Thu. Mar 23, 2023

K303

Academic Program [Oral B] | 01. Education and History of Chemistry | Oral B

[K303-2pm] 01. Education and History of Chemistry

Chair: Hirotoshi Mori, Izumi Imai
1:50 PM - 3:40 PM K303 (K303, Lecture Hall Bldg. [3F])

[K303-2pm-01] Practical computational chemistry course for a comprehensive understanding of organic, inorganic, and physical chemistry: from molecular interactions to chemical reactions

Nahoko Kuroki[1], Yuji Mochizuki[2], ○Hirotoshi Mori[1] (1. Chuo University, 2. Rikkyo Univeristy)

1:50 PM - 2:10 PM

[K303-2pm-02] Chemical education of community education and liberal arts education in the Times of Post Covid-19

○Sekai Iwama[1,2], Fumiyoshi Asahi[2], Ryu Takahashi[3] (1. Kumamoto Gakuen University, 2. Specified Nonprofit Corporation Otaru Kagakugizyutsu no Me wo Sodateru Kai, 3. Otaru City Council)

2:10 PM - 2:30 PM

[K303-2pm-03] SDGs in Chemistry in Context (American Chemical Society ed.) 9th edition - From the activities of Tohoku Association of Chemical Education

○Naoshi Watanabe[1], Kazuko Ogino[2], Hiroshi Kosugi[2], Daisuke Hojo[3], Yuko Masuyama[4], Hiroshi Ogino[2] (1. Miyagi University of Education, 2. Tohoku University, 3. Miyagi Prefecture Izumitateyama High School, 4. Miyagi Prefecture Teizan High School)

2:40 PM - 3:00 PM

[K303-2pm-05] Radical has the own semi-acidity or semi-basicity

○Hirosi Sano[1] (1. Laboratory of Global Energy Systeml)

3:20 PM - 3:40 PM

K202

Academic Program [Oral B] | 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry | Oral B

[K202-2pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Erik Lötstedt, Nahoko KUROKI
1:30 PM - 3:40 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-2pm-01] Development of cat-GRRM/MC/MD method realizing the process of crosslinked network structure formation using molecular catalysts

○YINGXIAO XI[1], Hironobu Fukuzawa[1], Shoji Fukunaga[1], Gota Kikugawa[2], Naoki Kishimoto[1] (1. Department of Chemistry, Tohoku University , 2. Institute of Fluid Science, Tohoku University)

1:30 PM - 1:50 PM

[K202-2pm-02] Quantum computation of time-dependent spin chain dynamics

○Erik Lötstedt[1], Lidong Wang[1], Ryuhei Yoshida[1], Youyuan Zhang[1], Kaoru Yamanouchi[1] (1. Department of Chemistry, School of Science, The University of Tokyo)

1:50 PM - 2:10 PM

[K202-2pm-03] Analysis of dynamical branching mechanisms based on the Reaction Space Projector

○Takuro Tsutsumi[1,2], Akifumi Fujita[3], Kenichiro Iwata[4], Yuriko Ono[5], Tetsuya Taketsugu[1,5] (1. Fac. Sci., Hokkaido Univ., 2. L-Station, Hokkaido Univ., 3. Sch. Sci., Hokkaido Univ., 4. Grad. School Chem. Sci. Eng., Hokkaido Univ., 5. WPI-ICReDD, Hokkaido Univ.)

2:20 PM - 2:40 PM

[K202-2pm-04] Quantum chemical analysis of coordination stability of flexible tripeptides and nickel ions self-assembling to form macrocyclic supramolecules

○Dapeng Zhang[1], Naoki Kishimoto[1], Ryosuke Miyake[2] (1. Tohoku University, 2. Ochanomizu University)

2:40 PM - 3:00 PM

[K202-2pm-05] Double layer differential capacitance calculation by absolute electrode potential controlled MD

○Ken Takahashi[1], Hirofumi Sato[1,2], Hiroshi Nakano[3] (1. Department of molecular

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engineering, Kyoto University, 2. Fukui Institute for Fundamental Chemistry, 3. CD-FMat, National Institute of Advanced Industrial Science and Technology (AIST))

3:00 PM - 3:20 PM

[K202-2pm-06] Theoretical investigation of atomic and electronic structures of supported metallic nanoparticles by large-scale DFT and machine learning

○Shengzhou Li[1,2], Tsuyoshi Miyazaki[2,1], Ayako Nakata[2,1] (1. University of Tsukuba, 2. National Institute for Materials Science)

3:20 PM - 3:40 PM

Academic Program [Oral B] | 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry | Oral B

[K202-2vn] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Takuro Tsutsumi, Yasuteru Shigeta
4:10 PM - 6:50 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-2vn-01] Comprehensive COSMO-RS Exploration of Highly CO_2 Selective Hydrogen-bonding Binary Absorbents

Shiori WATABE[1], ○Nahoko KUROKI[1,2], Hirotoshi MORI[1,3] (1. Chuo University, 2. JST ACT-X, 3. NEDO)

4:10 PM - 4:30 PM

[K202-2vn-02] Development and Applications of a Method for Designing Functional Molecules Based on Exploration of Chemical Space Accounting for Geometric Stability

○Takafumi Shiraogawa[1], Hasegawa Jun-ya[1] (1. Hokkaido Univ.)

4:30 PM - 4:50 PM

[K202-2vn-03] A Method for Predicting Physical Properties of Inorganic Materials Using Deep Learning Models and Proposing New Materials

○Hisanao Takahashi[1], Koji Tsuda[2], Masahito Hiroshima[1] (1. KYOCERA Corporation, 2. RIKEN)

4:50 PM - 5:10 PM

K203

Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B

[K203-2am] 04. Physical Chemistry -Properties-

Chair: Shun Dekura, Yoshiaki Shuku
9:00 AM - 11:30 AM K203 (K203, Lecture Hall Bldg. [2F])

[K203-2am-01] Theoretical study on electronic structure and single-molecule electron conductivity of annulene for design guideline of molecular circuits

○Naoka Amamizu[1], Keisuke Sasaki[1], Mitsuhiro Nishida[2], Masahiro Tsuda[1], Yuta Hayashi[1], Kazuki Honjo[2], Koki Masuda[2], Ryohei Kishi[1,3,4,5], Yasutaka Kitagawa[1,3,4,5,6] (1. Graduate School of Engineering Science, Osaka Univ., 2. Faculty of Engineering Science, Osaka Univ., 3. QIQB, Osaka Univ., 4. RCSEC, Osaka Univ., 5. ICS-OTRI, Osaka Univ., 6. SRN-OTRI, Osaka Univ.)

9:00 AM - 9:20 AM

[K203-2am-02] Theoretical study on stacking structure dependence of charge density distributions in finite-sized stacks of π-conjugated molecules

○Wataru Yoshida[1], Yasuteru Shigeta[2], Hiroshi Matsui[3], Ryohei Kishi[1,4,5,6], Yasutaka Kitagawa[1,4,5,6,7] (1. Graduate School of Engineering Science, Osaka University, 2. Center for Computational Sciences (CCS), University of Tsukuba, 3. Osaka Institute of Public Health, 4. Research Center for Solar Energy Chemistry (RCSEC), Osaka University, 5. Quantum Information and Quantum Biology (QIQB), Osaka University, 6. Innovative Catalysis Science Division Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, 7. Center for Spintronics Research Network (CSRN), Osaka University)

9:20 AM - 9:40 AM

[K203-2am-03] Proposal for the Mechanism on Preferred Electric Polarization and Chirality in Ferroelectric Triglycine Sulfate Crystals by Doping with Various Glycine Analogues

○Yukana Terasawa[1], Masaaki Ichiki[2], Toshio Kikuta[3], Masahito Tanaka[2], Toru Asahi[1] (1. Waseda Univ., 2. AIST, 3. The Univ. of Toyama)

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9:40 AM - 10:00 AM

[K203-2am-04] Topological band structures of polyhedral π conjugated molecule based triangular lattice

○Yoshiaki Shuku[1], Rie Suizu[1,2], Saya Nakano[3], Masahisa Tsuchiizu[3], Kunio Awaga[1] (1. Nagoya Univ., 2. JST PRESTO, 3. Nara Women's Univ.)

10:00 AM - 10:20 AM

[K203-2am-05] Low-barrier anhydrous proton conductivity based on proton tautomerism in single-crystalline azolium phosphates

○Shun Dekura[1], Kaito Nishioka[1], Hatsumi Mori[1] (1. ISSP, The Univ. of Tokyo)

10:30 AM - 10:50 AM

[K203-2am-06] Metallic State of Mixed Sequence Oligomer Salt that Models Doped PEDOT

○Kota Onozuka[1], Tomoko Fujino[1], Ryohei Kameyama[1], Shun Dekura[1], Kazuyoshi Yoshimi[1], Toshikazu Nakamura[2], Tatsuya Miyamoto[3], Takashi Yamakawa[3], Hiroshi Okamoto[3], Hatsumi Mori[1] (1. The Institute for Solid State Physics, The University of Tokyo, 2. Institute for Molecular Science, 3. Department of Advanced Materials Science, The University of Tokyo)

10:50 AM - 11:10 AM

[K203-2am-07] Investigation of carrier conduction in conductive polymer PEDOT/PSS using ultra-broadband spectroscopy

○Tetsu Sato[1], Zijing Guo[1], Yang Han[1], Naoki Takamura[1], Tatsuya Miyamoto[1], Noriaki Kida[1], Makiko Ogino[2], Yotarou Takahashi[2], Qingshuo Wei[3], Masaichi Mukaida[3], Hiroshi Okamoto[1] (1. Depat of Adv. Mat. Sci., Univ. of Tokyo, 2. Depat of Appl. Phys., Univ. of Tokyo, 3. AIST)

11:10 AM - 11:30 AM

Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B

[K203-2pm] 04. Physical Chemistry -Properties-

Chair: Kiyoshi Miyata, Ryohei Kishi

1:10 PM - 3:30 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-2pm-01] Ultrafast Spectroscopy of InP-based Core/shell Quantum Dots under Ultrahigh Pressure

○Daichi Eguchi[1], Naoto Tamai[1] (1. Kwansei Gakuin Univ.)

1:10 PM - 1:30 PM

[K203-2pm-02] Comparing the Raman and emission thermometry of a hydroxo-bridged molecular magnet

○KUNAL KUMAR[1], Olaf Stefanczyk[1], Szymon Chorazy[2], Koji Nakabayashi[1], Shin-ichi Ohkoshi[1] (1. University of Tokyo, 2. Jagiellonian University)

1:30 PM - 1:50 PM

[K203-2pm-03] Real-Time Tracking of Photon Upconversion Processes in Rare Earth Doped Nanoparticles using Ultrafast Spectroscopy

○Kiyoshi Miyata[1], Mako Takada[1], Kanji Sugioka[1], Shiori Miyazaki[1], Mitsunori Ohta[2], Ryusuke Mizoguchi[2], Ayumi Ishii[2], Ken Onda[1] (1. Kyushu University, 2. Teikyo Univ. of Sci.)

1:50 PM - 2:10 PM

[K203-2pm-04] Theoretical Study on Low-Lying Excited States Involved in Singlet Fission Process of Fused-ring Compounds Containing Diphenoquinone Structure

○Kenji Okada[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. QIQB, Osaka University, 3. RCSEC, Osaka University, 4. ICS-OTRI, Osaka Uniersity, 5. SRN-OTRI, Osaka University)

2:30 PM - 2:50 PM

[K203-2pm-05] Theoretical Study on Singlet Fission Dynamics in One-dimensional Molecular Aggregate Models: Dependence of Spatial Distributions of Correlated Triplet Pair on Structure of Aggregate

○Hajime Miyamoto[1], Kenji Okada[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. Center for Quantum Information and Quantum Biology, Osaka-University, 3. Research Center for Solar Energy Chemistry, Osaka University, 4. Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University, 5. Spintronics Research

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Network Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University)

2:50 PM - 3:10 PM

[K203-2pm-06] Theoretical study on relationship between open-shell character and intermolecular interaction energy in closely-π-stacked aggregates composed of antiaromatic molecules

○Ryota Sugimori[1], Masato Ikeuchi[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. RCSEC, Osaka University, 3. QIQB, Osaka University, 4. ICS-OTRI, Osaka University, 5. SRN-OTRI, Osaka University)

3:10 PM - 3:30 PM

Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B

[K203-2vn] 04. Physical Chemistry -Properties-

Chair: Sadahiro Masuo

4:10 PM - 5:10 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-2vn-01] Light Confinement of $CsPbBr_3$ Microplates Studied by Near-Field Imaging

○Seiju Hasegawa[1], Hina Hayashi[1], Kohei Imura[1] (1. Waseda Univ.)

4:10 PM - 4:30 PM

[K203-2vn-02] Elucidation of Adsorption Behavior of Perylene Bisimide Derivatives on Perovskite Nanocrystal Surface

○Naoki Kubo[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

4:30 PM - 4:50 PM

[K203-2vn-03] Atomically-precise synthesis and photoluminescence properties of water-soluble, NHC-protected Au_{13} clusters

○Dennis Alexander Buschmann[1], Shinjiro Takano[1], Tatsuya Tsukuda[1] (1. The University of Tokyo)

4:50 PM - 5:10 PM

K701

Academic Program [Oral B] | 06. Analytical Chemistry | Oral B

[K701-2pm] 06. Analytical Chemistry

Chair: Akihide Hibara, Takahito Ohshiro

2:20 PM - 3:40 PM K701 (K701, Lecture Hall Bldg. [7F])

[K701-2pm-01] Characterization of liquid gold used in traditional pottery and crafts

○Yoshihide MAENO Maeno[1,2], Takei Onoue[1], Shinnya Kitagawa[1], Hajime Ohtani[1], Yukiko Kikugawa[2], Yoshihiro Suzuki[2] (1. Nagoya Institute of Technology, 2. Noritake Co., Ltd)

2:20 PM - 2:40 PM

[K701-2pm-02] Development of Amino Acid Identification by Single Molecule Detection Method Towards Peptide Sequencing

○Takahito Ohshiro[1], Taniguti Masateru[1] (1. Osaka University)

2:40 PM - 3:00 PM

[K701-2pm-03] Digital PCR on an original microfluidic chip

○Kazuo Hosokawa[1], Hitoshi Ohmori[1] (1. RIKEN)

3:00 PM - 3:20 PM

[K701-2pm-04] Development of HPLC using phase-separation multiphase flow as as eluent

Noe Jallas[1], Daiki Ishikawa[1], Tetsuro Katayama[1], Aoi Kimura[1], ○Kazuhiko Tsukagoshi[1] (1. Doshisha University)

3:20 PM - 3:40 PM

K306

Academic Program [Oral B] | 08. Catalysts and Catalysis | Oral B

[K306-2am] 08. Catalysts and Catalysis

Chair: Akinobu Nakada, Tsuyoshi Takata

9:00 AM - 11:10 AM K306 (K306, Lecture Hall Bldg. [3F])

[K306-2am-01] Efficient hydrogen production by photo-redox-cascade catalyst composing dual photosensitizers and transparent hole acceptor

Nobutaka Yoshimura[1], Masaki Yoshida[2], ○Atsushi KOBAYASHI[1] (1. Hokkaido University, 2. Kwansei Gakuin University)

9:00 AM - 9:20 AM

[K306-2am-02] Local charge-carrier dynamics of a particulate Ga-doped $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ photocatalyst and the impact of Rh cocatalyst

○Kenji Katayama[1], Tatsuya Chugenji[1], Zhenhua Pan[1], Vikas Nandal[2], Kazuhiko Seki[2], Kazunari Domen[3] (1. Chuo University, 2. AIST, 3. The Univ. of Tokyo)

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9:20 AM - 9:40 AM

[K306-2am-03] Quantitative evaluation of the competition between oxidation of various reversible redox species and photocorrosion on chalcogenide photoanodes

○Yuu Shioiri[1], Keisuke Obata[1], Tomohiro Higashi[2], Yudai Kawase[1], Masao Katayama[1], Kazuhiro Takanabe[1] (1. The University of Tokyo, 2. University of Miyazaki)

9:40 AM - 10:00 AM

[K306-2am-04] Preparation of highly crystalline wurtzite CdS photocatalysts by a flux method

○Haruki Nagakawa[1], Tetsu Tatsuma[1] (1. IIS, The Univ. of Tokyo)

10:10 AM - 10:30 AM

[K306-2am-05] Development of $BaTaO_2N$ photocatalysts with distinctive carrier dynamics for one-step excitation overall water splitting

○Junie Jhon Magdadaro Vequizo[1], Jiadong Xiao[1], Shinji Nishimae[2], Takashi Hisatomi[1], Lu Daling[1], Tsuyoshi Takata[1], Akira Yamakata[3], Kazunari Domen[1,4] (1. Shinshu Univ., 2. ARPChem, 3. Okayama Univ., 4. The Univ. of Tokyo)

10:30 AM - 10:50 AM

[K306-2am-06] Synthesis of Nanocrystalline ATaO2N (A = Ca, Sr, Ba) for Photocatalytic Overall Water Splitting

○Jiadong XIAO[1], Takashi HISATOMI[1], Kazunari DOMEN[1,2] (1. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Nagano-shi, Nagano, 380-8553 Japan, 2. Office of University Professors, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo, 113-8656 Japan)

10:50 AM - 11:10 AM

K305

Academic Program [Oral B] | 08. Catalysts and Catalysis | Oral B

[K305-2pm] 08. Catalysts and Catalysis

Chair: Ken Motokura, Yusuke Kita
1:00 PM - 3:40 PM K305 (K305, Lecture Hall Bldg. [3F])

[K305-2pm-01] Highly-densed array of Iron-based metal catalyst nanoparticle showing high-temperature stability; Formation and the application to ultra-long carbon nanotube array

○Shunsuke Sakurai[1], Takashi Tsuji[1], Maho Yamada[1], Kenji Hata[1], Don N Futaba[1] (1. National Institute of Advanced Industrial Science and Technology)

1:00 PM - 1:20 PM

[K305-2pm-02] Understanding the Roles of Hydroxide in CO_2 Electroreduction on a Cu Electrode for Achieving Variable Selectivity

○MINGXU SUN[1], Miho Yamauchi[1] (1. Kyushu University)

1:20 PM - 1:40 PM

[K305-2pm-03] Development of the Ir-complex catalysts immobilized on functional polymer for formic acid dehydrogenation

○Keito Sawahara[1,2], Shinji Tanaka[2], Tetsuya Kodaira[2], Hajime Kawanami[2,1] (1. University of Tsukuba, 2. AIST)

1:40 PM - 2:00 PM

[K305-2pm-04] Iron-Catalyzed 1,4-Arylalkylation of 1,3-Enynes with Arylborates and Unactivated Alkyl Electrophiles

○Siming LU[1,2], Litian CHEN[1,2], Satsuki NOMURA, Katsuhiro ISOZAKI[1,2], Masaharu NAKAMURA[1,2] (1. Kyoto University, 2. Institute for Chemical Research)

2:00 PM - 2:20 PM

[K305-2pm-05] *In situ* formic acid dehydrogenation observation using a UV-vis-diffuse-reflectance spectroscopy system

○Risheng Li[1,2], Hajime Kawanami[1,2], Tetsuya Kodaira[2] (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

2:20 PM - 2:40 PM

[K305-2pm-06] Development of novel synthetic method for thiols using heterogeneous cobalt catalysts from hydrogen, elemental sulfur, and alkenes

○Xu Ke[1], Yamamoto Eiji[1], Murayama Haruno[1], Matsueda Hironobu[2], Sakata Hiroshi[2], Tokunaga Makoto[1] (1. kyushu university, 2. DIC Corporation)

2:40 PM - 3:00 PM

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[K305-2pm-07] Heterogeneous catalytic approach to the synthesis of cyclic carbonates and their decarboxylative transformations

○Sangita Karanjit[1], Emiko Tanaka[1], Ryota Sato[1], Kosuke Namba[1] （1. Tokushima University）

3:00 PM - 3:20 PM

[K305-2pm-08] Enantioselective [3+2] Annulation of Aromatic aldimines with Alkenes via C− H Activation by Half-Sandwich Scandium Catalysts

○Aniket Mishra[1], Xuefeng Cong[1], Masayoshi Nishiura[1], Zhaomin Hou[1] （1. RIKEN）

3:20 PM - 3:40 PM

K306

Academic Program [Oral B] | 08. Catalysts and Catalysis | Oral B

[K306-2pm] 08. Catalysts and Catalysis

Chair: Akihide Iwase, Osamu Tomita
1:50 PM - 3:40 PM K306 (K306, Lecture Hall Bldg. [3F])

[K306-2pm-01] Tuning interfacial energetics for enhanced H_2O_2 generation

○Zhenhua Pan[1], Junie Vequizo[3], Akira Yamakata[2], Chiheng Chu[4], Kenji Katayama[1] （1. Chuo University, 2. Okayama University, 3. Shinshu University, 4. Zhejiang University）

1:50 PM - 2:10 PM

[K306-2pm-02] Development of Green Molecular Transformation Mediated by Cobalt Complex and WO_3 System

○Keita Shichijo[1], Hisashi Shimakoshi[1] （1. Kyushu Univ.）

2:10 PM - 2:30 PM

[K306-2pm-03] Decomposition of Perfluoroalkyl Substances by Near-UV and Visible Light Irradiation to Semiconductor Nanocrystals

○Yoichi Kobayashi[1,2], Yusuke Sanada[1], Yuzo Arima[1], Yoshinori Okayasu[1], Yuki Nagai[1] （1. Ritsumeikan Univ., 2. PRESTO JST）

2:30 PM - 2:50 PM

[K306-2pm-04] Z-scheme hybrid photocatalysts consisting of conjugated polymer semiconductors and Ru(II) binuclear supramolecular photocatalyst for visible-light driven CO_2 reduction

○Noritaka Sakakibara[1], Ewan McQueen[2], Yusuke Tamaki[1], Sebastian Sprick[2], Osamu Ishitani[1,3] （1. Tokyo Tech., 2. Univ. of Strathclyde, 3. Hiroshima Univ.）

3:00 PM - 3:20 PM

[K306-2pm-05] Advances in Photocatalytic Hydrophosphination

○Rory Waterman[1] （1. University of Vermont）

3:20 PM - 3:40 PM

K506

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B

[K506-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Takahiro Matsumoto, Takuya Kochi
9:00 AM - 11:40 AM K506 (K506, Lecture Hall Bldg. [5F])

[K506-2am-01] Defluorohydrogenation of Acyl Fluorides by Secondary Phosphine Oxide as a Hydride Donor

○Myuto Kashihara[1], Ayaka Kataoka[2], Yasushi Nishihara[1] （1. RIIS, Okayama Univ., 2. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ.）

9:00 AM - 9:20 AM

[K506-2am-02] Effect of Carboxylate Coordination on Redox Properties and Substrate Oxidation Reactivity of Di(-oxido)dinickel(III) Complex

○Yuma Morimoto[1], Ryoichiro Ogumo[2], Shinobu Itoh[2] （1. Nagoya University, 2. Osaka University）

9:20 AM - 9:40 AM

[K506-2am-03] Aerobic oxidative reactivity of nickel complexes supported in napthyridines ligand scaffolds

○Shubham Deolka[1], Julia Khusnutdinova[1] （1. OIST ,JAPAN）

9:40 AM - 10:00 AM

[K506-2am-04] C_3 product formation by electrochemical CO_2 reduction for dinuclear Cu molecular catalyst

○Naonari Sakamoto[1], Keita Sekizawa[1], Soichi Shirai[1], Takamasa Nonaka[1], Takeo Arai[1], Shunsuke Sato[1], Takeshi Morikawa[1] （1. Toyota Central R&D Labs., Inc.）

10:00 AM - 10:20 AM

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[K506-2am-05] Synthesis and Redox Reaction of Copper- and Cobalt-Containing Zeolitic Imidazolate Frameworks

○Hiroki Nakahara[1], Masahito Kodera[1], Yutaka Hitomi[1] （1. Doshisha University）

10:20 AM - 10:40 AM

[K506-2am-06] Synthesis, structure and methane oxidation by dicopper complex with hydrophobic pocket

○Kyosuke FUJIKAWA[1], Yutaka HITOMI[1], Masahito KODERA[1,2] （1. Doshisha Univ., 2. JST CREST）

10:40 AM - 11:00 AM

[K506-2am-07] Dual Catalysis of Au_{25} Nanocluster Functionalized by Peptide Dendron Thiolate toward Cross-Dehydrogenative Coupling between Amines and Alkynes

○Kenta Iseri[1], Kyosuke Ueda[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] （1. Kyoto University）

11:00 AM - 11:20 AM

[K506-2am-08] Electrochemical and Photochemical CO_2 Reduction by Rhenium Porphyrin Complexes

○Jingru Liu[1], Kei Murata[1], Mengfei Wang[1], Kazuyuki Ishii[1], Yusuke Tamaki[2], Osamu Ishitani[2] （1. IIS, The Univ. of Tokyo, 2. Dept. of Chem., Tokyo Tech）

11:20 AM - 11:40 AM

K505

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B

[K505-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryota Matsuoka, Tomoyuki Haraguchi
9:00 AM - 11:30 AM K505 (K505, Lecture Hall Bldg. [5F])

[K505-2am-01] A 3D chiral networked MX compound

○Hao Liang[1], Kazuya Otsubo[1], Yuiga Nakamura[2], Shogo Kawaguchi[2], Hiroshi Kitagawa[1] （1. Kyoto University, 2. Japan Synchrotron Radiation Research Institute (JASRI), SPring-8）

9:00 AM - 9:20 AM

[K505-2am-02] Charge-transfer phase transition in a two-dimensional cyanido-bridged Co-W assembly with isoquinoline ligands

○Kazuki Nakamura[1], Shota Kobayashi[1], Koji Nakabayashi[1], Kenta Imoto[1], Shin-ichi Ohkoshi[1] （1. The Univ. of Tokyo）

9:20 AM - 9:40 AM

[K505-2am-03] Gate-Open-Close Vapochromism of Rhenium(I) Molecular Crystals Supported by Non-Covalent Interactions: In-Situ Observation of the Guest-Induced Structural Transformation Dynamics

○Yuki Matsuda[1], Ryota Nakamura[1], Yoshiki Ozawa[1], Keishiro Tahara[1], Toshikazu Ono[2], Nobuto Yoshinari[3], Takumi Konno[3], Kunihisa Sugimoto[4], Shintaro Kobayashi[5], Shogo Kawaguchi[5], Masaaki Abe[1] （1. Graduate School of Science, University of Hyogo, 2. Graduate School of Engineering, Kyushu University, 3. Graduate School of Science, Osaka University, 4. Department of Chemistry, Faculty of Science and Engineering, Kindai University, 5. SPring-8/JASRI）

9:40 AM - 10:00 AM

[K505-2am-04] Complexation behavior and luminescence enhancement of a pyridyl-containing triarylmethyl radical with silver(I)

○Takuto Mibu[1], Ryota Matsuoka[1], Tetsuro Kusamoto[1,2] （1. IMS, 2. JST-PRESTO）

10:00 AM - 10:20 AM

[K505-2am-05] Sequence Controll and Multi-stage Redox Composed of Single Metal containing Metallosupramolecular Polymeric Films for Electrochromic Study

○DINES CHANDRA SANTRA[1], Masayoshi HIGUCHI[1] （1. National Institute for Materials Science (NIMS)）

10:30 AM - 10:50 AM

[K505-2am-06] Development of visible-light responsive mutinuclear Zn complexes and Zn clusters based on Zn-Zn interaction

○Yoshimasa Wada[1,2], Takahiro Maruchi[2], Reon Ishii[2], Yusuke Sunada[1,2,3] （1. Institute of Industrial Science, The University of Tokyo, 2. Graduate School of Engineering, The University of Tokyo, 3. JST-PRESTO）

10:50 AM - 11:10 AM

[K505-2am-07] The spin-lattice magnetic relaxation of an

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S=1/2 copper(II)-substituted Keggin-type phosphotungstate

○Toshiharu Ishizaki[1], Yoji Inoue[1], Tomoji Ozeki[1] (1. Nihon Univ.)

11:10 AM - 11:30 AM

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B

[K505-2pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Norio Nakata, Shintaro Ishida
1:40 PM - 3:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-2pm-01] DNA Double Strand Breaks via Reductive O_2-Activation by Dicopper Complex: large acceleration by introducing an intercalator as DNA Binding Site

○Machi Hata[1], Hiroyuki Matsumoto[1], Yutaka Hitomi[1], Masahito Kodera[1] (1. Doshisha University)

1:40 PM - 2:00 PM

[K505-2pm-02] Room-temperature Conversion of CO_2 into Metal-Organic Frameworks

○Kentaro Kadota[1], Satoshi Horike[1,2] (1. Institute for Advanced Study, Kyoto University, 2. Graduate School of Engineering, Kyoto University)

2:00 PM - 2:20 PM

[K505-2pm-03] Synthesis of Lewis-base-coordinated Germabenzenylgermylenes Acting as a Ge Atom Source

○Ryohei Nishino[1], Yoshiyuki Mizuhata[1], Norihiro Tokitoh[1] (1. Institute for Chemical Research, Kyoto Univ.)

2:20 PM - 2:40 PM

[K505-2pm-04] Synthesis of Novel Silylboron Compounds Using Trialkylsilyl Anions

○Rikuro Takahashi[1], Hajime Ito[2,3] (1. Division ofApplied Chemistry, Graduate School of Engineering, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University, 3. WPI-ICReDD, Hokkaido University)

2:40 PM - 3:00 PM

[K505-2pm-05] Synthesis and Characterization of Alumanyl Complexes of Vanadium

○Pavel Zatsepin[1], Makoto Yamashita[1] (1. Nagoya University)

3:00 PM - 3:20 PM

[K505-2pm-06] Catalytic Hydrogenation of Carbonyl Compounds Using Crude H_2 as H_2 Source

○Mahiro Sakuraba[1], Sensuke Ogoshi[1], Yoichi Hoshimoto[1] (1. Osaka university)

3:20 PM - 3:40 PM

K404

Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- | Oral B

[K404-2am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Koji Kubota, Sobi Asako
9:00 AM - 11:40 AM K404 (K404, Lecture Hall Bldg. [4F])

[K404-2am-01] Low-Valent Titanium-Mediated Homolysis of Alcohol and Ether C-O Bonds

○Takuya Suga[1], Ryusei Takada[1], Yuuki Takahashi[1], Chinatsu Miki[1], Yutaka Ukaji[1] (1. Kanazawa University)

9:00 AM - 9:20 AM

[K404-2am-02] H_2 Purification through Sequential Hydrogenation/Dehydrogenation of *N*-Heterocycles Using Triarylborane Catalysts

○Taiki Hashimoto[1], Takahiro Asada[1], Sensuke Ogoshi[1], Yoichi Hoshimoto[1] (1. Graduate School of Engineering, Osaka University)

9:20 AM - 9:40 AM

[K404-2am-03] Synthesis and Reactivities of Cyclopentadienone Group 5 Metal Complexes

○Takuya Higashi[1], Shuhei Kusumoto[1], Kyoko Nozaki[1] (1. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[K404-2am-04] Silylation of Organic Halides with a Disilane Having Seven-Membered Dialkoxysilyl Groups Activated by Potassium *tert*-Butoxide

○Kenshiro Hitoshio[1], Hayate Saito[1], Jun Shimokawa[1], Hideki Yorimitsu[1] (1. Graduate School of Science, Kyoto University)

10:00 AM - 10:20 AM

[K404-2am-05] Experimental and DFT study on electrophilic and carbene-like reactivity of magnesium alkylidene carbenoids

○Koto Sekiguchi[1], Tsutomu Kimura[1] (1. Graduate School of Science, Tokyo University

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of Science)
10:40 AM - 11:00 AM

[K404-2am-06] Air-Tolerant and Extremely Fast Lithium-Based Birch Reduction Enabled by Mechanochemistry
○Yunpeng Gao[1], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)
11:00 AM - 11:20 AM

[K404-2am-07] Generation and Synthetic Applications of Calcium-Based Heavy Grignard Reagents under Mechanochemical Conditions
○Pan Gao[1], Julong Jiang[2], Satoshi Maeda[1,2], Koji Kubota[1,3], Hajime Ito[1,3] (1. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, 2. Department of Chemistry, Faculty of Science, Hokkaido University, 3. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University)
11:20 AM - 11:40 AM

Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- | Oral B

[K404-2pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takuya Kochi, Yuichiro Mutoh
1:00 PM - 3:40 PM K404 (K404, Lecture Hall Bldg. [4F])

[K404-2pm-01] Development of Palladium-catalyzed Oxidative Amination of 1,3-Diene and Elucidation of Catalytic Species
○Kazuki Tabaru[1], Tetsuaki Fujihara[2], Kazuyuki Torii[1], Takeyuki Suzuki[3], Yasushi Obora[1] (1. Fac. Chem. Matl. &Bioeng., Kansai Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. SANKEN, Osaka Univ.)
1:00 PM - 1:20 PM

[K404-2pm-02] Alkene Rotation as a Key Process in Chain Walking of a Palladium Catalyst and Its Effect on Selectivity of Reaction Pathways
○Kazuma Muto[1], Miho Hatanaka[1], Fumitoshi Kakiuchi[1], Takuya Kochi[1] (1. Keio. University)
1:20 PM - 1:40 PM

[K404-2pm-03] Virtual Ligand-Assisted Screening Strategy toward Finding Enabling Ligands for Transition Metal Catalysis
○Wataru Matsuoka[1,2], Yu Harabuchi[1,2,3], Satoshi Maeda[1,2,3] (1. Fac. of Sci., Hokkaido Univ., 2. JST-ERATO, 3. WPI-ICReDD, Hokkaido Univ.)
1:40 PM - 2:00 PM

[K404-2pm-04] Synthesis of SGLT2 Inhibitors by Means of Fukuyama Coupling Reaction
○Maheshwara Reddy Nadiveedhi[1], Sandeep Ramesharao Tapkir[1], Shaheen Kasim Mulani[1], Masahiko Seki[1,2], Kazushi Mashima[1] (1. Osaka University, 2. Tokuyama Corporation)
2:00 PM - 2:20 PM

[K404-2pm-05] Platinum-Catalyzed Stereospecific Synthesis of Silicon-Stereogenic Optically Active Silylboranes and Their Application
○Xihong Wang[1], Chi Feng[2], Koji Kubota[1,2], Hajime Ito[1,2] (1. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, 2. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University)
2:40 PM - 3:00 PM

[K404-2pm-06] Isolation and reactivity of allenynickel key reaction intermediates in Ni-catalyzed asymmetric propargylic substitution reactions
○Yusuke Miyazaki[1], Kenichi Michigami[2], Mitsuhiro Ueda[2], Masato Ohashi[2] (1. Osaka Prefecture Univ., 2. Osaka Metropolitan Univ.)
3:00 PM - 3:20 PM

[K404-2pm-07] Synthesis and Reactivity of Ni(0) Carbonyl Complexes Bearing *N*-Phosphine Oxide-Substituted Imidazolinylidene
○Yasuhiro Yamauchi[1], Yuta Uetake[1], Hidehiro Sakurai[1], Yoichi Hoshimoto[1], Sensuke Ogoshi[1] (1. Osaka university)
3:20 PM - 3:40 PM

K603

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B

[K603-2am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Takayuki Tanaka, Tetsuo Okujima

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9:00 AM - 11:30 AM K603 (K603, Lecture Hall Bldg. [6F])

[K603-2am-01] Single crystal field-effect transistor of tetrabenzoporphyrin with a one-dimensional columnar packing motif exhibiting efficient charge transport properties

○Hironobu Hayashi[1], JuanJuan Zhu[1], Kyohei Matsuo[1], Naoki Aratani[1], Hiroko Yamada[1] (1. Nara Institute of Science and Technology)

9:00 AM - 9:20 AM

[K603-2am-02] Synthesis and charge transpor properties of asymmetric 5,15-substituted tetrabenzoporphyrins

○Kazuya Miyazaki[1], Kyohei Matsuo[1], Naoki Aratani [1], Hiroko YAMADA[1] (1. Nara Institute of Science and Technology)

9:20 AM - 9:40 AM

[K603-2am-03] Deprotonation-Induced and Ion-Pairing-Modulated Diradical Properties of Partially Conjugated Pyrrole-Quinone Conjunction

○Shinya Sugiura[1], Takashi Kubo[2], Hiromitsu Maeda[1] (1. Ritsumeikan Univ., 2. Osaka Univ.)

9:40 AM - 10:00 AM

[K603-2am-04] Control of Aromatic Ring Inversion in Calix[3]pyrrole

○Yuya Inaba[1], Yu Kakibayashi[1], Yasuhide Inokuma[1,2] (1. Grad. Sch. Eng., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ.)

10:10 AM - 10:30 AM

[K603-2am-05] Synthesis and Redox properties of silver and nickel complexes of N-confused porphyrin dimer

○Osamu Iwanaga[1], Shigeki Mori[2], Masatoshi Ishida[3], Soji Shimizu[1], Hiroyuki Furuta[1,4] (1. Kyushu Univ., 2. Ehime Univ., 3. Tokyo Metropolitan Univ., 4. Ritsumeikan Univ.)

10:30 AM - 10:50 AM

[K603-2am-06] Panchromatic Absorption of Pyrrolopyrrole aza-BODIPY analogs Based on the Push-Pull Strategy

○Yitong Wang[1], Soji Shimizu[1] (1. Graduate School of Engineering, Kyushu University)

10:50 AM - 11:10 AM

[K603-2am-07] Synthesis and properties of electron-donor-substituted BODIPY-based contrast agents for two-photon-excitation-induced photoacoustic imaging

○Takahide Shimada[1], Ishida Masatoshi[2], Shigeki Mori[3], Soji Shimizu[1], Hiroyuki Furuta[4] (1. Graduate School of Engineering, Kyushu University, 2. Graduate School of Science, Tokyo Metropolitan University, 3. Advanced Research Support Center, Ehime University, 4. Research Organization of Science and Technology, Ritsumeikan University)

11:10 AM - 11:30 AM

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B

[K603-2pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Eiichi Kayahara, Ryo Sekiya

1:30 PM - 3:40 PM K603 (K603, Lecture Hall Bldg. [6F])

[K603-2pm-01] Investigation of cyclobisbiphenylenecarbonyl adopting a figure-of-eight structure

○Norihito Fukui[1,2], Junichiro Hirano[1], Owase Daisuke[1], Emiko Nishimoto[1], Yuki Sakamoto[1], Ren Takayanagi[1], Keita Tajima[1], Hiroshi Shinokubo[1] (1. Grad. Sch. of Eng., Nagoya Univ., 2. JST PRESTO)

1:30 PM - 1:50 PM

[K603-2pm-02] Atomic-resolution visualization of non-planar graphene nanoribbon by using transmission electron microscopy

○Hiroki Hanayama[1], Xuelin Yao[2], Koji Harano[3], Klaus Muellen[2], Eiichi Nakamura[4], Akimitsu Narita[1,2] (1. Okinawa Institute of Science and Technology Graduate University, 2. Max Plank Institute for Polymer Research, 3. National Institute for Materials Science, 4. The University of Tokyo)

1:50 PM - 2:10 PM

[K603-2pm-03] Synthesis and Optical Properties of Novel Cyclic Compounds Using Fluorescence Chromophores

○Takahiro Kakuta[1], Yuka Kanadzu[1], Ryota Nakanishi[1], Tada-aki Yamagishi[1] (1. Kanazawa University)

2:10 PM - 2:30 PM

[K603-2pm-04] Synthesis of polyacene utilizing

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coordination nanospaces

○Takumi Miura[1], Takashi Kitao[1,2], Takashi Uemura[1] （1. Grad. Sch. of Eng. The Univ. of Tokyo, 2. JST-PRESTO）

2:40 PM - 3:00 PM

[K603-2pm-05] Synthesis of gigantic nanocarbon molecules via optimization of macrocyclization by Design-of-Experiments and machine learning

○Misato Akiyoshi[1], Koki Ikemoto[1], Tatsuru Mio[1], Kaito Nishioka[1], Sota Sato[1], Hiroyuki Isobe[1] （1. The University of Tokyo）

3:00 PM - 3:20 PM

[K603-2pm-06] Synthesis of soluble backbone-unsubstituted π-conjugated molecules

○Shusei Fujiki[1], Kazuma Amaike[1], Akiko Yagi[1], Kenichiro Itami[1] （1. Nagoya University）

3:20 PM - 3:40 PM

K606

Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry- | Oral B

[K606-2am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Daichi Kitagawa, Yuichiro Tokoro

9:00 AM - 11:40 AM K606 (K606, Lecture Hall Bldg. [6F])

[K606-2am-01] Tunable Rigidochromism of Copper-Pyrazolate Complexes

○Yuichiro Watanabe[1], Benjamin Washer[2], Matthias Zeller[2], Sergei Savikhin[2], Lyudmila Slipchenko[2], Alexander Wei[2] （1. Kyoto University, 2. Purdue University）

9:00 AM - 9:20 AM

[K606-2am-02] Turn-on Vapoluminescence Behavior of Host– Guest Complex Crystals between Liquid Phosphorescence Molecules and Pillar[5]arenes

○Keisuke Wada[1], Yuya Oshima[2], Shunsuke Ohtani[1], Kenichi Kato[1], Yosuke Tani[2,3], Takashi Tachikawa[4], Tomoki Ogoshi[1,5] （1. Grad. Sch. Eng., Kyoto Univ., 2. Grad. Sch. Sci., Osaka Univ., 3. ICS-OTRI, Osaka Univ., 4. Mol. PhotoSci. Res. Center, Kobe Univ., 5. WPI-NanoLSI, Kanazawa Univ.）

9:20 AM - 9:40 AM

[K606-2am-03] Synergistic Effects of Molecular Machine and Photoluminescent Dye

○Ryojun Toyoda[1,2], Ben L. Feringa[2] （1. Tohoku University, 2. University of Groningen）

9:40 AM - 10:00 AM

[K606-2am-04] Intermolecular Photochromic Reaction in Rhodamine Spirolactam Derivatives

○Yuki Nagai[1], Genki Kawai[1], Yoshinori Okayasu[1], Yoichi Kobayashi[1,2] （1. Ritsumeikan Univ., 2. PRESTO JST）

10:00 AM - 10:20 AM

[K606-2am-05] Thermochromic afterglow of boronate co-crystals

○Kaede Kawaguchi[1], Masato Ito[1], Yuji Kubo[1] （1. Grad. Sch. Urban Environ. Sci., Tokyo Metropolitan Univ. ）

10:20 AM - 10:40 AM

[K606-2am-06] Ion-Pairing Electronic Properties Based on π-Stacked Ion Pairs

○Hiroki Tanaka[1], Yoichi Kobayashi[1], Ko Furukawa[2], Hiromitsu Maeda[1] （1. Ritsumeikan University, 2. Niigata University）

10:40 AM - 11:00 AM

[K606-2am-07] Solid State *Endo-Exo* Conformation Control of Benzyl-substituted Monofluorosumanene and its Mechanism

Minghong Li[1], Dongyi Zhou[1], Teppei Matsumura[3], ○Yumi Yakiyama[1,2], Nobuyuki Matsubayashi[3], Hidehiro Sakurai[1,2] （1. Grad. Sch. Eng., Osaka University , 2. ICS-OTRI, Osaka University , 3. Grad. Sch. Eng. Sci, Osaka University ）

11:00 AM - 11:20 AM

[K606-2am-08] Enantioselective crystallization of organic molecules manipulated by optical trapping with a circularly polarized laser beam

Tung-Ming Lin[1], Hao-Tse Su[1], An-Chieh Cheng[1,2], Keiji Sasaki[2], ○Teruki Sugiyama[1,3] （1. National Yang Ming Chiao Tung Univ., 2. Hokkaido Univ., 3. NAIST）

11:20 AM - 11:40 AM

Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry- | Oral B

[K606-2pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Atsuro Takai, Ryou Kubota

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2:00 PM - 3:40 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-2pm-01] Construction of Porous Organic Salts from Orthogonal Networks by the Combination with Square Planar Sulfonic Acids and Bulky Amines
○Kohei Okubo[1], Kouki Oka[1], Norimitsu Tohnai[1] (1. Osaka University)
2:00 PM - 2:20 PM

[K606-2pm-02] Shape-persistent porous crystals formed by flexible [2]catenanes
○Bohan Cheng[1], Hiroshi Sato[1] (1. Institute of Physical and Chemical Research)
2:20 PM - 2:40 PM

[K606-2pm-03] Adsorption Behaviors of Pillar[*n*]quinones for Volatile Halogenated Organic Compounds
○Shunsuke Ohtani[1], Onishi Katsuto[1], Tomoki Hirohata[2], Shinsuke Inagi[2], Jenny Pirillo[3], Yuh Hijikata[3], Motohiro Mizuno[4], Kenichi Kato[1], Tomoki Ogoshi[1,5] (1. Grad. Sch. Eng., Kyoto Univ., 2. Tokyo Institute of Technology, 3. WPI-ICReDD, Hokkaido Univ., 4. NanoMaRi, Kanazawa Univ., 5. WPI-NanoLSI, Kanazawa Univ.)
2:40 PM - 3:00 PM

[K606-2pm-04] Synthesis Stable and Crystalline Covalent Triazine Frameworks from CO_2
○Siquan Zhang[2], Loris Lombardo[1], Satoshi Horike[1,2] (1. Institute for Advanced Study, Kyoto University, 2. Graduate School of Engineering, Kyoto University)
3:00 PM - 3:20 PM

[K606-2pm-05] Spatial distribution of interaction forces derived from hydrophobic pockets visualized by 3D-AFM in liquid
○Moe Ogasawara[1], Rina Okumura[2], Masayuki Morimoto[3], Hitoshi Asakawa[1,2,3,4] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. College of Science and Engineering, Kanazawa University, 3. Nanomaterials Research Institute (NanoMaRi), Kanazawa University, 4. Nano Life Science Institute(WPI-NanoLSI), Kanazawa University)
3:20 PM - 3:40 PM

Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry- | Oral B

[K606-2vn] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Hiroshi Sato, Yuichiro Watanabe
4:10 PM - 6:20 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-2vn-01] Control of Guest Uptake/release Rates of Macrocyclic Cobalt(III) Dinuclear Metallohosts Having Aromatic Bridging Ligands
○Ryo Sudo[1], Yoko Sakata[1,2], Shigehisa Akine[1,2] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa University)
4:10 PM - 4:30 PM

[K606-2vn-02] Kinetic Control of Formation and Structural Conversion of Metallonanobelts Based on Interaction with Oligoethers
○Ryosuke Nakamura[1], Yoko Sakata[1,2], Shigehisa Akine[1,2] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute Kanazawa University)
4:30 PM - 4:50 PM

[K606-2vn-03] Real-time confocal imaging of formation and dynamics of a dipeptide-based coacervate
○Ryou Kubota[1], Yuchong Liu[1], Taro Hiroi[1], Itaru Hamachi[1,2] (1. Kyoto University, 2. JST ERATO)
4:50 PM - 5:10 PM

[K606-2vn-04] Repeated elongation and shrinkage of supramolecular fibers induced by surfactant micelle
○Torigoe Shogo[1], Kubota Ryou[1], Nagao Kazutoshi[1], Hamachi Itaru[1,2] (1. The Univ. of Kyoto, 2. JST-ERATO)
5:10 PM - 5:30 PM

[K606-2vn-05] Helical Charged π-Electronic Systems That Form Ion-Pairing Assemblies
○Rima Sengupta[1], Haruka Hashimoto[1], Yohei Haketa[1], Hiromitsu Maeda[1] (1. Ritsumeikan University)
5:40 PM - 6:00 PM

[K606-2vn-06] Catalyst-Free Click Reaction of Naphthalenediimides with Amines in Supramolecular Fibers

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○Minghan Tan[1], Masayuki Takeuchi[1], Atsuro Takai[1] （1. National Institute for Materials Science ）

6:00 PM - 6:20 PM

K602

Academic Program [Oral B] | 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry- | Oral B

[K602-2pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Eiji Shirakawa, Hajime Maeda
1:10 PM - 3:40 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-2pm-01] Improving the Efficiency of Triplet Dynamic Nuclear Polarization of Biomolecules Based on Zero-Field Splitting Control of Polarizing Agent Molecules

○Tomoyuki HAMACHI[1], Keita SAKAMOTO[1], Kenichiro TATEISHI[2], Tomohiro UESAKA[2], Nobuhiro YANAI[1,3] （1. Grad. Sch. Eng., Kyushu Univ., 2. RIKEN Nishina Center for Accelerator-Based Science, 3. FOREST, JST）

1:10 PM - 1:30 PM

[K602-2pm-02] Blue light driven C-C bond formation reaction via α-thiomethyl radicals derived from thioanisole derivatives

○Pijush Kanti Roy[1], Masahito Kodera[1], Yutaka Hitomi[1] （1. Doshisha Univ.）

1:30 PM - 1:50 PM

[K602-2pm-03] Dye and electron donor hybridized systems towards molecular probes using chemically induced dynamic nuclear polarization

○Koki Nishimura[1], Nobuhiro Yanai[1,2] （1. Grad. Sch. Eng., Kyushu Univ., 2. FOREST, JST）

1:50 PM - 2:10 PM

[K602-2pm-04] C– H Oxygenation by Simultaneous UV-Vis Light and Microwave Irradiation with Chlorine Dioxide

○Yuki Itabashi[1], Ai Sunami[1], Kei Ohkubo[1] （1. Osaka Univ.）

2:20 PM - 2:40 PM

[K602-2pm-05] Catalytic DDQ Photocatalysis: Direct Arene C-N Bond Formation

○Kaii Nakayama[1], Hidehiro Kamiya[1], Yohei Okada[1] （1. Tokyo University of Agriculture and Technology）

2:40 PM - 3:00 PM

[K602-2pm-06] Reductive Coupling Reaction between Aryl Bromides and Alkyl Pyridinium Salts Using Solid-state Photoredox Reaction

○Ryota Isshiki[1,2], Koji Kubota[1,2], Hajime Ito[1,2] （1. WPI-ICReDD, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University）

3:00 PM - 3:20 PM

[K602-2pm-07] Photochemical reductive cleavage of C-O bond of alkyl aryl ethers using carbazole photosensitizer activated by cesium carbonate

○Tatsushi Yabuta[1], Masahiko Hayashi[1], Ryosuke Matsubara[1] （1. Kobe university）

3:20 PM - 3:40 PM

K703

Academic Program [Oral B] | 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds- | Oral B

[K703-2am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Hiroaki Imoto, Kei Muto
9:00 AM - 11:30 AM K703 (K703, Lecture Hall Bldg. [7F])

[K703-2am-01] Skeletal Rearrangement of a Boron-Containing π-Conjugated Macrocycles Caused by Boron– Olefin Proximity Interaction

○Yukihiro Murata[1], Yoshiaki Shoji[1], Takanori Fukushima[1] （1. CLS, Tokyo Tech.）

9:00 AM - 9:20 AM

[K703-2am-02] Synthesis of Unsymmetric Bisphosphine Derivatives by the Strain-Release Three-Component Reaction of Propellane

○Hideaki Takano[1,2], Hitomi Katsuyama[1,2], Hiroki Hayashi[1,2], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2] （1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.）

9:20 AM - 9:40 AM

[K703-2am-03] Photoredox Dearomative Nucleophilic Addition of CO_2 Radial Anion to (Hetero)aromatics

○Saeesh Rajendra Mangaonkar[1,2], Hiroki

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Hayashi[1,2], Hideaki Takano[1,2], Wataru Kanna[3], Yu Harabuchi[1,2,3], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)
9:40 AM - 10:00 AM

[K703-2am-04] Tailor-made Synthesis of Fully and Differently Arylated Alkenes

○Kimiya Wada[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)
10:10 AM - 10:30 AM

[K703-2am-05] A Novel Jacobsen Reaction of 1,8-Diiodonaphthalene Induced by Ring Strain

○Kento Iwai[1], Noa Nishiguchi[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)
10:30 AM - 10:50 AM

[K703-2am-06] Regiodivergent Synthesis of Brominated Thienylpyridines Overriding the Inherent Substrate Bias

○Masahiro Hosoya[1], Kentaro Okano[1], Atsunori Mori[1,2] (1. Department of Chemical Science and Engineering, Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University)
10:50 AM - 11:10 AM

[K703-2am-07] Synthesis of π-Expanded Amines via Single-Electron Oxidant-Catalyzed Denitrogenative Benzannulation of Ynamine with Phthalazine

○Yasuhiro Okuda[1], Takuma Sato[1], Sou Takebe[1], Tomoki Inoue[1], Akihiro Orita[1] (1. Fac. of Eng., Okayama Univ. of Science)
11:10 AM - 11:30 AM

Academic Program [Oral B] | 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds- | Oral B

[K703-2pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Okano Kentaro, Tsuyoshi Mita
1:10 PM - 3:40 PM K703 (K703, Lecture Hall Bldg. [7F])

[K703-2pm-01] Peripheral Functionalization of Antiaromatic 5,15-Dioxaporphyrin

○Jiping Hao[1], Shigeki Mori[2], Soji Shimizu[1] (1. Graduate School of Engineering, Kyushu University, 2. Advanced Research Support Center (ADRES), Ehime University)
1:10 PM - 1:30 PM

[K703-2pm-02] Development of Heteroatom-Embedding Annulative π-Extension Reaction

○Kou Kawahara[1], Hideto Ito[1], Kenichiro Itami[1] (1. Nagoya University)
1:30 PM - 1:50 PM

[K703-2pm-03] Asymmetric Synthesis of Chiral Sulfimides Through the *O*-Alkylation of Chiral Sulfinamides

○Saori Tsuzuki[1], Taichi Kano[2] (1. Graduate School of Scienece, Kyoto University, 2. Graduate School of Engineering, Tokyo University of Agriculture and Technology)
1:50 PM - 2:10 PM

[K703-2pm-04] Deoxygenative Functionalization of Diarylketones

○Miki B Kurosawa[1], Moriaki Sakihara[1], Kenta Kato[1], Kei Muto[1], Junichiro Yamaguchi[1] (1. Waseda University)
2:10 PM - 2:30 PM

[K703-2pm-05] C_3-Symmetric Cage-shaped Phosphites: Structure Controls of Their Basicity, Chiral Environment, and Application to Rh-Catalyzed Asymmetric 1,4-Addition.

○Xiao Liu[1], Akihito Konishi[1], Makoto Yasuda[1] (1. Osaka University)
2:40 PM - 3:00 PM

[K703-2pm-06] Synthesis and Structure of [8]Heterocirculene by Use of Intramolecular Coupling [7]Thiaheterohelicene Derivatives

○Tatsuya Nakanishi[1], Hideji Osuga[1], Hidefumi Sakamoto[1] (1. Grad. Sch. Sys. Eng., Wakayama Univ.)
3:00 PM - 3:20 PM

[K703-2pm-07] Novel Pathways to Pentafluorosulfanylated Compounds via Thiolation and Oxidative Fluorination

○Yue Liu[1], Tim Gatzenmeier[1], Takashi Okazoe[1,2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. AGC Inc.)
3:20 PM - 3:40 PM

K705

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Academic Program [Oral B] | 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology- | Oral B

[K705-2pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Shintaro Kawamura, Takatsugu Murata
1:10 PM - 3:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-2pm-01] Stereoselective Addition of Sulfenate Species to Electrophiles as a Versatile Synthetic Method of Chiral Sulfoxides
○Jian Zhang[1], Keisuke Suzuki[2], Ken Ohmori[1] (1. Department of Chemistry, School of Science, Tokyo Institute of Technology., 2. Institute of Innovative Research, Tokyo Institute of Technology.)
1:10 PM - 1:30 PM

[K705-2pm-02] The Effect of Water in the Esterification Mediated by MNBA, Highly Efficient Dehydration Condensation Reagent
Takatsugu Murata[1], ○Nao Takabayashi[1], Isamu Shiina[1] (1. Tokyo University of Science)
1:30 PM - 1:50 PM

[K705-2pm-03] *Z*-Enamide Synthesis by Stereoselective Radical Fluoroalkylation Reaction
○Takuma Tagami[1], Daisuke Sekine[2], Yuma Aoki[1], Shintaro Kawamura[1,2], Mikiko Sodeoka[1,2] (1. RIKEN CSRS, 2. RIKEN CPR)
1:50 PM - 2:10 PM

[K705-2pm-04] Carboxylic Acid-Cooperative-Ru(bpga)-Catalyzed Highly Site-Selective C– H Oxygenation
○Daiki Doiuchi[1], Nanako Shimoda[1], Tatsuya Uchida[1,2,3,4] (1. Grad. Sch. Sci., Kyushu Univ., 2. Fac. Arts and Sci., Kyushu Univ., 3. WPI-I2CNER, Kyushu Univ., 4. JST-PRESTO)
2:10 PM - 2:30 PM

[K705-2pm-05] Visible-Light-Induced Carboamination of Styrenes with Carboxylic Acids and (Diarylmethylene)aminobenziodoxolones
○Daichi Okumatsu[1], Kensuke Kiyokawa[1], Satoshi Minakata[1] (1. Graduate School of Engineering, Osaka University)
2:40 PM - 3:00 PM

[K705-2pm-06] Tandem Enantioselective [2+2], [3+2] and [4+2] Cycloaddition Reactions of In Situ-generated *N*-Allenoylpyrazoles Induced by Chiral π – Cu(II) Catalysts
○Weiwei Guo[1], Masahiro Hori[1], Yoshihiro Ogura[1], Kazuki Nishimura[1], Kazuaki Ishihara[1] (1. Nagoya University)
3:00 PM - 3:20 PM

[K705-2pm-07] Enantioselective Radical Cation [2+2] and [4+2] Cycloadditions Using Chiral Iron(III) Catalyst with Photoirradiation
○Kei Katagiri[1], Haruna Kato[1], Shuhei Ohmura[1], Takahiro Horibe[1], Kazuaki Ishihara[1] (1. Nagoya University)
3:20 PM - 3:40 PM

Academic Program [Oral B] | 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology- | Oral B

[K705-2vn] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Muhammet Uyanik, Yuuya Kawasaki
4:10 PM - 6:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-2vn-01] Magnesium(II) and Sodium(I) Bisphenoxide Catalysts for Transesterification of Methyl (Meth)acrylate and Their Reaction Mechanisms
○Kazumasa Kon[1], Xue Zhao[2], Manussada Ratanasak[3], Chie Joko[2], Jun-ya Hasegawa[3], Kazuaki Ishihara[2] (1. Nagoya University Venture Business Laboratory, 2. Nagoya University, 3. Hokkaido University)
4:10 PM - 4:30 PM

[K705-2vn-02] Development of DACN based Multi-Molecular Connector and Its Application for Hybridization of Peptides
○Tomoya Hayashibara[1], Yuuki Seto[1], Yuutaro Taniguchi[1], Kazunobu Igawa[2], Kawasaki Yuuya[3], Katsuhiko Tomooka[1,3] (1. IMCE, Kyushu Univ., 2. FAST, Kumamoto Univ., 3. IGSES, Kyushu Univ.)
4:30 PM - 4:50 PM

[K705-2vn-03] Synthesis of polyhalogenated molecules by a general Cu-catalyzed halo-halofluoroalkylation of alkenes/alkynes with fluorinated carboxylic anhydrides
○SUBRATA MUKHERJEE[1], YUMA AOKI[1], SHINTARO KAWAMURA[1,2], MIKIKO SODEOKA[1,2] (1. RIKEN CSRS, 2. RIKEN CPR)
4:50 PM - 5:10 PM

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[K705-2vn-04] *E*-Selective Elongation Reaction of Aldehydes by Weinreb Amide-type Horner– Wadsworth– Emmons Reagent

○Hisazumi Tsutsui[1], Takatsugu Murata[1], Shintaro Hiraishi[1], Daiki Usukura[1], Hiroki Okano[1], Isamu Shiina[1] （1. Tokyo University of Science）

5:10 PM - 5:30 PM

[K705-2vn-05] Et_2Zn-Mediated Cross-coupling Reactions between Dibromoketones and Monobromo Carbonyl Compounds

○Aika Takeshima[1,2], Taichi Kano[1] （1. Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2. Graduate School of Science, Kyoto University）

5:40 PM - 6:00 PM

[K705-2vn-06] Design and synthesis of novel bifunctional organocatalysts for an enantioselective rearrangement of α-acyloxy-β-keto sulfides to α-acyloxy thioesters

○Julie Kong[1,2], Chloée Bournaud[1], Yasuhiro Yamashita[2], Shū Kobayashi[2], Giang Vo-Thanh[1] （1. Université Paris-Saclay, Institut de Chimie Moléculaire et des Matériaux d'Orsay, 2. The University of Tokyo, Department of Chemistry, School of Science）

6:00 PM - 6:20 PM

[K705-2vn-07] Development of Efficient Synthetic Method of Latanoprost Using an Organocatalyst

○Genki Kawauchi[1], Yurina Suga[1], Shunsuke Toda[1], Yujiro Hayashi[1] （1. Tohoku Univ.）

6:20 PM - 6:40 PM

D1443

Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B

[D1443-2am] 16. Natural Products Chemistry, Chemical Biology

Chair: Akihiro Ogura, Chikara Dohno
9:00 AM - 11:10 AM D1443 (1443, Bldg. 14 [4F])

[D1443-2am-01] Bioconjugation of Au_{25} nanocluster to trastuzumab

○Katarzyna Joanna Malawska[1], Shinjiro Takano[2], Kounosuke Oisaki[4], Haruaki Yanagisawa[3], Masahide Kikkawa[3], Tatsuya Tsukuda[2], Motomu Kanai[1] （1. Grad. Sch. Pharm. Sci., The Univ. of Tokyo, 2. Grad. Sch. Sci., The Univ. of Tokyo, 3. Grad. Sch. Med., The Univ. of Tokyo, 4. IRC3, AIST）

9:00 AM - 9:20 AM

[D1443-2am-02] Chemical reaction-driven “organ-to-organ” transfer of glycan-modified-HSA in living mouse

○Kenshiro Yamada[1], Tatsuya Kobayashi[1], Akari Mukaimine[2], Ambara Rachmat PRADIPTA[1], Katsunori Tanaka[1,2] （1. Tokyo Institute of Technology,School of Materials and Chemical Technology, Department of Chemical Science and Engineering, 2. RIKEN Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory）

9:20 AM - 9:40 AM

[D1443-2am-03] Development of novel psoralen-introduced triplex-forming oligonucleotides for the expansion of their target genome sequences

○Yu Mikame[1], Honoka Eshima[1], Juki Nakao[1], Tsuyoshi Yamamoto[1], Yoshiyuki Hari[2], Chikara Dohno[3], Takehiko Wada[4], Asako Yamayoshi[1] （1. Grad. Sch. Biomed. Sci., Nagasaki Univ, 2. Fac. of Pharm. Sci., Tokushima Bunri University, 3. SANKEN., Osaka Univ, 4. IMRAM., Tohoku Univ）

9:40 AM - 10:00 AM

[D1443-2am-04] Development of fluorescent probes for selective detection of intracellular free magnesium ion

○Akihiro Sakama[1], Rei Kumada[1], Yutaka Shindo[1], Naoko Iwasawa[1], Daniel Citterio[1], Kotaro Oka[1], Yuki Hiruta[1] （1. Keio University）

10:10 AM - 10:30 AM

[D1443-2am-05] Control of RNA repeat foci formation by photoswitchable RNA binding ligands

○Yusuke Fujiwara[1,2], Tomonori Shibata[1,2], Chikara Dohno[1,2], Kazuhiko Nakatani[1,2] （1. SANKEN, Osaka University, 2. CREST, JST）

10:30 AM - 10:50 AM

[D1443-2am-06] Targeted α-ray therapy using the reaction between acrolein and azide

○Yudai Ode[1], Ambara Rachmat PRADIPTA[1],

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Katsunori TANAKA[1,2] (1. Tokyo Institute of Technology, School of Materials and Chemical Technology, Department of Chemical Science and Engineering, 2. RIKEN Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory)
10:50 AM - 11:10 AM

Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B

[D1443-2pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Shoji Kobayashi, Takaaki Mitsuhashi
2:00 PM - 3:40 PM D1443 (1443, Bldg. 14 [4F])

[D1443-2pm-01] Study on enantio-selective enzymatic halocyclization using the CS method
○Takaaki Mitsuhashi[1], Jiazhuo Chen[2,1], Makoto Fujita[2,1] (1. IMS, 2. The Univ. of Tokyo)
2:00 PM - 2:20 PM

[D1443-2pm-02] Functional and structural analysis of the terpene synthase found from the genome of giant virus
○Youngcheol Jung[1], Takaaki Mitsuhashi[2], Miki Senda[3], Sota Sato[1], Toshiya Senda[3], Makoto Fujita[1,2] (1. Graduate School of Engineering, The Univ. of Tokyo, 2. Institute for Molecular Science, 3. High Energy Accelerator Research Organization)
2:20 PM - 2:40 PM

[D1443-2pm-03] Synthetic study of oxidative metabolites in mushrooms starting from ergosterol
○Edric Wilbert[1], Saki Nagayasu[1], Tomoka Taguri[1], Shoji Kobayashi[1] (1. Osaka Institute of Technology)
2:40 PM - 3:00 PM

[D1443-2pm-04] Development of anti-HBV agents through divergent and programmable synthesis of skeletally diverse alkaloidal scaffolds bearing Michael acceptors
○Nobuto Kaneko[1], Hiroki Kubota[2], Misao Himeno[1], Taketomo Kido[1], Atsushi Miyajima[1], Hiroki Oguri[1] (1. The University of Tokyo, 2. Tokyo University of Agriculture and Technology)
3:00 PM - 3:20 PM

[D1443-2pm-05] Development of Catalytic Asymmetric Mukaiyama-Michael Reaction and Its Application to Enantioselective Total Synthesis of Sesquiterpene Lactones
○Ryoji Sugiyama[1], Masahisa Nakada[1] (1. Waseda University)
3:20 PM - 3:40 PM

E1662

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[E1662-2am] 17. Biofunctional Chemistry, Biotechnology

Chair: Noriyuki Uchida, Shinya Hanashima
9:00 AM - 11:30 AM E1662 (1612, Bldg. 16 [1F])

[E1662-2am-01] Investigation of the relationship between hydration behavior and structural characteristics of carbohydrates by solution NMR measurements and molecular simulations
○Hiroaki Tatsuoka[1], Takumi Yamaguchi[1,2,3] (1. School of Materials Science, Japan Advanced Institute of Science and Technology, 2. Graduate School of Pharmaceutical Sciences, Nagoya City University, 3. Exploratory Research Center on Life and Living Systems (ExCELLS), National Institutes of Natural Sciences)
9:00 AM - 9:20 AM

[E1662-2am-02] Modification of membrane properties of small extracellular vesicle exosomes using lipid exchange
○Shinya Hanashima[1,2], Tomokazu Yasuda[1], Kazuya Kabayama[1], Koichiro M Hirosawa[3], Kenichi G. N. Suzuki[3] (1. Graduate School of Science, Osaka University, 2. Department of Engineering, Tottori University, 3. iGCORE, Gifu University)
9:20 AM - 9:40 AM

[E1662-2am-03] Development of Cancer-targeting Agents Based on Near-infrared-absorbing Diradical-platinum Complexes toward Photothermal Therapy
○Ryota Sawamura[1], Atsuko Masuya-Suzuki[2], Hao Thi Tran[3], Long Binh Vong[3], Yukio Nagasaki[3], Nobuhiko Iki[1] (1. Grad. Sch. Env.

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Stud., Tohoku Univ., 2. Grad. Sch. Sci. Tech. Innov., Yamaguchi Univ., 3. Grad. Sch. Pure Appl. Sci., Univ. of Tsukuba)
9:40 AM - 10:00 AM

[E1662-2am-04] Fabrication and Evaluation of Drug-Wrapped Adhesive Nanomaterials with epidermal regeneration ability
○Yota Shiba[1], Genta Yagami[1], Tadahiro Fuyama[1], Hideaki Sumiyoshi[2], Yutaka Inagaki[2], Yosuke OKamura[1,3] (1. Grad. Sch. of Eng., Tokai Univ., 2. Tokai Univ. Sch. of Med., 3. Micro/Nano Tech. Center, Tokai Univ.)
10:00 AM - 10:20 AM

[E1662-2am-05] Photoresponsive Membrane Deformation for Highly Efficient Encapsulation of Biomacromolecules and Its Application to *in vivo* Phage Display Method
○Noriyuki Uchida[1], Yunosuke Ryu[1], Teruhiko Matsubara[2], Toshinori Sato[2], Yasutaka Anraku[3], Takahiro Muraoka[1,4] (1. Tokyo Univ. Agri. and Tech., 2. Keio University, 3. The Univ. of Tokyo , 4. KISETC)
10:30 AM - 10:50 AM

[E1662-2am-06] Development of an amphiphilic peptide that self-assembles into helical fibers and controlling of bioadhesion properties by light
○Atsuya Yaguchi[1], Noriyuki Uchida[1], Itsuki Ajioka[2,3], Takahiro Muraoka[1,3] (1. Tokyo Univ. of Agri. and Tech., 2. Tokyo Med. and Dent. Univ., 3. KISTEC)
10:50 AM - 11:10 AM

[E1662-2am-07] Phase transfer of co-assembled peptide supramolecules
○Rie Wakabayashi[1], Hiroki Obayashi[1], Noriho Kamiya, Masahiro Goto (1. Faculty of Engineering, Kyushu University)
11:10 AM - 11:30 AM

E1661

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[E1661-2am] 17. Biofunctional Chemistry, Biotechnology

Chair: Tomohiro Doura, Tomonori Tamura
9:00 AM - 11:30 AM E1661 (1611, Bldg. 16 [1F])

[E1661-2am-01] Development of fast blinking fluorophores for real-time single-molecule super-resolution imaging
○Bochao Li[1], Toshiyuki Kowada[1], Takahiro Fujiwara[2], Shin Mizukami[1] (1. Tohoku Univ., 2. Kyoto Univ.)
9:00 AM - 9:20 AM

[E1661-2am-02] Optical regulation of intracellular protein localization using photochromic protein dimerizers
○Toshizo Sato[1], Toshiyuki Kowada[1,2], Satoshi Hamaguchi[1], Toshitaka Matsui[1,2], Shin Mizukami[1,2] (1. Graduate School of Life Sciences, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)
9:20 AM - 9:40 AM

[E1661-2am-03] pH-Responsive and Peptide Sequence-Specific Dynamic Covalent Bond Chemistry
○Yuto Ohno[1], Alexander Vinogradov[1], Hiroaki Suga[1] (1. The University of Tokyo)
9:40 AM - 10:00 AM

[E1661-2am-04] Discovery of CFA-type Covalent Inhibitors that Modulate Activity of Beta Oxidation Pathway Based on FBDD Approach
○ruikang Yin[1], Kazuya Inoue[1], Shohei Uchinomiya[1], Akio Ojida[1] (1. kyushu Universitity)
10:00 AM - 10:20 AM

[E1661-2am-05] Development of second generation NASA warhead for covalent inhibitors
○Masaharu Kawano[1], Shunsuke Murakawa[1], Tomonori Tamura[1], Itaru Hamachi[1,2] (1. Graduate School of Engineering, Kyoto University, 2. ERATO JST)
10:30 AM - 10:50 AM

[E1661-2am-06] New developments in *FixEL* method incorporating chemical sensors
○Takeharu Mino[1], Hiroshi Nonaka[1,2], Seiji Sakamoto[2], Mamoru Ishikawa[2], Itaru Hamachi[1,2] (1. Graduate School of Engineering, Kyoto University, 2. JST ERATO)

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10:50 AM - 11:10 AM

[E1661-2am-07] Chemogenetic regulation of adenosine A_{2A} receptor focusing on subtype selectivity of the antagonists

○Yuma Matsuoka[1], Tomohiro Doura[1], Shigeki Kiyonaka[1] (1. Nagoya University)

11:10 AM - 11:30 AM

E1662

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[E1662-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Satoshi Abe, Takahiro Muraoka
1:10 PM - 3:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-2pm-01] Modulation of the activity of enzyme assembled on DNA scaffold

○Peng Lin[1], Tomohiko Hayashi[2], Huyen Dinh[3], Eiji Nakata[1], Masahiro Kinoshita [1,4], Takashi Morii[1] (1. Kyoto University, 2. Niigata University, 3. Humboldt University of Berlin, 4. Chiba University)

1:10 PM - 1:30 PM

[E1662-2pm-02] Effect of charge around thiol group on promoting disulfide bonds-containing protein native structure formation

○Mai Kitamura[1], Takahiro Muraoka[1,2] (1. Tokyo University of Agriculture and Technology, 2. KISTEC)

1:30 PM - 1:50 PM

[E1662-2pm-03] Development of high-active protein folding promotors like enzyme

○Shunsuke Okada[1], Masaki Okumura[2], Takahiro Muraoka[1,3] (1. Tokyo Univ. of Agr. and Tech., 2. Tohoku Univ., 3. KISTEC)

1:50 PM - 2:10 PM

[E1662-2pm-04] In-cell protein crystal engineering for structure determination of intrinsically disordered protein

○Mariko Kojima[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)

2:10 PM - 2:30 PM

[E1662-2pm-05] Crystallization of ferritin directly from E. Coli cell lysate and structure determination.

○BASUDEV MAITY[1], Koki Date[1], Satoshi Abe[1], Takafumi Ueno[1] (1. TOKYO INSTITUTE OF TECHNOLOGY)

2:40 PM - 3:00 PM

[E1662-2pm-06] Engineering of in-cell protein crystals for the construction of solid materials

○Satoshi Abe[1], Junko Tanaka[1], Yuto Nakasuji[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)

3:00 PM - 3:20 PM

[E1662-2pm-07] *In-Cell* Engineering of Protein Crystals into Hybrid Solid Catalysts for Artificial Photosynthesis

○Tiezheng Pan[1], Basudev Maity[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)

3:20 PM - 3:40 PM

E1661

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[E1661-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Shuntaro Takahashi, Fumitaka Hashiya
1:10 PM - 3:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-2pm-01] Genome scale DNA assembly using modified primers

○Fumitaka Hashiya[1,6], Kaoru Onda[2], Kohei Nomura[2], Gao Yiuno[2], Hirotaka Murase[2], Kosuke Nakamoto[2], Masahito Inagaki[2], Haruka Hiraoka[2], Naoko Abe[2], Yasuaki Kimura[2], Natsuhisa Oka[3,4,6], Goro Terai[5,6], Kiyoshi Asai[5,6], Hiroshi Abe[1,2,6,7] (1. Nagoya University, Research Center for Materials Science, 2. Graduate School of Science, Nagoya University, 3. Department of Chemistry and Biomolecular Science, Gifu University, 4. Institute for Glyco-core Research (iGCORE), Gifu University, 5. Department of Computational Biology and Medical Sciences, University of Tokyo, 6. CREST, Japan Science and Technology Agency, 7. Institute for Glyco-core Research (iGCORE), Nagoya University)

1:10 PM - 1:30 PM

[E1661-2pm-02] Development of a DNA assembly technology using modified nucleic acids

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○Mikiya Kase[1], Masahito Inagaki[1], Haruka Hiraoka[1], Humitaka Hashiya[1], Naoko Abe[1], Yasuaki Kimura[1], Hiroshi Abe[1] (1. The Univ. of Nagoya)
1:30 PM - 1:50 PM

[E1661-2pm-03] Light-triggered control of rolling circle transcription aiming for RNA interference inside cells
○Yusuke Yonamine[1], Wei Jie Cheah[2], Hideyuki Mitomo[1], Kuniharu Ijiro[1] (1. RIES, Hokkaido Univ., 2. Grad. Sch. Life Sci., Hokkaido Univ.)
1:50 PM - 2:10 PM

[E1661-2pm-04] Improvement of chemical pseudo-primer extension reaction of L-*a*TNA based on reaction mechanism analysis
○Hikari Okita[1], Keiji Murayama[1], Hiroyuki Asanuma[1] (1. Nagoya Univ.)
2:10 PM - 2:30 PM

[E1661-2pm-05] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (87) : Prediction of ligand binding by hydration analysis of guanine quadruplex using high pressure
○Shuntaro Takahashi[1], Saki Matsumoto[1], Tatsuya Ohyama[1], Sudipta Bhowmik[2,3], Naoki Sugimoto[1,4] (1. Konan Univ. FIBER, 2. Calcutta Univ., 3. SBV Univ. MGMARI, 4. Konan Univ. FIRST)
2:40 PM - 3:00 PM

[E1661-2pm-06] Development of methods for the efficient ligation of staple nicks in DNA origami
○Arivazhagan Rajendran[1], Kirankumar Krishnamurthy[1], Eiji Nakata[1], Takashi Morii[1] (1. Kyoto University)
3:00 PM - 3:20 PM

[E1661-2pm-07] Photocatalytic profiling of G4 DNA-interacting proteins
○Ahmed Mostafa Abdelhady[1,2], Kazumitsu Onizuka[1,2], Tatsuki Masuzawa[3], Shinichi Sato[4], Keita Nakane[4], Takanori Oyoshi[3], Fumi Nagatsugi[1,2] (1. Graduate School of Science, Tohoku University, 2. IMRAM, Tohoku University, 3. Graduate School of Science and Technology, Shizuoka University, 4. FRIS, Tohoku University)
3:20 PM - 3:40 PM

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[E1661-2vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Takafumi Furuhata, Tomoshige Fujino
4:10 PM - 6:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-2vn-01] Intracellular artificial construction of droplets based on an amphiphilic YK peptide tag and client protein enrichment
○Masahiro Hashimoto[1], Takayuki Miki[1], Hiroki Takahashi[1], Sae Nakayama[1], Hisakazu Mihara[1] (1. Tokyo Institute of Technology, School of Life Science and Technology)
4:10 PM - 4:30 PM

[E1661-2vn-02] Pattern enrichment analysis for efficient peptide ligands selection from a phage library
○Takayuki Miki[1], Keigo Namii[1], Kenta Seko[1], Shota Kakehi[1], Hisakazu Mihara[1] (1. School of Life Science and Technology, Tokyo Instituite of Technology)
4:30 PM - 4:50 PM

[E1661-2vn-03] Improvement of the diversity of monobody and macrocyclic peptide libraries in mRNA display technology
○Shun Umemoto[1], Taishi Kondo[1], Tomoshige Fujino[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Nagoya University, 2. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)
4:50 PM - 5:10 PM

[E1661-2vn-04] Anti-azobenzene artificial antibodies for photocontrollable binding
○Tomoshige Fujino[1], Mamoru Funane[1], Naoya Murata[1], Tatsuyuki Yoshii[2], Gosuke Hayashi[1], Shinya Tsukiji[2], Hiroshi Murakami[1,3] (1. Graduate School of Engineering, Nagoya University, 2. Graduate School of Engineering, Nagoya Institute of Technology, 3. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)
5:10 PM - 5:30 PM

[E1661-2vn-05] A machine learning guided thiopeptide library design for the discovery of de novo

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thiopeptide binders

○Jun Shi Chang[1], Alexander Vinogradov[1], Yuki Goto[1], Hiroaki Suga[1] （1. Tokyo Univeristy）

5:40 PM - 6:00 PM

[E1661-2vn-06] Enzyme mediated one-pot synthesis of branched polyubiquitin (K48/K63) chain via photo-induced stepwise synthesis

○Phebee Angeline Devadasan Racheal[1], Takafumi Furuhata[1], Iori Murayama[1], Usano Toyoda[1], Akimitsu Okamato[1] （1. The Univ. of Tokyo）

6:00 PM - 6:20 PM

[E1661-2vn-07] Regulation of enzyme activity by perturbation to conformational change process using antibody mimetic "monobody"

○Ibuki Nakamura[1], Hiroshi Amesaka[2], Mizuho Hara[2], Kento Yonezawa[1], Hironari Kamikubo[1], Shun-ichi Tanaka[2], Shun Hirota[1], Takashi Matsuo[1] （1. Division of Materials Science, Nara Inst. Sci. Tech., 2. Department of Biomolecular Chemistry, Kyoto Prefectural University）

6:20 PM - 6:40 PM

K304

Academic Program [Oral B] | 18. Polymer | Oral B

[K304-2am] 18. Polymer

Chair: Shohei Saito, Yusuke Tsutsui

9:00 AM - 11:20 AM K304 (K304, Lecture Hall Bldg. [3F])

[K304-2am-01] Self-assembly of 2D Conjugated Covalent Organic Framework into 1D Electronically Conductive Nanotubes

○zhuowei LI[1], Takahiro Tsuneyuki[1], Samrat Ghosh[1], Takumi Nakazato[2], Masahiro Odawara[2], Wakana Matsuda[1], Masaki Nobuoka[1], Bin Chen[1], Rajendra Prasad Paitandi[1], Yusuke Tsutsui[1], Takayuki Tanaka[1], Masayuki Suda[1], Yoshihiro Miyake[2], Hiroshi Shinokubo[2], Shu Seki[1] （1. Kyoto University, 2. Nagoya University）

9:00 AM - 9:20 AM

[K304-2am-02] Fluorescent probe showing a two-step spectral change in response to polymer chain tension and strain-induced crystallization

○Kensuke Suga[1], Mitsuo Hara[2], Takuya Yamakado[1], Shohei Saito[1] （1. Grad. Sch. of Sci., Kyoto Univ., 2. Grad. Sch. of Eng., Nagoya Univ.）

9:20 AM - 9:40 AM

[K304-2am-03] Induction and Memory of Macromolecular Helicity: Kinetic Analysis Based on Helix Inversion Model

○Takaya Fujie[1], Takeshi Yamamoto[1], Michinori Suginome[1] （1. Kyoto University ）

9:40 AM - 10:00 AM

[K304-2am-04] The Effects of Dehydration Temperature and Monomer Chirality on Primitive Polyester Synthesis and Microdroplet Assembly

Rehana Afrin[1], Chen Chen[1], Davide Sarpa[2], Mahendran Sithamparam[3], Ruiqin Yi[1], Chaitanya Giri[4], Irena Mamajanov[1], H James Cleaves[1,5,6], Kuhan Chandru[3], ○Tony Z Jia[1,5] （1. Earth-Life Science Institute, Tokyo Institute of Technology, 2. The University of Southampton, 3. Space Science Centre (ANGKASA), Institute of Climate Change, National University of Malaysia, 4. Research and Information System for Developing Countries (RIS), 5. Blue Marble Space Institute of Science, 6. Earth and Planets Laboratory, Carnegie Institution of Washington）

10:00 AM - 10:20 AM

[K304-2am-05] Excessive molecular structure and properties determination of different types of Alkyl sulfonated polyimide (ASPI) with universal neural network potential (uNNP)

○Attila Taborosi[1], Michihisa Koyama[1], Yuki Nagao[2], Nobuyuki Zettsu[1] （1. Shinshu University, 2. Japan Advance Institute of Science and Technology）

10:20 AM - 10:40 AM

[K304-2am-06] Formation of latex films with high toughness

○Yuma Sasaki[1], Yuichiro Nishizawa[1], Hayato Suzuki[1], Takuma Kureha[3], Kazuya Uenishi[4], Kazuko Nakazono[5], Toshikazu Takata[6], Daisuke Suzuki[1,2] （1. Grad. Sch. of Textile Sci. &Tech.,

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Shinshu Univ., 2. RISM, Shinshu Univ., 3. Grad. Sch. of Sci. and Tech., Hirosaki Univ., 4. Yokohama Rubber Co., Ltd., 5. Dept. of Chemical Sci. and Engineering, Tokyo Tech, 6. Grad. Sch. of Advanced Sci. and Engineering, Hiroshima Univ.)
10:40 AM - 11:00 AM

[K304-2am-07] Ultrahighly Refractive and Degradable Thiourea Polymers with Dense and Multiple Intermolecular Hydrogen Bonds
○Seigo Watanabe[1], Kenichi Oyaizu[1] (1. Waseda Univ.)
11:00 AM - 11:20 AM

B445

Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B

[B445-2am] 19. Colloid and Interface Chemistry

Chair: Hirokazu Kobayashi, Kenshi Matsumoto
9:00 AM - 11:30 AM B445 (445, Bldg. 4 [4F])

[B445-2am-01] Flow Synthesis of 15 Elements Alloy Nanoparticles and Their Alcohol Electrooxidation Properties
○Hiroki Minamihara Minamihara[1], Kohei Kusada[1,2], Tomokazu Yamamoto[3], Takaaki Toriyama[3], Syo Matsumura[3], Osami Sakata[4], Shogo Kawaguchi[4], Yoshiki Kubota[5], Hiroshi Kitagawa[1] (1. Kyoto University, 2. JST PRESTO, 3. Kyusyu University, 4. JASRI/SPring-8, 5. Osaka Metropolitan University)
9:00 AM - 9:20 AM

[B445-2am-02] Monitor the Growth of ZnTe Microspheres in a PVP-contained Polyol System
○Yuen-ting Rachel Chau[1], Mai Thanh Nguyen[1], Tetsu Yonezawa[1] (1. Hokkaido University)
9:20 AM - 9:40 AM

[B445-2am-03] Quasi-Reversible Photoinduced Displacement of Perylenebisimide Derivatives from the Surface of ZnS Nanocrystals
○Daisuke Yoshioka[1], Yusuke Yoneda[2], I-Ya Chang[3], Hikaru Kuramochi[2], Kim Hyeon-Deuk[3], Yoichi Kobayashi[1,4] (1. Ritsumeikan Univ., 2. Inst. Mol. Sci., 3. Kyoto Univ., 4. PRESTO JST)
9:40 AM - 10:00 AM

[B445-2am-04] Colloidal Synthesis of Ag_8GeS_6 Quantum Dots Showing an Intense Near-IR Photoluminescence
○Nurmanita Rismaningsih[1], Junya Kubo[1], Tatsuya Kameyama[1], Norikazu Fujihira[2], Tsukasa Torimoto[1] (1. Graduate School of Engineering, Nagoya University, 2. Murata Manufacturing Co., Ltd.)
10:00 AM - 10:20 AM

[B445-2am-05] Au@Pd core-shell nanoparticles as high electrocatalyst for ethanol oxidation
○Jianhui Yang[1], Shinya Maenosono[1] (1. Japan Advanced Institute of Science and Technology)
10:30 AM - 10:50 AM

[B445-2am-06] Exploration of highly active multi-element nanoalloy catalyst and analysis of their structures by statistical method
○Yuto Maruta[1], Kohei Kusada[1], Okkyun Seo[3], Osami Sakata[3], Shogo Kawaguchi[3], Yoshiki Kubota[5], Hiromasa Kaneko[4], Takaaki Toriyama[2], Tomokazu Yamamoto[2], Yasukazu Murakami[2], Hiroshi Kitagawa[1] (1. Fac. of Science, Kyoto Univ., 2. Kyushu Univ., 3. JASRI, 4. Meiji Univ., 5. Osaka Metro. Univ.)
10:50 AM - 11:10 AM

[B445-2am-07] Element-Selective Observation of Dynamics in High-Entropy Alloy Nanoparticles with XAFS
○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Yoshiki Kubota[5], Shogo Kawaguchi[6], Toshiaki Ina[6], Kazuo Kato[6], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. Hakubi Center, Kyoto Univ., 3. URC, Kyushu Univ., 4. Grad. Sch. Eng., Kyushu Univ., 5. Grad. Sch. Sci., Osaka Metro. Univ., 6. JASRI/SPring-8)
11:10 AM - 11:30 AM

B444

Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B

[B444-2pm] 19. Colloid and Interface Chemistry

Chair: Toshiki Sawada, Yukikazu Takeoka
1:30 PM - 3:40 PM B444 (444, Bldg. 4 [4F])

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[B444-2pm-01] *In situ* structural analysis of liquid crystalline photo-alignment films at the interface of low-molecular-mass liquid crystals

○Chikara Kawakami[1], Mitsuo Hara[1], Shusaku Nagano[2], takahiro Seki[3] (1. Graduate School of Engineering, Nagoya University, 2. Department of Chemistry, Rikkyo University, 3. Emeritus Professor of Nagoya University)

1:30 PM - 1:50 PM

[B444-2pm-02] Thermo-responsive Gold nanorods reversible assembly flexible control with uniform orientation using DNA brushes

○JINGYAN YANG[1], Hideyuki Mitomo[2], Yu Sekizawa[1], Yusuke Yonamine[2], Kuniharu Ijiro[2] (1. Grad. Sch. Life Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ.)

1:50 PM - 2:10 PM

[B444-2pm-03] Vesicle adhesion induced by molecular recognition mimicking tissue formation

○Tomoya Kojima[1], Koichi Terasaka[1], Kouichi Asakura[1], Taisuke Banno[1] (1. Keio University)

2:10 PM - 2:30 PM

[B444-2pm-04] A Strategy to Make Commodity Plastics Self-Healable

○Yuta Fujisawa[1], Pier-luc Champagne[1], Yoshimitsu Itoh[1,2], Takuzo Aida[1,3] (1. The University of Tokyo, 2. JST PRESTO, 3. RIKEN CEMS)

2:40 PM - 3:00 PM

[B444-2pm-05] Supramolecular hydrogel capable of showing autonomous gel-to-sol-to-gel transition in response to oxidation

○Yuki Shintani[1], Hiroshi Katagiri[2], Masato Ikeda[1,3,4] (1. The United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University, 2. Graduate School of Organic Materials Science, Yamagata University., 3. Faculty of Engineering, Gifu University., 4. Institute for Glyco-core Research (iGCORE), Gifu University)

3:00 PM - 3:20 PM

[B444-2pm-06] High thermoelectric voltage of thermocell achieved by thermo-responsive dissolution of hydrogen bond donor

○Hirotaka Inoue[1], Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

3:20 PM - 3:40 PM

K206

Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B

[K206-2am] 20. Materials Chemistry -Basic and Application-

Chair: Naoki Tanaka, Yutaka Ie

9:00 AM - 11:30 AM K206 (K206, Lecture Hall Bldg. [2F])

[K206-2am-01] Optically tunable organic microdroplet lasers

○Hiroshi Yamagishi Yamagishi[1], Keitaro Fujita[1], Yohei Yamamoto[1] (1. University of Tsukuba)

9:00 AM - 9:20 AM

[K206-2am-02] Alkyl-π Liquid Electrets for Stretchable Mechanoelectric Generators

○Takashi Nakanishi[1], Akira Shinohara[1], Ravindra Kumar Gupta[1] (1. NIMS)

9:20 AM - 9:40 AM

[K206-2am-03] Bulk photovoltaic effect of ferroelectric liquid crystals based on extended π-conjugated units bearing lactic dimer units

○Masahiro Funahashi[1,2] (1. Kagawa Univ., 2. National Institute of Advanced Industrial Science and Technology)

9:40 AM - 10:00 AM

[K206-2am-04] Development of Functional Dye Films for Visualizing Volatile Organic Halogenated Compounds

○Kumpei Kozuka[1], Keiichi Imato[1], Yousuke Ooyama[1] (1. Hiroshima University)

10:00 AM - 10:20 AM

[K206-2am-05] Polymorphism and Mechanochromic Luminescence from Mesogenic Gold(I) Complex

○Andriani Furoida[1], Osamu Tsutsumi[1] (1. Ritsumeikan University)

10:30 AM - 10:50 AM

[K206-2am-06] Nonvolatile and highly-condensed π–gels based on alkyl–π functional molecular liquids

○Akito Tateyama[1,2], Masamichi Yamanaka[3], Takashi Nakanishi[1,2] (1. Hokkaido Univ., 2.

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NIMS, 3. Meiji Pharmaceutical Univ.)
10:50 AM - 11:10 AM

[K206-2am-07] Fabrication and analysis of periodic polymer structures induced by photopolymerization using scanning light
○Hirona Nakamura[1], Takuto Ishiyama[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology, 2. PRESTO, JST)
11:10 AM - 11:30 AM

Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B

[K206-2pm] 20. Materials Chemistry -Basic and Application-

Chair: Hajime Shigemitsu, Takashi Nakanishi
1:10 PM - 3:40 PM K206 (K206, Lecture Hall Bldg. [2F])

[K206-2pm-01] Amine and CO_2 Responsiveness of Ring-Perfluorinated Dye and Its Optical Properties
○Ryunosuke Kani[1], Yasuhiro Kubota[1], Toshiyasu Inuzuka[1], Kazumasa Funabiki[1] (1. Gifu University)
1:10 PM - 1:30 PM

[K206-2pm-02] Control of Molecular Alignment in Liquid-Crystalline Polymer Particles Synthesized by Dispersion Polymerization
○Tomoki Shigeyama[1], Kyohei Hisano[1], Osamu Tsutsumi[1] (1. Ritsumeikan Univ.)
1:30 PM - 1:50 PM

[K206-2pm-03] Development of Ladder-Type Fused pi-Conjugated Units Bearing Spirocyclopentadithiophenes for Non-Fullerene Acceptors in Organic Solar Cells
○Kai Wang[1], Takuji Seo[1], Hajime Nitta[1], Seihou Jinnai[1,2], Yutaka Ie[1,2] (1. Osaka Univ., 2. ICS-OTRI, Osaka Univ.)
1:50 PM - 2:10 PM

[K206-2pm-04] Effect of the tether length of reagents with two reactive sites on the band gap of single-walled carbon nanotubes
○Yui Konno[1], Rina Morooka[1], Tatsunari Morishita[1], Pei Zhao[2], Daiki Uchida[1], Michio Yamada[1], Masahiro Ehara[2], Yutaka Maeda[1] (1. Tokyo Gakugei University, 2. Institute for molecular science)
2:10 PM - 2:30 PM

[K206-2pm-05] Biomolecular Machines as Functional Building Blocks in Programmed Nanostructures
○Kiyoshi Morishita[1,2], PK Hashim[1], Haruaki Yanagisawa[1], Masahide Kikkawa[1], Hideki Taguchi[3], Takuzo Aida[1,2] (1. The University of Tokyo, 2. RIKEN CEMS, 3. Tokyo Institute of Technology)
2:40 PM - 3:00 PM

[K206-2pm-06] Regulation of reversible self-assembly ability by substitution and deletion of amino acid residues of elastin peptide $(FPGVG)_n$ analogs
○Keitaro Suyama[1], Shogo Sumiyoshi[2], Marin Shimizu[2], Naoki Tanaka[2], Keisuke Tomohara[1], Suguru Taniguchi[3], Iori Maeda[4], Takeru Nose[1,2] (1. Faculty of Arts and Science, Kyushu University, 2. Department of Chemistry, Faculty and Graduate School of Science, Kyushu University, 3. Division of Biomedical Sciences, Fukuoka Dental College, 4. Department of Physics and Information Technology, Kyushu Institute of Technology)
3:00 PM - 3:20 PM

[K206-2pm-07] Characterization of Artificial Protein Nanocage-Cross-Linked-hydrogels
○Nasu Erika[1], Norifumi Kawakami[1], Ryoichi Arai[2], Kenji Miyamoto[1] (1. Keio University, 2. Shinshu University)
3:20 PM - 3:40 PM

K303

Academic Program [Oral B] | 21. Energy and Related Chemistry, Geo and Space Chemistry | Oral B

[K303-2am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Akira Yamakata, Masayuki Yagi
9:00 AM - 11:30 AM K303 (K303, Lecture Hall Bldg. [3F])

[K303-2am-01] Temperature control of nanowire/hexagonal prismatic WO_3 structure with a high performance for photoelectrochemical water oxidation
○Tomohiro Katsuki[1], Debraj Chandra[1], Yuta Tsubonouchi[1], Norihisa Hoshino[1], Zaki Zahran[1], Masayuki Yagi[1] (1. Grad. School of Sci. and Tech., Niigata Univ)

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9:00 AM - 9:20 AM

[K303-2am-02] Development of Visible-Light Photomeltable Azobenzenes and Their Application as Solar Thermal Fuels

○Dennis Kwaria[1,2], Keegan McGehee[1,2], Suyi Liu[1,2], Yoshihiro Kikkawa[2], Shotaro Ito[3], Yasuo Norikane[2,1] (1. Graduate School of Pure and Applied Science, University of Tsukuba, 2. Research Institute for Advanced Electronics and Photonics, National Institute of Advanced Industrial Science and Technology (AIST), 3. Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST))

9:20 AM - 9:40 AM

[K303-2am-03] Near-infrared Light Induced Mechanical Motions of Organic Crystals Coated with Photothermal Conversion Materials

○Yuki Hagiwara[1], Dong Wook Kim[2], Shodai Hasebe[1], Mingchao Zhang[2], Toru Asahi[1], Hideko Koshima[1], Metin Sitti[2] (1. Waseda University, 2. Max Planck Institute for Intelligent Systems)

9:40 AM - 10:00 AM

[K303-2am-04] Quantitative description to stabilize local pH shift in a solar-driven water splitting device and demonstration of coupled reductive upgrading of biomass feedstock

○Keisuke Obata[1,2], Michael Schwarze[3], Roel van de Krol[2,3], Reinhard Schomäcker[3], Fatwa firdaus Abdi[2] (1. The Univ. of Tokyo, 2. Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 3. Technische Universität Berlin)

10:10 AM - 10:30 AM

[K303-2am-05] n Type Carbon Nanotubes with Extremely High Thermal Stability in Air Produced by Doping with Organic Superbases

○Shohei Horike[1,2,3,4], Qingshuo Wei[3], Kouki Akaike[3], Kazuhiro Kirihara[3], Masakazu Mukaida[3], Yasuko Koshiba[1,2], Kenji Ishida[1,2] (1. Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University, 3. National Institute of Advanced Industrial Science and Technology (AIST), 4. PRESTO, Japan Science and Technology Agency)

10:30 AM - 10:50 AM

[K303-2am-06] Development of Paleo-redox indicators for paleocean surface using chlorophyll-derived substances

○Kenta Asahina[1], Satoshi Takahashi[2], Ryosuke Saito[3], Kunio Kaiho[4], Yasuhiro Oba[5] (1. National Institute of Advanced Industrial Science and Technology, 2. Nagoya University, 3. Yamaguchi University, 4. Tohoku University, 5. Hokkaido University)

10:50 AM - 11:10 AM

[K303-2am-07] Atmospheric ozone as an indicator of earthquake generation

○Hiroshi Sakugawa[1] (1. Hiroshima University)

11:10 AM - 11:30 AM

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Academic Program [Oral B] | 01. Education and History of Chemistry | Oral B

[K303-2pm] 01. Education and History of Chemistry

Chair: Hirotoshi Mori, Izumi Imai

Thu. Mar 23, 2023 1:50 PM - 3:40 PM K303 (K303, Lecture Hall Bldg. [3F])

[K303-2pm-01] Practical computational chemistry course for a comprehensive understanding of organic, inorganic, and physical chemistry: from molecular interactions to chemical reactions

Nahoko Kuroki[1], Yuji Mochizuki[2], ○Hirotoshi Mori[1] （1. Chuo University, 2. Rikkyo Univeristy）

1:50 PM - 2:10 PM

[K303-2pm-02] Chemical education of community education and liberal arts education in the Times of Post Covid-19

○Sekai Iwama[1,2], Fumiyoshi Asahi[2], Ryu Takahashi[3] （1. Kumamoto Gakuen University, 2. Specified Nonprofit Corporation Otaru Kagakugizyutsu no Me wo Sodateru Kai, 3. Otaru City Council）

2:10 PM - 2:30 PM

[K303-2pm-03] SDGs in Chemistry in Context (American Chemical Society ed.) 9th edition - From the activities of Tohoku Association of Chemical Education

○Naoshi Watanabe[1], Kazuko Ogino[2], Hiroshi Kosugi[2], Daisuke Hojo[3], Yuko Masuyama[4], Hiroshi Ogino[2] （1. Miyagi University of Education, 2. Tohoku University, 3. Miyagi Prefecture Izumitateyama High School, 4. Miyagi Prefecture Teizan High School）

2:40 PM - 3:00 PM

[K303-2pm-05] Radical has the own semi-acidity or semi-basicity

○Hirosi Sano[1] （1. Laboratory of Global Energy Systeml）

3:20 PM - 3:40 PM

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反応有機・無機・物理化学を総合的に理解するための実践的な計算化学コース：分子間相互作用から化学反応まで

（中央大学[1]・立教大学[2]）黒木 菜保子[1]・○望月 祐志[2]・○森 寛敏[1]

Practical computational chemistry course for a comprehensive understanding of organic, inorganic, and physical chemistry: from molecular interactions to chemical reactions

([1]*Department of Applied Chemistry, Chuo University,* [2]*Department of Chemistry, Rikkyo University*) Nahoko Kuroki,[1] Yuji Mochizuki,[2] Hirotoshi Mori[1]

In all fields of chemistry, it has become essential to use quantum chemical calculations and machine learning for explaining and predicting chemical phenomena. However, it is challenging to apply textbook knowledge to practical research. In this study, we developed teaching material based on computational chemistry to promote the integration of knowledge from all fields of chemistry, including organic, inorganic, and physical chemistry, to bridge the gap between classroom learning and chemistry research. This experimental material, which comprehensively covers weak intermolecular interactions and chemical reactions, is expected to help students conduct purposeful research activities after being assigned to a laboratory.

Keywords : Upper-Division Undergraduate; Physical Chemistry; Computational Chemistry; Computer-Based Learning; Internet/Web-Based Learning

あらゆる化学の分野において、化学現象の説明や予測に、量子化学計算や機械学習を用いることが必要不可欠になっている。[1] しかし、教科書の知識を実践的な研究に応用することは、一般に学部生にとってハードルの高いものとなる。本研究では、有機化学、無機化学、物理化学など化学のあらゆる分野の知識の統合理解を促進し、教室での学習と、研究室レベルの実践的化学研究のギャップを埋めるための、計算化学に基づく教材を開発・公開した。[2,3] この実験教材は、弱い分子間相互作用や化学反応などを、最新の計算化学理論に基づき段階的かつ網羅的に扱っている（**図 1**）。学生が研究室に配属後に、目的意識を持って研究活動を行う助けとなることが期待される。

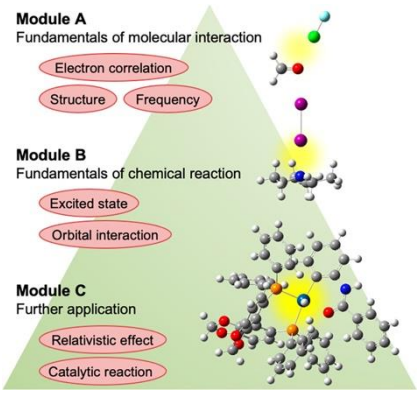


図 1　計算化学を基として開発した統合的化学教育モジュール

1) Comprehensive Physical Chemistry Learning Based on Blended Learning: A New Laboratory Course, , N. Kuroki, H. Mori, *J. Chem. Edu.* **2021**, 12, 3884-3870.
2) Practical computational chemistry course for a comprehensive understanding of organic, inorganic, and physical chemistry: from molecular interactions to chemical reactions, N. Kuroki, Y. Mochizuki, H. Mori, *J. Chem. Edu.* **2023**, *in press*.
3) *Computational Chemistry Course*. https://sites.google.com/g.chuo-u.ac.jp/jce2022/home (accessed 2022-12-11)

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ポストコロナにおける社会教育と教養教育としての化学教育

(熊本学園大商学部[1]・NPO 法人小樽青少年科学技術の芽を育てる会[2]・小樽市議会[3]・NPO 法人 Nextday[4]・小樽市科学教育ネットワーク[5])
○岩間世界[1,2,5]・旭史悦[2,5]・高橋龍[2,3,5]・佐々木束[4]

Chemical education of community education and liberal arts education in the times of post Covid-19

([1]*Department of Commerce, Kumamoto Gakuen Univ.,* [2]*Specified Nonprofit Corporation Otaru Kagakugizyutsu no Me wo Sodateru Kai,* [3]*Otaru City Council,* [4] *Specified Nonprofit Corporation Nextday,* [5] *Otaru-city science education network,*)
○IWAMA, Sekai[1,2,5]; ASAHI, Fumiyoshi[2,5]; TAKAHASHI, Ryu[2,3,5]; SASAKI, Tsugane[4]

Hear we report the current situation and problems of science education for the children under COVID-19 calamity in Otaru city. Otaru city is a mid-west part city of Hokkaido with a population of 108,000 in end of 2022 is suffering from depopulation from 1960s (It has been halved in 50 years; middle of 1960s had 210,000 population.). We report practical examples that the face-to-face science experience held while taking care of the COVID-19.

Keywords : Science (Chemical) Education for Post Covid-19; Regional Disparities of Science Education; Specified Nonprofit Corporation Activity; Liberal Arts; Overcoming Population Decline

新型コロナウイルス感染症(COVID-19)の影響により，2022 年も 2019 年以前の教育環境に戻れていない。筆者は文系大学における教養課程の「化学」を担当しているが，3 年間対面形式の講義が実施できず，主に講義動画のオンデマンド配信による遠隔講義を余儀なくされている。コロナ禍前は高校までにおいて実験に触れる機会が少なかった学生が多いことも考慮し，半期に 4，5 回程度演示実験を行うことを前提に講義を組み立てていたが，動画においては撮影に向かない実験もあり，文系学生にとっては，人生で最後に化学（科学）を学ぶ機会が講義動画の視聴となってしまうことは，化学（科学）への親近感という面において大きな問題であると考えている。

社会教育においては，筆者らは 2012 年から小樽市において，主に小中高校生を対象にした各種科学教室を主催し，コロナ禍以降は望遠鏡工作教室，プログラミング体験・工作教室，科学実験教室など年 15 事業程度（実施回数としては 30 回程度）を行っている。ZOOM 等を用いたリアルタイム双方向によるオンライン型工作教室も実施したが，小樽市においては家庭におけるネット環境や保護者の ICT リテラシー差が激しく [1]，主催行事としては 21 年度に工作教室を 1 事業（2 回）実施したのみである。また，実施においては，実施人員がボランティアベースとなるため，メンバー間での考え方が運営に大きく影響する。コロナ禍が 3 年間継続する中において，コロナ禍以前には戻らないことを前提にするのか，コロナ禍がいずれ終結する（コロナ禍前に完全に戻る）ことを前提に考えるのかで，実施事業の内容や運営の細部に大きな違いとなって現出してきている。本発表では，上述した現状についての報告と，筆者が関与している教養教育の受講学生と社会教育における参加者とその保護者からのアンケート調査の結果を考察することにより，ポストコロナの化学（科学）教育について考える嚆矢としたい。

1) 小樽市，令和 3 年小樽市教育委員会第 3 回定例会議事録, pp8-11, 2021 年 4 月

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Chemistry in Context（アメリカ化学会） 第 9 版 に見られる SDGs ～東北化学教育研究会の活動から～

(宮城教育大学[1]・.東北大学[2]・.宮城県泉 館山高等学校[3]・宮城県貞山高等学校[4])
○渡辺 尚[1]・荻野 博[2]・小杉 紘史[2]・北條 大輔[3]・増山 裕子[4]・荻野 和子[2]

SDGs in Chemistry in Context (American Chemical Society) 9th edition - From the activities of Tohoku Chemical Education Research Group

([1]*Miyagi University of Education,* [2]*Tohoku University,* [3]*Miyagi Prefecture Izumitateyama High School*, [4]*Miyagi Prefecture Teizan High School*) ○Naoshi Watanabe, [1] Hiroshi Ogino, [2] Hiroshi Kosugi, [2] Daisuke Hojo , [3] Yuko Masuyama, [4] Kazuko Ogino[2]

The Tohoku Association of Chemical Education[1)] started in 1994 and has continued for 29 years to date. Since its inception, overseas chemistry textbooks (high school science and university liberal arts level) have been used. We have been reading Chemistry in Context（9th Ed）[2)] since April 2019. In this book, I took a bird's-eye view from the perspective of the SDGs and compared it with Japanese high school chemistry textbooks. We investigated Goals 3, 9, and 12, among the 17 goals of the SDGs. As a result, in the 9th Edition, we found word elements that met our purpose in many chapters, although we could hardly find corresponding words in Japanese high school chemistry textbooks. Interestingly, Green Chemistry, which is considered to be closely related to SDGs, can be found here and there in some textbooks in Japan, but in the 9th Edition, the word is actively used, appearing a total of 41 times. The difference is remarkable.

Keywords : Chemical Education, Chemistry Textbooks, Sustainable Development Goals(SDGs), Chemistry in Context, Tohoku Association of Chemical Education

東北化学教育研究会[1)]は 1994 年に始まり、現在まで 29 年の長きに渡って継続している。発足当時から主に海外の化学教科書（高校理系や大学教養レベル）の輪読を行い、2019 年 4 月より Chemistry in Context (9th Ed)[2)]を輪読している。この本を SDGs の視点から俯瞰して日本の高校化学の教科書と比較した。SDGs の 17 の目標のうち、Goal3,9,12 の項目について調べた。その結果は日本の高校化学の教科書では該当する単語を殆ど見出すことが出来なかったが、9th Edition では目的に合致する言葉の要素が多くの章の中に見出せた。興味深いことに、SDGs に大いに関係があると考えられる Green Chemistry については日本では一部の教科書で散見することができたが、9th Edition では積極的にその単語が使用され、のべ 41 回も登場しその違いが顕著である。

Sustainable Development Goals - SDGs		本文中の回数
GOAL 3	**Good Health**[1)] and **Well-Being**[2)]	[1)]6 回, [2)]5 回
GOAL 9	Industry, **Innovation**[1)] and **Infrastructure**[2)]	[1)]7 回, [2)]9 回
GOAL 12	Responsible **Consumption**[1)] and **Production**[2)]	[1)]65 回, [2)]504 回 [1)] and [2)]の並列表記 6 回

1) 東北化学教育研究会の活動. 荻野和子, *高分子.* **2008**, *57*, 208-209.
2) American Chemical Society, Chemistry in Context, 9th ed., 2018. McGraw-Hill.

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ラジカルにも一種の酸性・塩基性が認められる

（地球エネルギーシステム研）○佐野 寛

Radical has the own semi-acidity or semi-basicity

(Lab.of Global energy system) ○Hirosi Sano

A new chem-formula shows the realistic shape of bonding **electron-pair**. Otherwise, a **radical** is not electron-pair but single electron. Then, the **radical** electron should be shown as half arrow.（so that the half arrows can be adaptable for one electron-pair）.Almost of **radical** reactions have poor chemical *selectivity*. Exceptionally, such radical as O_2 or NO has some chemical selectivity, to react with only electron-donating radicals. They may be called "semi-acidic radical".

Keywords : new formula, radical electron, 1 electron-bond, radical reaction selectivity, semi acid-basicity

新構造式は結合電子対を線/で表示する。イオン反応は電子対↗が他の空軌道¨を攻撃して電子対結合/を生成する(∴極性に支配され,選択性が高い)。一方、ラジカル電子を片矢羽で表示[1)]（'02,'03 日化）すると、束ねて結合線/(=電子対)になるので好都合である。

ラジカルは本来、ラジカル電子と空軌道とを持つので、ラジカル同士の反応は電子対生成となる。したがってラジカル反応は本質的に選択性が低い。だが NO ラジカルや 0_2ビラジカルは、自己会合し難く、電子供与性のラジカルと好んで反応する。いわば「半・酸性」のラジカルといえる。そこでラジカル自身に酸・塩基概念を導入すると選択性が説明できる。ラジカルは、ルイス酸(空軌道¨を持つ)または塩基（ローンペア↗を持つ）とは、反応し難い。それはラジカル同士が電子対結合を生成できるのに対し、①ラジカル＋酸(空軌道)⇛ 一電子結合を；②ラジカル＋塩基(電子対)⇛ 三電子結合を；しか形成できないからである。

ラジカルを半酸性,半塩基性で分類すると：[半･酸性ラジカル] Cl 原子,Br 原子,HO,NO,NO_2, O_2；[両性ラジカル] H原子、H_3C、R_3C、ϕ_3C ；[半･塩基性ラジカル] Na 原子、･･･となりラジカルの選択性発現が説明できる。

1)佐野寛： 2002年春･日化 2E7-42「ラジカル表現」；同秋･日化 2B5-07「活性酸素の構造」

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[K202-2pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Erik Lötstedt, Nahoko KUROKI

Thu. Mar 23, 2023 1:30 PM - 3:40 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-2pm-01] Development of cat-GRRM/MC/MD method realizing the process of crosslinked network structure formation using molecular catalysts

○YINGXIAO XI[1], Hironobu Fukuzawa[1], Shoji Fukunaga[1], Gota Kikugawa[2], Naoki Kishimoto[1] （1. Department of Chemistry, Tohoku University , 2. Institute of Fluid Science, Tohoku University）

1:30 PM - 1:50 PM

[K202-2pm-02] Quantum computation of time-dependent spin chain dynamics

○Erik Lötstedt[1], Lidong Wang[1], Ryuhei Yoshida[1], Youyuan Zhang[1], Kaoru Yamanouchi[1] （1. Department of Chemistry, School of Science, The University of Tokyo）

1:50 PM - 2:10 PM

[K202-2pm-03] Analysis of dynamical branching mechanisms based on the Reaction Space Projector

○Takuro Tsutsumi[1,2], Akifumi Fujita[3], Kenichiro Iwata[4], Yuriko Ono[5], Tetsuya Taketsugu[1,5] （1. Fac. Sci., Hokkaido Univ., 2. L-Station, Hokkaido Univ., 3. Sch. Sci., Hokkaido Univ., 4. Grad. School Chem. Sci. Eng., Hokkaido Univ., 5. WPI-ICReDD, Hokkaido Univ.）

2:20 PM - 2:40 PM

[K202-2pm-04] Quantum chemical analysis of coordination stability of flexible tripeptides and nickel ions self-assembling to form macrocyclic supramolecules

○Dapeng Zhang[1], Naoki Kishimoto[1], Ryosuke Miyake[2] （1. Tohoku University, 2. Ochanomizu University）

2:40 PM - 3:00 PM

[K202-2pm-05] Double layer differential capacitance calculation by absolute electrode potential controlled MD

○Ken Takahashi[1], Hirofumi Sato[1,2], Hiroshi Nakano[3] （1. Department of molecular engineering, Kyoto University, 2. Fukui Institute for Fundamental Chemistry, 3. CD-FMat, National Institute of Advanced Industrial Science and Technology (AIST)）

3:00 PM - 3:20 PM

[K202-2pm-06] Theoretical investigation of atomic and electronic structures of supported metallic nanoparticles by large-scale DFT and machine learning

○Shengzhou Li[1,2], Tsuyoshi Miyazaki[2,1], Ayako Nakata[2,1] （1. University of Tsukuba, 2. National Institute for Materials Science）

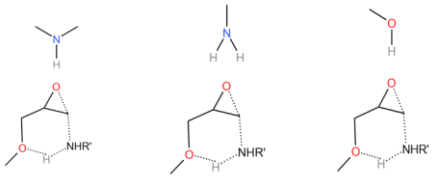
3:20 PM - 3:40 PM

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Development of cat-GRRM/MC/MD method realizing the process of crosslinked network structure formation using molecular catalysts

([1]*Department of Chemistry, Tohoku University*, [2]*Institute of Fluid Science, Tohoku University*)
○Yingxiao Xi,[1] Hironobu Fukuzawa,[1] Shoji Fukunaga,[1] Gota Kikugawa,[2] Naoki Kishimoto[1]
Keywords: Molecular Dynamics; Quantum chemical calculation; Chemical reaction simulation; Network polymer; Catalytic effect

Epoxy resin is a commonly used matrix in carbon fiber reinforced plastic, which can be obtained from the base epoxy resin and amine curing agent by curing reaction. The excellent physical properties of epoxy resin result from the three-dimensional (3D) cross-linked structures and can be determined experimentally, despite being time-consuming and costly. Molecular dynamics (MD) methods are commonly used to simulate the physical properties of network polymers from their molecular structures but ignore chemical reaction processes. Quantum chemistry calculations can explain reaction mechanisms and provide reaction energies but not in the case of models over thousands of atoms. And in epoxy amine reactions, additional alcohol or amine molecules can act as catalysts for the reaction.[1]



We developed a cat-GRRM/MC/MD method that combines the Global Reaction Route Mapping (GRRM)[2] program with the reaction simulation involved in the MD method in which reaction kinetics is realized in a Monte Carlo (MC) manner. In this study, the *ab initio* molecular-orbital calculation (RHF/3-21G) was combined with the GRRM to simulate the reaction pathways through which proton donor molecules, such as alcohols and amines (R-OH，$R\text{-}NH_2$, R-NH), act as molecular catalysts (autocatalysis). The energy values obtained by GRRM were applied to the MD simulation. In the chemical reaction simulation, we used a large-scale atomic/molecular massively parallel simulator (LAMMPS)[3] to simulate the crosslinking process of epoxy resin. In this way, the properties of the resin can be tested with minimal parameters while considering the reaction process and mechanism. The deviation between the simulation and experimental results for physical properties of the epoxy resin were successfully reduced using the cat-GRRM/MC/MD method compared with the model without considering the catalytic effect.

1) J.-E. Ehlers, N.G. Rondan, L.K. Huynh, H. Pham, M. Marks, T.N. Truong, *Macromolecules* **2007**, *40*, 4370. 2) S. Maeda, K. Ohno, K. Morokuma, *Phys. Chem. Chem. Phys*. **2013**, *15*, 3683. 3) S. Plimpton, *J. Comp. Phys*. **1995**, *117*, 1.

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Quantum computation of time-dependent spin chain dynamics

(*Department of Chemistry, School of Science, The University of Tokyo*)
○Erik Lötstedt, Lidong Wang, Ryuhei Yoshida, Youyuan Zhang, Kaoru Yamanouchi
Keywords: Quantum computing, error mitigation, time-dependent dynamics, Heisenberg spin chain

Quantum computers are considered promising for the simulation of quantum many-particle systems which are hard to be simulated using classical computers. However, currently available quantum computers, also called noisy intermediate-scale quantum (NISQ) devices, suffer from noise caused by the decoherence of the qubits and imperfect quantum gate operations. Therefore, output of the NISQ devices carry large systematic errors which must be mitigated before meaningful results can be obtained.

In this contribution,[1] we simulate the time-dependent dynamics of a three-site spin chain using three qubits of the superconducting qubit type quantum computer *ibm_kawasaki*.[2] The spin chain is described by the Heisenberg XXX Hamiltonian,

$$H = J\left(\sigma_x^{(2)}\sigma_x^{(1)} + \sigma_y^{(2)}\sigma_y^{(1)} + \sigma_z^{(2)}\sigma_z^{(1)} + \sigma_x^{(1)}\sigma_x^{(0)} + \sigma_y^{(1)}\sigma_y^{(0)} + \sigma_z^{(1)}\sigma_z^{(0)}\right), \quad (1)$$

where J is the coupling strength and $\sigma_\alpha^{(i)}$ ($\alpha = x, y, z$) is a Pauli operator operating on site i. We calculate the time-dependent wave function $|\psi(t)\rangle$ by the Suzuki-Trotter approximation, using $N = 8$ Suzuki-Trotter steps. The initial state is $|\psi(0)\rangle = |110\rangle$. The resulting quantum circuits contain 48 CNOT gates. To mitigate the error, we use a combination of the Clifford data regression (CDR) and the Pauli twirling (PT). The positions of the non-Clifford gates replaced by Clifford gates in the CDR are optimized at time $t = \pi\hbar/J$.

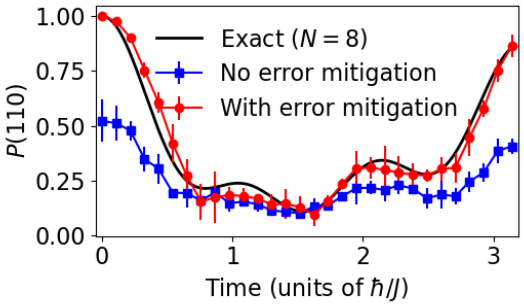


Fig. 1. Time-dependent population in the $|110\rangle$ state.

The time-dependent population $P(110) = |\langle 110|\psi(t)\rangle|^2$ in the $|110\rangle$ state simulated using *ibm_kawasaki* is shown in Fig. 1. Without error mitigation (blue squares in Fig. 1), the time-dependent population $P(110)$ is largely different from the exact result (black solid line). The time-dependent population obtained after the error mitigation (red circles) reproduces well the exact curve within an error of $|P(110) - P_{\mathrm{exact}}(110)| < 0.1$ in the time interval of $0 \le t \le \pi\hbar/J$. Our results imply that the Suzuki-Trotter method combined with the error mitigation by CDR and PT can be used for accurate simulation of spin chain dynamics on quantum computers.

This research is partly supported by the UTokyo Quantum Initiative. We acknowledge support from the DIC Corporation through the AQUABIT project.

1) E. Lötstedt, L. Wang, R. Yoshida, Y. Zhang, and K. Yamanouchi, submitted for publication (2023).
2) IBM Quantum team, https://quantum-computing.ibm.com (2021), *ibm_kawasaki* v1.3.20.

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反応空間投影法によるペリ環状反応の動的分岐機構解析

（北大院理[1]・北大 L-Station[2]・北大理[3]・北大院総合化学[4]・北大 WPI-ICReDD[5]）
○堤　拓朗[1,2]・藤田聡文[3]・岩田健一郎[4]・小野ゆり子[5]・武次徹也[1,5]
Analysis of dynamical branching mechanisms based on the Reaction Space Projector ([1]*Fac. Sci., Hokkaido Univ.*, [2]*L-Station, Hokkaido Univ.*, [3]*Sch. Sci., Hokkaido Univ.*, [4]*Grad. School Chem. Sci. Eng., Hokkaido Univ.*, [5]*WPI-ICReDD, Hokkaido Univ.*) ○Takuro Tsutsumi,[1,2] Akifumi Fujita,[3] Kenichiro Iwata,[4] Yuriko Ono,[5] Tetsuya Taketsugu[1,5]

Recently, the tris-pericyclic reaction leading to three different cycloadducts was reported, and the reaction mechanism was discussed in the low-dimensional subspace defined by internal coordinates.[1] However, selecting coordinate axes relies on chemical intuition and experiences. To avoid such ambiguity, we have developed the Reaction Space Projector (ReSPer) that uniquely defines principal coordinates by exploiting a dimension reduction technique, which reproduce a structural distance relationship of a set of reference structures.[2] Here, we reveal dynamical branching mechanisms of the tris-pericyclic reaction based on static reaction path calculations, *ab initio* molecular dynamics simulations, and ReSPer analyses.[3]
Keywords : Reaction Space Projector, Ab initio molecular dynamics, Reaction path, Dynamical branching, Low-dimensional potential energy landscape

ペリ環状反応は、極性反応、ラジカル反応と並ぶ有機化学の基礎反応である。Houk らは 1 つの遷移状態構造から 3 つの環化付加体を与えるペリ環状反応を報告し（**Fig. 1**）、反応経路解析や *ab initio* 分子動力学（AIMD）計算により分岐比や反応機構を議論した[1]。先行研究では AIMD トラジェクトリを解析するために、反応に関与する内部座標により定義される部分空間を利用したが、これらの自由度選択は解析者の化学的知見に強く依存している。近年、我々は次元縮約法の導入により、座標選択に関する恣意性を排除した部分空間構築法である反応空間投影法（ReSPer）を開発し、低次元反応空間に基づく AIMD 古典軌道解析を展開してきた[2]。本研究では、ReSPer を **Fig. 1** に示したペリ環状反応に適用し、二次元反応空間に基づく分岐反応描像を明らかにする。

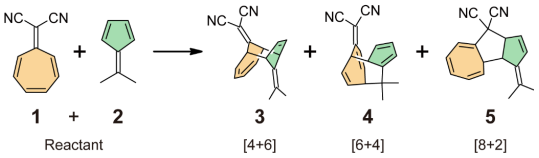


Figure 1. Target pericyclic reaction.[1]

本研究では、はじめに反応物（**1**+**2**）と環化付加体（**3**, **4**, **5**）を結ぶ反応経路を求め、AIMD 計算を実行することで、**3**:**4**:**5** = 93:4:3 の分岐比を得た。次に ReSPer を用いて反応経路に沿った参照構造により定義された二次元ポテンシャルエネルギー地形を作成した。最後に二次元空間に AIMD トラジェクトリを射影することで、分岐生成物（**4**, **5**）へ進行する AIMD トラジェクトリはポテンシャルエネルギーが平坦化する領域から動的効果に分岐することを見出した。発表当日は二次元反応空間構築により見出された本ペリ環状反応経路の特徴や動的分岐機構について報告する[3]。

[1] X. Xue *et al.*, *J. Am. Chem. Soc.*, **2019**, 141, 1217.　[2] **T. Tsutsumi**, *et al.*, *Chem. Commun. (Feature Article)*, **2021**, 57, 11734.　[3] T. Tsutsumi, A. Fujita, K. Iwata, Y. Ono, T. Taketsugu, *submitted*.

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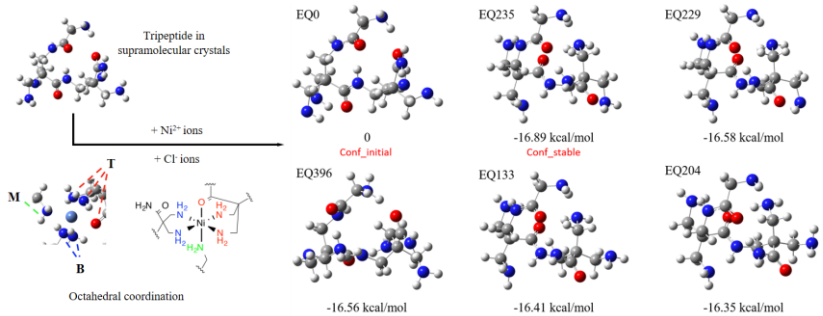
Quantum chemical analysis of coordination stability of flexible tripeptides and nickel ions self-assembling to form macrocyclic supramolecules

([1]*Graduate School of Science, Tohoku University,* [2]*Graduate School of Humanities and Sciences, Ochanomizu University*) ○ Dapeng Zhang,[1] Naoki Kishimoto1,[1] Ryosuke Miyake[2]

Keywords: Quantum Chemical Calculation; Self-assembly; Flexible Tripeptide; Macrocyclic Metal Complexes; Conformation Search

Giant cyclic structures reported by Miyake *et al.*[1], $[M_{14}L_{14}]^{28+}$ and $[M_{12}L_{12}]^{24+}$, and catenane structure $[M_{28}L_{28}]^{56+}$, can be formed by self-assembly of octahedral coordination between nickel ions (M) and flexible tripeptides (L). The amino and carboxyl groups in the tripeptide can act as the monodentate, bidentate, and tridentate sites, forming the octahedral coordination with a nickel ion. In this study, we propose an indirect and feasible approach to uncover the causes of self-assembly by analyzing the coordination stability through the chemical calculations on simple models.

The calculations were performed by using B3LYP method. The polarizable continuum model (PCM) was applied to describe solvent effects. Anharmonic Downward Distortion Following algorithm (ADDF)[2] coded in Global Reaction Route Mapping program[3] (GRRM) was used to search for stable conformations in water. Our research shows the conformation extracted from the crystal can rotate its functional groups to form intramolecular hydrogen interactions, and transform into more stable conformations. The Sphere Contraction Walk algorithm (SCW)[4] and Two-Point Scaled Hypersphere Search algorithm (2PSHS)[5] were used to calculate possible reaction pathways connecting the conformers obtained by ADDF calculation. Our results can confirm that the crystal structure of tripeptide has the advantage of formation under the influence of sufficient Ni^{2+} ions and counter anions.



1) R. Miyake, A. Ando, et al., *J. Am. Chem. Soc.,* **2019**, 141, 22, 8675-8679. 2) S. Maeda, T. Taketsugu, et al., *Bull. Chem. Soc. Jpn.,* **2014**, 87, 1315-1334. 3) S. Maeda, Y. Harabuchi, et al., GRRM17, see http://iqce.jp/GRRM/index_e.shtml 4) S. Maeda, K. Ohno., *J. Chem. Phys.,* **2006**, 124, 174306. 5) S. Maeda, K. Ohno., *Chem. Phys. Lett.,* **2005**, 404, 95-99.

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絶対電極電位制御 MD による電気二重層微分容量計算

（京大院工[1]・京大 FIFC[2]・産総研 CD-FMat[3]）○高橋 健[1]・佐藤 啓文[1,2]・中農 浩史[3]
Double layer differential capacitance calculation by absolute electrode potential controlled MD
([1]*Department of molecular engineering, Kyoto University*, [2]*Fukui Institute for Fundamental Chemistry*, [3]*CD-FMat, National Institute of Advanced Industrial Science and Technology*) ○ Ken Takahashi[1], Hirofumi Sato[1,2], Hiroshi Nakano[3]

Differential capacitance at an electrode-electrolyte interface indicates a degree of the electrolyte response to the electrode potential change. It is defined with respect to the potential difference with the reference electrode in a 3-electrode setup, i.e., to the absolute potential of the working electrode. Polarizable classical molecular dynamics (MD) simulation is applied to a Pt(111)/NaF aqueous solution interface to evaluate the differential capacitance profile and obtain molecular insights about its potential dependence. Working electrode / electrolyte / counter electrode setup is used and the working electrode potential is controlled by tuning the potential difference. By choosing a parameter that reproduces quantum chemical calculation results in determining the electrode atomic charges, the agreement in the calculated differential capacitance profile with the experiment is improved in comparison to the conventional parameter.
Keywords : Molecular dynamics (MD) simulation; Differential capacitance

電気二重層の微分容量は、電極の電位変化に対する電解液の応答を表す指標であり、電極電位に依存する。三極測定実験では作用電極-参照電極間の電位差、すなわち作用電極の絶対電位が制御される。電極が電子分極可能な古典分子動力学(MD)法を Pt(111)/NaF 水溶液系に適用し、作用電極-電解液-対極からなるセルにおいて作用電極-対極間の電位差を適切に選ぶことで作用電極の絶対電位を制御し、各電位における電極電荷密度(Fig. a)を電位で微分することで微分容量プロファイルを計算した(Fig. b)。電極の原子電荷を決定する際に必要な Hubbard パラメーターU^0を量子化学計算の結果を再現できるもの(8.5 eV/e^2)にすることで、極大値、極大となる電位について、電極を完全導体として扱う従来のもの(21.9 eV/e^2)を用いた場合に比べ、実験(PZC で極大値 40-80 μF/cm^2 をとる)[1]との一致が改善した[2]。微分容量の電位依存性について分子論的に解析した結果については当日報告する。

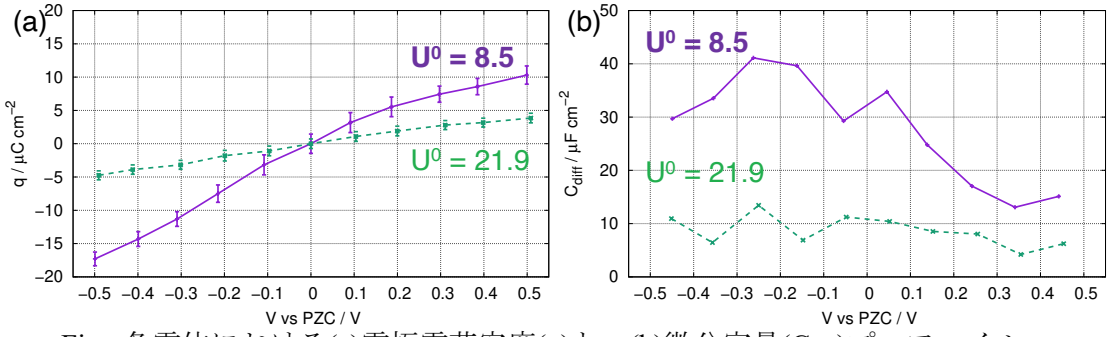


Fig. 各電位における(a)電極電荷密度(q)と、(b)微分容量(C_{diff})プロファイル。

[1] T. Pajkossy and D. Kolb, *Electrochemistry commun.* **5**, 283 (2003).
[2] K. Takahashi, H. Sato, and H. Nakano, *to be submitted.*

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Investigation of atomic and electronic structure of supported metallic nanoparticles by large-scale DFT and machine learning

([1]*University of. Tsukuba*, [2]*National Institute for Materials Science*)
○Shengzhou Li,[1,2] Tsuyoshi Miyazaki,[2,1] Ayako Nakata[2,1]
Keywords: Metallic Nanoparticles; Catalyst; Large-scale DFT Calculation; Machine Learning

Metallic nanoparticles (NPs) show high catalytic reactivity, and the combination of nanoparticles and substrate is one of the important factors to affect the reactivity. Besides this, the particle sizes and shapes also play an important role.[1,2] To treat nano-scale metallic nanoparticles on substrates, large calculation models with several thousand atoms are required. In this study, we have investigated the interaction between a gold nanoparticle (AuNP) and MgO substrate (Fig. 1) using our own large-scale DFT code, CONQUEST[3].

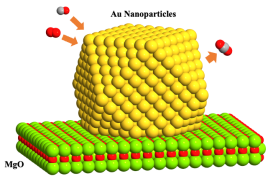


Fig. 1. Au nanoparticle on MgO (100) surface.

First, we calculated AuNPs in several sizes from 1 nm (13 atoms) to 5 nm (2057 atoms) with three different structures (Oh, Ih and Dh). It was found that the shape of the nanoparticle clearly affects the atomic and electronic structures. As the particle sizes increase, it becomes difficult to distinguish which atom has more characteristic electronic structures, i.e., which site can be an active site. Combination with machine learning has enabled it to find characteristic sites efficiently in large complex system.

Principal component analysis (PCA) and K-means clustering show the clear site-dependence of the electronic structure of the surface atoms (Fig. 2). Analysis using decision tree suggests that the major difference between inside and surface Au atoms comes from the local DOS (LDOS) around -6.9 ~ -6.1 eV (pink region in Fig. 3). The LDOS for surface Au atoms have smaller amplitudes in this energy region, which suggests the different energy position of *d* orbitals for surface atoms.

The analysis for the NPs supported on MgO substrate will be also reported in the presentation.

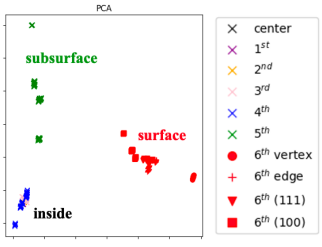


Fig. 2. PCA result for electronic structure of AuNP.

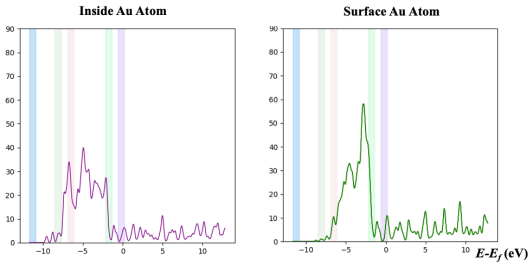


Fig. 3. Decision tree results for electronic structure of AuNP.

1) T. Mitsudome, et al., *J. Am. Chem. Soc*. **2015**, *137*, 13452-13455. 2) H. Y. Kim, et al., *J. Am. Chem. Soc*. **2012**, *134*, 1560-1570. 3) A. Nakata, et al., *J. Chem. Phys*. **2020**, *152*, 164112.

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[K202-2vn] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Takuro Tsutsumi, Yasuteru Shigeta

Thu. Mar 23, 2023 4:10 PM - 6:50 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-2vn-01] Comprehensive COSMO-RS Exploration of Highly CO_2 Selective Hydrogen-bonding Binary Absorbents

Shiori WATABE[1], ○Nahoko KUROKI[1,2], Hirotoshi MORI[1,3] （1. Chuo University, 2. JST ACT-X, 3. NEDO）

4:10 PM - 4:30 PM

[K202-2vn-02] Development and Applications of a Method for Designing Functional Molecules Based on Exploration of Chemical Space Accounting for Geometric Stability

○Takafumi Shiraogawa[1], Hasegawa Jun-ya[1] （1. Hokkaido Univ.）

4:30 PM - 4:50 PM

[K202-2vn-03] A Method for Predicting Physical Properties of Inorganic Materials Using Deep Learning Models and Proposing New Materials

○Hisanao Takahashi[1], Koji Tsuda[2], Masahito Hiroshima[1] （1. KYOCERA Corporation, 2. RIKEN）

4:50 PM - 5:10 PM

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高 CO_2 選択吸収性な水素結合性混合溶媒開発のための第一原理統計熱力学計算

（中央大理工[1]・JST ACT-X[2]・NEDO[2]）渡部 栞[1]・○黒木 菜保子[1,2]・森 寛敏[1,3]
Comprehensive COSMO-RS Exploration of Highly CO_2 Selective Hydrogen-bonding Binary Absorbents ([1]*Chuo University*, [2]*JST ACT-X*, [3]*NEDO*) Shiori Watabe,[1] ○Nahoko Kuroki,[1,2] Hirotoshi Mori,[1,3]

Improving the carbon capture efficiency with reducing the cost is mandatory for popularizing carbon capture, utilization, and storage (CCUS). Considering the objectives of green chemistry and engineering, here we show a theoretical exploration of the CO_2-absorbing capacity of a set of 1,527,030 deep eutectic solvents (DESs). Exhaustive statistical thermodynamic calculations followed the previous experiments that DESs, including choline chloride, would have better CO_2-absorbing capacity than those composed of non-ionic hydrogen bonding species in the case that choline chloride is used as a hydrogen-bonding acceptor. Quantitative evaluation of hydrogen-bonding interaction also indicated that the CO_2-absorbing capacity would increase further when choline chloride is used as a hydrogen-bonding donor.
Keywords : Hydrogen-bonding mixed solvents; Deep eutectic solvents; Carbon dioxide; Selectivity; Fast screening

効率的で持続可能な CO_2 吸収液の開発は、化学工学や環境化学分野で注目されている。現在、化学吸収法を原理とした「アミン水溶液」がプラント化されているが、その揮発毒性や液体再生時のエネルギーコストが問題視されていた。そこで我々は、カチオンとアニオンの組合せで構成される「イオン液体」に着目し、CO_2 を物理的に吸収する可能性を検討してきた。第一原理統計熱力学計算・機械学習・合成・測定により、CO_2 吸収量に優れたホスホニウム系イオン液体 $[P_{66614}][PFOS]$ の具現化に成功したものの、粘度の高さや分離選択性の低さが課題として残された[1,2]。

これらの課題を克服する新たなガス吸収液として、近年注目されているのが、水素結合によって揮発毒性を抑える混合有機溶媒「深共融溶媒 (DES)」である。DES の構成要素には、水素結合ドナー・アクセプターがあるが、どちらの性質を調整すれば目的の機能を発現可能か自明ではない。本研究の目的は、高 CO_2 選択吸収性な DES の設計指針を探索することである。統計熱力学計算 Conductor like Screening Model for Realistic Solvation (COSMO-RS) により、混合組成の異なる 1,527,030 種類の溶媒について CO_2 分離選択性を評価するファストスクリーニングを行った。探索された溶液を構成する分子の特徴を幾何的・電子的特徴の観点から評価した[3]。

1) N. Kuroki, Y. Suzuki, D. Kodama, F. A. Chowdhury, H. Yamada, H. Mori, *ChemRxiv* **2022** (DOI:10.26434/chemrxiv-2022-t1m69).
2) Y. Suzuki, D. Kodama, H. Mori, N. Kuroki, F. A. Chowdhury, H. Yamada, *Ind. Eng. Chem. Res.* **2022**, *61*, 16584.
3) N. Kuroki, S. Watabe, H. Mori, *ChemRxiv* **2022** (DOI:10.26434/chemrxiv-2022-bwc99).

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構造安定性を考慮した化学空間の探索による機能性分子設計法の開発と応用

（北大触媒研 [1]）○白男川 貴史 [1]・長谷川 淳也 [1]

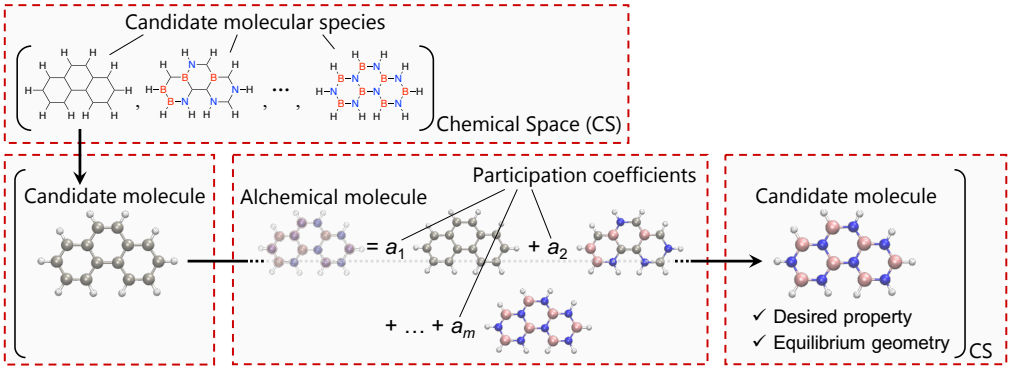
Development and Applications of a Method for Designing Functional Molecules Based on Exploration of Chemical Space Accounting for Geometric Stability

([1]*Institute for Catalysis, Hokkaido University*) ○Takafumi Shiraogawa,[1] Jun-ya Hasegawa[1]

The rational design of molecules is important for accelerating discoveries of functional molecules and materials. The design of functional molecules is regarded as searching for molecules with desired functionalities in chemical space populated by candidate molecules. Considering the geometric stability of molecules during the search process is crucial for designing realistic molecules. Here, we propose a method for designing functional molecules by exploring chemical space while explicitly accounting for geometric stability[1,2]. The proposed method allows the simultaneous prediction of functional molecule in the equilibrium structure and its target desired property without empirical data. The applicability is proven by obtaining molecules with the desired energy-related functionalities and electric dipole moments in various chemical spaces: (BF, CO), (N_2, CO), (CH_4, NH_3), 18 BN-doped benzene derivatives, and 3.1×10^5 BN-doped phenanthrene derivatives.

Keywords : Design of Functional Molecules; Chemical Space; Quantum Chemistry; Inverse Molecular Design

分子の合理設計は、機能分子・材料の開発の加速のために重要である。機能分子設計は、候補分子に占められた化学空間における所望の機能を有する分子の探索とみなせる。現実的な分子を設計するためには、設計過程で構造安定性を考慮する必要がある。本研究では、構造安定性を考慮して化学空間の効率的探索を行う機能分子設計法を開発した [1,2]。開発した方法は、経験的データなしで平衡構造における機能分子とその所望の物性を同時に予測する。この方法を(BF, CO)、(N_2, CO)、(CH_4, NH_3)、18 の BN ドープベンゼン誘導体、 3.1×10^5 の BN ドープフェナントレン誘導体の化学空間に応用し、所望のエネルギー関連機能と電気双極子能率をもつ分子の設計に成功した。



1) T. Shiraogawa, J. Hasegawa, *J. Phys. Chem. Lett.* **2022**, *13*, 8620–8627.
2) T. Shiraogawa, J. Hasegawa, *ChemRxiv* **2023**. DOI: 10.26434/chemrxiv-2023-zddx7.

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Attention 機構を用いた無機材料の物性予測深層学習モデルの構築および材料提案

（京セラ株式会社[1]・理化学研究所 革新知能統合研究センター[2]）○高橋 久尚[1]・津田 宏治[2]・廣島雅人[1]
Modeling Attention-base Deep Learning Algorithm for Predicting Some Properties of Inorganic Compounds and Suggestion of Promising Materials ([1]*KYOCERA Corporation*, [2]*RIKEN Center for Advanced Intelligence Project*) ○ Hisanao Takahashi, Koji Tsuda[2], Masahito Hiroshima[1]

Prediction models with Self-Attention structures, such as Roost and CrabNet, have garnered attention because Self-Attention enables models to learn individual element representations based on their chemical environment. However, the existing Self-Attention model yields low prediction accuracy when predicting structure-dependent material properties for lack of structural information of compounds as input. In this research, based on the existing Self-Attention model, we set both elemental and structural information, especially the space group number and lattice constant, as input information and successfully construct a prediction model that is more versatile than existing methods.
Keywords : Materials Informatics; Inorganic Compounds, Self-Attention; Deep Learning

自然言語処理における BERT モデルや画像認識における Vision Transformer のように、Transformer を用いた深層学習モデルは様々な分野において既存手法を上回る性能が確認されている。Transformer の Encoder を無機化学に応用した物性予測モデルとして Roost や CrabNet[1]がある。しかしこれらのモデルは、入力情報が化合物の組成に限定されており、構造依存の強い物性を高精度に予測することは困難である。本研究では、CrabNet のアーキテクチャをベースに、単純な構造情報(格子情報や対称性)を入力情報に加え、再学習することで汎用性の高い物性予測モデルの構築を行った。

本研究を通して得られた学習済みモデルは、既存手法と比較して幅広い範囲の物性を高精度に予測可能であり、特に磁気モーメントを予測するタスクにおいては、予測結果が Slater-Pauling 曲線に即したものとなった。

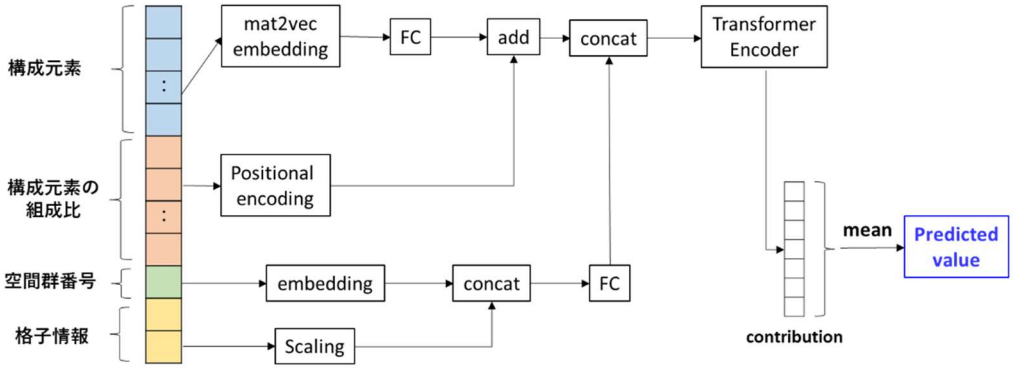


Fig.1 Schematic image of our model.

1) A.Wang, S.Kauwe, R. Murdock, and T. Sparks, *npj Comput Mater*, **2021**, *7*, 77.

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Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B

[K203-2am] 04. Physical Chemistry -Properties-

Chair: Shun Dekura, Yoshiaki Shuku

Thu. Mar 23, 2023 9:00 AM - 11:30 AM K203 (K203, Lecture Hall Bldg. [2F])

[K203-2am-01] Theoretical study on electronic structure and single-molecule electron conductivity of annulene for design guideline of molecular circuits

○Naoka Amamizu[1], Keisuke Sasaki[1], Mitsuhiro Nishida[2], Masahiro Tsuda[1], Yuta Hayashi[1], Kazuki Honjo[2], Koki Masuda[2], Ryohei Kishi[1,3,4,5], Yasutaka Kitagawa[1,3,4,5,6] （1. Graduate School of Engineering Science, Osaka Univ., 2. Faculty of Engineering Science, Osaka Univ., 3. QIQB, Osaka Univ., 4. RCSEC, Osaka Univ., 5. ICS-OTRI, Osaka Univ., 6. SRN-OTRI, Osaka Univ.）

9:00 AM - 9:20 AM

[K203-2am-02] Theoretical study on stacking structure dependence of charge density distributions in finite-sized stacks of π-conjugated molecules

○Wataru Yoshida[1], Yasuteru Shigeta[2], Hiroshi Matsui[3], Ryohei Kishi[1,4,5,6], Yasutaka Kitagawa[1,4,5,6,7] （1. Graduate School of Engineering Science, Osaka University, 2. Center for Computational Sciences (CCS), University of Tsukuba, 3. Osaka Institute of Public Health, 4. Research Center for Solar Energy Chemistry (RCSEC), Osaka University, 5. Quantum Information and Quantum Biology (QIQB), Osaka University, 6. Innovative Catalysis Science Division Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, 7. Center for Spintronics Research Network (CSRN), Osaka University）

9:20 AM - 9:40 AM

[K203-2am-03] Proposal for the Mechanism on Preferred Electric Polarization and Chirality in Ferroelectric Triglycine Sulfate Crystals by Doping with Various Glycine Analogues

○Yukana Terasawa[1], Masaaki Ichiki[2], Toshio Kikuta[3], Masahito Tanaka[2], Toru Asahi[1] （1. Waseda Univ., 2. AIST, 3. The Univ. of Toyama）

9:40 AM - 10:00 AM

[K203-2am-04] Topological band structures of polyhedral π conjugated molecule based triangular lattice

○Yoshiaki Shuku[1], Rie Suizu[1,2], Saya Nakano[3], Masahisa Tsuchiizu[3], Kunio Awaga[1] （1. Nagoya Univ., 2. JST PRESTO, 3. Nara Women's Univ.）

10:00 AM - 10:20 AM

[K203-2am-05] Low-barrier anhydrous proton conductivity based on proton tautomerism in single-crystalline azolium phosphates

○Shun Dekura[1], Kaito Nishioka[1], Hatsumi Mori[1] （1. ISSP, The Univ. of Tokyo）

10:30 AM - 10:50 AM

[K203-2am-06] Metallic State of Mixed Sequence Oligomer Salt that Models Doped PEDOT

○Kota Onozuka[1], Tomoko Fujino[1], Ryohei Kameyama[1], Shun Dekura[1], Kazuyoshi Yoshimi[1], Toshikazu Nakamura[2], Tatsuya Miyamoto[3], Takashi Yamakawa[3], Hiroshi Okamoto[3],

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Hatsumi Mori[1] （1. The Institute for Solid State Physics, The University of Tokyo, 2. Institute for Molecular Science, 3. Department of Advanced Materials Science, The University of Tokyo ）

10:50 AM - 11:10 AM

[K203-2am-07] Investigation of carrier conduction in conductive polymer PEDOT/PSS using ultra-broadband spectroscopy

○Tetsu Sato[1], Zijing Guo[1], Yang Han[1], Naoki Takamura[1], Tatsuya Miyamoto[1], Noriaki Kida[1], Makiko Ogino[2], Yotarou Takahashi[2], Qingshuo Wei[3], Masaichi Mukaida[3], Hiroshi Okamoto[1] （1. Depat of Adv. Mat. Sci., Univ. of Tokyo, 2. Depat of Appl. Phys., Univ. of Tokyo, 3. AIST）

11:10 AM - 11:30 AM

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分子回路設計指針構築に向けたアヌレンの電子状態と単分子電気伝導性に関する理論研究

（阪大院基礎工[1]・阪大基礎工[2]・阪大 QIQB[3]・阪大 RCSEC[4]・阪大 ICS-OTRI[5]・阪大 SRN-OTRI[6]）○甘水 君佳[1]・佐々木 啓介[1]・西田 光博[2]・津田 雅大[1]・林 優太[1]・本城 一樹[2]・益田 晃希[2]・岸 亮平[1,3,4,5]・北河 康隆[1,3,4,5,6]

Theoretical study on electronic structure and single-molecule electron conductivity of annulene for design guideline of molecular circuits ([1]*Graduate School of Engineering Science, Osaka Univ.,* [2]*Faculty of Engineering Science, Osaka Univ.*, [3]*QIQB, Osaka Univ.,* [4]*RCSEC, Osaka Univ.*, [5]*ICS-OTRI, Osaka Univ.*, [6]*SRN-OTRI, Osaka Univ.*) ○Naoka Amamizu,[1] Keisuke Sasaki,[1] Mitsuhiro Nishida,[2] Masahiro Tsuda,[1] Yuta Hayashi,[1] Kazuki Honjo,[2] Koki Masuda,[2] Ryohei Kishi,[1,3,4,5] Yasutaka Kitagawa,[1,3,4,5,6]

To realize molecular devices which consist of functional single-molecules, it is necessary to make molecular circuits by combing the molecules. In this study, to obtain a design guideline for molecular circuits, a relationship between electronic structure and single-molecule electron conductivity of [18]annulenes is investigated as models of the molecular parallel circuit, by using the elastic scattering Green's function method and density functional theory. According to the calculation results, the conductivity of [18]annulene can be changed by introducing electron donating or withdrawing groups to the annulene. These results are explained by the spin polarization of [18]annulene and energy interaction between the molecule and electrodes. Therefore, it is suggested that the conductivity of molecular circuits can be controlled by the substituent.

Keywords : Molecular Electronics, Molecular Circuit, Quantum Chemical Calculation, Density Functional Theory

分子エレクトロニクスとは、電子素子としての機能を有する単分子素子の実現を目指す分野である[1)]。このような単分子素子によるデバイスを構築するには、それらを組み合わせて電気回路を作る必要があると考えられる。本研究では[18]アヌレンを2つの単分子素子を並列に繋いだ分子並列回路とみなし(Fig. 1)、種々の置換基の導入によって電子状態を変化させた場合の電気伝導性変化を密度汎関数理論法と弾性散乱 Green 関数法による伝導性計算によって求めた。結果として、置換基によって分子回路の開殻性とα電子およびβ電子の分布が変化し、それによって伝導性の制御が可能であることが示唆された。結果の詳細は当日報告する。

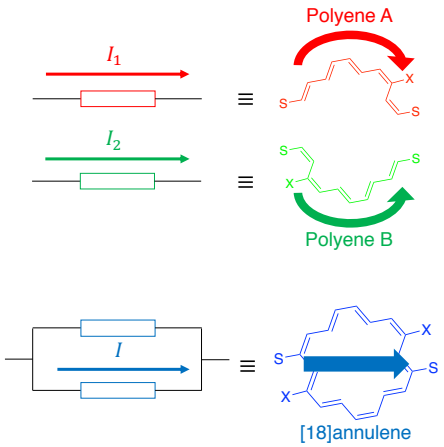


Fig. 1 モデル分子

1) D. Xiang et al., *Chem. Rev.*, **116**, 4318 (2016).

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Theoretical study on stacking structure dependence of charge density distributions in finite-sized stacks of π-conjugated molecules

([1]*Graduate School of Engineering Science, Osaka University,* [2]*Center for Computational Sciences (CCS), University of Tsukuba*, [3]*Osaka Institute of Public Health*, [4]*Reseach Center for Solar Energy Chemistry (RCSEC), Osaka University*, [5]*Quantum Information and Quantum Biology (QIQB), Osaka University*, [6]*Innovative Catalysis Science Division Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University*, [7]*Spintronics Research Network Division Institute for Open and Transdisciplinary Research Initiatives (SRN-OTRI), Osaka University*) ○ Wataru Yoshida,[1] Yasuteru Shigeta,[2] Hiroshi Matsui,[3] Ryohei Kishi,[1,4,5,6] Yasutaka Kitagawa[1,4,5,6,7]

Keywords: *Quantum Chemical Calculation; Intermolecular Electronic Conjugation; π-Conjugated Molecular Aggregate; Electronic Oxidation State; Charge Transfer*

Electronic properties of organic charge-transfer complexes composed of charge-donating and charge-accepting π-conjugated units are known to be characterized by the charge density distribution on each monomer.[1] Clarifying the relationship between structures, charge density distributions, and properties of molecular aggregates is important for establishing design strategies for versatile functional molecular materials. Previously, we theoretically investigated nonlinear optical (NLO) properties of π-stacked trimers of π-radical species and found that the third-order NLO properties of the trimers are enhanced significantly in the one-electron oxidation state when the stacking distance becomes large.[2] In this study, we have further investigated effects of the stacking distance and the electron oxidation state on electron correlations and charge density distributions in several π-stacked aggregate models consisting of closed- and open-shell molecules.

We constructed π-stacked trimer models of methyl radicals (CH_3) and ethylenes (C_2H_4) (Figure 1a) and compared the net Hirshfeld charges (Figure 1b) on each monomer in the neutral and one-electron oxidation states calculated at the UCCSD/6-31+G* level. The results show that the amplitude of the positive charge on the central monomer is larger than that on the terminal monomer in the one-electron oxidation state as the stacking distance R increases. We have discussed the origin of this trend in terms of electron correlation and orbital expansion effects.

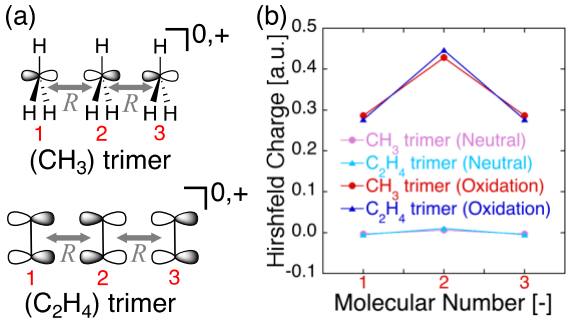


Fig. 1. Structures of (CH_3)- and (C_2H_4)-trimer models (a), and results of the net Hirshfeld charge on each monomer at R = 3.0 Å (b).

1) K. P. Goetz et al., *J. Mater. Chem. C*, **2**, 3065 (2014). 2) W. Yoshida et al., *ACS Omega*, **6**, 3046 (2021).

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様々なグリシン類縁体ドープによる強誘電体硫酸トリグリシン結晶における電気分極とキラリティの偏りのメカニズムの提案

（早大院先理[1]・早大材研[2]・産総研センシング[3]・富大工[4]・産総研計量標準[5]・早大理[6]・早大ナノ・ライフ[7]）○寺澤有果菜[1,2]・一木正聡[3]・喜久田寿郎[4]・田中真人[5]・朝日透[6,7]

Proposal for the Mechanism on Preferred Electric Polarization and Chirality in Ferroelectric Triglycine Sulfate Crystals by Doping with Various Glycine Analogues

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In the field of conductive, dielectric, and magnetic materials, the development of stable functional materials shows greatly improved by introducing chiral components. Although α-alanine-doped triglycine sulfate (TGS) is used for infrared sensors due to its high pyroelectricity, the mechanism has not been reported previously. Therefore, in this study, some glycine analogues are doped to TGS crystals in order to investigate the effect to the electric polarization, and the mechanism of forming single domain structure adding the perspective of chirality, which is deeply related to the electric polarization is discussed.

Keywords : Ferroelectricity; Electric Polarization; Chirality

導電性・誘電性・磁性材料の分野では、キラル成分を導入することで、多様な機能性材料が創出されている。α-アラニンドープ硫酸トリグリシン（TGS）結晶は焦電性が高いため、FT-IR のセンサ材料として使用されているが、その機構は未解明である[1)]。そこで、本研究では、TGS 結晶にいくつかのグリシン類縁体をドープし、電気分極への影響を調べるとともに、電気分極に深く関わるキラリティの観点からも、その機構を議論する[2,3)]。

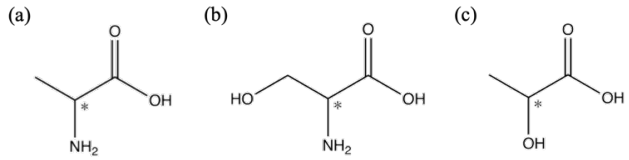


Figure 1 Molecular structure of dopants. (a) alanine, (b) serine, (c) lactic acid. The mark * represents the asymmetric carbon.

1) A. Alomari, *J. Mater. Sci: Mater. Electron*, **2022**, *33*, 4350-4359, 2) Y. Terasawa *et al*., *IEEJ Trans. Sens. Micromach.*, **2022**, 142, 205−213, 3) Y. Terasawa *et al*., *JJAP under review*.

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立体π共役系の作る三角格子のトポロジカルなバンド構造

（名大院理[1]・JST さきがけ[2]・奈良女子大理[3]）○珠玖 良昭[1]・水津 理恵[1,2]・中野 沙耶[3]・土射津 昌久[3]・阿波賀 邦夫[1]
Topological band structures of polyhedral π conjugated molecule based triangular lattice ([1]*Department of Chemistry, Nagoya University*, [2]*JST PRESTO*, [3]*Department of Physics, Nara Women's University*) ○Yoshiaki Shuku,[1] Rie Suizu,[1,2] Saya Nakano,[3] Masahisa Tsuchiizu,[3] Kunio Awaga[1]

Electronic structures of graphene and related materials attracted much attention, because of their exotic physical properties arising from their unique electronic band structures such as Dirac cone and flat band. Band structure of graphene includes Dirac cone which provides massless fermions. In contrast, the effective mass of flat band which has no energy dispersion can be regarded as infinitely heavy. The structural models of flat band are also actively investigated, because it has possibility to provide ferromagnetism and superconductivity. Previously, we prepared radical anion salts of polyhedral π conjugated molecules and demonstrated their highly symmetric crystal structures and their unique electronic band structure by the tight-binding method.[1,2)] In the band structure of these crystal structures, both the Dirac cone and flat band are always included reflecting the symmetry of polyhedral π conjugated molecules. Based on these results, we systematically calculated electronic band structures of the triangle lattice, which consist of polyhedral π conjugated molecules, by changing intramolecular and intermolecular interactions as parameters. The origin of their topological band structures will be discussed in detail.
Keywords : Triptycene; Triangle Lattice; Dirac Cone; Flat Band

近年、ディラックコーンやフラットバンドといった特徴的な分散を含むバンド構造や、そこから発現する物理が注目を集めている。グラフェンンの特異な物性は、ディラックコーンにおける有効質量 0 の電子の振る舞いとして議論されている。エネルギー分散のないフラットバンドはこれとは対照的に電子の有効質量を重い極限として考えることができ、強磁性や超伝導の起源として期待されることから注目を集めている。我々は、*p*-TT や NDI-Δのような分子が 3 回軸をもつように 3 つのπ平面が接続された分子（立体π共役分子）を構成要素とすることで、グラフェンや数学的に予測された K_4 炭素といった sp^2 炭素同素体の等構造の構築に成功している[1,2)]。それらの構造を基にした強束縛近似によるバンド計算から、分子性炭素同素体のバンド構造には炭素同素体にも見られるディラックコーンに加えて、フラットバンドが必然的に含まれることを提案している。我々は、立体π共役系の作る構造に興味を持ち様々な類縁体を作製しているが、本研究ではこれらのバンド構造をより深く理解するために、相互作用を系統的に変化させた三角格子のモデル構造において、強束縛近似によるバンド計算を行った。発表では、このようなモデル構造におけるトポロジカルなバンド構造の起源について詳細に議論する。

1) A. Mizuno *et al*. *J. Am. Chem. Soc.* **2015**, *137*, 7612-7615.
2) Y. Shuku *et al*. *Chem. Commun.* **2018**, *54*, 3815-3818.

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リン酸アゾリウム単結晶におけるプロトン互変異性に基づく低障壁無水プロトン伝導

（東大物性研）○出倉 駿・西岡 海人・森 初果

Low-barrier anhydrous proton conductivity based on proton tautomerism in single-crystalline azolium phosphates (*The Institute for Solid State Physics, The University of Tokyo*) ○Shun Dekura, Kaito Nishioka, Hatsumi Mori

Anhydrous proton (H^+) conductors have attracted attention as solid H^+ electrolytes that can operate without humidification and in the medium temperature range above 100 °C. In previous studies on molecular single crystals, molecular motions responsible for intra-molecular H^+ transfer has been considered essential for H^+ conduction; however, it is often accompanied by high activation energies of several eV.[1–4] In this study, we focused on H^+ tautomerism, which is a fast interconversion between states with different H^+ positions in a molecule, as a new conduction mechanism to replace molecular motion. Azolium phosphate single crystals were prepared, where imidazolium (ImH^+) is replaced with 1,2,3-triazolium (1,2,3-$TrzH^+$) or 5-aminotetrazolium (5AmTetzH^+), which can exhibit H^+ tautomerism (Figure a,b). The results showed that the introduction of H^+ tautomerism can systematically achieve low-barrier anhydrous H^+ conductivity (Figure c).

Keywords : Proton Conductor; Molecular Solid; Azole; Phosphate; Tautomerism

加湿不要かつ 100 °C 以上の中温域で動作可能なプロトン(H^+)の固体電解質として、無水 H^+伝導体が注目されている。分子性単結晶を用いた先行研究では、水素結合ネットワークの構築と分子間 H^+移動に加え、分子内 H^+移動を担う分子運動が重要であると考えられてきたが、結晶中分子運動の制御は困難であり、しばしば数 eV の高い活性化エネルギーを伴うことが課題であった [1–4]。本研究では分子運動に置き換わる新たな機構として、分子中 H^+位置が異なる状態間の高速相互変換である H^+互変異性に着目した。イミダゾリウム (ImH^+)を H^+互変異性能を有する 1,2,3-トリアゾリウム (1,2,3-$TrzH^+$) または 5-アミノテトラゾリウム (5AmTetzH^+)に置き換えたリン酸アゾリウム 単結晶を作製し (Figure a,b)、各塩のアゾリウム分子を含む伝導方向の単結晶無水 H^+伝導度を比較したところ、H^+互変異性の導入によって系統的に低障壁な無水 H^+伝導性を実現できることが明らかになった (Figure c)。

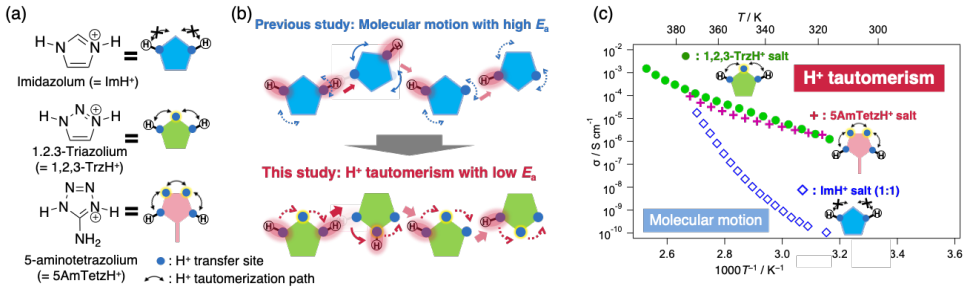


Figure. (a) Structures of the azolium molecules. (b) Schematic image of the new strategy utilizing H^+ tautomerism. (c) Temperature dependences of anhydrous H^+ conductivities of the azolium phosphates.

[1] Y. Sunairi, SD, HM *et al.*, *J. Phys. Soc. Jpn.* **2020**, *89*, 051008. [2] Y. Hori, SD, HM, *et al.*, *J. Phys. Chem. Lett.* **2021**, *12*, 5390. [3] SD, HM, *et al.*, *Solid State Ionics* **2021**, *372*, 115775. [4] SD, M. Mizuno, HM, *Angew. Chem. Int. Ed.* **2022**, *61*, e202212872.

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Metallic State of Mixed Sequence Oligomer Salt that Models Doped PEDOT

([1]*The Institute for Solid State Physics, The University of Tokyo*, [2]*Institute for Molecular Science,* [3]*Department of Advanced Materials Science, The University of Tokyo*)
○Kota Onozuka[1], Tomoko Fujino[1], Ryohei Kameyama[1], Shun Dekura[1], Kazuyoshi Yoshimi[1], Toshikazu Nakamura[2], Tatsuya Miyamoto[3], Hiroshi Okamoto[3], Hatsumi Mori[1]
Keywords: Charge-transfer salts; Oligothiophene; Molecular crystal; Electrical conductivity; Radical cation

Conjugated polymers (e.g., doped poly(3,4-ethylenedioxythiophene) (PEDOT)) (Figure 1a, left) are commonly employed materials in organic electronic devices. However, due to the wide molecular-weight distribution, detailed structural information could not be obtained, limiting research on the mechanism of conductivity and methods to control conductivity[1]. To solve these problems, we reported oligomer models for doped PEDOT (i.e., ***n*O•*X***, n = 2–3, X = BF_4, ClO_4, PF_6, $H_y(SO_4)_z$, Figure 1)[2), 3), 4)].

In this study, we extended the oligomers by introducing mixed sequences. The multiple units are assembled in a precisely designed sequence that are intrinsic structural determinants of the oligomers. We designed and synthesized **4PS** with a sequence of P-S-S-P composed of the oxygen/sulfur-substituted unit **S** and unit **P** (Figure 1a, right).

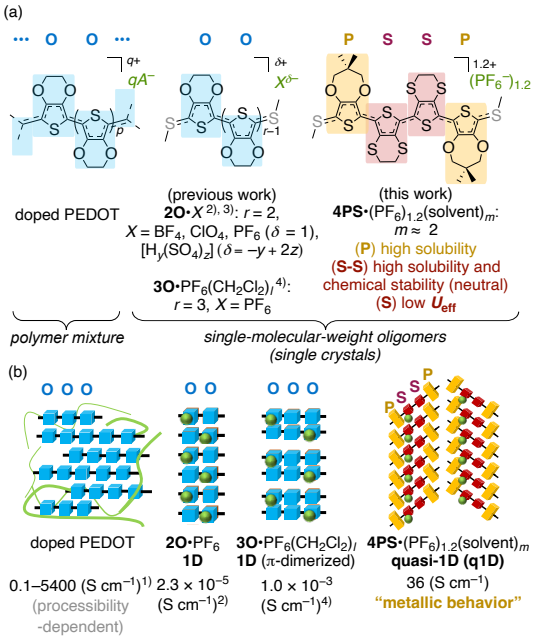


Figure 1. (a) Chemical structures of doped PEDOT, **2O•*X***, **3O•**$PF_6(CH_2Cl_2)_l$, and **4PS•**$(PF_6)_{1.2}(solvent)_m$ with structural-unit designators above each structure. (b) Illustrating packing structures. The assignment for **4PS•**$(PF_6)_{1.2}(solvent)_m$ composition formula is discussed in the text. Cubes: polymer and oligomer units. Green strings and circles: counter anions for donors.

The single-crystal XRD analysis of **4PS•**$(PF_6)_{1.2}(solvent)_n$ showed that it forms a pitched π-stack packing structure. The room temperature conductivity σ_{rt} of the single crystal was 36 S/cm, a six-order magnitude higher than that of **2O•**PF_6. Above room temperature, a metallic state was observed. The dramatic improvement of the conductivity can be attributed to the reduction of Coulomb repulsion energy, band filling, and higher dimensionality by introduction of mix sequence.

1) H. Shi *et al*., *Adv. Electron. Mater.* **2015**, *1*, 1500017. 2) R. Kameyama *et al*., *Chem. Eur. J.* **2021**, *27*, 6696. 3) R. Kameyama *et al*., *J. Mater. Chem. C*, **2022**, *10*, 7543. 4) R. Kameyama *et al*., *Phys. Chem. Chem. Phys,* **2022**, *24*, 9130.

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超広帯域分光を用いた導電性高分子 PEDOT/PSS のキャリア伝導の研究

(東大新領域[1]・東大工[2]) ○佐藤 鉄[1]・紫荊 郭[1]・陽 韓[1]・高村 直幹[1]・宮本 辰也[1]・貴田 徳明[1]・荻野 慎子[2]・高橋 陽太郎[2]・慶碩 衛[3]・向田 雅一[3]・岡本 博[1]

Investigation of carrier conduction in conductive polymer PEDOT/PSS using ultra-broadband spectroscopy ([1]*Depat of Adv. Mat. Sci., Univ. of Tokyo*, [2]*Depat of Appl. Phys., Univ. of Tokyo*, [3]*AIST*) ○Tetsu Sato,[1] Zijing Guo,[1] Yang Han,[1] Naoki Takamura,[1] Tatsuya Miyamoto,[1] Noriaki Kida,[1] Makiko Ogino,[2] Yotarou Takahashi,[2] Qingshuo Wei,[3] Masaichi Mukaida,[3] Hiroshi Okamoto[1]

The conductivity of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) (PEDOT/PSS) films are known to change significantly depending on different assembling morphologies of PEDOT molecules within the polymer. In this study, spin-coated PEDOT/PSS films were immersed in ethylene glycol (EG) or drop casted by sulfuric acid to get films with DC conductivities of approximately 1000 S/cm and 1700 S/cm, respectively. THz time-domain spectroscopy and infrared-visible reflection spectroscopy were applied to these samples to derive ultra-broadband complex optical conductivity spectra in the terahertz to visible range. These spectra can be well reproduced by the Drude-Lorentz model, which is the sum of the Drude response of carriers and Lorentz-oscillator responses of molecular vibrations. Carrier-density and mobility values were precisely evaluated from analyses of the Drude response.
Keywords : PEDOT/PSS; electrical conductivity; ultra-broadband spectroscopy; optical conductivity spectra; Drude model

フレキシブルな透明電極としての応用が期待されるポリ(3,4ーエチレンジオキシチオフェン)/ポリ(スチレンスルホン酸)(PEDOT/PSS)薄膜では、ポリマー内の PEDOT 分子の集積状態によって伝導度が大きく変化することが知られている。本研究では、スピンコート法で作製した PEDOT/PSS 薄膜にエチレングリコールへの浸漬処理あるいは硫酸 drop 処理を施すことによって、それぞれ、約 1000 S/cm および 1700 S/cm の直流伝導度を示す試料を得た。これらの試料に対し、THz 時間領域分光と赤外-可視反射分光を適用し、テラヘルツから可視域にわたる超広帯域複素光学伝導度スペクトルを導出した。このスペクトルは、Drude-Lorentz モデルを適用することにより、キャリアによる Drude 応答と分子振動による Lorentz 振動子の応答の和として再現することが可能である。さらに、Drude 応答の解析から、キャリアの移動度や密度を定量的に評価できる。当日は、測定手法及び電気伝導を特徴づけるパラメータについて、詳細な報告を行う。

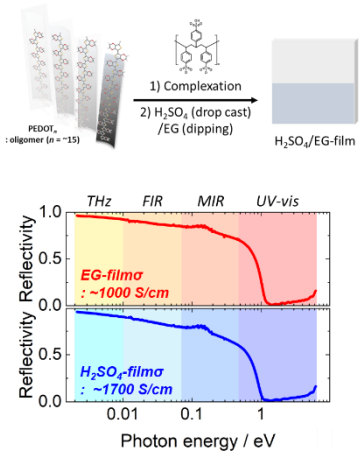


Figure1. PEDOT/PSS 薄膜の成膜過程(上)と得られた 2 試料の超広帯域反射スペクトル(下)

1) S. He et al., *Polymers*, **2018**, *10*, 1065, 2) M. Yamashita et al., *Appl. Phys. Lett.*, **2011**, *99*, 143307

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Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B

[K203-2pm] 04. Physical Chemistry -Properties-

Chair: Kiyoshi Miyata, Ryohei Kishi

Thu. Mar 23, 2023 1:10 PM - 3:30 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-2pm-01] Ultrafast Spectroscopy of InP-based Core/shell Quantum Dots under Ultrahigh Pressure

○Daichi Eguchi[1], Naoto Tamai[1] (1. Kwansei Gakuin Univ.)

1:10 PM - 1:30 PM

[K203-2pm-02] Comparing the Raman and emission thermometry of a hydroxo-bridged molecular magnet

○KUNAL KUMAR[1], Olaf Stefanczyk[1], Szymon Chorazy[2], Koji Nakabayashi[1], Shin-ichi Ohkoshi[1] (1. University of Tokyo, 2. Jagiellonian University)

1:30 PM - 1:50 PM

[K203-2pm-03] Real-Time Tracking of Photon Upconversion Processes in Rare Earth Doped Nanoparticles using Ultrafast Spectroscopy

○Kiyoshi Miyata[1], Mako Takada[1], Kanji Sugioka[1], Shiori Miyazaki[1], Mitsunori Ohta[2], Ryusuke Mizoguchi[2], Ayumi Ishii[2], Ken Onda[1] (1. Kyushu University, 2. Teikyo Univ. of Sci.)

1:50 PM - 2:10 PM

[K203-2pm-04] Theoretical Study on Low-Lying Excited States Involved in Singlet Fission Process of Fused-ring Compounds Containing Diphenoquinone Structure

○Kenji Okada[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. QIQB, Osaka University, 3. RCSEC, Osaka University, 4. ICS-OTRI, Osaka Uniersity, 5. SRN-OTRI, Osaka University)

2:30 PM - 2:50 PM

[K203-2pm-05] Theoretical Study on Singlet Fission Dynamics in One-dimensional Molecular Aggregate Models: Dependence of Spatial Distributions of Correlated Triplet Pair on Structure of Aggregate

○Hajime Miyamoto[1], Kenji Okada[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. Center for Quantum Information and Quantum Biology, Osaka-University, 3. Research Center for Solar Energy Chemistry, Osaka University, 4. Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University, 5. Spintronics Research Network Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University)

2:50 PM - 3:10 PM

[K203-2pm-06] Theoretical study on relationship between open-shell character and intermolecular interaction energy in closely-π-stacked aggregates composed of antiaromatic molecules

○Ryota Sugimori[1], Masato Ikeuchi[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. RCSEC, Osaka University, 3. QIQB, Osaka University, 4. ICS-OTRI, Osaka University, 5. SRN-OTRI, Osaka University)

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3:10 PM - 3:30 PM

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InP 系コアシェル量子ドットにおける超高圧下での超高速分光

（関学院理）○江口 大地・玉井 尚登
Ultrafast Spectroscopy of InP-based Core/shell Quantum Dots Under Ultrahigh Pressure
([1]*Graduate School of Science, Kwansei Gakuin University*)○Daichi Eguchi, Naoto Tamai

Quantum dots (QDs) exhibit size-dependent electronic structures different from the bulk due to a quantum size effect. The elementary exciton processes of QDs also show size-dependent behavior. Although the exciton dynamics at ambient pressure has been extensively studied, that under ultrahigh pressure has been little examined. In this study, we applied pressure to InP core/shell QDs using a diamond anvil cell and examined the elementary exciton dynamics by femtosecond transient absorption spectroscopy.
Keywords : Diamond Anvil Cell; Ultrahigh Pressure; Ultrafast Spectroscopy

物質への圧力印加は、原子間距離を変化させ、電子構造を制御する手法である。半導体量子ドット (QDs) は、電子-正孔対である励起子を微小空間に閉じ込めたナノ結晶であり、量子サイズ効果が発現し粒径に応じた電子構造を有している。QDs へ圧力を印加し、定常状態での物性変化を解析した報告例はあるものの [1]、パルス励起後に生成するホット電子の緩和過程といった非平衡状態の圧力依存性は未解明な点が残されている。そこで本研究では、InP 系コアシェル QDs にダイヤモンドアンビルセル (DAC) で圧力を印加し、その励起子素過程をフェムト秒過渡吸収分光 (fs-TA) 測定で明らかにしたので報告する。

ホットインジェクション法により、ワンポットで InP/ZnS QDs の合成を行った。透過型電子顕微鏡観察の結果から、InP コアは 2.4±0.6 nm、InP/ZnS QDs は 2.7±0.6 nm であった。定常光の吸収と発光スペクトル測定から、励起子吸収の極大吸収波長と極大発光波長は InP コアに比べて InP/ZnS QDs では赤方偏移しており、発光量子収率は 200 倍程度上昇していることから、InP コアに対して ZnS シェルがエピタキシャル成長したことが分かった。合成した InP/ZnS QDs に DAC を用いて、圧力を印加すると励起子吸収及び極大発光波長が青方偏移した (Figure 1)。この印加圧力での粒径変化は 5%以下であるため、青方偏移は量子サイズ効果によるものではなく、粒径変化に伴う電子状態の変化に起因していると考えている [2]。fs-TA 測定では、励起子吸収のブリーチが観測され、この信号も圧力印加することで定常光の吸収スペクトルと同様に青方偏移した。このブリーチダイナミクスの立ち上がりは、ホット電子の緩和過程に対応し、この緩和速度は圧力を印加することで早くなっていることが分かった。

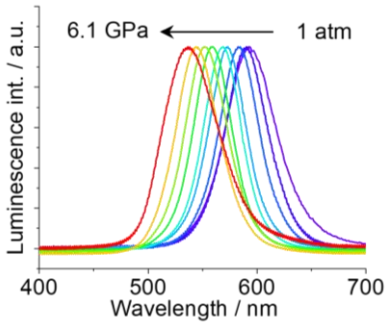


Figure 1. Pressure-dependent luminescence spectra of InP/ZnS QDs (λ_{ex} = 400 nm).

[1] Z. Lin *et al.*, *Angew. Chem. Int. ed.* **2021**, *60*, 9772. [2] B. Zou *et al.*, *Nanoscale Horiz.* **2020**, *5*, 1233.

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Comparing the Raman and emission thermometry of a hydroxo-bridged molecular magnet

([1]*Graduate School of Science, University of Tokyo*, [2]*Faculty of Chemistry, Jagiellonian University*) ○KUNAL KUMAR[1], Olaf Stefanczyk[1], Szymon Chorazy[2], Koji Nakabayashi[1], Shin-ichi Ohkoshi[1]

Keywords: Raman thermometer, emission thermometer, single molecule magnet, low-frequency Raman spectroscopy, ab-initio calculation

The design of multi-functional materials with an ability to perform multiple task is being studied by the researchers globally due to its potential application in diverse fields.[1] Our lab has shown that magnetism of molecular compounds can be controlled by various external stimuli such as – light, pressure, humidity, etc. Learning from these experiences, we synthesized three materials with the general formula $[Dy_x^{III}Y_{1-x}^{III}(phen)_2(\mu\text{-}OH)_2(H_2O)_2]\cdot[Au^I(SCN)_2]_2\cdot phen\cdot 0.5MeCN\cdot 0.5H_2O$ (x = 0 (**DyAu**), 0.1 (**$Dy_{0.1}Y_{0.9}Au$**), 0.02 (**$Dy_{0.02}Y_{0.98}Au$**); phen = 1,10–phenanthroline) containing lanthanide(III) ions (Ln^{3+}) and bis(thiocyanato)gold(I) ions (Figure 1a).[2] They have centrosymmetric P-1 space group with central Ln^{3+} ions coordinated by two water molecules, two hydroxide ions, and two phen ligands. The charge of cationic components $\{Dy^{III}(phen)_2(H_2O)_2(\mu\text{–}OH)\}^{+2}$ are balanced by the presence of $\{[Au^I(SCN)_2]^-\}_2$–moiety consists of two Au(I) atoms with two thiocyanide ions.

All complexes' crystals exhibit several distinct Raman active vibrations in the LF region (Figure 1b). We considered the compounds to be a prime choice to investigate their thermometric ability because they don't absorb any light in the visible spectrum. We determined the ratio of anti-Stokes and Stokes peaks for three distinct phonons associated with the thiocyanidometallate vibrations, which are centered at 27, 108, and 304 cm^{-1}. To determine the utility of such a thermal sensor, we further tested **DyAu**'s capacity for temperature sensing in a variety of benchtop solvents (ethanol, water, methanol, acetone, acetonitrile, isopropanol, etc.). Thermal sensing ability of all three compounds were compared using Raman as well as emission properties. Additionally, **$Dy_{0.02}Y_{0.98}Au$** reveal field-induced single molecule magnet behaviour.

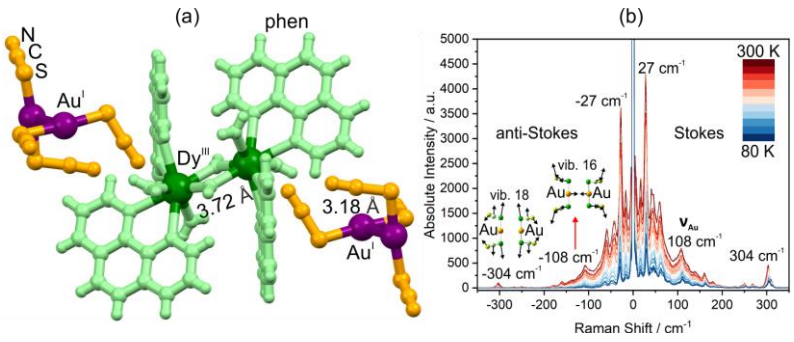


Figure 1. Representative crystal structure of **DyAu** (a) and Raman spectrum of **DyAu** at various temperature in the low-frequency region.

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nat. Photonics* **2014**, *8*, 65. 2) K. Kumar, O. Stefanczyk, S. Chorazy, K. Nakabayashi, S. Ohkoshi, *Adv. Optical Mater.* **2022**, *10*, 2201675.

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Real-Time Tracking of Photon Upconversion Processes in Rare Earth Doped Nanoparticles using Ultrafast Spectroscopy

([1]*Kyushu University*, [2] *Teikyo Univ. of Sci.*) ○Kiyoshi Miyata,[1] Mako Takada,[1] Kanji Sugioka,[1] Shiori Miyazaki,[1] Mitsunori Ohta[2], Ryusuke Mizoguchi[2], Ayumi Ishii[2], Ken Onda[1]

Keywords: Photon upconversion; Lanthanide; Nanoparticle; Time-resolved photoluminescence spectroscopy; Emissive materials

Trivalent lanthanide ions-based up-conversion nanoparticles (UCNPs) are expected as photon up-conversion luminescent materials due to their high photochemical stability, significant anti-Stokes shift, and narrow emission line width [1-3]. In this study, we have tracked the emission intensity changes from multiple emission levels for Yb-Tm UCNPs in real time, mainly by time-resolved luminescence measurements (TR-PL), to analyze the energy transfer mechanism and the effect of the surface coating of the nanoparticles.

Figure 1(a) shows the UC emission spectrum observed when Yb^{3+} is excited at 980 nm and the assignments of the transitions to each emission line. Emission lines from multiple levels due to UC emission were observed in a range from 460 nm to 800 nm. Figure 1(b) shows the time evolution of the UC emission intensity from $^1D_2$, $^1G_4$, and $^3F_{2,3}$ of Tm^{3+} observed after excitation with nanosecond pulsed light. Among these levels, the emission increase from $^3F_{2,3}$ occurs on the fastest time scale (0.1 μs), indicating that $^3F_{2,3}$ is occupied in the first UC. The time constant for the emission enhancement of higher-lying $^1D_2$ (0.24 ms) is faster than the time constant for the emission enhancement from the $^1G_4$ level (0.35 ms). Therefore, it is suggested that the UC process from $^3F_{2,3}$ to $^1G_4$ is due to the energy transfer from Yb^{3+} via the $^3F_{2,3} \rightarrow {}^3H_4$ relaxation, while the UC from the $^3F_{2,3}$ to the $^1D_2$ level is due to the energy transfer in the $^3F_{2,3}$ level between Tm^{3+} ions.

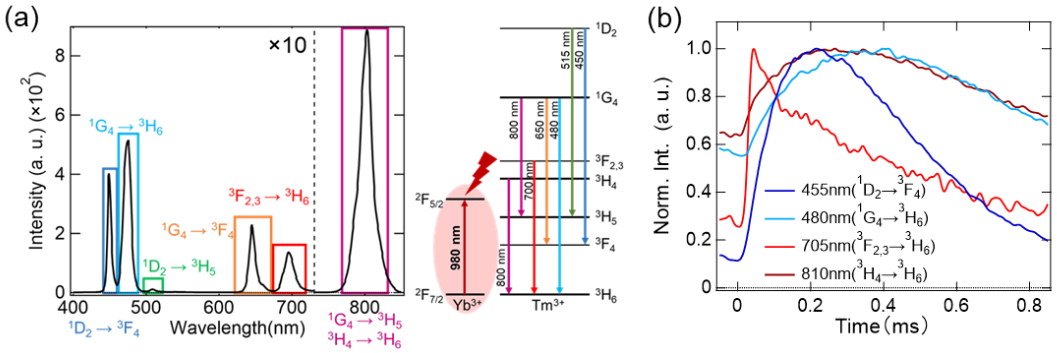


Figure. 1. (a) Spectra of UC emission of Yb-Tm UCNP observed with 980 nm excitation: 400~730 nm: excitation intensity 3.1×10^2 mW/cm^2, 730~850 nm: excitation intensity 1.5×10^2 mW/cm^2. (b) Temporal change of emission intensity from $^1D_2$, $^1G_4$, $^3F_{2,3}$ levels after pulsed excitation at 980 nm.

Refs: [1] A. Ishii, M. Hasegawa, *Sci. Rep.* **2017**, *7*, 1. [2] W. Liu, et al. *Angew. Chemie* **2021**, *133*, 7117. [3] A. Ishii, T. Miyasaka, *Adv. Photonics Res.* 2022, DOI: 10.1002/adpr.202200222

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ジフェノキノン骨格を含有する縮合環化合物の一重項分裂過程に関与する低励起状態の理論研究

（阪大院基礎工[1]・阪大 QIQB[2]・阪大 RCSEC[3]・阪大 ICS-OTRI[4]・阪大 SRN-OTRI[5]）
○岡田 健治[1]・岸 亮平[1,2,3,4]・北河 康隆[1,2,3,4,5]

Theoretical Study on Low-Lying Excited States Involved in Singlet Fission Process of Fused-ring Compounds Containing Diphenoquinone Structure ([1]*Graduate School of Engineering Science, Osaka University,* [2]*QIQB, Osaka University,* [3]*RCSEC, Osaka University,* [4]*ICS-OTRI, Osaka University,* [5]*SRN-OTRI, Osaka University*) ○ Kenji Okada,[1] Ryohei Kishi,[1,2,3,4] Yasutaka Kitagawa[1,2,3,4,5]

Singlet fission (SF) is a photophysical process in which a singlet exciton splits into two triplet excitons.[1] SF has attracted intense attention due to its potential to improve the photoelectric conversion efficiency of solar cells. Matching conditions for the energy levels of low-lying singlet and triplet excited states at the monomer level have been proposed,[1] and open-shell singlet molecules with mediate diradical character y_0 tend to satisfy the criteria.[2] In this study, we focused on 4,4'-diphenoquinone structure, which exhibits weak diradical character. Quantum chemical calculations revealed that dark nπ* states (S_1 and S_2) and the bright ππ* state S_3 satisfy the SF energy matching condition. We further investigated low-lying excited states of several fused-ring compounds containing 4,4'-diphenoquinone as a substructure to examine their possibilities as candidates for novel SF materials.

Keywords : Singlet Fission; Quantum Chemical Calculations; Carbonyl Compounds

一重項分裂(SF)は光励起により生成した 1 つの一重項励起子が 2 つの三重項に分裂する過程であり、太陽電池への応用による光電変換効率の向上が期待されている。候補分子の探索においては分子レベルでは一重項及び三重項励起状態の励起エネルギーに関する条件 $E(S_1) \geq 2E(T_1)$を満たすことが求められる[1]。また、分子の開殻性を表すジラジカル因子 y_0 を用いたスクリーニング方法が提案されており、0.2~0.5 程度の y_0 を持つ弱～中間的な開殻性を示す分子が上記のエネルギー整合条件を満たす傾向にある[2]。本研究では 4,4'-ジフェノキノン骨格を含有する縮合環化合物を対象に量子化学計算による検討を行った。4,4'-ジフェノキノンは Figure 1 に示したようなジラジカル的な共鳴構造の寄与が存在するため $y_0 = 0.3$ と開殻性を示す。励起状態計算の結果、S_1, S_2 は対称禁制な nπ*遷移と対応し、他方で光学的許容な ππ*遷移は S_3 と対応することがわかった。これらの状態の励起エネルギーはいずれも T_1 の励起エネルギーの二倍よりも大きいか同程度であるためエネルギー整合条件を満たす。さらに、この結果に基づき 4,4'-ジフェノキノンを部分骨格として有する種々の分子を設計したところ、その多くは新たに SF 分子の候補となる可能性があることを見出した。

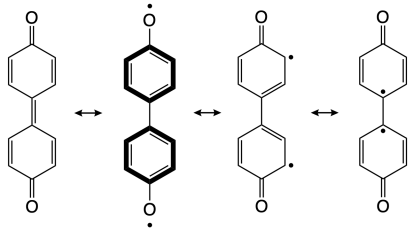


Figure 1. Resonance structures of 4,4'-diphenoquinone.

1) M. B. Smith, J. Michl, *Chem. Rev*. **2010**, *110*, 6891.
2) T. Minami, M. Nakano, *J. Phys. Chem. Lett.* **2012**, *3*, 145.

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一次元分子集合系における一重項分裂ダイナミクスに関する理論研究:三重項励起子移動の影響

（阪大院基礎工[1]・阪大 QIQB[2]・阪大 RCSEC[3]・阪大 ICS-OTRI[4]・阪大 SRN-OTRI[5]）○宮本 孟[1]・岡田 健治[1]・岸 亮平[1,2,3,4]・北河 康隆[1,2,3,4,5]
Theoretical study on singlet fission dynamics in one-dimensional molecular aggregate models: dependence of spatial distribution of correlated triplet pair on structure of aggregate ([1]*Graduate School of Engineering Science, Osaka University*, [2]*QIQB, Osaka University,* [3]*RCSEC, Osaka University,* [4] *ICS-OTRI, Osaka University,* [5]*SRN-OTRI, Osaka University*) Masato Ikeuchi,[1] Ryota Sugimori,[1]○Ryohei Kishi,[1,2,3,4] Yasutaka Kitagawa,[1,2,3,4,5]

Singlet Fission (SF) is a photophysical process in which one singlet exciton splits into two triplet excitons in organic molecular aggregates, and has been pointed out to have potential to improve photoelectronic conversion efficiency in organic solar cells. Recently, control of correlated triplet exciton pair states as the intermediate states of SF has been examined. In this study, we discussed correlation between structure-SF property in one dimensional molecular aggregate in which triplet exciton transfer integral and spatial distribution of triplet pair states are taken into account.

Keywords : Singlet Fission; Quantum Master Equation; Molecular Aggregate; Exciton Dynamics; Pentacene

一重項分裂(SF)とは、一重項励起子(S_1)が二つの三重項励起子(T_1)に分裂する現象であり、有機太陽電池におけるキャリア電流増加への応用可能性が指摘されている [1]。近年、SF の中間体として生じる相関三重項対(TT)状態の空間的分離過程の制御に関する研究が進められている [2]。このような三重項励起子対の分布に影響を与える因子には、結晶や有限分子集合系に見られるように、部分的に不均一な欠陥の存在といった配列のパターンが挙げられる。このような配列パターンの変化が SF ダイナミクスや相関 TT 対の空間的分離過程に与える影響を議論することは、高速かつ高収率な SF 分子及び有限分子集合系の設計に重要であると考えられる。

モデル系として、図 1 のような分子(黒丸)の間の電子カップリングが赤と青で異なる(A)均一および(B)不均一一次元 N 量体を考える。まず SF に関わる一重項励起(S_1S_0)状態、電荷移動(CT)状態、相関 TT 状態を用いたモデルハミルトニアンを構築し、電子カップリングをパラメータ的に用い、相関 TT 対の空間的分離が促進される条件を検討した。また、この条件を満たしうるペンタセン二量体配置での量子化学計算の結果を用いて、量子マスター方程式法 [3]により SF 速度や TT 分離ダイナミクスの検討を行った。図 1(B)の構造における青色の部分の SF 速度が S_1 移動より十分に速く、かつ両端では三重項移動積分が速いときに著しく相関 TT 間距離が大きくなることが明らかになった。

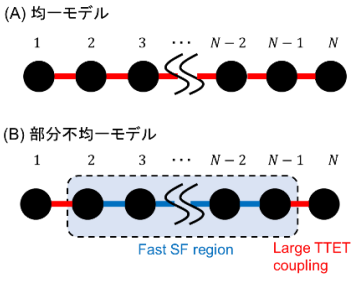


Fig.1. Model structure of one-dimensional aggregate system.

1) M. B. Smith, J. Michl *Chem. Rev.* **2010**, *110*, 6891. 2) K. Miyata et al., Chem. Rev. 2019, 119, 6, 4261. 3) M. Nakano et al., *J. Comput, Chem*. **2019**, *40*, 89.

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近接したπ積層反芳香族分子集合系における開殻性と分子間相互作用エネルギーの関係についての理論研究

(阪大院基礎工[1]・阪大 RCSEC[2]・阪大 QIQB[3]・阪大 ICS-OTRI[4]・阪大 SRN-OTRI[5])
○杉森亮太[1]・池内雅登[1]・岸亮平[1234]・北河康隆[12345]

Theoretical study on relationship between open-shell character and intermolecular interaction energy in closely-π-stacked aggregates composed of antiaromatic molecules

([1]*Graduate School of Engineering Science, Osaka University*, [2]*RCSEC, Osaka University,* [3]*QIQB, Osaka University*, [4]*ICS-OTRI, Osaka University,* [5]*SRN-OTRI, Osaka University*)
○Ryota Sugimori[1], Masato Ikeuchi[1], Ryohei Kishi[1234], Yasutaka Kitagawa[12345]

π-Stacked antiaromatic molecular aggregates are expected as candidates for novel functional materials, from the viewpoints of the possibility for utilizing intermolecular conjugation and the excellent external-field-induced response properties. In this study, we discuss the relationship between the open-shell character in the monomer and intermolecular stabilization energy in the π-stacked antiaromatic molecular aggregates, by calculating the intermolecular interaction energy for aggregate models of several antiaromatic molecules.
Keyword: π-stacked aromaticity, antiaromatic molecules, intermolecular interaction, quantum chemical calculation.

$4n$ 個の π 電子をもつ環状 π 共役分子である反芳香族分子は小さな HOMO-LUMO gap (Δ_{hl})を有し、比較的不安定な分子として知られている。一方、摂動論に基づけば、$4n\pi$ 電子系の小さな Δ_{hl} は、優れた応答物性や特異な分子集合構造の形成の起源としても期待される。後者に関しては、小さな Δ_{hl} により分子間に大きな軌道相互作用が生じることで、近接した対面 π 積層構造の実現可能性が指摘されており[1]、集合系の安定化機構や分子間の非局在化による電子、光学物性の向上など、分子材料の新規機能発現・制御機構として期待されている。実験的には、反芳香族ポルフィリン分子である Ni^{II}-ノルコロール分子が近接した分子配置に伴う構造や物性変化が報告されたが[2]、数えるほどしかない。これは、反芳香族分子の近接 π 積層による安定化機構が十分に明らかになっていないことが原因の一つと考えられる。

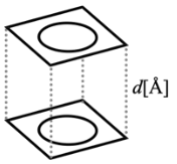


Fig. 1 CBD 積層二量体モデル

交換、核間反発効果の存在下で近接した π 積層構造を実現するには、分子間にこれらに匹敵する安定化効果が働く必要がある。分子間軌道相互作用による安定化の程度は、Δ_{hl} を通じて単量体の一重項状態の開殻性と関係づけられる可能性がある。そこで、本研究では、単分子が持つ開殻性と分子間のエネルギー安定化の関係を検討する。具体的には、種々の反芳香族分子の集合系モデルに対して、分子間相互作用エネルギーを高精度量子化学計算により算出し、エネルギー分割解析を行った。Fig.1 に示すシクロブタジエン(CBD)二量体モデルに対する計算と解析の結果から、近接した π 積層構造の実現には、(1)単量体の局所安定構造と y が増大可能な構造がエネルギー的に近いこと、(2)軌道相互作用だけでなくそれ以外の相互作用エネルギーの寄与を考慮した設計や制御が重要であることが明らかになった。

[1] C. Corminboeuf et. al., *Org. Lett.*, **9**, 3263 (2007). [2] R. Nozawa et al., *Nat. Commun*., **7**, 13620 (2016); *Nat. Commun*. **10**, 3576 (2019); H. Kawashima et al., *J. Am. Chem. Soc.*, **143**, 10676 (2021).

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[K203-2vn] 04. Physical Chemistry -Properties-

Chair: Sadahiro Masuo

Thu. Mar 23, 2023 4:10 PM - 5:10 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-2vn-01] Light Confinement of $CsPbBr_3$ Microplates Studied by Near-Field Imaging

○Seiju Hasegawa[1], Hina Hayashi[1], Kohei Imura[1] （1. Waseda Univ.）

4:10 PM - 4:30 PM

[K203-2vn-02] Elucidation of Adsorption Behavior of Perylene Bisimide Derivatives on Perovskite Nanocrystal Surface

○Naoki Kubo[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University）

4:30 PM - 4:50 PM

[K203-2vn-03] Atomically-precise synthesis and photoluminescence properties of water-soluble, NHC-protected Au_{13} clusters

○Dennis Alexander Buschmann[1], Shinjiro Takano[1], Tatsuya Tsukuda[1] （1. The University of Tokyo）

4:50 PM - 5:10 PM

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$CsPbBr_3$ マイクロプレートにおける光閉じ込めモードの近接場イメージング

（早大院先進理工[1]）○長谷川 誠樹[1]・林 ひな[1]・井村 考平[1]
Light Confinement of $CsPbBr_3$ Microplates Studied by Near-Field Imaging ([1]*Graduate School of Advanced Science and Engineering, Waseda University*) ○ Seiju Hasegawa,[1] Hina Hayashi,[1] Kohei Imura[1]

Lead halide perovskite (LHP) microcrystals exhibit strong light confinement and is expected to be applied for low threshold lasing and so on. Visualization and understanding of the light confinement are essential for the applications. Spatial resolution of a conventional microscope is limited by the diffraction limit of light. As the spatial feature of a localized mode excited in LHP microcrystals is smaller than the spatial resolution, visualization of the localized mode has been little reported. We performed visualization of the localized mode excited in a $CsPbBr_3$ microplate using a scanning near-field optical microscope. We revealed from the imaging that visualized spatial characteristic in the microplate is originated from the Fabry-Pérot mode.
Keywords : Near-Field, Lead halide perovskite, Light confinement

ハロゲン化鉛ペロブスカイト（LHP）のマイクロ結晶は，高い光閉じ込め効果を示すことから，低閾値レーザー媒質などへの応用が期待される。この光閉じ込めモードを可視化し理解することは，LHP マイクロ結晶を応用する上で重要である。しかし，従来の光学顕微鏡の空間分解能は，光の回折限界によって制限されるため，光閉じ込めモードの空間構造を可視化することが困難である。本研究では，光の回折限界を超えた空間分解計測が可能な近接場光学顕微鏡を用いて $CsPbBr_3$ マイクロプレートに励起される光閉じ込めモードの可視化と帰属を行うことを目的とした。

Fig. 1(a)に化学気相成長法で合成した $CsPbBr_3$ マイクロプレートの走査型電子顕微鏡像を示す。図中のスケールバーは 1 μm である。プレートは直方体であり，1 辺の長さは長辺約 1.4 μm，短辺約 1.3 μm であった。複数のプレートに対するサイズ評価の結果，合成されたプレートの 1 辺は 1 ~ 6 μm，厚みは 200 ~ 500 nm であった。Fig. 1(b)にマイクロプレートの近接場透過像（観測波長: 約 550 nm）を示す。スケールバーは 500 nm である。図中の点線はプレートの概形を示し，図中の明暗は透過光の強弱に対応する。プレートの内部に格子構造が観測された。格子構造の間隔は観測波長に依存する。電磁気学計算においても同様の格子構造が構造体内部に可視化された。Fabry-Pérot モードによって形成される定在波は，構造内部に格子状の空間特性を示すと予測される。このことは，観測された格子構造が Fabry-Pérot モードに帰属されることを示唆する。

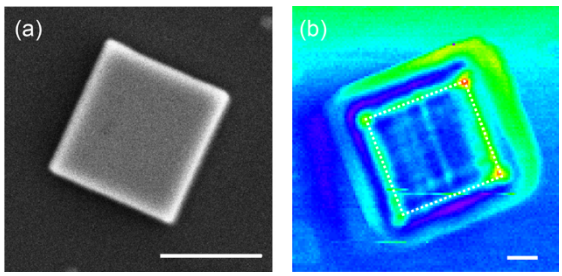


Fig. 1. (a) Scanning electron micrograph of a $CsPbBr_3$ microplate (side length: ~ 1.4, 1.3 μm). Scale bar: 1 μm. (b) Near-filed transmission image of a microplate (side length: ~ 1.7 μm) taken at a wavelength near 550 nm. Dotted line: approximate shape of the microplate. Scale bar: 500 nm.

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Elucidation of Adsorption Behavior of Perylene Bisimide Derivatives on Perovskite Nanocrystal Surface

(*Kwansei Gakuin University*) ○Naoki Kubo, Mitsuaki Yamauchi, Sadahiro Masuo
Keywords: Perylene Bisimide; Perovskite Nanocrystal; Self-Assembly; Energy Transfer; Quantum Dot

$CsPbBr_3$ perovskite nanocrystals (PNCs) have attracted much attention as outstanding photosensitizer because of their strong light absorption which can transfer singlet and triplet energy to surface-bonded accepter molecules. Especially, assemblies of the PNC and π-conjugated molecules can show unique photoluminescence (PL) properties such as efficient photon upconversion at low excitation intensity. However, the π-conjugated molecules easily undergo self-assembly on the nanocrystal surface, which significantly changes their PL properties[1]. Therefore, the evaluation of adsorption behavior of the molecule on the PNC surface is of importance. Herein, we investigated the adsorption and assembling behaviors of perylene bisimide derivatives (PBI, Fig.1a) on the PNC surface. Furthermore, we examined the PL properties of PNC-PBI assemblies depending on adsorption condition of the PBI.

Upon mixing the PNC and a PBI having carboxy groups on both ends as adhesion moieties (**PBI1**) in chloroform, the absorption spectrum of **PBI1** blueshifted (Fig. 1b). Therefore, the formation of PBI aggregates having face-to-face stacked structure on the PNC surface was revealed. On the other hand, no spectral change was observed from a mixture of the PNC and a PBI having a carboxy group on a one end (**PBI2**), indicating the adsorption of **PBI2** monomer (Fig. 1b). These results suggest that the hydrogen bonding between carboxy groups promotes the aggregation of PBI on the PNC surface. Furthermore, the energy transfer between the PNC and PBI was evaluated by measuring the PL spectra (Fig. 1c). As a result, PL quenching of PNC was observed in both PBIs, suggesting the energy transfer from the PNC to PBI. Moreover, the **PNC-PBI2** showed the PL enhancement of **PBI2** by the energy transfer, while the **PNC-PBI1** showed the quenching of **PBI1**. According to these results, we revealed that the adsorption condition of PBI significantly affects the PL properties of PNC-PBI assemblies.

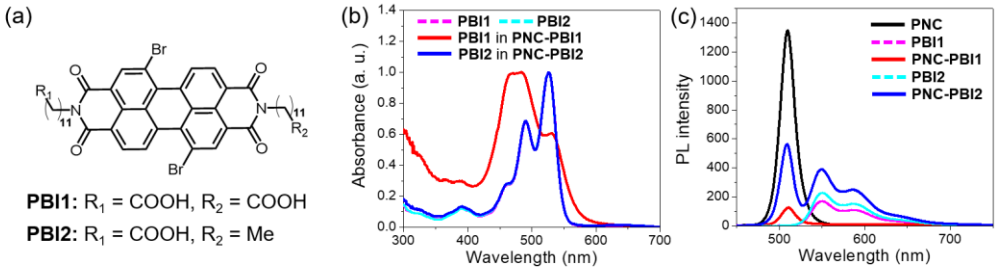


Fig. 1 (a) Molecular structures of **PBI1** and **PBI2**. (b) UV/Vis absorption spectra of the sole PBI and the PBI in mixtures of PNC-PBI. (c) PL spectra of the sole PNC and PBI and PNC-PBI mixtures (λ_{ex} = 405 nm).

1) M. Yamauchi, S. Masuo, *Chem. Eur. J.* **2019**, *25*, 167-172.

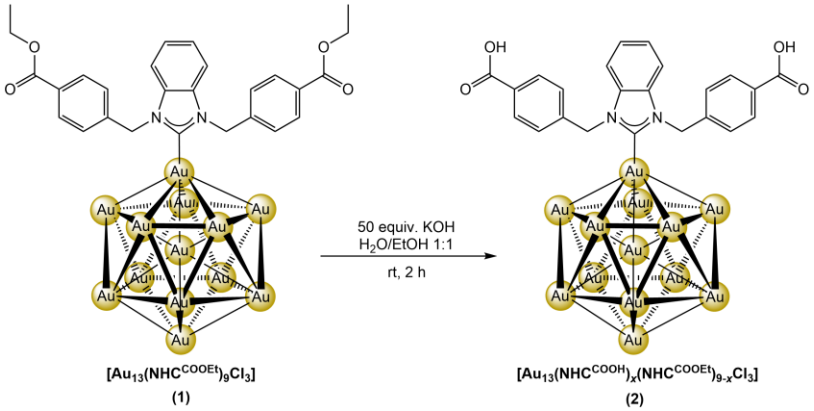
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Atomically-precise synthesis and photoluminescence properties of water-soluble, NHC-protected Au_{13} clusters

([1] *Catalytic Chemistry Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo*) ○Dennis A. Buschmann,[1] Shinjiro Takano,[1] Tatsuya Tsukuda[1]
Keywords: NHC-protected Gold Clusters, Gold Superatoms, Photoluminescence

Atomically-precise Au clusters not only impress with their bright photoluminescence,[1] but gained significant importance in medicinal applications as well.[2] In non-aqueous media, the nuclearity and structural motif is governed by stabilizing ancillary ligands, such as thiolate or phosphide ligands.[3,4] We recently reported on the enhancement of both the stability and photoluminescence properties of Au clusters stabilized by N-heterocyclic carbenes (NHCs).[5,6]

Here, we wish to report on the extension of the previously established synthesis of NHC-protected Au clusters toward water-soluble systems. Mono- and bis(benzimidazolium)ligands were synthesized, featuring ethyl 4-(chloromethyl)-benzoate as wingtip moieties. The respective Au complexes are feasible via standard synthesis routes, using $(Me_2S)AuCl$ and K_2CO_3. Atomically-precise Au_{13} clusters (**1**) were obtained by treatment of the NHC-Au complexes with stoichiometric amounts of $NaBH_4$, with the monodentate NHC-Au cluster showing a photoluminescence quantum yield (PLQY) of 3%. The transformation into water-soluble systems was achieved via saponification of the ester group in basic aqueous media, producing the corresponding carboxybenzyl-protected Au clusters (**2**) with high PLQYs (monodentate NHC: 3% in MeOH, 2% in H_2O; bidentate NHC: 27% in MeOH, 8% in H_2O).



Scheme 1. Transformation of benzoate-benzimidazole Au_{13} (**1**) into carboxybenzyl-benzimidazole Au_{13} (**2**) by saponification. Ligands, except for one NHC ligand, are omitted for improved visualization.

1) H. Hirai, T. Tsukuda *et al.*, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207290. 2) S. Palmal, N. R. Jana, *WIREs Nanomed. Nanotechnol.* **2014**, *6*, 102. 3) Z. Wu, J. Xie *et al.*, *Angew. Chem. Int. Ed.* **2020**, *59*, 9934. 4) S. Takano, T. Tsukuda *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 8380. 5) M. R. Narouz, T. Tsukuda, C. M. Crudden *et al.*, *Nat. Chem.* **2019**, *11*, 419. 6) M. R. Narouz, T. Tsukuda, C. M. Crudden *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 14997.

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Academic Program [Oral B] | 06. Analytical Chemistry | Oral B

[K701-2pm] 06. Analytical Chemistry

Chair: Akihide Hibara, Takahito Ohshiro

Thu. Mar 23, 2023 2:20 PM - 3:40 PM K701 (K701, Lecture Hall Bldg. [7F])

[K701-2pm-01] Characterization of liquid gold used in traditional pottery and crafts

○Yoshihide MAENO Maeno[1,2], Takei Onoue[1], Shinnya Kitagawa[1], Hajime Ohtani[1], Yukiko Kikugawa[2], Yoshihiro Suzuki[2] （1. Nagoya Institute of Technology, 2. Noritake Co., Ltd）

2:20 PM - 2:40 PM

[K701-2pm-02] Development of Amino Acid Identification by Single Molecule Detection Method Towards Peptide Sequencing

○Takahito Ohshiro[1], Taniguti Masateru[1] （1. Osaka University）

2:40 PM - 3:00 PM

[K701-2pm-03] Digital PCR on an original microfluidic chip

○Kazuo Hosokawa[1], Hitoshi Ohmori[1] （1. RIKEN）

3:00 PM - 3:20 PM

[K701-2pm-04] Development of HPLC using phase-separation multiphase flow as as eluent

Noe Jallas[1], Daiki Ishikawa[1], Tetsuro Katayama[1], Aoi Kimura[1], ○Kazuhiko Tsukagoshi[1] （1. Doshisha University）

3:20 PM - 3:40 PM

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Characterization of liquid gold used in traditional pottery and crafts

([1]*Graduate School of Engineering, Nagoya Institute of Technology*, [2] *Noritake Co., Ltd*)
○Yoshihide Maeno,[1,2] Takei Onoue,[1] Shinya Kitagawa,[1] Hajime Ohtani,[1] Yukiko Kikugawa,[2] Yoshihiro Suzuki,[2]

Keywords: Liquid gold; Balsam sulfide; Characterization; ESI-IMS-MS; Py-GC-MS/SCD; MALDI-TOFMS

"Liquid gold" has been used for long time in decoration of traditional pottery and crafts. One of the main component of liquid gold is "gold resinate", which is a reaction product of tetrachloroauric(III) acid and "balsam sulfide". Balsam sulfide is obtained by the reaction of balsam, a complex natural product, with inorganic sulfur. Although the liquid gold is common material for decoration, neither gold resinate nor balsam sulfide has been characterized due to their complexity. In this study, we analyzed balsam sulfide and gold resinate using various methods such as pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), matrix assisted laser desorption/ionization time-of-fright mass spectrometry (MALDI-TOFMS) and electrospray ionization-ion mobility spectrometry-mass spectrometry (ESI-IMS-MS).

First, sulfur containing components in balsam sulfide were analyzed by a combination of Py-GC-MS and Py-GC-sulfur chemiluminescence detector (SCD). The peaks, separated in GC, for sulfur compounds were assigned by SCD and their mass values were measured by MS for the identification. It was confirmed that balsam sulfide contains the compounds composed of an α-pinene unit and 1-3 sulfur atoms as the low molecular weight products. In addition, as high molecular weight components, the compounds composed of 2 or 3 α-pinene units and sulfur atoms were detected and identified by MALDI-TOFMS.

Then, balsam sulfide and gold resinate were analyzed by ESI-IMS-MS. The analysis of balsam sulfide resulted in signals observed as two groups in a 2D heatmap of *m*/*z* and drift time. In the analysis of gold resinate, a new group was found in the 2D map. The slope in the *m*/*z* - drift time relation for the new group is approximately the same as that for one group for balsam sulfide. However, the new group shows smaller drift time at the same *m*/*z* value and the difference in two groups corresponded to approximately 200 in *m*/*z* value. This result indicated that the compounds in the new group contains a gold atom (atomic weight: 197). The MS/MS analyses of compounds in the new group revealed that they composed of Au, S, Cl, α-pinene and cymene yielded from α-pinene. That is, it was found that α-pinene sulfides (or cymene sulfides) were reacted with Au and yielded the compounds of 600 to 1000 Da.

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ペプチド配列解析にむけた１分子検出法によるアミノ酸識別法の開発

（阪大[1]）大城 敬人[1]、小本 祐貴[1]、谷口 正輝[1]

Development of single molecule detection method for methylation-modified microRNA analysis ([1]*Osaka University*, [2] *Tokyo University of Science*) ○ Takahito Ohshiro[1], Yuki Komoto[1], Ayumu Asai[1], Masamitsu Konno[2], Hideshi Ishii[1], Masateru Taniguchi[1]

Peptides are one of the most important components of living organisms, and are responsible for the expression of various functions. In this study, single molecule quantum measurements using nanogap electrode devices were used to discriminate amino acids including L- and D-bodies, which are the building blocks of peptides. By machine learning the signals, we created a learning unit with high discriminative power. Using this device, single molecule signals obtained from mixed amino acid solutions were evaluated, and more than 80% of the signals were successfully discriminated.

Keywords : Peptide ; Single-Molecule Detection; Tunnel-Current; Amino acid

ペプチドは，アミノ酸のユニットからなる生体高分子で，様々な機能発現することからシーケンシングの開発に近年興味が高まってきている．これまで，我々はトンネル電流を指標として１分子ごとのコンダクタンスの高速計測可能なセンサー開発を行ってきた．そこで我々は，高速リードが可能なシーケンサーとして，１分子量子シーケンサーをもちいたペプチドシーケンシング法を提案する．

１分子量子シーケンサーとは，ナノギャップ電極間を通過する一本鎖生体高分子の各ﾓﾉﾏｰ種の違いを，トンネル電流を指標としたシグナルの違いによって配列決定をする方法である [1-4]．本研究では，ナノギャップ電極デバイスを用いた１分子量子計測により，ペプチドの構成要素であるＬ体およびＤ体を含むアミノ酸の識別を行った．得られたシグナルを，機械学習を用いて分子種を識別可能な学習を作成した．これをもとに，ペプチド鎖のシグナルのアミノ酸種の再構成を行った．

微小ギャップ電極で，1uM のアミノ酸水溶液を 0.54-0.58 nm のギャップ間距離に調整した電極によって計測した．その時，分子がギャップ間を通過するときに，分子を介したトンネル電流の増加現象が観察された．観察されたシグナル波形を，１２シグナル領域にたたみこんだ特徴量やコンダクタンス値の変化量を指標をもとに機械学習を行い，作成した識別器を用いて，各アミノ酸のＬ体,D 体を含む３９種のアミノ酸の１分子の識別評価を行った．その結果，50%をこえる高い確率で，識別に成功した．この学習器を用いて，別に作成した４種の混合アミノ酸溶液の計測シグナルについて，識別を行った．その結果，シグナルの識別精度は８０％となり，混合比と反映したシグナル数の比を再現することに成功した．

以上のことから，本計測法がアミノ酸種の違いを精度よく識別できる可能性があることから，ペプチドシーケンサへの応用の可能性が示されたといえる．

[1] Ohshiro T. et al., Sci.Rep., (2019), 9, 3886 [2] Ohshiro T. et al., Sci.Rep. (2018), 8,8517. [3] Ohshiro T. et al., Sci. Rep. (2021),11,19304. [4] Ohshiro T. et al., Micromachines (2020), 11, 982.

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独自のマイクロ流体チップを用いたデジタル PCR

（理研 [1]）○細川 和生 [1]・大森 整 [1]
Digital PCR on an Original Microfluidic Chip ([1]*Materials Fabrication Laboratory, RIKEN Cluster for Pioneering Research*) ○Kazuo Hosokawa,[1] Hitoshi Ohmori[1]

Digital PCR enables sensitive and precise analysis for nucleic acids without calibration. However, the commercialized digital PCR instruments are expensive and not yet in widespread use. We have developed a microfluidic chip which realizes digital PCR using only common laboratory equipment such as a thermo-cycler and a fluorescence microscope. The measurements well agreed with the theory in the range of 1.3×10^{1}~1.3×10^{4} copies/μL of human genomic DNA.
Keywords : Digital PCR; Microfluidic Chip

デジタル PCR はキャリブレーション不要で高感度・高精度な核酸分析法である．しかしながら市場にあるデジタル PCR は高価な専用装置を必要とするため，広く普及しているとは言えない．本研究では独自のマイクロ流体チップにより，専用装置を用いることなく，一般的なサーモサイクラーと蛍光顕微鏡のみでデジタル PCR を可能とした．

マイクロ流体チップは PDMS を素材とし，表面に一辺 50 μm，深さ 100 μm のウエルを 24,840 個備えている．市販のヒトゲノム DNA を試料とし，*RNase P* 遺伝子（各ゲノムに 1 コピーだけある）を検出する TaqMan リアルタイム PCR 試薬と混合した．混合物をマイクロ流体チップのウエルに導入し, PDMS をコートしたガラス基板で封入した．ガラス基板側をサーモサイクラー（Arktik, ThermoFisher）のヒートブロックに接触させて 40 サイクルのサーマルサイクルを行った．この際に試料・試薬の蒸発を防ぐため，手製の水ホルダーを用いて PDMS マイクロ流体チップを水で覆った．反応後のチップを倒立型蛍光顕微鏡（Ti-U, ニコン）で観察したところ，ウエルの蛍光強度に明暗の違いが明確に見られ，明るいウエルの個数は DNA 濃度に応じて変化した（Fig. 1）．明るいウエルの個数を画像処理ソフト（ImageJ）によってカウントしたところ, 明るいウエルにだけ *RNase P* 遺伝子があったと仮定してポアソン統計により計算した個数とよく一致した．

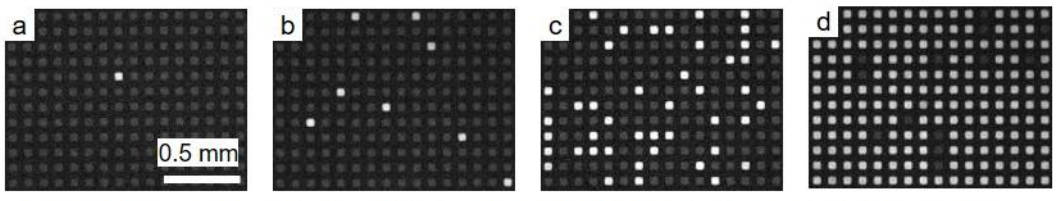


Fig. 1. Fluorescence images of the results of digital PCR with varying concentrations of the target DNA; (a) 13 copes/μL, (b) 130 copies/μL, (c) 1.3×10^{3} copies/μL, and (d) 1.3×10^{4} copies/μL.

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相分離混相流を溶離液として使用する HPLC の開発

(同志社大院理工[1]) Noe Jallas[1]・石川 大輝[1]・片山 哲朗[1]・木村 葵[1]・○塚越 一彦[1]

Development of HPLC using phase-separation multiphase flow as an eluent ([1]*Applied Chemistry, Graduate School of Science and Engineering, Doshisha University*) Noe Jallas[1], Daiki Ishikawa[1], Tetsuro Katayama[1], Aoi Kimura[1], ○Kazuhiko Tsukagoshi[1]

A new type of multiphase flow was generated by delivering two-phase separation mixed solutions into the flow device. We call this phase-separation multiphase flow. In this study we used two-phase separation mixed solutions as an eluent in a commercially available high-performance liquid chromatography (HPLC) system equipped with a normal packed separation column. We examined the effect of phase-separation multiphase flow on a packed column separation in HPLC, using a water/acetonitrile/ethyl acetate ternary mixed solution.

Keywords : Phase-separation multiphase flow, high-performance liquid chromatography, two-phase separation mixed solution

水/親水性/疎水性有機溶媒混合溶液のような二相分離混合溶液は、温度／圧力変化で相変化し、回分式容器内では上層と下層に相分離する。我々は、それを微小領域に送液しながら、温度／圧力変化で相変化させると、動的液–液界面を有する新たな混相流が得られることを見出した。この流れを相分離混相流という。これまで、キャピラリーチューブやマイクロチャネル内に相分離混相流の一つとして創出される環状流（管径方向分配流；tube radial distribution flow, TRDF）を用いて、クロマトグラフィー（管径方向分配クロマトグラフィー；tube radial distribution chromatography, TRDC)、抽出、混合、反応器の開発に取り組んできた[1]。今回、二相分離混合溶液として水/アセトニトリル/酢酸エチル３成分混合溶液を、充填カラムを備えた市販 HPLC システムの溶離液として使用した。相分離混相流が、HPLC に与える新たな分離モード（相分離モード）について報告する。

市販 HPLC システムは、主に送液ポンプ（LC-20AT、島津製作所)、UV-VIS 検出器（SPD-20A、島津製作所)、ODS カラム（Shim-pack HT-ODS、粒子径 2 μm、島津製作所)で構成された。カラム温度は 20 または 5℃に維持した。溶離液には、水/アセトニトリル/酢酸エチル３成分混合溶液を用いた。流速は 100 μ Lmin^{-1} とした。

水/アセトニトリル/酢酸エチル混合溶液(A; 20:60:20 体積比および B; 70:23:7 体積比)を溶離液として、1-Naphthol (NA) と 2,6-Naphthalenedisulfonic acid (NDS)を 20 および 5℃で分析した。20°C のとき、A では分離は見られず、B では NDS、NA の順で溶出した(逆相モード)。5°C では、A では NA、NDS の順で溶出した（相分離モード）。B では NDS、NA の順で溶出し、20°C の時より大幅に分離係数が改善された（逆相＋相分離モード）。すなわち、5°C で溶離液 A と B を用いたとき、カラム内での相分離混相流の創出が分離挙動に影響を与えた。相図からの情報とも矛盾しない。HPLC の新規分離モードとして、その分離メカニズムを考察した[2]。

[1] K. Tsukagoshi, *BUNSEKI KAGAKU (Review)*, **71,** 25-39 (2022).
[2] K. Horikawa, S. Kinoshita, K. Tsuchiya, and K. Tsukagoshi, *Anal. Sci.*, **38**, 731-736 (2022).

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Academic Program [Oral B] | 08. Catalysts and Catalysis | Oral B

[K306-2am] 08. Catalysts and Catalysis

Chair: Akinobu Nakada, Tsuyoshi Takata

Thu. Mar 23, 2023 9:00 AM - 11:10 AM K306 (K306, Lecture Hall Bldg. [3F])

[K306-2am-01] Efficient hydrogen production by photo-redox-cascade catalyst composing dual photosensitizers and transparent hole acceptor

Nobutaka Yoshimura[1], Masaki Yoshida[2], ○Atsushi KOBAYASHI[1] （1. Hokkaido University, 2. Kwansei Gakuin University）

9:00 AM - 9:20 AM

[K306-2am-02] Local charge-carrier dynamics of a particulate Ga-doped $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ photocatalyst and the impact of Rh cocatalyst

○Kenji Katayama[1], Tatsuya Chugenji[1], Zhenhua Pan[1], Vikas Nandal[2], Kazuhiko Seki[2], Kazunari Domen[3] （1. Chuo University, 2. AIST, 3. The Univ. of Tokyo）

9:20 AM - 9:40 AM

[K306-2am-03] Quantitative evaluation of the competition between oxidation of various reversible redox species and photocorrosion on chalcogenide photoanodes

○Yuu Shioiri[1], Keisuke Obata[1], Tomohiro Higashi[2], Yudai Kawase[1], Masao Katayama[1], Kazuhiro Takanabe[1] （1. The University of Tokyo, 2. University of Miyazaki）

9:40 AM - 10:00 AM

[K306-2am-04] Preparation of highly crystalline wurtzite CdS photocatalysts by a flux method

○Haruki Nagakawa[1], Tetsu Tatsuma[1] （1. IIS, The Univ. of Tokyo）

10:10 AM - 10:30 AM

[K306-2am-05] Development of $BaTaO_2N$ photocatalysts with distinctive carrier dynamics for one-step excitation overall water splitting

○Junie Jhon Magdadaro Vequizo[1], Jiadong Xiao[1], Shinji Nishimae[2], Takashi Hisatomi[1], Lu Daling[1], Tsuyoshi Takata[1], Akira Yamakata[3], Kazunari Domen[1,4] （1. Shinshu Univ., 2. ARPChem, 3. Okayama Univ., 4. The Univ. of Tokyo）

10:30 AM - 10:50 AM

[K306-2am-06] Synthesis of Nanocrystalline ATaO2N (A = Ca, Sr, Ba) for Photocatalytic Overall Water Splitting

○Jiadong XIAO[1], Takashi HISATOMI[1], Kazunari DOMEN[1,2] （1. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Nagano-shi, Nagano, 380-8553 Japan, 2. Office of University Professors, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo, 113-8656 Japan）

10:50 AM - 11:10 AM

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Efficient hydrogen production by photo-redox-cascade catalyst composing dual photosensitizers and transparent hole acceptor

([1]*Hokkaido University*, [2]*Kwansei Gakuin University*) Nobutaka Yoshimura,[1] Masaki Yoshida,[2] ○Atsushi Kobayashi[1]

Keywords: Photosensitization; Hydrogen production; Electron mediator; Charge separation

Z-scheme water-splitting photocatalysis, which utilizes a two-step photoexcitation process with a water oxidation catalyst (WOC), water reduction catalyst (WRC), and redox mediator (RM), is a powerful strategy for converting a wide spectrum of solar energy to chemical energy and storing it as H_2 and O_2; it also ensures the water-splitting and electron-transfer potentials are sufficient. However, thermodynamically favorable back reactions at the WOC–RM and RM–WRC interfaces remain a bottleneck issue. Thus, a new strategy of regulating the electron transfer direction (from WOC to WRC via RM) is strongly required. In this work, with the aim of suppressing back reactions at the WRC–RM interface, we constructed a three-step photoredox cascade catalyst, **HCRu**-Zr-**RuCP^6**-Zr-**RuP^6**@Pt-TiO_2 (**PRCC-1**), by assembling two Ru(II)-based molecular photosensitizers (PSs), **RuP^6** and **RuCP^6**,[1] and a visible-light-transparent RM, **HCRu**,[2] on the surface of a Pt-TiO_2 nanoparticle catalyst via water-stable Zr^{4+}–PO_3 bonds (Fig. 1a). During photocatalytic H_2 evolution in aqueous $[Co(bpy)_3]SO_4$ (16.4 mM), the H_2 production and turnover number per PS molecule (PS TON) of **PRCC-1** (28.9 μmol and 116, respectively) were approximately 1.9-times greater than those without **HCRu** (15.2 μmol and 60.7, respectively) after 6 h of irradiation (Fig. 1b). Considering that **HCRu** has a more negative redox potential than **RuCP^6**, the improved activity of **PRCC-1** was ascribed to the enhanced charge-separation between the dual PS layers and $[Co(bpy)_3]^{2+}$ RM owing to electron mediation via **HCRu**.

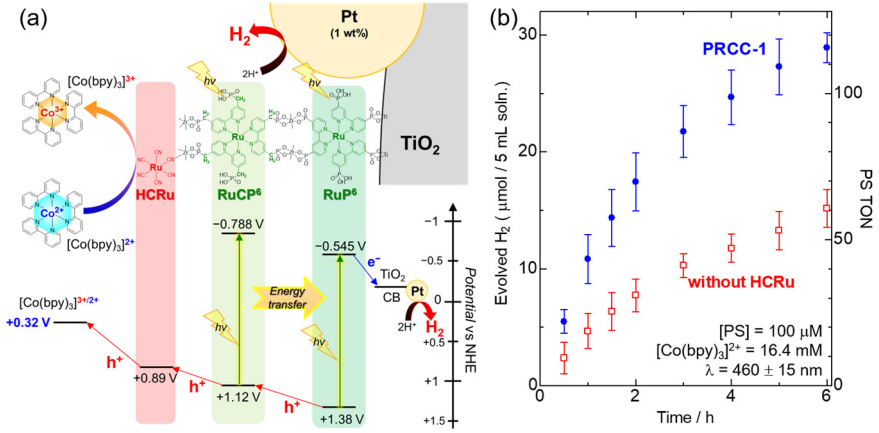


Fig. 1. (a) Schematic energy diagram and (b) photocatalytic H_2 production of **PRCC-1**.

1) N. Yoshimura, A. Kobayashi, M. Yoshida, M. Kato, *Chem. Eur. J.* **2020**, *26*, 16939.

2) H. Kitano, A. Kobayashi, M. Yoshida, M. Kato, *Sustainable Energy Fuels* **2018**, *2*, 2609.

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Local charge-carrier dynamics of a particulate Ga-doped $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ photocatalyst and the impact of Rh cocatalyst

([1] *Chuo University*, [2] *AIST*, [3] *The University of Tokyo*) ○Kenji Katayama,[1] Tatsuya Chugenji,[1] Zhenhua Pan,[1] Vikas Nandal,[2] Kazuhiko Seki[2], Kazunari Domen, 3

Keywords: Charge Carrier Dyanmics; Microscopy; Photocatalyst; LTCA; Co-catalyst

Charge carrier dynamics of highly active p-type photocatalytic particle materials were clarified for particle-by-particle observation. We could distinguish the difference in the charge carrier responses due to co-catalysts by the local observation of each spot of the particles. The photocatalyst was Ga-doped $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ (Ga-LTCA), which is a promising p-type photocatalyst for solar hydrogen generation. We could make this measurement possible with our home-built time-resolved microscopy combined with informatics analysis such as image recovery and clustering of time-resolved data.[1] We could successfully identify the electron trapping at the co-catalyst sites (Rh) from the difference in the charge carrier behavior.[2]

In our measurement, a pulse light with a pattern is illuminated to a sample, and the time-resolved phase-contrast image sequence is obtained with nanosecond time resolution. (Figure left) We could clearly detect time-resolved local responses at each photocatalytic particle or agglomerates. By selecting one of the regions, the time responses at all the image regions were analyzed by the clustering analysis, which provided the categorization of different charge carrier types. (Figure right top) We could assign each response due to the surface-trapped electrons and holes.

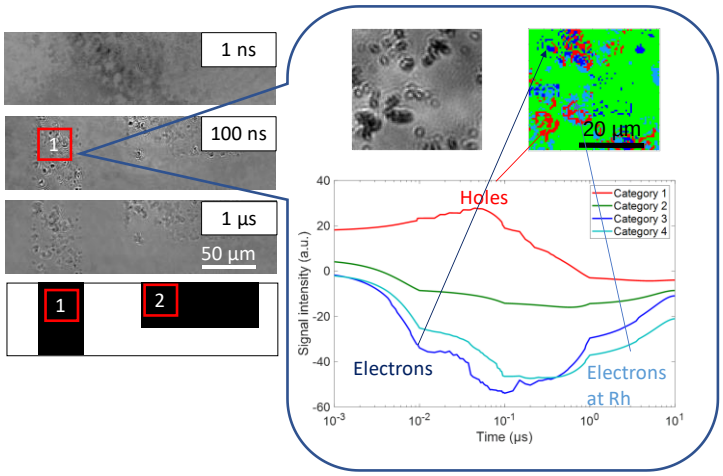


Figure The time-resolved image sequence for the particulate Rh doped Ga-LTCA. The bottom drawing corresponds to the pattern of the pump light illumination. The square 1 was cut off and the time responses were analyzed by the clustering analysis to categorize the responses depending on the charge types. The categorized map and the corresponding responses are shown at the bottom, which corresponds to holes and two types of electrons.

1) M. Ebihara, et al. *Nat. Commun.*. **2021**, *12*, 3716. 2) T. Chugenji, et al. *PCCP*. **2022**, *24*, 17485.

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Quantitative evaluation of the competition between oxidation of various reversible redox species and photocorrosion on chalcogenide photoanodes

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute for Tenure Track Promotion, University of Miyazaki,* [3]*Environmental Science Center, The University of Tokyo*)
○Yuu Shioiri,[1] Keisuke Obata,[1] Tomohiro Higashi,[2] Yudai Kawase,[1] Masao Katayama[1,3] and Kazuhiro Takanabe[1]
Keywords: Photocatalyst; Photoanode; Metal Chalcogenides; Photocorrosion

Metal chalcogenides (CdS, CdSe) are attractive photoactive materials for organic synthesis and water splitting due to their visible-light response.[1] They, however, often suffer from self-photocorrosion.[1] The clarification of the kinetics of the photocorrosion is beneficial to utilize these semiconductors for solar energy conversions. Therefore, we quantitatively evaluated the competitive behavior between oxidation reactions of different redox species with various redox potentials and photocorrosion of photoanodes. The ferrocene (E° = 0.4 V vs. SHE) and bromide (E° = 1.1 V vs. SHE) were used as redox species. Electrochemical oxidation of the redox species using a Pt electrode and photoelectrochemical oxidation using a CdS single crystal photoanode were conducted with a three-electrode cell. The Pt electrode was used as an ideal electrode, which can oxidize the redox species at 100% faradaic efficiency (FE) without the corrosion. UV–vis measurements were conducted after chronoamperometries, and the oxidized species in the electrolyte were quantified by its absorbance.

Figure. 1a and **b** show the results of oxidation of ferrocene and bromide, respectively. The FE of ferrocene oxidation was almost 100%. On the other hand, the FE of bromide oxidation was around 3.6%. The oxidation of bromide on the CdS photoanode competes with the photocorrosion. Based on these results, the kinetics of the photocorrosion seems to sharply rise between their redox potentials indicating the challenge to perform oxygen evolution (E° = 1.23 V vs. SHE). The present methodology will provide a design guideline to perform stable photoelectrochemical conversions, such as organic synthesis, based on their thermodynamics.

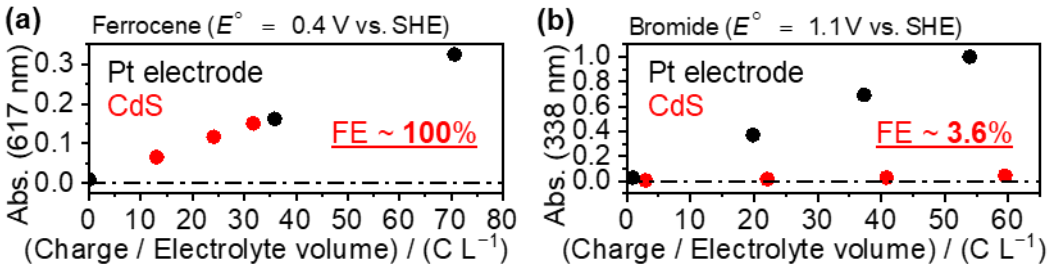


Figure. 1 Oxidation of **(a)** ferrocene **(b)** bromide by a Pt electrode and a CdS photoanode evaluated from the absorbance in the electrolyte by UV-vis measurements.

[1] Meissner, D. and Memming, R., *J. Phys. Chem.*, **1988**, *92*, 3476–3483.

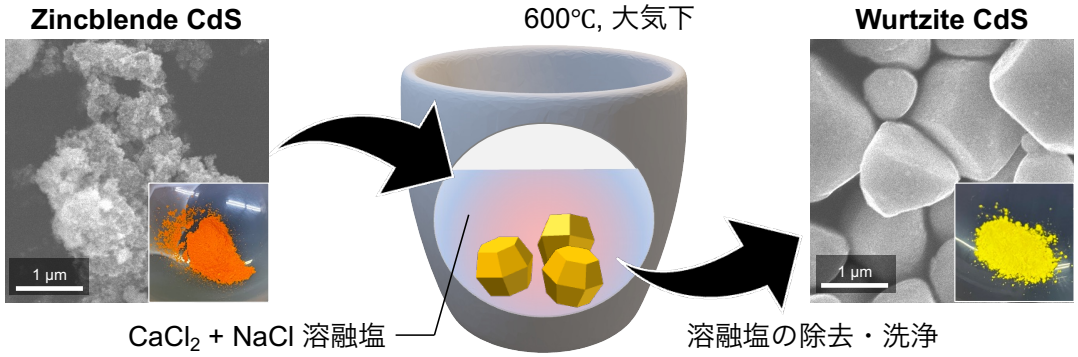
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溶融塩処理による高結晶性ウルツ鉱型 CdS 光触媒の作製

（東大生研）○長川 遥輝・立間 徹
Preparation of Highly Crystalline Wurtzite CdS Photocatalysts by a Flux Method (*Institute of Industrial Science, The University of Tokyo*) ○Haruki Nagakawa, Tetsu Tatsuma

Among many photocatalysts, CdS has attracted attention because of its conduction and valence band levels suitable for water splitting. CdS usually has zincblende or wurtzite structure. Zincblende CdS transforms at around 600 °C to wurtzite CdS, which is known to exhibit a higher photocatalytic activity. However, since S atoms in CdS are easily substituted with O atoms at high temperatures, the heat treatment has been conducted mostly in a hydrogen sulfide atmosphere or in vacuum. In this study, highly crystalline wurtzite CdS particles have been successfully prepared by heat treatment of zincblende CdS in a mixed molten salt. This method does not require a vacuum or highly toxic hydrogen sulfide conditions as in conventional annealing methods. The obtained wurtzite CdS photocatalyst with a Pt cocatalyst shows hydrogen evolution activity under visible light, in the presence of sulfide sacrificial reagents. The activity is ~50-fold higher than that of the zincblende CdS precursor and about twice as high as that of wurtzite CdS prepared by vacuum annealing.
Keywords : Photocatalysis; Cadmium Sulfide; Hydrogen Production; Molten Salt

光触媒の中でも、硫化カドミウム(CdS)は水の分解に適したバンド構造を持つため注目されている。CdS は通常、閃亜鉛鉱型またはウルツ鉱型の結晶構造を示す。閃亜鉛鉱型 CdS は 600℃付近でウルツ鉱型 CdS に転移し、より高い光触媒活性を示すようになる。しかし、CdS は高温で S が O に置換されやすいため、熱処理は硫化水素雰囲気中や真空中で行われてきた。本研究では、溶融塩中で閃亜鉛鉱型 CdS を熱処理することにより、結晶性の高いウルツ鉱型 CdS を簡便に作製することに成功した[1)]。この方法は、従来のような真空条件や毒性の強い硫化水素を必要としない。得られたウルツ鉱型 CdS に白金を担持し、S^{2-}犠牲試薬を含む溶液中で可視光照射した際、高い水素生成活性を示した。この活性は、前駆体として用いた閃亜鉛鉱型 CdS の約 50 倍、真空中での焼成によって作製したウルツ鉱型 CdS の約 2 倍であった。



1) Highly crystalline wurtzite CdS prepared by a flux method and application to photocatalysis. H. Nagakawa, T. Tatsuma, *ACS Appl. Energy Mater.* **2022**, *5*, 14652.

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Development of $BaTaO_2N$ photocatalysts with distinctive carrier dynamics for one-step excitation overall water splitting

([1]RISM, *Shinshu University*, [2]*ARPCHEM, Tokyo University,* [3]*Okayama University,* [4]*Office of the University Professors, Tokyo University*) ○Junie Jhon M. Vequizo,[1] Jiadong Xiao,[1] Shinji Nishimae,[2] Takashi Hisatomi,[1] Lu Daling,[1] Tsuyoshi Takata,[1] Akira Yamakata,[3] Yasunori Inoue,[2] Kazunari Domen[1,4]

Keywords: $BaTaO_2N$; photocatalysts; overall water splitting; cocatalyst; carrier dynamics

$BaTaO_2N$ (BTON) is an attractive perovskite oxynitride material and visible-light responsive photocatalyst, owing to its suitable band structures for hydrogen and oxygen evolution reactions. To date, several strategies have been employed to produce BTON with considerably less defects such as flux-assisted approach.[1-2] However, the one-step excitation overall water splitting (OE-OWS) utilizing BTON as the photocatalysts remains elusive to achieve. Herein, we report BTON that demonstrates OE-OWS and unravel its characteristics suitable for simultaneous production of H_2 and O_2 in pure water condition and under visible light irradiation.

The BTON was synthesized using amorphous Ta_2O_5 as a Ta precursor and blended with $BaCO_3$ as a Ba precursor, followed by nitridation under NH_3 gas. With suitable hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) cocatalysts, the BTON split water to H_2 and O_2 at the nearly stoichiometric ratio (2.3 and 1.1 μmol/h for H_2 and O_2, respectively), suggesting successful observation of OWS utilizing BTON as the photocatalysts. The carrier dynamics of BTON synthesized from amorphous Ta_2O_5 was investigated by transient absorption spectroscopy to reveal its distinctive characteristics compared to other BTONs nitrided using the commercially available Ta_2O_5 precursors and with the addition of fluxes. Under 470 nm laser pulse excitation, the mid-IR absorption spectra of photocarriers in BTON exhibited monotonic increase behavior towards lower probe energies, indicating notable free carrier absorption characteristics, as depicted in Figure 1. This absorption feature has not been observed previously for BTON synthesized using conventional Ta_2O_5 precursor.[1] Detailed results will be presented at the conference.

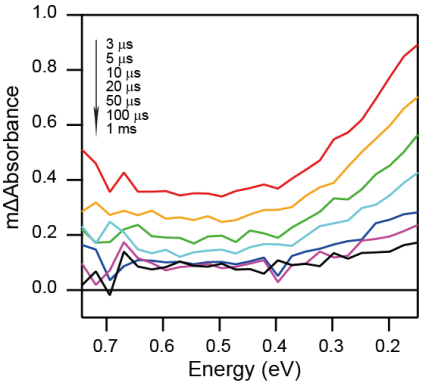


Figure 1. Transient absorption spectra of BTON BTON nitrided at 1173 K for 5 h under 470 nm laser pulses excitation. Measurement condition: room temperature and in N_2 (20 Torr).

References:

1) Z. Wang et al, Nature Communication, **12**, 1005 (2021), 2) S. Jadhav et al, *J. Mater. Chem. A 8*, 1127 (2020). 3) M. Higashi et al, *Chem. Mater.* 21, 1543 (2009).

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Synthesis of Nanocrystalline $ATaO_2N$ (A = Ca, Sr, Ba) for Photocatalytic Overall Water Splitting

([1]*Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Nagano-shi, Nagano, 380-8553 Japan*, [2]*Office of University Professors, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo, 113-8656 Japan*) ○Jiadong Xiao,[1] Takashi Hisatomi,[1] Kazunari Domen[1, 2]

Keywords: Ta-Based Oxynitrides; Overall Water Splitting (OWS); Nanosized Single Crystal; Solar Hydrogen

Particulate semiconductors having simultaneously a narrow bandgap, high degree of crystallinity and a few tens of nanometer size hold great promise for efficient solar-to-chemical energy conversion, but fabrication of such materials remains a great challenge.[1] This work demonstrates a simple synthetic approach to $ATaO_2N$ (A = Ca, Sr, Ba) nanocrystals by applying TaS_2 and $A(OH)_2$ (A = Ca, Sr, Ba) as the precursor and molten $SrCl_2$ as a flux. The developed approach allows control over different light absorption edges, particle sizes and degrees of crystallinity via tuning the synthetic parameters. As a showcase material, the fabricated $SrTaO_2N$ features a high degree of crystallinity (Fig. 1a), a typical light absorption edge of 600 nm (Fig. 1b), and particle sizes of around 50 nm (Fig. 1c-g). This material exhibited superior photocatalytic sacrificial hydrogen (Fig. 1h) and oxygen (Fig. 1i) evolution performance to the previously reported $SrTaO_2N$ photocatalysts. Efficient Z-scheme OWS applying Ir/Pt/Cr_2O_3-decorated $SrTaO_2N$ as the hydrogen evolution photocatalyst was achieved.

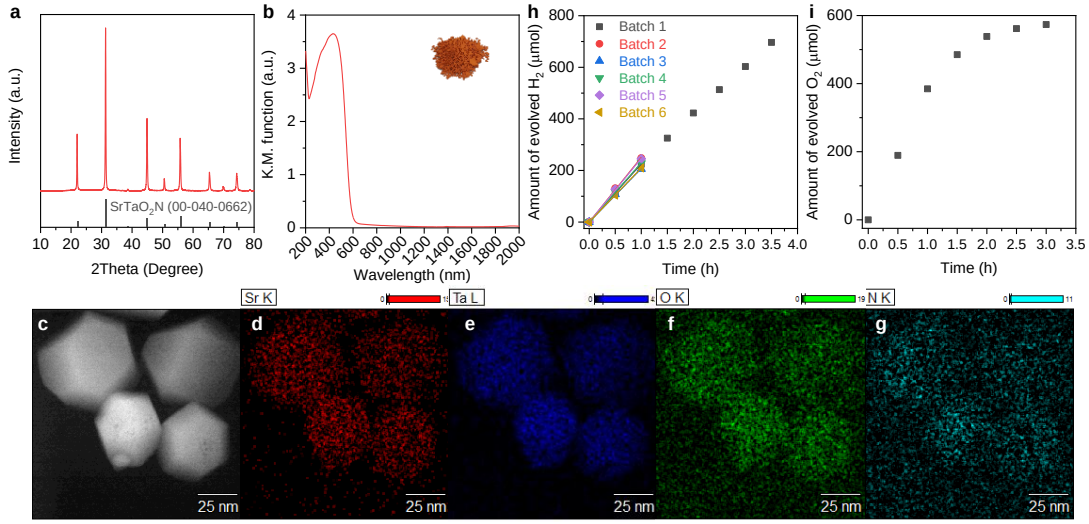


Figure 1. (a) X-ray diffraction pattern, (b) diffuse reflectance spectrum, (c-g) scanning transmission electron microscopy-energy dispersive X-ray spectroscopy maps of the prepared $SrTaO_2N$. Time course of photocatalytic (h) hydrogen and (i) oxygen evolution over Ir/Pt/Cr_2O_3-decorated $SrTaO_2N$ and CoO_x-decorated $SrTaO_2N$, respectively, under visible light.

1) Q. Wang, K. Domen, *Chem. Rev.* **2020**, *120*, 919.

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Academic Program [Oral B] | 08. Catalysts and Catalysis | Oral B

[K305-2pm] 08. Catalysts and Catalysis

Chair: Ken Motokura, Yusuke Kita

Thu. Mar 23, 2023 1:00 PM - 3:40 PM K305 (K305, Lecture Hall Bldg. [3F])

[K305-2pm-01] Highly-densed array of Iron-based metal catalyst nanoparticle showing high-temperature stability; Formation and the application to ultra-long carbon nanotube array

○Shunsuke Sakurai[1], Takashi Tsuji[1], Maho Yamada[1], Kenji Hata[1], Don N Futaba[1] (1. National Institute of Advanced Industrial Science and Technology)

1:00 PM - 1:20 PM

[K305-2pm-02] Understanding the Roles of Hydroxide in CO_2 Electroreduction on a Cu Electrode for Achieving Variable Selectivity

○MINGXU SUN[1], Miho Yamauchi[1] (1. Kyushu University)

1:20 PM - 1:40 PM

[K305-2pm-03] Development of the Ir-complex catalysts immobilized on functional polymer for formic acid dehydrogenation

○Keito Sawahara[1,2], Shinji Tanaka[2], Tetsuya Kodaira[2], Hajime Kawanami[2,1] (1. University of Tsukuba, 2. AIST)

1:40 PM - 2:00 PM

[K305-2pm-04] Iron-Catalyzed 1,4-Arylalkylation of 1,3-Enynes with Arylborates and Unactivated Alkyl Electrophiles

○Siming LU[1,2], Litian CHEN[1,2], Satsuki NOMURA, Katsuhiro ISOZAKI[1,2], Masaharu NAKAMURA[1,2] (1. Kyoto University, 2. Institute for Chemical Research)

2:00 PM - 2:20 PM

[K305-2pm-05] *In situ* formic acid dehydrogenation observation using a UV-vis-diffuse-reflectance spectroscopy system

○Risheng Li[1,2], Hajime Kawanami[1,2], Tetsuya Kodaira[2] (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

2:20 PM - 2:40 PM

[K305-2pm-06] Development of novel synthetic method for thiols using heterogeneous cobalt catalysts from hydrogen, elemental sulfur, and alkenes

○Xu Ke[1], Yamamoto Eiji[1], Murayama Haruno[1], Matsueda Hironobu[2], Sakata Hiroshi[2], Tokunaga Makoto[1] (1. kyushu university, 2. DIC Corporation)

2:40 PM - 3:00 PM

[K305-2pm-07] Heterogeneous catalytic approach to the synthesis of cyclic carbonates and their decarboxylative transformations

○Sangita Karanjit[1], Emiko Tanaka[1], Ryota Sato[1], Kosuke Namba[1] (1. Tokushima University)

3:00 PM - 3:20 PM

[K305-2pm-08] Enantioselective [3+2] Annulation of Aromatic aldimines with Alkenes via C− H Activation by Half-Sandwich Scandium Catalysts

○Aniket Mishra[1], Xuefeng Cong[1], Masayoshi Nishiura[1], Zhaomin Hou[1] (1. RIKEN)

3:20 PM - 3:40 PM

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鉄系金属触媒ナノ粒子アレイにおいて高温での粒子間凝集を抑制する基材表面の多層構造について　-触媒 CVD 法による長尺カーボンナノチューブ合成への応用-

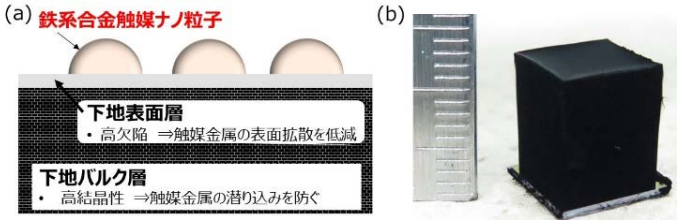
（産総研 [1]）○桜井 俊介 [1]・辻 享志 [1]・山田 真保 [1]・畠 賢治 [1]・Futaba Don[1]
Highly-densed array of Iron-based metal catalyst nanoparticle showing high-temperature stability; Formation and the application to ultra-long carbon nanotube array ([1]*National Institute of Advanced Industrial Science and Technology*) ○Shunsuke Sakurai[1], Takashi Tsuji[1], Maho Yamada[1], Kenji Hata[1], Don N. Futaba[1]

In order to achieve a high-density formation of iron-based metal nanoparticle catalysts at high temperatures without aggregation between nanoparticles, we examined various metal oxide multilayer films formed on a flat silicon substrate and investigated their effects on the catalysts. As shown in Figure 1, it was found that the multi-layer structure with a very thin (about 1 nm) oxide layer having many defects deposited on a highly crystalline metal oxide layer contributes significantly to the high temperature stability (750°C) of dense (10-15 nm spacing) arrays of iron nanoparticles (3-5 nm in diameter). The nanoparticle arrays prepared on the above mentioned double-layered (DL) support were applied to the synthesis of long carbon nanotubes by catalytic CVD at high temperatures, and were able to achieve both superior growth rate and growth lifetime, resulting in the synthesis of carbon nanotube assemblies exceeding 1 cm height within 60 minutes for the first time.
Keywords : Nanoparticle; Catalyst; Carbon Nanotube; Iron

高温で利用する鉄系金属のナノ粒子触媒を、基材表面上に高密度に配列し、かつナノ粒子間の凝集を回避し優れた安定性を発現させることを目的とし、平坦なシリコン基板表面に種々の金属酸化物多層膜を基材として形成し、その影響を調査した。

その結果図 1a に示すように、結晶性の高い金属酸化物膜の上に、ごく薄く（1 nm 程度）欠陥の多い酸化物層が成膜された構造が、鉄ナノ粒子（直径 3-5 nm）高密度（10-15 nm 間隔）アレイの高温安定性（750℃）に大きく寄与することが明らかにされた。

上記のように２層構造を有する下地層を用いて調整された触媒ナノ粒子アレイは、高温での触媒 CVD 法による長尺カーボンナノチューブの高速成長 [1]に適用され、従来法と比べて優れた成長速度と成長寿命が両立でき、60 分で 1 cm を超えるカーボンナノチューブ集合体の合成に初めて成功した（図 1b）。



1) S. Sakurai, M. Yamada, J. He, K. Hata, D. N. Futaba, *J. Phys. Chem. Lett.*, **2022**, *13*, 1879-1885.

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Understanding the Roles of Hydroxide in CO_2 Electroreduction on a Cu Electrode for Achieving Variable Selectivity

(*[1]Department of Chemistry, Graduate School of Science, Kyushu University, [2]IMCE, Kyushu University, [3]WPI-I[2]CNER, Kyushu University, [4]K-NETs, Kyushu University, [5]WPI-AIMR, Tohoku University*) ○Mingxu Sun[1] and Miho Yamauchi [1, 2, 3, 4, 5]

Keywords: CO_2 reduction reaction; hydroxide; work function; electroadsorption; variable selectivity

Hydroxide-derived copper (OH/Cu) electrodes exhibit excellent performance for the electrocatalytic CO_2 reduction reaction (CO_2RR). However, the role of hydroxide (OH) in CO_2RR remains controversial and the origin of the selectivity enhancement emerging on OH/Cu has not been fully understood. The center of the debate has been what product selectivity can be improved by OH formation, not intrinsic natures of the electrode surface. Thus, in this study, we evaluated the influence of the OH on CO_2RR by preparing Cu electrode with different amount of surface OH.

We synthesized three electrodes characterized by significantly different OH amounts: small (**Cu foil**), moderate (**M-OH/Cu**), and large amounts of OH (**L-OH/Cu**), in which the **M-OH/Cu** and **L-OH/Cu** were prepared by electrooxidation method followed by reduction with different degree. The CO_2RR performance was evaluated at current densities from −10 to −80 mA cm^{-2} using a gastight H-type glass cell.

Scanning electron microscopy (SEM) suggested that the pristine **Cu foil** has a relatively flat surface, whereas needle-like nanostructures are formed on the surface of the **M-OH/Cu** and **L-OH/Cu**. The OH amount on the Cu surface was characterized by electroadsorption technique, which is the first time used for OH amount evaluation.[1] The electroadsorption suggested that the amount of OH and the OH-to-Cu^0 ratio on **L-OH/Cu** were 4.7 times and 2.7 times, respectively, larger than those on **M-OH/Cu**, whereas obvious adsorption was not observed on **Cu foil**. Fig. 1 presents Faradaic efficiencies (FE) for CO_2RR on prepared Cu electrodes. **Cu foil** showed a high CH_4 selectivity with an average CH_4 FE of 67% and **M-OH/Cu** provided a C_{2+} FE of 71%. **L-OH/Cu** having large OH amount exhibited a lower C_{2+} FE (54%) than **M-OH/Cu** (71%) but the ratio of C_{2+}-to-CH_4 on **L-OH/Cu** is higher than 355 (Fig. 1). Density functional theory calculation conducted by Prof. A. Staykov represented that the OH coverage modifies the work function (WF) of Cu surfaces (Fig. 2) and the reaction energetics for the formation of *CHO and *COCHO, which are deeply related to the variable selectivity observed on the Cu electrodes.[1]

1) M. Sun, A. Staykov, M. Yamauchi, *ACS Catalysis* **2022,** *12* (24), 14856.

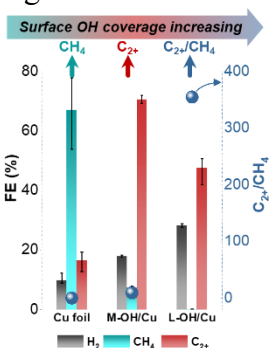


Fig.1. Faradaic efficiency (FE) and the ratio of C_{2+}-to-CH_4 in CO_2RR.

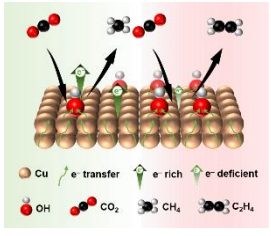


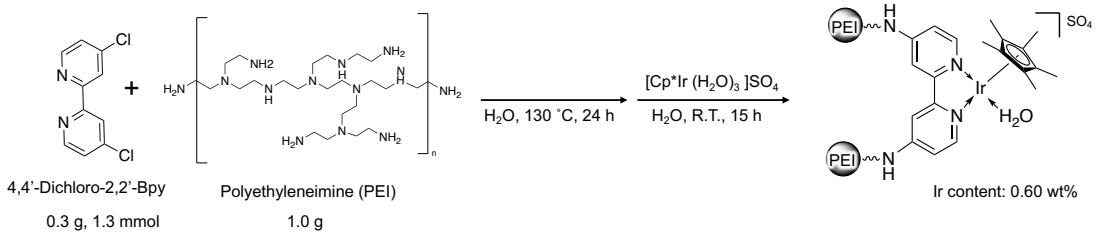
Fig.2. Roles of OH with low (left) and high coverage (right) on Cu electrodes.

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Development of the Ir-complex catalysts immobilized on functional polymer for formic acid dehydrogenation

([1] *Graduate School of Science and Technology, University of Tsukuba*, [2] *Interdisciplinary Research Center for Catalytic Chemistry, AIST,* [3] *Research Institute for Chemical Process Technology, AIST*) ○Keito Sawahara,[1,2] Shinji Tanaka,[2] Tetsuya Kodaira,[3] Hajime Kawanami[1,2]
Keywords: *Hydrogen, Immobilized catalysts, Formic acid, Polymer*

Due to the recent attention on hydrogen energy, we have proposed the use of formic acid (FA) as a hydrogen carrier.[1,2] Because FA has a high hydrogen storage capacity (53 kg/m^3, 4.3 wt%), and has several advantages such as high stability, low toxicity, low flammability, and ease of storage and reserve. Recently, we reported the efficient homogeneous Ir catalysts for formic acid dehydrogenation (FADH),[1,2] and these catalysts enabled the production of high-pressure hydrogen gas above 150 MPa at 80 ˚C.



Scheme 1. Synthetic scheme of Ir catalysts immobilized on polymer

For the practical use of FADH, immobilization of these catalysts is necessary in the flow-type continuous hydrogen production. Herein, we synthesized the Ir-based catalysts immobilized on functional polymers and evaluated these catalytic properties toward FADH activity and durability for a long-time reaction.

Scheme 1 shows a synthetic scheme of the Ir catalysts immobilized on polyethyleneimine (PEI).[3] As prepared catalysts showed high activities for FADH, and the total Turn Over Number (TON) of 7-cycle tests was 1.9×10^5 (Figure 1). In addition, we confirmed no decrease in Turn Over Frequency (TOF) values during 7-cycle tests (TOF = 1.5×10^4 h^{-1}). The details of catalyst synthesis, catalytic reaction and high-pressure hydrogen production are presented.

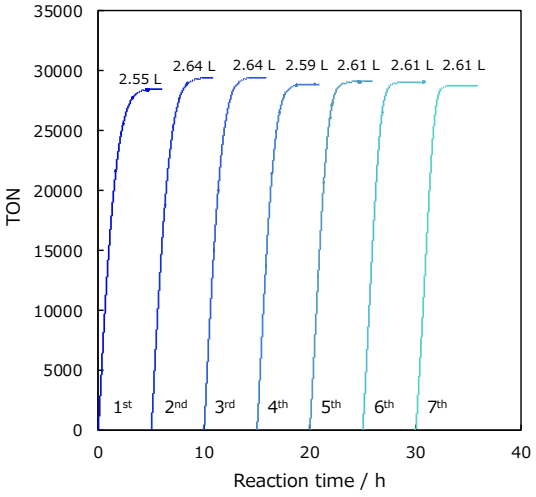


Figure 1. Formic acid dehydrogenation using the immobilized Ir catalysts

1) H. Kawanami, M. Iguchi, Y. Himeda, *Inorg. Chem.* **2020**, 59, 4191. 2) M. Iguchi, Y. Himeda, Y. Manaka, H. Kawanami, *ChemSusChem* **2016**, 9, 2749. 3) Japan Patent Application 2022-139988 (2022.09.02)

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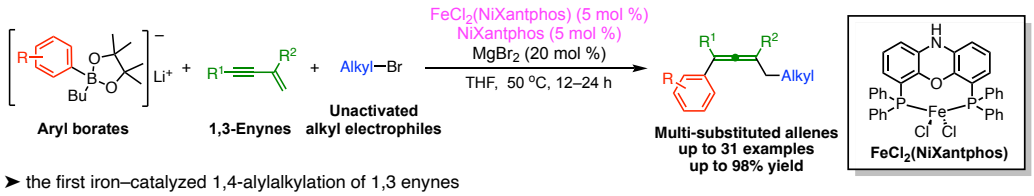
Iron-Catalyzed 1,4-Arylalkylation of 1,3-Enynes with Arylborates and Unactivated Alkyl Electrophiles

(*Institute for Chemical Research, and Graduate School of Engineering, Kyoto University*)
○Siming Lu, Litian Chen, Satsuki Nomura, Katsuhiro Isozaki, Masaharu Nakamura
Keywords: Three Component Coupling Reaction; Iron-NiXantphos complex catalyst; 1,4-Arylalkylation; Alkyl Electrophiles; Arylborates

Allene is one of the most versatile building blocks to construct complex molecular scaffolds in natural products and pharmaceuticals.[1] In recent years, transition metal-catalyzed 1,4-arylalkylations of 1,3-enynes have been proved a powerful strategy for the efficient synthesis of multi- or tetra-substituted allenes. Although the first-row transition metal catalysts significantly improved and complemented this reaction based on the single electron transfer process, only few reports have been published to this date.[2] Herein, we report the first iron-catalyzed radical 1,4-arylalkylation of 1,3-enynes with arylborates and unactivated alkyl electrophiles to afford tetra-substituted allenes (Scheme 1).

The three–component coupling reaction proceeds smoothly under mild conditions in the presence of magnesium bromine and catalytic amounts of iron–NiXantphos complex, providing the corresponding multi-substituted allenes in good to excellent yields. During the scope studies, we observed that several functional and heterocyclic substituent groups are well-tolerated in this reaction, demonstrating a broad substrate scope. Following the screening of several types of alkyl electrophiles, we noticed that the stability of the alkyl radical had a great impact on the reaction yields. To further prove this hypothesis, we performed several competitive or mechanistic reactions including radical scavenge reactions. In this presentation, we will report the detailed ligand screening and scope studies and discuss the possible reaction mechanism.

Scheme 1



➤ the first iron–catalyzed 1,4-alylalkylation of 1,3 enynes

1. Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis,* Wiley-VCH, New York, 1984.
2. a) Terao, J.; Bando, F.; Kambe, N. *Chem. Commun.* **2009**, 7336–7338; b) Wang, F.; Wang, D.; Zhou, Y.; Liang, L.; Lu, R.; Chen, P.; Lin, Z.; Liu, G. *Angew. Chem. Int. Ed.* **2018**, *57*, 7140–7145; c) Zhu, X.; Deng, W.; Chou, M. F.; Ye, C.; Jian, W.; Zeng, Y.; Jiao, Y.; Ge, L.; Li, Y.; Zhang X.; Bao H. **2019**, *141*, 548–559; d) Zhang, K.; Bian, K.; Li, C.; Sheng, J.; Li, Y.; Wang X. *Angew. Chem. Int. Ed.* **2019**, *58*, 5069–5074. e) Li, Y.; Bao H. *Chem. Sci.*, **2022**, *13*, 8491–8506.

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In situ formic acid dehydrogenation observation using a UV-vis-diffuse-reflectance spectroscopy system

([1]*Graduate School of Science and Technology, University of Tsukuba*, [2] *National Institute of Advanced Industrial Science and Technology*) ○Risheng Li,[1,2] Tetsuya Kodaira,[2] Hajime Kawanami[1,2]

Keywords: In-situ monitoring, UV-vis, homogeneous Ir catalyst.

In recent decades, formic acid (FA) is regarded as one of the most promising liquid hydrogen carriers, which possesses a high hydrogen content (53 g of H_2/L) and is nontoxic, and has garnered considerable attention.

With regard to formic acid dehydrogenation (FADH), researchers have mainly focused on the development of efficient catalysts; thus, a myriad of homogeneous catalysts have been developed so far[1-3]. However, few in situ measurements have been reported during the gas generation to understand the FADH reaction mechanism in the presence of homogeneous catalysts. One of the barriers to employing conventional in situ measurements of the absorption spectra is the presence of gas-liquid mixed phases. Herein, we developed a new in situ UV-vis-diffuse-reflectance spectroscopy technology to monitor the

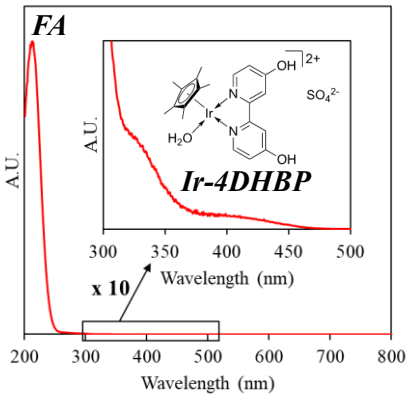


Fig.1 The absorption spectra of the sample

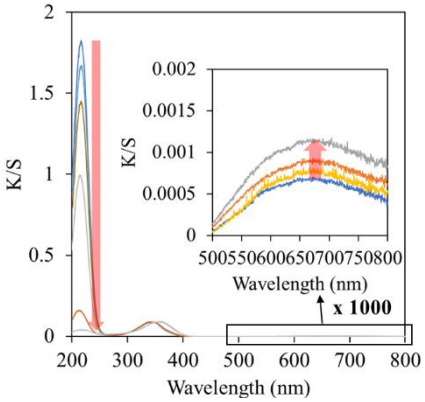


Fig.2 The absorption spectra of long-term experiments

FADH reaction. The results (Figure 1) showed a clear signal at 215 nm corresponding to the FA in the sample and the weak signals of the catalyst (Ir-4DHBP) were obtained as well. Moreover, we applied our new technology to monitor the sample in the long-term experiment (> 14h), and it was found that the peak of the FA decreased gradually which indicated the consumption of the FA and a new signal appeared in the range from 650 to 700 nm which probably corresponds to the intermediate in the process of the catalyst decomposition. In this presentation, we will introduce the detail in the mechanism of the catalyst decomposition investigated by our new technology.

1) H. Kawanami et al., *Adv. Inorg. Chem.*, 2017, **70**, 395-427. 2) M. Younas et al., *Int. J. Hydrogen Energy*, 2022, **47**, 11694-11724. 3) I. Dutta et al., Adv. Energy Mater., 2022, 12, 2103799.

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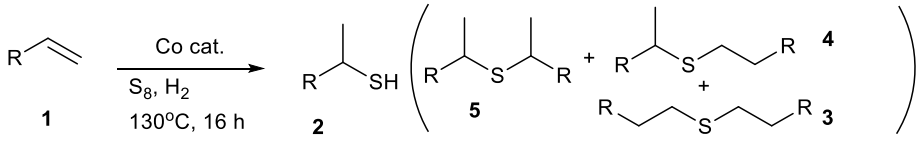
固体コバルト触媒を用いた水素、硫黄、アルケンを原料とするチオール類の新合成法開発

(九大院理[1]・DIC 株式会社[2]) ○許 柯[1]・山本 英治[1]・村山 美乃[1]・松枝 宏尚[2]・坂田 浩[2]・徳永 信[1]

Development of novel synthetic method for thiols using heterogeneous cobalt catalysts from hydrogen, elemental sulfur, and alkenes ([1]*Graduate School of Science, Kyushu University*, [2]DIC Corporation) ○Ke Xu,[1] Eiji Yamamoto,[1] Haruno Murayama,[1] Hironobu Matsueda,[2] Hiroshi Sakata,[2] Makoto Tokunaga[1]

Thiols are important organic sulfur compounds widely applied in medicinal chemistry and materials science. Alkyl thiols with the different alkyl chains are used as gas odorization and perfumes in the relation to the special smells. Industrial thiol synthesis using hydrogen sulfide and alkenes as the starting materials have been reported. However, the use of hydrogen sulfide process for the thiol synthesis remains ongoing challenges due to the high toxicity. In this study, we developed a novel catalytic synthesis of thiols using elemental sulfur as the sulfur source since the sulfur is easy to handle. Alkyl olefins (**1**) were used as the alkene substrate and the reactions were carried out under high-pressure H_2 gas atmosohere. The results of the investigation showed H_2 pressure under 7 MPa and solvent-free conditions, the reaction of alkene and sulfur, Co catalyst, at 130ºC for 16 h gave the thiol in acceptable yield and the dialkylmonosulfanes (**3**-**5**) as the by-product were confirmed (Scheme 1).
Keywords : Thiols; Cobalt; Sulfur; Hydrogen; dialkylmonosulfanes

チオール類は創薬化学や材料科学の分野でもしばしば利用される重要な有機硫黄化合物である。例えば、この硫黄化合物は構造の違いによって異なる匂いを持つため香料やガス添加剤等にも使用されている。工業的なアルキルチオールの合成法ではアルケンと硫化水素を原料とした触媒的合成法が用いられている。しかし硫黄源かつ水素源となる硫化水素は、高い毒性を持つため安全性と設備管理の面で懸念がある。そこで本研究では、硫化水素の取り扱い容易な代替反応剤として硫黄と水素を用いて、アルケンを基質原料とするチオール類の新しい触媒的合成法の開発を目指した研究を行った。
アルキルオレフィン類(**1**)を基質として反応の最適化を検討した。様々な検討の結果、水素圧下、**1** に対し、無溶媒条件下で固体コバルト触媒と硫黄を添加し、130ºC、16 時間反応を行うと、アルカン-2-チオール(**2**)が良い収率で得られた。また、副生成物としてジアルキルモノスルファン類(**3-5**)が、それぞれ合成し確認した。(Scheme 1)



Scheme 1. Catalytic thiol synthesis using hydrogen and sulfur

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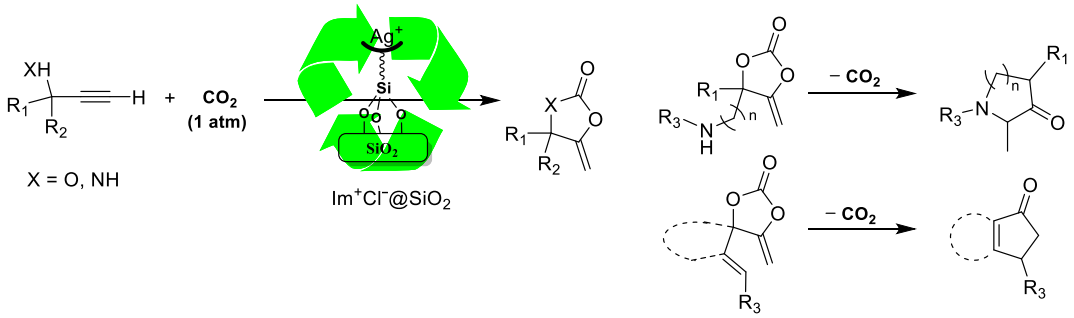
Heterogeneous catalytic approach to the synthesis of cyclic carbonates and their decarboxylative transformations

(*[1]Graduate School of Pharmaceutical Science, Tokushima University*) ○Sangita Karanjit[1], Emiko Tanaka[1], Ryota Sato[1], Kosuke Namba[1]

Keywords: heterogeneous catalyst, carbondioxide conversion, Silver catalyst, Decarboxylation

CO_2 has been regarded as a nontoxic, abundant, nonflammable, and renewable one-carbon (C1) feedstock for the synthesis of a variety of value-added chemicals. There have been numerous advances on the metal-catalyzed synthesis of various organic compounds utilizing CO_2 as a C1 source. Among them, the reactions of CO_2 with unsaturated alcohols and amines to afford carbonates and carbamates through carboxylative cyclization process is one of the promising green routes. These compounds have wide range of application in organic synthesis for being important building blocks and potential biological activity. Silver has the potential to activate alkynes and has been extensively studied for chemical transformation of CO_2. Most of the studies have concentrated on homogeneous catalysis using relatively large amounts of Ag based catalysts[1]. Compared to homogeneous systems, heterogeneous system is advantageous for development of green and sustainable society in terms of good activity and reusability.

We recently developed a heterogeneous silver catalyst by the immobilization of silver catalyst on silica support via alkoxysilane linkage ($Im^+Cl^-@SiO_2$)[2]. We carried out the CO_2 transformation reactions with propargyl alcohols and amines using the synthesized silver catalyst $Im^+Cl^-@SiO_2$. The active catalysts were synthesized or generated in situ which performed the reactions with excellent yields of the corresponding carbonates and carbamates under mild condition with good activity and reusability. In addition, the product cyclic carbonates were converted to various value-added products by decarboxylation processes.



1) S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H.-M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn*. **2011**, *84*, 698.

2) S. Karanjit, E. Tanaka, L. K. Shrestha, A. Nakayama, K. Ariga, and K. Namba, *Catal. Sci. Technol.* **2022**, *12*, 3778.

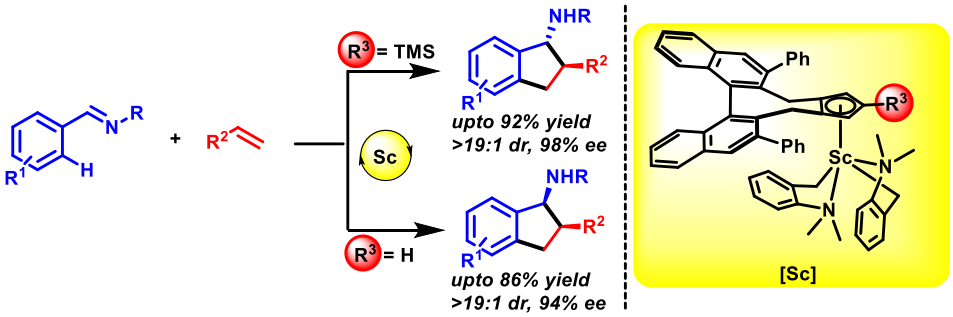
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Enantioselective [3+2] Annulation of Aromatic aldimines with Alkenes via C−H Activation by Half-Sandwich Scandium Catalysts

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science*)
○Aniket Mishra,[1] Xuefeng Cong,[1] Masayoshi Nishiura,[1] Zhaomin Hou[1]
Keywords: C−H activation, Annulation, Scandium, Rare-earth-metal, Asymmetric synthesis

Chiral aminoindanes are valuable structural motifs found in numerous drugs and bioactive molecules. Therefore, the development of a selective and efficient route for the synthesis of densely functionalized chiral aminoindanes is of high interest and importance. In principle, enantioselective formal [3+2] annulation of aromatic aldimines with alkenes via *ortho* aryl C–H bond activation is among the most straightforward and atom-efficient approach for the synthesis of multisubstituted chiral aminoindanes. However, such approach has remained unsuccessful, presumably due to the lack of suitable chiral catalysts. Recently, we have found that half-sandwich rare-earth-alkyl complexes can serve as efficient catalysts for the [3+2] annulation of aldimines and alkenes via C–H activation.[1] These studies invoked us to examine the feasibility of the asymmetric annulation by using chiral half-sandwich rare-earth-alkyl catalyst.

Herein, we demonstrate the first diastereodivergent asymmetric [3+2] annulation of aromatic aldimines with styrenes via C–H bond activation by chiral half-sandwich scandium catalysts. This protocol offers the atom-efficient synthesis of both the *trans* and *cis* diastereoisomers of multisubstituted chiral aminoindanes in high yield along with excellent diastereo- and enantioselectivity by fine-tuning the sterics around the metal-center. Apart from styrenes, aliphatic α-olefins, norbornene, 1,3-dienes were all suitable for the asymmetric transformation.



1) (a) X. Cong, G. Zhan, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2020**, *143*, 5531. (b) X. Cong, Q. Zhuo, N. Hao, Z. Mo, G. Zhan, Z. Mo, M. Nishiura, Z. Hou, *Angew. Chem., Int. Ed.* **2022**, *134*, e202115996.

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[K306-2pm] 08. Catalysts and Catalysis

Chair: Akihide Iwase, Osamu Tomita

Thu. Mar 23, 2023 1:50 PM - 3:40 PM K306 (K306, Lecture Hall Bldg. [3F])

[K306-2pm-01] Tuning interfacial energetics for enhanced H_2O_2 generation

○Zhenhua Pan[1], Junie Vequizo[3], Akira Yamakata[2], Chiheng Chu[4], Kenji Katayama[1] (1. Chuo University, 2. Okayama University, 3. Shinshu University, 4. Zhejiang University)

1:50 PM - 2:10 PM

[K306-2pm-02] Development of Green Molecular Transformation Mediated by Cobalt Complex and WO_3 System

○Keita Shichijo[1], Hisashi Shimakoshi[1] (1. Kyushu Univ.)

2:10 PM - 2:30 PM

[K306-2pm-03] Decomposition of Perfluoroalkyl Substances by Near-UV and Visible Light Irradiation to Semiconductor Nanocrystals

○Yoichi Kobayashi[1,2], Yusuke Sanada[1], Yuzo Arima[1], Yoshinori Okayasu[1], Yuki Nagai[1] (1. Ritsumeikan Univ., 2. PRESTO JST)

2:30 PM - 2:50 PM

[K306-2pm-04] Z-scheme hybrid photocatalysts consisting of conjugated polymer semiconductors and Ru(II) binuclear supramolecular photocatalyst for visible-light driven CO_2 reduction

○Noritaka Sakakibara[1], Ewan McQueen[2], Yusuke Tamaki[1], Sebastian Sprick[2], Osamu Ishitani[1,3] (1. Tokyo Tech., 2. Univ. of Strathclyde, 3. Hiroshima Univ.)

3:00 PM - 3:20 PM

[K306-2pm-05] Advances in Photocatalytic Hydrophosphination

○Rory Waterman[1] (1. University of Vermont)

3:20 PM - 3:40 PM

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Tuning interfacial energetics for enhanced H_2O_2 generation

Zhenhua Pan[1*], Junie Vequizo[2], Akira Yamakata[3], Chiheng Chu[4], Kenji Katayama[1]
(1. Chuo University, 2. Shinshu University, 3. Okayama University 4. Zhejiang University)
*Email: zhenhua.20y@g.chuo-u.ac.jp

Solar-driven H_2O_2 generation over a particulate photocatalyst has attracted much attention. Yet, the efforts in designing high-performance particulate photocatalysts are largely impeded by inefficient charge separation. Because charge separation in a particulate photocatalyst is driven by asymmetric interfacial energetics between its reduction and oxidation sites, enhancing this process demands nanoscale tuning of interfacial energetics on the prerequisite of not impairing the kinetics and selectivity for H_2O_2 generation. In this study, we realized this target with a general strategy involving the application of a core/shell type cocatalyst that is demonstrated on various photocatalytic systems. Particularly, this strategy was highlighted on a $BiVO_4$ system for overall H_2O_2 photosynthesis. A core/shell type Ag/Pd cocatalyst was selectively deposited on the reduction facets of $BiVO_4$, where the Ag core formed a low Schottky barrier with $BiVO_4$ at its reduction site for enhancing charge separation and Pd shell preserved the surface kinetics and selectivity for H_2O_2 generation (Figures 1a-1d). Time-resolved spectroscopy and numerical simulations suggest the $BiVO_4$/Ag junction enhanced the asymmetric interfacial energetics as expected. With successful interfacial energetics tuning, $BiVO_4$ exhibits high overall H_2O_2 photosynthesis among inorganic photocatalysts, with an apparent quantum yield (AQY) of 3.0% and a solar-to-H_2O_2 conversion (STH) efficiency of 0.73% at full spectrum, as well as an AQY of 13.1% at 420 nm (Figures 1e-1f).

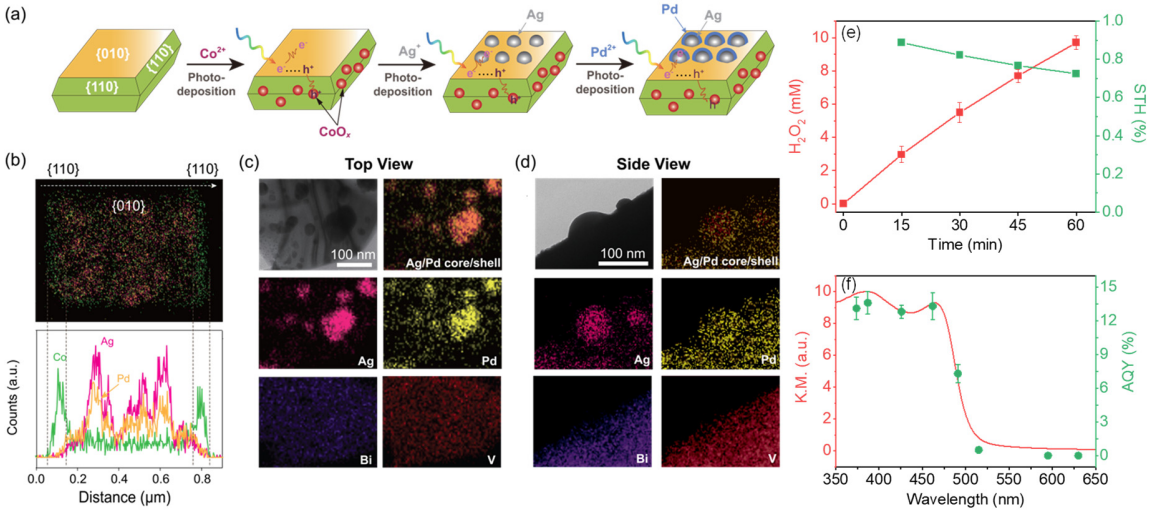


Figure 1 (a) Stepwise and facet-selective photodeposition of Co, Ag and Pd on $BiVO_4$. (b) EDS elemental mapping and line profile of CoO_x/$BiVO_4$/(Ag/Pd). (c)-(d) STEM-EDS elemental mapping of Ag/Pd particles loaded on $BiVO_4$. (e) Time courses of photocatalytic H_2O_2 generation over CoO_x/$BiVO_4$/(Ag/Pd) and the corresponding STH efficiency. (f) AQY of H_2O_2 photosynthesis over CoO_x/$BiVO_4$/(Ag/Pd) as a function of the incident light wavelength.

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[2] T. Liu, Z. Pan*, K. Kato, J.J.M. Vequizo, R. Yanagi, X. Zheng, W. Yu., A. Yamakata, S. Hu, K. Katayama, C. Chu*, A general interfacial-energetics-tuning strategy for enhanced artificial photosynthesis, *Nat. Commun.*, Accepted.

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酸化タングステンとコバルト錯体の最適ペアで実現するクリーン物質変換

（九大院工）○七條 慶太・嶌越 恒
Development of green molecular transformation mediated by cobalt complex and WO_3 system
(*Graduate School of Engineering, Kyushu University*) ○Keita Shichijo, Hisashi Shimakoshi

We report the green and sustainable organic transformation catalyzed by the WO_3 and a cobalt complex, synthesized from vitamin B_{12} in our group, during visible light irradiation in air at room temperature. The visible light driven methyl benzoate formation from benzotrichloride was effectively promoted by this catalytic system with utilizing methanol as electron donor, reactant, and solvent.
Keywords : Tungsten Oxide (WO_3), Cobalt Complex, Visible Light, Organic Transformation.

酸化タングステン（WO_3）は可視光応答性の光触媒として注目されており、水の酸化反応や有機物の酸化分解反応へ応用する研究が行われている[1]。一方で、WO_3 を触媒として利用する有機物質変換はほとんど例がなく未開拓の領域である。我々は、現在までに天然由来のコバルト錯体であるビタミン B_{12} と金属酸化物光触媒を組み合わせた触媒システムによる有機物質変換反応を開発してきた。ここでは酸化チタン（TiO_2）を利用することで光駆動型の物質変換反応を達成している[2]。一方で、可視光を利用できる優れた WO_3 を利用した触媒システム・物質変換反応の開発は未だ達成できていない。近年我々は、ビタミン B_{12} を化学修飾したコバルト錯体は中心金属のコバルトの還元電位が+0.3 V 正にシフトし、それに伴って WO_3 に可視光を照射した際に生じる励起電子によって触媒活性種の Co(I)種を生成可能であることを見出した。そこで本研究では、酸化タングステン(WO_3)と新規に合成した B_{12} 由来コバルト錯体を用いた触媒システムを利用することにより、可視光を駆動力とするクリーンな有機物質変換反応の開発を目指す(Figure 1. (a))。

触媒システムに利用するコバルト錯体(**π1**)は、天然のビタミン B_{12} から 2 ステップで合成に成功した。合成したコバルト錯体と WO_3 をメタノール中に加え、窒素雰囲気下で可視光（$\lambda \geq 420$ nm）を照射しながら拡散反射スペクトルを測定すると、90 分間の照射後に 470 nm 付近に Co(I)種由来の明瞭なピークを観測できた(Figure 1. (b))。また、本触媒システムを利用してトリクロロメチルベンゼンからエステルを合成する反応を実行した。その結果、収率 82%で目的のエステルを合成することに成功した(Scheme 1)。

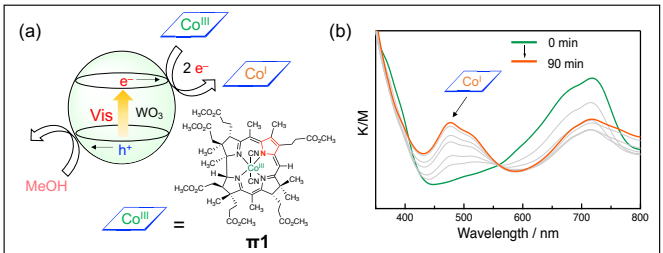
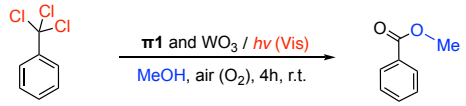


Figure 1. (a) Photocatalytic system composed of cobalt complex and WO_3. (b) DR-UV-vis spectra during visible light irradiation.

Scheme 1. Ester formation from benzotrichloride by **π1** and WO_3.



[1] R. Abe, H. Takami, N. Murakami, B. Ohotani, *J. Am. Chem. Soc.*, **2008**, *130*, 7780–7781.
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半導体ナノ結晶と近紫外・可視光を用いたパーフルオロアルキル化合物の分解

（立命館大生命科学[1]・JST さきがけ[2]）○小林 洋一[1,2]・真田優介[1]・有馬 佑蔵[1]・岡安 祥徳[1]・永井 邑樹[1]

Decomposition of Perfluoroalkyl Substances by Near-UV and Visible Light Irradiation to Semiconductor Nanocrystals ([1]*College of Life Sciences, Ritsumeikan University,* [2]*PRESTO JST*) ○Yoichi Kobayashi,[1,2] Yusuke Sanada,[1] Yuzo Arima,[1] Yoshinori Okayasu,[1] Yuki Nagai[1]

Perfluoroalkyl substances (PFAS) are practically used in various industries, while their extremely high stability causes serious environmental persistence. Several decomposition methods such as heating over 300 degree Celsius and irradiation of deep ultraviolet light have been reported, however, decompositions under more mild conditions are desired. In this study, we report that PFAS can be decomposed into F^- ions using near UV and visible LED light irradiation using metal-doped semiconductor nanocrystals (NCs) at room temperature under atmospheric pressure.

Keywords : Organic Fluoride Compounds; Polytetrafluoroethylene; Perfluorooctanesulfonic acid; Semiconductor nanocrystals; Photocatalysts

パーフルオロアルキル化合物（PFAS）は表面処理剤をはじめとして多くの産業で用いられる一方、近年その高い化学的安定性による環境残留性と難分解性が問題となっている。PFAS の分解にあたっては強熱や深紫外光照射など様々な手法が試みられているものの、より温和な条件での分解が求められている。

近年我々は、銅イオンをドープした硫化亜鉛（Cu-ZnS）、酸化亜鉛（ZnO）、硫化カドミウム（CdS）ナノ結晶 (NCs)などを用いて、常温常圧でそれらと PFAS の混合水溶液に近紫外・可視 LED 光を照射することにより、PFAS の中でも特に環境負荷が懸念されるペルフルオロオクタンスルホン酸（PFOS）や、化学的安定性が極めて高いテフロンをフッ化物イオンに分解することに成功している。本発表では、これらの成果、およびその考えられるメカニズムについて発表する。

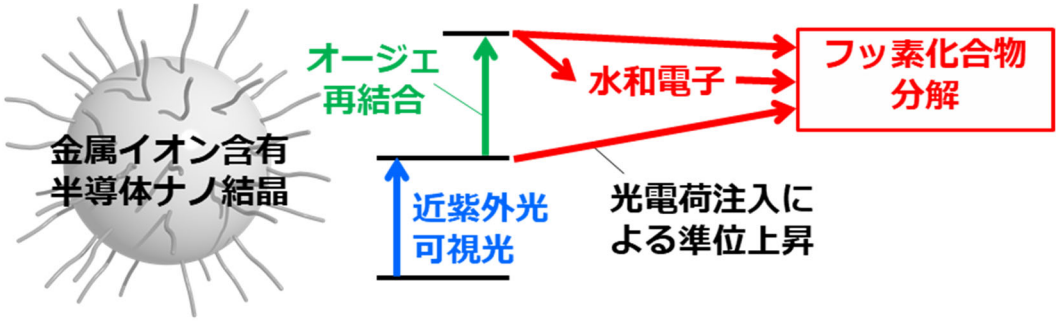


Fig. 1　Plausible mechanism of the visible (near UV)-light-induced decomposition of PFAS using semiconductor NCs.

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共役ポリマー半導体と Ru(II)二核超分子光触媒からなる Z スキーム型ハイブリッド光触媒を用いた可視光駆動 CO_2 還元

（東工大理[1]・Univ. of Strathclyde[2]・広島大理[3]）○榊原 教貴[1]・Ewan McQueen[2]・玉置 悠祐[1]・Sebastian Sprick[2]・石谷 治[1,3]

Z-scheme hybrid photocatalysts consisting of conjugated polymer semiconductors and Ru(II) binuclear supramolecular photocatalyst for visible-light driven CO_2 reduction ([1]*School of Science, Tokyo Institute of Technology*, [2] *Department of Pure and Applied Chemistry, University of Strathclyde*, [3] *Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Noritaka Sakakibara,[1] Ewan McQueen,[2] Yusuke Tamaki,[1] Sebastian Sprick,[2] Osamu Ishitani[1,3]

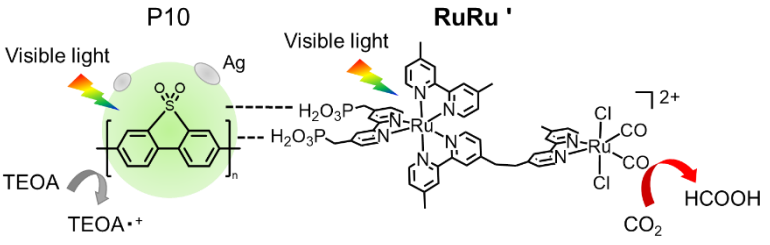
Hybrid photocatalysts consisting of a semiconductor and a supramolecular photocatalyst are promising for visible-driven CO_2 conversion to useful fuels.[1)] In this study, we have developed new Z-scheme hybrid photocatalysts consisting of various linear conjugated polymer semiconductors[2)] and a Ru(II) binuclear supramolecular photocatalyst (**RuRu'**). Especially, the hybrid photocatalyst with poly(dibenzo[*b,d*]thiophene sulfone) (P10) on which Ag was loaded as an electron sink,[1)] i.e., **RuRu'**/Ag/P10, worked as a highly efficient photocatalyst for CO_2 reduction to formic acid with 96% selectivity under visible light (λ = 460 nm) irradiation: its apparent quantum yield was 9.2±0.68% at 460-nm light irradiation and turnover number of formic acid production was over 320000 after 95 h light irradiation.

Keywords : Polymer semiconductor; Supramolecular photocatalyst; CO_2 reduction; Z-scheme

半導体と超分子光触媒からなるハイブリッド光触媒は、可視光を有効利用し CO_2 を有用資源へと変換する高性能なシステムの構築に向けて大変有望である[1)]。本研究では半導体として、モノマーの選択により多様な構造を設計でき、光物理的、電子的性質を制御可能な共役ポリマー[2)]を活用した。この共役ポリマー上に Ru(II)二核超分子光触媒（**RuRu'**）を固定化し、Z スキーム型新規ハイブリッド光触媒を開発した。

共役ポリマーとしてポリジベンゾ[*b,d*]チオフェンスルホン（P10）を用い、電荷分離促進のために Ag を共担持[1)]したハイブリッド光触媒（**RuRu'**/Ag/P10）を、*N,N'*-ジメチルアセトアミド／トリエタノールアミン（TEOA）中に懸濁させ可視光（λ=460 nm）を照射したところ、CO_2 を 96%の選択率でギ酸へと還元した。本ハイブリッド光触媒は、460 nm におけるギ酸生成の見かけの量子収率が 9.2±0.68%、光照射 95 時間後のギ酸生成の触媒回転数が 32 万回という、非常に高い光触媒特性を示した。

1) A. Nakada, H. Kumagai, M. Robert, O. Ishitani, K. Maeda, *Acc. Mater. Res.* **2021**, 2, 458.
2) C. M. Aitchison, R. S. Sprick, *Nanoscale* **2021**, 13, 634-646.



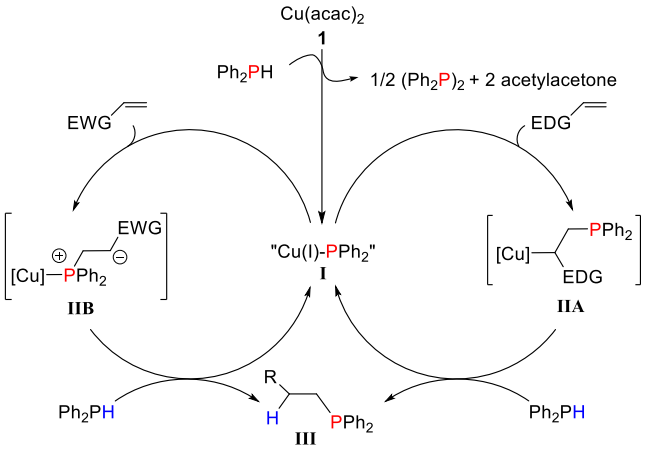
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Advances in Photocatalytic Hydrophosphination

([1]*Department of Chemistry, University of Vermont*) ○Rory Waterman[1]
Keywords: Hydrophosphination; Phosphine; Photocatalysis; Copper; Zirconium

An important challenge for chemists is increasingly efficient routes to element–carbon bonds, as characterized by energetic costs and atom economy, among other factors. An atom-economical route for element–carbon bond formation is the metal-catalyzed addition of an E–H bond across an unsaturated substrate, generally termed heterofunctionalization. For hydrophosphination or P–C bond formation, challenges in substrate scope, selectivity, and catalyst have loomed.[1] Many catalysts are known,[2] and a rich variety of mechanisms have been uncovered in these reactions.[3] Starting from poor initial hydrophosphination catalysis with zirconium compounds, a family of earth abundant, highly active, and selective catalysts have been discovered and investigated, and photocatalysis is critical to this activity.

Simple copper catalysts that may be the most active known but are certainly the most synthetically accessible.[5] Under visible or UV photolysis, $Cu(acac)_2$ is highly active for the hydrophosphination a range of phosphine and unsaturated substrates. These reactions are on a scale of minutes to hours, allowing for broad testing of hydrophosphination with a wide variety of substrates, making this the go-to catalyst for synthetic screening. The mechanism of this catalysis diverges based on substrate. After a common reduction step with sacrificial phosphine substrate, the active copper(I) catalyst can either undergo an insertion-based mechanism of the phosphido ligand can attack an electron poor alkene. Spectroscopic and computational analysis point to a LUMO with significant Cu–P σ* character. This would indicate that photocatalysis for early and late metals are similar and therefore may extend to other π-basic ligands. Analysis of mechanism with respect to expanding the substrate scope of hydrophosphination and addressing related challenges will be detailed.



1) Bange, C. A.; Waterman, R. *Chem. Eur. J.* **2016**, *22*, 12598. 2) Novas, B. T.; Waterman, R. *ChemCatChem* **2022**, *14*, e202200988. 3) Rosenberg, L. *ACS Catal.* **2013**, *3*, 2845. 4) Dannenberg, S. G.; Waterman, R. *Chem. Commun*. **2020**, *56*, 14219. 5) Dannenberg, S. G.; Seth, Jr., D. M.; Finfer, E. J.; Waterman, R. *ACS Catal.* **2022** *accepted*.

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[K506-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Takahiro Matsumoto, Takuya Kochi

Thu. Mar 23, 2023 9:00 AM - 11:40 AM K506 (K506, Lecture Hall Bldg. [5F])

[K506-2am-01] Defluorohydrogenation of Acyl Fluorides by Secondary Phosphine Oxide as a Hydride Donor

○Myuto Kashihara[1], Ayaka Kataoka[2], Yasushi Nishihara[1] (1. RIIS, Okayama Univ., 2. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ.)

9:00 AM - 9:20 AM

[K506-2am-02] Effect of Carboxylate Coordination on Redox Properties and Substrate Oxidation Reactivity of Di(-oxido)dinickel(III) Complex

○Yuma Morimoto[1], Ryoichiro Ogumo[2], Shinobu Itoh[2] (1. Nagoya University, 2. Osaka University)

9:20 AM - 9:40 AM

[K506-2am-03] Aerobic oxidative reactivity of nickel complexes supported in napthyridines ligand scaffolds

○Shubham Deolka[1], Julia Khusnutdinova[1] (1. OIST ,JAPAN)

9:40 AM - 10:00 AM

[K506-2am-04] C_3 product formation by electrochemical CO_2 reduction for dinuclear Cu molecular catalyst

○Naonari Sakamoto[1], Keita Sekizawa[1], Soichi Shirai[1], Takamasa Nonaka[1], Takeo Arai[1], Shunsuke Sato[1], Takeshi Morikawa[1] (1. Toyota Central R&D Labs., Inc.)

10:00 AM - 10:20 AM

[K506-2am-05] Synthesis and Redox Reaction of Copper- and Cobalt-Containing Zeolitic Imidazolate Frameworks

○Hiroki Nakahara[1], Masahito Kodera[1], Yutaka Hitomi[1] (1. Doshisha University)

10:20 AM - 10:40 AM

[K506-2am-06] Synthesis, structure and methane oxidation by dicopper complex with hydrophobic pocket

○Kyosuke FUJIKAWA[1], Yutaka HITOMI[1], Masahito KODERA[1,2] (1. Doshisha Univ., 2. JST CREST)

10:40 AM - 11:00 AM

[K506-2am-07] Dual Catalysis of Au_{25} Nanocluster Functionalized by Peptide Dendron Thiolate toward Cross-Dehydrogenative Coupling between Amines and Alkynes

○Kenta Iseri[1], Kyosuke Ueda[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto University)

11:00 AM - 11:20 AM

[K506-2am-08] Electrochemical and Photochemical CO_2 Reduction by Rhenium Porphyrin Complexes

○Jingru Liu[1], Kei Murata[1], Mengfei Wang[1], Kazuyuki Ishii[1], Yusuke Tamaki[2], Osamu Ishitani[2] (1. IIS, The Univ. of Tokyo, 2. Dept. of Chem., Tokyo Tech)

11:20 AM - 11:40 AM

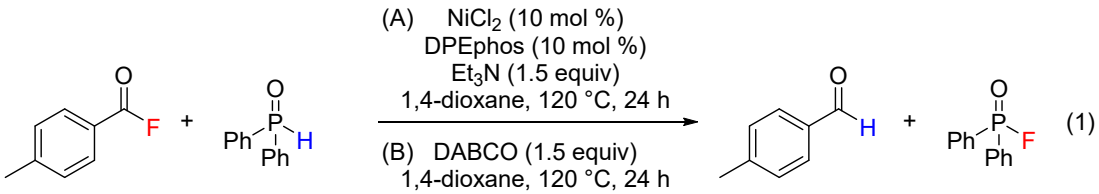
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Defluorohydrogenation of Acyl Fluorides by Secondary Phosphine Oxide as a Hydride Donor

([1] *Research Institute for Interdisciplinary Science, Okayama University,* [2] *Graduate School of Natural Science and Technology, Okayama University*)
○Myuto Kashihara,[1] Ayaka Kataoka,[2] Yasushi Nishihara[1]
Keywords: Acyl Fluorides; Secondary Phosphine Oxides; Aldehydes; Nickel Catalysts

Acyl fluorides are a class of compounds containing a carbonyl–fluorine bond. They are more stable than other acyl halides, but more reactive than the corresponding esters and amides. This moderate reactivity has recently attracted attention and opened up new fields to utilize acyl fluorides as easy-to-handle electrophiles.[1] Another synthetically useful feature is two possible reaction modes: acyl coupling (RCOF as the RCO source) and decarbonylative coupling (RCOF as the R source). Late transition metal catalysts are especially suitable for controlling selectivity and expanding the variation of transformations.

Following our reports on the transformation of acyl fluorides,[2] we this time employed secondary phosphine oxide as a nucleophile under nickel catalysis. However, unlike the reported decarbonylative phosphorylation of amides,[3] only a trace amount of the expected tertiary phosphine oxide was obtained. Instead, we observed clear formation of the corresponding aldehyde and phosphinic fluoride resulting from the exchange of hydrogen with fluorine. After optimizing the reaction conditions, the defluorohydrogenation of *p*-toluic fluoride by diphenylphosiphine oxide was found to be efficiently catalyzed by $NiCl_2$/DPEphos system in the presence of a base (eq. 1(A)). Moreover, the same reaction turned out to be also promoted by use of a base alone. Utilizing the proper base, aldehydes were formed in yields comparable to those obtained under nickel-catalyzed conditions (eq. 1(B)).



1) Y. Ogiwara, N. Sakai, *Angew. Chem., Int. Ed.* **2020**, *59*, 574.
2) a) Z. Wang, X. Wang, Y. Nishihara, *Chem. Commun.* **2018**, *54*, 13969. b) X. Wang, Z. Wang, Y. Nishihara, *Chem. Commun.* **2019**, *55*, 10507. c) L. Fu, Q. Chen, Z. Wang, Y. Nishihara, *Org. Lett.* **2020**, *22*, 2350.
3) C. Liu, M. Szostak, *Angew. Chem., Int. Ed.* **2017**, *56*, 12718.

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Effect of Carboxylate Coordination on Redox Properties and Substrate Oxidation Reactivity of Di(*μ*-oxido)dinickel(III) Complex

○Yuma Morimoto[1], Ryoichiro Ogumo[2], Shinobu Itoh[2] ([1]*Grad. School of Eng., Nagoya Univ.*, [2]*Grad. School of Eng., Osaka Univ.*)

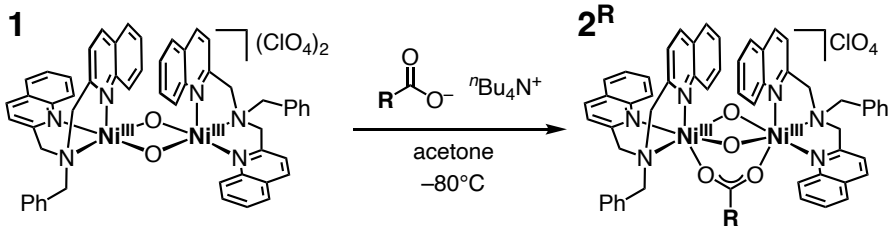
In several metalloenzymes, di(*μ*-oxido)dimetal species are invoked as the key reactive intermediate in the enzymatic oxidation reactions. Dinuclear-metal centers embedded in metalloenzymes are often bridged by a carboxylate group as found in soluble methane monooxygenase (*s*MMO). Although numerous numbers of model complexes of such dinuclear metal centers have been developed, there is no report focusing on the effect of carboxylate bridging ligand on the electronic structure and the reactivity of the di(*μ*-oxido)dimetal species. We herein report the enhancement of the oxidation reactivity of a di(*μ*-oxido)dinickel(III) complex by coordination of a series of carboxylate anions.

To an acetone solution (273 K) of di(*μ*-hydroxido)dinickel(II) complex (**H**) was added an equimolar amount of hydrogen peroxide to generate di(*μ*-hydroxido)dinickel(III) complex (**1**). The complex **1** is characterized by UV–vis and resonance Raman spectroscopy and CSI-MS. X-ray diffraction analysis of its single crystal further endorsed the formation of **1**. Its reduction potential was determined to be –0.56 V vs Fc/Fc^+ with square-wave voltammogram.

Addition of a series of carboxylates ($RCOO^-$, R: Ph, *p*-MeO-Ph, *p*-Cl-Ph, *p*-NO_2-Ph, $(CH_3)_3C$, $CHCl_2$) into the solution of **1** generated an adduct complex ($\mathbf{2^R}$) at 193 K (Scheme 1). Titration experiments and CSI-MS measurement suggested the formation of 1:1 adducts with the association constant of 9.0×10^4 M^{-1}. The benzoate adducts $\mathbf{2^{Ph}}$ oxidized xanthene to xanthydrol as the major product together with xanthone a minor product, where the kinetic deuterium isotope effect (KIE) value was determined as 19. Notably, the coordination of benzoate accelerated the reaction rate for the xanthene oxidation by 16-fold, although the reduction potential of the complex was shifted to the negative direction. The characterization and reactivity studies were also conducted for the other carboxylate adducts. A linear relationship was found between the logarithm of second-order reaction rate constants (log *k*) and the pK_b of the carboxylate anions, which suggested the increase of electron density on the oxide ligand is a key factor in the hydrogen abstraction reaction.

Keywords : Di(μ-oxido)dimetal Complex; Hydrogen Peroxide; Reactive Oxidant; Benzoate Anion; Redox Property

Scheme 1. Formation of $\mathbf{2^R}$ from **1** and carboxylate.



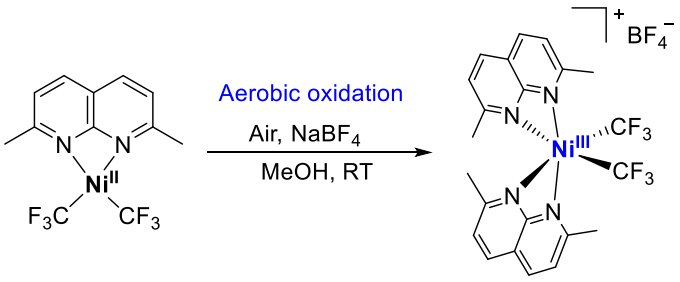
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Aerobic oxidative reactivity of nickel complexes supported by naphthyridine ligands

([1]*Coordination Chemistry and Catalysis Unit*, *Okinawa Institute of Science and Technology Graduate University*) ○Shubham Deolka[1], Govindarajan Ramadoss,[1], Eugene Khaskin,[1] Julia R. Khusnutdinova*[1]

Keywords: Nickel; Naphthyridine; Trifluoromethylation; Oxygen atom transfer.

Our group's longstanding interest is in the development of new ligand platform for selective bond activation. We focused our attention on naphthyridine as a versatile fragment for building up both binucleating and mononucleating ligands. Naphthyridine is well-known for its ability to bridge between two metals forming close metal-metal distances, which gave us inspiration to use it for selective formation of heterobimetallic complexes for bimetallic cooperative bond activation. [1]



While studying coordination chemistry of naphthyridines with Ni, we discovered that simple and substituted naphthyridines tend to form mononuclear Ni complexes.[2] when bis-trifluoromethyl Ni precursor was used. Moreover, these complexes could be easily oxidized by air to give rare examples of aerobically formed, stable Ni(III) bis-trifluoromethyl complexes. Furthermore, we then studied their reactivity in light-induced radical C-H bond trifluoromethylation [3].

In this talk, we will discuss more detailed studies of the aerobic reactivity of organometallic Ni complexes and their application of aerobic oxidation of phosphines, sulfides, alcohols and stilbenes using molecular oxygen as a terminal oxidant.

References:

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[3] Nagib, D. et.al, *Nature*. **2011**, 480, 224−228..

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2 核 Cu 分子触媒の CO_2 電解還元による C_3H_7OH 生成

(豊田中研)○坂本 直柔・関澤 佳太・白井 聡一・野中 敬正・荒井 健男・佐藤 俊介・森川 健志
C_3 product formation by electrochemical CO_2 reduction for dinuclear Cu molecular catalyst. (*Toyota Central R&D Labs., Inc.*,) ○Naonari Sakamoto, Keita Sekizawa, Soichi Shirai, Takamasa Nonaka, Takeo Arai, Shunsuke Sato, and Takeshi Morikawa,

The propanol (C_3H_7OH) with high energy density and high market price as a CO_2 reduction product is one of the desired compounds when practicality is considered. To produce propanol, which requires three molecules of CO_2 and 18 electrons, a new molecular design strategy must be considered, different from the conventional molecular catalysts for two-electron reduction products (CO, HCOOH) formation. Herein, we demonstrated that a new Cu molecular catalyst can exhibit both CO_2 adsorption/retention and intermediate retention properties, enabling the production of C_3H_7OH beyond C_2 products. Detailed *operando* analyses also revealed high robustness during the reaction, which has been a problem with conventional Cu molecular catalysts. New molecular design guidelines are provided as one of the basic structures of molecular catalysts for the synthesis of CO_2 reduction products that require C-C coupling.

Keywords: CO_2 reduction, Molecular catalyst, C_3 products, CO_2 adsorption, operando analysis

CO_2 還元生成物として高エネルギー密度、高い市場価格のプロパノールは実用性を考慮する際に望まれる化合物の一つである。3 分子の CO_2 と 18 電子を必要とするプロパノール生成のためには、従来の 2 電子還元物(CO, HCOOH)生成分子触媒とは異なる、新たな戦略による分子設計が求められる。

本発表では、CO_2 の吸着・保持能力と反応中間体の保持能力を兼ね備えた新規 Cu2 核分子触媒による水溶液中 CO_2 電解還元反応におけるプロパノール生成実証を示す。*Operando* X 線吸収分光法から、従来の Cu 分子触媒の問題点であった反応中の高い堅牢性も兼ね備えていることが明らかとなった。また、電極上の分子触媒の分析は局在表面プラズモン共鳴を利用した *operando* 分光分析を用い、DFT 計算と組み合わせることで主要な反応中間体の検出・同定、プロパノール生成反応機構解明に向けた検討を行った。C-C カップリングを必要とする CO_2 還元生成物合成のための分子触媒の基本構造の 1 つとして新たな指針を与えるものである。

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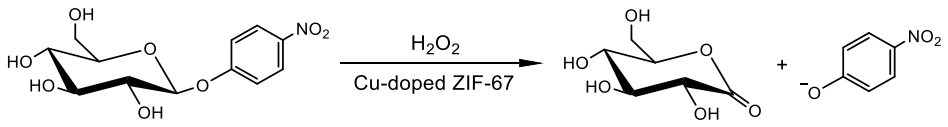
Synthesis and Redox Reaction of Copper- and Cobalt-Containing Zeolitic Imidazolate Frameworks

(*Graduate School of Science and Engineering, Doshisha University*) ○Hiroki Nakahara, Masahito Kodera, Yutaka Hitomi

Keywords: Cobalt, Copper, Metal-organic framework; Redox

There are many enzymes containing copper ions in the active center, including lytic polysaccharide monooxygenase (LPMO), dopamine β-monooxygenase, peptidylglycine α-hydroxylating monooxygenase, which reductively activate oxygen and oxidize C–H bonds, laccase, which couples phenols with oxidation to reduce oxygen to water by four electrons, and superoxide dismutase, which disproportionates superoxide anion radicals. The copper ions present in these enzymes are mainly coordinated with imidazole in the histidine side chain, and there is also a vacant coordination position in which oxygen or superoxide anion radicals are coordinated. In addition, these copper ions have a redox cycle that goes back and forth between monovalent and divalent copper in the enzyme catalytic cycle. For these reasons, a number of copper complexes with vacant coordination positions have been synthesized to reproduce the function of these copper-containing enzymes.

Previously we reported that Cu-doped ZIF-8, which is one of zeolitic imidazolate frameworks and composed of 2-methylimidazole and zinc ion, exhibits excellent superoxide dismutase-like activity. In this study, we focused on ZIF-67, which is a cobalt analog of ZIF-8 and is more stable than ZIF-8 [1]. Cu-doped ZIF-67 was prepared by mixing a methanol solution containing copper(II) acetate and cobalt(II) nitrate and a methanol solution of 2-methylimidazole, followed by standing at 50°C for 6 ~24 hours. In this study, we evaluated LPMO-like activity of Cu-doped ZIF-67. LPMOs are mononuclear copper-containing enzymes that catalyze oxidative depolymerization of crystalline polysaccharides, such as cellulose and chitin, in a reaction that depends on an electron donor and dioxygen or hydrogen peroxide on the mononuclear copper site located at the surface of the enzymes [2]. The LPMO-like reactivity of Cu-doped ZIF-67 was evaluated using the oxidation reaction of *p*-nitrophenyl-β-D-glucopyranoside [3], which is a model compound of polysaccharides, with hydrogen peroxide as an oxidant in aqueous media.



References
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2) G. R. Hemsworth *et al. Trends Biotechnol.*, **2015**, *33*, 747-761.
3) A. L. Concia *et al. Inorg. Chem.* **2017**, *56*, 1023-1026.

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疎水ポケットを持つ二核銅錯体の合成、構造、メタン酸化触媒活性

（同志社大院理工[1], CREST[2]）○藤川　恭祐[1]・人見　穣[1]・小寺　政人[1,2]

Synthesis, structure, and methane oxidation by dicopper complex with hydrophobic pocket([1]*Graduate School of Science and Engineering, Doshisha University,* [2]*CREST*) ○ Kyosuke Fujikawa[1], Yutaka Hitomi[1], Masahito Kodera[1,2]

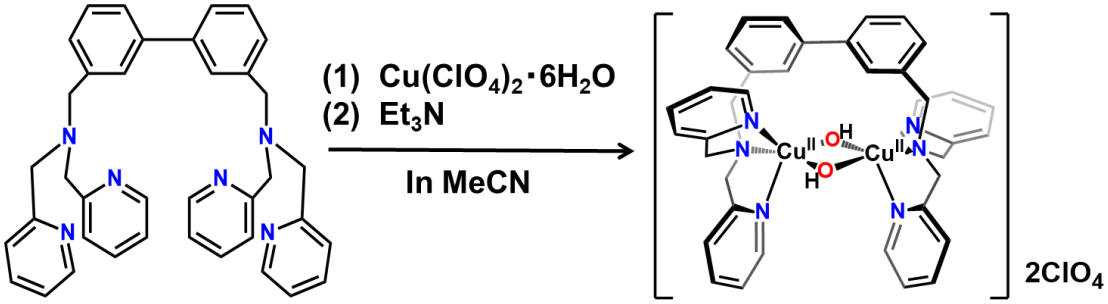
Selective conversion of methane to methanol is a difficult chemical process due to the strong C-H bond and easy overoxidation. This is catalyzed by sMMO and pMMO, Fe and Cu methane monooxygenases, under ambient conditions. $Cu_2(\mu\text{-}O\bullet)$ species were proposed by DFT studies as the active species of methane oxidation by pMMO and Cu ion exchange zeolite.[1,2] Thus, we have focused on multicopper complexes as the methane oxidation catalysts.

In previous work, we found that a copper complex of Medpa tridentate ligand, $[Cu(Medpa)]^{2+}$ (**1**) gives a large TOF 120 min^{-1} in the cyclohexane oxidation with H_2O_2 and proposed that **1** reacts with H_2O_2 to form $Cu^{II}_2(\mu\text{-}O\bullet)(\mu\text{-}OH)$ as the active species. In this study, we synthesized a new dinucleating ligand L, having two dpa units connected by a biphenyl tether. It forms a dicopper complex $[Cu_2L(\mu\text{-}OH)_2]^{2+}$ (**2**). The crystal structure revealed that a hydrophobic pocket is located between the dicopper center and the biphenyl group. **2** efficiently catalyzed the methane oxidation with H_2O_2. Here, we report the synthesis, crystal structure, and methane oxidation.

Keywords; methane oxidation; dicopper complex; dinucleating ligand; H_2O_2-activation; hydrohibic pocket

メタンのメタノールへの選択的酸化は困難な化学プロセスである．一方，鉄及び銅酵素である sMMO や pMMO はこの反応を常温, 常圧で触媒する. DFT 計算から $Cu_2(\mu\text{-}O\bullet)$が pMMO や Cu イオン交換ゼオライトによるメタン酸化の活性種として提案されている[1, 2]．そこで，我々はマルチ銅錯体に注目して研究を行なってきた．

これまでに我々は，三座配位子 Medpa の単核銅(II)錯体$[Cu(Medpa)]^{2+}$(**1**) が H_2O_2 によるシクロヘキサン酸化を TOF 120 min^{-1} という高速で触媒することを見出し，その酸化活性種として $Cu(II)_2(\mu\text{-}O\bullet)$を提案した．本研究では，dpa をビフェニルテザーでつないだ新たな二核化配位子 L を合成した。これは、二核銅錯体$[Cu_2L(\mu\text{-}OH)_2]^{2+}$(**2**)を生成した．**2** はメタン酸化(TON:50)，シクロヘキサン酸化(TON: 1200)において高い反応性を示した．今回は，**2** の合成、構造、メタン酸化活性などについて報告する．



[1] K. Yoshizawa, et. al., *Inorg. Chem*. **2013**, *52*, 7907−7917
[2] Edward I. Solomon, et al. *J. Am. Chem. Soc.* **2021**, 143, 19, 7531–7540

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ペプチドデンドロン修飾金 25 核ナノクラスターの二重触媒作用によるアミンとアルキンの脱水素型クロスカップリング

（京大化研・京大院工）○井芹 建太・上田 恭輔・磯﨑 勝弘・中村 正治

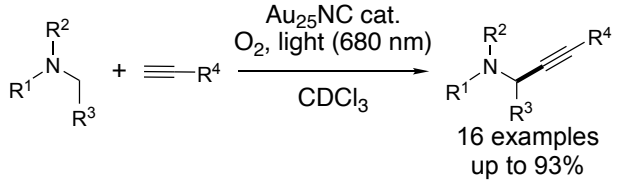
Dual Catalysis of Au_{25} Nanocluster Functionalized by Peptide Dendron Thiolate toward Cross-Dehydrogenative Coupling between Amines and Alkynes. (*Institute for Chemical Research and Graduate School of Engineering, Kyoto University*) ○Kenta ISERI, Kyosuke UEDA, Katsuhiro ISOZAKI, Masaharu NAKAMURA

Peptide dendron thiolate-functionalized gold nanoclusters, $[Au_{25}(SR)_{18}]^-$, exert dual catalysis upon photooxidative C–H alkynylation of amines to give propargyl amines. In the presence of the catalytic gold nanoclusters, tertiary amines and terminal alkynes were cross-coupled dehydrogenatively in $CDCl_3$ under an oxygen atmosphere and the visible light irradiation (680 nm), to give various propargylamine products. The dual-catalysis can be accounted for by the different roles of the kernel and staple moieties of the gold nanocluster.

Keywords : Gold Nanocluster; Dual Catalyst; Cross Dehydrogenative Coupling; Supramolecular Catalyst; Photocatalyst.

金ナノクラスターは，数十の金原子からなる核とそれを修飾する有機配位子から成り，金錯体や，金ナノ粒子，バルクの金とは異なる電子状態，反応性を持つことから高活性な触媒となる事が期待されている。最も盛んに研究されているチオラート保護金 25 核ナノクラスター（$Au_{25}NC$）は，末端アルキンの活性化を経た A^3 カップリング反応の触媒として作用することが報告されている [1]。我々の研究室では，これまでに多数の水素結合点を有するペプチドデンドロンチオラートにより保護された $Au_{25}NC$ の合成を行い，その光触媒作用によりアミノアルコールの酸化的環化反応が効率よく進行することを見出している [2]。本研究では，$Au_{25}NC$ がアミン類の光酸化と末端アルキンの活性化において二重触媒として働き，アミンとアルキンの脱水素型クロスカップリング反応が効率よく進行することを見出した。

触媒量の $Au_{25}NC$ の存在下，第三級アミンと末端アルキンを酸素雰囲気において重クロロホルム中で混合し，680 nm の可視光照射を行った結果プロパルギルアミン生成物が得られた。アミン，アルキンそれぞれについて基質検討を行い，16 種類のプロパルギルアミン生成物が得られた。$Au_{25}NC$ にアルキニル配位子を導入したクラスターを合成し，同ナノクラスターが光触媒，及び本反応における二重触媒として作用することを確認した。本講演では，ペプチドデンドロンチオラート配位子の超分子反応場としての作用，および反応機構研究に基づいた想定反応機構についても発表する。



(1) (a) Li R.; Das, A.; Wang, S.; Chen, Y.; Jin, R. *Chem. Commun.* **2016,** *52,* 14298–14301. (b) Adachi, Y.; Kawasaki, H.; Nagata, T.; Obora, Y. *Chem. Lett.* **2016,** *45,* 1457–1459.
(2) Isozaki, K.; Nakamura, M. et al, *ACS Catal.* **2021,** *11,* 13180–13187.

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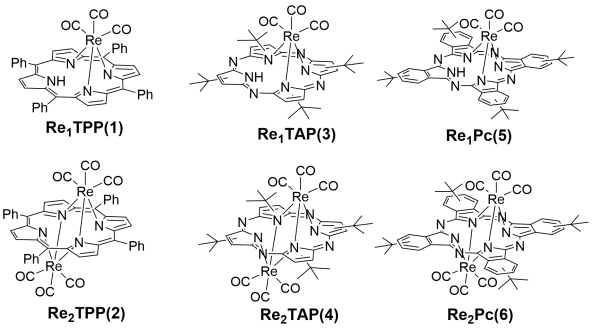
Electrochemical and Photochemical CO_2 Reduction by Rhenium Porphyrin Complexes

([1]*Institute of Industrial Science, the University of Tokyo*, [2]*School of Science, Tokyo Institute of Technology*, [3]*Graduate School of Advanced Science and Engineering, Hiroshima University*)
○ Jingru Liu,[1] Kei Murata,[1] Mengfei Wang,[1] Kazuyuki Ishii,[1] Yusuke Tamaki,[2] Osamu Ishitani[2,3]

Keywords: Electrochemistry; Carbon Dioxide Reduction; Rhenium Complexes;

CO_2 reduction has attracted much attention as it enables to convert CO_2 to useful chemicals and construct sustainable carbon neutral system. Rhenium-bipyridine complexes have been reported to exhibit catalytic activity in the electrochemical and photochemical CO_2 reduction.[1),2)] In those cases, the tricarbonyl rhenium(I) ($[Re(CO)_3]^+$) unit is regarded as important roles in the expression of the catalytic activity. Meanwhile, porphyrinic complexes such as metalloporphyrins and metallophthalocyanines have been also known to work as catalysts for the CO_2 reduction.[3)] The large π-conjugated system of the macrocyclic ligands could contribute to catalyze the reaction at low overpotentials.

In this study, we investigated the catalytic activities toward the electrochemical and photochemical CO_2 reduction of the 6 complexes constituted by a combination of the $[Re(CO)_3]^+$ unit(s) and the porphyrinic ligand (TPP: tetraphenylporphyrin, TAP: tetraazaporphyrin, Pc: phthalocyanine).[4)-6)] In the cyclic voltammograms under CO_2 atmosphere, the catalytic currents attributed to the CO_2 reduction were observed in complexes **1** – **5**. The large current increase occurred at the second reduction potential in all cases. The catalytic current increased in the order of TAP < Pc < TPP, and with the decreasing number of the $[Re(CO)_3]^+$ unit. In addition to these behaviors, the photocatalytic activities of the rhenium complexes will be discussed in the presentation.



1) J. Hawecker, R. Ziessel, J. -M. Lehn, *J. Chem. Soc*., *Chem. Commun*. **1984**, 328–330. 2) Y. Tamaki, K. Koike, T. Morimoto, Y. Yamazaki, O. Ishitani, *Inorg. Chem*. **2013**, *52*, 11902−11909 3) C. Costentin, M. Robert, J. -M. Savéant, *Chem. Soc. Rev*. **2013**, *42*, 2423–2436. 4) M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Jr. Meyer, *J. Am. Chem. Soc.* **1975**, *97*, 3952–3965. 5) K. Murata, Y. Koike, K. Ishii, *Chem. Commun.* **2020**, *56*, 13760–13763. 6) M. f. Wang, K. Murata, K. Ishii, *Chem. Eur. J.*, **2021**, *27*, 8994–9002.

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[K505-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryota Matsuoka, Tomoyuki Haraguchi

Thu. Mar 23, 2023 9:00 AM - 11:30 AM K505 (K505, Lecture Hall Bldg. [5F])

[K505-2am-01] A 3D chiral networked MX compound

○Hao Liang[1], Kazuya Otsubo[1], Yuiga Nakamura[2], Shogo Kawaguchi[2], Hiroshi Kitagawa[1] （1. Kyoto University, 2. Japan Synchrotron Radiation Research Institute (JASRI), SPring-8）

9:00 AM - 9:20 AM

[K505-2am-02] Charge-transfer phase transition in a two-dimensional cyanido-bridged Co-W assembly with isoquinoline ligands

○Kazuki Nakamura[1], Shota Kobayashi[1], Koji Nakabayashi[1], Kenta Imoto[1], Shin-ichi Ohkoshi[1] （1. The Univ. of Tokyo）

9:20 AM - 9:40 AM

[K505-2am-03] Gate-Open-Close Vapochromism of Rhenium(I) Molecular Crystals Supported by Non-Covalent Interactions: In-Situ Observation of the Guest-Induced Structural Transformation Dynamics

○Yuki Matsuda[1], Ryota Nakamura[1], Yoshiki Ozawa[1], Keishiro Tahara[1], Toshikazu Ono[2], Nobuto Yoshinari[3], Takumi Konno[3], Kunihisa Sugimoto[4], Shintaro Kobayashi[5], Shogo Kawaguchi[5], Masaaki Abe[1] （1. Graduate School of Science, University of Hyogo, 2. Graduate School of Engineering, Kyushu University, 3. Graduate School of Science, Osaka University, 4. Department of Chemistry, Faculty of Science and Engineering, Kindai University, 5. SPring-8/JASRI）

9:40 AM - 10:00 AM

[K505-2am-04] Complexation behavior and luminescence enhancement of a pyridyl-containing triarylmethyl radical with silver(I)

○Takuto Mibu[1], Ryota Matsuoka[1], Tetsuro Kusamoto[1,2] （1. IMS, 2. JST-PRESTO）

10:00 AM - 10:20 AM

[K505-2am-05] Sequence Controll and Multi-stage Redox Composed of Single Metal containing Metallosupramolecular Polymeric Films for Electrochromic Study

○DINES CHANDRA SANTRA[1], Masayoshi HIGUCHI[1] （1. National Institute for Materials Science (NIMS)）

10:30 AM - 10:50 AM

[K505-2am-06] Development of visible-light responsive mutinuclear Zn complexes and Zn clusters based on Zn-Zn interaction

○Yoshimasa Wada[1,2], Takahiro Maruchi[2], Reon Ishii[2], Yusuke Sunada[1,2,3] （1. Institute of Industrial Science, The University of Tokyo, 2. Graduate School of Engineering, The University of Tokyo, 3. JST-PRESTO）

10:50 AM - 11:10 AM

[K505-2am-07] The spin-lattice magnetic relaxation of an *S*=1/2 copper(II)-substituted Keggin-type phosphotungstate

○Toshiharu Ishizaki[1], Yoji Inoue[1], Tomoji Ozeki[1] （1. Nihon Univ.）

11:10 AM - 11:30 AM

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A 3D chiral networked MX compound

([1]*Graduate School of Science, Kyoto University,* [2]*Japan Synchrotron Radiation Research Institute (JASRI), SPring-8*) ○ Hao Liang,[1] Kazuya Otsubo,[1] Yuiga Nakamura,[2] Shogo Kawaguchi,[2] Hiroshi Kitagawa[1]

Keywords: Metal–Organic Framework; Mixed-Valence Compounds; Ladder Compounds; Crystal Structure; Electronic States

MX-ladder is a new family of metal–organic ladder compound based on mixed-valence halogen-bridged transition-metal complex (MX-chain), which shows unique electronic states, and physical properties.[1] Although we have synthesized a variety of MX-ladder compounds, the so-called two-legged MX-ladder, four-legged MX-tube, and ghost-legged MX-sheet,[2–5] the development of 3D-extended type MX compound is still challenging. In this work, for the first time, we successfully synthesized a new 3D networked MX-type compound, $[Pt(en)(dpye)I]_2(NO_3)_4$ (en: ethylenediamine, dpye: 1,2-Di(4-pyridyl)ethane).

The target compound was synthesized from following two steps:

(a) $2Pt(en)(NO_3)_2 + 2dpye \rightarrow [Pt(en)(dpye)]_2(NO_3)_4$ (**1**)

(b) $[Pt(en)(dpye)]_2(NO_3)_4 + I_2 \rightarrow [Pt(en)(dpye)I]_2(NO_3)_4$ (**2**)

Figure 1 shows the X-ray crystal structure of **2** at 100 K. **2** crystallizes in tetragonal $P4_12_12$ or $P4_32_12$ space group due to spontaneous resolution. Macrocyclic Pt units are helically aligned with a 4-fold periodicity along the *c*-axis and bridged by I^- with each other to form a 3D networked structure. Focusing on the MX-chain part, the bridging I^- sites are disordered with a half occupancy around the midpoint between adjacent Pt ions, indicating that electronic state within one MX-chain is in the mixed-valence charge-density-wave state (CDW: $\cdots Pt^{2+}\cdots I–Pt^{4+}–I\cdots Pt^{2+}\cdots I–Pt^{4+}–I\cdots$), as also confirmed by optical measurements. Details are presented.

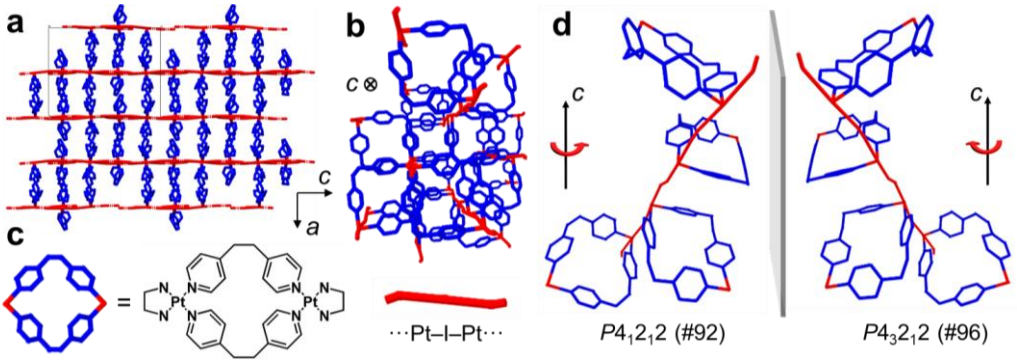


Figure 1. Crystal structure of compound **2** ($P4_12_12$ form). (a) View along *b*-axis. (b) View along *c*-axis. (c) Building block. (d) Two enantiomers. The en unit, H_2O and NO_3^- have been omitted for clarity.

1) Otsubo, K. et al. *CrystEngComm*, **2014**, *16*, 6277. 2) Kobayashi, A. et al. *J. Am. Chem. Soc.*, **2006**, *128*, 12066. 3) Otsubo, K. et al. *Nat. Mater.*, **2011**, *10*, 291. 4) Otake, K. et al. *Nat. Commun.*, **2020**, *11*, 843. 5) Hashiguchi, R. et al. *Angew. Chem., Int. Ed.*, **2017**, *56*, 3838.

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Charge-transfer phase transition in a two-dimensional cyanido-bridged Co-W assembly with isoquinoline ligands

([1]*Graduate School of Science, University of Tokyo*) ○Kazuki Nakamura,[1] Shota Kobayashi,[1] Koji Nakabayashi,[1] Kenta Imoto,[1] Shin-ichi Ohkoshi[1]

Keywords: Charge-transfer induced phase transition, molecular magnets

Molecular-based magnets have attracted attention from various fields such as chemistry, physics, and material science. Combinations between phase transitions and magnetic properties lead to development for magnetic switching materials. Cyanido-bridged assemblies are suitable for such materials because we can select metal ions to show spin crossover and charge transfer which provide phase transitions and change of spin states.[1] We have reported some cyanido-bridged Co-W assemblies showing photo-induced phase transitions as well as thermal phase transitions derived from a charge transfer between Co^{II}-W^{V} and Co^{III}-W^{IV} states.[2,3] Herein, we report a new cyanido-bridged Co-W assembly including isoquinoline as ligands, $[\{Co(isoquinoline)_4\}_2\{W(CN)_8\}_2]\cdot 4H_2O$ (**CoWIsoq**).

The purple single crystal was obtained by reacting a mixed solution of Ethanol/H_2O including $CoCl_2\cdot 6H_2O$ and isoquinoline with an aqueous solution containing $Cs_3[W(CN)_8]\cdot 2H_2O$ at room temperature using slow diffusion method. The crystal structure of **CoWIsoq** at 300 K has a two-dimensional cyanido-bridged Co-W layers and also the π-π interaction between layers because of ligands (Figure 1). The product of the molar magnetic susceptibility (χ_M) and temperature (T) vs. T plot of **CoWIsoq** shows the thermal phase transition derived from the charge transfer between Co^{II}-W^{V} (purple) and Co^{III}-W^{IV} (orange) states (Figure 2). In addition, the photo-induced phase transition was observed in the variable temperature UV-vis spectra and magnetic measurements with a 980 nm diode laser.

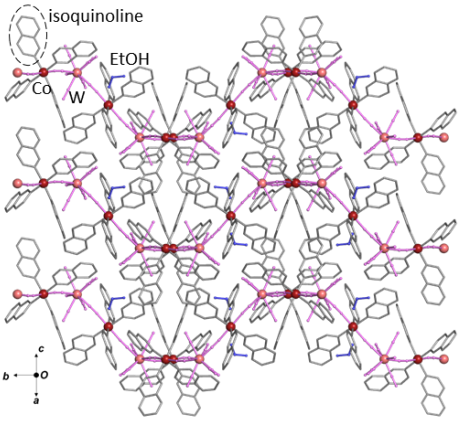


Fig.1 Crystal structure of **CoWIsoq** at 300 K viewed from (101) plane.

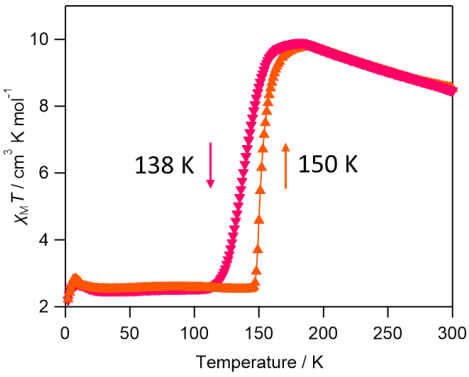


Fig. 2. $\chi_M T$-T plot of **CoWIsoq** under 5000 Oe.

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nature Photonics*, 2014, **8**, 65.
2) S. Ohkoshi, S. Ikeda, T. Hozumi, T. Kashiwagi, K. Hashimoto, *J. Am. Chem. Soc.*, 2006, **128**, 5320.
3) K. Nakamura, K. Nakabayashi, K. Imoto, S. Ohkoshi, *Inorg. Chem. Front.*, 2023. *doi*: *10.1039/D2QI02321K*.

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Gate-Open-Close Vapochromism of Rhenium(I) Molecular Crystals Supported by Non-Covalent Interactions: In-Situ Observation of the Guest-Induced Structural Transformation Dynamics

([1]*Graduate School of Science*, *University of Hyogo*, [2]*Graduate School of Engineering, Kyushu University*, [3]*Graduate School of Science*, *Osaka University*, [4]*Department of Chemistry*, *Faculty of Science and Engineering*, *Kindai University*, [5]*SPring-8/JASRI*) ○ Yuki Matsuda,[1] Ryota Nakamura,[1] Yoshiki Ozawa,[1] Keishiro Tahara,[1] Toshikazu Ono,[2] Nobuto Yoshinari,[3] Takumi Konno,[3] Kunihisa Sugimoto,[4] Shintaro Kobayashi,[5] Shogo Kawaguchi,[5] Masaaki Abe[1]

Keywords: Molecular Crystals; Multiple Non-Covalent Interactions; Vapor-Induced Emission Enhancement; Gate-Open-Close Behavior; In-Situ Powder X-ray Diffraction Analysis

Recently, vapochromic materials, which adsorb guest molecules to exhibit reversible changes of the photoluminescence property, have been the subject of intense research. It is essential for this property to design and control the molecular arrangement in the crystalline state. In this work, a novel luminescent molecular rhenium(I) complex *fac*-ReBr(CO)$_3$(ppt) (**1**), where ppt = 2-pyridyl-4-phenylthiazole, has been synthesized and characterized. Complex **1** has a non-porous guest-free crystal (**1**) (Type O) and several solvated crystals, and they are molecular crystals supported by multiple non-covalent interactions. The solvated crystals have been formulated **1**·***n*Sol**, where n = 0.5 (Type A) or 1 (Type B). We have also investigated the vapochromic behavior of guest-free **1**. The crystal has given an emission peak at 574 nm upon irradiation at 365 nm. The emission wavelength has displayed a blue shift by ca. 20 nm under volatile organic compound (VOC) vapors. We have also observed vapor-induced emission enhancement (VIEE). Interestingly, in spite of the non-porous structure, guest-free crystal **1** has showed gate-open-close behavior, and this result has been suggested by adsorption isotherm measurement. The guest-adsorption process has been monitored by synchrotron *in-situ* powder X-ray diffraction (*in-situ* PXRD) analysis (SPring-8, BL02B2). During the structural transformation from Type O to Type A or B, no intermediates have been observed, indicating crystal-to-crystal transformation. In addition, guest-substitution process has also occurred between several solvated crystals (Type A and Type B). However, this process was irreversible, suggesting that the strength of the host-guest interactions varied depending on the kinds of solvents. The guest-induced and guest-exchange structural transformation dynamics is shown in Fig. 1.

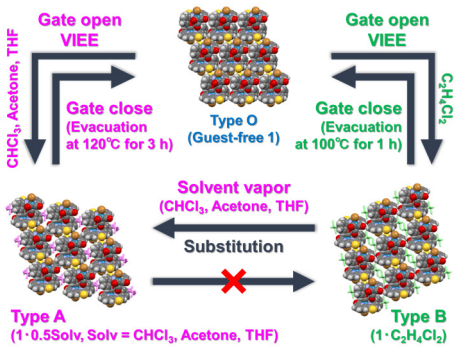


Fig. 1. Crystal-to-crystal transformation dynamics

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ピリジル含有トリアリールメチルラジカルの銀(I)イオンとの錯形成挙動と発光増強

(分子研[1]・JST さきがけ[2]) ○壬生 託人[1]・松岡 亮太[1]・草本 哲郎[1,2]

Complexation behavior and luminescence enhancement of a pyridyl-containing triarylmethyl radical with silver(I)

([1]*IMS*, [2]*JST-PRESTO*) ○Takuto Mibu,[1] Ryota Matsuoka,[1] Tetsuro Kusamoto[1,2]

Luminescent radicals, which exhibit fluorescence from the lowest doublet excited state, have been attracting much attention in recent years. Our group have reported various luminescent triarylmethyl radicals containing pyridyl groups such as PyBTM (Fig. a) and the enhancement of these luminescence properties by coordination to metal ions such as gold(I), zinc(II), etc.[1-2]. In this study, we investigated the complexation behavior of PyBTM with silver(I). Two PyBTM molecules coordinated to a silver(I) ion in the crystalline state (Fig. b), whereas PyBTM forms a 1:1 complex with silver(I) in solution, as suggested by the titration experiment (Fig. c). In addition, as the added silver(I) ion increased, the photoluminescence intensity increased and the maximum emission wavelength was redshifted (Fig. d). These results indicate the luminescence enhancement of the radical by complexation with silver(I).

Keywords : radical; luminescence; metal complexes; silver(I)

発光性ラジカルはその励起二重項状態からの発光に基づき、高効率 EL などへの応用が期待される有用な化合物群である。当グループでは PyBTM (Fig. a) などのピリジル基を含む発光性トリアリールメチルラジカル群を合成し、これらの金(I)や亜鉛(II)イオンなどへの錯形成に伴う発光特性の向上を明らかにしてきた[1-2]。本研究では PyBTM と銀(I)イオンの錯形成挙動と光学特性の相関について調査した。

結晶中では銀(I)イオンと PyBTM が 1:2 のモル比で錯形成していることが明らかになったが(Fig. b)、溶液中での滴定実験の結果、吸収スペクトルに等吸収点が観測され、銀(I)イオンと PyBTM が 1:1 のモル比で錯形成していることが示唆された(Fig. c)。また銀(I)イオンの当量増加に従い、発光の強度増加及び長波長シフトが観測され、ラジカル配位子の錯形成に伴う発光増強が明らかとなった(Fig. d)。

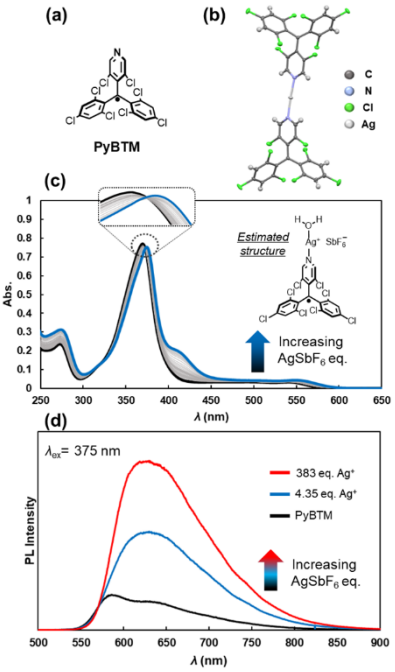


Fig. (a) Chemical structure of PyBTM. (b) Crystal structure of $[Ag(PyBTM)_2]^+$ at 123 K. The SbF_6^- counter anion is omitted for clarity. (c) Absorption spectral change of PyBTM (30 μM) upon the addition of $AgSbF_6$ (0–4.8 eq.) in CH_2Cl_2 at r.t. (d) Emission spectral change of PyBTM (30 μM) upon the addition of $AgSbF_6$ in CH_2Cl_2 at r.t.

1) Y. Hattori, T. Kusamoto and H. Nishihara, *Angew. Chem. Int. Ed.* **2015**, *54*, 3731–3734.
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Sequence Control and Multi-stage Redox Composed of Single Metal Containing Metallosupramolecular Polymeric Films for Electrochromic Study

(National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. Tel & Fax: 029-860-4721, E-mail: HIGUCHI.Masayoshi@nims.go.jp) ○ Dines Chandra Santra and Masayoshi Higuchi.

Keywords: *Metallo-supramolecular polymer, Single Metal, Sequence controlled, Multi-stage redox, Electrochromism*

Electrochromic (EC) materials and EC devices (ECDs) have always been regarded as a considerable developing research field. The well-regulated optical properties of EC materials have unique application in the field of solar control windows, e-displays, mirrors and camouflage materials. Compared with conventional EC materials such as WO_3 and viologens, the metallo-supramolecular polymers (MSPs) acquire various benefits, including simplistic film preparation, fast color change, high optical contrast and fine-tuning of the working potential by structure modification.[1,2] MSPs, a new class of EC materials, have gained popularity and demonstrated advantages among them. Because of their high complexing action and robust metal-ligand charge transfer (MLCT) activity, terpyridine ligands are typically used in the MSP systems.

In this work, we propose a facile strategy to realize multistage electrochromism by designing and synthesizing a unsymmetric ditopic ligand. Using the ligands, we have prepared single metal containing MSP. The final MSPs have exceptional solubility and stability. Three reversible redox couples and color transformations are revealed by the MSP film upon different potential (Fig. 1). The EC performances of single metal MSP revealed continuous modulation over the visible region, high optical contrast, fast response time, high coloration contrast, outstanding cyclic reversibility, and optical memory time at once.

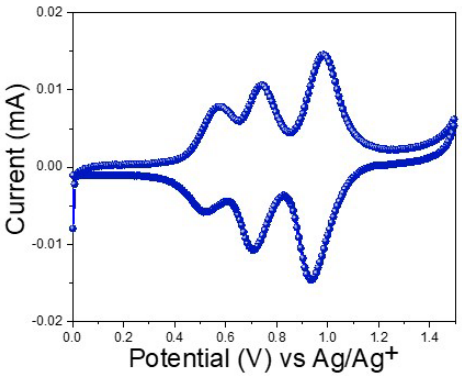


Fig.-1. A cyclic voltamogram of the MSP in 0.1 M $LiClO_4$/acetonitrile.

References.

1) M. Higuchi, *J. Mater. Chem. C*, **2013**, 1, 3408. 2) R. Reynolds, *Chem. Rev*., **2010**, 110,1, 268

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亜鉛間相互作用に基づく、亜鉛複核錯体・クラスターの可視光機能開拓

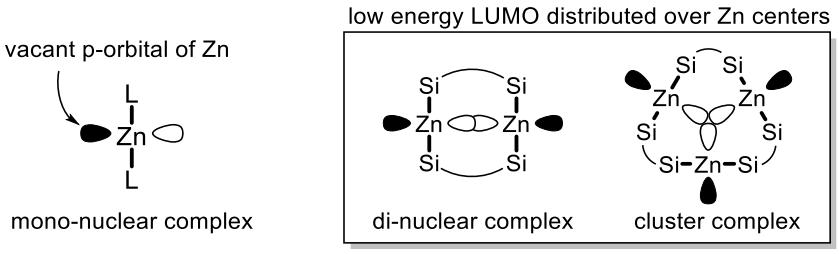
（東大生研[1]・東大院工[2]・JST さきがけ[3]）○和田 啓幹[1,2]・丸地 貴大[2]・石井 玲音[2]・砂田 祐輔[1,2,3]

Development of visible-light responsive mutinuclear Zn complexes and Zn clusters based on Zn-Zn interaction ([1]*Institute of Industrial Science, The University of Tokyo*, [2]*Graduate School of Engineering, The University of Tokyo*, [3]*JST-PRESTO*) ○Yoshimasa Wada,[1,2] Takahiro Maruchi,[2] Reon Ishii,[2] Yusuke Sunada[1,2,3]

It has been widely known that Zn(II)-based complexes are colorless and therefore “silent” toward visible-light[1]. In this research, we developed a visible-light “active” Zn complex[2] and a cluster molecule based on a theoretical molecular design introducing interatomic orbital interaction between Zn centers. Using sterically bulky oligosilyl-ligands resulted in electron deficient and coordinatively unsaturated Zn(II) centers, which in turn induced interaction between empty p-orbital of Zn centers and formed energetically stabilized LUMO over Zn centers. Owing to the decreased LUMO energy level, visible-light absorption was realized. We believe our findings open up untapped possibility for inexpensive and less-toxic Zn-based photo functional materials such as photocatalysts and chromic sensors, as well as emitting materials for light-emitting diodes.

Keywords : multinuclear Zn complex; Zn cluster molecule; intermetallic interaction; visible-light absorption; theoretical calculation

亜鉛は錯体中において 2 価の d^{10} 電子配置をとることに由来し、可視光応答を示さず、無色ないし白色の化合物であることが教科書事実として知られてきた[1]。本研究では、亜鉛原子間に働く軌道間相互作用に注目し、これを適切に利用する分子設計に基づき、実際に可視光吸収を示す有色の亜鉛複核錯体[2]・クラスター分子を開発したのでこれを報告する。立体的にかさ高い二座のケイ素配位子(Si–Si)を用い、電子不足かつ高度に配位不飽和な 2 配位の亜鉛(II)中心を形成させることにより、複数の亜鉛原子の空 p 軌道からなる低エネルギーの LUMO が生じた。その結果、HOMO-LUMO 間のエネルギー差が大幅に低下し、可視光領域に吸収を示した。本研究結果により、亜鉛を中心金属として用いた様々な可視光機能材料への展開が大いに期待される。



1) C.E. Housecroft and A.G. Sharpe, **2018**, Inorganic chemistry, Fifth edition. Edition (Pearson).
2) Y. Wada, T. Maruchi, R. Ishii, and Y. Sunada, *available at SSRN*, DOI : 10.2139/ssrn.4197384.

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The spin-lattice magnetic relaxation of an *S*=1/2 copper(II)-substituted Keggin-type phosphotungstate

([1]*College of Humanities and Sciences, Nihon University*) ○Toshiharu Ishizaki, Yoji Inoue, Tomoji Ozeki

Keywords: Magnetic property, Polyoxometalate, Copper(II), *S*=1/2

Magnetic relaxation behaviors of 3d transition metal based *S*=1/2 systems have been attracted much attention owing to the intrinsic quantum properties and the long magnetic relaxation time.[1] In this presentation, the spin-lattice magnetic relaxation behavior of an *S*=1/2 copper(II)-substituted Keggin-type phosphotungstate $[(n\text{-}C_4H_9)N]_4H[PW_{11}O_{39}Cu]$ (**1**) is reported.

AC magnetic susceptibility measurements revealed that the polyoxometalate-based spin-1/2 system exhibits a slow magnetic relaxation in applied static magnetic field (H_{dc}) at low temperatures (Figure 1). The longest relaxation time of 260 ms was obtained at 1.8 K and in an applied H_{dc} of 3000 Oe for a 5% magnetically diluted powder of **1**, $[(n\text{-}C_4H_9)N]_4H[PW_{11}O_{39}Cu_{0.05}Zn_{0.95}]$ (**dil.1**). The value is larger than that for an *S*=1/2 monocopper(II)-substituted Keggin-type silicotungstate of 92 ms obtained at 1.8 K and in an H_{dc}=5000 Oe, and comparable to those of other *S*=1/2 systems with organic ligands that exhibits the spin coherence.[1,2] The relaxation time analysis indicates that the Raman spin-lattice magnetic relaxation process dominates at all measured temperatures in an H_{dc}=5000 Oe. The extracted Raman exponent *n* of 2.68 is smaller than *S*=1/2 systems with organic ligands, which implies the decrease in relaxation time at higher temperatures is likely to be moderate.[3]

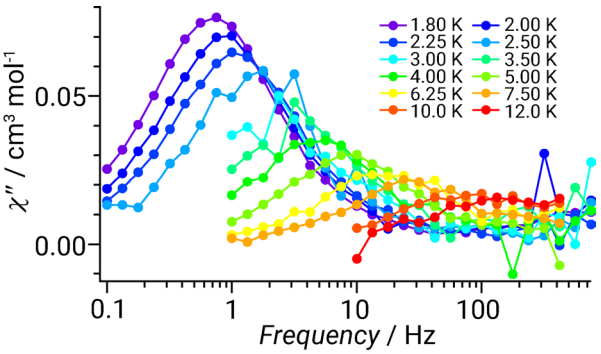


Figure 1 A plot of χ'' vs. ac frequency plot of **dil.1** in an applied static field of 5000 Oe at indicated temperatures.

A part of this work was conducted in Institute for Molecular Science, supported by "Adavanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Proposal Number JPMXP1222MS1035. This work is also supported by JSPS Core-to-Core program.

1) J. van Slageren et al., *Nat. Commun.*, **2014**, *5*, 5304. 2) D. E. Freedman, *ACS Cent. Sci.*, **2015**, *1*, 488. 3) R. Sessoli *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 11234.

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[K505-2pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Norio Nakata, Shintaro Ishida

Thu. Mar 23, 2023 1:40 PM - 3:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-2pm-01] DNA Double Strand Breaks via Reductive O_2-Activation by Dicopper Complex: large acceleration by introducing an intercalator as DNA Binding Site

○Machi Hata[1], Hiroyuki Matsumoto[1], Yutaka Hitomi[1], Masahito Kodera[1] （1. Doshisha University）

1:40 PM - 2:00 PM

[K505-2pm-02] Room-temperature Conversion of CO_2 into Metal-Organic Frameworks

○Kentaro Kadota[1], Satoshi Horike[1,2] （1. Institute for Advanced Study, Kyoto University, 2. Graduate School of Engineering, Kyoto University）

2:00 PM - 2:20 PM

[K505-2pm-03] Synthesis of Lewis-base-coordinated Germabenzenylgermylenes Acting as a Ge Atom Source

○Ryohei Nishino[1], Yoshiyuki Mizuhata[1], Norihiro Tokitoh[1] （1. Institute for Chemical Research, Kyoto Univ.）

2:20 PM - 2:40 PM

[K505-2pm-04] Synthesis of Novel Silylboron Compounds Using Trialkylsilyl Anions

○Rikuro Takahashi[1], Hajime Ito[2,3] （1. Division ofApplied Chemistry, Graduate School of Engineering, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University, 3. WPI-ICReDD, Hokkaido University）

2:40 PM - 3:00 PM

[K505-2pm-05] Synthesis and Characterization of Alumanyl Complexes of Vanadium

○Pavel Zatsepin[1], Makoto Yamashita[1] （1. Nagoya University）

3:00 PM - 3:20 PM

[K505-2pm-06] Catalytic Hydrogenation of Carbonyl Compounds Using Crude H_2 as H_2 Source

○Mahiro Sakuraba[1], Sensuke Ogoshi[1], Yoichi Hoshimoto[1] （1. Osaka university）

3:20 PM - 3:40 PM

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DNA Double Strand Breaks via Reductive O_2-Activation by Dicopper Complex: large acceleration by introducing an intercalator as DNA Binding Site

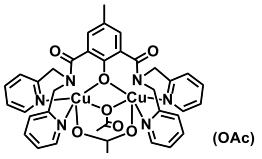
(*Graduate School of Science and Engineering, Doshisha University*) ○Machi Hata, Hiroyuki Matsumoto, Yutaka Hitomi, Masahito Kodera

Keywords: Dicopper Complex with intercalator; DNA double strand breaks; Reductive O_2-activation; Cytotoxicity; DNA binding ability

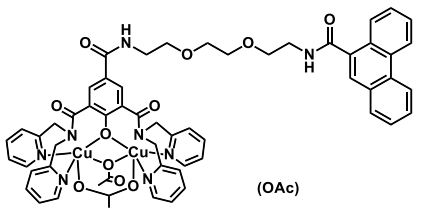
DNA double-strand breaks (dsb) are important reactions for gene editing and therapeutic applications. Bleomycin is an anticancer drug, and its iron complex, Fe-BLM is the strongest DNA cutter and catalyzes single- and double-strand breaks, ratio of which is reported to be in the range 1:3 to 1:20.[1] Burst of dsb by Fe-BLM via reductive O_2-activation with dithiothreitol (DTT) was reported, but the mechanism has not been clarified yet.[2] Metal complexes able to reproduce burst of DNA dsb may be useful to gain some insight into the mechanism. Various metal complexes have been developed to mimic oxidative DNA cleavage by Fe-BLM. Roelfes reported that a N4Py iron(II) complex $[Fe(MeCN)(N4Py)](ClO_4)_2$ (**3**) shows high activity in the oxidative DNA cleavage as a model compound of Fe-BLM.

Recently, we reported that a dicopper complex of *p*-cresol-2,6-bis(amide-tether-dpa) ligand (HL1) $[Cu_2(\mu\text{-}OAc)_2(L1)](OAc)$ (**1**) oxidatively cleaves DNA double-strand in the presence of AscNa.[3] **1** (30 μM) converted 26% of supercoiled plasmid DNA to linear form in 1 min via reductive O_2-activation with AscNa (150 μM), being much more active than **3**. The kinetic and spectroscopic studies showed that **1** is rapidly reduced to Cu(I)Cu(II) and Cu(I)Cu(I) species, both of which are involved in the rate-limiting three electron reduction of O_2 to HO• responsible for DNA cleavage. Moreover, measurement of the DNA binding revealed that rigid DNA binding within the 16 base pair intervals is essential for DNA dsb.

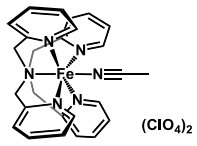
In this study, we synthesized a new dinucleating ligand (HL2) having a DNA binding site to improve DNA binding. HL2 forms a dicopper complex $[Cu_2(\mu\text{-}OAc)_2(L2)](OAc)$ (**2**), which largely accelerated DNA dsb, much faster than **1**.



1



2



3

[1] Q. Li, T. A. van den Berg, B. L. Feringa, G. Roelfes, *Dalton Trans.* **2010**, *39*, 8012.
[2] R. J. Steighner, L. F. Povirk, *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 8350.
[3] M. Hata, Y. Kadoya, Y. Hitomi, M.Kodera, *Bull. Chem. Soc. Jpn.*, **2022**, *95*, 1546.

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Room-temperature Conversion of CO_2 into Metal-Organic Frameworks

([1]*Institute for Advanced Study, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*) ○Kentaro Kadota[1] and Satoshi Horike[1,2]

Keywords: Metal-Organic Frameworks, CO_2 utilization, Porosity

Facile conversion of CO_2 into valuable chemicals and materials is a significant challenge to a carbon-neutral society. CO_2 is an attractive renewable carbon resource with the high natural abundance.[1] Due to the inherent inertness of CO_2, conversion of CO_2 into functional materials at ambient conditions is a significant challenge regardless of the materials.

Metal−organic frameworks (MOFs) are porous materials that consist of metal ions and bridging linkers. CO_2 storage/separation and catalysts using MOFs have been extensively studied last few decades. On the other hand, MOF synthesis from CO_2 remains unexplored. Carboxylates are a representative MOF linker, e.g. benzene-1,4-dicarboxylate. Meanwhile, the di- or tri-carboxylates, which are suitable as MOF linkers, present difficulties in the synthesis from CO_2 because the high-energy reaction conditions and multistep reactions are required.

We focused on carbamate as a CO_2-derived MOF linker instead of conventional carboxylates. Amines (*R*-NH_2) readily react with CO_2 to produce carbamates (*R*-$NCOO^-$). In this work, piperazine (H_2PZ) was employed as a source of CO_2-derived carbamate linker, piperazine 1,4-dicarbamate ($[PZ(CO_2)_2]^{2-}$: PDC). We demonstrated one-pot, room-temperature synthesis of MOFs, $[Zn_4O(PDC)_3]$ (**1**), from CO_2 (**Figure 1**). We comprehensively studied the crystal structure of **1** by synchrotron X-ray analysis and the stabilization of PDC in the MOF lattice by temperature-programmed desorption and DFT calculations.[2]

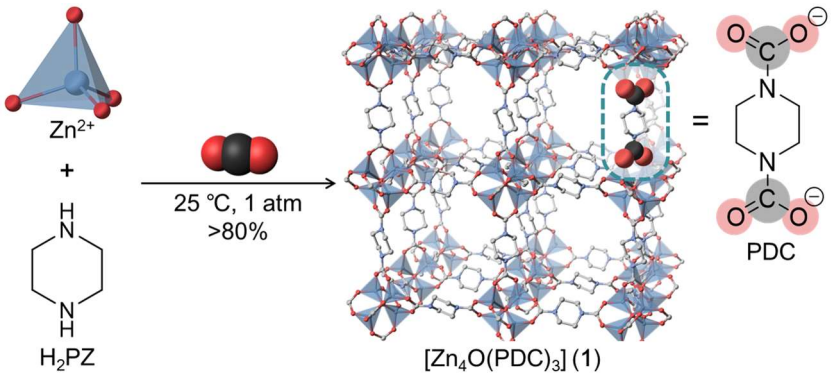


Figure 1. Schematic illustration of formation of **1** via *in situ* conversion of CO_2 into PDC.

1) Q. Liu *et al*., *Nat. Commun.*, 2015, **6**, 5933. 2) K. Kadota *et al*., *J. Am. Chem. Soc.*, 2021, **143**, 16750.

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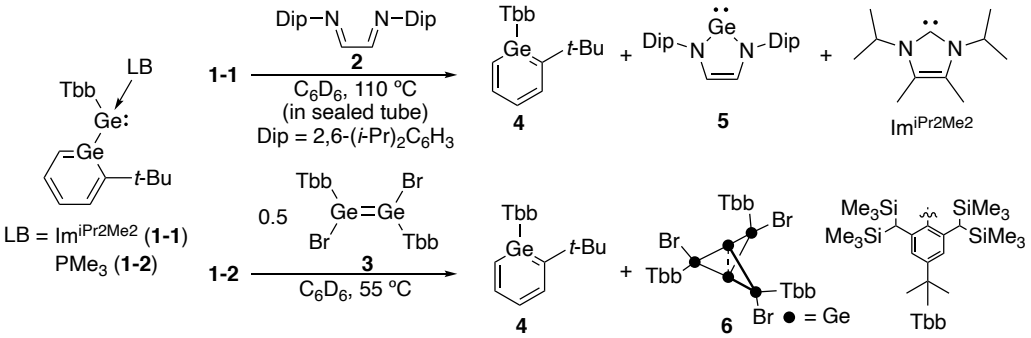
Ge 原子供与体として働くルイス塩基配位ゲルマベンゼニルゲルミレンの合成

（京大化研）◯西野 龍平・水畑 吉行・時任 宣博
Synthesis of Lewis-base-coordinated Germabenzenylgermylenes Acting as a Ge Atom Source
(Institute for Chemical Research, Kyoto University) ◯Ryohei Nishino, Yoshiyuki Mizuhata, Norihiro Tokitoh

We have recently reported a novel Ge atom transfer reaction using a germabenzenyl anion, a Ge-analogue of phenyl anion. We report here the synthesis of Lewis-base complexes of germabenzenylgermylene, which is the key intermediate of the Ge atom transfer reaction. The Ge atom transfer reactions using synthesized complexes will also be discussed.
Keywords : Germanium; Phenyl Anion; Single Atom Transfer Reaction; Germabenzene; Germylene

近年、Si, Ge, Pb 低配位化学種を用いた単原子輸送反応が報告されるようになり、単原子等価体としての活用が期待されている [1]。一方最近我々は、フェニルアニオンのゲルマニウム類縁体であるゲルマベンゼニルアニオンを用いた Ge 原子の輸送反応を報告している。種々の検証により、この反応においてゲルマベンゼニルゲルミレンが重要な中間体であることが分かった。本発表ではゲルマベンゼニルゲルミレンのルイス塩基錯体 **1-1**, **1-2** としての合成およびその反応性について報告する。

1-1 の C_6D_6 溶液を耐圧 NMR 管中 110 ºC で 24 時間加熱すると、対応するゲルマベンゼン **4** が生成した。また、この反応をジイミン **2** 存在下で行うと、**4** に加えて *N*-ヘテロ環状ゲルミレン **5** が生成し、**2** へ Ge 原子が輸送されたことが強く示唆された。一方、PMe_3 錯体 **1-2** は C_6D_6 中 60 ºC で 5 時間加熱すると完全に消失した。この系において **2** を添加しても **5** は生成しなかったものの、ジブロモジゲルメン **3** 存在下で熱分解を行うと **3** に Ge 原子が輸送され、ペンタゲルマ[1.1.1]プロペラン **6** が得られた。



References: 1 K. M. Krebs, D. Hanselmann, H. Schubert, K. Wurst, M. Scheele, L. Wesemann, *J. Am. Chem. Soc.* **2019**, *141*, 3424; Y. Wang, C. A. Tope, Y. Xie, P. Wei, J. L. Urbauer, H. F. Schaefer, G. H. Robinson, *Angew. Chem. Int. Ed.* **2020**, *59*, 8864; C. Wilhelm, D. Raiser, H. Schubert, C. P. Sindlinger, L. Wesemann, *Inorg. Chem.* **2021**, *60*, 9268; T. Koike, T. Nukazawa, T. Iwamoto, *J. Am. Chem. Soc.* **2021**, *143*, 14332; M. Chen, Z. Zhang, Z. Qiao, L. Zhao, Z. Mo, *Angew. Chem. Int. Ed.* **2022**, e202215146 (doi: 10.1002/anie.202215146).

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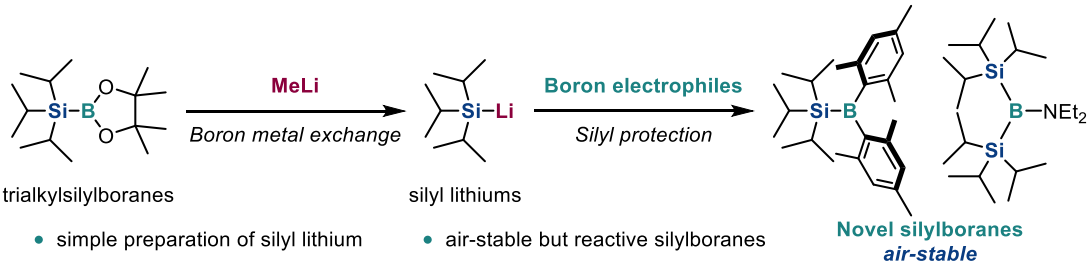
Synthesis of Novel Silylboron Compounds Using Trialkylsilylanions

([1]*Graduate School of Chemical Science and Engineering, Hokkaido University*, [2]*Graduate School of Engineering, Hokkaido University,* [3]*WPI-ICReDD, Hokkaido University*)
○Rikuro Takahashi,[1] Hajime Ito[2,3]

Keywords: Silylborane; Organosilicon Compounds; Organoboron Compounds; Silyl Anions; DFT Calculations

Silylboron compounds are a class of interelement compounds that contain an Si–B bond. The Si–B bond is generally inactive, but various reactivity was known using transition-metal catalysis which can activate the Si–B bond by the oxidative addition and transmetalation. In addition, the stoichiometric amount of base can coordinate to the boron. However, most silylboron compounds are unstable under air condition and decomposed by hydrolysis. Some stable silylboron compounds have been reported until today, but they require electronic stabilization or steric protection around boron atoms.[1]

We previously developed a general synthesis of sterically hindered trialkylsilylboranes by catalytic Si–H borylation reactions and realized that these reagents could be used as silyl anion equivalents via the boron metal exchange reactions.[2] We consider that these bulky silyl moieties can be utilized as protecting groups of the reactive boron center. Here, we found that the introduction of TIPS groups into silylborane compounds improves their stability, providing a new strategy for the design of stable silylborane compounds. The products, TIPS–$BMes_2$ and $(TIPS)_2B–NEt_2$ are air stable and isolable by column chromatography. In addition, we studied the reactivity of TIPS–$BMes_2$ with carbon monoxide and obtained a spiro compound, accompanied by the cleavage of the carbon-oxygen triple bond and the dearomatization of the mesityl group. DFT studies were conducted to understand the reaction mechanism.



1) a) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.***2002**, *124*, 8816. b) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc*. **2007**, *129*, 758. c) Zhou, Z.; Wakamiya, A.; Kushida, T.; Yamaguchi, S. *J. Am. Chem. Soc.***2012**, *134*, 4529.
2) Shishido, R.; Uesugi, M.; Takahashi, R.; Mita, T.; Ishiyama, T.; Kubota, K.; Ito, H. *J. Am. Chem. Soc*. **2020**, *142*, 14125.

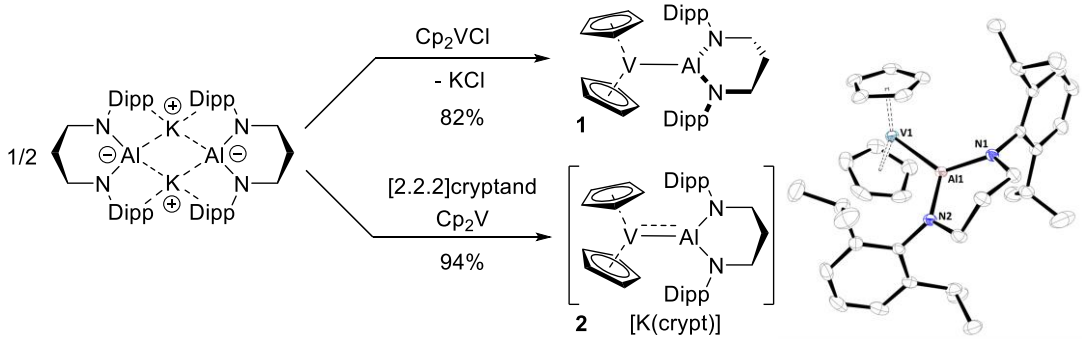
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Synthesis and Characterization of Alumanyl Complexes of Vanadium

(*Graduate School of Engineering, Nagoya University*) ○Pavel Zatsepin, Makoto Yamashita
Keywords: Aluminium, Vanadium, Alumanyl ligand, oxidation state, unpaired electron

Anionic aluminium(I) nucleophiles, alumanyl anions, have recently captivated the inorganic chemistry community.[1] Alumanyl anions are isolobal with carbenes and hence feature a strongly donating, Lewis basic electron pair while simultaneously bearing an empty *p*-orbital imparting electrophilicity at the same Al centre. Unlike carbenes however, investigations of transition metal(TM)-alumanyl coordination chemistry are scarce. The existing literature on TM-alumanyls is focused mainly on late metals.[2] Late TMs are relatively electronegative compared to Al so late TM–Al bonds tend to be polarised such that the TM centre bears a partial negative (δ^-) charge and Al bears a partial positive (δ^+) charge. Our group has recently reported rare earth-alumanyl complexes of Sc(III) and Y(III) in which this situation is reversed.[3] However, these d^0 metal complexes give little opportunity to explore the electronic effects of a σ-donating/π-accepting Al(I) ligand on a more electropositive metal. In this work we report the first example of a group-5 element bound to such an aluminium moiety.

With yields exceeding 80%, on scales of hundreds of milligrams the V(III) complex [Cp_2VAl(NN)] (**1**) (NN = *N,N'*-(2,6-diisopropylphenyl)propylenediamide) and 1-electron-reduced counterpart [Cp_2VAl(NN)][K(crypt)] (**2**) (crypt = [2.2.2]cryptand) could be prepared. These are first examples of group-5 complexes possessing a TM–Al bond. Reaction of [Cp_2VAl(NN)] with hydrogen yields the 18-electron complex [$Cp_2V(\mu_2\text{-}H)_2Al(NN)$] which possesses a shorter V–Al distance than that of its precursor in the solid state. The features of these compounds will be discussed in the presentation.



(Left) Scheme of synthesis of **1** and **2**. (Right) X-ray structure of **1** with H atoms omitted.

Refs: 1. Most recent review: Coles, M. P.; Evans, M. J. *Chem. Commun.* **2023**, doi: 10.1039/D2CC05963K 2. Representative examples: (a) McManus, C. *et al. Chem. Sci.* **2021**, *12*, 13458. (b) Morisako, S. *et al. Angew. Chem. Int. Ed.* **2019**, *58*, 15031 3. (a) Sugita, K.; Yamashita, M. *Chem. Eur. J.* **2020**, *26*, 4520. (b) Feng. G. *et al. J. Am. Chem. Soc.* **2022**, *144*, 22662.

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Catalytic Hydrogenation of Carbonyl Compounds Using Crude H_2 as H_2 Source

(*Department of Applied Chemistry, Faculty of Engineering, Osaka University*)
○Mahiro Sakuraba, Sensuke Ogoshi, Yoichi Hoshimoto
Keywords: Triarylborane; Frustrated Lewis Pair; Hydrogenation; Alcohol; Crude Hydrogen

Molecular hydrogen (H_2) is generally produced via multi-step purification processes of a gaseous mixture (crude H_2) including H_2, CO, CO_2, and so on, and then used in the synthesis of both bulk and fine chemicals. Given that those crude H_2 can be produced from a variety of hydrocarbon resources such as biomass and agricultural/livestock wastes, a direct use of crude H_2 for the hydrogenation of unsaturated molecules should be beneficial as in-depth purification processes to produce H_2 can be bypassed.[1] Here, we report a triarylborane-catalyzed hydrogenation of carbonyl compounds using the mixture of H_2, CO, and CO_2.[2]

Hydrogenation of aldehydes was reported to proceed in the presence of CO when Rh and/or Ru complexes were used;[3] however, hydrogenation of 1-naphtaldehyde (**1**) took place only in 18% under H_2/CO/CO_2 (20 atm each), albeit **2** was afforded in 98% under H_2 (20 atm) (Figure 1). Subsequently, we explored the use of $B(C_6F_5)_3$, which would generate a frustrated Lewis pair between 1,4-dioxane,[4] affording **2** in 63%; however, the hydrogenation of **1** was again suppressed by CO and/or CO_2. Thus, we have optimized the structure of triarylboranes. As a result, $B(3,5\text{-}Br_2\text{-}2,6\text{-}F_2\text{-}C_6H)_3$ exhibited a superior catalytic activity, and **2** was eventually obtained in 91% in 4-methyltetrahydropyrane.

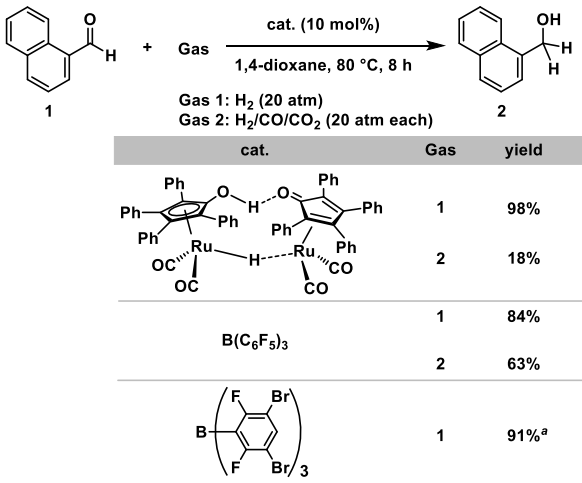


Figure 1. Catalytic hydrogenation of 1-naphtaldehyde. [*a*] 4-Metyltetrahydropyrane was used as a solvent.

1) T. Hashimoto, T. Asada, S. Ogoshi, Y. Hoshimoto, *Sci. Adv*. **2022**, *8*, eade0189. 2) Y. Hoshimoto, S. Ogoshi, *Jpn. Tokugan* 2022-195051. 3) (a) L. Diab, T. Šmejkal, J. Geier, B. Breit, *Angew. Chem. Int. Ed.* **2009**, *48*, 8022. (b) K. Takahashi, K. Nozaki, *Org. Lett.* **2014**, *16*, 5846. 4) S. A. Weicker, D. W. Stephan, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1003.

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Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- | Oral B

[K404-2am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Koji Kubota, Sobi Asako

Thu. Mar 23, 2023 9:00 AM - 11:40 AM K404 (K404, Lecture Hall Bldg. [4F])

[K404-2am-01] Low-Valent Titanium-Mediated Homolysis of Alcohol and Ether C-O Bonds

○Takuya Suga[1], Ryusei Takada[1], Yuuki Takahashi[1], Chinatsu Miki[1], Yutaka Ukaji[1] (1. Kanazawa University)

9:00 AM - 9:20 AM

[K404-2am-02] H_2 Purification through Sequential Hydrogenation/Dehydrogenation of *N*-Heterocycles Using Triarylborane Catalysts

○Taiki Hashimoto[1], Takahiro Asada[1], Sensuke Ogoshi[1], Yoichi Hoshimoto[1] (1. Graduate School of Engineering, Osaka University)

9:20 AM - 9:40 AM

[K404-2am-03] Synthesis and Reactivities of Cyclopentadienone Group 5 Metal Complexes

○Takuya Higashi[1], Shuhei Kusumoto[1], Kyoko Nozaki[1] (1. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[K404-2am-04] Silylation of Organic Halides with a Disilane Having Seven-Membered Dialkoxysilyl Groups Activated by Potassium *tert*-Butoxide

○Kenshiro Hitoshio[1], Hayate Saito[1], Jun Shimokawa[1], Hideki Yorimitsu[1] (1. Graduate School of Science, Kyoto University)

10:00 AM - 10:20 AM

[K404-2am-05] Experimental and DFT study on electrophilic and carbene-like reactivity of magnesium alkylidene carbenoids

○Koto Sekiguchi[1], Tsutomu Kimura[1] (1. Graduate School of Science, Tokyo University of Science)

10:40 AM - 11:00 AM

[K404-2am-06] Air-Tolerant and Extremely Fast Lithium-Based Birch Reduction Enabled by Mechanochemistry

○Yunpeng Gao[1], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)

11:00 AM - 11:20 AM

[K404-2am-07] Generation and Synthetic Applications of Calcium-Based Heavy Grignard Reagents under Mechanochemical Conditions

○Pan Gao[1], Julong Jiang[2], Satoshi Maeda[1,2], Koji Kubota[1,3], Hajime Ito[1,3] (1. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, 2. Department of Chemistry, Faculty of Science, Hokkaido University, 3. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University)

11:20 AM - 11:40 AM

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低原子価チタンを用いたアルコール・エーテルの C-O 結合ホモリシス

（金沢大院自然）○菅 拓也・高田 琉星・高橋 勇気・三木 稚夏・宇梶 裕

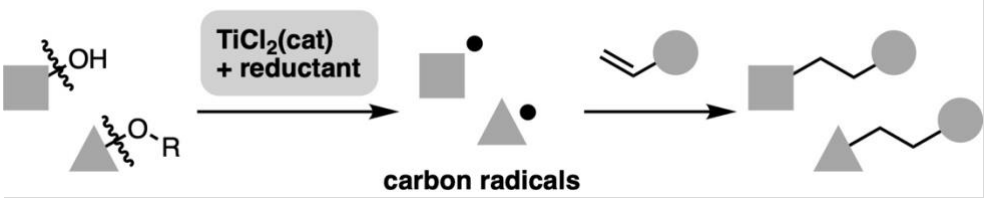
Low-Valent Titanium-Mediated Homolysis of Alcohol and Ether C-O Bonds (*Graduate School of Natural Science and Technology, Kanazawa University*) ○Takuya Suga, Ryusei Takada, Yuuki Takahashi, Chinatsu Miki, Yutaka Ukaji

Carbon-oxygen (C-O) bonds are thermodynamically stable covalent bonds, whereas their polarized nature allows us to utilize them as carbocation equivalents. However, their tolerance against homolytic cleavage has hampered the use of alcohols and ethers in the radical chemistry. To tackle this challenge, we developed several low-valent titanium reagents capable of homolytically cleaving C-O bonds. In particular, the $TiCl_2$(cat)-based low-valent titanium reagent (cat = catecholate) cleaved non-activated C-O bonds of tertiary, secondary and primary alcohols. Furthermore, it also activated ether C-O bonds with the assistance of appropriate chelation. These phenomena were successfully utilized to alkene insertion reactions. $TiCl_2$(cat) was easily accessible from very cheap bulk chemicals: $TiCl_4$ and catechol.

Keywords : Radicals; Titanium; Alcohols; Ethers

C-O 結合は熱力学的に安定な共有結合であるが、その分極した性質から、合成化学的にはカルボカチオンの等価体とみなされる。一方、一般的な C-O 結合はホモリシスに対してはほとんど不活性と言ってよく、アルコールやエーテルの C-O 結合を炭素ラジカルの等価体として直接利用することは容易ではない。

我々は、これらの不活性 C-O 結合のホモリシスを惹起する低原子価チタン反応剤の開発を行った。その結果、$TiCl_2$(cat) (cat = catecholate)から発生させた反応剤が不活性な第三級、二級そして一級のアルコールの C-O 結合をホモリティックに切断する性質を示すことを見出した[1]。さらに、キレーション効果を利用することにより、この反応剤はエーテル結合すらも切断した。これらの現象は、アルケン挿入反応に利用可能であった。$TiCl_2$(cat)は、非常に安価なバルクケミカルである四塩化チタンとカテコールから容易に合成できる。



1) T. Suga, Y. Takahashi, C. Miki, Y. Ukaji, *Angew. Chem. Ind. Ed.* **2022**, *61*, e202112533.

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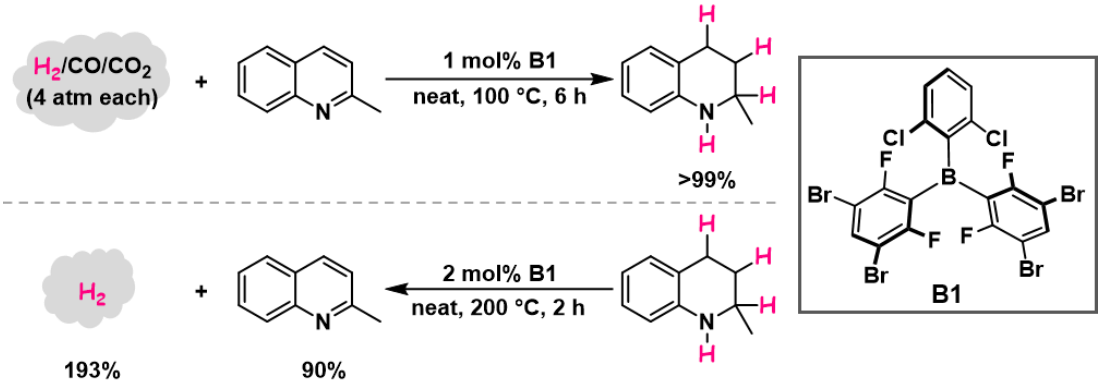
H_2 Purification through Sequential Hydrogenation/Dehydrogenation of *N*-Heterocycles Using Triarylborane Catalysts

(*Graduate School of Engineering, Osaka University*) ○Taiki Hashimoto, Takahiro Asada, Sensuke Ogoshi, Yoichi Hoshimoto

Keywords: Triarylboranes; *N*-Heteroaromatics; Hydrogen; Liquid Organic Hydrogen Careers; Frustrated Lewis Pairs

Molecular hydrogen (H_2) has been hailed as one of the most important energy carriers of the future, based on its high gravimetric energy density and the low environmental impact of its combustion product.[1] Most of H_2 in industrial use is currently produced from a variety of hydrocarbon sources including biomass through the in-depth purification of crude H_2, which is a gaseous mixture of H_2, CO, CO_2, and other components. Processes for the removal of such contaminants prior to H_2 storage are of importance to prevent the deactivation of metal-based catalysts used in fuel cells and the chemical industry; however, bypassing these purification processes is desirable, given their energy consumption and environmental impact, which ultimately increases the cost of the produced H_2. Here, we developed triarylboranes for the catalytic hydrogenation of *N*-heteroaromatic compounds in the co-presence of substantial amounts of CO, CO_2, CH_4, and H_2O, which is commensurate to a simultaneous separation and storage of H_2 (Scheme 1).[2]

We found that hydrogenation of 2-methylquinoline proceeded in the presence of a catalytic amount of **B1** and a gaseous mixture of H_2/CO/CO_2. Moreover, the **B1**-catalyzed dehydrogenation from 2-methyltetrahydroquinoline also proceeded.



Scheme 1. Catalytic hydrogenation/dehydrogenation of *N*-heterocycles.

1) K. Liu, C. Song, V. Subramani, Hydrogen and Syngas Production and Purification Technologies, Wiley-VCH 2009. 2) T. Hashimoto, T. Asada, S. Ogoshi, Y. Hoshimoto, *Sci. Adv.* **2022**, *8*, eade0189.

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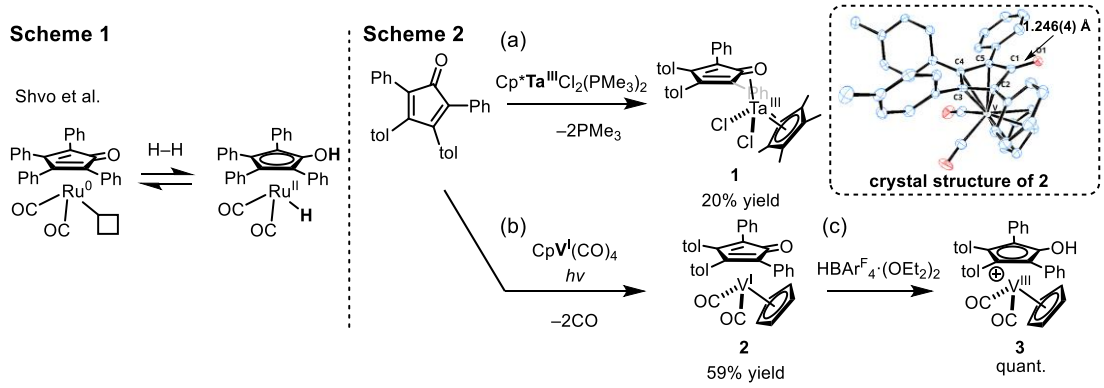
Synthesis and Reactivities of Cyclopentadienone Group 5 Metal Complexes

([1]*Graduate School of Engineering, The University of Tokyo*) ○Takuya Higashi,[1] Shuhei Kusumoto,[1] Kyoko Nozaki[1]

Keywords: Cyclopentadienone; Vanadium; Tantalum; Metal–Ligand Cooperativity

Cyclopentadienone(=CpO)/hydroxycyclopentadienyl(=CpOH) late transition-metal complexes have been well-studied as an active metal–ligand bifunctional catalyst in hydrogenation.[1,2] The reaction of the complex with, e.g., H_2 is driven by the electron transfer from the metal to the CpO ligand (**Scheme 1**). In this study, we applied the system to unprecedented low-valent group 5 metals that have stronger reducing characters[3] than late transition metal counterparts.

The reaction of tetraarylcyclopentadienone with $Cp^*Ta^{III}Cl_2(PMe_3)_2$ gave CpO tantalum(III) complex **1**, in which π-orbital of the ligand C=O bond was bound to the metal center in an η^2-fashion (**Scheme 2a**). On the other hand, the reaction with $CpV^{I}(CO)_4$ resulted in the formation of η^4-CpO vanadium(I) complex **2**, which was fully characterized by single crystal XRD analysis (**Scheme 2b**). The structural analysis for **2** clarified that it had the longest C–O bond length of 1.246(4) Å on the ligand among the family of analogous CpO metal complexes. This observation suggests a large electron transfer from the low-valent vanadium center to the CpO ligand. The redox activity of the CpO vanadium(I) complex **2** was confirmed by the reaction with a proton source. Upon addition of $HBAr^F{}_4{\cdot}(OEt_2)_2$ to the solution of **2**, the formation of CpOH vanadium complex **3** was confirmed (**Scheme 2c**). Notably, IR measurements for **3** identified the disappearance of the signal for the carbonyl of the CpO ligand and the increased ν(CO) value for metal-carbonyls. These spectral changes elucidated the oxidation of the vanadium center from I to III.



1) a) Blum, Y.; Shvo, Y. *Isr. J. Chem.* **1984**, *24*, 144. b) Shvo, Y.; Czarkie, D.; Rahamim, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7400. 2) Higashi, T.; Kusumoto, S.; Nozaki, K. *J. Am. Chem. Soc.* **2021**, *143*, 12999. 3) Beaumier, E. P.; Pearce, A. J.; See, X. Y.; Tonks, I. A. *Nat. Rev. Chem.* **2019**, *3*, 15.

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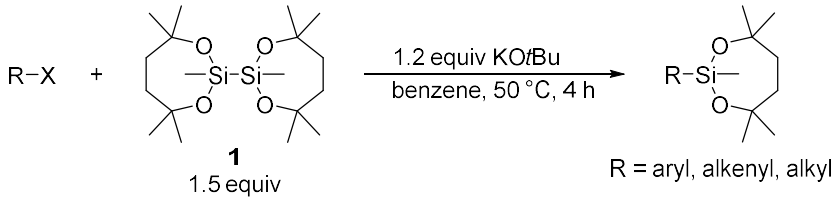
Silylation of Organic Halides with a Disilane Having Seven-Membered Dialkoxysilyl Groups Activated by Potassium *tert*-Butoxide

(*Graduate School of Science, Kyoto University*) ○Kenshiro Hitoshio, Hayate Saito, Jun Shimokawa, Hideki Yorimitsu

Keywords: Silylation; Alkoxysilane; Disilane; Organic Halide

We recently reported the discovery of a dialkoxysilyl group bearing a bulky 7-membered ring that has both excellent stability and on-demand reactivity.[1] This silyl group is stable even during transformations using $LiAlH_4$ and *n*BuLi. Still, it is reactive in cross-coupling, Tamao–Fleming oxidation, and bromination under suitable conditions. While seeking for new methods to introduce this useful silyl group, we focused on the silylation of aryl halides using a silylanion species *in situ* generated from a disilane and an alkoxide base.[2]

We first synthesized tetraalkoxydisilane **1** from commercially available 1,1,2,2-tetrachloro-1,2-dimethyldisilane and 2,5-dimethyl-2,5-hexanediol. Disilane **1** was obtained as a white solid that was found to be stable under air for at least 4 months. Next, we optimized the reaction conditions for silylation of aryl halides with **1**. After optimization, the conditions "1.5 equiv **1**, 1.2 equiv KO*t*Bu, 4 h, 50 ℃ in benzene using aryl chlorides as substrates" were found to be optimal. In this silylation reaction, KO*t*Bu was specifically effective as an activator. We also attempted to introduce silyl groups other than dioxasilepanyl group under the reaction conditions, however, silylation reaction did not proceed at all and an aryl chloride was fully recovered. During the investigation of substrate scope, we found that silylation of alkenyl and alkyl chlorides also takes place. In addition, we conducted some experiments using organic chlorides to disclose the reaction mechanism. Our current mechanistic hypothesis is that chlorine-potassium exchange initially occurs between organic chlorides and *in situ* generated silylpotassium species, followed by the generation of organopotassium species and a chlorosilane.



1) H. Saito, J. Shimokawa, H. Yorimitsu, *Chem. Sci.* **2021**, *12*, 9546. 2) a) H. Watanabe, K. Higuchi, M. Kobayashi, M. Hara, Y. Koike, T. Kitahara, Y. Nagai, *J. Chem. Soc., Chem. Commun.* **1977**, 534. b) C. Grogger, B. Loidl, H. Stueger, T. Kammel, B. Pachaly, *J. Organomet. Chem.* **2006**, *691*, 105.

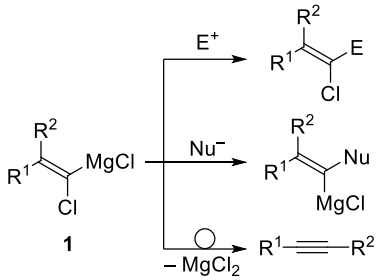
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Experimental and DFT Study on Electrophilic and Carbene-Like Reactivity of Magnesium Alkylidene Carbenoids

([1]*Graduate School of Science, Tokyo University of Science*) ○Koto Sekiguchi,[1] Tsutomu Kimura[1]

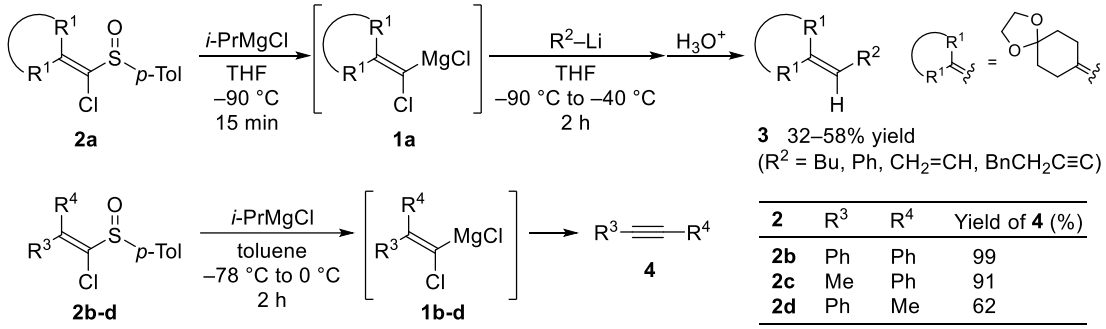
Keywords: Magnesium Alkylidene Carbenoid; 1-Chlorovinyl *p*-Tolyl Sulfoxide; DFT Calculation; Nucleophilic Substitution; Fritsch–Buttenberg–Wiechell Rearrangement

Magnesium alkylidene carbenoids **1** are reactive intermediates in which magnesium and chlorine atoms are connected to a vinylic carbon atom (Scheme 1). Magnesium alkylidene carbenoids **1** have an ambiphilic reactivity, namely, magnesium alkylidene carbenoids **1** act not only as nucleophiles but also as electrophiles. Furthermore, as the name suggests, magnesium alkylidene carbenoids **1** have a carbene-like reactivity. We studied on the electrophilic reactivity and carbene-like reactivity of magnesium alkylidene carbenoids **1**.



Scheme 1. Reactivity of magnesium alkylidene carbenoids **1.**

Magnesium alkylidene carbenoid **1a** was generated from 1-chlorovinyl *p*-tolyl sulfoxide **2a** and *i*-PrMgCl via the sulfoxide/magnesium exchange reaction (Scheme 2). Nucleophilic substitution of magnesium alkylidene carbenoid **1a** with organolithium reagents occurred at the vinylic carbon atom to give substituted alkenes **3** in 32–58% yield. Reaction mechanism of nucleophilic substitution at the vinylic carbon atom was studied by DFT calculations. Activation energy for the reaction of magnesium alkylidene carbenoid with acetylide via the 1,2-metallate rearrangement was estimated to be 20.0 kcal/mol, and it was lower than that of the S_N2 reaction of chloroalkene with acetylide by 7.7 kcal/mol. When magnesium alkylidene carbenoids **1b-d** were left without organolithium reagents, 1,2-rearrangement occurred to give terminal alkynes **4** in 62–99% yield.



2	R^3	R^4	Yield of **4** (%)
2b	Ph	Ph	99
2c	Me	Ph	91
2d	Ph	Me	62

Scheme 2. Nucleophilic substitution of magnesium alkylidene carbenoid **1a** with organolithium reagents and 1,2-rearrangement of magnesium alkylidene carbenoids **1b-d.**

1) T. Kimura, *Synthesis* **2017**, *40*, 3835.

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Air-Tolerant and Extremely Fast Lithium-Based Birch Reduction Enabled by Mechanochemistry

([1]*Graduate School of Engineering, Hokkaido University,* [2]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University*) ○Yunpeng Gao,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Keywords: Ball milling, Birch reduction, Lithium, Mechanochemistry, Synthetic methods

Birch reduction has been widely used in organic synthesis for over half a century as a powerful method to dearomatize arenes.[1] However, the conventional Birch reduction reaction using liquid ammonia requires laborious procedures. Although several remarkable ammonia-free modifications have been reported, these solution-based protocols still require an inert atmosphere and strictly dehydrated conditions. The development of an operationally simple, efficient, and scalable protocol remains a challenge.

Based on our experiences with mechanochemical synthesis with bulk metals,[2] we hypothesized that the development of mechanochemical lithium-based Birch reduction might overcome these issues. The *in-situ* mechanical agitation provided by ball milling would accelerate the activation of bulk metal. Meanwhile, the reduced contact of the reactive organometallic species with gaseous oxygen and water under solvent-less conditions leads to significant tolerance of atmospheric conditions. In this study, we have achieved the first mechanochemical approach for lithium-based ammonium-free Birch reduction *in air* at room temperature using a ball mill. The entire synthetic procedure can be conducted under atmospheric conditions without any special precautions or elaborate synthetic techniques. Owing to the *in-situ* mechanical activation of lithium metal, the mechanochemical Birch reduction was extremely fast and completed within *one minute* for a broad range of substrates. The rapid and selective Birch reduction of bioactive targets showcased the generality of this mechanochemical protocol. The success of the gram-scale reduction within one minute implies the possibility of highly efficient scaled-up synthesis.[3]



1) A. J. Birch, *J. Chem. Soc.* **1944**, 430. 2) a) R. Takahashi, A. Hu, P. Gao, Y. Gao, Y. Pang, T. Seo, J. Jiang, S. Maeda, H. Takaya, K. Kubota, H. Ito, *Nat. Commun.* **2021**, *12*, 6691. b) P. Gao, J. Jiang, S. Maeda, K. Kubota, H. Ito, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207118. 2) Y. Gao, K. Kubota, H. Ito, **2022**, *submitted.*

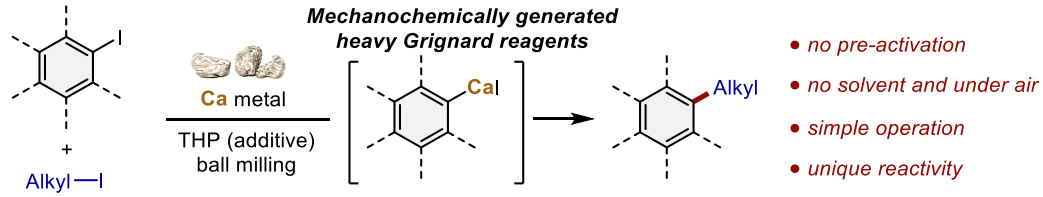
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Generation and Synthetic Applications of Calcium-Based Heavy Grignard Reagents under Mechanochemical Conditions

([1]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University*, [2]*Department of Chemistry, Faculty of Science, Hokkaido University*, [3]*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University*)
○Pan Gao,[1] Julong Jiang,[2] Satoshi Maeda,[1,2] Koji Kubota,[1,3] and Hajime Ito[1,3]
Keywords: Calcium; Ball Mill; Mechanochemistry; Cross-Electrophile Coupling; Solid-State Reaction

In sharp contrast to the use of conventional magnesium-based Grignard reagents (R−MgX), the application of calcium-based heavy Grignard reagents (R−CaX) remains poorly explored. This is mainly due to the lack of experimentally simple ways to access such organocalcium nucleophiles from readily available starting materials under mild conditions. The direct synthesis from organic halides with calcium metal would be a versatile route to obtain organocalcium reagents. However, due to the relatively high atomization energy of calcium metal, pre-activation of the calcium metal is necessary. One reliable pre-activation method is first dissolving the calcium metal in liquid ammonia and then quickly removing the solvent by distillation at low temperature to provide highly reactive and pyrophoric calcium powder. Rieke calcium metal can also be prepared by reduction of CaX_2 with lithium biphenylide. The requirements for toxic ammonia or harsh reduction conditions, dry organic solvents, and strict control of the reaction temperature greatly impede the widespread use of calcium-based carbon nucleophiles in organic synthesis.

Based on our experiences with mechanochemical organic synthesis using a ball mill,[2] we hypothesized that the mechanical impact could provide sufficient energy to overcome the relatively high atomization energy of calcium metal, which would allow the efficient activation of calcium metal and thus make the direct generation of organocalcium reagents feasible. In this study, using the mechanochemical method, we have achieved for the first time the generation of calcium-based heavy Grignard reagents from commercially available, unactivated calcium metal without applying any pre-activation process. Furthermore, we present the first example of the alkylation of arylcalcium nucleophiles with alkyl electrophiles to form carbon−carbon bonds, which has not been reported using previous pre-activation methods for the direct generation of organocalcium compounds.[3] This operationally simple approach will significantly advance the synthetic organic chemistry of organocalcium compounds.



1) A. Koch, Q. Dufrois, M. Wirgenings, H. Görls, S. Krieck, M. Etienne, G. Pohnert, M. Westerhausen, *Chem. Eur. J.* **2018**, 2*4*, 16840. 2) R. Takahashi, A. Hu, P. Gao, Y. Gao, Y. Pang, T. Seo, J. Jiang, S. Maeda, H. Takaya, K. Kubota, H. Ito, *Nat. Commun.* **2021**, *12*, 6691. 3) P. Gao, J. Jiang, S. Maeda, K. Kubota, H. Ito, *Angew. Chem. Int. Ed.* **2022**, DOI: *10.1002/anie.202207118*.

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Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- | Oral B

[K404-2pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takuya Kochi, Yuichiro Mutoh

Thu. Mar 23, 2023 1:00 PM - 3:40 PM K404 (K404, Lecture Hall Bldg. [4F])

[K404-2pm-01] Development of Palladium-catalyzed Oxidative Amination of 1,3-Diene and Elucidation of Catalytic Species

○Kazuki Tabaru[1], Tetsuaki Fujihara[2], Kazuyuki Torii[1], Takeyuki Suzuki[3], Yasushi Obora[1] （1. Fac. Chem. Matl. &Bioeng., Kansai Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. SANKEN, Osaka Univ.）

1:00 PM - 1:20 PM

[K404-2pm-02] Alkene Rotation as a Key Process in Chain Walking of a Palladium Catalyst and Its Effect on Selectivity of Reaction Pathways

○Kazuma Muto[1], Miho Hatanaka[1], Fumitoshi Kakiuchi[1], Takuya Kochi[1] （1. Keio. University）

1:20 PM - 1:40 PM

[K404-2pm-03] Virtual Ligand-Assisted Screening Strategy toward Finding Enabling Ligands for Transition Metal Catalysis

○Wataru Matsuoka[1,2], Yu Harabuchi[1,2,3], Satoshi Maeda[1,2,3] （1. Fac. of Sci., Hokkaido Univ., 2. JST-ERATO, 3. WPI-ICReDD, Hokkaido Univ.）

1:40 PM - 2:00 PM

[K404-2pm-04] Synthesis of SGLT2 Inhibitors by Means of Fukuyama Coupling Reaction

○Maheshwara Reddy Nadiveedhi[1], Sandeep Ramesharao Tapkir[1], Shaheen Kasim Mulani[1], Masahiko Seki[1,2], Kazushi Mashima[1] （1. Osaka University, 2. Tokuyama Corporation）

2:00 PM - 2:20 PM

[K404-2pm-05] Platinum-Catalyzed Stereospecific Synthesis of Silicon-Stereogenic Optically Active Silylboranes and Their Application

○Xihong Wang[1], Chi Feng[2], Koji Kubota[1,2], Hajime Ito[1,2] （1. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, 2. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University）

2:40 PM - 3:00 PM

[K404-2pm-06] Isolation and reactivity of allenynickel key reaction intermediates in Ni-catalyzed asymmetric propargylic substitution reactions

○Yusuke Miyazaki[1], Kenichi Michigami[2], Mitsuhiro Ueda[2], Masato Ohashi[2] （1. Osaka Prefecture Univ., 2. Osaka Metropolitan Univ.）

3:00 PM - 3:20 PM

[K404-2pm-07] Synthesis and Reactivity of Ni(0) Carbonyl Complexes Bearing *N*-Phosphine Oxide-Substituted Imidazolinylidene

○Yasuhiro Yamauchi[1], Yuta Uetake[1], Hidehiro Sakurai[1], Yoichi Hoshimoto[1], Sensuke Ogoshi[1] （1. Osaka university）

3:20 PM - 3:40 PM

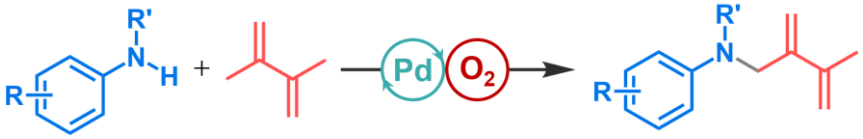
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Development of Palladium-catalyzed Oxidative Amination of 1,3-Diene and Elucidation of Catalytic Species

([1] *Faculty of Chemistry, Materials & Bioengineering, Kansai University.*, [2] *Graduate School of Engineering, Kyoto University,* [3] *SANKEN, Osaka University*)
○Kazuki Tabaru,[1] Tetsuaki Fujihara,[2] Kazuyuki Torii,[1] Takeyuki Suzuki,[3] Yasushi Obora[1]
Keywords: Oxidative coupling; Palladium complex; Palladium nanoclusters; Disilane; 1,3-Diene

Palladium-catalyzed coupling reaction is a powerful tool in organic chemistry. Especially, oxidative coupling is one of the most straightforward coupling reactions.[1] This strategy is based on the oxidation of two hydrogen atoms where the coupling event occurs, succeeding in an atom- and step-economical reaction. It is well known that metal complexes are key intermediates including monometallic active sites in the proposed mechanism. However, the practical catalytic system involved a variety of catalytic species differing from a metal complex such as metal nanoparticles and metal nanoclusters, which exhibits a unique catalytic activity due to their reaction fields and dynamics.[2]

Here, we developed palladium-catalyzed aerobic oxidative amination of 1,3-diene. This reaction readily furnished nitrogen containing 1,3-dienes from commercially accessible feedstocks. The use of palladium complex with disilane allowed the reaction to proceeded with a high-chemo selectivity rather than electrophilic additions to 1,3-diene such as 1,4-hydroamination. Results of X-ray absorption spectroscopy (XAS) indicated our system involved unique palladium catalyst species contributing to the formation of products. Transmission electron microscopy and other X-ray techniques such as small angle X-ray scattering (SAXS) and X-ray diffraction (XRD) suggested the presence of palladium nanoparticles generated through the reduction by disilane. To obtain detailed understandings of the reaction, we evaluated both complex and nanoparticles catalyst reaction routes by computational studies and solution-phase XAS analysis.



- ✓ *Aerobic oxidative amination of 1,3-diene*
- ✓ *Characterization by XAS, SAXS, XRD…*
- ✓ *Computational studies*

1) K. Tabaru, Y. Obora, *Eur. J. Org. Chem.*, **2022**, e202200618.
2) a) M. V. Polynski, V. P. Ananikov, *ACS Catal.*, **2019**, *9*, 3991. b) F. Garnes-Portolés, R. Greco, J. Oliver-Meseguer, J. Castellanos-Soriano, M. C. Jiménez, M. López-Haro, J. C. Hernández-Garrido, M. Boronat, R. Pérez-Ruiz, A. Leyva-Pérez, *Nat. Cat.*, **2021**, *4*, 293.

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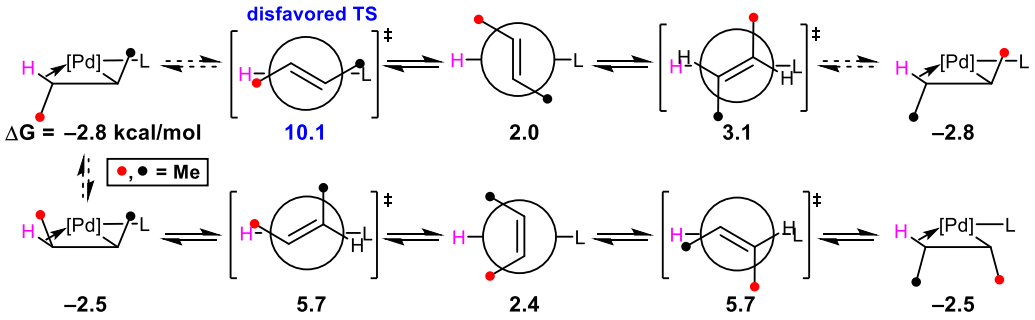
Alkene Rotation as a Key Process in Chain Walking of a Palladium Catalyst and Its Effect on Selectivity of Reaction Pathways

(*Faculty of Science and Technology, Keio University*) ○Kazuma Muto, Miho Hatanaka, Fumitoshi Kakiuchi, Takuya Kochi

Keywords: Alkene Rotation, DFT Calculation, Palladium Catalyst, Chain Walking, Deuterium Labeling Study

Alkene rotation around the metal–alkene bond in complexes is one of the most fundamental elementary processes in organometallic chemistry, and the energy barrier of alkene rotation has been studied experimentally[1] and theoretically[2] for various alkene complexes. There have been numerous organometallic catalytic reactions involving the alkene rotation step, especially right before migratory insertion. However, it has rarely been recognized as key steps such as turnover-limiting or selectivity-determining steps in catalytic cycles. Chain walking is a process where alkylmetal species move along aliphatic carbon chains through repetitive β-hydride elimination, alkene rotation, and migratory insertion. During the course of our theoretical and experimental studies on the catalytic reactions proceeding via nondissociative chain walking of 1,10-phenanthroline palladium catalysts, we obtained some results indicating that the alkene rotation step mostly has the highest energy barrier in the chain walking process.

Explorations of nondissociative chain walking pathways of an *n*-propylpalladium species by DFT calculation suggested that the transition states on the alkene isomerization pathways only located during the alkene rotation. Alkene dissociation from the alkene hydrido complex and associative alkene exchange were also calculated and found to be less favorable than the nondissociative chain walking pathway. Theoretical calculation of palladium complexes with longer alkyl groups also provided similar results to the propylpalladium complex. In addition, it was suggested that chain walking of the palladium center between internal carbons proceeds via palladium hydride complexes ligated to cis alkene intermedites, although cis alkenes are thermodynamically less stable than trans alkenes. The preference of cis alkene intermediates was supported by a deuterium-labeling experiment of remote arylative substitution using a 1,10-phenanthroline palladium catalyst.[3]



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(2) T. Sperger, I. A. Sanhueza, I. Kalvet, F. Schoenebeck, *Chem. Rev.* **2015**, *115*, 9532.
(3) K. Muto, T. Kumagai, F. Kakiuchi, T. Kochi, *Angew. Chem. Int. Ed.* **2021**, *60*, 24500.

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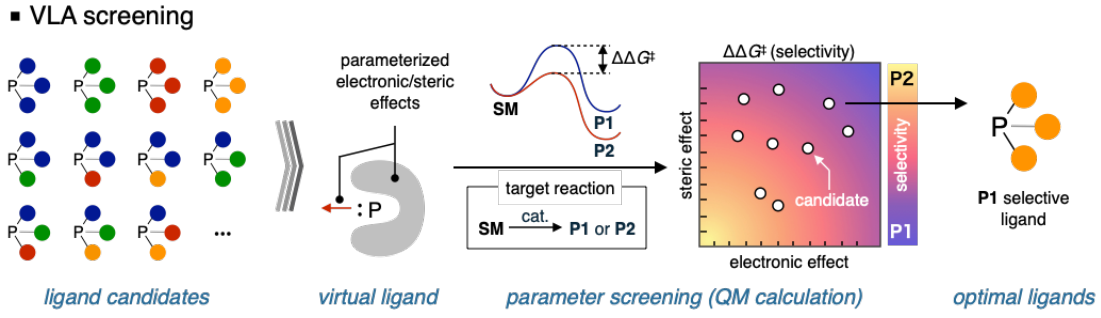
遷移金属触媒のインシリコ設計を指向したバーチャル配位子法の開発と配位子スクリーニングへの応用

(北大院理[1]・JST-ERATO[2]・北大 WPI-ICReDD[3]) ○松岡 和[1,2]・原渕 祐[1,2,3]・前田 理[1,2,3]
Virtual Ligand-Assisted Screening Strategy toward Finding Enabling Ligands for Transition Metal Catalysis ([1]*Faculty of Science, Hokkaido University*, [2]*JST-ERATO,* [3]*WPI-ICReDD, Hokkaido University*) ○Wataru Matsuoka,[1,2] Yu Harabuchi,[1,2,3] Satoshi Maeda[1,2,3]

Ligand screening is a crucial step in the development of transition metal catalysis. Conventionally, this process has been carried out by an empirical trial-and-error approach, which can be time consuming and resource intensive. To streamline this process, we have previously proposed a computational method called virtual ligand-assisted (VLA) screening.[1] In this method, quantum chemical calculations are performed using virtual ligands which reproduce and parameterize the electronic and steric effects of real ligands. By optimizing the electronic and steric parameters of the virtual ligands to maximize the efficiency and/or selectivity of the desired reaction, the optimal features of ligands for the reaction can be rapidly identified. In this presentation, we applied VLA screening to the Suzuki-Miyaura cross-coupling reaction of *p*-chlorophenyltriflate and succeeded to find phosphine ligands that exhibits high chemoselectivity.

Keywords : in silico ligand screening; virtual ligand; transition metal catalysis; quantum chemical calculation; transition state theory

遷移金属触媒反応の開発において、目的の反応に最適な配位子を選ぶことは極めて重要である。従来、この配位子スクリーニングは実験的なトライアンドエラーによって達成されてきたが、最適配位子を見出すまでに多大な時間や資源を必要とするという問題があった。この課題に対して、我々は、量子化学計算に基づいて最適配位子を提案するバーチャル配位子アシスト(VLA)スクリーニングという手法を提案している[1)]。本手法では、配位子の電子効果と立体効果を近似するバーチャル配位子を用いて量子化学計算を行う。バーチャル配位子の電子・立体パラメータを目的の反応に対して最適化することで、最適配位子の性質を簡便に特定することが可能である。今回我々は、*p*-クロロフェニルトリフレートの鈴木–宮浦クロスカップリング反応に対して VLA スクリーニングを適用し、高い化学選択性を発現するホスフィン配位子を見出すことに成功した。



1) Matsuoka, W.; Harabuchi, Y.; Maeda, S. *ACS Catal.* **2022**, *12*, 3752–3766.

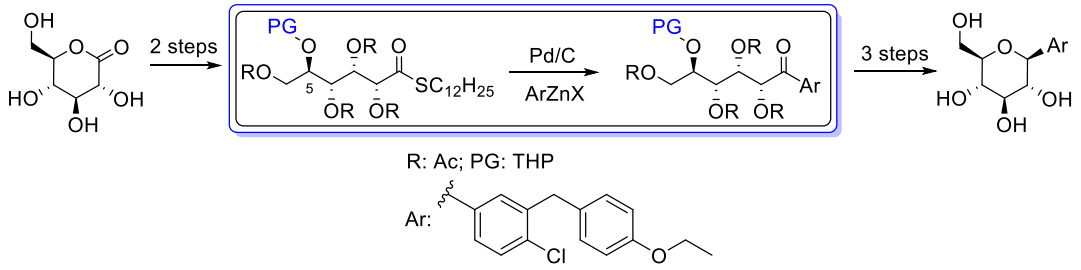
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Synthesis of SGLT2 Inhibitors by Means of Fukuyama Coupling Reaction

([1]*Graduate School of Pharmaceutical Sciences, Osaka University*, [2]*Tokuyama Corporation, Tsukuba*) ○ N. Maheshwara Reddy[1], Tapkir Sandeep Ramesharao[1], Shaheen Kasim Mulani[1], Masahiko Seki[1,2] and Kazushi Mashima[1]

Keywords: SGLT2 Inhibitors, Pd/C-catalysed reactions, Fukuyama coupling, arylzinc reagents

The sodium glucose co-transporter 2 (SGLT2) has received considerable attention in recent years as a target for the treatment of type 2 diabetes mellitus (T2DM)[1,2]. In this context, dapagliflozin currently represents one of the most advanced SGLT2 inhibitor due to its high efficacy and safety. The present study describes a novel synthesis of dapagliflozin via Fukuyama coupling reaction[3] of a D-gluconolactone-derived thioester with aryl zinc reagents producing the corresponding multifunctional aryl ketones in high yield at ambient temperature, followed by THP deprotection, base catalysed cyclization, silane reduction and final deacetylation. This newly developed protocol is highlighted by the high cumulative yields, mild reaction conditions and use of readily removable acetyl protecting groups.



1) J. Talode, D. Kato, H. Nagae, H. Tsurugi, M. Seki, and K. Mashima, *J. Org. Chem.* **2020**, *85*, 12382 2) B. Komoroski, N. Vachharajani, D. Boulton, D. Kornhauser, M. Geraldes, L. Li, M. Pfister *Clinical Pharmacology & Therapeutics* **2009**, *85*(5), 520. 3) M. Seki, M. Hatsuda, Y. Mori, S. Yoshida, S. Yamada, T. Shimizu, *Chem. Eur. J.* **2004**, 10, 6102.

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Platinum-Catalyzed Stereospecific Synthesis of Silicon-Stereogenic Optically Active Silylboranes and Their Application

([1]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), HokkaidoUniversity*, [2]*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University*) ○Xihong Wang,[1] Chi Feng,[2] Koji Kubota,[1,2] Hajime Ito[1,2]

Keywords: Chiral Silicon Chemistry; Chiral Hydrosilane; Chiral Silylborane; Stereospecific Reaction; Borylation Reaction

Since its first synthesis by Suginome and Ito in 1996, silylborane has shown attractive features in synthetic organic chemistry, especially as a powerful silyl transfer reagent.[1] Although silicon-stereogenic optically active silylborane has a strong potential to allow the introduction of silicon-stereogenic silyl groups into various molecules, the synthesis of such silicon-stereogenic silylboranes is so far unprecedented. Very recently, we reported a platinum- or rhodium-catalyzed borylation of hydrosilanes following the pioneering study of an iridium-catalyzed Si–H borylation reported by Hartwig,[2] which provides access to trialkylsilylboranes with bulky alkyl groups and dialkylarylsilylboranes.[3] Based on this study, we envisioned that the synthesis of chiral silylboranes could be achieved via the stereospecific transition-metal-catalyzed Si–H borylation of the corresponding chiral hydrosilanes.

Silicon-stereogenic optically active silylboranes were successfully obtained via a stereospecific $Pt(PPh_3)_4$-catalyzed Si–H borylation of silicon-stereogenic hydrosilanes in high yield and perfect enantiospecificity (up to 99% *ee*, >99% *es*) with retention of the configuration. Furthermore, the usefulness of silicon-stereogenic silylborane is proven to keep perfect stereospecificity in the generation of the unprecedented chiral silyl nucleophile, silicon–silicon bond-forming reactions, transition-metal-catalyzed carbon–silicon bond-forming cross-coupling reactions, and a conjugate addition reaction (>99% *es*).



1) J.-J. Feng, W. Mao, L. Zhang, M. Oestreich, *Chem. Soc. Rev.* **2021**, *50*, 2010. 2) T. A. Boebel, J. F. Hartwig, *Organometallics* **2008**, *27*, 6013. 3) R. Shishido, M. Uesugi, R. Takahashi, T. Mita, T. Ishiyama, K. Kubota, H. Ito, *J. Am. Chem. Soc.* **2020**, *142*, 14125.

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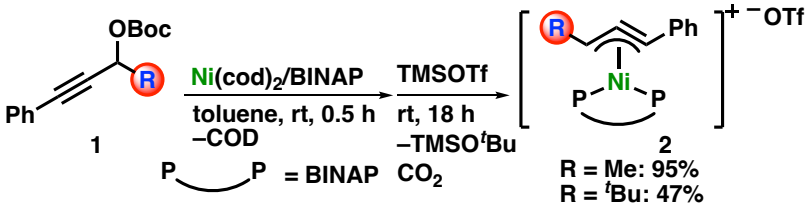
Isolation and reactivity of allenylnickel complexes in Ni-catalyzed propargylic substitution reactions

([1]*Graduate School of Science, Osaka Prefecture University*, [2]*Graduate School of Science, Osaka Metropolitan University*) ○ Yusuke Miyazaki,[1] Kenichi Michigami,[1,2] Mitsuhiro Ueda,[1,2] Masato Ohashi[1,2]

Keywords: Allenylnickel complex; Propargylic substitution; Ni-catalyzed reaction; Propargylic amine; Reaction intermediate

The catalytic propargylic substitution reaction has been realized as an efficient method for the synthesis of alkyne- or allene-containing organic molecules.[1] In particular, the palladium catalysis is one of the most powerful synthetic tools, in which allenylpalladium complexes are involved as key intermediates.[2] Recently, Tsuji, Kawatsura, and co-workers reported the nickel-catalyzed asymmetric propargylic amination of propargylic carbonates, which allowed access to the corresponding chiral propargylic amines in high yields with excellent enantioselectivity.[3] However, allenylnickel congeners, plausible key intermediates in nickel-catalyzed system, have not been isolated thus far. We herein disclosed the first example of the synthesis and reactivity of a series of allenylnickel complexes having BINAP ligand.

Treatment of alkyne complexes, which were prepared by the reaction of propargylic *tert*-butyl carbonate (**1**) with an equimolar amount of Ni(cod)$_2$/BINAP, with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dry toluene at room temperature for 18 h gave the corresponding cationic η^3-allenylnickel complexes (**2-Me** and **2-^{t}Bu**) in 95% and 47% yield, respectively. These molecular structures of **2-Me** and **2-^{t}Bu** were unambiguously determined by X-ray diffraction analysis. The reaction of **(*R*)-2-Me** with *N*-methylaniline gave the propargylic amine in high enantioselectivity, which is comparable to that observed in the Ni-catalyzed asymmetric propargylic amination, albeit low yield.



1. a) J. A. Marshall, M. A. Wolf, *J. Org. Chem.***1996**, *61*, 3238. b) X. Huang, S. Wu, W. Wu, P. Li, C. Fu, S. Ma, *Nat. Commun.* **2016**, *7*, 12382.
2. a) P. J. Stang, C. M. Crittell, A. M. Arif, *Organometallics* **1993**, *12*, 4799. b) J. M. A. Wouters, R. A. Klein, C. J. Elsevier, *Organometallics* **1994**, *13*, 4586. c) K. Tstutsumi, T. Kawase, K. Kakiuchi, S. Ogoshi, Y. Okada, H. Kurosawa, *Bull. Chem. Soc. Jpn.* **1992**, *72*, 2687. d) S. Ogoshi, T. Nishida, T. Shinagawa, H. Kurosawa, *J. Am. Chem. Soc.* **2001**, *123*, 7164.
3. K. Watanabe, Y. Miyazaki, M. Okubo, B. Zhou, H. Tsuji, M. Kawatsura, *Org. Lett.* **2018**, *20*, 5448.

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Synthesis and Reactivity of a Nickel-Carbonyl Complex Bearing *N*-Phosphine-Oxide-Substituted Imidazolinylidenes

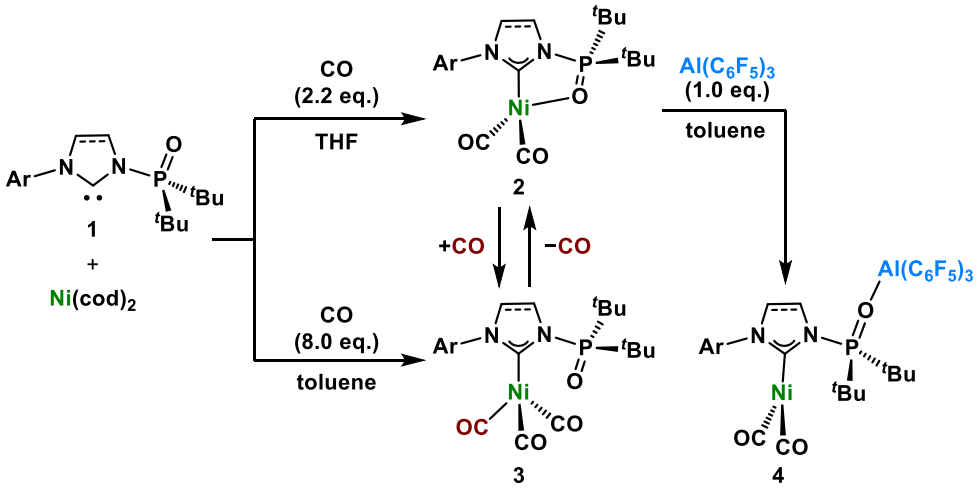
([1]*Graduate School of Engineering, Osaka University*) ○Yasuhiro Yamauchi,[1] Yoichi Hoshimoto,[1] Yuta Uetake,[1] Hidehiro Sakurai,[1] Sensuke Ogoshi[1]

Keywords: Nickel; Carbon Monoxide; *N*-Heterocyclic Carbenes; Triarylaluminium; Heterobimetallic Complexes

A variety of Ni(0) carbonyl complexes bearing *N*-heterocyclic carbenes (NHCs), namely (NHC)Ni(CO)$_n$ (n = 2 or 3), have been synthesized for the comparison of the steric and electronic properties of NHCs.[1] However, there have been no reports on NHCs that can afford both di- and tri-carbonyl complexes. Herein, we report a selective synthesis of both nickel di- and tri-carbonyl complexes bearing *N*-phosphine-oxide-substituted imidazolinylidenes[2] as well as their interconversion under the ambient conditions.[3]

Treatment of a solution of **1** and Ni(cod)$_2$ with CO afforded either (κ-*C*,*O*-**1**)Ni(CO)$_2$ (**2**) or (κ-*C*-**1**)Ni(CO)$_3$ (**3**) quantitatively depending on the reaction conditions. Stirring **2** under the CO atmosphere resulted in the formation of **3** in excellent yields. In addition, complex **3** was again converted to **2** under the reduced pressure.

Reaction of **2** with Al(C$_6$F$_5$)$_3$ yielded heterobimetallic Ni/Al complexes (**4**), in which the carbene moiety coordinates to the nickel as well as the oxygen atom coordinates to the aluminum.



Scheme 1. Synthesis and reactivity of (κ-*C*,*O*-**1**)Ni(CO)$_2$ (**2**) or (κ-*C*-**1**)Ni(CO)$_3$ (**3**).

1) a) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841. b) H. V. Huynh, *Chem. Rev.* **2018**, *118*, 9457. 2) Y. Hoshimoto, S. Ogoshi, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 327. 3) Y. Yamauchi, Y. Hoshimoto, T. Kawakita, T. Kinoshita, Y. Uetake, H. Sakurai, S. Ogoshi, *J. Am. Chem. Soc.* **2022**, *144*, 8818.

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Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B

[K603-2am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Takayuki Tanaka, Tetsuo Okujima

Thu. Mar 23, 2023 9:00 AM - 11:30 AM K603 (K603, Lecture Hall Bldg. [6F])

[K603-2am-01] Single crystal field-effect transistor of tetrabenzoporphyrin with a one-dimensional columnar packing motif exhibiting efficient charge transport properties

○Hironobu Hayashi[1], JuanJuan Zhu[1], Kyohei Matsuo[1], Naoki Aratani[1], Hiroko Yamada[1]
（1. Nara Institute of Science and Technology）

9:00 AM - 9:20 AM

[K603-2am-02] Synthesis and charge transpor properties of asymmetric 5,15-substituted tetrabenzoporphyrins

○Kazuya Miyazaki[1], Kyohei Matsuo[1], Naoki Aratani [1], Hiroko YAMADA[1] （1. Nara Institute of Science and Technology）

9:20 AM - 9:40 AM

[K603-2am-03] Deprotonation-Induced and Ion-Pairing-Modulated Diradical Properties of Partially Conjugated Pyrrole-Quinone Conjunction

○Shinya Sugiura[1], Takashi Kubo[2], Hiromitsu Maeda[1] （1. Ritsumeikan Univ., 2. Osaka Univ.）

9:40 AM - 10:00 AM

[K603-2am-04] Control of Aromatic Ring Inversion in Calix[3]pyrrole

○Yuya Inaba[1], Yu Kakibayashi[1], Yasuhide Inokuma[1,2] （1. Grad. Sch. Eng., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ.）

10:10 AM - 10:30 AM

[K603-2am-05] Synthesis and Redox properties of silver and nickel complexes of N-confused porphyrin dimer

○Osamu Iwanaga[1], Shigeki Mori[2], Masatoshi Ishida[3], Soji Shimizu[1], Hiroyuki Furuta[1,4]
（1. Kyushu Univ., 2. Ehime Univ., 3. Tokyo Metropolitan Univ., 4. Ritsumeikan Univ.）

10:30 AM - 10:50 AM

[K603-2am-06] Panchromatic Absorption of Pyrrolopyrrole aza-BODIPY analogs Based on the Push-Pull Strategy

○Yitong Wang[1], Soji Shimizu[1] （1. Graduate School of Engineering, Kyushu University）

10:50 AM - 11:10 AM

[K603-2am-07] Synthesis and properties of electron-donor-substituted BODIPY-based contrast agents for two-photon-excitation-induced photoacoustic imaging

○Takahide Shimada[1], Ishida Masatoshi[2], Shigeki Mori[3], Soji Shimizu[1], Hiroyuki Furuta[4]
（1. Graduate School of Engineering, Kyushu University, 2. Graduate School of Science, Tokyo Metropolitan University, 3. Advanced Research Support Center, Ehime University, 4. Research Organization of Science and Technology, Ritsumeikan University）

11:10 AM - 11:30 AM

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高効率な電荷輸送特性を示す一次元カラム構造を形成したテトラベンゾポルフィリンの単結晶電界効果トランジスタ

（奈良先端大先端科技）○林 宏暢・Zhu Juanjuan・松尾 恭平・荒谷 直樹・山田 容子
Single crystal field-effect transistor of tetrabenzoporphyrin with a one-dimensional columnar packing motif exhibiting efficient charge transport properties (*Graduate School of Science and Technology, Nara Institute of Science and Technology*) ○Hironobu Hayashi, Juanjuan Zhu, Kyohei Matsuo, Naoki Aratani, Hiroko Yamada

Due to the large and rigid π-system, tetrabenzoporphyrins are promising candidates as efficient p-type semiconducting materials. In this study, the charge transport properties of 5,15-bis(triisopropylsilylethynyl)tetrabenzoporphyrin (TIPS-H_2BP) and its metal complexes were investigated. Their crystals were grown by drop-casting the toluene solution on the octadecyltrichlorosilane modified Si/SiO_2 surface. The single crystal field-effect transistors of TIPS-H_2BP clearly exhibited better hole mobility than its metal complexes. The long-range one-dimensional columnar structure of TIPS-H_2BP contributed to the efficient charge transport property, whereas the charge transport was suppressed in the case of the metal complexes because of their “triad-like” structures in the column.
Keywords : Precursor method; Tetrabenzoporphyrin; Organic field-effect transistor; Hole mobility; Single crystal

テトラベンゾポルフィリンは剛直で大きなπ共役系であり、優れた p 型有機半導体材料として注目を集めている。本研究では、5,15-位にトリイソプロピルシリルエチニル基を導入したテトラベンゾポルフィリン（TIPS-H_2BP）とその金属錯体の電荷輸送特性を、単結晶トランジスタ（SCFET）作製により評価した（Figure 1）。TIPS-H_2BP は BP ユニットが効果的にπ–πスタックしたカラム構造に起因する効率的な電荷輸送特性（2.16 cm^2/Vs）を発現した。一方、亜鉛錯体および銅錯体も同様のカラム構造を形成したが、単結晶中での「triad-like 構造」により電荷輸送が妨げられた結果、TIPS-H_2BP と比べて低い電荷輸送特性（~0.1–0.2 cm^2/Vs）を示すことを明らかにした [1]。

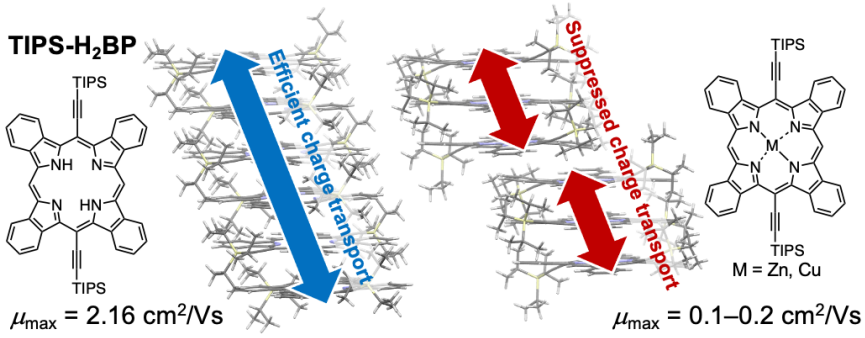


Figure 1. Packing structures and hole mobilities of TIPS-H_2BP and its metal complexes.

1) J. Zhu, H. Hayashi, M. Chen, C. Xiao, K. Matsuo, N. Aratani, L. Zhang, H. Yamada, *J. Mater. Chem. C* **2022**, *10*, 2527.

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非対称型 5,15 置換テトラベンゾポルフィリンの合成と電荷輸送特性

（奈良先端大先端科技）○宮﨑 和哉・松尾 恭平・荒谷 直樹・山田 容子

Synthesis and charge transport properties of asymmetric 5,15-substituted tetrabenzoporphyrins

(*Graduate School of Science and Technology, Nara Institute of Science and Technology*) ○ Kazuya Miyazaki, Kyohei Matsuo, Naoki Aratani, Hiroko Yamada

Tetrabenzoporphyrins (TBPs) are promising organic semiconductors due to the rigid structure and two-dimensionally extended π-conjugation. However, the tendency of 5,15-substituted TBPs to form one-dimensional crossed π-stacking structure is disadvantageous for organic field-effect transistor (OFET) applications utilizing polycrystalline thin films. We found that asymmetric TBP derivative with different substituents at 5 and 15 positions preferentially form two-dimensional slipped π-stacking structures to maintain steric and electronic balance of its aggregate. Their synthesis, crystal structures, and OFET characteristics will be presented.

Keywords : Tetrabenzoporphyrin; Crystal structure analysis; Organic field-effect transistors

テトラベンゾポルフィリン(TBP)は剛直で二次元的に広がったπ共役系を有する色素骨格であり、優れた有機半導体材料として注目を集めている。一方、5,15 位に置換基を導入した TBP 誘導体は置換基の衝突を避けるために TBP ユニットが 90 度回転してπスタックした一次元的な交差積層構造を形成しやすい傾向があり、多結晶膜を活性層とする有機電界効果トランジスタ(OFET)の応用には不利であった。今回、我々は 5,15 位に異なる種類の置換基を導入した TBP 誘導体(**TIPS-Ph-TBP**)を合成し、単結晶 X 線構造解析を行ったところ、TBP ユニットが 180 度回転した上でずれて積層した二次元的なπスタック構造を優先的に形成することを見出した(Figure 1)。これは非対称な分子が交差積層した場合、立体的・電子的な釣り合いが取れず不利になるため、ずれたπスタック構造が熱力学的により安定になったためだと考えられる。発表では、OFET 作製・評価についても議論する予定である。

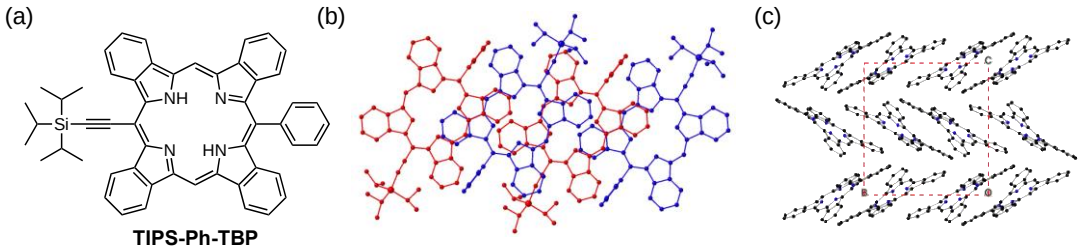


Figure 1. (a) Molecular structure and (b, c) packing structures of **TIPS-Ph-TBP**.

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部分的に共役したピロール-キノン架橋型π電子系：脱プロトン化およびイオンペア形成によるジラジカル性の発現と変調

（立命館大生命科学[1]・阪大院理[2]）○杉浦 慎哉[1]・久保 孝史[2]・前田 大光[1]
Deprotonation-Induced and Ion-Pairing-Modulated Diradical Properties of Partially Conjugated Pyrrole-Quinone Conjunction ([1]*College of Life Sciences, Ritsumeikan University*, [2]*Graduate School of Science, Osaka University*) ○Shinya Sugiura,[1] Takashi Kubo,[2] Hiromitsu Maeda[1]

Quinoidal molecules based on di**p**yrrolyldiketone **b**oron complexes (**QPB**s), in which pyrrole units were connected by a partially conjugated system as a singlet spin coupler, were synthesized. **QPB**, which was stabilized by the introduction of a benzo unit at the pyrrole β-positions, formed a closed-shell tautomer conformation that showed near-infrared absorption. The deprotonated species, **QPB**$^{-}$ and **QPB**$^{2-}$, showing over 1000-nm absorption, were formed by the addition of bases, providing ion pairs in combination with countercations. Cation-dependent diradical properties were observed in **QPB**$^{2-}$, whose singlet-state diradical was more stable than the triplet-state diradical.
Keywords : pyrrole derivatives; quinoidal derivatives; diradical property; ion pairs; π-conjugated systems

拡張π電子系キノン誘導体は、ジラジカル特性や長波長領域の吸収を示すことから、多様な分野で注目されている。本研究では、ピロールを基盤としたキノンユニットを、共役の寄与が大きい交差共役系であるジケトンホウ素錯体で架橋した新規π電子系（**QPB**s）の開拓をめざした（Figure 1a）。**QPB** は閉殻系を示し、ピロールのπ拡張による安定化が観察された。一方、塩基による脱プロトン化によって、近赤外領域の吸収を示す **QPB**$^{-}$および **QPB**$^{2-}$が形成され、多様なカチオンとのイオンペア形成が可能であることを見出した。また、ジアニオン体 **QPB**$^{2-}$は理論計算や ESR からジラジカル性が確認され、ESR の温度依存性から一重項状態がより安定であることが示唆された（Figure 1b）。**QPB**$^{2-}$の安定性やジラジカル性が対カチオンによって変化し、イオンペアリングによるスピン状態の制御が可能であることを明らかにした。[1)]

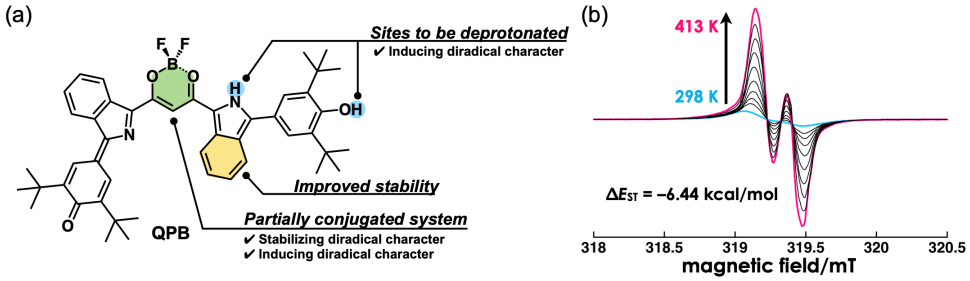


Figure 1. (a) Conceptual diagram of **PB**-based quinoidal molecules (**QPB**s) and (b) variable-temperature ESR spectral change of **QPB**$^{2-}$.

1) Sugiura, S.; Kubo, T.; Haketa, Y.; Shigeta, Y.; Sakai, H.; Hasobe, T.; Maeda, H. to be submitted.

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Control of Aromatic Ring Inversion in Calix[3]pyrrole

([1]*Grad. Sch. Eng., Hokkaido Univ.*, [2]*WPI-ICReDD, Hokkaido Univ.*) ○Yuya Inaba,[1] Yu Kakibayashi,[1] Yasuhide Inokuma[1,2]

Keywords: Calix[3]pyrrole; Ring inversion; Strained molecules; Boron complex; Planar chirality

Inversion of aromatic rings in macrocyclic compounds such as calixarenes or calixpyrroles can dynamically change their conformations and alter their reactivity, host-guest interactions, and chirality. In this work, we investigated aromatic ring inversion behaviors of calix[3]pyrrole[1], a ring contracted analogue of calix[4]pyrrole, and its derivatives.

Pyrrole ring inversion in calix[3]pyrrole **1** was rapid in solution to be observed as a time averaged C_3 symmetric molecule in ^{1}H NMR spectrum (**Fig. 1a**). Upon binding of fluoride anion, **1** adopts cone-like conformation to have hydrogen-bonds with fluoride efficiently. When two pyrrole rings of **1** were replaced with furan and thiophene rings to give **2**, its nonplanar conformations became chiral. Though two enantiomers of **2** were separated by chiral HPLC and exhibited mirror-image CD spectra, **2** underwent racemization via aromatic ring inversion in *n*-hexane/*i*-PrOH (v/v = 1/1) at room temperature with a half-life of 2.1 hours at 298 K (**Fig. 1b**). When **2** was methylated at NH site to give **3** in 50% yield, aromatic ring inversion was effectively suppressed. Enantiomers of **3** were successfully separated using chiral HPLC, and no racemization was observed for over a month at room temperature. The crystal structure of one of the enantiomers showed partial cone conformation that can be assigned as (R_p, S_p, S_p) with respect to thiophene, furan, and pyrrole plane respectively (**Fig. 1c**). This difference in racemization behaviors between **2** and **3** were applied for chiral recognition during *N*-methylation using chiral ammonium salt.

Furthermore, when the ring inversion in **1** was inhibited in its boron complex **4** (**Fig. 1d**), a drastic change was observed in its reactivity towards acids. While **1** caused rapid ring cleavage upon treatment with TFA, boron complex **4** showed amphophilic behavior with the macrocycle withstanding acidic conditions by reversible protonation at pyrrole ring.

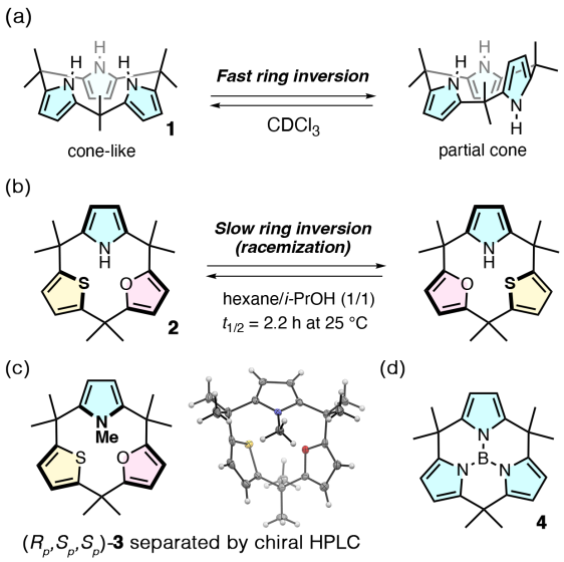


Fig. 1. (a) Pyrrole ring inversion in **1**, (b) aromatic ring inversion-based racemization of **2**, (c) molecular and crystal structure of (R_p, S_p, S_p)-**3** separated by chiral HPLC, and (d) molecular structure of **4**.

1) Y. Inaba, Y. Nomata, Y. Ide, J. Pirillo, Y. Hijikata, T. Yoneda, A. Osuka, J. L. Sessler, Y. Inokuma, *J. Am. Chem. Soc.*, **2021**, *143*, 12355–12360.

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Synthesis and Redox Properties of Silver and Nickel Complexes of N-confused Porphyrin Dimer

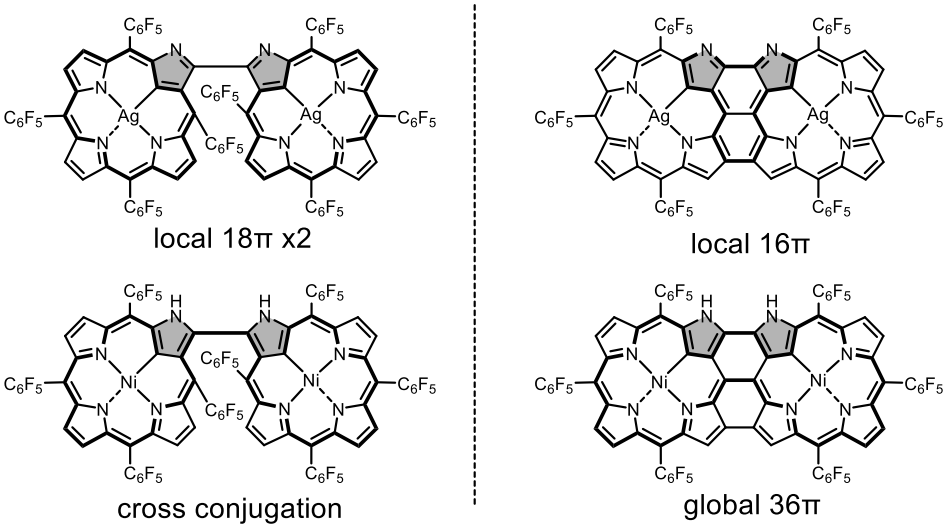
([1]*Graduate School of Engineering, Kyushu University*, [2]*Advanced Research Support Center, Ehime University,* [3]*Graduate School of Science, Tokyo Metropolitan University,* [4]*Research Organization of Science and Technology, Ritsumeikan University*) ○Osamu Iwanaga,[1] Shigeki Mori,[2] Masatoshi Ishida,[3] Soji Shimizu,[1] Hiroyuki Furuta[1,4]

Keywords: N-Confused Porphyrin; Dimeric Structure; π-Electronic System; Redox Properties

Owing to the unique near-infrared optical properties and molecular wires, various dimeric porphyrins and their related analogues have been developed so far.[1] The distance and orientation of the porphyrin units are essential factors in controlling the interchromophore electronic interactions and communications.

In this study, as a monomer unit of the dimeric porphyrin analogues, N-confused porphyrin (NCP) was used to synthesize singly- and triply-linked dimers. Owing to the NH tautomerism, NCP can provide the dianionic and trianionic coordination environments depending on the valence states of the central metal ions. In the case of dimers, the NH tautomerism and orientation of NCP units can change the interchromophore electronic interactions and communications. The unique optical and electrochemical properties of the NCP dimers were investigated by UV/vis/NIR absorption and NMR spectroscopy, electrochemical measurements, and theoretical calculations.

In this presentation, the detail of the synthesis and properties of a series of NCP dimers will be presented.



1) a) A. Osuka, H. Shimidzu, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135. b) N. Yoshida, H. Shimidzu, A. Osuka, *Chem. Lett.* **1998**, 55. c) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Angew. Chem. Int. Ed.* **1999**, *38*, 176.

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Panchromatic Absorption of Pyrrolopyrrole aza-BODIPY analogs Based on the Push-Pull Strategy

(*Graduate School of Engineering, Kyushu University*) ○Yitong Wang, Soji Shimizu
Keywords: BODIPY, NIR Chromophore, Panchromatic Absorption

The creation of novel push-pull chromophores and studies on their attractive properties including intramolecular charge-transfer (ICT) bands and nonlinear optical properties are attracting research interest because of their impact on next-generation electronic and optoelectronic devices. Tetracyanobuta-1,3-diene (TCBD) is a powerful electron-accepting unit, which is easily integrated into activated alkynes via a [2+2] cycloaddition-retroelectrocyclization (CA-RE) reaction.[1]

With these in mind, a push-pull unit consisting of triphenylamine and TCBD was linked to aza-BODIPY analogues called pyrrolopyrrole aza-BODIPYs (PPABs),[2] resulting in panchromatic visible/near-infrared chromophores (Figure 1). The charge transfer from the push-pull units to the PPAB core can be controlled by the linker units: in the case of the 2,5-thienylene liker the red-shift of the absorption is more significant compared with the 1,4-phenylene linker. In both cases, the fluorescence emission was quenched probably due to the charge separation and recombination in the excited state. Cyclic voltammetry (CV) and differential pulse voltammograms (DPV) revealed multistep electrochemical reduction properties for both compounds.

In this presentation, the synthesis, and optical and electrochemical properties of these panchromatic PPABs will be presented.

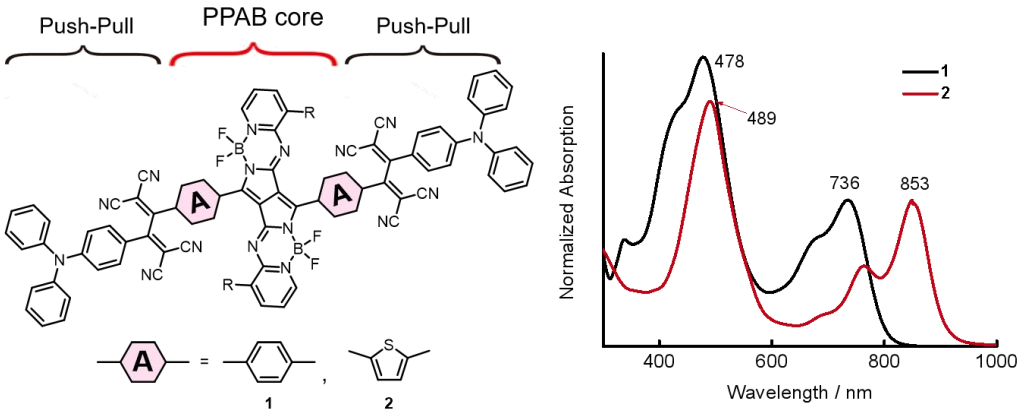


Figure 1. Structures of panchromatic PPABs and the UV/vis/NIR absorption spectra in chloroform.

1) T. Michinobu, D. François, *Angew. Chem., Int. Ed.* **2018**, *57*, 3552.
2) S. Shimizu, T. Iino, Y. Araki, N. Kobayashi, *Chem. Commun.* **2013**, *49*, 1621.

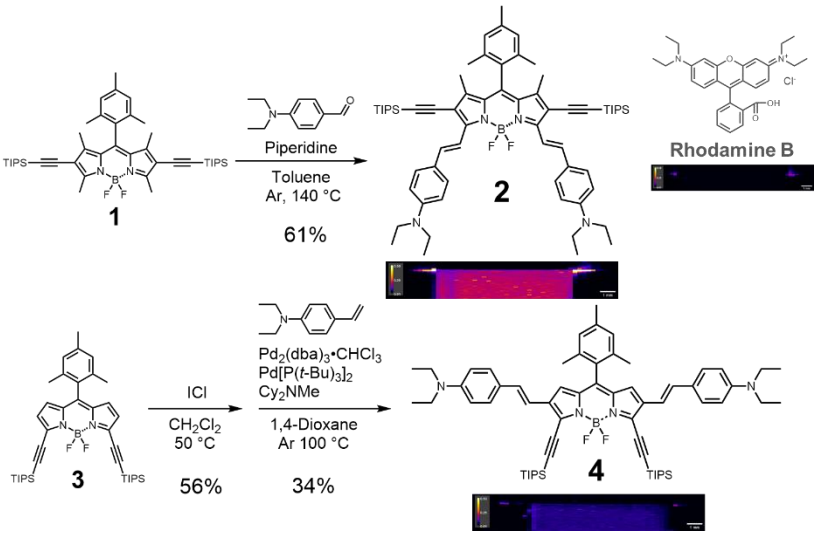
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二光子励起光音響イメージング造影剤を指向した電子ドナーを有する BODIPY 誘導体の合成と光学特性

（九大院工[1]・都立大院理[2]・立命館大総合科学技術研究機構[3]）○嶋田隆秀[1]・石田真敏[2]・清水宗治[1]・古田弘幸[3]
Synthesis and properties of electron-donor-substituted BODIPY-based contrast agents for two-photon-excitation-induced photoacoustic imaging (*[1]Graduate School of Engineering, Kyushu University, [2]Graduate School of Science, Tokyo Metropolitan University, [3]Research Organization of Science and Technology, Ritsumeikan University*) ○ Takahide Shimada,[1] Masatoshi Ishida,[2] Soji Shimizu,[1] Hiroyuki Furuta[3]

In recent years, the creation of novel contrast agents for two-photon excitation-induced photoacoustic imaging has attracted attention to visualizing deep tissues with high spatial resolution in the bio-imaging application. Considering the high transparency of the second near-infrared light in body tissues, the combined technology of nonlinear photoacoustic imaging can improve the imaging resolution and depth of the target tissue. Herein, we report the synthesis of novel D-π-A-π-D type BODIPY derivatives (i.e., **2** and **4**) having ethynyl (-C≡C-) groups and electron-donating diethylaniline substituents bridged by ethylene (-C=C-) at arbitrary positions in the BODIPY backbone. The resulting BODIPY derivatives exhibit intense photoacoustic signals induced by two-photon excitation compared to the reference dye, namely Rhodamine B. The structure-property relationship will be reported in this presentation.
Keywords : BODIPY; Photoacoustic imaging; Two-photon excitation

近年、深部組織の可視化を指向して、生体透過性の高い第二近赤外光を活用する二光子励起光音響造影剤が注目されている。本研究では、エチニル基(−C≡C−)およびエチレン（−C=C−）で架橋された電子ドナー性のジエチルアニリン置換基を有する D-π-A-π-D 型 BODIPY 誘導体(**2** および **4**)を設計・合成し、光学特性評価を行った。得られた誘導体では二光子吸収に誘起される高い光音響信号を観測した。また、比較として用いた Rhodamine B では光音響イメージング画像が観測できない程の低い励起光強度でも、**2**および **4** では光音響イメージング画像を観測することに成功している。本発表では、色素分子の合成および構造と光音響特性の相関について、詳細を報告する。



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[K603-2pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Eiichi Kayahara, Ryo Sekiya

Thu. Mar 23, 2023 1:30 PM - 3:40 PM K603 (K603, Lecture Hall Bldg. [6F])

[K603-2pm-01] Investigation of cyclobisbiphenylenecarbonyl adopting a figure-of-eight structure

○Norihito Fukui[1,2], Junichiro Hirano[1], Owase Daisuke[1], Emiko Nishimoto[1], Yuki Sakamoto[1], Ren Takayanagi[1], Keita Tajima[1], Hiroshi Shinokubo[1] （1. Grad. Sch. of Eng., Nagoya Univ., 2. JST PRESTO）

1:30 PM - 1:50 PM

[K603-2pm-02] Atomic-resolution visualization of non-planar graphene nanoribbon by using transmission electron microscopy

○Hiroki Hanayama[1], Xuelin Yao[2], Koji Harano[3], Klaus Muellen[2], Eiichi Nakamura[4], Akimitsu Narita[1,2] （1. Okinawa Institute of Science and Technology Graduate University, 2. Max Plank Institute for Polymer Research, 3. National Institute for Materials Science, 4. The University of Tokyo）

1:50 PM - 2:10 PM

[K603-2pm-03] Synthesis and Optical Properties of Novel Cyclic Compounds Using Fluorescence Chromophores

○Takahiro Kakuta[1], Yuka Kanadzu[1], Ryota Nakanishi[1], Tada-aki Yamagishi[1] （1. Kanazawa University）

2:10 PM - 2:30 PM

[K603-2pm-04] Synthesis of polyacene utilizing coordination nanospaces

○Takumi Miura[1], Takashi Kitao[1,2], Takashi Uemura[1] （1. Grad. Sch. of Eng. The Univ. of Tokyo, 2. JST-PRESTO）

2:40 PM - 3:00 PM

[K603-2pm-05] Synthesis of gigantic nanocarbon molecules via optimization of macrocyclization by Design-of-Experiments and machine learning

○Misato Akiyoshi[1], Koki Ikemoto[1], Tatsuru Mio[1], Kaito Nishioka[1], Sota Sato[1], Hiroyuki Isobe[1] （1. The University of Tokyo）

3:00 PM - 3:20 PM

[K603-2pm-06] Synthesis of soluble backbone-unsubstituted π-conjugated molecules

○Shusei Fujiki[1], Kazuma Amaike[1], Akiko Yagi[1], Kenichiro Itami[1] （1. Nagoya University）

3:20 PM - 3:40 PM

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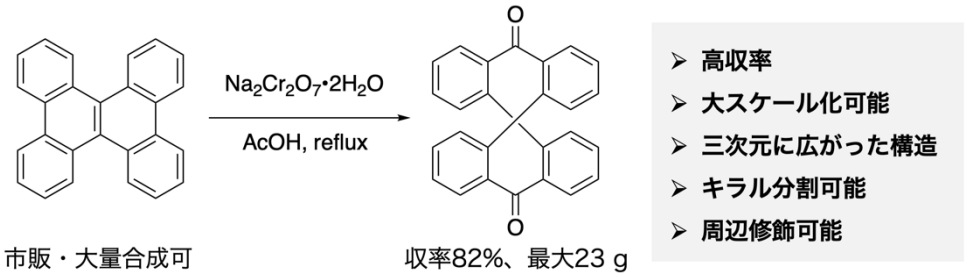
８の字型分子シクロビスビフェニレンカルボニルの機能探求

（名大院工 [1]・JST さきがけ [2]）○福井 識人 [1,2]・平野 純一朗 [1]・尾初瀬 大祐 [1]・西本 絵美子 [1]・坂本 祐樹 [1]・高柳 蓮 [1]・田島 慶太 [1]・忍久保 洋 [1]
Investigation of Cyclobisbiphenylenecarbonyl Adopting a Figure-of-eight Structure ([1]*Graduate School of Engineering, Nagoya University*, [2]*JST PRESTO*)○Norihito Fukui,[1,2] Junichiro Hirano,[1] Daisuke Owase,[1] Emiko Nishimoto,[1] Yuki Sakamoto,[1] Ren Takayanagi,[1] Keita Tajima,[1] Hiroshi Shinokubo[1]

Non-planar π-systems exhibit a variety of attractive properties. The development of readily accessible non-planar π-systems is helpful in promoting the investigation of these π-systems as novel functional materials. In particular, figure-of-eight molecules are fascinating due to their chirality and topology. However, a figure-of-eight molecule capable of large-scale preparation has been unexplored. In this presentation, we report that cyclobisbiphenylenecarbonyl (CBBC) is a figure-of-eight molecule, which is available in a large amount. We also disclose the fundamental properties of CBBC.
Keywords : Figure-of-eight Molecule; Non-planar π-Systems; Cyclobisbiphenylenecarbonyl; Oxidative Cleavage; Inner Modification

非平面π共役分子は三次元に広がった共役系を有し、平面π共役分子とは異なる多彩な機能を示す。したがって、大量合成可能な非平面π共役分子の創製は様々な応用を探る上で重要な基盤を与える。特に、８の字型分子は共役系のねじれの向きに応じて異なるキラリティーを示す。そのため、キラリティーに由来する光学特性や分子認識に注目が寄せられ、広く研究されている。しかし、大量合成可能な８の字型分子は報告がない。

ジベンゾ[*g*,*p*]クリセンの骨格内部の二重結合を酸化的に開裂することでシクロビスビフェニレンカルボニル（CBBC）が簡便に合成できることが 1934 年に Suszko と Schilak によって報告されている [1)]。また、1980 年には CBBC の結晶構造が報告されている [2)]。本研究では、この CBBC が大量合成可能な８の字型分子であることを示すとともに、その類縁体の合成を行なった。また、CBBC のキラル分割を実施するとともに、光学特性ならびに反転挙動の評価を行なった。



1) J. Suszko, R. Schilak, *Roczniki Chemii* **1934**, *14*, 1216. 2) T. S. Cameron, C. Chan, D. G. Morris, A. G. Shepherd, *Can. J. Chem.* **1980**, *58*, 777.

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Atomic-resolution visualization of non-planar graphene nanoribbon by using transmission electron microscopy

([1]*Organic and Carbon Nanomaterials unit, Okinawa Institute of Science and Technology Graduate University*, [2]*Max Plank Institute for Polymer Research,* [3]*Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS),* [4]*Department of Chemistry, The University of Tokyo*) ○Hiroki Hanayama,[1] Xuelin Yao,[2] Koji Harano,[3] Klaus Müllen,[2] Eiichi Nakamura,[4] Akimitsu Narita

Keywords: Graphene nanoribbon; Transmission electron microscopy

Synthesis of atomically precise graphene nanostructures was achieved by the development of the "bottom-up" method and revealed the unique chemical properties depending on their structures.[1] While these structures were mostly planar, the non-planar graphene nanoribbon (GNR) has attracted much attention because they are expected to have unprecedented chiroptic, mechanical, and electromagnetic properties. However, their structural characterization is very challenging. Scanning probe microscopy can visualize the planar structure at atomic resolution, but the high resolution cannot be achieved for non-planar structure.

Here we report the observation of fjord-GNR,[2] non-planar GNR with helically twisted structure, by using transmission electron microscopy (TEM). The isolation of a single GNR was achieved by covalent anchoring to an amino group introduced on the tip of carbon nanohorn and washing out excess GNRs. Moreover, the edge-chlorination reaction assisted the structural analysis of GNR by increasing the contrast in TEM images (Figure 1a). The dotted contrast of Cl atoms in TEM image was well reproduced by simulation analysis (Figure 1b).

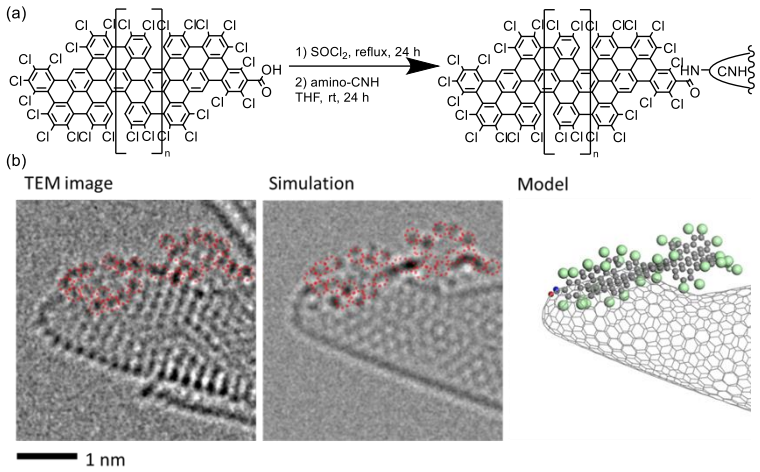


Figure 1. TEM observation of a non-planar graphene nanoribbon. (a) Molecular structure of chlorinated fjord-edged GNR (Cl-FGNR) and reaction with amino-functionalized carbon nanohorn. (b) TEM image, its simulation, and a corresponding molecular model of Cl-FGNR.

1) A. Narita, et al. *Chem. Sci.* **2019**, *10*, 964. 2) Yao, X.et al. *J. Am. Chem. Soc.* **2021**, *143*, 5654.

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発光色素を利用した新規環状化合物の合成と光学特性

（金沢大[1]）○角田 貴洋[1]・金津 有伽[1]・中西 良太[1]・山岸 忠明[1]
Synthesis and Optical Properties of Novel Cyclic Compounds Using Fluorescence Chromophores ([1]*Kanazawa University*) ○ Takahiro Kakuta,[1] Yuka Kanadzu,[1] Ryota Nakanishi,[1] Tada-aki Yamagishi[1]

Cyclic compounds have host-guest interactions properties to incorporate guest molecules inside a cavity. Fluorescence cyclic compounds based on fluorescent dyes and π-conjugated structure have been reported to change their optical properties through host-guest interactions. Since optical properties of these compounds were changed by selectively interacting with a guest molecule, they are expected to be applied as sensing materials. On the other hand, many fluorescence compounds show emission in solution. Therefore, it is difficult to use in the solid state. In this study, we synthesized novel fluorescence cyclic compounds (TPE Rings) based on tetraphenylethene (TPE). Because TPE exhibits strong emission in the solid state, TPE Rings showed emission in film state. The optical properties of the cyclic compounds are become different depending on cross-linking aromatic compounds.
Keywords : Tetraphenylethene; Cyclic structures; Metal ions; Host-guest interaction

環状化合物は、内部空孔にゲスト分子を取り込むホストーゲスト相互作用を示す。環状化合物のうち、蛍光色素や π 共役系で構成されたものは、発光性環状化合物としてホストーゲスト相互作用により光学特性変化すると報告されている。光学特性の変化は、空孔サイズに見合うゲスト分子に選択的に生じるため、センシング材料としての応用が期待される。一方、多くの発光色素が溶液中で発現することから、固体状態での利用は制限されていた。本研究では、固体状態で強い発光特性を示す、テトラフェニルエテンを基本とする新規発光性環状化合物 (TPERings) を合成した (Figure 1)。ベンゼン環で架橋した TPE Rings (BR) は、$CHCl_3$ 中で 249 nm と 337 nm に吸収ピークを示した。加えて、270 nm の励起光により 455 nm に発光ピークを示した。これに対して、アントラセンやフェナントレンで架橋した、AR や PhR は、より超波長域に発光を示した。これは、結合する芳香族化合物により環の平面性が変化したためと考えられる。

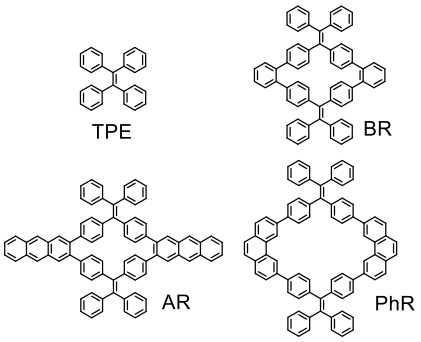


Figure 1. Chemical structures of TPE, BR, AR and PhR.

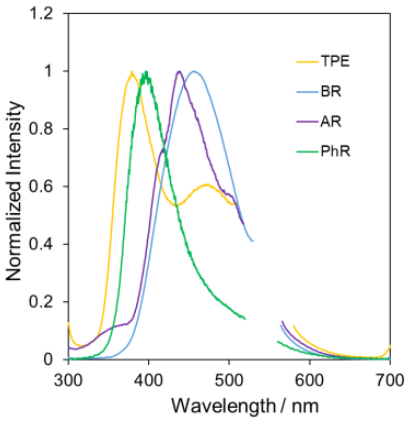


Figure 3. Fluorescence spectra of TPE, BR, AR and PhR in CH_3Cl exited at 270 nm.

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Synthesis of Polyacene Utilizing Coordination Nanospaces

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*JST-PRESTO*)
○Takumi Miura,[1] Takashi Kitao,[1,2] Takashi Uemura[1]
Keywords: Metal–Organic Framework; Polyacene; Annulation reaction

Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings. The intriguing feature of acenes—evolution of physical properties with an increase in the benzene ring number—fascinated a wide spectrum of researchers. However, the synthesis of long acenes has been challenging due to their low solubility and inherent chemical instability. Since the first synthesis of pentacene in 1912,[1] the length of acenes has been gradually increased (one benzene ring at a time) via solution and on-surface synthesis, reaching dodecacene (12 rings), the longest acene reported so far.[2]

Here, we present a new methodology to extend the acene systems, mediated by a metal–organic framework (MOF), achieving the first synthesis of polymeric acenes with numerous benzene rings, namely polyacene.[3] The strategy involves two steps: controlled synthesis of a polymeric hydroacene as a precursor within the MOF nanochannels, and the subsequent conversion into polyacene via dehydro-aromatization reaction (**Fig. 1**). The geometrical constraints of the MOF allowed for suppression of unfavorable crosslinking reactions, providing the linearly extended polymeric precursor. A series of characterizations, including solid-state NMR, UV/vis/NIR, and FT-IR spectroscopy measurements, confirmed the formation of polyacene that was overwhelmingly longer than the previously reported ones. The bulk-scale synthesis of polyacene will open up a new avenue toward not only unveiling the unique topological properties of the acene series but also its future applications in organic electronics and spintronics.

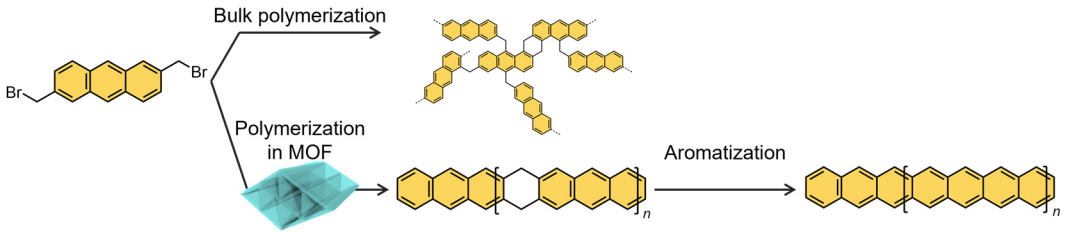


Fig. 1 Synthetic procedure of polyacene using a MOF.

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2) F. Eisenhut, *et al*., *ACS Nano* **2020**, *14*, 1011.
3) T. Kitao, T. Miura, T. Uemura, *et al*., *submitted* (ChemRxiv, DOI: 10.26434/chemrxiv-2022-151bv).

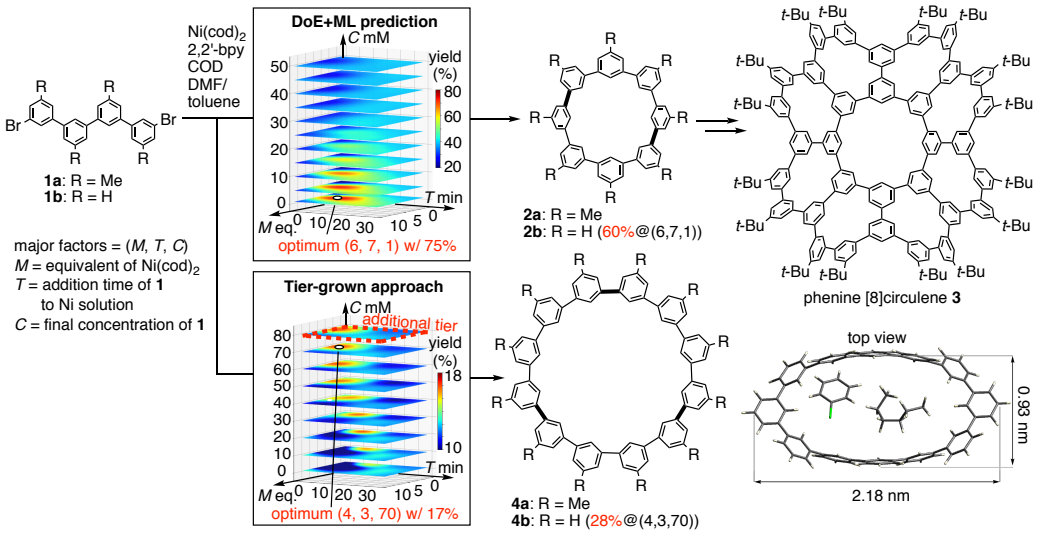
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Synthesis of Gigantic Nanocarbon Molecules via Optimization of Macrocyclization by Design-of-Experiments and Machine Learning

(*Department of Chemistry, The University of Tokyo*) ○Misato Akiyoshi, Koki Ikemoto, Tatsuru Mio, Kaito Nishioka, Sota Sato, Hiroyuki Isobe

Keywords: Design-of-Experiments, Machine Learning, Macrocyclization, Nanocarbon Molecules, Coupling

Establishing models of scientific phenomena is an important part of science, and rational mechanistic models of reactions have been traditionally elucidated via one-factor-at-a-time optimizations in synthetic experiments. In this study, we developed a method to elucidate empirical models of reactions via Design-of-Experiments (DoE) optimization with machine learning (ML) supplements.[1,2] The empirical model was first established for a 3D parameter space of oligomeric macrocyclization of **1**. Three factors, *M* = equivalent of $Ni(cod)_2$, *T* = addition time of **1** and *C* = final concentration of **1**, were adopted for optimization, runs were specified by DoE, and the model was generated as heatmaps of yields with ML supplements through examinations of four ML methods. The yield of dimer (**2b**) was consequently improved to 60%, which allowed for synthesis of phenine [8]circulene (**3**) with a molecular formula of $C_{256}H_{240}$. This "DoE+ML" approach of model constructions was further developed, and the heatmap empirical model was rationally expanded for trimerization to **4** by integrating an additional tier without ruining efficient space coverage of DoE. This tier-grown approach led to synthesis of the largest congener of [*n*]cyclo-*meta*-phenylene with *n* = 12.



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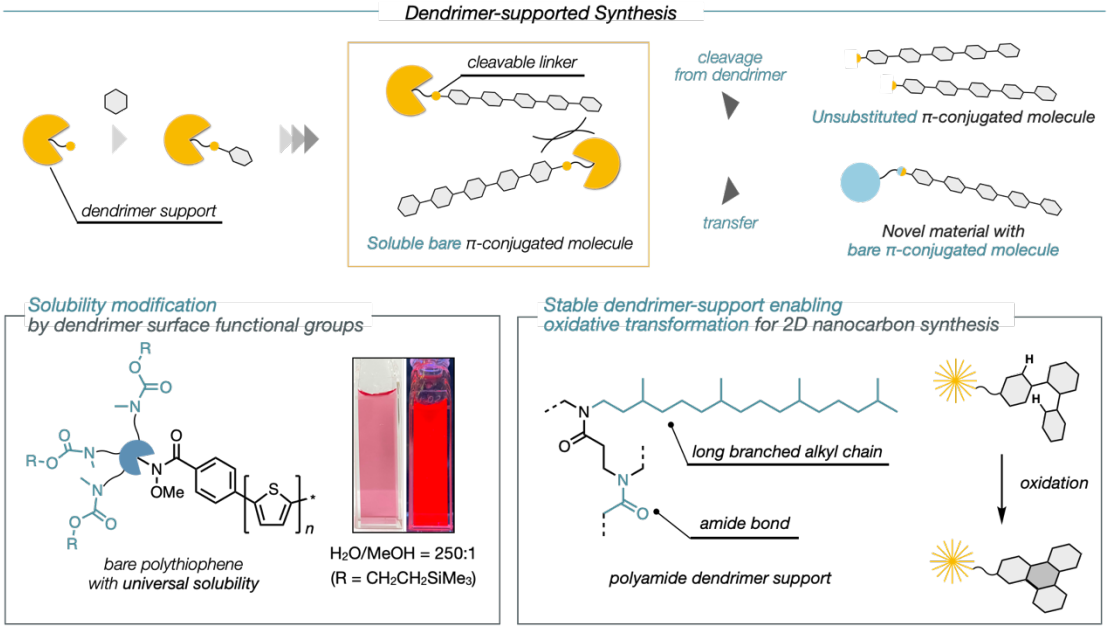
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Synthesis of Soluble Backbone-unsubstituted π-Conjugated Molecules

([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*) ○ Shusei Fujiki,[1] Kazuma Amaike,[1] Akiko Yagi,[1,2] Kenichiro Itami[1,2]

Keywords: *Molecular Nanocarbons; Insoluble Compound; Dendrimer*

π-Conjugated molecules including aromatic polymers and nanographenes are promising molecular entities for electronic devices. Because of their strong intermolecular interactions, planar π-conjugated molecules easily form aggregates. In order to suppress the aggregation, long alkyl or alkoxy chains are often installed as substituents. Since the substituents cause the change of physical properties, a synthetic method for bare, namely backbone-unsubstituted, π-conjugated molecules is highly demanded. Recently, we reported a novel synthetic method to access bare aromatic polymers.[1] In this synthetic method, bare aromatic polymers can be synthesized on huge poly(aryl alkyl ether) dendrimers in order to prevent aggregation. Since the thus-obtained dendrimer-ligated aromatic polymers are highly soluble to hexane, THF and chloroform, they can be transformed to truly unsubstituted cognate and hybridized with non-organic materials such as protein and silica gel. In addition, solubility modification can be achieved by introducing carbamate groups to the dendrimer surface. The bare polythiophenes attached to the dendrimer containing 18 carbamate groups have universal solubility from hexane to water/methanol = 250:1. Since the poly(aryl alkyl ether) dendrimer is fragile under oxidative reaction condition, more stable dendrimer support was also designed to expand the synthetic scope of our strategy. Thus, a stable polyamide dendrimer bearing 16 long branched alkyl chains on its periphery was synthetized and oxidative synthesis of bare two-dimentional π-conjugated molecules were examined on the polyamide dendrimer support.



[1] Fujiki, S.; Amaike, K.; Yagi, A.; Itami, K. *Nat. Commun.* **2022**, *13*, 5358.

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[K606-2am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Daichi Kitagawa, Yuichiro Tokoro
Thu. Mar 23, 2023 9:00 AM - 11:40 AM K606 (K606, Lecture Hall Bldg. [6F])

[K606-2am-01] Tunable Rigidochromism of Copper-Pyrazolate Complexes

○Yuichiro Watanabe[1], Benjamin Washer[2], Matthias Zeller[2], Sergei Savikhin[2], Lyudmila Slipchenko[2], Alexander Wei[2] （1. Kyoto University, 2. Purdue University）

9:00 AM - 9:20 AM

[K606-2am-02] Turn-on Vapoluminescence Behavior of Host– Guest Complex Crystals between Liquid Phosphorescence Molecules and Pillar[5]arenes

○Keisuke Wada[1], Yuya Oshima[2], Shunsuke Ohtani[1], Kenichi Kato[1], Yosuke Tani[2,3], Takashi Tachikawa[4], Tomoki Ogoshi[1,5] （1. Grad. Sch. Eng., Kyoto Univ., 2. Grad. Sch. Sci., Osaka Univ., 3. ICS-OTRI, Osaka Univ., 4. Mol. PhotoSci. Res. Center, Kobe Univ., 5. WPI-NanoLSI, Kanazawa Univ.）

9:20 AM - 9:40 AM

[K606-2am-03] Synergistic Effects of Molecular Machine and Photoluminescent Dye

○Ryojun Toyoda[1,2], Ben L. Feringa[2] （1. Tohoku University, 2. University of Groningen）

9:40 AM - 10:00 AM

[K606-2am-04] Intermolecular Photochromic Reaction in Rhodamine Spirolactam Derivatives

○Yuki Nagai[1], Genki Kawai[1], Yoshinori Okayasu[1], Yoichi Kobayashi[1,2] （1. Ritsumeikan Univ., 2. PRESTO JST）

10:00 AM - 10:20 AM

[K606-2am-05] Thermochromic afterglow of boronate co-crystals

○Kaede Kawaguchi[1], Masato Ito[1], Yuji Kubo[1] （1. Grad. Sch. Urban Environ. Sci., Tokyo Metropolitan Univ. ）

10:20 AM - 10:40 AM

[K606-2am-06] Ion-Pairing Electronic Properties Based on π-Stacked Ion Pairs

○Hiroki Tanaka[1], Yoichi Kobayashi[1], Ko Furukawa[2], Hiromitsu Maeda[1] （1. Ritsumeikan University, 2. Niigata University）

10:40 AM - 11:00 AM

[K606-2am-07] Solid State *Endo-Exo* Conformation Control of Benzyl-substituted Monofluorosumanene and its Mechanism

Minghong Li[1], Dongyi Zhou[1], Teppei Matsumura[3], ○Yumi Yakiyama[1,2], Nobuyuki Matsubayashi[3], Hidehiro Sakurai[1,2] （1. Grad. Sch. Eng., Osaka University , 2. ICS-OTRI, Osaka University , 3. Grad. Sch. Eng. Sci, Osaka University ）

11:00 AM - 11:20 AM

[K606-2am-08] Enantioselective crystallization of organic molecules manipulated by optical trapping with a circularly polarized laser beam

Tung-Ming Lin[1], Hao-Tse Su[1], An-Chieh Cheng[1,2], Keiji Sasaki[2], ○Teruki Sugiyama[1,3] （1. National Yang Ming Chiao Tung Univ., 2. Hokkaido Univ., 3. NAIST）

11:20 AM - 11:40 AM

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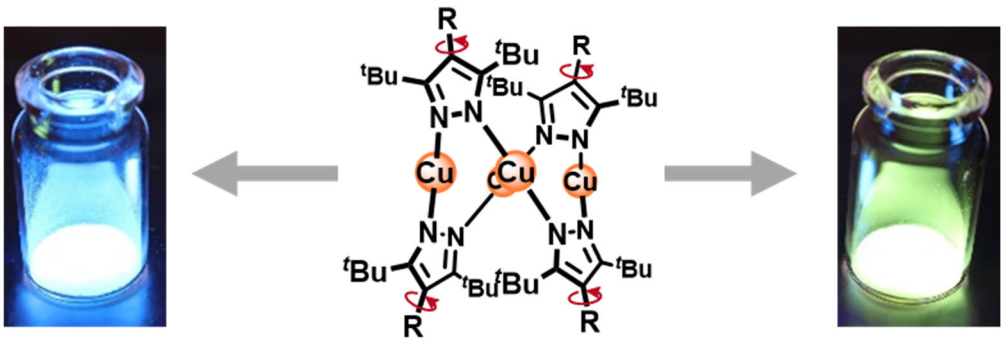
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Tunable Rigidochromism of Copper-Pyrazolate Complexes

([1]*Graduate School of Engineering, Kyoto University*, [2]*Department of Chemistry, Purdue University*) ○Yuichiro Watanabe,[1] Benjamin M. Washer,[2] Matthias Zeller,[2] Sergei Savikhin,[2] Lyudmila V. Slipchenko,[2] Alexander Wei[2]

Keywords: Solid-state Phosphorescence; Cluster Complexes; Steric Effect; Rigidochromism; Conformation Analysis

Copper(I) ions and pyrazoles can self-assemble into macrocyclic clusters with intense solid-state phosphorescence at ambient temperatures. We are investigating a series of tetranuclear Cu–pyrazolate (Cu_4pz_4) complexes having five different substituents at C4, including known complex **1** (R = H, λ_{em}: 559 nm)[1,2,3] plus four new complexes **2**–**5** (R = F, λ_{em}: 513 nm, Cl, Br, and CH_3, λ_{em}: 457–458 nm). Remarkably, X-ray crystal and computational analyses indicate the photoemission energies correlate with changes in their van der Waals volume (V_{vdW}) of the remote C4 substituents rather than electronic factors. These remote substituent effects are steric in nature and support a tunable rigidochromism with emissions ranging from yellow to deep blue, confirmed by TD-DFT calculations.[4] As pyrazole ligands increase in structural complexity, polymorphs with different luminescent wavelengths emerge that allow rigidochromic behavior to be tuned by extrinsic physical and chemical stimuli (i.e. heat, and hydrocarbon vapor treatment).



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Turn-on Vapoluminescence Behavior of Host–Guest Complex Crystals between Liquid Phosphorescence Molecules and Pillar[5]arenes

(*[1]Grad. Sch. of Eng., Kyoto Univ., [2]Grad. Sch. of Sci., Osaka Univ. [3]ICS-OTRI, Osaka Univ. [4]Mol. PhotoSci. Res. Center, Kobe Univ. [5]Kanazawa Univ., WPI-NanoLSI*)
○Keisuke Wada,[1] Yuya Oshima,[2] Shunsuke Ohtani,[1] Kenichi Kato,[1] Yosuke Tani,[2,3] Takashi Tachikawa,[4] Tomoki Ogoshi[1,2]
Keywords: Pillar[5]arene; Phosphorescence; Vapoluminescence; Host–Guest Complex

Room-temperature phosphorescence (RTP) of metal-free organic molecules is a critical research topic because of its potential application in biological imaging, optoelectronic materials, and sensing materials. Therefore, development of the organic RTP materials has been actively studied. Recently, some research groups have successfully improved the phosphorescence lifetime and quantum yield by using cyclic host molecules such as cyclodextrins and cucurbiturils to confine phosphorescent guest molecules.[1)] However, most of these studies focused only on the suppression of molecular motion by the confinement of phosphorescent guest in the cavity.

Pillar[5]arenes are cyclic molecules composed of diethoxybenzene and exhibit electron-donor properties. Therefore, pillar[5]arenes are able to form charge-transfer complex with electron-poor guest molecules via host–guest systems. In this study, host–guest complex crystals were obtained by immersing crystalline pillar[5]arenes in a liquid phosphorescent molecule (**DMOS**) (Fig. 1a). The phosphorescent emission observed from neat **DMOS** was effectively quenched by complexation (Fig. 1b). This is because charge-transfer complex formation between pillar[5]arene and **DMOS** occurred. In addition, *n*-hexane vapor, which is a guest molecule of pillar[5]arenes, pushed out **DMOS** from the pillar[5]arene cavity, and phosphorescent emission was recovered (Fig. 1c). As a result, the host–guest complex crystals showed guest vapor-induced turn-on phosphorescent emission.

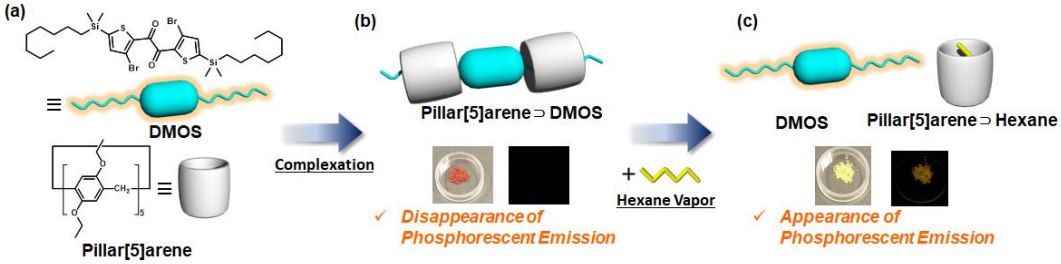


Fig. 1. (a) Chemical structures of pillar[5]arene and **DMOS**. (b) Quenching of phosphorescent emission induced by complexation. (c) Turn-on phosphorescent emission triggered by exposure to *n*-hexane vapor.

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Synergistic Effects of Molecular Machine and Photoluminescent Dye

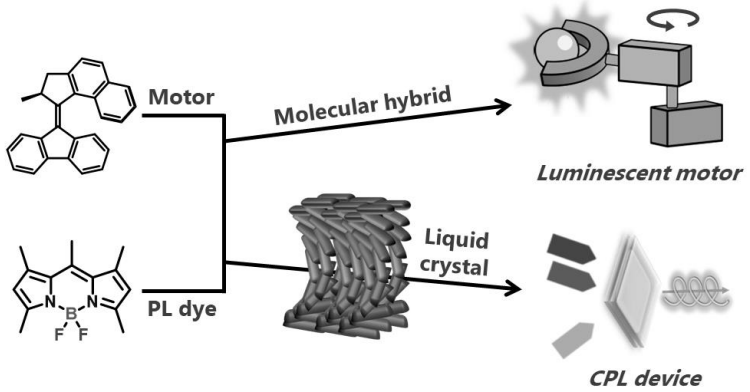
([1]*Graduate School of Science, Tohoku University*, [2]*Faculty of Science and Engineering, University of Groningen*) ○Ryojun Toyoda,[1,2] Ben L. Feringa[2]
Keywords: Molecular machine; BODIPY; Photoluminescence

After the successful development of light-driven molecular motors in the past decades, the next challenge is to combine the unidirectional rotary motion of these nano-machines with other light-mediated functions. Especially, photoluminescence (PL) properties are expected in terms of single-molecule imaging and development of photoswichable devices.

Here, a light-driven rotary molecular motor with a PL dye is developed, not compromising its motor function.[1] In this molecule, a well-known PL dye BODIPY is attached perpendicular to the upper half plane of the 2nd generation molecular motor. This design suppresses direct conjugation between the two functional groups, successfully affording efficient rotary motion and bright PL. This feature is advantageous for tracking the motion of the motor. Interestingly, the two photofunctions can be addressed by a proper choice of excitation wavelengths and solvents, and synergistic effects are observed between the two photofunctional moieties such as visible-light-driven motor rotation, switchable PL and chirality transfer from the motor to the otherwise achiral BODIPY part.

Furthermore, when a molecular motor and an achiral BODIPY are mixed in liquid crystal media, circularly polarized luminescence (CPL) with a high PL quantum yield and a large dissymmetry factor is generated.[2] Tuning of the color of the CPL and the retention time of the photoprogrammed helicity is achieved making use of a variety of molecular motors and PL dyes. This system opens possibilities for pixilated displays with externally addressable polarization.

The utility of PL for exploiting the potential of molecular machines is demonstrated.



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ローダミンスピロラクタム誘導体における分子間フォトクロミック反応

(立命館大生命科学[1]・JST さきがけ[2]) ○永井 邑樹[1]・河合 彦希[1]・岡安 祥徳[1]・小林 洋一[1,2]

Intermolecular Photochromic Reaction in Rhodamine Spirolactam Derivatives ([1]*College of Life Sciences, Ritsumeikan University*, [2]*PRESTO JST*) ○ Yuki Nagai,[1] Genki Kawai,[1] Yoshinori Okayasu,[1] Yoichi Kobayashi[1,2]

Understanding the effects of intermolecular interaction on photochromism leads to unique photofunctions, especially in molecular assemblies and condensed phases. In this research, the excitation dynamics of a perylene-substituted rhodamine spirolactam derivative (Rh-Pe, Fig. 1a) was investigated using transient absorption spectroscopy. As a result, we found its photochromic reaction dependent on intermolecular interaction. The ring-closing form of Rh-Pe has no absorption above 500 nm, but the ring-opening form, which shows an absorption peak at 570 nm, is generated under UV irradiation (365 nm). Interestingly, the back reaction from the ring-opening to ring-closing form was accelerated as the concentration and the excitation intensity is higher (Fig. 1b). This indicates that the back reaction is affected by intermolecular interaction between the ring-opening forms.

Keywords : Photochromism; Perylene; Radical Anion; Charge Separation; Transient Absorption Spectroscopy

近年、超分子集合体や凝縮系材料にフォトクロミック分子を導入し、巨視的性状を劇的に光制御しようとする試みが盛んに行われている。こうした系において、分子間相互作用によってフォトクロミック反応を制御することができれば、分子集合系ならではの光機能の開発に繋がる。本研究では、ペリレン置換ローダミンスピロラクタム誘導体 (Rh-Pe, Fig. 1a) の励起ダイナミクスを過渡吸収分光法により追跡した。この結果、分子間反応に依存するフォトクロミック反応を見出した。

Rh-Pe の閉環体は波長 500 nm 以下にしか吸収を持たないが、紫外光 (波長 365 nm) を照射すると波長 570 nm に極大吸収を示す開環体が生成する。興味深いことに、この開環体から閉環体への熱戻り反応は濃度が高いほど、また励起光強度が強いほど速くなった (Fig. 1b)。このことから、熱戻り反応の速度は開環体濃度に依存しており、開環体同士の相互作用に影響を受けることが示唆された。

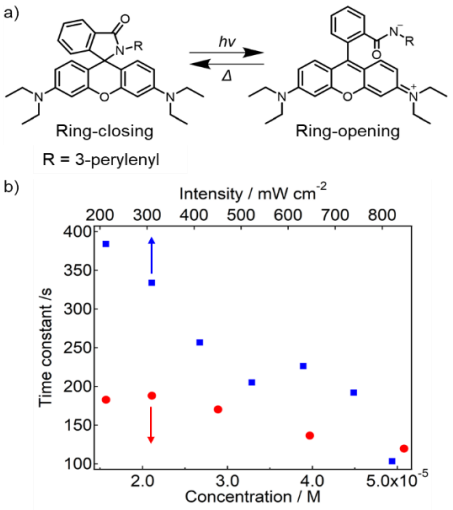


Fig. 1 a) Photochromic reaction of Rh-Pe, b) Time constants of the back reaction in acetonitrile in various concentrations (Excitation intensity: 350 mW cm^{-2}) and under various excitation intensities (Conc.: 5.8×10^{-5} M).

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ボロネート共結晶のサーモクロミック残光

（都立大院都市環境）○川口 楓・伊藤 正人・久保 由治
Thermochromic afterglow of boronate co-crystals ([1]*Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*) ○Kaede Kawaguchi, Masato Ito, Yuji Kubo

Recently, it has been reported that some donor-acceptor (D–A) linked compounds exhibit thermochromic dual phosphorescence at cryogenic temperature[1, 2]. Herein, we found that solid-state benzene-1,4-diboronic acid (**BDBA**), in spite of its no D–A structure, exhibited a thermochromic dual phosphorescence under 150 K. Notably, **BDBA**-doped co-crystal using trimethylolpropane (**TMP**) as a host material enabled it to detect a change in the afterglow with increasing temperature up to 40 ºC (Fig. 1a). According to the theoretical calculations, it was revealed that the dual phosphorescence was owing to the emission from T_1 and T_2, where the slow T_2–T_1 internal conversion (IC) due to their different excited-state structure would be the origin of dual phosphorescence (Fig. 1b). Further, it was clarified that the geometry relaxation at singlet excited state plays an important role in the intersystem crossing of **BDBA**.

Keywords: Thermochromic emission; Room-temperature phosphorescence; Afterglow; Excited-state dynamics; Boronic acid

近年, いくつかのドナー–アクセプター (D–A) 型化合物がサーモクロミック二重燐光を示すことが報告されており [1, 2]，いずれも細胞内温度プローブや極低温温度センサーへの応用が期待されている．今回我々は，ベンゼン-1,4-ジボロン酸 (**BDBA**) の固体が，D–A 型構造を持たないにも関わらず、サーモクロミック燐光特性を示すことを見出した．さらに，トリメチロールプロパン (**TMP**) をホストとして用いた共結晶化によりサーモクロミック燐光挙動を室温領域 (313 K) まで引き上げることに成功した (Fig. 1a) ．この光学特性を理論計算と合わせて調査したところ，二重燐光はそれぞれ T_1 と T_2 からの発光であり，両状態の最安定構造が異なることにより T_2–T_1 内部転換が遅いことが原因であると示唆された (Fig. 1b) ．さらに，**BDBA** の項間交差において一重項励起状態における構造緩和が重要な役割を果たすことがわかった．

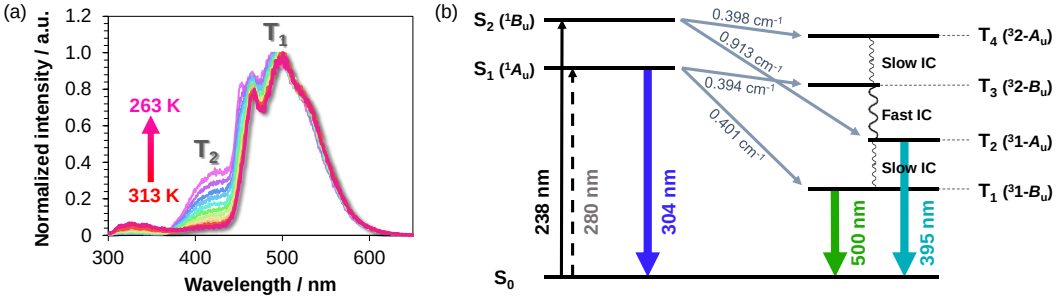


Fig. 1. (a) Temperature dependent delayed emission spectra of **BDBA/TMP** co-crystal (λ_{ex} = 254 nm, delay: 50 ms, [**BDBA**] = 0.05 mol%). (b) Plausible Jablonski diagram of **BDBA** based on the theoretical calculations.

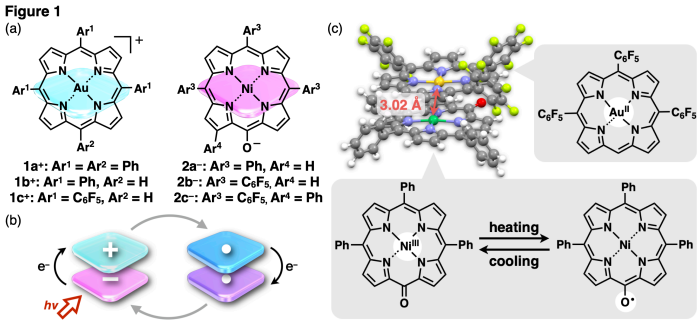
1) G. Zhang *et al.*, *Nat. Commun.*, **2021**, *12*, 1364.
2) E. Zysman-Colman *et al.*, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202206681.

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荷電 π 電子系の積層構造を基盤としたイオンペアリング電子物性

（立命館大生命科学[1]・新潟大研究推進機構[2]）○田中 宏樹[1]・小林 洋一[1]・古川 貢[2]・前田 大光[1]
Ion-Pairing Electronic Properties Based on π-Stacked Ion Pairs ([1]*College of Life Sciences, Ritsumeikan University*, [2]*Centre for Instrumental Analysis, Niigata University*) ○Hiroki Tanaka,[1] Yoichi Kobayashi,[1] Ko Furukawa,[2] Hiromitsu Maeda[1]

Porphyrin ion pairs, the charge of which is delocalized in the core units, were found to form solid-state assemblies and solution-state π-stacked ion pairs (*π-sips*) according to the peripheral electron-donating (EDG) and electron-withdrawing groups (EWG). The electronic states of the charged π-electronic systems were controlled, and the electron transfer by external stimuli such as light and solvents and resulting radical pair were observed for the ion pair of *meso*-EWG cation and *meso*-EDG anion. The ESR in frozen toluene revealed the formation of a closely stacked structure by the magnetic dipole interaction and temperature-dependent spin transfer behavior.
Keywords : charged π-electronic systems; porphyrins; ion pairs; electron transfer; radicals



多様な周辺修飾が可能なポルフィリンの拡張されたπ平面に対する電荷の付与は、荷電π電子系の重要な形成戦略の一つである。[1] そこで本研究では、ポルフィリン Au^{III} 錯体とメゾヒドロキシポルフィリンの脱プロトン体を導入したイオンペアを HSAB 則に基づいたイオンペアメタセシスにより合成し、電子供与性・求引性置換基の導入による機能発現および集合化を検討した（Figure 1a）。溶液中でカチオンとアニオンが近接した積層イオンペア（*π-sip*）の形成が、環電流効果と対イオンの近接に起因した ^{1}H NMR 化学シフトから示唆された。このとき、CD_2Cl_2 中の濃度可変 NMR における化学シフト変化から、**1b**$^+$-**2b**$^-$と **1c**$^+$-**2b**$^-$のヘテロ 2 量化定数をそれぞれ 3.5×10^4, 2.8×10^5 M^{-1} と求め、カチオンの電子状態が*π-sip* の安定性に影響することを見出した。また、*π-sip* のアニオンを光励起することにより電子移動が可能であり、イオンの電子状態に起因して過渡種であるラジカルペアの寿命を制御できることを見出した（Figure 1b）。[2,3] さらに、トルエン中の **1c**$^+$-**2a**$^-$は基底状態で電子移動が誘起され、ラジカルペアを形成することを明らかにした。このとき、凍結非極性溶媒中で生成した 2 種類のラジカルが近接積層し、スピン–スピン相互作用により温度に依存した電子スピン分布のスイッチングが可能であることを解明した（Figure 1c）。[2]

1) Review: Yamasumi, K. et al. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2252; 2) Tanaka, H. et al. *J. Am. Chem. Soc.* **2022**, *144*, 21710; 3) Tanaka, H. et al. *Chem. Eur. J.* **2023**, *29*, in press (DOI: 10.1002/chem.202203957).

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ベンジル位置換モノフルオロスマネン結晶の *endo-exo* 配向制御とそのメカニズム

（阪大院工[1]・阪大 ICS-OTRI[2]・阪大院基礎工[3]）李 明洪[1]・周 冬一[1]・松村 徹平[3]・○燒山 佑美[1,2]・松林 伸幸[3]・櫻井 英博[1,2]

Solid State *Endo-Exo* Conformation Control of Benzyl-substituted Monofluorosumanene and its Mechanism ([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka University,* [3]*Graduate School of Engineering Science, Osaka University*) Minghong Li,[1] Dongyi Zhou,[1] Teppei Matsumura,[3] ○Yumi Yakiyama,[1,2] Nobuyuki Matsubayashi, [3]Hidehiro Sakurai[1,2]

Two hydrogens on the benzylic carbon of curved-p conjugated sumanene are placed on the different geometry, the outer (*exo*) and the inner (*endo*) sides of the bowl. It is known that their position is interconvertible via bowl flipping phenomenon in the solution state. We recently found that the *exo*:*endo* ratio of monosuluorosumanene, which also show the bowl inversion in the solution state, significantly changed in the crystalline state depending on the crystallization solvent. In this presentation, we will show its mechanism on the basis of experimental and theoretical investigations by means of DFT calculations and molecular dynamics simulations.
Keywords : Bowl Inversion; Curved-π Conjugated Molecule; Diastereomeric Mixture; Molecular Dynamics

お椀型分子スマネンの周縁ベンジル位炭素に結合している 2 つの水素原子は、それぞれお椀の外側（*exo* 位）と内側（*endo* 位）に位置し、異なる環境下にある。うち 1 つをフッ素原子で置換したモノフルオロスマネン **1** は、溶液中で *endo* 体（$\mathbf{1}_{endo}$）および *exo* 体（$\mathbf{1}_{exo}$）との平衡状態にあり、$\mathbf{1}_{endo}$ が熱力学的にわずかに安定である（Figure 1）。また既報の周縁フッ素置換スマネンと同様、スマネンと等構造の結晶を与える[1]。今回、**1** の溶液および固体中における *exo*:*endo* 比を種々の溶媒条件にて ^{1}H NMR およびそこから得られる単結晶の構造解析データから調査したところ、特にアセトンを溶媒とした際に、*exo*:*endo* 比が溶液中と固体中とで逆転することを見いだした（Table 1）。そのメカニズムについて量子化学計算並びに分子動力学計算により考察するとともに、*exo*:*endo* 比の変化がもたらす物理的性質の違いについても検討を行ったので報告する。

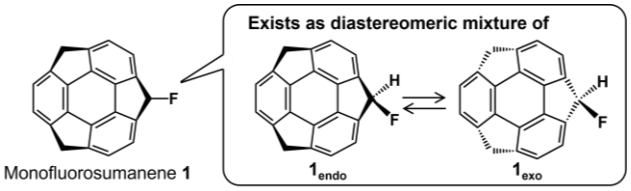


Figure 1. モノフルオロスマネン **1**。

◆ In solution State: ^{1}H NMR

Temperature (K)	Solvent (*endo* : *exo*)	
	$CDCl_3$	Acetone-d_6
373	-	-
348	-	-
323	-	-
298	72:28	64:36
273	74:26	70:30
243	76:24	78:22
193	80:20	90:10

***Endo* is favorable**

◆ In Solid State: Single Crystal

Prep. Temp (K)	Single Crystal (*endo* : *exo*)		
	DCM	Acetone	DMF
373	-	-	-
348	-	-	-
323	-	**31:69**	**20:80**
298	50:50	**20:80**	**17:83**
273	-	-	-
243	60:40	**30:70**	**24:72**
193	45:55	**36:64**	-

***Exo* is favorable (acetone and DMF)**

Table 1. 溶液および結晶中における *exo-endo* 比の変化。

1) a) M. Li, J.-Y. Wu, K. Sambe, Y. Yakiyama, T. Akutagawa, T. Kajitani, T. Fukushima, K. Matsuda, H. Sakurai, *Mater. Chem. Front.* **2022**, *6*, 1752. b) M. Li, X. Chen, Y. Yakiyama, J. Wu, T. Akutagawa, H. Sakurai, *Chem. Commun.* **2022**, *58*, 8950.

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Enantioselective Crystallization of Organic Molecules Manipulated by Optical Trapping with a Circularly Polarized Laser Beam

([1]*Deratment of Applied Chemistry, National Yang Chiao-Tung University*, [2]*Research Institute for Electronic Science, Hokkaido University*, [3]*Division of Materials Science, Nara Institute of Science and Technology*) Tung-Ming Lin,[1] Hao-Tse Su,[1] An-Chieh Cheng,[1,2] Keiji Sasaki,[2] ○Teruki Sugiyama[1,3]

Keywords: Enantioselective Crystallization; Optical Trapping; Circularly Polarized Light; Crystal Enantiomeric Excess; Ethylenediamine Sulfate

For the last decade and a half, our group has explored the possibility of the optical trapping method for crystal chemistry and has demonstrated control of nucleation, crystal growth, and polymorphism for various compounds.[1-3] We have called this crystallization method "optical trapping-induced crystallization (OTIC)". In this method, optical forces, gradient and scattering forces, with a focused laser beam sequentially capture molecules/clusters at the focal spot in sample solutions, realizing spatiotemporally controlled nucleation. Also, laser polarization-dependent polymorphism and its control mechanism have been intensively examined so far. This work presents the enantioselective crystallization of ethylenediamine sulfate (EDS) by the OTIC method with a circularly polarized (CP) laser beam.

When the laser beam is focused on the air/solution interface of the sample solution, only one EDS crystal is generated at the laser focus in one run. The enantiomorph (*l*- or *d*-form) of the resultant chiral crystals is identified in situ by a rotating-analyzer method. The experiment is repeated several dozen times with right- or left-handed CP (*r*-CP or *l*-CP) laser beams. The calculated crystal enantiomeric excess (CEE) (below Table) shows that optical trapping with a focused CP laser beam produces a significant chiral bias in the generation number of two enantiomorphs. In the presentation, some plausible mechanisms in enantioselective crystallization induced by OTIC will be discussed from the viewpoint of thermodynamics and helical optical force upon nucleation.

Table Generation number of *d*- and *l*-forms for right- or left-handed CP light and its calculated crystal enantiomer excess.

Polarization	*r*-CP	*l*-CP
l-Form	23	39
d-Form	37	21
Total run	60	60
CEE (%)	23	-30

1) T. Sugiyama, S.-F. Wang *J. Photochem. Photobiol. C: Photochem. Rev.* **2022**, *52*, 100530. 2) T. Sugiyama, K. Yuyama, and H. Masuhara, *Acc*. *Chem*. *Res*. **2012**, *45*, 2012. 3) T. Sugiyama, T. Adachi, H. Masuhara, *Chem*. *Lett.* **2007**, *36*, 1480.

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[K606-2pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Atsuro Takai, Ryou Kubota

Thu. Mar 23, 2023 2:00 PM - 3:40 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-2pm-01] Construction of Porous Organic Salts from Orthogonal Networks by the Combination with Square Planar Sulfonic Acids and Bulky Amines

○Kohei Okubo[1], Kouki Oka[1], Norimitsu Tohnai[1] (1. Osaka University)

2:00 PM - 2:20 PM

[K606-2pm-02] Shape-persistent porous crystals formed by flexible [2]catenanes

○Bohan Cheng[1], Hiroshi Sato[1] (1. Institute of Physical and Chemical Research)

2:20 PM - 2:40 PM

[K606-2pm-03] Adsorption Behaviors of Pillar[*n*]quinones for Volatile Halogenated Organic Compounds

○Shunsuke Ohtani[1], Onishi Katsuto[1], Tomoki Hirohata[2], Shinsuke Inagi[2], Jenny Pirillo[3], Yuh Hijikata[3], Motohiro Mizuno[4], Kenichi Kato[1], Tomoki Ogoshi[1,5] (1. Grad. Sch. Eng., Kyoto Univ., 2. Tokyo Institute of Technology, 3. WPI-ICReDD, Hokkaido Univ., 4. NanoMaRi, Kanazawa Univ., 5. WPI-NanoLSI, Kanazawa Univ.)

2:40 PM - 3:00 PM

[K606-2pm-04] Synthesis Stable and Crystalline Covalent Triazine Frameworks from CO_2

○Siquan Zhang[2], Loris Lombardo[1], Satoshi Horike[1,2] (1. Institute for Advanced Study, Kyoto University, 2. Graduate School of Engineering, Kyoto University)

3:00 PM - 3:20 PM

[K606-2pm-05] Spatial distribution of interaction forces derived from hydrophobic pockets visualized by 3D-AFM in liquid

○Moe Ogasawara[1], Rina Okumura[2], Masayuki Morimoto[3], Hitoshi Asakawa[1,2,3,4] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. College of Science and Engineering, Kanazawa University, 3. Nanomaterials Research Institute (NanoMaRi), Kanazawa University, 4. Nano Life Science Institute(WPI-NanoLSI), Kanazawa University)

3:20 PM - 3:40 PM

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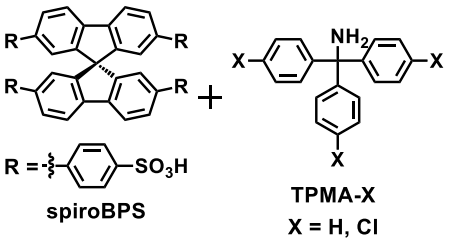
Construction of Porous Organic Salts from Orthogonal Networks by the Combination with Square Planar Sulfonic Acids and Bulky Amines

(*Graduate School of Engineering, Osaka University*) ○Kohei Okubo, Kouki Oka, Norimitsu Tohnai

Keywords: *Hydrogen bond; Organic salts; Porous material*

Porous materials based on organic molecules have been aggressively investigated because of their diversity and functionalization of voids by molecular design. We have constructed porous organic salts (**POS**s) through the formation of tetrahedral supramolecular clusters with various aromatic sulfonic acids and bulky amines such as triphenylmethylamine (**TPMA**).[1] However, **POS**s have been constructed only from diamond networks based on the geometry of supramolecular clusters, and the diversification of these structures is still under development.

In the current work, in order to diversify the porous structure of **POS**s, we used 2,2',7,7'-tetrakis[*p*-sulfophenyl]-9,9'-spirobifluorene (**spiroBPS**), square planar sulfonic acid and **TPMA** or *para*-chlorinated **TPMA** (**TPMA-Cl**) to construct **POS**s with different networks from the diamond shape (**Scheme 1**). The obtained structures were constructed from novel orthogonal networks with 2-fold interpenetration or helical networks with non-interpenetration, depending on the bulkiness at the *para* position of **TPMA** derivatives (**Figure 1a**). The non-interpenetrated structure showed unique gas adsorption properties at 77 K, selectively adsorbing only oxygen among oxygen and nitrogen (**Figure 1b**).



Scheme 1.

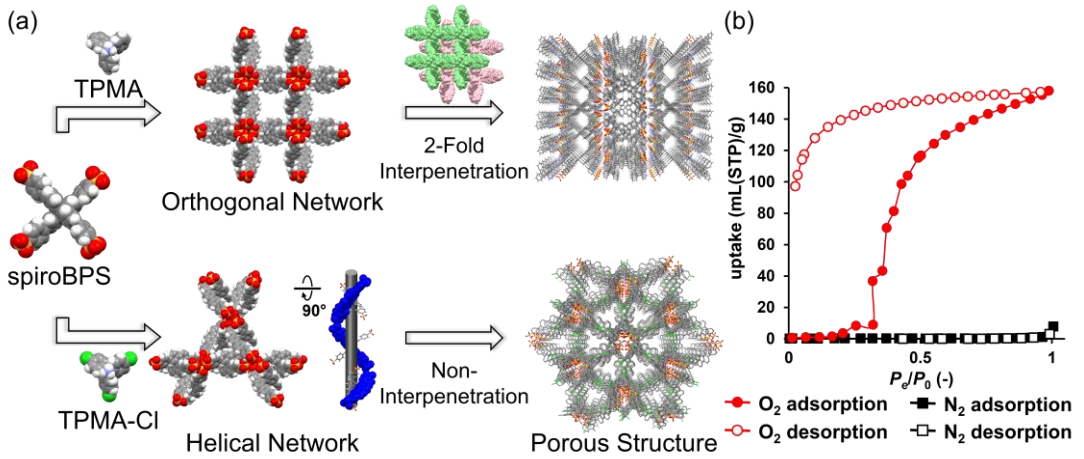


Figure 1. (a) Schematic images of the construction of **POS**s using **spiroBPS**/**TPMA** or **TPMA-Cl**. (b) Gas adsorption isotherms of **spiroBPS**/**TPMA-Cl** at 77 K.

1) N. Tohnai, *et al*., *Cryst. Growth. Des*., **2012**, *12*, 4600.

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Shape-persistent porous crystals formed by flexible [2]catenanes

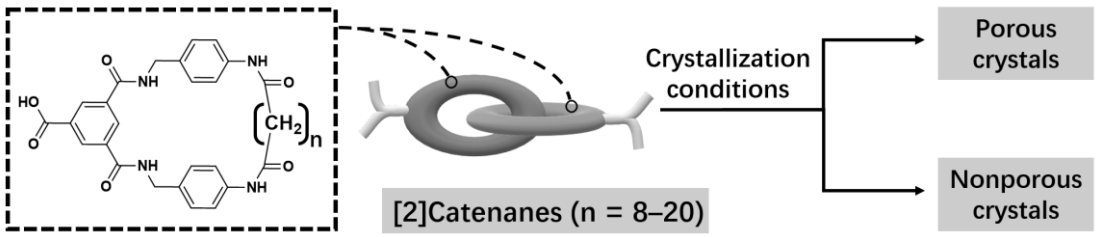
([1]*Center for Emergent Matter Science, RIKEN;* [2]*JST-PRESTO*) ○Bohan Cheng[1], Hiroshi Sato[1,2]

Keywords: Catenane; Porous crystal

Polymers and gels formed by mechanically interlocked structures such as catenane[1] or rotaxane[2] have attracted massive research interests over the last decade because interlocked structures will introduce unique flexibility to the materials. However, interlocked catenane structure was rarely reported[3] as porous crystals, since crystallinity and flexibility seem to be contradictory.

Recently, our research team reported an elastic porous crystal[4] formed by the reaction of a carboxylic acid-appended [2]catenane and metal ions. The crystal exhibit rubber-like properties, changing its structure reversibly in response to mechanical pressure. We found that the key to the unique mechanical properties is the reversible intramolecular hydrogen bonds that exist in the [2]catenane. Here we design a new family of [2]catenanes that can form intramolecular hydrogen bonds between the amide groups. These [2]catenanes have saturated alkyl moieties in the macrocycles, and we successfully synthesized [2]catenanes with different macrocycle sizes (n = 8–20).

Interestingly, some of the [2]catenanes were found to selectively self-assemble into porous or nonporous molecular crystals, depending on the crystallization conditions. For example, in porous crystals obtained from [2]catenanes with moderate macrocycle sizes (n = 14–16), the coexistence of intra- and intermolecular hydrogen bonds resulted in the formation of one-dimensional channels of approximately 0.6 nm in diameter, in which the crystallization solvent was incorporated as guest molecules. Furthermore, the guest adsorption properties of the molecular crystals formed by these [2]catenanes will be discussed in the presentation.



1) T. Hagiwara, Y. Murano, Y. Watanabe, T. Hoshi and T. Sawaguchi, *Tetrahedron Lett.*, 2012, **53**, 2805–2808. 2) Q. Lin, L. Li, M. Tang, S. Uenuma, J. Samanta, S. Li, X. Jiang, L. Zou, K. Ito and C. Ke, *Chem*, 2021, **7**, 2442–2459. 3) G. Zhang, O. Presly, F. White, I. M. Oppel and M. Mastalerz, *Angew. Chem. Int. Ed.*, 2014, **53**, 5126–5130. 4) W. Meng, S. Kondo, T. Ito, K. Komatsu, J. Pirillo, Y. Hijikata, Y. Ikuhara, T. Aida and H. Sato, *Nature*, 2021, **598**, 298–303.

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Adsorption Behaviors of Pillar[*n*]quinones for Volatile Halogenated Organic Compounds

(*[1]Grad. Sch. Eng., Kyoto Univ., [2]Tokyo Tech., [3]WPI-ICReDD, Hokkaido Univ., [4]NanoMaRi, Kanazawa Univ., [5]WPI-NanoLSI, Kanazawa Univ.*)
○ Shunsuke Ohtani[1], Katsuto Onishi[1], Tomoki Hirohata[2], Shinsuke Inagi[2], Jenny Pirillo[3], Yuh Hijikata[3], Motohiro Mizuno[4], Kenichi Kato[1], Tomoki Ogoshi[1,5]
Keywords: Host−Guest Chemistry; Volatile Halogenated Organic Compounds; Macrocyclic Molecule

There are growing concerns about halogenetad organic compounds in the atomosphere because of the damage to human health and the environment. In particular, fluorocarbon gases such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), which were used as refrigerants in cooling technologies, have significant environmental impacts because of their long lifetime and high ozone depletion in the stratosphere and global warming potential. In addition, volatile halogenated organic compound (VHOC) solvents have been widely used in industrial fields such as synthesis of other chemicals, metal cleaning, paints and automotive aerosols, however, the long-time exposure of such solvents is known to be harmful and cause cancer both in human and animals. Therefore, the developments of capture and strorage technologies for them has gained more importance.

In this work, we discovered that the electron-deficient macrocycle pillar[*n*]quinone (**P[*n*]Q**)[1,2] crstals showed uptake behaviors for toxic and environmentally-harmful halogeneted organic compounds such as fluorocarbon gases and VHOC vapors (Fig. 1). Further investigation using FT-IR, solid-state NMR and computational analyses revealed that the driving forces of the uptake of VHOCs with **P[*n*]Q**s were their electron-deficient macrocyclic scaffolds and weakly-basic oxygen atoms at C=O on the both rims of **P[*n*]Q**s. In addition, it should be emphasized that a crystalline host–guest complex between **P[5]Q** and CH_2Cl_2 showed exceptional thermal and long-term stability, that is, the VHOC molecules could be strongly confined inside the crystal lattice of **P[5]Q**.



Fig. 1 Schematic representation of capture and storage of halogenated compounds by **P[*n*]Q** crystals.

1) Cao, D. R.; Kou, Y. H.; Liang, J. Q.; Chen, Z. Z.; Wang, L. Y.; Meier, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 9721–9723. 2) Hirohata, T.; Shida, N.; Uekusa, H.; Yasuda, N.; Nishihara, H.; Ogoshi, T.; Tomita, I.; Inagi, S. *Chem. Commun.* **2021**, *57*, 6360–6363.

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Synthesis of Stable and Crystalline Covalent Triazine Frameworks from CO_2

Siquan Zhang[1], Loris Lombardo[2], Satoshi Horike[1,2]*(1. Graduate School of Engineering, Kyoto University 2. Institute for Advanced Study, Kyoto University)

ABSTRACT

Crystalline covalent triazine frameworks (CTFs) are aromatic nitrogen-rich and promising for practical appications. In this work, a stable and crystalline covalent triazine framework based on interpenetrated-stacking was synthesized from CO_2 and melamine with solvent-thermal condition. The product showing interpenetration crystal structure was confirmed by PXRD and HR-TEM. This CTF shows BET surface area of S_{BET}= 945 m^2 g^{-1} and high CO_2 and water adsorption ability (5.3 wt% for CO_2 and 53 wt% for H_2O in 298 K). The crystal structure shows high stability in strong acid (6M HCl), strong base (6M NaOH), and boiling water for 24 hours. We studied proton conductivity for this compound and it showed σ = 0.03 S cm^{-1} in 85 ^oC and 95% RH upon post modification of Oxone.

CO_2 • crystalline • triazine • porous framework • proton conductivity.

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液中 3 次元走査型 AFM による疎水性ナノポケット周辺の相互作用力分布の可視化

(金沢大院自然[1]・金沢大理工[2]・金沢大ナノマリ[3]・金沢大 WPI-NanoLSI[4]) ○小笠原 萌[1]・奥村 里菜[2]・森本 将行[3]・淺川 雅[1,2,3,4]
Spatial distribution of interaction forces derived from hydrophobic pockets visualized by 3D-AFM in liquid ([1]*Graduate School of Natural Science and Technology, Kanazawa University*, [2]*College of Science and Engineering, Kanazawa University*, [3]*Nanomaterials Research Institute (NanoMaRi), Kanazawa University*, [4]*Nano Life Science Institute (WPI-NanoLSI), Kanazawa University*) ○Moe Ogasawara,[1] Rina Okumura,[2] Masayuki Morimoto,[3] Hitoshi Asakawa[1,2,3,4]

Three-dimensional atomic force microscopy (3D-AFM) has been developed as a "structural measurement technique" for solid-liquid interfaces with sub-nm spatial resolution and pN force sensitivity. Based on the performance, the 3D-AFM should be able to apply as an "interaction force measurement." This study demonstrates a 3D-AFM investigation of characteristic interaction forces derived from hydrophobic nanopockets in self-assembled monolayers of small organic molecules. Our results suggest that 3D-AFM can visualize the distribution of interaction forces in nanospaces at the single molecule scale, promising to contribute to the elucidation of molecular recognition mechanisms.
Keywords : Three-dimensional AFM; Intermolecular interaction; Hydrophobic pocket; Molecular recognition

3 次元走査型原子間力顕微鏡（3D-AFM）はサブナノメートル空間分解能とピコニュートン力分解能を有する固液界面の「構造計測手法」として開発されてきた。一方で、この高い空間・力分解能に基づく「相互作用力計測手法」としても発展できると考えている。本研究では、3D-AFM が有機小分子の自己組織化単分子層中に形成された疎水性ナノポケットに由来する特徴的な相互作用力分布を可視化できることを実証した。今後、空間に広がる相互作用力分布を 1 分子スケールで可視化できる 3D-AFM 技術は分子識別メカニズムの解明などに貢献することが期待される。

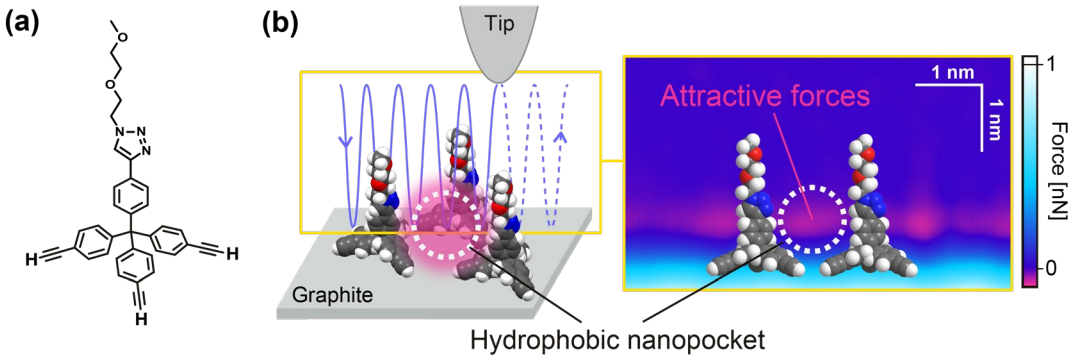


Fig. 1. (a) Chemical structure. (b) Hydrophobic nanopockets in self-assembled monolayers investigated by 3D-AFM in water.

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[K606-2vn] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Hiroshi Sato, Yuichiro Watanabe

Thu. Mar 23, 2023 4:10 PM - 6:20 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-2vn-01] Control of Guest Uptake/release Rates of Macrocyclic Cobalt(III) Dinuclear Metallohosts Having Aromatic Bridging Ligands

○Ryo Sudo[1], Yoko Sakata[1,2], Shigehisa Akine[1,2] （1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa University）

4:10 PM - 4:30 PM

[K606-2vn-02] Kinetic Control of Formation and Structural Conversion of Metallonanobelts Based on Interaction with Oligoethers

○Ryosuke Nakamura[1], Yoko Sakata[1,2], Shigehisa Akine[1,2] （1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute Kanazawa University）

4:30 PM - 4:50 PM

[K606-2vn-03] Real-time confocal imaging of formation and dynamics of a dipeptide-based coacervate

○Ryou Kubota[1], Yuchong Liu[1], Taro Hiroi[1], Itaru Hamachi[1,2] （1. Kyoto University, 2. JST ERATO）

4:50 PM - 5:10 PM

[K606-2vn-04] Repeated elongation and shrinkage of supramolecular fibers induced by surfactant micelle

○Torigoe Shogo[1], Kubota Ryou[1], Nagao Kazutoshi[1], Hamachi Itaru[1,2] （1. The Univ. of Kyoto, 2. JST-ERATO）

5:10 PM - 5:30 PM

[K606-2vn-05] Helical Charged π-Electronic Systems That Form Ion-Pairing Assemblies

○Rima Sengupta[1], Haruka Hashimoto[1], Yohei Haketa[1], Hiromitsu Maeda[1] （1. Ritsumeikan University）

5:40 PM - 6:00 PM

[K606-2vn-06] Catalyst-Free Click Reaction of Naphthalenediimides with Amines in Supramolecular Fibers

○Minghan Tan[1], Masayuki Takeuchi[1], Atsuro Takai[1] （1. National Institute for Materials Science ）

6:00 PM - 6:20 PM

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芳香族架橋配位子を有する大環状コバルト(III)二核メタロホストのゲスト出入り速度の制御

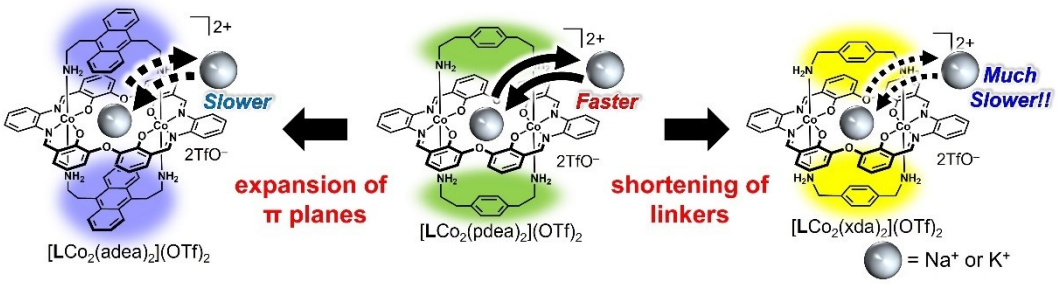
（金沢大院自然[1]・金沢大 NanoLSI[2]）○須藤 涼[1]・酒田 陽子[1,2]・秋根 茂久[1,2]

Control of Guest Uptake/release Rates of Macrocyclic Cobalt(III) Dinuclear Metallohosts Having Aromatic Bridging Ligands ([1]*Graduate School of Natural Science and Technology, Kanazawa University*, [2]*Nano Life Science Institute, Kanazawa University*)
○Ryo Sudo,[1] Yoko Sakata,[1,2] Shigehisa Akine[1,2]

We synthesized a series of cobalt(III) macrocyclic metallohosts having two bridging aromatic ligands. We investigated the effect of the structure of the bridging ligands on the guest uptake/release rate. We found that the guest exchange rate became slower by the introduction of bulky ligands or narrowing the distance between the ligands and the cavity.
Keywords：*Guest Recognition; Ligand Exchange; Metallohost; Bridging Ligand; Alkali Metal*

環状ホスト分子の空孔の開口部の大きさを制御できれば、ゲストの出入り速度を調節できる高機能性ホストとしての応用が期待される。我々は、二つの saloph 部位を有する環状コバルト(III)二核メタロホストの軸位にピペリジンを導入した $[\mathbf{L}Co_2(pip)_4](OTf)_2$ (pip = piperidine) との配位子交換により、架橋配位子として 1,6-ヘキサンジアミン[1]や *p*-フェニレンジエタナミン(= pdea)を導入する戦略を開発してきた。本研究では、$[\mathbf{L}Co_2(adea)_2](OTf)_2$ (adea = 9,10-anthracenediethanamine) と $[\mathbf{L}Co_2(xda)_2](OTf)_2$ (xda = *p*-xylylenediamine)を新たに合成し、「π平面の大きさ」と「架橋鎖の長さ」のゲスト出入り速度に対する影響を検討することとした。

「π平面の大きさ」のゲスト出入り速度に対する影響を調べるために、$[\mathbf{L}Co_2(pdea)_2](OTf)_2$ と $[\mathbf{L}Co_2(adea)_2](OTf)_2$ の Na^+出入り速度定数を決定した。Na^+出入り速度定数はそれぞれ 0.17 s^{-1}, 0.031 s^{-1} であり、嵩高い架橋配位子を導入することでゲスト出入りにおけるブロック効果を増大させることに成功した。また、「架橋鎖の長さ」のゲスト出入り速度に対する影響を調べるために、$[\mathbf{L}Co_2(pdea)_2](OTf)_2$ と $[\mathbf{L}Co_2(xda)_2](OTf)_2$ の K^+から Na^+へのゲスト交換速度を調べた。$[\mathbf{L}Co_2(pdea)_2](OTf)_2$ の場合では 5 分以内に完結したゲスト交換は、$[\mathbf{L}Co_2(xda)_2](OTf)_2$ では数日間から数ヶ月程度にまで抑制されることが分かった。このように、「架橋鎖の長さ」がゲスト出入りに大きく影響することが分かった。



1) Sakata, Y.; Okada, M.; Akine, S. *Chem. Eur. J.* **2021**, *27*, 2284-2288.

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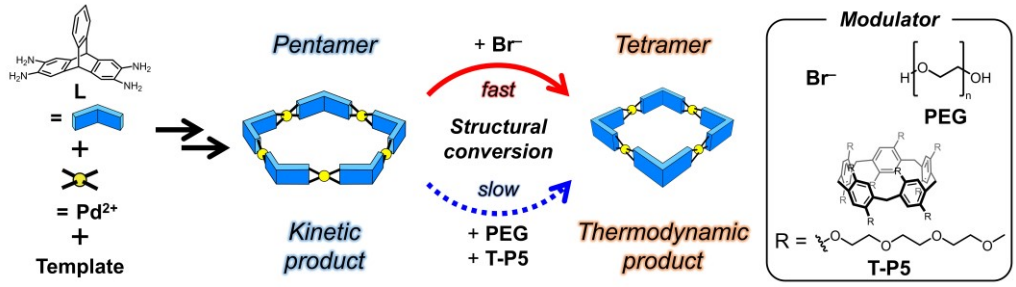
オリゴエーテルとの相互作用を利用したメタロナノベルトの形成と構造変換の速度論的制御

（金沢大院自然[1]・金沢大 NanoLSI[2]）○中村 亮介[1]・酒田 陽子[1,2]・秋根 茂久[1,2]
Kinetic Control of Formation and Structural Conversion of Metallonanobelts Based on Interaction with Oligoethers ([1] *Graduate School of Natural Science and Technology, Kanazawa University*, [2] *Nano Life Science Institute Kanazawa University*) ○Ryosuke Nakamura,[1] Yoko Sakata,[1,2] Shigehisa Akine[1,2]

We have previously found that a kinetically stable pentanuclear metallonanobelt can be selectively formed by using a pillar[6]arene derivative **T-P6** as a template during the self-assembly of 2,3,6,7-tetraaminotriptycene **L** and Pd^{2+}. In this work, we succeeded in speed tuning of structural conversion from the kinetically stable pentanuclear metallonanobelt to the thermodynamically stable tetranuclear metallonanobelt by additives. The addition of bromide ion to the pentanuclear metallonanobelt drastically accelerated the structural conversion. The structural conversion was suppressed by adding a pillar[5]arene derivative with oligoether chains or polyethylene glycols.
Keywords : Macrocycle; Self-assembly; Template Effect; Guest Recognition; Kinetic Control

自己集合型金属錯体の構造変換を速度論的に制御できれば、さまざまな金属配位結合を駆動力とする自己集合過程を精密に制御するための重要な指針を与え得る。我々はこれまでに 2,3,6,7-テトラアミノトリプチセン **L** と Pd^{2+}のテンプレート自己集合によって準安定な五核メタロナノベルトの選択的形成に成功し、これが熱力学的に安定な四核メタロナノベルトへと数十日かけて非常にゆっくりと構造変換することを見出している[1]。本研究では、この比較的遅い構造変換の速度をさまざまなモジュレーターの添加により精密に制御することに成功した。

Pd-N 間の結合の組み替えを促進することが明らかとなっている臭化物イオン[2]を五核メタロナノベルトに対して添加すると、構造変換は大幅に加速した。一方、メタロナノベルトと多点水素結合を形成することが明らかとなっているオリゴエーテル鎖を導入したピラー[5]アレーン誘導体やポリエチレングリコール(PEG)を添加すると、構造変換は抑制された。特に分子量 2×10^4 を超える PEG を用いた場合では顕著な構造変換の抑制がみられた。



1) Y. Sakata, R. Yamamoto, D. Saito, S. Akine, *et al., Inorg. Chem.* **2018**, *57*, 15500-15506.
2) Y. Sakata, R. Nakamura, T. Hibi, S. Akine, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217048.

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Real-time confocal imaging of formation and dynamics of a dipeptide-based coacervate

([1]*Graduate School of Engineering, Kyoto University*, [2]*JST ERATO*) ○Ryou Kubota,[1] Yuchong Liu,[1] Taro Hiroi,[1] Itaru Hamachi[1,2]

Keywords: Self-assembly; Liquid-liquid phase separation; Confocal microscopy

Coacervates are liquid-like membraneless supramolecules formed through liquid-liquid phase separation. Coacervates are important for development of functional soft materials and understanding/controlling of biological functions due to their ability of molecular sequestration and reaction acceleration. To date, the inner assembly structure of coacervates have been investigated mainly by cryogenic electron microscopy. However, the dynamic aspect of the inner assembly structure, like formation processes and structural fluctuation, have not been studied yet. Very recently, we reported a novel structural motif for liquid-liquid phase separation, *tert*-butyl phenylalanylphenylalaninate (FF–OtBu).[1] In this research, we found that a kind of FF–OtBu derivatives forms coacervate droplets whose inner assembling structure can be observed by confocal-based super-resolution microscopy. Real-time super-resolution imaging visualized that the inner structure of the coacervate consists of a three-dimensional structurally-fluctuated sponge-like network (Figure). We also found unique dynamic behaviors of the coacervate; the network crosslinks are repeatedly engaged/disengaged with each other at several millisecond scale. Furthermore, during fusion process, the coacervate droplets showed a stochastically 'kissing' behavior, in which the outer network structures between different coacervates temporarily contact with each other. In this presentation, we will discuss a unique formation behavior of a dipeptide-based coacervate revealed by real-time super-resolution imaging. Such real-time observation of the dynamic behaviors of the coacervate would provide a way to understand and control the physicochemical properties of coacervates.

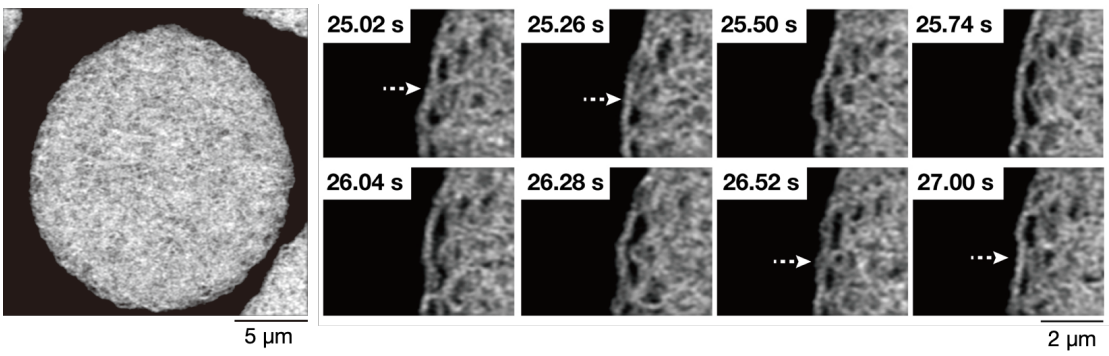


Figure (Left) Super-resolution microscopic image of a dipeptide-based coacervate. (Right) Real-time confocal images of structural fluctuation of the sponge-like network. White arrows indicate the position of dynamically engaged/disengaged crosslinks.

1. R. Kubota, S. Torigoe, I. Hamachi, ***J. Am. Chem. Soc.*** 144, 15155 (2022).

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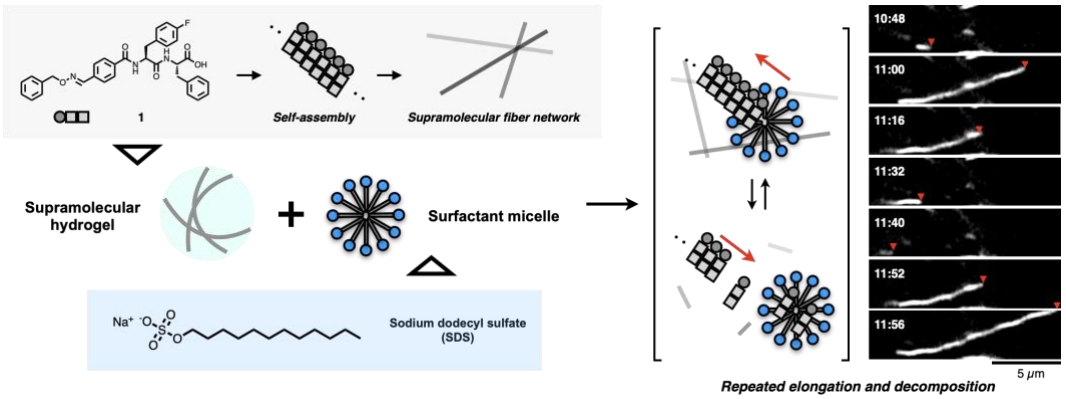
Repeated elongation and shrinkage of supramolecular fibers induced by surfactant micelle

([1]*Graduate School of Engineering, Kyoto University*, [2]*JST-ERATO*) ○Shogo Torigoe,[1] Ryou Kubota,[1] Kazutoshi Nagao,[1] Itaru Hamachi,[1,2]

Keywords: *Supramolecular, Surfactant, Non-equilibrium dynamics, Confocal microscopy*

In living cells, formation and decomposition of biological self-assembled constructs like cytoskeleton dynamically proceed to control functions such as cell motility and transport spatiotemporally. For example, microtubules are formed by polymerization of GTP-bound tubulin dimers and depolymerized triggered by hydrolysis of GTP to GDP inside the polymerized tubulin. Furthermore, the polymerization and depolymerization of microtubules are also known to be precisely regulated by interactions with binding proteins (e.g. XMAP-215). Inspired by biological non-equilibrium self-assembly, synthetic chemists attempted to construct artificial supramolecular fibers that spontaneously grow and shrink driven by chemical reactions.[1] However, repeated growth and shrinkage through non-covalent interactions among different types of supramolecules have not been reported so far.

In this study, we describe our discovery of the repeated elongation/shrinkage behavior of peptide-based nanofibers[2] in the presence of an SDS micelle (SDS: sodium dodecyl sulfate) (Figure, left). We started real-time confocal imaging after addition of the SDS micelle to the peptide hydrogel containing a fluorescent probe. Real-time confocal imaging visualized that both elongating and shrinking nanofibers were simultaneously observed and that such the dynamic behavior continued for more than 12 h. After addition of the micelle, the fiber morphology was changed from shorter straight fibers to longer curved fibers, suggesting that the longer curved fibers would consist of both the peptide hydrogelator and SDS. We also found that a few of fibers exhibited unique dynamic behaviors such as repeated elongation and shrinkage (Figure, right). Diifferent dynamic behaviors was observed that depend on chemical properties of surfactants. In this presentation, we report these non-equilibrium dynamics and the possible mechanism in detail.



1) J. Boekhoven, *et. al. Science* **2015**, 349, 1075. 2) R. Kubota *et al. Nat. Commun.* **2020**, *11*, 4100.

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Helical Charged π-Electronic Systems That Form Ion-Pairing Assemblies

(*College of Life Sciences, Ritsumeikan University*) ○Rima Sengupta, Haruka Hashimoto, Yohei Haketa, Hiromitsu Maeda

Keywords: π-electronic systems; pyrrole derivatives; helical structures; ion pairs; assemblies

Ion-pairing assemblies in anisotropic arrangement of charged π-electronic species formed aggregates as single crystals, supramolecular gels, and liquid crystals.[1] Structures and properties of ion-pairing assemblies depend on the constituent cations and anions. While various planar π-electronic cations have been investigated as building blocks of ion-pairing assemblies, cations with helical structures have been scarcely explored. Helical metal complexes of π-conjugated ligands are essential for their fascinating chiral electronic and electrooptical properties and applications in host-guest recognition, molecular knots, and chiral separation. In this regard, we have prepared a series of ion pairs based on α-arylbidipyrrin–Au^{III} complexes (Figure 1a) as stable helical π-electronic cations via ion-pair metathesis. The ion pairs exhibited absorption and phosphorescence emission in the NIR region. The solid-state structures of these ion pairs appeared as single helices with Au^{III} adopting a distorted square planar geometry (Figure 1b). The ion pairs existed as racemic mixtures in the crystal states, and the assembling modes depended on coexisting counteranions. In the solid-state assembly of the Cl^- ion pair, each row consists of *P* and *M* enantiomers (Figure 1c(i)), whereas the packing diagrams of the $AuCl_4^-$ and $PCCp^-$ ion pairs consist of *P* and *M* enantiomers alternately arranged in rows (Figure 1c(ii)). Electrostatic and dispersion forces are the major contributors for stabilizing the ion-pairing assemblies as suggested by energy decomposition analysis (EDA).[2]

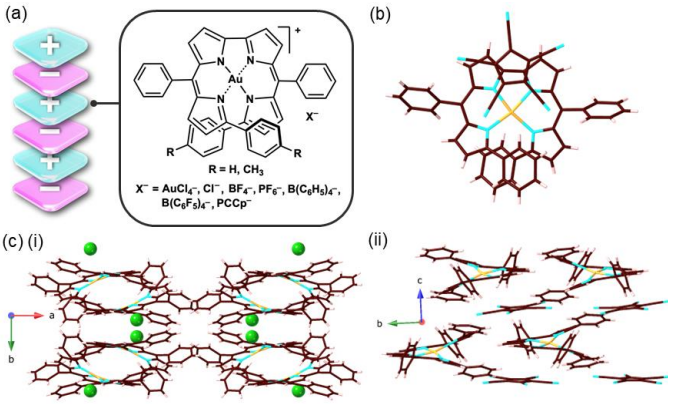


Figure 1 (a) α-Arylbidipyrrin–Au^{III} complexes as building blocks of ion-pairing assemblies, (b) single-crystal X-ray structure as a *P*-type helix in a $PCCp^-$ (pentacyanocyclopentadienide) ion pair, and (c) packing diagrams of (i) Cl^- ion pair and (ii) $PCCp^-$ ion pair viewed along *c* and *a* axes, respectively.

1) Reviews: (a) Haketa, Y.; Urakawa, K.; Maeda, H. *Mol. Syst. Des. Eng.* **2020**, *5*, 757. (b) Yamasumi, K.; Maeda, H. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2252.

2) Sengupta, R.; Hashimoto, H.; Haketa, Y.; Maeda, H. manuscript in preparation.

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Catalyst-Free Click Reaction of Naphthalenediimides with Amines in Supramolecular Fibers

([1]*Molecular Design and Function Group*, *National Institute for Materials Science: NIMS*)
○Minghan Tan,[1] Masayuki Takeuchi,[1] Atsuro Takai[1]

Keywords: Supramolecular Polymer; Spatiotemporal Dynamics; Catalyst-Free Click Reaction; π-Conjugated Molecules; Naphthalenediimide

Implementing chemical reactivity into synthetic supramolecular polymers of π-conjugated molecules has been attracting increasing attention in the context of dynamic supramolecular materials. However, the development of *in situ* chemical reaction within the supramolecular polymers is still in its infancy because one needs to design an optimal π-conjugated monomers having excellent reactivity under mild conditions possibly without byproducts or a catalyst. We have previously found a catalyst-free click reaction of an ethynyl-substituted naphthalenediimide (NDI) with amines at ambient tenperature.[1,2)] In this presentation, we report that the click reaction within supramolecular fibers of NDIs triggers changes in the morphological and optical properties, and that these macroscopic changes depend on the type of NDIs and amines (Figure 1).

NDI compounds that have two ethynyl groups at the π-core and the amide and trialkoxyphenyl groups at the imide side chains formed supramolecular polymers in non-polar solvents upon gradual cooling from 363 K to 298 K. The click reaction of **S-NDI2** supramolecular polymers with a monoamine afforded short fibrous assemblies of the amine mono-adduct *via* transient intermediate assemblies.[3)] On the other hand, the *in situ* reaction with 1,4-diaminobutane produced two-dimensionally extended fibrous networks owing to the efficient intra- and inter-supramolecular cross-linking (Figure 1).[3)] The characteristic reaction kinetics of the click reaction within the supramolecular polymers and the unique reactivity of the chiral supramolecular polymers will be also discussed.

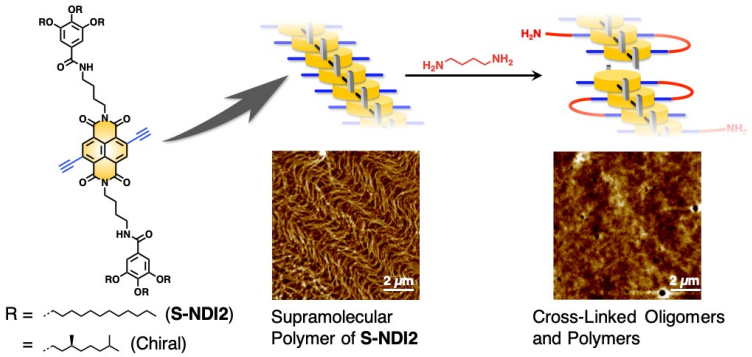


Figure 1 *In situ* click reaction of **S-NDI2** supramolecular fibers with 1,4-diaminobutane.

1) A. Takai, M. Takeuchi, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 44. 2) M. Tan, M. Takeuchi, A. Takai, *Chem. Commun.* **2022**, *58*, 7196. 3) M. Tan, M. Takeuchi, A. Takai, *Chem. Sci.* **2022**, *13*, 4413.

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[K602-2pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Eiji Shirakawa, Hajime Maeda

Thu. Mar 23, 2023 1:10 PM - 3:40 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-2pm-01] Improving the Efficiency of Triplet Dynamic Nuclear Polarization of Biomolecules Based on Zero-Field Splitting Control of Polarizing Agent Molecules

○Tomoyuki HAMACHI[1], Keita SAKAMOTO[1], Kenichiro TATEISHI[2], Tomohiro UESAKA[2], Nobuhiro YANAI[1,3] (1. Grad. Sch. Eng., Kyushu Univ., 2. RIKEN Nishina Center for Accelerator-Based Science, 3. FOREST, JST)

1:10 PM - 1:30 PM

[K602-2pm-02] Blue light driven C-C bond formation reaction via α-thiomethyl radicals derived from thioanisole derivatives

○Pijush Kanti Roy[1], Masahito Kodera[1], Yutaka Hitomi[1] (1. Doshisha Univ.)

1:30 PM - 1:50 PM

[K602-2pm-03] Dye and electron donor hybridized systems towards molecular probes using chemically induced dynamic nuclear polarization

○Koki Nishimura[1], Nobuhiro Yanai[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. FOREST, JST)

1:50 PM - 2:10 PM

[K602-2pm-04] C– H Oxygenation by Simultaneous UV-Vis Light and Microwave Irradiation with Chlorine Dioxide

○Yuki Itabashi[1], Ai Sunami[1], Kei Ohkubo[1] (1. Osaka Univ.)

2:20 PM - 2:40 PM

[K602-2pm-05] Catalytic DDQ Photocatalysis: Direct Arene C-N Bond Formation

○Kaii Nakayama[1], Hidehiro Kamiya[1], Yohei Okada[1] (1. Tokyo University of Agriculture and Technology)

2:40 PM - 3:00 PM

[K602-2pm-06] Reductive Coupling Reaction between Aryl Bromides and Alkyl Pyridinium Salts Using Solid-state Photoredox Reaction

○Ryota Isshiki[1,2], Koji Kubota[1,2], Hajime Ito[1,2] (1. WPI-ICReDD, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University)

3:00 PM - 3:20 PM

[K602-2pm-07] Photochemical reductive cleavage of C-O bond of alkyl aryl ethers using carbazole photosensitizer activated by cesium carbonate

○Tatsushi Yabuta[1], Masahiko Hayashi[1], Ryosuke Matsubara[1] (1. Kobe university)

3:20 PM - 3:40 PM

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Improving the Efficiency of Triplet Dynamic Nuclear Polarization of Biomolecules Based on Zero-Field Splitting Control of Polarizing Agent Molecules

([1]*Grad. Sch. Eng., Kyushu Univ.*, [2]*RIKEN Nishina Center for Accelerator-Based Science*, [3]*FOREST, JST*) ○Tomoyuki Hamachi,[1] Keita Sakamoto,[1] Kenichiro Tateishi,[2] Tomohiro Uesaka,[2] Nobuhiro Yanai[1,3]

Keywords: Dynamic nuclear polarization; Photoexcited triplet electron; Nuclear magnetic resonance; Zero field splitting

Dynamic nuclear polarization (DNP) improves the sensitivity of nuclear magnetic resonance (NMR) by transferring the spin polarization of electron spins to nuclear spins. However, common DNP based on radicals requires cryogenic temperatures (~1 K) to obtain a high electron spin polarization (~100%) at thermal equilibrium. In contrast, DNP using photoexcited triplet electron spins (triplet-DNP) can produce hyperpolarization at milder conditions since the triplet spin polarization is high (~70%) independent of temperature.[1]

However, conventional polarizing agents such as pentacene show broaden ESR spectra in the random orientation due to the dipole interaction between triplet electron spins (zero field splitting, ZFS), and this leads to a lower polarization transfer efficiency to target molecules. In this study, we developed new water-soluble polarizing agents with controlled ZFS and succeeded in improving the nuclear spin polarization of water molecules.

ZFS parameters of two novel water-soluble pentacene derivatives, (pentacene-6,13-diylbis(thiophene-5,2-diyl))dimethanol (PTDM) and (pentacene-6,13-diylbis(4,1-phenylene))dimethanol (PPDM), were compared (Fig. 1). ESR spectrum of photo-excited triplet state of PTDM was sharper than that of PPDM thanks to its smaller *D* and *E* values (Fig. 2). The polarization transfer from PTDM and PPDM to water molecules by triplet-DNP will also be reported.

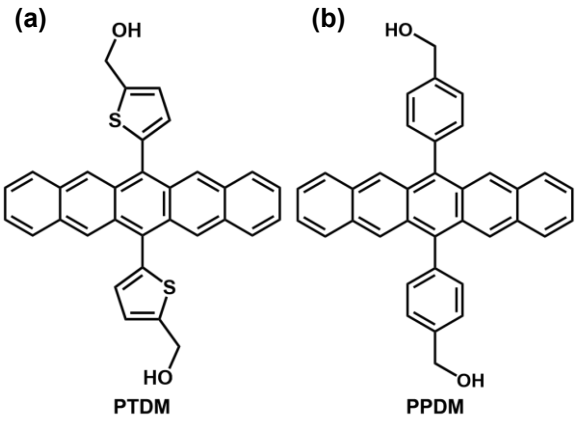


Figure 1. Chemical structures of (a) PTDM and (b) PPDM.

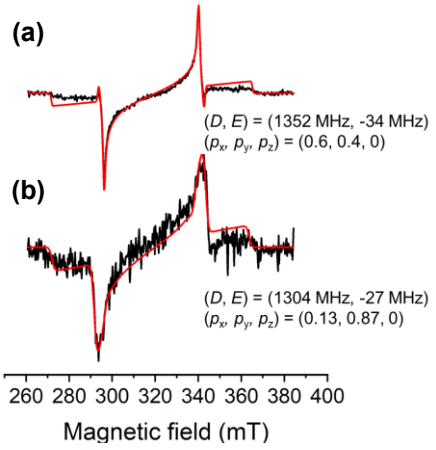


Figure 2. ESR spectra of (a) PTDM and (b) PPDM.

1) a) W. Th. Wenckebach et al., *Chem. Phys. Lett.*, **1990**, *165*, 6-10. b) N. Yanai et al., *Chem. Commun.*, **2020**, *56*, 7217-7232.

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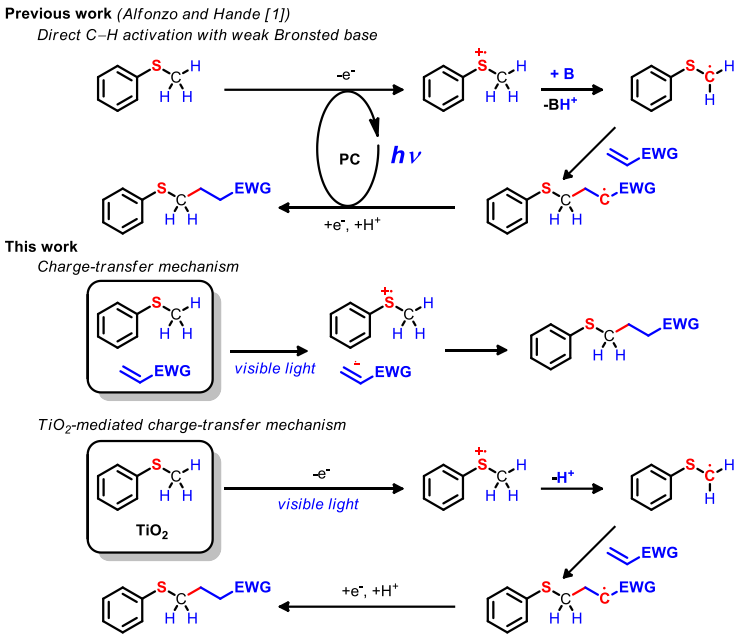
Blue Light Driven C–C Bond Formation Reaction via α-Thiomethyl Radicals Derived from Thioanisole Derivatives

(*Graduate School of Science and Engineering, Doshisha University*) ○ Pijush Kanti Roy, Masahito Kodera, Yutaka Hitomi

Keywords: C–C Bond Formation; Thioanisole; Charge Transfer Complex; Titanium Dioxide; Oxidative Cyclization

Photochemical C–H activation of thioethers to α-thioalkyl radical is an attractive strategy for subsequent C–C bond formation; in 2020, Alfonzo and Hande reported that thioethers' C–H activation, as shown in Scheme 1, produces α-thioalkyl radicals, which afford alkylated products with electron-deficient olefins in the presence of photoredox and weak Brønsted base catalysis [1].

We found that the reactions between thioanisole derivatives and benzylmalononitrile, one of the electron-deficient olefins, proceed by irradiating their charge transfer complexes with blue light even without a photosensitizer. However, the reactions between thioanisole derivatives and *N*-alkyl maleimide derivatives do not proceed under the same conditions, except for the reaction using 4-nitrothioanisole. However, to our delight, the reactions were promoted in the presence of titanium dioxide under blue light irradiation. In our previous work, TiO_2 can selectively transform toluene to benzaldehyde under blue light irradiation in the presence of dioxygen [2]. Therefore, we propose that an interfacial charge transfer occurs from thioanisole derivatives to the conduction band of TiO_2 under blue light irradiation, resulting in π-cation radical formation and deprotonation (Scheme 1).



Scheme 1 Strategy for formation of thioalkyl radicals and subsequent carbon-carbon bond formation

1) E. Alfonzo and S. M. Hande *ACS Catal.* **2020**, *10*, 12590. 2) K. Aitsuki, D. Fukushima, H. Nakahara, K. Yo, M. Kodera, S. Okunaka, H. Tokudome, T. Koitaya, Y. Hitomi, *New J. Chem*. **2022**, *46*, 9010.

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光で駆動する超核偏極分子プローブを志向した色素と電子ドナーの複合化

（九大院工[1]・JST 創発[2]）○西村 亘生[1]・楊井 伸浩[1, 2]
Dye and electron donor hybridized systems towards molecular probes using chemically induced dynamic nuclear polarization ([1]*Graduate School of Engineering, Kyushu University*, [2]*FOREST JST*) ○Koki Nishimura,[1] Nobuhiro Yanai,[1, 2]

Photochemically induced nuclear polarization[1] (CIDNP) is a powerful technique to improve the sensitivity of NMR/MRI. However, it has not yet been applied to MRI in vivo because the polarization generates by bimolecular reactions, which is inefficient under low concentration. In this study, we aimed to create a new molecular probe by hybridization of a dye and an electron donor to achieve CIDNP through an intramolecular reaction. We focused on fluorescein derivatives, which show high CIDNP efficiency under high magnetic fields[2]. Among them, a pair of eosin Y and phenol derivatives showed the highest enhancement factor under moderate magnetic field (1.4 T), indicating that they are useful for the application of MRI. In this presentation, we will report the results of CIDNP measurement using hybridized molecules of these candidates and we discuss about suitable molecular design for molecular probe.

Keywords : Dynamic nuclear polarization; Photo-excited triplet state; Magnetic resonance; Electron transfer

光化学誘起動的核偏極[1]（CIDNP）は、光照射のみで NMR/MRI の高感度化を達成する有用な技術である。しかし、偏極生成過程が二分子反応である為に、低濃度下では効率が悪く、生体応用に至っていない。そこで、本研究では色素と電子ドナーを複合化し、分子内反応によって CIDNP を達成することで、新たな分子プローブを創出することを目標とした。初めに、高磁場下で高い CIDNP 効率を示すフルオレセイン誘導体に着目した[2]。その内、エオシン Y とフェノール誘導体の組み合わせは、中程度の磁場（1.4 T）下でも高い偏極倍率を示し、MRI への応用に向けて有用であった。そこで、実際にこれらの色素と電子ドナー分子を複合化し CIDNP 効率を評価した。その結果を基に最適な分子プローブの設計について議論する。

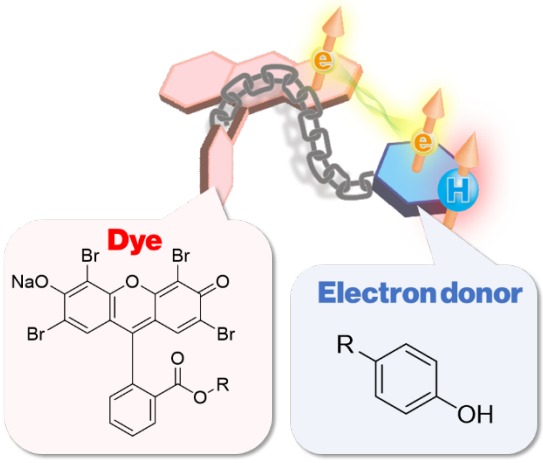


図 1. 分子内 CIDNP に向けた分子設計

1) O. B. Morozova and K. L. Ivanov, *ChemPhysChem*, **2019**, 20, 197-215.
2) A. Sobol, F. Torres, A. Aicher, A. Renn and R. Riek, *J. Chem. Phys*., **2019**, 151, 234201.

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二酸化塩素を用いたマイクロ波と紫外可視光同時照射による C–H 結合の酸素化反応

（阪大先導的学際研[1]・阪大高等共創研[2]）○板橋勇輝[1]・角南 愛[1]・大久保敬[1,2]

C–H Oxygenation by Simultaneous UV-Vis Light and Microwave Irradiation with Chlorine Dioxide ([1]Institute for Open and Transdisciplinary Research Initiatives, Osaka University, [2]Institute for Advanced Co-Creation Studies, Osaka University) ○Yuki Itabashi[1], Ai Sunami[1] and Kei Ohkubo[1,2]

The direct oxidation reaction to convert methane to methanol and formic acid at room temperature and normal pressure has been considered one of the most difficult reactions because methane is a stable gas due to the strong C–H bond (BDE 105 kcal mol^{-1}), resulting in low reactivity. When chlorine dioxide is activated under light irradiation, oxygen and chlorine radical are generated. The chlorine radical acts as a strong hydrogen abstracting reagent, because of the high bond formation energy of H–Cl (102 kcal mol^{-1}). The chlorine radical abstracts the strong C–H of the methane. This is followed by the addition of oxygen to methyl radicals, leading to the final products of metanol and formic acid.[1] This study aimed to further improve the efficiency of this reaction. The simultaneous irradiation of visible light and microwaves activated chlorine dioxide and reaction intermediates, and efficiently converted methane to methanol and formic acid. This microwave-assisted photochemical technique was applicable to C–H polymer substrates, and afforded hydrophilization by oxidation of C–H bonds to OH and COOH groups on the plastic surface. The analyses suggest that the reactivity of simultaneous irradiation is different from that of individual irradiation.

Keywords : C–H Oxidation; Photochemical Reaction; Microwave; Hydrophilization; Chlorine Dioxide

メタンからメタノール，ギ酸へ常温常圧で変換する直接酸化反応は、メタンが気体であり，かつ C–H が強固であるため(BDE 105 kcal mol^{-1})，反応性が低く，最高難度化学変換とされてきた．二酸化塩素を光によって活性化すると，酸素と塩素ラジカルが生成する．塩素ラジカルは，水素引き抜きによる H–Cl の結合生成エネルギーが 102 kcal mol^{-1} であることから，強力な水素引き抜き剤として働く．塩素ラジカルがメタンの強固な C–H を引き抜き，それにより生成するメチルラジカルに対して，酸素が付加することでメタンの酸化反応が進行する[1]．本研究ではこの反応の効率をさらに向上させることを目的とし、可視光とマイクロ波を同時照射することにより，二酸化塩素および反応中間体を活性化し，メタンを酸化してメタノールおよびギ酸へと効率的に変換できることを見出した．この手法は，ポリプロピレンやポリエチレンテレフタラートをはじめとする高分子樹脂に対しても適用可能であり[2]，プラスチック表面の C−H 結合を酸化し OH 基および COOH 基を導入することで，表面の親水化を達成した．分析結果から同時照射は，単独照射と反応性が異なることを見出した．

1) K. Ohkubo, K. Hirose, *Angew. Chem., Int. Ed*. **2018**, *57*, 2126. 2) K. Ohkubo, H. Asahara, T. Inoue, *Chem. Commun.* **2019**, *55*, 4723.

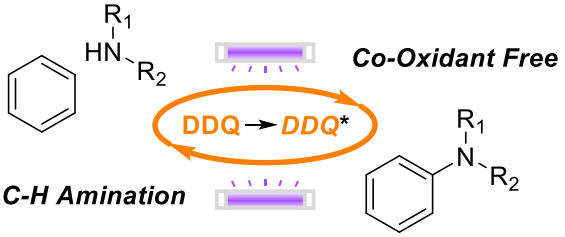
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触媒量の DDQ 光触媒による芳香環 C-H アミノ化反応

（東農工大院）○中山 海衣・神谷 秀博・岡田 洋平*
Catalytic DDQ Photocatalysis: Direct Arene C-N Bond Formation (*Tokyo University of Agriculture and Technology*) ○Kaii Nakayama, Hidehiro Kamiya, Yohei Okada*

2,3-dichloro-5,6-dicyanoquinone (DDQ) is known as a powerful oxidant in synthetic organic chemistry. However, the requirement of adding more than stoichiometric amounts and the limited recycling methods of 2,3-dichloro-5,6-dicyano-hydroquinone ($DDQH_2$) which is generated after DDQ oxidations are disadvantages in terms of environmental viewpoint and atom economy. To overcome this weakness, researchers have studied a co-oxidant that regenerates $DDQH_2$ into DDQ; particularly, *tert*-butyl nitrite (TBN) and molecular oxygen (O_2) co-oxidant system which was reported by Hu *et al.* has been used in catalytic DDQ oxidation.[1] Fukuzimi and Ohkubo *et al.* described the phenol synthesis using the combination of catalytic DDQ photocatalysts and the TBN/O_2 co-oxidant system.[2] Since we have been developing the reactions which are promoted by TiO_2 photocatalytic oxidation, TiO_2 may have the potential to re-activate $DDQH_2$ to DDQ. We report that direct arene C-N bond formation was serendipitously found by catalytic DDQ photocatalysts without co-oxidants.
Keywords: DDQ, Photocatalysis, Catalytic Amount, Arene C-N Bond Formation, Co-Oxidant

DDQ は有用な有機酸化剤として知られ、様々な有機合成反応に利用されている。しかしながら、一般的に量論量の添加が必要とされること、反応後に生成する $DDQH_2$ を再利用する手段が少ないことから、環境負荷やアトムエコノミーの観点で問題を抱えている。ゆえに、DDQ の添加を触媒量に抑えるため、系中で $DDQH_2$ を DDQ へと再生させる研究が盛んに進められている。現在よく用いられている手法は、Hu らによって報告された TBN と O_2 を組み合わせた再酸化システムであり、[1] さらに福住、大久保らは、TBN/O_2 再酸化システムを用いた、触媒量の DDQ 光触媒によるフェノールの合成に成功している。[2] 我々のグループでは、酸化チタン光触媒による一電子酸化を起点として進行する反応開発を行っており、酸化チタン光触媒が TBN/O_2 の代替となって光励起 DDQ を触媒サイクルさせることが可能であると考えた。本発表では、意外なことに、再酸化剤の添加無しで触媒量の光励起 DDQ による芳香環 C-H アミノ化反応が観測されたため、その結果について報告する。



(1) Shen, Z.; Dai, J.; Xiong, J.; He, X.; Mo, W.; Hu, B.; Sun, N.; Hu, X. *Adv. Synth. Catal.* **2011**, *353*, 3031–3038.
(2) Ohkubo, K.; Fujimoto, A.; Fukuzumi, S. *J. Am. Chem. Soc.* **2013**, *135*, 5368–5371.

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固体フォトレドックス反応を用いた芳香族臭化物とアルキルピリジニウム塩との還元的カップリング反応

（北大 WPI-ICReDD[1]・北大院工[2]）○一色 遼大[1,2]・久保田 浩司[1,2]・伊藤 肇[1,2]
Reductive Coupling Reaction between Aryl Bromides and Alkyl Pyridinium Salts Using Solid-state Photoredox Reaction ([1]*WPI-ICReDD, Hokkaido University*, [2]*Graduate School of Engineering, Hokkaido University*) ○Ryota Isshiki,[1,2] Koji Kubota,[1,2] Hajime Ito[1,2]

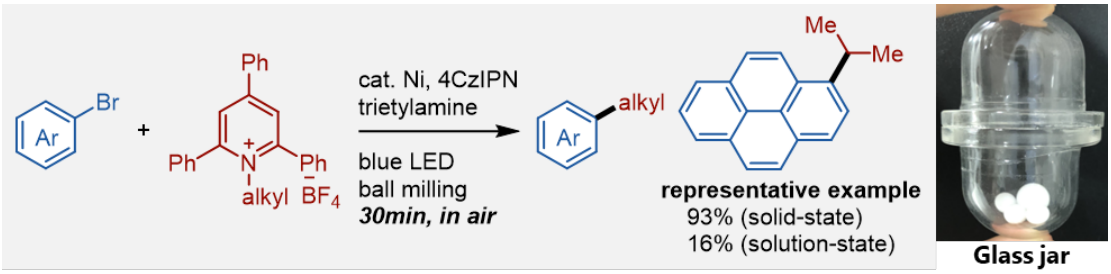
Photoredox reactions utilize the strong oxidizing and reducing potential of excited photocatalysts to generate radical species under mild conditions. These reactions have gained great attentions of organic chemists because of their high functional group tolerance and safety. However, there still have some issues such as complicated degassing operations and long reaction time because they are carried out under solution-state.

In this study, we have developed solid-state nickel/photoredox catalyzed reductive coupling reaction between aryl bromides and alkyl pyridinium salts using blue LED irradiated ball-milling techniques.[1)] This method has the advantages over solution conditions, for example, environmentally friendliness, simple operation, and time economical method. And alkylation of poorly soluble aryl bromides proceeded more efficiently than in solution.

Keywords : Photoredox Reaction; Ball-mill; Nickel; Reductive Coupling; Mechanochemistry

フォトレドックス反応では、励起された光触媒の強力な酸化・還元力を利用することで、温和な条件下ラジカル種を発生させることができる。高い官能基許容性や安全性から多くの化学者達の注目を集め、爆発的に報告数を伸ばしている。しかし、多量の溶媒を用いた希薄条件で反応を実施するため、煩雑な脱気操作が必要な点や反応の完結に長い反応時間が必要な点等の課題が残されていた。

今回我々は、ガラス製反応器を用い青色 LED 照射下、ニッケル触媒とフォトレドックス触媒を添加し、芳香族臭化物とアルキルピリジニウム塩とをボールミル中で撹拌すると還元的アルキル化反応が進行することを見出した[1)]。本反応は有機溶媒を使用しない高い環境調和性、空気下で反応を実施できる操作の簡便さ、短時間で反応が完結するタイムエコノミーの観点で優れている。また、溶液系では実施が困難な難溶性化合物のアルキル化反応が、溶液系と比較して効率的に進行することも見出した。



1) In solution, see: Deaminative Reductive Arylation Enabled by Nickel/Photoredox Dual Catalysis. Yi, J.; Badir, S. O.; Kammer, L. M.; Ribagorda, M.; Molander, G. A. *Org. Lett.* **2019**, *21*, 3346.

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炭酸セシウムにより活性化されたカルバゾール光増感剤を用いたアルキルアリールエーテルの C-O 結合の光還元的切断反応

（神大大教[1]・神大院理[2]）○藪田　達志[1]・林　昌彦[2]・松原　亮介[2]

Photochemical reductive cleavage of C-O bond of alkyl aryl ethers using carbazole photosensitizer activated by cesium carbonate ([1]*Institute for Promotion of Higher Education, Kobe University*, [2]*Graduate School of Science, Kobe University*) ○ Tatsushi Yabuta,[1] Masahiko Hayashi,[2] Ryosuke Matsubara[2]

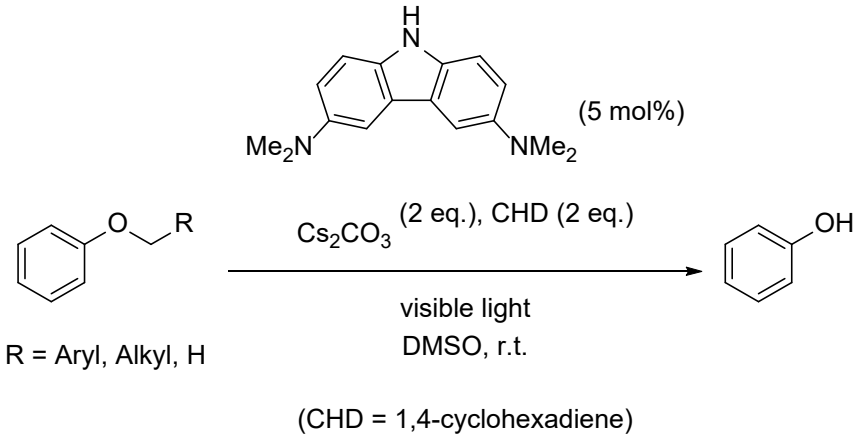
Alkyl aryl ethers which are abundant compounds in natural and synthesized molecules attract attention as a chemical source. However, there are relatively scarce methods to convert to other functional groups from ether group due to the stability of ether C-O bonds. Therefore, development of effective conversion method of the ether C-O bonds is desirable.

Recently, we achieved to effectively cleave the ether C-O bonds using carbazole photosensitizer and revealed that cesium carbonate activates carbazole photosensitizer. Herein, we report the substrate scope and the effect of cesium carbonate to photochemical properties revealed by spectroscopic analysis.

Keywords : Photoreaction; ether bond; reductive cleavage; carbazole; cesium carbonate

アルキルアリールエーテルは自然界や合成化学品中に普遍的に存在する化合物であり、有機合成原料として注目されている。しかし、エーテル結合は非常に安定な結合であるため、他の官能基へ変換する反応は少ない。そのため、効率的な変換反応の開発が求められている。

最近、演者らはカルバゾール光増感剤によってエーテル結合を効率的に切断する反応を開発した[1)]。物性評価を行う中で炭酸セシウムがカルバゾール光増感剤を活性化していることを明らかにした。発表では、基質一般性の詳細や、炭酸セシウムがカルバゾールに及ぼす光学物性への影響について報告する。



1) Yabuta, T.; Hayashi, M.; Matsubara, R. *J. Org. Chem.* **2021**, *86*, 2545.

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[K703-2am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Hiroaki Imoto, Kei Muto
Thu. Mar 23, 2023 9:00 AM - 11:30 AM K703 (K703, Lecture Hall Bldg. [7F])

[K703-2am-01] Skeletal Rearrangement of a Boron-Containing π-Conjugated Macrocycles Caused by Boron– Olefin Proximity Interaction

○Yukihiro Murata[1], Yoshiaki Shoji[1], Takanori Fukushima[1] (1. CLS, Tokyo Tech.)

9:00 AM - 9:20 AM

[K703-2am-02] Synthesis of Unsymmetric Bisphosphine Derivatives by the Strain-Release Three-Component Reaction of Propellane

○Hideaki Takano[1,2], Hitomi Katsuyama[1,2], Hiroki Hayashi[1,2], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

9:20 AM - 9:40 AM

[K703-2am-03] Photoredox Dearomative Nucleophilic Addition of CO_2 Radial Anion to (Hetero)aromatics

○Saeesh Rajendra Mangaonkar[1,2], Hiroki Hayashi[1,2], Hideaki Takano[1,2], Wataru Kanna[3], Yu Harabuchi[1,2,3], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

9:40 AM - 10:00 AM

[K703-2am-04] Tailor-made Synthesis of Fully and Differently Arylated Alkenes

○Kimiya Wada[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

10:10 AM - 10:30 AM

[K703-2am-05] A Novel Jacobsen Reaction of 1,8-Diiodonaphthalene Induced by Ring Strain

○Kento Iwai[1], Noa Nishiguchi[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

10:30 AM - 10:50 AM

[K703-2am-06] Regiodivergent Synthesis of Brominated Thienylpyridines Overriding the Inherent Substrate Bias

○Masahiro Hosoya[1], Kentaro Okano[1], Atsunori Mori[1,2] (1. Department of Chemical Science and Engineering, Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University)

10:50 AM - 11:10 AM

[K703-2am-07] Synthesis of π-Expanded Amines via Single-Electron Oxidant-Catalyzed Denitrogenative Benzannulation of Ynamine with Phthalazine

○Yasuhiro Okuda[1], Takuma Sato[1], Sou Takebe[1], Tomoki Inoue[1], Akihiro Orita[1] (1. Fac. of Eng., Okayama Univ. of Science)

11:10 AM - 11:30 AM

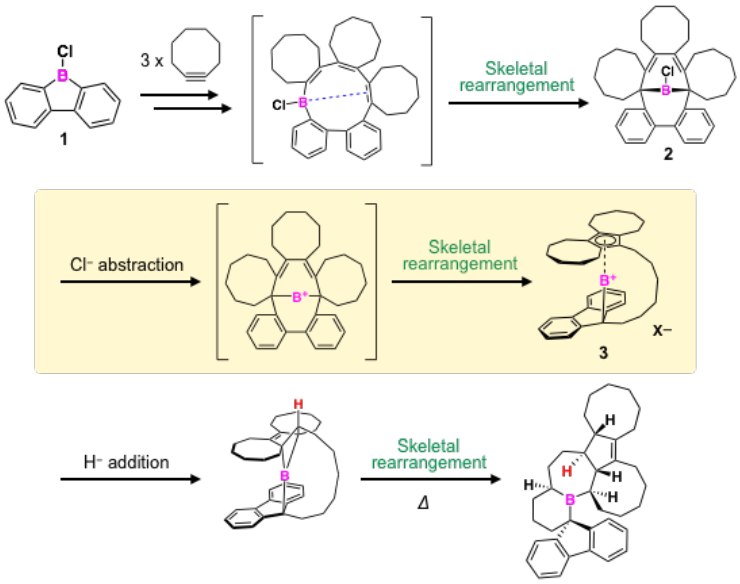
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ホウ素とオレフィンの近接相互作用による含ホウ素環状π共役化合物の骨格転位反応

（東工大化生研[1]・東工大物質理工[2]）○村田 幸優[1,2]・福島 孝典[1,2]・庄子 良晃[1,2]
Skeletal Rearrangement of a Boron-Containing π-Conjugated Macrocycles Caused by Boron-Olefin proximity Interaction ([1]*Lab. Chem. Life Sci., Tokyo Tech.*, [2]*Sch. Mater. and Chem. Tech., Tokyo Tech.*) ○Yukihiro Murata,[1,2] Takanori Fukushima,[1,2] Yoshiaki Shoji[1,2]

We recently reported a multiple insertion reaction of a strain-activated alkyne derivative into a B–C bond of 9-chloro-9-borafluorene, giving a boron-containing π-conjugated macrocycle. Within this macrocycle, a close intramolecular interaction between boron and olefin operates, to cause unique skeletal rearrangement into a boron-bridged bicyclic product. We found that this product further undergoes a skeletal rearrangement involving multiple C–C bonds formation/cleavage. Here we discuss the effect of boron–olefin proximity interaction on the unique skeletal rearrangement reactions.
Keywords : Boron; 1,2-Carboboration; Olefin; π-Coordination; Skeletal Rearrangement

オレフィンがπ配位したホウ素錯体は、ヒドロホウ素化や Frustrated Lewis Pair による小分子活性化反応など、多様な反応の中間体として想定されてきた。最近我々は、環歪みにより活性化されたアルキンが、9-ボラフルオレン誘導体 **1** のホウ素–炭素結合に連続的に挿入する反応を報告している[1]。この反応で得られる含ホウ素マクロサイクルにおいて、ホウ素とオレフィンとの間に近接相互作用が働くことで骨格転位反応が進行し、ホウ素架橋 10 員環化合物 **2** が生成することを見いだしている[1]。単結晶 X 線構造解析および理論計算から、**2** においてもホウ素–オレフィン近接相互作用が強く働いていることが予測された。そこで、ホウ素–オレフィン近接相互作用をより増大させる目的で、**2** の B–Cl 結合からの Cl^- 引き抜き反応を検討したところ、複数の C–C 結合形成／切断を伴う骨格転位が進行し、ボロセニウムイオン **3** が得られることを見いだした。さらに、**3** の変換反応により、複雑な三次元骨格からなる有機ホウ素化合物が得られることも明らかにした。本発表では、これらの骨格転位反応におけるホウ素–オレフィン近接相互作用の寄与について議論する。



[1] Y. Murata, K. Matsunagi, J. Kashida, Y. Shoji, C. Özen, S. Maeda T. Fukushima, *Angew. Chem. Int. Ed.* **2021**, 60, 14630.

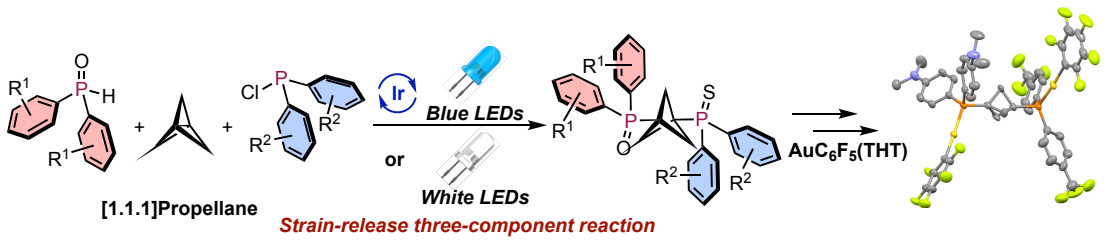
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プロペランのひずみ解消を駆動力とする三成分反応による非対称ビスホスフィン誘導体の合成

(北大 WPI-ICReDD[1]・JST-ERATO[2]・北大院理[3]) ○髙野 秀明[1,2]・勝山 瞳[1,2]・林 裕樹[1,2]・前田 理[1,2,3]・美多 剛[1,2]
Synthesis of Unsymmetric Bisphosphine Derivatives by the Strain-Release Three-Component Reaction of Propellane ([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*) ○Hideaki Takano[1,2], Hitomi Katsuyama[1,2], Hiroki Hayashi[1,2], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2]

[1.1.1]Propellane is a highly strained cyclic hydrocarbon due to the charge-shift bond that connects two bridgehead carbon atoms. By the release of ring strain, [1.1.1]propellane easily reacts with various nucleophiles and radical species to generate bicycle[1.1.1]pentane (BCP) derivatives which are regarded as isosteres of *p*-phenylene, alkyne, and *tert*-butyl group. Although BCPs possessing two phosphorous functional groups are expected to be used as new linker molecules for supramolecular chemistry, to the best of our knowledge, there have been few reports for the synthesis of BCP-bisphosphine compounds. Herein, we develop a three-component reaction (3CR) of [1.1.1]propellane with a phosphine oxide and a chlorophosphine, each of which has different substituents on the phosphorous atom, under photoirradiation. This 3CR affords unsymmetric bisphosphine derivatives possessing a BCP skeleton. One of the obtained BCP-bisphosphine derivatives was transformed through the reduction followed by the reaction with gold salt into the corresponding gold complex, of which structure was confirmed by X-ray analysis.
Keywords : Propellane; Bisphosphine ligands; Three-component reaction; Photochemical reaction; Quantum chemical calculations

[1.1.1]プロペランは橋頭位同士が電荷シフト結合により結合した架橋構造を持つ脂環式炭化水素であり、極めて大きな環ひずみを有するため、様々な求核剤やラジカルと容易に反応し、*p*-フェニレンやアルキン、*tert*-ブチル基の等価体として利用可能なビシクロ[1.1.1]ペンタン(BCP)骨格を与える。BCP 骨格に配位性のリン原子が二つ導入されたビスホスフィン誘導体は、有機超分子の新たなリンカー部位としての利用が期待できるが、その報告例が極めて少ない。今回我々は、光照射条件下、[1.1.1]プロペランと、それぞれ異なる置換基を有するホスフィンオキシドとクロロホスフィンの三成分反応により、BCP 骨格を有する非対称ビスホスフィン誘導体の合成に成功した。得られた誘導体から三工程を経て金錯体へ誘導し、その立体構造を X 線結晶構造解析により確認した。



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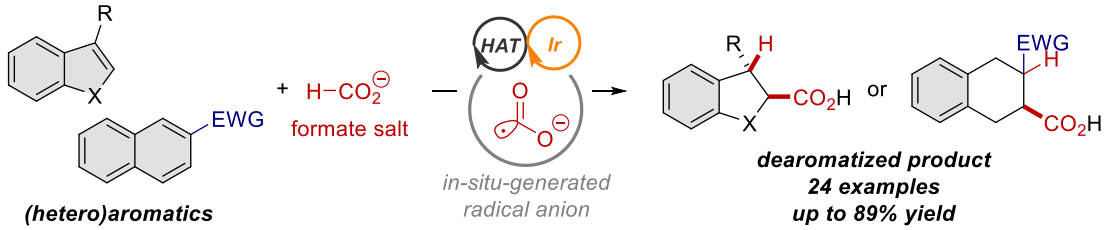
Photoredox Dearomative Nucleophilic Addition of CO_2 Radical Anion to (Hetero)aromatics

([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*) ○Saeesh R. Mangaonkar,[1,2] Hiroki Hayashi,[1,2] Hideaki Takano,[1,2] Wataru Kanna,[3] Yu Harabuchi,[1,2,3] Satoshi Maeda,[1,2,3] Tsuyoshi Mita[1,2]

Keywords: Photoredox; Carbon Dioxide Radical Anion; Dearomative Carboxylation; Formate Salts; Hydrogen Atom Transfer

Aromatic and heteroaromatic compounds are ubiquitous synthetic starting materials and many types of reactions have been developed for their dearomative functionalization. This synthetic methodology is highly effective because it converts stable aromatics into dearomatized products, which can be converted into potential synthetic intermediates.[1]

The carbon dioxide radical anion ($CO_2^{\bullet-}$) is a highly reactive intermediate that is mostly accessed through electrochemical reduction of CO_2.[2] Given its reactive radical character, $CO_2^{\bullet-}$ is rapidly emerging in modern organic chemistry. The generated radical species is known to exhibit high reactivity toward unsaturated double bonds in single-electron reduction manner (the release of stable CO_2) or in Giese-type reaction manner especially for electron-deficient alkenes and styrene derivatives.[3] We have herein developed a robust and efficient method for introducing $CO_2^{\bullet-}$ to stable heteroaromatics such as furan and indole analogues *via* photoredox-HAT conditions using *fac*-[Ir(dFppy)$_3$] as a photoredox catalyst, HCO_2Cs as a metal formate identified as a C1 source, and DABCO as a hydrogen atom transfer (HAT) catalyst, in DMSO solvent at 100 °C under the irradiation from blue LEDs, affording synthetically useful α-oxy and α-amino acid derivatives in moderate to high yields. In addition, when using electron-deficient naphthalene derivatives, both single-electron reduction and Giese-type addition occurred simultaneously to produce dearomatized tetrahydronaphthalene derivatives in good yields.[4] Furthermore, the reaction with CO_2 as an additional C1 sources gave the corresponding synthetically useful dicarboxylic acids.



1) W.-T. Wu, L. Zhang, S.-L. You, *Chem. Soc. Rev.* **2016**, *45*, 1570-1580. 2) Y. You, W. Kanna, H. Takano, H. Hayashi, S. Maeda, T. Mita *J. Am. Chem. Soc.* **2022**, *144*, 3685-3695. 3) S. N. Alektiar, Z. K. Wickens, *J. Am. Chem. Soc.* **2021**, *143*, 13022-13028. 4) S. R. Mangaonkar, H. Hayashi, H. Takano, W. Kanna, S. Maeda, T. Mita. *ACS Catal.* **2023**, *13*, *in revision*.

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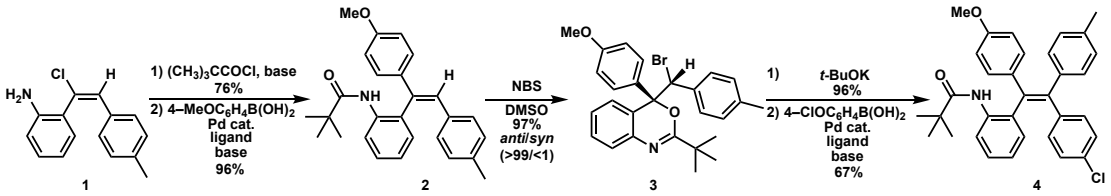
テトラアリールアルケンの選択的自在合成

（高知工大 環境理工）○和田貴巳也・岩井健人・西脇永敏
Tailor-made Synthesis of Fully and Differently Arylated Alkenes (School of Environmental Science and Engineering, Kochi University of Technology)○Khimiya Wada, Kento Iwai, Nagatoshi Nishiwaki

Despite the usefulness of tetraarylalkenes as functional materials, their synthesis with high stereo- and regioselectivity is one of the challenging projects[1]. We synthesized triaarylalkenes **2** using stereoselective hydrohalogenation[2] of alkyne as a key step and subsequent Suzuki-Miyaura cross coupling. When the produced alkene **2** was subjected to bromination, intramolecular ring closure also proceeded to afford benzoxazine **3**. In this reaction, solvent was a crucial factor to determine diastereomeric ratio of **3**, and a single stereoisomer of **3** was successfully obtained when DMSO was used as a solvent. The ring opening reaction efficiently proceeded with a stereospecific mode upon treatment with base. Finally, we achieved synthesis of tetraarylalkenes by Suzuki-Miyaura cross coupling.
Keywords: Pseudo-intramolecular reaction, Stereoselective bromination, Tetraarylalkene, Benzoxazine, Aggregation induced emission

テトラアリールアルケンは機能性材料として幅広く用いられている。一方で、4つの異なるアリール基を導入する手法については立体および位置選択性の制御の観点から多くの課題が残されている [1]。そのような背景の下、今回我々は当研究室で開発したアルキンの立体選択的なハロゲン化水素化法 [2]を利用することで、高選択的なテトラアリールアルケンの合成法の開発を目指した。

まず、我々の手法により合成した(*E*)-ハロエテニルアニリン **1** を *N*-アシル化した後、カップリング反応を行なうことでトリアリールアルケン **2** を得た。次に、アルケニル水素のブロモ化を試みたところ、アミド部位での閉環を伴ったブロモ化反応が進行し、ベンゾオキサジン **3** が生成することを明らかにした。本過程では 2 種類のジアステレオマーが生成したものの、溶媒に DMSO を用いることで一方の異性体のみ得ることに成功した。次いでアンチ脱離を利用し、**3**の立体を保持したままブロモアルケンに変換した後、鈴木ー宮浦クロスカップリングを行なうことで高選択的なテトラアリールアルケン **4** の合成を達成した。



1) Jiao, J.; Nakajima, K.; Nishihara, Y. *Org. Lett*. **2013**, *15*, 3294–3297.
2) *Eur. J. Org. Chem.* **2021**, 5747–5755.

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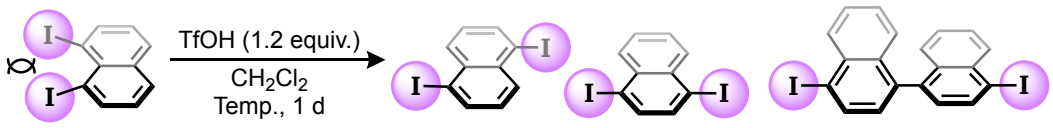
骨格歪みを利用した 1,8-ジヨードナフタレンの新奇 Jacobsen 反応

（高知工大環境理工）○岩井健人・西口乃亜・西脇永敏
A Novel Jacobsen Reaction of 1,8-Diiodonaphthalene Induced by Ring Strain (*School of Environmental Science and Engineering, Kochi University of Technology*) ○Kento Iwai, Noa Nishiguchi, Nagatoshi Nishiwaki

Jacobsen rearrangement is a disproportionation of substituted benzenes, which usually requires harsh conditions.[1,2] In the present work, we studied on the halo-Jacobsen reaction under mild conditions by using ring strain caused by intramolecular steric repulsion. When 1,8-Diiodonaphthalene distorted by steric repulsion between iodo groups was reacted with stoichiometric amounts of triflic acid at room temperature, the reaction smoothly underwent to afford positional isomer **2** and **3**. Noteworthy, 4,4'-diiodo-1,1'-binaphthyl **4** was additionally obtained as a side-product. The formation of **4** indicates that deiodonative homo-coupling reaction underwent under acidic conditions, which predominantly proceeded at –40 °C. Further studies on the reaction mechanism were also performed.
Keywords：*Halo-Jacobsen reaction*; *1,8-Diiodonaphthalene*; *Halogen dance*; *Steric repulsion*; *Ring strain*

Jacobsen 転位は置換ベンゼン間で置換基が移動する不均化反応であり、反応の進行には厳しい反応条件を必要とする[1,2]。今回我々は置換基間の立体反発による環歪みを利用することにより穏和な条件下での halo-Jacobsen 転位を達成した。

ヨウ素原子間の立体反発により歪んだ 1,8-ジヨードナフタレン **1** にトリフルオロメタンスルホン酸を作用させたところ室温で速やかに反応が進行し、ヨード基が移動した **1** の位置異性体 **2**, **3** が主生成物として得られた。さらに本反応では、4,4'-ジヨード-1,1'-ビナフチル **4** が副生していた。**4** は酸性条件下での脱ヨウ素を伴うホモカップリングという新奇な反応様式により生成している。反応温度の検討を行なったところ、-40 °C でビナフチル **3** がほぼ選択的に得られることを明らかにした。その他、反応機構の検討やビナフチル **3** の変換反応について検討を行なったのでその詳細について発表する。



Temp. (°C)	2	3	4
25	30%	16%	10%
–40	3%	12%	74%

1. Suzuki, H. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1642-1650; 2. Suzuki, H.; Yoshida, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 287-288.

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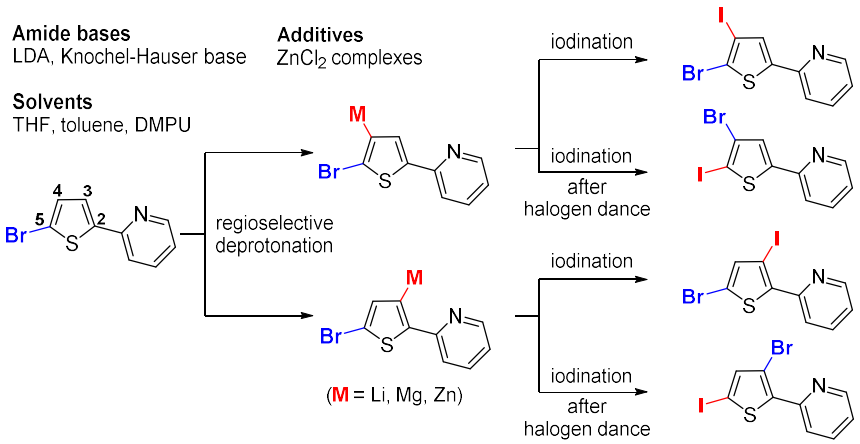
Regiodivergent Synthesis of Brominated Thienylpyridines Overriding the Inherent Substrate Bias

([1]*Department of Chemical Science and Engineering, Kobe University*, [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Masahiro Hosoya,[1] Kentaro Okano,[1] Atsunori Mori[1,2]

Keywords: Regioselective Deprotonation; Halogen Dance; Thienylpyridine

Thienylpyridine scaffold is one of the most attracting biaryl compounds, which is expected to be applied in the wide range of fields such as pharmaceuticals, β-strand peptidic mimics, metal chelators, photochromic compounds, and fluorescent materials. To stimulate the wide application of thienylpyridine, its regiodivergent synthesis is highly pursued. However, pyridine works as a powerful directing group in the functionalization of thienylpyridine, and the 3-position on the thiophene is preferably deprotonated or functionalized. Therefore, the functionalization at the 4-position is challenging because the inherent substrate bias derived from the directing effect of pyridine has to be overridden.

Our investigation began with the screening of the reaction conditions for the regiocontrolled deprotometalation. Treatment of the bromothienylpyridine with LDA in THF resulted in deprotonation mainly at the 3-position. After extensive optimization, appropriate choice of solvent and additive allowed the regioselective deprotonation at both 3- and 4-positions. Subsequently, in situ transmetalation[1] and halogen dance[2] of the corresponding organometallic species could be switched by additives and reaction temperature as well as the above reaction conditions. This method successfully enabled the synthesis of the four iodinated isomers from the single starting bromothienylpyridine. We will present the detailed screening of the reaction conditions and discuss the mechanistic insight into the regiodivergent synthesis of the brominated thienylpyridines.



1) Inoue, K.; Feng, Y.; Mori, A.; Okano, K. *Chem. Eur. J.* **2021**, *27*, 10267. 2) Schnürch, M.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046.

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一電子酸化触媒を用いたイナミンとフタラジンの脱窒素型環化によるパイ拡張アミンの合成

（岡山理大工）○奥田 靖浩・佐藤 拓磨・武部 蒼・井上 友熙・折田 明浩

Synthesis of π-Expanded Amines via Single-Electron Oxidant-Catalyzed Denitrogenative Benzannulation of Ynamine with Phthalazine

(*Fac. of Eng., Okayama Univ. of Science*) ○Yasuhiro Okuda, Takuma Sato, Sou Takebe, Tomoki Inoue, Akihiro Orita

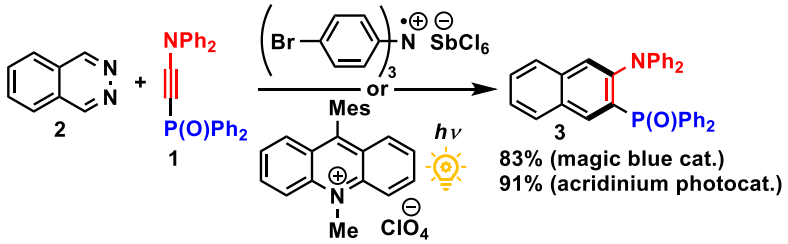
π-Expanded triarylamines have been widely used as hole-transport and luminescent materials. Recently we developed a π-expanding triarylamine synthesis via palladium-catalyzed dephosphinylative Sonogashira–Hagihara coupling of phosphinyl ynamine **1** with aryl halides and the subsequent intramolecular Friedel–Crafts cyclization[1]. We herein introduce a metal-free single-electron oxidant-promoted radical cation Diels–Alder cycloaddition of **1** with phthalazine.

When ynamine **1** and phthalazine (**2**) were treated with catalytic amount of magic blue as a single-electron oxidant, the desired π-expanded amine **3** was obtained in 83% yield. Acridinium photocatalyst/white LED irradiation-promoted denitrogenative benzannulation was achieved 91% yield. In this presentation, we also discuss the following dephosphinylative cyclization of **3** to synthesize π-expanded carbazoles.

Keywords : Ynamine; Acridinium Photocatalyst; Radical Cation; Diels–Alder Reaction; Dephosphinylation

拡張パイ共役系を含むトリアリールアミン誘導体は、正孔輸送材料や発光材料など機能性化合物として幅広く利用されている。以前、我々はパラジウム触媒によるホスフィニルイナミン **1** とアリールハライドとの薗頭－萩原カップリングおよび分子内 Friedel–Crafts 環化によりパイ拡張アミンを合成した[1]。本発表では、イナミン **1** を用いた新たなパイ拡張戦略としてフタラジンとのラジカルカチオン Diels–Alder 環化を開発した結果について紹介する。

まず、イナミン **1** とフタラジン (**2**) に一電子酸化剤としてマジックブルーを触媒量添加すると、脱窒素型環化によりパイ拡張アミン **3** が 83% 収率で得られた。また、白色 LED 照射によるアクリジニウム光触媒反応では 91% 収率を達成した。さらに本研究では **3** の脱ホスフィニル型縮環によりパイ拡張カルバゾールも合成したので、その内容についても述べる。



1) Y. Okuda, M. Fujimoto, H. Akashi, A. Orita, *J. Org. Chem.* **2021**, *86*, 17651.

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[K703-2pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Okano Kentaro, Tsuyoshi Mita

Thu. Mar 23, 2023 1:10 PM - 3:40 PM K703 (K703, Lecture Hall Bldg. [7F])

[K703-2pm-01] Peripheral Functionalization of Antiaromatic 5,15-Dioxaporphyrin

○Jiping Hao[1], Shigeki Mori[2], Soji Shimizu[1] (1. Graduate School of Engineering, Kyushu University, 2. Advanced Research Support Center (ADRES), Ehime University)

1:10 PM - 1:30 PM

[K703-2pm-02] Development of Heteroatom-Embedding Annulative π-Extension Reaction

○Kou Kawahara[1], Hideto Ito[1], Kenichiro Itami[1] (1. Nagoya University)

1:30 PM - 1:50 PM

[K703-2pm-03] Asymmetric Synthesis of Chiral Sulfimides Through the *O*-Alkylation of Chiral Sulfinamides

○Saori Tsuzuki[1], Taichi Kano[2] (1. Graduate School of Scienece, Kyoto University, 2. Graduate School of Engineering, Tokyo University of Agriculture and Technology)

1:50 PM - 2:10 PM

[K703-2pm-04] Deoxygenative Functionalization of Diarylketones

○Miki B Kurosawa[1], Moriaki Sakihara[1], Kenta Kato[1], Kei Muto[1], Junichiro Yamaguchi[1] (1. Waseda University)

2:10 PM - 2:30 PM

[K703-2pm-05] C_3-Symmetric Cage-shaped Phosphites: Structure Controls of Their Basicity, Chiral Environment, and Application to Rh-Catalyzed Asymmetric 1,4-Addition.

○Xiao Liu[1], Akihito Konishi[1], Makoto Yasuda[1] (1. Osaka University)

2:40 PM - 3:00 PM

[K703-2pm-06] Synthesis and Structure of [8]Heterocirculene by Use of Intramolecular Coupling [7]Thiaheterohelicene Derivatives

○Tatsuya Nakanishi[1], Hideji Osuga[1], Hidefumi Sakamoto[1] (1. Grad. Sch. Sys. Eng., Wakayama Univ.)

3:00 PM - 3:20 PM

[K703-2pm-07] Novel Pathways to Pentafluorosulfanylated Compounds via Thiolation and Oxidative Fluorination

○Yue Liu[1], Tim Gatzenmeier[1], Takashi Okazoe[1,2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. AGC Inc.)

3:20 PM - 3:40 PM

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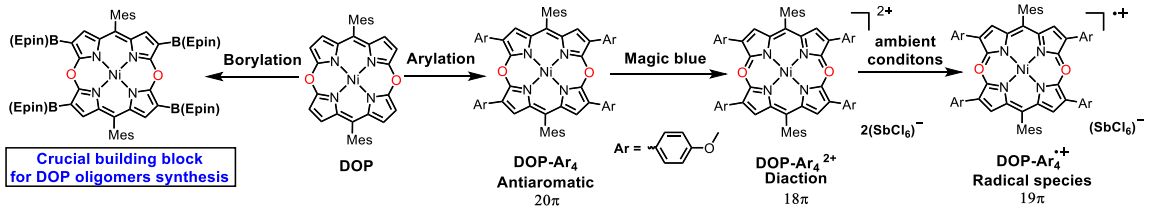
Peripheral Functionalization of Antiaromatic 5,15-Dioxaporphyrin

([1]*Graduate School of Engineering, Kyushu University,* [2]*Advanced Research Support Center (ADRES), Ehime University*) ○Jiping Hao,[1] Shigeki Mori,[2] Soji Shimizu[1]

Keywords: 5,15-Dioxaporphyrin; Aromaticity/Antiaromaticity; Redox Chemistry

Heteroatom-containing porphyrin analogues, exhibiting air stability and antiaromaticity, have been attracting considerable attention. Among these analogues, 5,15-dioxaporphyrin (DOP) was synthesized for the first time in our laboratory by a nucleophilic substitution reaction of a bis(α,α'-dibromodipyrrin) nickel complex with benzaldoxime followed by an *in-situ* annulation of the α-hydroxy-substituted intermediate.[1] In our previous study, we revealed unique reactivities of DOP in a nucleophilic ring-opening reaction and chemical oxidation reaction. In the electrochemical oxidation, DOP was transformed from the 20π-antiaromatic neutral state to the 19π-radical cation and further to the 18π-aromatic dication, whereas the chemical oxidation of DOP with $AgPF_6$ and $NOSbF_6$ provided a β,β-linked dimeric and tetrakis-β-nitrated DOP, respectively, due to the high reactivity of the radical cation species at the β-pyrrolic positions.[1,2] In this study, to prevent the dimerization and nitration upon oxidation and investigate redox behaviors of DOP, tetraaryl-substituted DOP (DOP-Ar_4) was synthesized.

DOP-Ar_4 was synthesized by bromination of DOP and subsequent Suzuki-Miyaura coupling reaction. The neutral DOP-Ar_4 was oxidized with two molar equivalents of Magic blue to provide a 18π dication species. During the oxidation process, 19π radical cation species was also obtained. The aromatic nature of the dication species was confirmed by the down-field chemical shifts of β-pyrrolic protons. The stepwise oxidation processes were also revealed by the titration study of the absorption spectra. Structures at all the oxidation states were characterized by single-crystal X-ray diffraction analysis. In addition to the oxidation reaction, an efficient strategy to construct tetraborylated DOP as a key building block for DOP oligomers was also developed. In this presentation, the reactions and properties of a series of DOP compounds will be reported.



Scheme 1. A various reaction of DOP.

1) A. Nishiyama, M. Fukuda, S. Mori, K. Furukawa, H. Fliegl, H. Furuta, S. Shimizu, *Angew. Chem. Int. Ed*. **2018**, *57*, 9728.

2) A. Nishiyama, Y. Tanaka, S. Mori, H. Furuta, S. Shimizu, *J. Porphyrins Phthalocyanines* **2020**, *24*, 355.

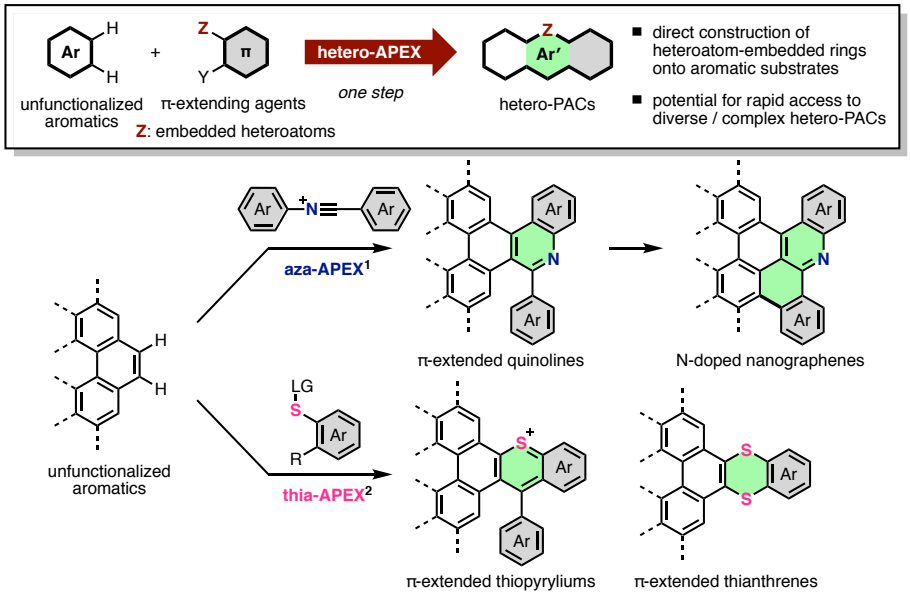
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Development of Heteroatom-Embedding Annulative π-Extension Reaction

([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules, Nagoya University*) ○Kou P. Kawahara,[1] Hideto Ito,[1] Kenichiro Itami,[1,2]

Keywords: *heteroatom-embedded polycyclic aromatic compounds; annulative π-extension reaction; quinoline; thiopyrylium salt; thianthrene*

Heteroatom-embedded polycyclic aromatic compounds (hetero-PACs) have gathered great attention in various areas of science and technologies.[1] With conventional synthetic methods, hetero-PACs are prepared via multi-step reaction processes. These methods result in lower total yield and longer reaction time, so that development of more efficient synthetic methods for hetero-PACs has been highly desired. In this context, we report development of heteroatom-embedding annulative π-extension (hetero-APEX) reactions.[2] Hetero-APEX reaction realizes a one-step construction of heteroaromatic moieties onto unfunctionalized aromatics using appropriate heteroatom-embedded π-extending agents. To date, we developed diarylnitrilium salts[2a] and *S*-succinimidated arenethiols[2b,c] as novel π-extending agents for hetero-APEX. Using these agents, we achieved direct synthesis of π-extended quinolines, π-extended thiopyrylium salts and π-extended thianthrenes by aza-APEX[2a] and thia-APEX[2b,c] reactions from unfunctionalized aromatic substrates. Moreover, synthesis of *N*-doped nanographenes and measurements of absorption/emission properties of newly synthesized hetero-PACs were demonstrated as highlights of this study.



[1] a) Stępień, M. *et al. Chem. Rev.* **2017**, *117*, 3479. b) Borissov, A. *et al. Chem. Rev.* **2022**, *122*, 565.
[2] a) Kawahara, K. P. *et al. Angew. Chem., Int. Ed.* **2020**, *59*, 6383. b) Kawahara, K. P. *et al. Chem. Commun.* **2023**, *Advance Article*. DOI: 10.1039/D2CC06706D. c) Kawahara, K. P. *et al., submitted.*

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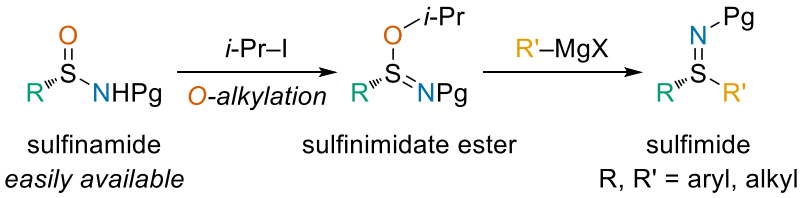
Asymmetric Synthesis of Chiral Sulfimides through the *O*-Alkylation of Chiral Sulfinamides

([1]*Graduate School of Scienece, Kyoto University*, [2]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Saori Tsuzuki,[1,2] Taichi Kano[2]

Keywords: Sulfimide; Sulfinamide; Sulfinimidate ester; Organosulfur compound; Stereospecific reaction

Chiral sulfimides, the aza-analogue of sulfoxides, are valuable compounds in organic synthesis and medicinal chemistry. Conventional methods to access chiral sulfimides involve the asymmetric imidation of sulfides with electrophilic imidating agents.[1] However, most of these methodologies suffer from the use of expensive transition-metal catalysts and imidating agents that are difficult to prepare or handle. Moreover, a significant difference in the steric and/or electronic properties of the two carbon substituents on the sulfur atom is required to achieve high enantioselectivity.

Herein we report an efficient method for preparing sulfimides from easily available chiral sulfinamides.[2] A variety of chiral alkyl or aryl sulfinamides are easily available.[3] The key step of this method is a stereospecific oxygen-selective alkylation of chiral sulfinamides, and it is accomplished by using a suitable alkylating agent, base, and solvent. The obtained chiral sulfinimidate esters are transformed to chiral sulfimides by the nucleophilic addition of the Grignard reagents under simple conditions. This transformation allows for access to the enantioenriched diaryl or dialkyl sulfimides bearing two similar carbon substituents, which are difficult to synthesize by the traditional method. Moreover, kinetic studies implied that aryl sulfimides having ortho-substituents are prone to racemization.



[1] V. Bizet, C. M. M. Hendriks, C. Bolm, *Chem. Soc. Rev.* **2015**, *44*, 3378. [2] S. Tsuzuki, T. Kano, *submitted*. [3] a) Y. Aota, T. Kano, K. Maruoka, *Angew. Chem. Int. Ed.* **2019**, *58*, 17661. b) Y. Aota, T. Kano, K. Maruoka, *J. Am. Chem. Soc.* **2019**, *141*, 19263. c) Y. Maeda, S. Hamada, Y. Aota, K. Otsubo, T. Kano, K. Maruoka, *J. Org. Chem.* **2022**, *87*, 3652.

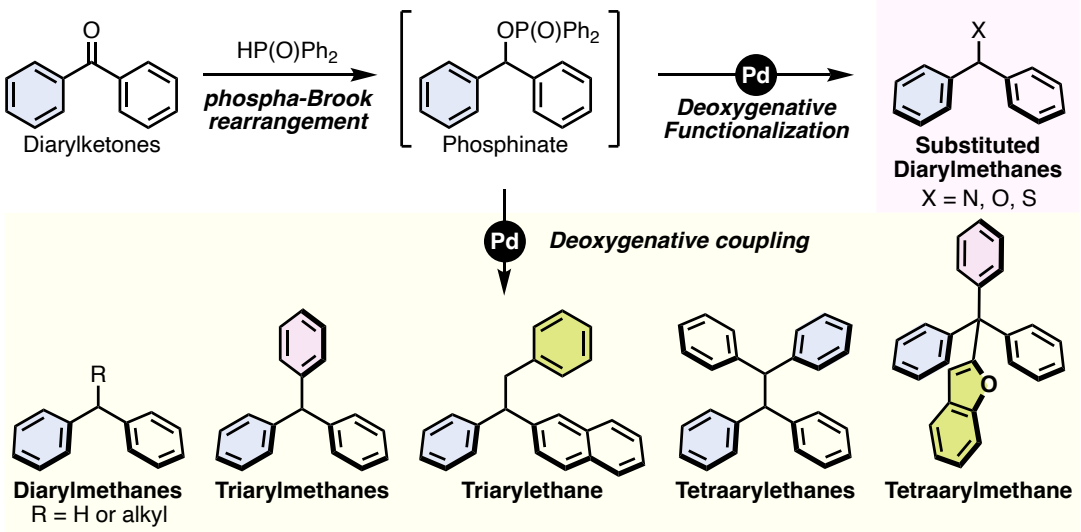
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Deoxygenative Functionalization of Diarylketones

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*Institute for Advanced Study, Waseda University*)
○Miki B. Kurosawa,[1] Moriaki Sakihara,[1] Kenta Kato,[1] Kei Muto,[2] Junichiro Yamaguchi[1]
Keywords: Diarylketones; Phospha-Brook Rearrangement; Deoxygenative Reaction; Palladium

Multiply arylated alkanes are widely used as pharmaceuticals, natural products, and organic materials. Since these are important structures, the synthesis of multiply arylated alkanes has long been investigated. Particularly recently, excellent catalytic and efficient syntheses of these alkanes have been reported using readily available building blocks and state-of-the-art methodologies. While various syntheses of multiply arylated alkanes have been reported, thus far, there is no unified synthetic protocol from the same starting materials.

Herein, we have developed a unified synthesis of multiply arylated alkanes from diarylketones. The key for this reaction is the readily generation of phosphinates from diarylketones with diphenylphosphine oxides via a phospha-Brook rearrangement.[1] Using this method, we have succeeded in synthesizing five different types of multiply arylated alkanes (diarylmethanes, diarylethane, triarylmethanes, triarylethane, tetraarylethanes and tetraarylmethane) from diarylketones in a single step (one-pot).[2] Additionally, substituted diarylmethanes were obtained by using various nucleophiles (diborylmethanes, amines, phenols, and thiols) toward phosphinates.



1) Kurosawa, M. B.; Isshiki, R.; Muto, K.; Yamaguchi, J. *J. Am. Chem. Soc.* **2020**, *142,* 7386–7392.
2) Kurosawa, M. B.; Kato, K.; Muto, K.; Yamaguchi, J. *Chem. Sci.* **2022**, *13,* 10743–10751.

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C_3-Symmetric Cage-shaped Phosphites: Structure Controls of Their Basicity, Chiral Environment, and Application to Rh-Catalyzed Asymmetric 1,4-Addition.

(*Graduate School of Engineering, Osaka University*) ○Xiao Liu, Akihito Konishi, Makoto Yasuda

Keywords: Chiral Ligand; C_3-Symmetric; Phosphite; Asymmetric Catalysis; 1,4-Addition.

The design of chiral metal ligands plays a vital role in asymmetric transition-metal catalyzed synthesis, which assists in furnishing exclusive single enantiomer product. In the history of developing chiral ligands, ligands with C_2-symmetry have received a great deal of attention and research.[1] Nevertheless, the ligands having higher axial symmetry like the C_3-symmetric ligands were reported barely, although they may result in high chiral recognition in the catalytic system.[2] On the other hand, in our laboratory, we previously designed and synthesized the C_3-symmetric cage-shaped borate **1** (Figure **1A**), its unique propeller-like chiral auxiliary allows the product with a high enantiomeric excess (90% *ee*) when applied to an asymmetric catalyst in the allylation of the aldehyde with allyl-tributyl stannane.[3]

In this work, utilizing the three homochiral binaphthol backbone of cage-shaped borate, the central atom is displayed from boron to phosphorus. A C_3-symmetric chiral cage-shaped phosphite **2a** (Figure **1B**) was designed and synthesized. **2a** as a chiral metal ligand has been applied to Rh-catalysis asymmetric conjugate addition. It gives the product in a high yield (80%) with high enantiomeric excess (94% *ee*) when cyclohexene-1-one is used for conjugate addition with phenylboronic acid. Along with this successful application, we attempted to change the tethered group from C–H to Si–Me of cage-shaped phosphite to establish a stricter chiral environment. A chiral cage-shaped phosphite **2b** was synthesized and investigated in the same reaction. Although a higher reaction temperature is required, introduce **2b** still shows a better performance of enantioselectivity (98% *ee*) demonstrating the formation of a more robust chiral auxiliary environment.

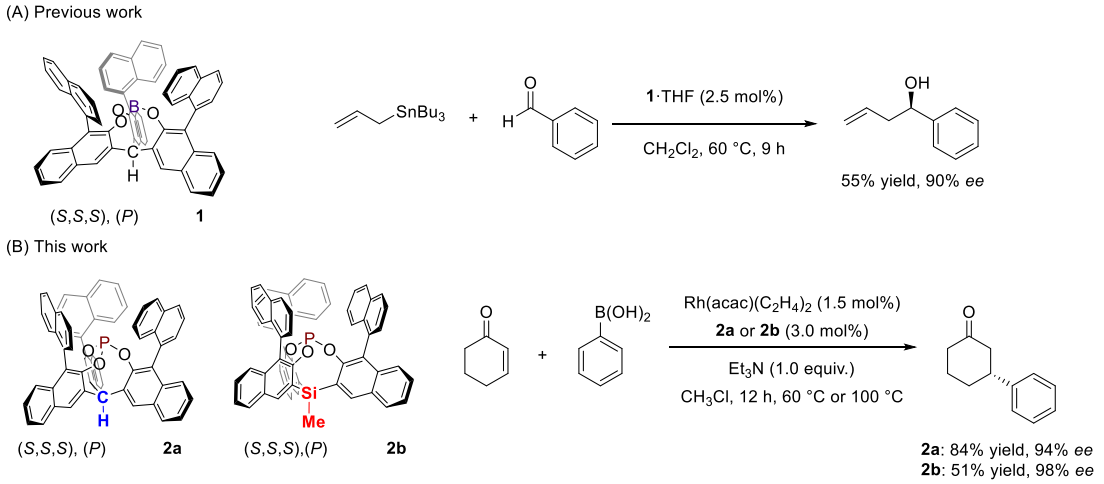


Figure 1. A) The chiral cage-shaped borate (**1**) applied in asymmetric allylation; B) The chiral cage-shaped phosphite (**2a** and **2b**) applied in Rh-catalysis asymmetric conjugate addition.

1) T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691-1693. 2) M. T. Reetz, H. Guo, J.-A. Ma, R. Goddard, R. J. Mynott, *J. Am. Chem. Soc.* **2009**, *131*, 4136–4142. 3) A. Konishi, K. Nakaoka, H. Maruyama, H. Nakajima, T. Eguchi, A. Baba, M. Yasuda, *Chem. Eur. J.* **2017**, *23*, 1273 – 1277.

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Synthesis and Structure of [8]Heterocirculene by Use of Intramolecular Coupling [7]Thiaheterohelicene Derivatives

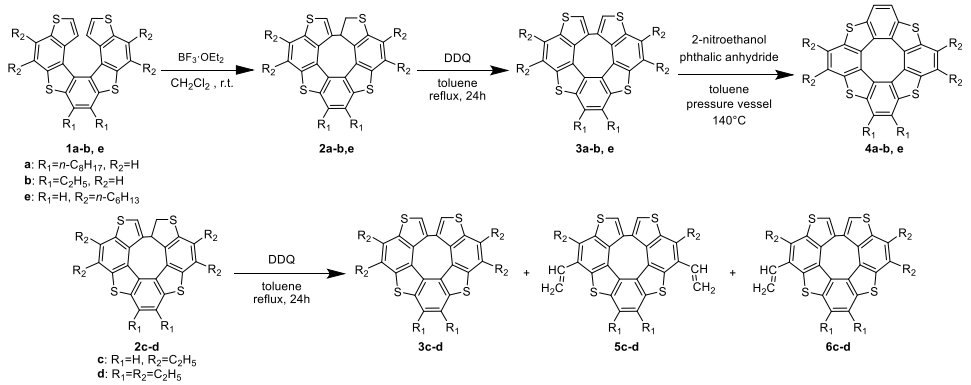
(*Graduate School of System Engineering, Wakayama University*) ○Tatsuya Nakanishi, Hideji Osuga, Hidefumi Sakamoto

Keywords: [7]Thiaheterohelicene; Intramolecular Coupling Reaction; Aromatization Reaction; [8]Heterocirculene; Diels-Alder Reaction

Helicenes are *ortho*-condensed polycyclic aromatic compounds, in which aromatics are angularly annulated to give helically-shaped molecules. We have already reported the synthesis of a number of [7]thiaheterohelicene derivatives.

In the course of these works, we found that the treatment of the [7]thiaheterohelicenes with Lewis acids gave intramolecular coupling products in which the terminal thiophene ring was not aromatized on only one side. On the other hand, the previous reports[1] have shown that the reaction of the [7]thiaheterohelicene with Lewis acids does not proceed. We also found that the reaction of the coupling product with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone(DDQ) gave the annulated heterohelicene derivatives. Since the obtained compound has the substructure of the [8]heterocirculene, the synthesis of [8]heterocirculenes using the cyclized product as a starting material is investigated. [8]Heterocirculenes has a cyclooctadiene-like structures and anti-aromatic 8π-electron systems, and their structures and properties would attract considerable interest.

In this work, the intramolecular coupling reaction of alkyl substituted [7]thiaheterohelicene derivatives was achieved by treatment with $BF_3 \cdot OEt_2$. And aromatization reaction of coupling product with DDQ gave annulated heterohelicene derivatives in quantitative yield. We will report the synthesis and structure of the [8]heterocirculene starting from the aromatized intramolecular coupling products of the alkyl substituted [7]thiaheterohelicene derivatives. We will also report the regioselective dehydrogenative reaction of the side alkyl chains in the reaction pathway.



1) a) M. B. Groen, H. Schadenberg, H. Wynberg, *J. Org. Chem.*, **1971**, *36*, 2797. b) J. H. Dopper, H. Wynberg, *J. Org. Chem.*, **1975**, *40*, 3398.

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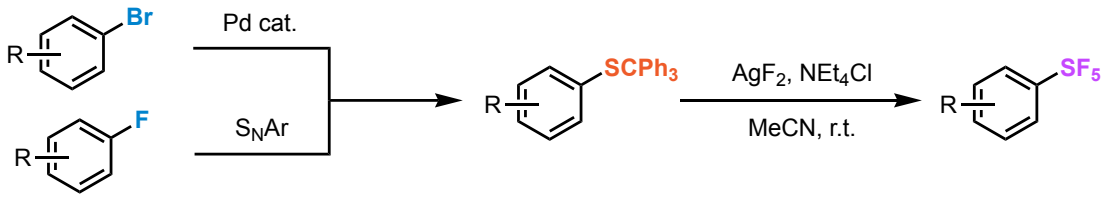
Novel Pathways to Pentafluorosulfanylated Compounds *via* Thiolation and Oxidative Fluorination

([1]*Graduate School of Engineering, the University of Tokyo,* [2] *AGC Inc.*) ○Yue Liu,[1] Tim Gatzenmeier, [1] Takashi Okazoe, [1,2] Kyoko Nozaki[1]

Keywords: Pentafluorosulfanyl Group; Silver Difluoride; Oxidative Fluorination; Cross-Coupling Reaction; S_NAr Reaction

A novel synthetic methodology towards pentafluorosulfanylated aromatic compounds ($ArSF_5$ compounds) through an efficient, two-step protocol from a variety of raw materials was developed, with substantially improved yields having been achieved over a broader substrate scope than has ever been realized. Crucially, the synthesis of $ArSF_5$ compounds has remained prohibitively inefficient since the first such report by W. A. Sheppard in 1960.[1] The latest synthetic method reported by Togni *et al.* in 2019 uses trichloroisocyanuric acid (TCICA) and KF to obtain $ArSF_4Cl$ intermediates which are then converted to the corresponding $ArSF_5$ compounds by AgF. Unfortunately, this multi-step synthetic route suffers from low to moderate (31–55%) overall yields and involves hydrolytically-sensitive $ArSF_4Cl$ intermediates, requires long reaction times, and spans a limited scope lacking in electron-rich examples.[2] The present discussion relates to our recent disclosure of direct oxidative fluorination of diaryl disulfides and aryl thiols into $ArSF_5$ compounds utilizing a system of AgF_2 and tetraalkylammonium halides.[3] These findings have prompted the supposition that this oxidative fluorination system can be applied to an even wider variety of sulfur-containing intermediates, bringing $ArSF_5$ compounds into ever nearer reach of applied synthetic chemists.

Aryl trityl sulfides (ArSTr) were found to convert smoothly to $ArSF_5$ compounds in a single, high-yielding step under modified reaction conditions. However, as only a limited number of ArSTr syntheses from aryl bromides and fluorides have been reported in the literature,[4,5] a thorough investigation into their synthesis by way of both cross-coupling and S_NAr reactions was performed. In summary, $ArSF_5$ compounds can now be accessed from aryl halides in two steps *via* thiolation followed by oxidative fluorination, with net combined yields reaching as high as 95% of theory.



1) W. A. Sheppard *J. Am. Chem. Soc.* 1960, 82, 4751. 2) A. Togni, *Angew. Chem. Int. Ed.* **2019**, 58, 1950. 3) T. Okazoe, T. Gatzenmeier, K. Nozaki WIPO Patent WO 2022/186304 Al, 2022. 4) R. Fasan *Chem. Comm.* **2012**, *48*, 1461. 5) M. C. Stefan *Organometallics* **2021**, *40*, 83.

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[K705-2pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Shintaro Kawamura, Takatsugu Murata
Thu. Mar 23, 2023 1:10 PM - 3:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-2pm-01] Stereoselective Addition of Sulfenate Species to Electrophiles as a Versatile Synthetic Method of Chiral Sulfoxides

○Jian Zhang[1], Keisuke Suzuki[2], Ken Ohmori[1] （1. Department of Chemistry, School of Science, Tokyo Institute of Technology., 2. Institute of Innovative Research, Tokyo Institute of Technology.）

1:10 PM - 1:30 PM

[K705-2pm-02] The Effect of Water in the Esterification Mediated by MNBA, Highly Efficient Dehydration Condensation Reagent

Takatsugu Murata[1], ○Nao Takabayashi[1], Isamu Shiina[1] （1. Tokyo University of Science）

1:30 PM - 1:50 PM

[K705-2pm-03] *Z*-Enamide Synthesis by Stereoselective Radical Fluoroalkylation Reaction

○Takuma Tagami[1], Daisuke Sekine[2], Yuma Aoki[1], Shintaro Kawamura[1,2], Mikiko Sodeoka[1,2] （1. RIKEN CSRS, 2. RIKEN CPR）

1:50 PM - 2:10 PM

[K705-2pm-04] Carboxylic Acid-Cooperative-Ru(bpga)-Catalyzed Highly Site-Selective C– H Oxygenation

○Daiki Doiuchi[1], Nanako Shimoda[1], Tatsuya Uchida[1,2,3,4] （1. Grad. Sch. Sci., Kyushu Univ., 2. Fac. Arts and Sci., Kyushu Univ., 3. WPI-I2CNER, Kyushu Univ., 4. JST-PRESTO）

2:10 PM - 2:30 PM

[K705-2pm-05] Visible-Light-Induced Carboamination of Styrenes with Carboxylic Acids and (Diarylmethylene)aminobenziodoxolones

○Daichi Okumatsu[1], Kensuke Kiyokawa[1], Satoshi Minakata[1] （1. Graduate School of Engineering, Osaka University）

2:40 PM - 3:00 PM

[K705-2pm-06] Tandem Enantioselective [2+2], [3+2] and [4+2] Cycloaddition Reactions of In Situ-generated *N*-Allenoylpyrazoles Induced by Chiral π– Cu(II) Catalysts

○Weiwei Guo[1], Masahiro Hori[1], Yoshihiro Ogura[1], Kazuki Nishimura[1], Kazuaki Ishihara[1] （1. Nagoya University）

3:00 PM - 3:20 PM

[K705-2pm-07] Enantioselective Radical Cation [2+2] and [4+2] Cycloadditions Using Chiral Iron(III) Catalyst with Photoirradiation

○Kei Katagiri[1], Haruna Kato[1], Shuhei Ohmura[1], Takahiro Horibe[1], Kazuaki Ishihara[1] （1. Nagoya University）

3:20 PM - 3:40 PM

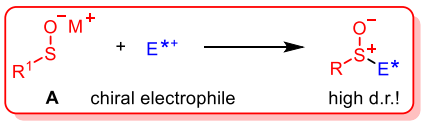
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Stereoselective Addition of Sulfenate Species to Electrophiles as a Versatile Synthetic Method of Chiral Sulfoxides

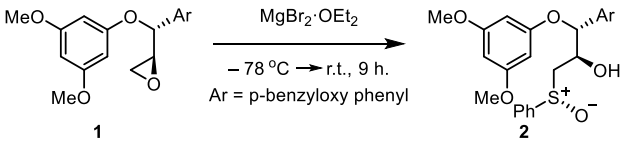
([1]*Department of Chemistry, Tokyo Institute of Technology*, [2]*Institute of Innovative Research, Tokyo Institute of Technology*) ○Jian Zhang,[1] Keisuke Suzuki,[2] Ken Ohmori[1]
Keywords: sulfenate species, stereoselective, chiral sulfoxides.

During a course of our synthetic study on bioactive natural flavonoids, we found that epoxide **1** allows the nucleophilic attack of the sulfenate species **A** to give *β*-hydroxy sulfoxide **2** with *anti*-stereochemistry, albeit in a poor yield. Stimulated by these results, we assumed that this method would serve as a useful way to access various chiral sulfoxides, and thus, we decided to pursuit this reaction.
First of all, we examined the diastereoselective ring-opening of epoxide by sulfenate anion **A**, and found that $MgBr_2 \cdot OEt_2$ accelerates the reaction significantly, giving corresponding *β*-hydroxy sulfoxides in high yield with *anti*-selectivity. Secondly, we attempted the reaction of oxetane derivatives with **A** and discovered that an addition of catalytic $Sc(OTf)_3$ allows the diastereoselective synthesis of *γ*-hydroxy sulfoxides in excellent yield with high *anti*-selectivity. Finally, we successfully demonstrated the axial-to-central chirality transfer with allenes and sulfenate anion **A**, giving the *S*-chirogenic sulfoxide compounds in complete selective manner.

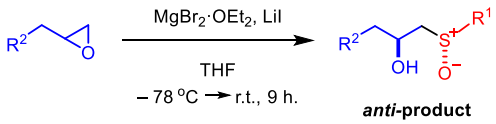
This work



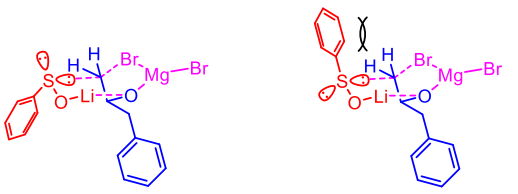
Preliminary results



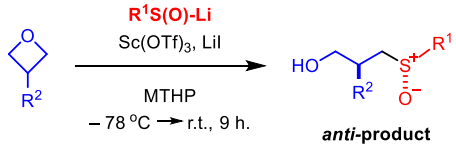
A) with epoxides



R^1 = *n*-Hex	R^2 = Ph	72% yield, 18:1 d.r.
2-NAP	Ph	96% yield, >20:1 d.r.
2-NAP	Cl	98% yield, >20:1 d.r.

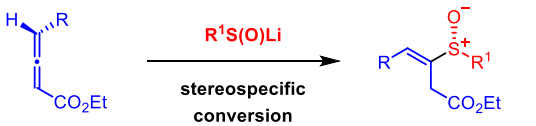


B) with oxetanes

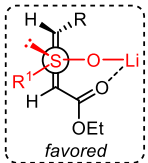


R^1 = *n*-Hex	R^2 = Ph	96% yield, >20:1 d.r.
n-Hex	*c*-Hex	95% yield, >20:1 d.r.
2-NAP	Ph	98% yield, >20:1 d.r.
2-NAP	Bn	95% yield, >20:1 d.r.

C) with allenes



R = Me	R^2 = *c*-Hex	91% yield, 95% ee
^{t}Bu	dodecyl	91% yield, >99% ee
Ph	*c*-Hex	91% yield, >99% ee
Ph	dodecyl	90% yield, >99% ee

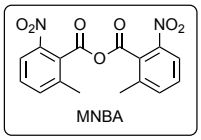


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迅速脱水縮合剤 MNBA を用いたエステル化反応に与える水の影響

（東理大理）村田 貴嗣・○高林 奈央・椎名 勇
The Effect of Water in the Esterification Mediated by MNBA, Highly Efficient Dehydration Condensation Reagent (*Faculty of Science, Tokyo University of Science*) Takatsugu Murata, ○Nao Takabayashi, Isamu Shiina

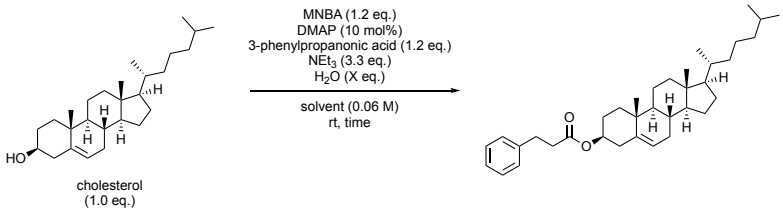
As a highly efficient dehydration condensation reagent, 2-methyl-6-nitrobenzoic anhydride, MNBA has been utilized for the ester bond formation and the amide bond formation. Notably, the number of reports on utilization to derivatization in microscale analysis has remarkably increased. The water content of substances in microscale analysis should be considered. Therefore, we have investigated the effect of water in the esterification mediated by MNBA.
Keywords : Dehydration Condensation; Esterification; MNBA; Microscale Analysis



2-メチル-6-ニトロ安息香酸無水物[1]、すなわち MNBA はこれまでに迅速脱水縮合剤として多くのエステル結合形成、アミド結合形成反応に用いられてきた。近年、生体内分子の微量分析を実施する際の汎用縮合剤としても広く用いられ、利用例が著しく増加している[2,3]。一方で、水が共存した場合に、この反応がどのように阻害されるかについては今まで調査が行われてこなかった。そこで我々は、MNBA を用いたエステル化反応に与える水の影響について調査することとした。

本研究では、基質に生合成産物であるコレステロールを選択し、縮合剤に MNBA を用いて、触媒量の DMAP の存在下で 3-フェニルプロパン酸とのエステル化反応を行った[1]。まず、反応次数を調査するために各反応時間で反応を実施した。その後、各試薬が反応に何次に相関するかを調査した。続いて、あらかじめ水を溶かし込んだ溶媒を用いて反応を実施し、反応に与える水の影響の調査に取り組んだ。

今回我々は、MNBA を用いたエステル化反応が混合酸無水物を経由していることを実験的に示した。また、水が共存した場合のエステル化反応に与える水の影響の調査を行うことで、反応に水がどのように作用しているかを明らかにした。さらに、これらの結果を踏まえ、微量分析に採用可能な反応条件として、含水条件でも無水条件と同等の収率が与えられる条件を調査した。本講演ではこれらの詳細を報告する。



1) I. Shiina, R. Ibuka, M. Kubota, *Chem. Lett.*, **2002**, *31*, 286–287.
2) K. Yamashita, M. Takahashi, S. Tsukamoto, M. Numazawa, M. Okuyama, S. Honma, *J. Chromatogr. A.*, **2007**, *1173*, 120–128.
3) Z. Hubler, D. J. Adams, *et al*., *Nature*, **2018**, *560*, 372–376.

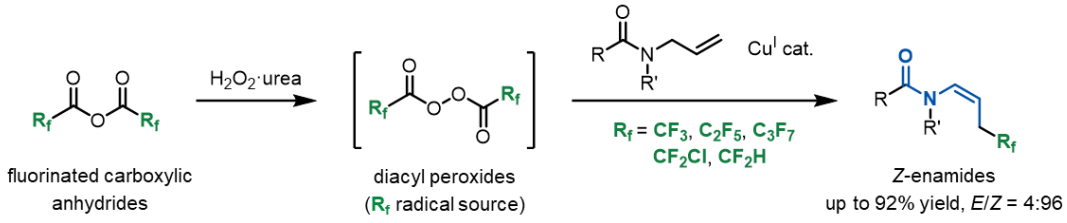
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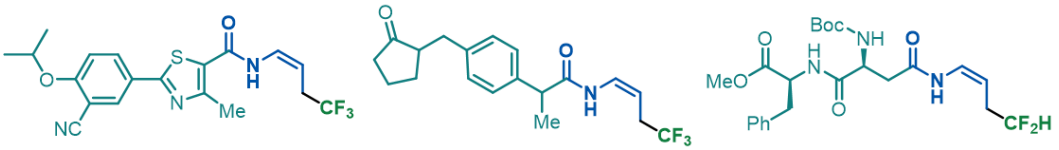
Z-Enamide Synthesis by Stereoselective Radical Fluoroalkylation Reaction

(1*RIKEN Center for Sustainable Resource Science*, 2*RIKEN Cluster for Pioneering Research*)
○Takuma Tagami,[1] Daisuke Sekine,[2] Yuma Aoki,[1] Shintaro Kawamura,[1,2] Mikiko Sodeoka[1,2]
Keywords: *Z*-Enamides; Stereoselective Reaction; Radical Reaction; Allylic Fluoroalkylation; Metallacycle Intermediates

Z-Enamides are important motif as synthetic building blocks and bioactive molecules. Thus, stereoselective *Z*-enamide synthesis has long been studied. The methods based on polar reactions have been established, whereas radical approaches to *Z*-enamide synthesis is rarely known due to difficulty of the controlling stereochemistry. The previous stereoselective synthesis involving radical species required directing group on the substrate, such as inducing intramolecular hydrogen bonding and steric repulsion of the substituents, which strongly limited the substrate scope. Therefore, a typical method for controlling the stereoselectivity is highly demanded in the radical-involving *Z*-enamide synthesis to expand their chemical space, because radical reactions usually allowed to introduce unique functional groups that is difficult to be achieved by polar reactions.

In this work, we developed a novel method for *Z*-enamide synthesis by stereoselective radical fluoroalkylation of *N*-allylamides, which does not require the directing substituents. The fluoroalkylated *Z*-enamides were obtained by copper-catalyzed reaction of *N*-allylamides with diacyl peroxides that were prepared from fluorinated carboxylic anhydrides and urea·H_2O_2 in-situ and employed as a perfluoroalkyl radical source. This method could introduce various fluoroalkyl groups (R_f) by changing fluorinated carboxylic anhydrides, and also apply to a late-stage functionalization of bioactive molecules. Furthermore, the obtained products were derivatized to various *N*-containing fluoroalkyl molecules in order to prove their utility as a building block. In addition to the reaction development, its mechanistic studies including kinetic experiments were performed to elucidate the origin of the unusual *Z*-selectivity outcome. The details will be discussed in the presentation.





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Carboxylic Acid-Cooperative Ru(bpga)-Catalyzed Highly Site-Selective C–H Oxygenation

([1]*Graduate School of Science, Kyushu University*, [2]*Faculty of Arts and Science, Kyushu University,* [3]*International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University*, [4]*Japan Science and Technology Agency (JST) PRESTO*) ○Daiki Doiuchi,[1] Nanako Shimoda,[1] Tatsuya Uchida[1,2,3,4]

Keywords: C–H Oxidation; Acid-Cooperative Catalysis; Hydrogen Peroxide; Site-Selective Oxidation; Ruthenium Catalyst

C–H oxygenation is a useful and powerful tool for the short-step and atom-economic organic synthesis.[1] Recently, highly practical and site-selective C–H oxygenation has been revealed by using Ru(bpga) [bpga: *N*,*N*-bis(2-pyridylmethyl)glycinamide] **1a** as the catalyst, albeit with requiring atom-economically unfavored hypervalent iodine regent as the terminal oxidant.[2,3] Fortunately, during these studies, we found that the C–H oxidation dramatically accelerated through hydrogen bonding between an oxo ligand and a carboxylic acid. On the other hand, in non-heme-enzymatic catalysis, carboxylate ligands have been known to activate H_2O_2 to give the putative metal(oxo) species. Thus, ruthenium-catalyzed oxidation combined with these acid-cooperative effects was thought to be able to use hydrogen peroxide, an environmentally friendly and atom-economic reagent, as the terminal oxidant.

Based on this consideration, we investigated the acid-cooperative C–H oxidations using Ru(bpga) catalysts and hydrogen peroxide, and achieved a highly practical and useful catalytic site-selective C–H oxygenation by introducing Ru(bpga)(H-maleate)$_2$ complex **1b** as the catalyst (Figure 1).[4] Intramolecular acid-cooperative complex **1b** with hydrogen peroxide presented excellent site-selectivity on even late-stage C–H oxygenation, and high turnover frequency (up to 600 rph). The C–H oxygenation allowed wide functional group tolerance; the substrates bearing nitro, cyanide, alcohol, sulfonamide, carbamate, pyridine, and amine groups can also produce oxygenated compounds with excellent site-selectivity.

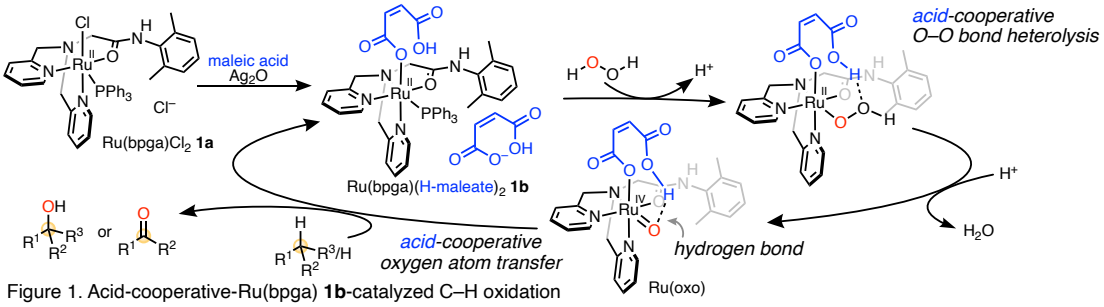


Figure 1. Acid-cooperative-Ru(bpga) **1b**-catalyzed C–H oxidation

1) D. Doiuchi, T. Uchida, *Synthesis*, **2021**, *53*, 3235–3246.

2) D. Doiuchi, T. Nakamura, H. Hayashi, T. Uchida, *Chem. Asian J.* **2020**, *15*, 762–765.

3) D. Doiuchi, T. Uchida, *Org. Lett.* **2021**, *23*, 7301–7305.

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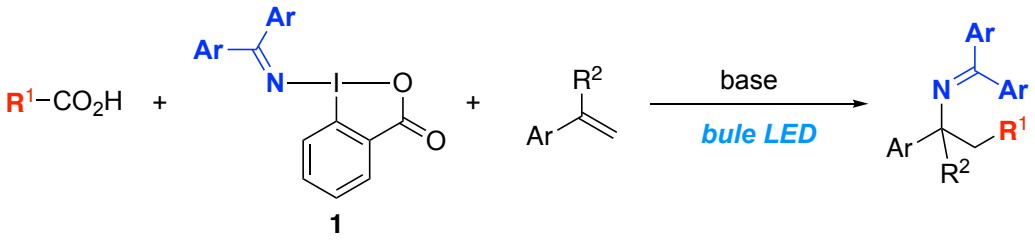
Visible-Light-Induced Carboamination of Styrenes with Carboxylic Acids and (Diarylmethylene)aminobenziodoxolones

(*Graduate School of Engineering, Osaka University*) ○ Daichi Okumatsu, Kensuke Kiyokawa, Satoshi Minakata

Keywords: Alkenes; Amination; Carboxylic Acids; Hypervalent Iodine; Radical Reaction

Amines are an important class of compounds that have wide applications in organic synthesis, medicinal chemistry, and material science. An intermolecular carboamination of alkenes that enables the simultaneous construction of C−C and C−N bonds is one of the most attractive strategies for the rapid synthesis of complex amines. Although a radical carboamination using readily available carboxylic acids as a carbon radical precursor would be a useful method, existing methods require the pre-preparation of carboxylic acid derivatives such as redox-active esters, diacyl peroxides, and oxime esters.[1,2] Carboxylic acids have never been used directly as a carbon radical precursor for carboamination.

We recently reported the synthesis of (diarylmethylene)aminobenziodoxolones (**1**) and their application in the radical amination of silyl ketene acetals.[3] In this reaction, the iodine reagent **1** was found to function both as a single-electron oxidant and an iminyl radical source. In addition, we also found that **1** can function as a photoexcited oxidant under the irradiation of visible-light[4] and enables single-electron oxidation of carboxylates to generate an alkyl radical species. Based on these findings, we have achieved the carboamination of styrenes using carboxylic acids and **1** in the presence of a base under irradiation of blue LEDs. This method allows the use of various styrene derivatives and aliphatic carboxylic acids generating primary, secondary, and tertiary alkyl radicals, leading to a wide range of complex amines. In addition, (diarylmethylene)amino groups in the products could be easily transformed by acid hydrolysis and hydride reduction, providing the corresponding primary amines and (diarylmethyl)amines, respectively.



1) H. Jianga, A. Studer, *Chem. Soc. Rev*. **2020**, *49*, 1790. 2) T. Patra, P. Bellotti, F. Strieth-Kalthoff, F. Glorius, *Angew. Chem., Int. Ed.* **2020**, *59,* 3172. 3) K. Kiyokawa, D. Okumatsu, S. Minakata, *Angew. Chem., Int. Ed.* **2019**, *58,* 8907. 4) S. G. E. Amos, D. Cavalli, F. Le Vaillant, J. Waser, *Angew. Chem., Int. Ed.* **2021**, *60,* 23827.

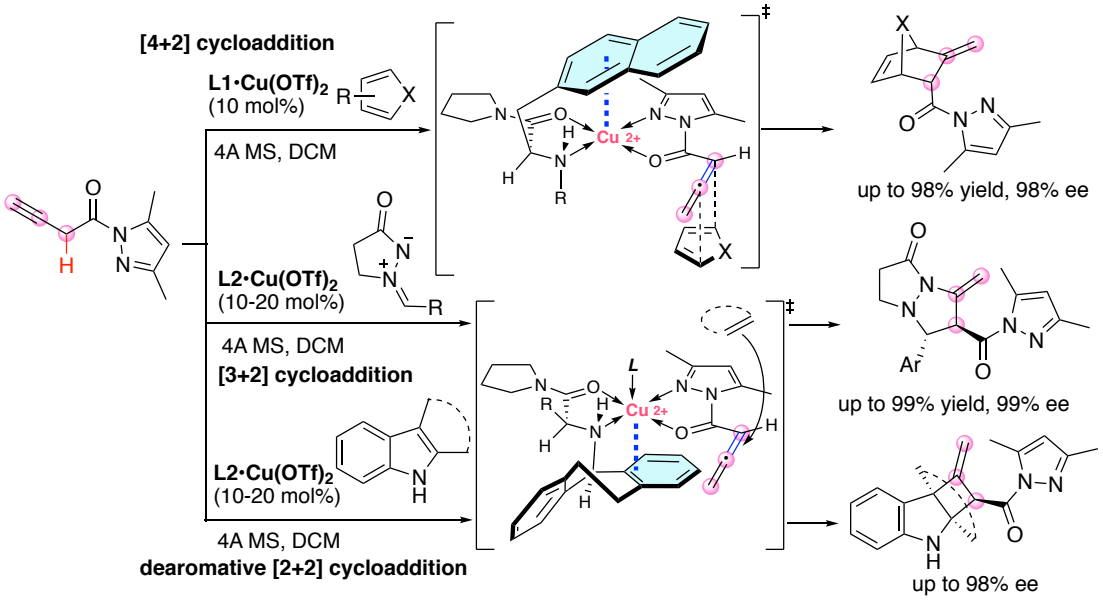
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Tandem Enantioselective [4+2], [3+2] and [2+2] Cycloaddition Reactions of *In Situ*-generated *N*-Allenoylpyrazoles Induced by Chiral π–Cu(II) Catalyst

(*Graduate School of Engineering, Nagoya University*) ○ Weiwei Guo, Masahiro Hori, Yoshihiro Ogura, Kazuki Nishimura, Kazuaki Ishihara

Keywords: Isomerization; *N*-Allenoylpyrazole; Cycloaddition; Chiral π–copper(II) complex; Enantioselectivity

Allenes are important building blocks, and derivatation of products *via* their cycloadditions could be a powerful strategy for constructing carbocyclic and heterocyclic rings. The synthesis of allenes and developing their enantioselective cycloaddition reactions, however, still present challenge. Here, we report chiral π–copper(II) complex[1]-catalyzed isomerization of *N*-(but-3-ynoyl)-3,5-dimethyl-1*H*-pyrazoles to *in situ* generate *N*-allenoylpyrazoles and successive enantioselective [4+2], [3+2] and [2+2] cycloaddition reactions. The asymmetric environment created by intramolecular π–Cu(II) interaction gives the corresponding adducts in high yields with excellent enantioselectivity. To the best of our knowledge, it is the first successful method for Lewis acid-catalyzed one-pot enantioselective cycloaddition of *N*-allenoylpyrazoles.



References

1. For recent examples of π–Cu(II) catalysis, see: (a) K. Ishihara, K. Nishimura, K. Yamakawa, *Angew. Chem. Int. Ed.*, **59**, 17641 (2020); (b) K. Nishimura, Y. Wang, Y. Ogura, J. Kumagai, K. Ishihara, *ACS Catal.*, **12**, 1012 (2022); (c) K. Nishimura, K. Ishihara, *Synlett*, **33**, 585 (2022).

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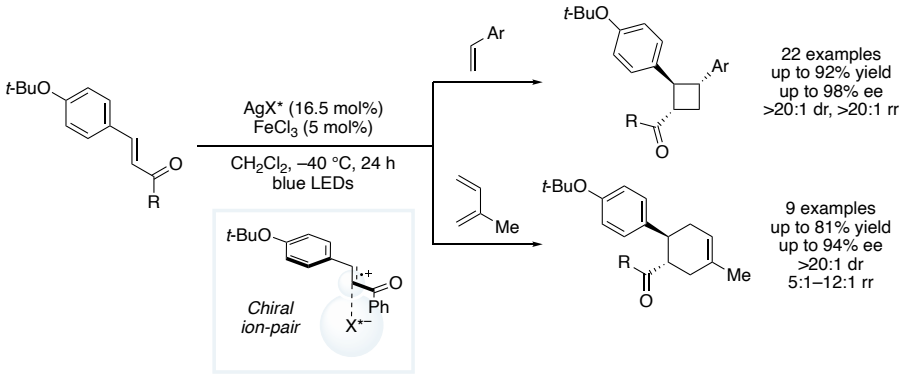
Enantioselective Radical Cation [2+2] and [4+2] Cycloadditions Using Chiral Iron(III) Catalyst with Photoirradiation

(*Graduate School of Engineering, Nagoya University*) ○Kei Katagiri, Haruna Kato, Shuhei Ohmura, Takahiro Horibe, Kazuaki Ishihara

Keywords: Radical Cation; Cycloaddition; Chiral Iron(III) Catalyst; Chiral Counter Anion; Photoirradiation

Radical cations are open-shell cationic species that are usually generated by the one-electron oxidation of neutral molecules. As their behavior is distinct from those of cations generated by two-electron processes (e.g., protonation, heterolysis, and coordination to Lewis acids), considerable effort has been directed toward using radical cations as alternative cationic intermediates for organic reactions. On the other hand, asymmetric catalysis to promote enantioselective radical cation reactions remains a major challenge in contemporary organic synthesis. However, over the last few years, Luo and Nicewicz have independently developed a novel class of chiral photoredox catalysts that provided the targeted products with modest enantioselectivity.[1] These pioneering studies have demonstrated the feasibility of controlling the reactivity of such labile species in order to accomplish highly enantioselective reactions.

We have already developed radical cation cycloadditions using iron(III) salts as effective and earth-abundant one-electron oxidants. According to our previous reports,[2] the X-ray crystallographic analysis of a radical cation generated by $FeCl_3$ reveals a structure with a tight ion pair between the radical cation and $FeCl_4^-$. These findings inspired us to develop a chiral version of this iron(III) catalysis. Here, we report that an iron(III) salt containing a relatively weakly coordinating chiral anion is able to catalyze enantioselective radical cation [2+2] cycloadditions under irradiation with blue LEDs. To demonstrate the practical utility of this approach, we also explored enantioselective [4+2] cycloadditions to afford unusual regioisomers, highlighting the complementarity of our method to well-known Lewis-acid-mediated [4+2] cycloadditions.



1) a) Z. Yang, H. Li, S. Li, M.-T. Zhang, S. Luo, *Org. Chem. Front.* **2017**, *4*, 1037. b) P. D. Morse, T. M. Nguyen, C. L. Cruz, D. A. Nicewicz, *Tetrahedron* **2018**, *74*, 3266.
2) T. Horibe, S. Ohmura, K. Ishihara, *J. Am. Chem. Soc.* **2019**, *141*, 1877.

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[K705-2vn] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Muhammet Uyanik, Yuuya Kawasaki
Thu. Mar 23, 2023 4:10 PM - 6:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-2vn-01] Magnesium(II) and Sodium(I) Bisphenoxide Catalysts for Transesterification of Methyl (Meth)acrylate and Their Reaction Mechanisms

○Kazumasa Kon[1], Xue Zhao[2], Manussada Ratanasak[3], Chie Joko[2], Jun-ya Hasegawa[3], Kazuaki Ishihara[2] (1. Nagoya University Venture Business Laboratory, 2. Nagoya University, 3. Hokkaido University)

4:10 PM - 4:30 PM

[K705-2vn-02] Development of DACN based Multi-Molecular Connector and Its Application for Hybridization of Peptides

○Tomoya Hayashibara[1], Yuuki Seto[1], Yuutaro Taniguchi[1], Kazunobu Igawa[2], Kawasaki Yuuya[3], Katsuhiko Tomooka[1,3] (1. IMCE, Kyushu Univ., 2. FAST, Kumamoto Univ., 3. IGSES, Kyushu Univ.)

4:30 PM - 4:50 PM

[K705-2vn-03] Synthesis of polyhalogenated molecules by a general Cu-catalyzed halo-halofluoroalkylation of alkenes/alkynes with fluorinated carboxylic anhydrides

○SUBRATA MUKHERJEE[1], YUMA AOKI[1], SHINTARO KAWAMURA[1,2], MIKIKO SODEOKA[1,2] (1. RIKEN CSRS, 2. RIKEN CPR)

4:50 PM - 5:10 PM

[K705-2vn-04] *E*-Selective Elongation Reaction of Aldehydes by Weinreb Amide-type Horner– Wadsworth– Emmons Reagent

○Hisazumi Tsutsui[1], Takatsugu Murata[1], Shintaro Hiraishi[1], Daiki Usukura[1], Hiroki Okano[1], Isamu Shiina[1] (1. Tokyo University of Science)

5:10 PM - 5:30 PM

[K705-2vn-05] Et_2Zn-Mediated Cross-coupling Reactions between Dibromoketones and Monobromo Carbonyl Compounds

○Aika Takeshima[1,2], Taichi Kano[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2. Graduate School of Science, Kyoto University)

5:40 PM - 6:00 PM

[K705-2vn-06] Design and synthesis of novel bifunctional organocatalysts for an enantioselective rearrangement of α-acyloxy-β-keto sulfides to α-acyloxy thioesters

○Julie Kong[1,2], Chloée Bournaud[1], Yasuhiro Yamashita[2], Shū Kobayashi[2], Giang Vo-Thanh[1] (1. Université Paris-Saclay, Institut de Chimie Moléculaire et des Matériaux d'Orsay, 2. The University of Tokyo, Department of Chemistry, School of Science)

6:00 PM - 6:20 PM

[K705-2vn-07] Development of Efficient Synthetic Method of Latanoprost Using an Organocatalyst

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○Genki Kawauchi[1], Yurina Suga[1], Shunsuke Toda[1], Yujiro Hayashi[1] （1. Tohoku Univ.）

6:20 PM - 6:40 PM

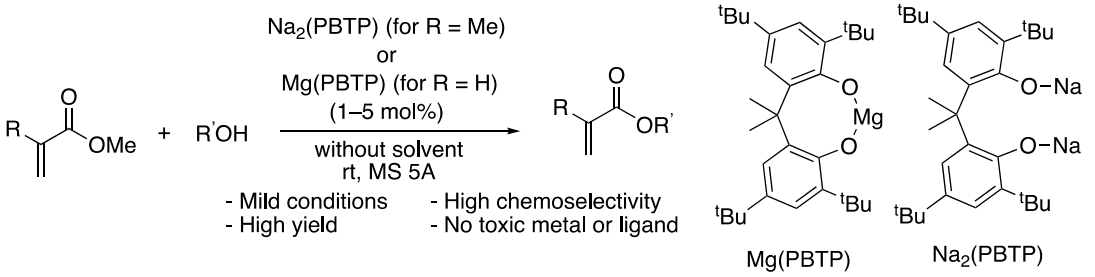
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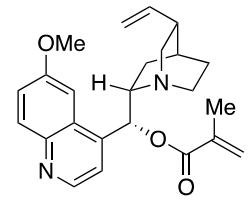
Magnesium(II) and Sodium(I) Bisphenoxide Catalysts for Transesterification of Methyl (Meth)acrylate and Their Reaction Mechanisms

(*[1]Venture Business Laboratory, Nagoya University, [2]Graduate School of Engineering, Nagoya University, [3] Section of Theoretical Catalytic Chemistry, Institute for Catalysis, Hokkaido University*) ○ Kazumasa Kon,[1]Xue Zhao,[2] Manussada Ratanasak,[3] Chie Joko,[2] Jun-ya Hasegawa,[3] Kazuaki Ishihara[2]

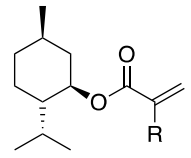
Keywords: Transesterification; Acrylate; Methacrylate; Chemoselective; DFT Calculation

Chemoselective transesterification of methyl acrylate (MA) and methyl methacrylate (MMA) is the important synthetic method to produce (meth)acrylates because (meth)acrylates are useful for various industrial applications. Previously, we developed Mg(II) and Na(I) catalysts derived from 2,6-di-*tert*-butyl-4-methylphenol (BHT–H) for the chemoselective transesterification of MA and MMA, respectively.[1] In this presentation, we report the development of bulky Mg(II) and Na(I) bisphenoxides derived from 6,6'-(propane-2,2'-diyl)bis(2,4-di-*tert*-butyl)phenol (PBTP-H_2) as more active catalysts for chemoselective transesterification of MA and MMA.[2] Various primary and secondary alcohols, diols, triols and thermally unstable alcohols provided the corresponding (meth)acrylates in high yield without Michael adducts. The X-ray diffraction analyses of Mg(II) and Na(I) complexes succeeded, and DFT calculations were conducted to understand reaction mechanisms.



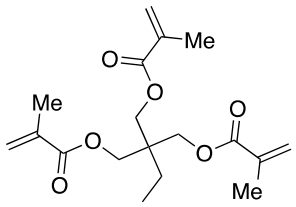


3 h, >99% yield
[Na(BHT): 6 h, >99% yield]



R = Me, 0.5 h, >99% yield
[Na(BHT): 3 h, 99% yield]

R = H, 24 h, >99% yield
[$Mg(BHT)_2$: 48 h, 90% yield]



2.5 mol%, 38 h, >99% yield
[Na(BHT): 5 mol%, 48 h, >99% yield]

1) Ng, J. Q.; Arima, H.; Mochizuki, T.; Toh, K.; Matsui, K.; Ratanasak, M.; Hasegawa, J.; Hatano, M.; Ishihara, K. *ACS Catal.* **2021**, *11*, 199–207. 2) Zhao, X.; Ratanasak, M.; Kon, K.; Hasegawa, J.; Ishihara, K. *Chem. Sci.* **2022**, accepted.

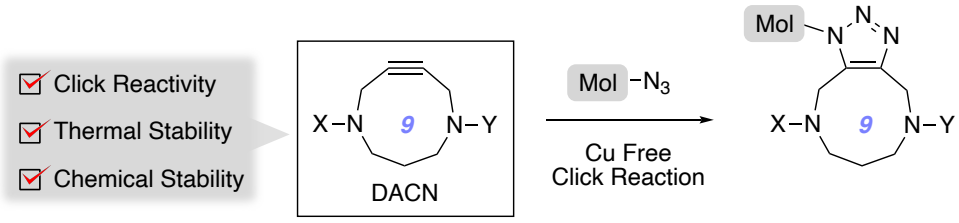
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多分子連結型 DACN 誘導体の開発とペプチド複合化への応用

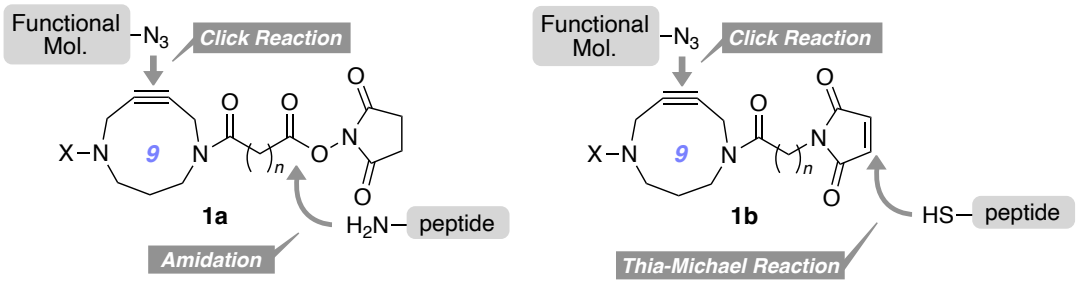
(九大院総理工[1]・熊大先端科学[2]・九大先導研[3])
○林原 智也[1]・瀬戸 祐樹[1]・谷口 優太郎[1]・井川 和宣[2]・河崎 悠也[3]・友岡 克彦[1,3]
Development of DACN based Multi-Molecular Connector and Its Application for Hybridization of Peptides ([1]*IGSES, Kyushu Univ.*, [2]*FAST*, *Kumamoto Univ.*, [3]*IMCE*, *Kyushu Univ.*) ○Tomoya Hayashibara,[1] Yuki Seto,[1] Yutaro Taniguchi,[1] Kazunobu Igawa,[2] Yuuya Kawasaki,[3] Katsuhiko Tomooka[1,3]

To expand the chemistry of our previously developed 4,8-diazacyclononyne (DACN), we designed and synthesized DACN-NHS ester **1a** and DACN-maleimide **1b**. The details of their synthesis and applications for labeling of peptides will be presented.
Keywords : DACN; Huisgen Reaction; Click Reaction; Labeling Reaction

先に我々は無触媒クリック反応素子 4,8-diazacyclononyne (DACN)を開発し，これが熱的，化学的に安定でありながら高い反応性を有することを明らかにしている．[1,2,3)]



本研究では DACN を生体分子の高度複合化に利用することを目指して，DACN-NHS エステル **1a**，DACN マレイミド **1b** を開発した．これらは無触媒条件下で アジドと Huisgen 反応するとともに，それぞれアミンとの縮合反応によりアミド結合を形成，もしくは，チオール類との thia-Michael 反応により C–S 結合を形成することができる．発表時には **1a**, **1b** の合成と反応の詳細，およびペプチドの複合化への応用について報告する．



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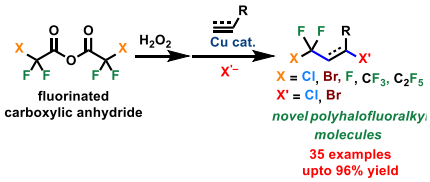
Synthesis of Polyhalogenated Molecules by a General Cu-Catalyzed Halo-Halofluoroalkylation of Alkenes/Alkynes with Fluorinated Carboxylic Anhydrides

([1]*RIKEN CSRS*, [2]*RIKEN CPR*) ○Subrata Mukherjee,[1] Yuma Aoki,[1] Shintaro Kawamura,[1,2] Mikiko Sodeoka,[1,2]

Keywords: Organofluorine molecules; Fluoroalkyaltion; Halo-fluoroalkyaltion; Fluorinated carboxylic anhydride; Copper catalyst

Fluoroalkyl compounds have been recently regarded as a promising candidate in development of small drugs and agrochemicals. In particular, compounds having fluoroalkyl group and another halogen atom on the vicinal carbons could be a versatile building block for novel organofluorine compounds. A three-component halo-fluoroalkylation reaction of alkenes and alkynes using halide salts is a highly useful synthetic method for them. However, to the best of our knowledge, a general three component reaction that allows the free choice of the combinations of fluoroalkyl (R_f) and halogen (X) groups to be introduced across a multiple bond was not known in literature.[1]

In this work, we developed a general Cu-catalyzed three-component 1,2-halo-fluoroalkylation reaction of alkenes and alkynes by using the combination of commercially available-fluorinated carboxylic anhydrides (R_f = CF_2Cl, CF_2Br, CF_3, C_2F_5, C_3F_7) and alkali metal halides (X = Cl, Br) for the synthesis of unique polyhalogenated fluoroalkyl molecules. The carboxylic anhydride was utilized in the reaction by forming diacyl peroxide with H_2O_2 in situ and used for the reaction.[2] We found that the use of bipyridyl-type ligand is essential for realizing high product selectivity by suppression of contamination of undesired halogen derived from the carboxylic anhydride to the product. Derivatization of the products was also performed to prove synthetic utility of this methodology. Furthermore, the reaction mechanism focusing on ligand effect was examined by experimental and theoretical investigations.



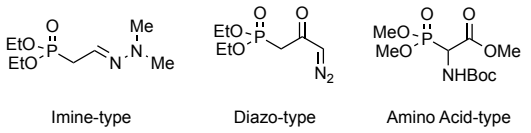
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E-Selective Elongation Reaction of Aldehydes by Weinreb Amide-type Horner–Wadsworth–Emmons Reagent

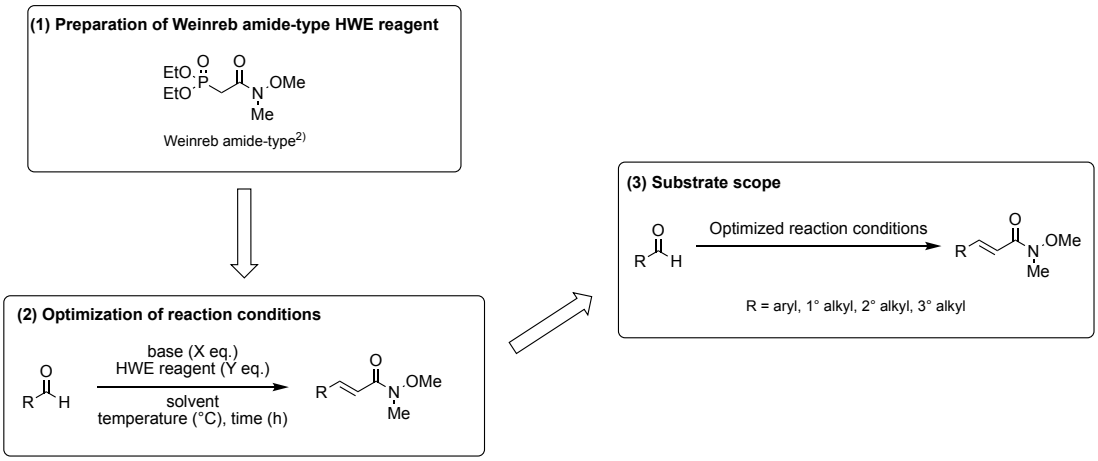
(*Faculty of Science, Tokyo University of Science*) Takatsugu Murata,○Hisazumi Tsutsui, Shintaro Hiraishi, Daiki Usukura, Hiroki Okano, Isamu Shiina

Keywords: Horner–Wadsworth–Emmons Reaction; Elongation Reaction; Weinreb Amide



Horner–Wadsworth–Emmons (HWE) reaction is an often-utilized method in variable syntheses. The products obtained in these syntheses are valuable for functional group conversion reactions. Some researchers reported HWE reagents that facilitate functional transformations. However, only simple optimization of the reaction conditions and structural investigations of a few compounds have been examined in the above reports. Therefore, it is required to develop the HWE reaction facilitating to convert products into related ones easily. We recently accomplished total synthesis of antibiotic tanzawaic acid B[1] through the *E*-selective HWE reaction using the Weinreb amide-type HWE reagent[2] developed by Nuzillard *et al*.

As shown in the figure below, we will report three items: (1) a Large-scale synthetic method of the Weinreb amide-type HWE reagent was developed; (2) HWE reaction using the Weinreb amide-type HWE reagent was reinvestigated[3–5]; (3) Limitation of the substrate scope was defined, and the effective substrate-conversion using this reagent was clarified.



1) Unpublished results.
2) J.-M. Nuzillard, A. Boumendjel, G. Massiot, *Tetrahedron Lett*, **1989**, *30*, 3779–3780.
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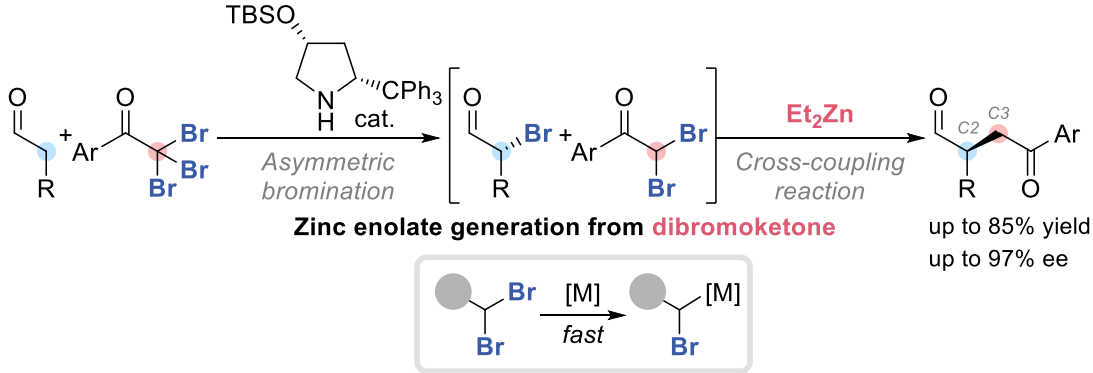
Et_2Zn-Mediated Cross-Coupling Reactions between Dibromoketones and Monobromo Carbonyl Compounds

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Graduate School of Science, Kyoto University*) ○Aika Takeshima,[1,2] Taichi Kano[1]

Keywords: Organocatalysis; Chemoselectivity; Bromine; Diethylzinc

Chiral 1,4-dicarbonyls are core structures found in natural products and pharmaceuticals. As they are useful synthetic intermediates, the development of efficient methods for their catalytic asymmetric synthesis is highly desirable. The construction of the C2–C3 bond is one of the strategies commonly used for the formation of chiral 1,4-dicarbonyl compounds. Although effective methods that employ chiral auxiliaries have been reported,[1] few methods have been developed for catalytic asymmetric variants to synthesize enantioenriched 1,4-dicarbonyl compounds.[2]

Here, we have developed a novel route to synthesize chiral or racemic 1,4-dicarbonyl compounds.[3] Chiral 1,4-dicarbonyl compounds can be obtained via the enantioselective bromination of aldehydes using a chiral secondary amine catalyst and a subsequent cross-coupling reaction between the resulting chiral α-bromoaldehydes and α,α-dibromoacetophenones.[4] α,α-Dibromoketones generate zinc enolates through a diethylzinc-mediated halogen–metal exchange and react with α-bromocarbonyl compounds to furnish 1,4-dicarbonyl compounds via a second generation of zinc enolates. This cross-coupling reaction is enabled by the chemoselective formation of zinc enolates from α,α-dibromoketones in the presence of α-bromocarbonyl compounds. This approach provides various chiral 1,4-dicarbonyl compounds with high enantioselectivity from readily available aldehydes and α,α,α-tribromoketones under mild conditions.



[1] D. Kaldre, I. Klose, N. Maulide, *Science* **2018**, *361*, 664. [2] a) H.-Y. Jang, J.-B. Hong, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2007**, *129*, 7004. b) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 78. [3] A. Takeshima, T. Kano, *Angew. Chem. Int. Ed.* **2022**, e202217496. [4] A. Takeshima, M. Shimogaki, T. Kano, K. Maruoka, *ACS Catal.* **2020**, *10*, 5959.

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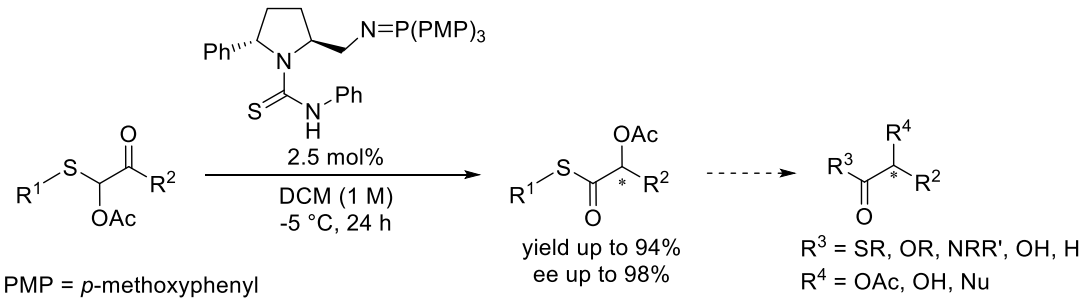
Design and Synthesis of Novel Bifunctional Organocatalysts for Enantioselective Rearrangement of α-Acyloxy-β-Keto Sulfides to α-Acyloxy Thioesters

(Institut de Chimie Moléculaire et des Matériaux d'Orsay, Univ. Paris-Saclay;[1] Department of Chemistry, School of Science, The Univ. of Tokyo[2]) ○ Julie KONG[1,2], Chloée BOURNAUD[1], Yasuhiro YAMASHITA[2], Shū KOBAYASHI[2], Giang VO-THANH[1]

Keywords: Bifunctional Organocatalyst; Enantioselective Rearrangement; Brønsted Base; Hydrogen-bonding; Protonation

Organocatalysis is a metal-free synthetic methodology established as a highly attractive area in modern organic synthesis and green chemistry because it prevents metal pollution. Applications of organocatalysts have notably made it possible to promote numerous efficient enantioselective reactions giving access to new synthetic routes for natural and non-natural products.[1)] Among them, chiral bifunctional organocatalysts associated with hydrogen-bond donors represent an interesting new class of catalysts. They allow a better asymmetric induction by simultaneous activation of nucleophiles and electrophiles while keeping chiral scaffolds in their proximity.

In this project, we designed new bifunctional organocatalysts bearing an iminophosphorane and a thiourea moiety that function as Brønsted bases and hydrogen-bond donors respectively.[2)] Additionally, L-proline structure was introduced as a rigid chiral source for asymmetric induction. This organocatalyst has been employed for asymmetric rearrangement of α-acyloxy-β-keto sulfides to furnish α-acyloxy thioesters in excellent yields with high enantioselectivities. The starting material formed via a Pummerer rearrangement was deprotonated by the iminophosphorane function. This deprotonation led to the generation of an enolate and allowed its addition to the acetate. Then enantioselective protonation occurred to deliver the final product. This reaction gave up to 94% yield and up to 98% ee of the products in 2.5 mol% catalyst loading. The product underwent plenty of chemical transformations, making it a good molecular platform for forming a variety of compounds with wide applications, such as derivatives of lactic acids used as food additives or cosmetics.



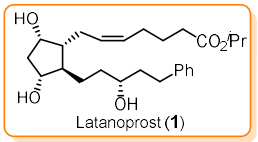
1) Enders, D. *et al*. *Nat. Chem*., **2010**, *2*, 167.
2) Dixon, D. J. *et al*. *J. Am. Chem. Soc*., **2015**, *137*, 15992.

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Development of Efficient Synthetic Method of Latanoprost Using an Organocatalyst

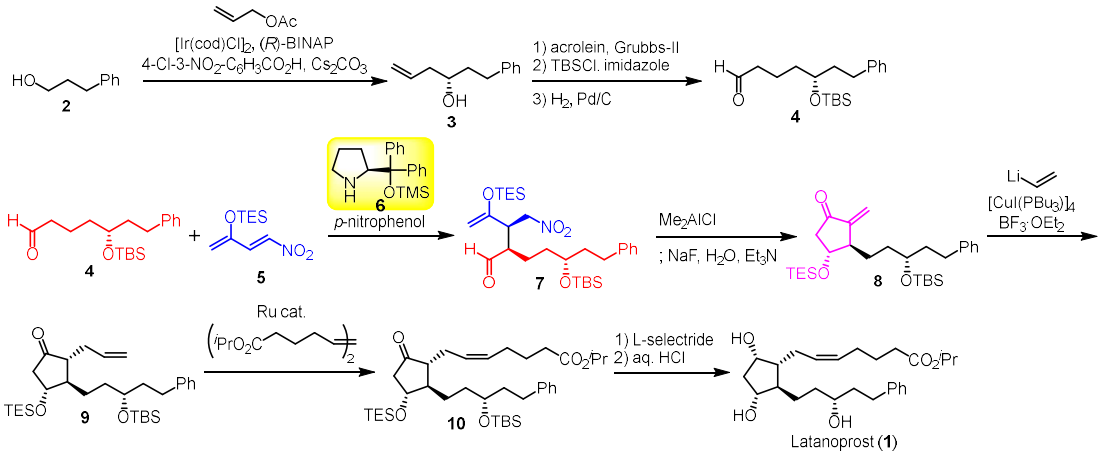
(*Graduate School of Science, Tohoku University*) ○Genki Kawauchi, Yurina Suga, Shunsuke Toda, Yujiro Hayashi

Keywords: Total Synthesis; Organocatalyst; Asymmetric Synthesis; Prostaglandin; Michael Reaction



Latanoprost (**1**) is a prostaglandin $F_{2\alpha}$ derivative developed by Pfizer for the treatment of glaucoma. As for the structural feature, it posesses four contiguous stereocenters including two side chains on the five-membered ring. In this presentation, we describe the efficient asymmetric total synthesis of latanoprost (**1**). The key reaction consists of asymmetric Michael reaction of aldehyde and nitroalkene catalyzed by diphenylprolinol silyl ether,[1] followed by intramolecular Mukaiyama aldol reaction for the formation of five-membered ring.

Asymmetric allylation[2] of 3-phenyl-1-propanol (**2**) afforded chiral alcohol **3**. Then, cross metathesis with acrolein, and protection by TBS group followed by hydrogenation provided ω-side chain **4**. The key asymmetric Michael reaction of aldehyde **4** and nitroalkene **5** catalyzed by diphenylprolinol silyl ether **6** afforded compound **7** in good diastereoselectivity. Then, cyclopropane skeleton was constructed through intramolecular Mukaiyama aldol reaction, followed by elimination of HNO_2 to provide compound **8**. Conjugate addition of vinyl copper reagent afforded compound **9**. The introduction of α-side chain through *Z*-selective cross metathesis[3] gave compound **10**. Diastereoselective reduction followed by deprotection afforded latanoprost (**1**).



1) Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem. Int. Ed.* **2005**, *44*, 4212. 2) I. S. Kim, M. Y. Ngai, M. J. Krische, *J. Am. Chem. Soc.* **2008**, *130*, 6340. 3) J. Li, T. S. Ahmed, C. Xu, B. M. Stoltz, R. H. Grubbs, *J. Am. Chem. Soc.* **2019**, *141*, 154.

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[D1443-2am] 16. Natural Products Chemistry, Chemical Biology

Chair: Akihiro Ogura, Chikara Dohno

Thu. Mar 23, 2023 9:00 AM - 11:10 AM D1443 (1443, Bldg. 14 [4F])

[D1443-2am-01] Bioconjugation of Au_{25} nanocluster to trastuzumab

○Katarzyna Joanna Malawska[1], Shinjiro Takano[2], Kounosuke Oisaki[4], Haruaki Yanagisawa[3], Masahide Kikkawa[3], Tatsuya Tsukuda[2], Motomu Kanai[1] （1. Grad. Sch. Pharm. Sci., The Univ. of Tokyo, 2. Grad. Sch. Sci., The Univ. of Tokyo, 3. Grad. Sch. Med., The Univ. of Tokyo, 4. IRC3, AIST）

9:00 AM - 9:20 AM

[D1443-2am-02] Chemical reaction-driven “organ-to-organ” transfer of glycan-modified-HSA in living mouse

○Kenshiro Yamada[1], Tatsuya Kobayashi[1], Akari Mukaimine[2], Ambara Rachmat PRADIPTA[1], Katsunori Tanaka[1,2] （1. Tokyo Institute of Technology,School of Materials and Chemical Technology, Department of Chemical Science and Engineering, 2. RIKEN Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory）

9:20 AM - 9:40 AM

[D1443-2am-03] Development of novel psoralen-introduced triplex-forming oligonucleotides for the expansion of their target genome sequences

○Yu Mikame[1], Honoka Eshima[1], Juki Nakao[1], Tsuyoshi Yamamoto[1], Yoshiyuki Hari[2], Chikara Dohno[3], Takehiko Wada[4], Asako Yamayoshi[1] （1. Grad. Sch. Biomed. Sci., Nagasaki Univ, 2. Fac. of Pharm. Sci., Tokushima Bunri University, 3. SANKEN., Osaka Univ, 4. IMRAM., Tohoku Univ）

9:40 AM - 10:00 AM

[D1443-2am-04] Development of fluorescent probes for selective detection of intracellular free magnesium ion

○Akihiro Sakama[1], Rei Kumada[1], Yutaka Shindo[1], Naoko Iwasawa[1], Daniel Citterio[1], Kotaro Oka[1], Yuki Hiruta[1] （1. Keio University）

10:10 AM - 10:30 AM

[D1443-2am-05] Control of RNA repeat foci formation by photoswitchable RNA binding ligands

○Yusuke Fujiwara[1,2], Tomonori Shibata[1,2], Chikara Dohno[1,2], Kazuhiko Nakatani[1,2] （1. SANKEN, Osaka University, 2. CREST, JST）

10:30 AM - 10:50 AM

[D1443-2am-06] Targeted α-ray therapy using the reaction between acrolein and azide

○Yudai Ode[1], Ambara Rachmat PRADIPTA[1], Katsunori TANAKA[1,2] （1. Tokyo Institute of Technology, School of Materials and Chemical Technology, Department of Chemical Science and Engineering, 2. RIKEN Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory）

10:50 AM - 11:10 AM

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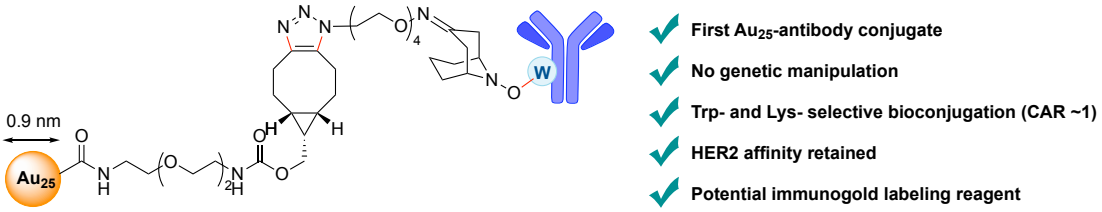
Bioconjugation of Au_{25} nanocluster to trastuzumab

([1]*Graduate School of Pharmaceutical Sciences, The University of Tokyo*, [2]*Graduate School of Science, The University of Tokyo,* [3]*Interdisciplinary Research Center for Catalytic Chemistry (IRC3) National Institute of Advanced Industrial Science and Technology (AIST),* [4]*Graduate School of Medicine, The University of Tokyo*) ○Katarzyna Joanna Malawska,[1] Shinjiro Takano,[2] Kounosuke Oisaki,[3] Haruaki Yanagisawa,[4] Masahide Kikkawa,[4] Tatsuya Tsukuda[2], Motomu Kanai[1]

Keywords: Bioconjugation; Tryptophan; Gold nanocluster; Immunogold labelling; Antibody conjugate

Cryogenic Electron Microscopy (Cryo-EM) is a dynamic field of structural biology, but despite many advances, the images obtained by cryo microscopes remain extremely noisy. One way to tackle this problem is to apply labelling with heavy metal particles such as colloidal gold. Recent years saw a surge in reports on special types of particles called gold nanoclusters. Compared to colloidal gold, their synthesis requires special skills, but they are more stable, their core is smaller, and they can be covalently attached to proteins which makes them excellent candidates for high-resolution electron probing of proteins. Bioconjugation of larger gold nanoclusters such as Au_{71}, Au_{102}, and Au_{144} with the aim to create an antibody-based label for Cryo-EM has already been described in the literature. Reported methods mostly relied on time-consuming genetic manipulation on protein to install additional cysteine residue, whose free thiol would serve as an actual bioconjugation handle.

In this presentation, we report the first example of bioconjugation of an Au_{25} gold nanocluster to protein, without genetic manipulation. The novelty of the method is the application of mild tryptophan-selective bioconjugation protocol which was fine-tuned since the first report to make it compatible with gold nanoclusters. Currently, easier-to-handle keto-ABNOH derivatives can be applied in the reaction instead of keto-ABNO radicals, under aqueous neutral buffered conditions and strain-promoted alkyne-azide cycloaddition is employed to secure cluster on protein. The utility of the method is demonstrated on whole monoclonal antibody trastuzumab. We present successful separation of the Au_{25} conjugate and compare it with the conjugate synthesized by conventional lysine-selective bioconjugation under Cryo-EM.



1) Y. Seki, T. Ishiyama, D. Sasaki, J. Abe, Y. Sohma, K. Oisaki, M. Kanai, *J. Am. Chem. Soc.* **2016**, *138*, 10798.

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化学反応を駆動力とする糖鎖アルブミン分子のマウス体内で「臓器間」移動

（東工大物質理工 [1]・理研 開拓研究本部 田中生体研 [2]）○山田 健士郎 [1]・小林 達也 [1]・向峯 あかり [2]・プラディプタ アンバラ [1]・田中 克典 [1,2]

Chemical reaction-driven “organ-to-organ” transfer of glycan-modified-HSA in living mouse ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Biofunctional Synthetic Chemistry Laboratory*, *Cluster for Pioneering Research, RIKEN*) ○ Kenshiro Yamada[1], Tatsuya Kobayashi[1], Akari Mukaimine[2], Ambara R. Pradipta,[1] Katsunori Tanaka[1,2]

N-type glycans have essential roles in cell and protein interactions. Previously, we reported glycan-modified human serum albumin (HSA) that could accumulate specifically in cancer cells. Also, we have developed pattern recognition studies of the glycan-modified HSA to recognize various cancers. In this study, we designed a strategy to move glycan molecules from the original target to the new target in living animals by switching their pattern recognition. The details will be discussed in the symposium.

Keywords：Glycan pattern recognition; Click reaction; N-glycan; In vivo synthesis

N 型糖鎖は生体内での細胞・タンパク質間での相互作用において重要な役割を果たす生体分子である。これまでに我々は、アルブミンに N 型糖鎖約 10 分子を修飾した糖鎖アルブミン分子が、がん細胞周辺に集積すること，さらに糖鎖の修飾パターンに応じて種々のがん細胞へ異なる強度の認識（パターン認識）が発現することを見出し [1)]、糖鎖アルブミン分子を用いたがん治療研究へと発展させてきた [2)]。糖鎖パターン認識のさらなる活用法として, 糖鎖修飾パターンを生体内でスイッチすることで標的が更新され、新たな標的へと生体内を移動する糖鎖アルブミン分子の開発を試みた。本発表では、生体内での化学反応スイッチによるパターン認識更新の検討について述べる。

1) I. Smirnov, R. Sibgatullina, S. Urano, T. Tahara, P. Ahmadi, Y. Watanabe, A. R. Pradipta, A. Kurbangalieva, K. Tanaka, *Small* **2020**, *16*, 2004831.
2) K. Vong, T. Tahara, S. Urano, I. Nasibullin, K. Tsubokura, Y. Nakao, A. Kurbangalieva, H. Onoe, Y. Watanabe, K. Tanaka, *Sci. Adv.* **2021**, *7*, eabg4038.

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新規ソラレン導入型三重鎖形成核酸の開発と標的ゲノム配列の拡張性評価

（長崎大院医歯薬[1]・徳島文理大薬[2]・大阪大産研[3]・東北大多元研[4]）○三瓶悠[1]・江島穂乃香[1]・中尾樹希[1]・山本剛史[1]・張功幸[2]・堂野主税[3]・和田健彦[4]・山吉麻子[1]

Development of novel psoralen-introduced triplex-forming oligonucleotides for the expansion of their target genome sequences ([1]*Grad. Sch. Biomed. Sci, Nagasaki Univ,* [2]*Fac. of Pharm. Sci., Tokushima Bunri University* [3]*SANKEN, Osaka Univ,* [4]*IMRAM*) ○Yu Mikame,[1] Honoka Eshima,[1] Juki Nakao,[1] Tsuyoshi Yamamoto,[1] Yoshiyuki Hari,[2] Dohno Chikara,[3] Wada Takehiko,[4] Asako Yamayoshi[1]

Triplex-forming oligonucleotide (TFO) is an oligonucleotide that forms sequence-specific Hoogsteen hydrogen bonds with a double-stranded DNA (dsDNA). However, the Hoogsteen hydrogen bonds can only be formed between a purine base of A/T (or G/:C) base pairs of dsDNA and a TFO. If the target base pair in dsDNA is interchanged (T/A or C/G base pair), it becomes a mismatched base pair with TFO, reducing the thermodynamic stability of the triplex structure. This is one of the most significant barriers to the practical application of TFO as nucleic acid medicine.

On the other hand, psoralen derivatives are known as DNA intercalators that react with pyrimidine bases. Thus, we hypothesized that the introduction of psoralen into the mismatched site of TFO could improve the thermodynamic stability of the triplex *via* intercalation. In this study, we synthesized a novel compound with psoralen at C-1 position of deoxyribose (1Ps-dRib) and introduced 1Ps-dRib at the mismatch base pair formation site in the TFO (OPTO). Moreover, we evaluated the thermodynamic stability of the triplex composed of OPTO and DNA duplex with mismatched sites and found that introduction of 1Ps-dRib stabilized the triplex structure significantly.

Keywords : Triplex forming oligonucleotide; Psoralen; Hoogsteen hydrogen bond; Thermodynamic stability

三重鎖形成核酸（TFO）はフーグスティーン型塩基対を介して、二本鎖 DNA と配列特異的に三重鎖形成する核酸である。しかしながらフーグスティーン型塩基対は、二本鎖 DNA の主溝において A/T 塩基対（あるいは G/C 塩基対）のプリン塩基側（A or G）と TFO との間でしか形成されず、標的 DNA の塩基対が入れ替わった場合（T/A あるいは C/G 塩基対）には TFO とミスマッチ塩基対となるため、三重鎖構造の熱力学的安定性の低下を招く。これが TFO の核酸医薬としての実用化を妨げる要因の一つとなっている。

一方、小分子化合物であるソラレン類は DNA 塩基間にインターカレートすることが知られている。そこで我々は、上述のミスマッチ塩基対部位にソラレンを導入することで、インターカレーションによる三重鎖構造の安定化が可能であると考えた。本研究では、デオキシリボース 1 位にソラレンを導入した新規化合物（1Ps-dRib）を合成し、TFO 鎖中のミスマッチ塩基対部位に 1Ps-dRib を導入した新規ソラレン導入型 TFO（OPTO）を開発した。OPTO とミスマッチ部を有する標的 DNA 配列との三重鎖構造の熱力学的安定性を評価した結果、有意な安定化効果が得られ、OPTO による標的配列の拡張が可能であることが示唆された。本発表ではその詳細について報告する。

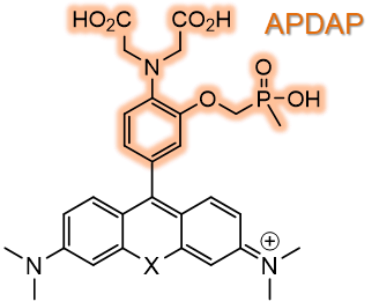
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細胞内遊離マグネシウムイオン動態の選択的可視化を可能にする新規蛍光プローブの開発

（慶大理工）○坂間 亮浩・熊田 怜・新藤 豊・岩澤 尚子・チッテリオ ダニエル・岡 浩太郎・蛭田 勇樹
Development of fluorescent probes for selective detection of intracellular free magnesium ion (*Keio University*) ○Akihiro Sakama, Rei Kumada, Yutaka Shindo, Naoko Iwasawa, Daniel Citterio, Kotaro Oka, Yuki Hiruta

Magnesium ion (Mg^{2+}) plays multiple important roles in cells; however, the mechanisms are still unclear. The research on Mg^{2+} has the potential to contribute to the elucidation of the mechanisms of diseases and the discovery of new biological phenomena. Fluorescence imaging is one of the methods for clarifying intracellular ion dynamics. However, the conventional Mg^{2+} fluorescent probes lack the selectivity for free Mg^{2+} and color variation. To solve these issues, we designed and synthesized rhodamine-type fluorescent probes, KMG-301APDAP and KMG-501APDAP, which possess free Mg^{2+}-selective ligand APDAP. The basic properties of these probes, such as responsiveness to Mg^{2+} and calcium ion (Ca^{2+}), were evaluated.
Keywords : Functional Fluorescent Probe; Cell Imaging; Magnesium Ion

マグネシウムイオン（Mg^{2+}）は細胞内において様々な重要な役割を担っているが、その詳しいメカニズムは解明されていない。したがって、細胞内 Mg^{2+} に関する研究は疾患のメカニズム解明や新たな生命現象の発見に貢献できる可能性を持つ。細胞内イオン動態を明らかにする方法として蛍光イメージングが挙げられる。しかしながら、既存の Mg^{2+} 蛍光プローブは、遊離 Mg^{2+} への選択性とカラーバリエーションに問題がある。そこで、遊離 Mg^{2+} に高い選択性を有するリガンドである APDAP[1] を導入した新規ローダミン系蛍光プローブ KMG-301APDAP と KMG-501APDAP を設計し、合成を行った。これらプローブについて、Mg^{2+} やカルシウムイオン（Ca^{2+}）への応答性等の基礎特性の評価を行った。



KMG-301APDAP (X = O)
KMG-501APDAP (X = $SiMe_2$)

1) Walter, E. R. H.; Fox, M. A.; Parker, D.; Williams, J. A. G. *Dalton Trans.* **2018**, *47*, 1879–1887.

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日本化学会 第103春季年会 (2023)

RNA 反復配列を標的とした光応答性リガンドによる細胞内 RNA foci の形成制御

（阪大産研[1]・CREST, JST[2]）○藤原 侑亮[1,2]・柴田 知範[1,2]・堂野 主税[1,2]・中谷 和彦[1,2]

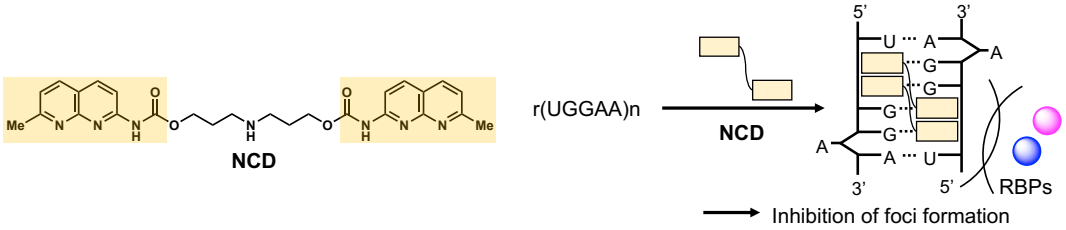
Control of RNA repeat foci formation by photoswitchable RNA binding ligands ([1]*SANKEN, Osaka University*, [2]*CREST, JST*) ○ Yusuke Fujiwara,[1,2] Tomonori Shibata,[1,2] Chikara Dohno,[1,2] Kazuhiko Nakatani[1,2]

RNAs with r(UGGAA) repeat sequences bind to RNA-binding proteins (RBPs) as scaffolds and form structures called RNA foci. Although RNA foci have been shown to change their components and localization depending on the surrounding environment, their individual roles remain unknown. Thus, techniques to regulate RNA foci formation spatiotemporally are needed for elucidating their dynamics. So far, we reported that NCD (Naphthyridine Carbamate Dimer), which binds to r(UGGAA) repeats, competed with RBPs to bind RNA and inhibited RNA foci formation[1]. In this research, we report NCTA, a photoswitchable RNA ligand that binds to r(UGGAA) repeats. Thermal stability analysis suggested that NCTA increased the binding ability to the UGGAA/UGGAA mismatch by UV light irradiation. Treating NCTA to model cells controlled the formation of RNA foci with r(UGGAA) repeats depending on light stimulation.

Keywords : Photoswitch; Nucleic acid; RNA foci; Phase separation; Repeat RNA

r(UGGAA)反復配列をもつ RNA は、RNA 結合タンパク質(RBPs)の足場となり、RNA foci とよばれる構造体を形成する。RNA foci は環境や時間変化に応じてその構成や局在が変化することが知られているが、その個々の役割の理解のためには、時空間特異的に RNA foci の形成を制御する技術が必要である。

当研究室ではこれまでに、r(UGGAA)反復配列に結合するリガンド NCD (Naphthyridine carbamate dimer)が RBPs と競合して RNA と結合し、細胞内において RNA foci 形成を阻害することを報告した(図)[1]。本研究では NCD 2 つをアゾベンゼンで繋げた、光応答性 r(UGGAA)リガンド NCTA について報告する。NCTA は 365 nm (UV)光および 460 nm(可視)光照射により、アゾベンゼン部位がそれぞれ *Z* 体 *E* 体に異性化する。また、UGGAA/UGGAA ミスマッチ配列をもつヘアピン RNA の熱融解曲線の解析から、NCTA は UV 光照射に応答して結合能力が活性化することが示唆された。さらに、r(UGGAA)反復配列を発現するモデル細胞系に NCTA を処理したところ、RNA foci の形成を UV 光依存的に制御することを見出した。



1) Shibata T. *et al. Nat. Commun.* **2021**, *12*, 236.

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アクロレインとアジドの反応を利用した標的α線治療

（東工大物質理工[1]・理研 開拓研究本部 田中生体研[2]）○大出 雄大[1]・プラディプタ アンバラ[1]・田中 克典[1,2]

Targeted α-ray therapy using the reaction between acrolein and azide ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Biofunctional Synthetic Chemistry Laboratory*, *Cluster for Pioneering Research, RIKEN*) ○Yudai Ode,[1] Ambara R. Pradipta,[1] Katsunori Tanaka[1,2]

Adverse drug reactions are the decisive risk factor associated with cancer chemotherapy. In recent years, the development of targeted alpha therapy to overcome the problem has been impressive.[1] Previously, we have discovered that acrolein is overproduced in cancer cells and negligible in healthy cells.[2] Moreover, we found that aryl azides could react selectively with the acrolein of cancer cells to give diazo compounds, which could further react with the nearest organelle to form a covalent bond inside the cancer cells. In this study, we designed a targeted alpha therapy using the azide-acrolein reaction and utilized various alpha-ray emitters. Their antitumor effects have been investigated, and the details will be discussed in the symposium.

Keywords： Targeted Alpha Therapy; Cancer; Acrolein; 1,3-Dipolar cycloaddition; Aryl azide

がん治療分子の開発において、副作用の問題を避けるため、標的がん細胞のみを攻撃する分子標的治療（ミサイル療法）の研究が盛んである[1)]。この一つとして、放射性治療分子を投与して、がん組織近傍から放射線治療を行う RI 内用療法が挙げられる。今回我々は、この RI 内用療法の新候補として、がん細胞内での有機合成化学反応と様々なα線放出核種を融合させた方法を考案した。

これまでに我々の研究室では、がん細胞内でアクロレインが大量に発生していることを発見した[2)]。さらにアジド分子ががんから産生されるアクロレインと選択的に反応することにより、アジド由来分子ががん細胞内に効果的に留まる現象を見出している。これはがん患者のサンプルでも効果的に起こり、ヒトにも一般的な現象である。そこで、アジド分子に対して様々なα放出核種で標識した新規分子をデザインし、がん細胞内での生体内合成反応による集積効果とα線放出核種を用いた分子によるがん殺傷効果を期待した。本研究では、放射性前駆体分子の合成、α放出核種による標識効率の検討、さらに動物実験による腫瘍増加の抑制評価と生体内分布の評価を行なったので、これらの経緯について報告する。

1) K. Fujiki, Y. Kanayama, S. Yano, N. Sato, T. Yokokita, P. Ahmadi, Y. Watanabe, H. Haba, K. Tanaka, *Chem. Sci.* **2019**, *10*, 1936.
2) T. Tanei, A. R. Pradipta, K. Morimoto, M. Fujii, M. Arata, A. Ito, M. Yoshida, E. Saigitbatalova, A. Kurbangalieva, J.-I. Ikeda, E. Morii, S. Noguchi, K. Tanaka, *Adv. Sci*. **2019**, *6*, 1801479.

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[D1443-2pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Shoji Kobayashi, Takaaki Mitsuhashi

Thu. Mar 23, 2023 2:00 PM - 3:40 PM D1443 (1443, Bldg. 14 [4F])

[D1443-2pm-01] Study on enantio-selective enzymatic halocyclization using the CS method

○Takaaki Mitsuhashi[1], Jiazhuo Chen[2,1], Makoto Fujita[2,1] (1. IMS, 2. The Univ. of Tokyo)

2:00 PM - 2:20 PM

[D1443-2pm-02] Functional and structural analysis of the terpene synthase found from the genome of giant virus

○Youngcheol Jung[1], Takaaki Mitsuhashi[2], Miki Senda[3], Sota Sato[1], Toshiya Senda[3], Makoto Fujita[1,2] (1. Graduate School of Engineering, The Univ. of Tokyo, 2. Institute for Molecular Science, 3. High Energy Accelerator Research Organization)

2:20 PM - 2:40 PM

[D1443-2pm-03] Synthetic study of oxidative metabolites in mushrooms starting from ergosterol

○Edric Wilbert[1], Saki Nagayasu[1], Tomoka Taguri[1], Shoji Kobayashi[1] (1. Osaka Institute of Technology)

2:40 PM - 3:00 PM

[D1443-2pm-04] Development of anti-HBV agents through divergent and programmable synthesis of skeletally diverse alkaloidal scaffolds bearing Michael acceptors

○Nobuto Kaneko[1], Hiroki Kubota[2], Misao Himeno[1], Taketomo Kido[1], Atsushi Miyajima[1], Hiroki Oguri[1] (1. The University of Tokyo, 2. Tokyo University of Agriculture and Technology)

3:00 PM - 3:20 PM

[D1443-2pm-05] Development of Catalytic Asymmetric Mukaiyama-Michael Reaction and Its Application to Enantioselective Total Synthesis of Sesquiterpene Lactones

○Ryoji Sugiyama[1], Masahisa Nakada[1] (1. Waseda University)

3:20 PM - 3:40 PM

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結晶スポンジ法を用いた酵素的不斉ハロ環化反応の研究

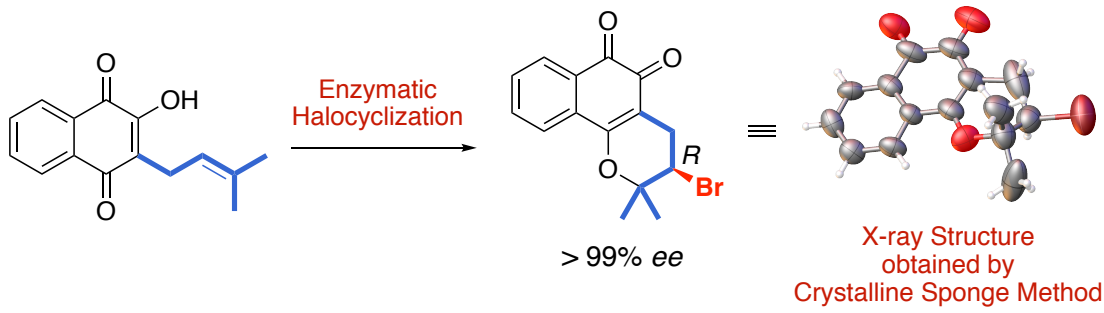
（分子研[1]・東大院工[2]）○三橋 隆章[1]・Jiazhuo Chen[1,2]・藤田 誠[1,2]
Study on enantio-selective enzymatic halocyclization using the CS method ([1]*Institute for Molecular Science*, [2] *Graduate School of Engineering, The University of Tokyo*) ○Takaaki Mitsuhashi,[1] Jiazhuo Chen,[1,2] Makoto Fujita[1,2]

Enzymatic halogenation is valuable because it proceeds in a mild condition and achieve selective halogenation. In this study, we tried a halo-cyclization reaction, using vanadium-dependent haloperoxidases. Previously, only unselective or diastereo-selective halocyclizations by this kind of enzymes were reported. However, we achieved an enantio-selective enzymatic halocyclization. In addition, the CS method[1)] was used for the structure determination of enzyme products. This method is known to be suitable for the structure elucidation of halogenated compounds[2)], and actually greatly facilitated this study.

Keywords : Crystalline Sponge Method; Structure Determination; Enzyme Reaction; Halogenase; Meroterpenoid

酵素を用いたハロゲン化反応は、温和な条件で進行し、選択的な反応を達成できるなどの利点がある。本研究では、バナジウム依存型ハロペルオキシダーゼを用い、酵素的なハロ環化反応を試みた。これまでの研究では、非立体選択的もしくはジアステレオ選択的なハロ環化反応しか達成されていなかったところ、本研究では、エナンチオ選択的なハロ環化反応を達成することができた。

また本研究において、酵素反応産物の構造決定には、結晶スポンジ法[1)]を使用した。ハロゲン化した化合物は、結晶スポンジ法と特に相性が良いことが知られているが[2)]、実際に、本研究にて得られたハロ環化反応産物も結晶スポンジ法により容易に構造決定することができた。本研究にて得られた酵素反応産物の絶対立体配置の決定は、結晶スポンジ法以外の方法では容易とは言えず、結晶スポンジ法の使用が研究の迅速化に貢献したと言える。



1) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita, *Nature* **2013**, *495*, 461. 2) J. Chen, T. Kikuchi, K. Takagi, H. Kiyota, K. Adachi, T. Mitsuhashi, M. Fujita, *Chem. Lett.* **2022**, *51*, 85.

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Functional and Structural analysis of the Terpene Synthase Found from the Genome of Giant Virus

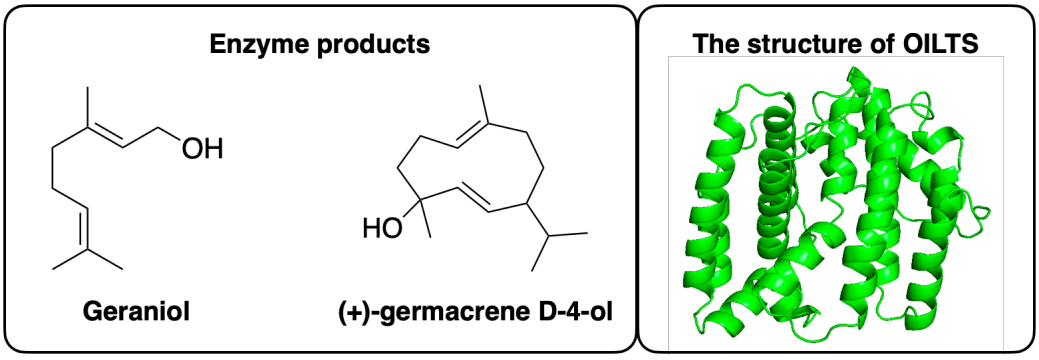
([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institue of Molecular Science,* [3]*High Energy Accelerator Research Organization*) ○Youngcheol Jung,[1] Takaaki Mitsuhashi,[2] Miki Senda,[3] Sota Sato,[1] Toshiya Senda,[3] Makoto Fujita[1,2]

Keywords: Giant Virus; Natural Product; Terpenoid; Protein X-ray Crystallography; Crystalline Sponge Method

A giant virus first reported in 2003[1)] is an unusual virus having unique characteristics such as large particle and genome. Thus far, many researchers investigate the genome of a giant virus, genes related to protein translation, immune system and primary metabolism have been reported. However, the research on genes specially related to secondary metabolites has not been investigated yet. In this study, we noticed an exitance of a gene encoding a terpene synthase designated as OILTS in a genome data of a giant virus, Orpheovirus IHUMI-LCC2,[2)] and analyzed its function and structure, using the crystalline sponge method and protein X-ray crystallography, respectively.

As a result, we revealed that OILTS was class I terpene synthase converting farnesyl diphosphate and geranyl diphosphate into (+)-germacrene D-4-ol and geraniol, respectively. Moreover, the X-ray structure of OILTS obtained in this study is the first X-ray structure of the viral terpene synthase.

This work showed that the natural product biosynthetic enzyme OILTS in the giant virus really works and produce the natural products. We thus speculate that giant viruses produce natural products in nature. Even though an actual role of natural products from giant viruses is still unclear, we believe that further analysis of natural products from giant viruses would deepen the understand of the ecology of giant viruses.



1) B. L. Scola, S. Audic, C. Robert, L. Jungang, X. D. Lamballerie, M. Drancourt, R. Birtles, J. -M. Claverie, D. Raolt, *Science* **2003**, *299*, 2033. 2) J. Andreani, J. Y. B. Khalil, E. Bastiste, I. Hasni, C. Michelle, D. Raoult, A. Levasseur, B. La Scola, *Front. Microbiol.* **2018**, *8*, 2643.

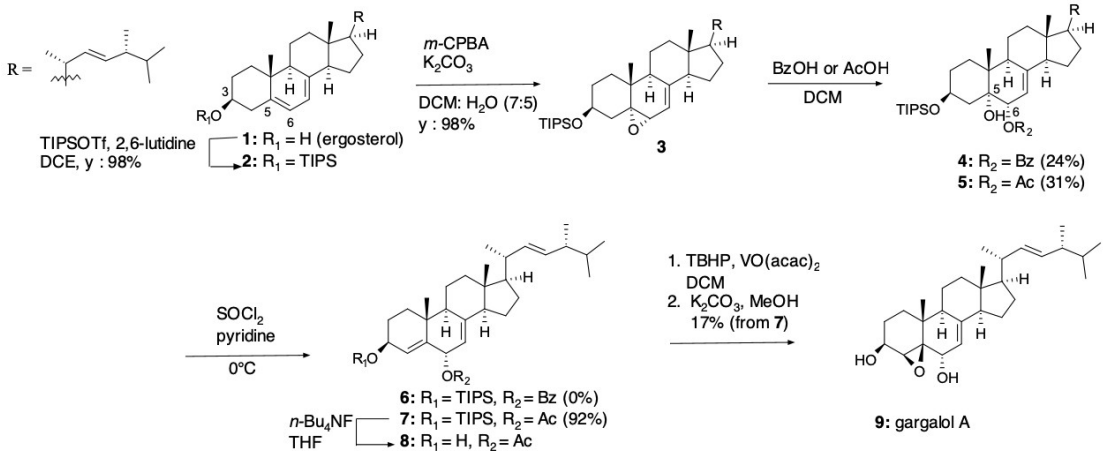
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Synthetic study of oxidative metabolites in mushrooms starting from ergosterol

([1]*Faculty of Engineering, Osaka Institute of Technology*, [2]*Graduate School of Engineering, Osaka Institute of Technology*) ○Edric Wilbert[1], Saki Nagayasu[2], Tomoka Taguri[1], Shoji Kobayashi[1]

Keywords: Ergosterol; Oxidative Metabolites; Gargalol A; Epoxide; Mushroom Ingredients

Mushrooms are widely consumed as health food and their health-promoting functions are thought to be partially attributed to the steroidal metabolites contained. This study focuses on straightforward syntheses of oxidized steroidal metabolites from ergosterol (**1**), a presumed biosynthetic precursor. The following scheme shows the synthetic route of gargalol A (**9**) isolated from the edible mushroom *Grifola gargal*.[1] The C3-hydroxyl group in **1** was first protected as its TIPS ether, and the C5-C6 olefin was epoxidized to give α-epoxide **3** in regio- and stereoselective manners. Nucleophilic epoxide opening by benzoic or acetic acids proceeded stereoselectively, giving rise to α-benzoate **4** and α-acetate **5** probably via S_N1 reaction pathways. Subsequent dehydration was achieved with thionyl chloride and pyridine. Interestingly, the benzoate **4** was inert under these conditions while the acetate **5** smoothly underwent dehydration to give **7** in 92% yields. It is likely that the sterically hindered benzoyl group inhibited chlorination of the C5-alcohol. Removal of the TIPS group in **7** turned out problematic because of the instability of the resulting allylic alcohol **8**. Eventually, careful isolation of the intermediate (**8**) followed by epoxidation using TBHP/$VO(acac)_2$ and deacetylation gave gargalol A (**9**) whose spectra matched the natural product.[1] Although an overall yield was moderate, such straightforward synthesis gives valuable insights into the biosynthetic routes of steroidal metabolites.



1) J. Wu, J.-H. Choi, M. Yoshida, H. Hirai, E. Harada, K. Masuda, T. Koyama, K. Yazawa, K. Noguchi, K. Nagasawa, H. Kawagishi, *Tetrahedron* **2011**, *67*, 6576.

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Development of anti-HBV agents through divergent and programmable synthesis of skeletally diverse alkaloidal scaffolds bearing Michael acceptors

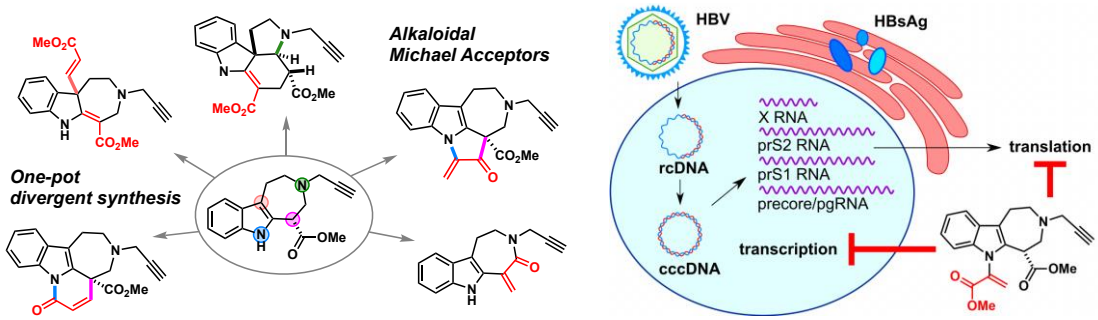
([1]*Graduate School of Science, The University of Tokyo,* [2]*Graduate School of Engineering, Tokyo University of Agriculture and Technology,* [3]*Institute for Quantitative Biosciences, The University of Tokyo*) ○Nobuto Kaneko,[1] Hiroki Kubota,[2] Misao Himeno,[3] Taketomo Kido,[3] Atsushi Miyajima,[3] Hiroki Oguri[1]

Keywords: Indole Alkaloids; Hepatitis B; Michael acceptor; Covalent inhibitor; Skeletal diversification

Small molecules with a Michael acceptor exhibit potent biological activities by forming a covalent bond with their target proteins. In this study, a series of nitrogen-containing scaffolds bearing Michael acceptors was designed and synthesized based on the structural motifs relevant to the covalent drugs and natural products exhibiting antiviral activity.

We devised site-selective reactions of the common tricyclic intermediate with methyl propiolate at the four potentially nucleophilic sites involving indole N1, C3, ester alpha position, and aliphatic nitrogen, and achieved divergent synthesis of five alkaloidal Michael acceptors in a programmable manner within two steps.[1,2] This approach allowed rapid and collective synthesis of the alkaloidal Michael acceptors with distinct reactivities and steric hindrances against nucleophilic groups of cellular biomolecules.

Three Michael acceptors were found to exert potent *in vitro* inhibitory activities against hepatitis B virus (HBV) proliferation with low toxicity, and substantially reduced the levels of relaxed circular DNA (rcDNA) and covalently closed circular DNA (cccDNA). The optimal lead candidates are likely to suppress either RNA transcription from cccDNA or protein translation from HBV RNA, which would be a distinct mechanism of action from existing nucleic acid based anti-HBV drugs.[3,4]



1) Chen, P.; Cao, L.; Li, C. *J. Org. Chem.* **2009**, *74*, 7533. 2) Mizoguchi, H.; Oikawa, H.; Oguri, H. *Nat. Chem.* **2014**, *6*, 57. 3) Pei, Y.; Wang, C.; Yan, S. F.; Liu, G. *J. Med. Chem.* **2017**, *60*, 6461. 4) Tsukuda, S.; Watashi, K. *Antiviral Res.* **2020**, *182*, 104925.

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触媒的不斉向山-Michael 反応の開発とセスキテルペンラクトン類不斉全合成への活用

（早大院先進理工）○杉山 亮司・中田 雅久

Development of Catalytic Asymmetric Mukaiyama-Michael Reaction and Its Application to Enantioselective Total Synthesis of Sesquiterpene Lactones (*Graduate School of Advanced Science and Engineering, Waseda University*) ○Ryoji Sugiyama, Masahisa Nakada

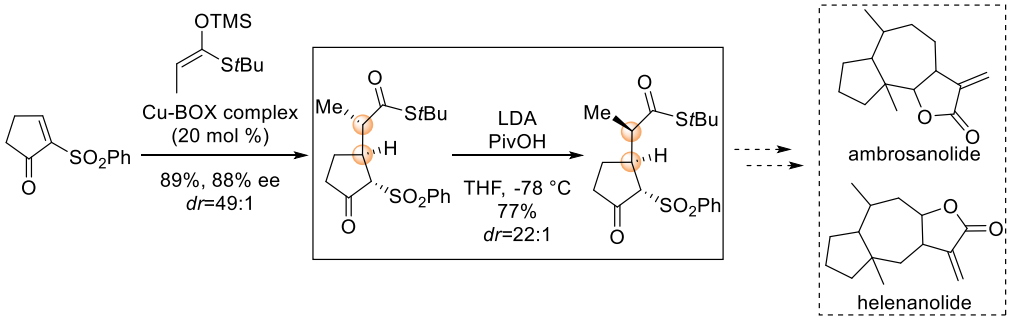
The Mukaiyama-Michael reaction is a carbon-carbon bond-forming reaction, generating an asymmetric carbon as well as a 1,5-dicarbonyl functional group, and its asymmetric catalysis has been widely studied. However, the highly enantio- and diastereoselective catalytic asymmetric Mukaiyama-Michael reaction of cyclic α-alkylidene β-keto compounds has never been reported. The catalytic asymmetric Mukaiyama-Michael reaction of α-phenyl sulfonyl cyclopentenone and silyl enol ethers of propionic acid *tert*-butyl thioester afforded the product in 89% yield with 88% ee as a single diastereomer when a 20 mol % Cu (II)–BOX complex was used. Inversion of the configuration of the α-position of thioester in the product was achieved with LDA and pivalic acid. These reactions enabled preparation of possible four diastereomers. The products are useful chiral building blocks and will be used for the enantioselective total syntheses of sesquiterpene lactones.

Keywords : Mukaiyama-Michael reaction, asymmetric catalysis, cyclic α-alkylidene β-ketosulfone, sesquiterpene lactone, stereoselective synthesis

向山-Michael 反応は炭素-炭素結合形成により、合成上有用な 1,5-ジカルボニル化合物を与え、また、新たな不斉中心を構築可能であるため、不斉反応への展開が広く行われてきた。しかし、環状α-アルキリデン β-ケト化合物の向山-Michael 反応による高エナンチオ、高ジアステレオ選択的な連続不斉中心構築は未だに達成されていない。

我々は、α-フェニルスルホニルシクロペンテノンの触媒的不斉向山-Michael 反応が単一ジアステレオマーの生成物を収率 89%、88% ee で与えることを見出した。また、生成物のチオエステルのα位は LDA とピバリン酸を反応させることで高立体選択的に反転することができ、4 種類の可能な立体異性体の自在な構築が可能となった。

開発した不斉触媒反応の生成物は合成上有用なキラル化合物であり、得られた 2 種類の立体異性体を活用したセスキテルペンラクトン類の不斉全合成を行った。



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Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[E1662-2am] 17. Biofunctional Chemistry, Biotechnology

Chair: Noriyuki Uchida, Shinya Hanashima

Thu. Mar 23, 2023 9:00 AM - 11:30 AM E1662 (1612, Bldg. 16 [1F])

[E1662-2am-01] Investigation of the relationship between hydration behavior and structural characteristics of carbohydrates by solution NMR measurements and molecular simulations

○Hiroaki Tatsuoka[1], Takumi Yamaguchi[1,2,3] （1. School of Materials Science, Japan Advanced Institute of Science and Technology, 2. Graduate School of Pharmaceutical Sciences, Nagoya City University, 3. Exploratory Research Center on Life and Living Systems (ExCELLS), National Institutes of Natural Sciences）

9:00 AM - 9:20 AM

[E1662-2am-02] Modification of membrane properties of small extracellular vesicle exosomes using lipid exchange

○Shinya Hanashima[1,2], Tomokazu Yasuda[1], Kazuya Kabayama[1], Koichiro M Hirosawa[3], Kenichi G. N. Suzuki[3] （1. Graduate School of Science, Osaka University, 2. Department of Engineering, Tottori University, 3. iGCORE, Gifu University）

9:20 AM - 9:40 AM

[E1662-2am-03] Development of Cancer-targeting Agents Based on Near-infrared-absorbing Diradical-platinum Complexes toward Photothermal Therapy

○Ryota Sawamura[1], Atsuko Masuya-Suzuki[2], Hao Thi Tran[3], Long Binh Vong[3], Yukio Nagasaki[3], Nobuhiko Iki[1] （1. Grad. Sch. Env. Stud., Tohoku Univ., 2. Grad. Sch. Sci. Tech. Innov., Yamaguchi Univ., 3. Grad. Sch. Pure Appl. Sci., Univ. of Tsukuba）

9:40 AM - 10:00 AM

[E1662-2am-04] Fabrication and Evaluation of Drug-Wrapped Adhesive Nanomaterials with epidermal regeneration ability

○Yota Shiba[1], Genta Yagami[1], Tadahiro Fuyama[1], Hideaki Sumiyoshi[2], Yutaka Inagaki[2], Yosuke OKamura[1,3] （1. Grad. Sch. of Eng., Tokai Univ., 2. Tokai Univ. Sch. of Med., 3. Micro/Nano Tech. Center, Tokai Univ.）

10:00 AM - 10:20 AM

[E1662-2am-05] Photoresponsive Membrane Deformation for Highly Efficient Encapsulation of Biomacromolecules and Its Application to *in vivo* Phage Display Method

○Noriyuki Uchida[1], Yunosuke Ryu[1], Teruhiko Matsubara[2], Toshinori Sato[2], Yasutaka Anraku[3], Takahiro Muraoka[1,4] （1. Tokyo Univ. Agri. and Tech., 2. Keio University, 3. The Univ. of Tokyo , 4. KISETC）

10:30 AM - 10:50 AM

[E1662-2am-06] Development of an amphiphilic peptide that self-assembles into helical fibers and controlling of bioadhesion properties by light

○Atsuya Yaguchi[1], Noriyuki Uchida[1], Itsuki Ajioka[2,3], Takahiro Muraoka[1,3] （1. Tokyo Univ. of Agri. and Tech., 2. Tokyo Med. and Dent. Univ., 3. KISTEC）

10:50 AM - 11:10 AM

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[E1662-2am-07] Phase transfer of co-assembled peptide supramolecules

○Rie Wakabayashi[1], Hiroki Obayashi[1], Noriho Kamiya, Masahiro Goto （1. Faculty of Engineering, Kyushu University）

11:10 AM - 11:30 AM

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溶液 NMR 計測と分子シミュレーションを用いた糖鎖の立体構造と水和挙動の連関の解明

(北陸先端大マテリアル[1]・名市大院薬[2]・自然科学研究機構 ExCELLS[3])
○龍岡　博亮[1]・山口　拓実[1,2,3]

Investigation of the relationship between hydration behavior and structural characteristics of carbohydrates by solution NMR measurements and molecular simulations ([1]*School of Materials Science,Japan Advanced Institute of Science and Technology,* [2]*Graduate School of Pharmaceutical Sciences,Nagoya City University,* [3]*Exploratory Research Center on Life and Living Systems (ExCELLS), National Institutes of Natural Sciences*) ○Hiroaki Tatsuoka,[1] Takumi Yamaguchi[1,2,3]

The biological function of oligosaccharides is provided mainly through the interaction with lectins. The conformation, dynamics and hydration structure of oligosaccharides are potential factors for regulating the selectivity and affinity in carbohydrate recognitions. However, analyzing carbohydrate hydration still remains a challenge. In this study, we performed NMR analyses and molecular simulations to approach the hydration behavior of oligosaccharides.

We focused on disaccharides, Manα1-3Manα, Manα1-2Manα and Glcα1-3Manα, which are the structures appearing at the non-reducing end of high mannose-type oligosaccharides involved in the quality control of glycoproteins in the endoplasmic reticulum. The synthesized disaccharides were solved in a water/DMSO mixed solvent to adjust proton exchange rates. NMR analyses of the disaccharides indicated that the exchange of carbohydrate hydroxyl protons with water protons occurred at different rates among the three disaccharides. Moreover, Glcα1-3Manα made the water–water interaction more efficient than the others. Molecular simulations of the disaccharides showed that water molecules bridging between carbohydrate residues were significantly found in Glcα1-3Manα. These results suggest that water molecules strongly associated with oligosaccharides promote the structuring of the surrounding water.
Keywords : Oligosaccharide; NMR; Hydration; MD Simulation; Conformation

糖鎖の生物機能メカニズムには、糖鎖の立体構造や運動性に加え、水和構造も密接に影響していると考えられる。しかし、糖鎖の水和に関しての知見は、未だ限られている。本研究では、核磁気共鳴(NMR)法と分子シミュレーションを活用し、糖鎖の水和挙動の探査に取り組んだ。

配列や結合様式の違いによる水との相互作用の差異を調べるため、小胞体内に見られる高マンノース型糖鎖の非還元末端の二糖構造、Glcα1-3Manα、Manα1-3Manα、および Manα1-2Manα に着目し、解析対象とした。合成した各二糖を、プロトン交換速度をコントロールするために水と DMSO を一定の割合で混合した溶媒へ溶かし、NMR 解析を行った。H/D 同位体効果を利用した NMR 計測の結果、これらの二糖構造では、糖の水酸基と水とのプロトン交換速度に違いがあることが示された。また、Glcα1-3Manα 溶液では水分子の挙動が異なっており、水ー水間の相互作用が強く働くことが分かった。さらに分子シミュレーションにより、各二糖と水分子との間の水素結合を調べたところ、Glcα1-3Manα では糖残基間を架橋する水分子が顕著に確認された。これらの結果から、糖鎖と強く結びついた水分子が、周囲の水の構造化を進めることが示唆された。

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脂質交換反応を利用した細胞外小胞エクソソームの膜物性改変法の検討

（阪大院理[1]・鳥取大工[2]・岐阜大 iGCORE[2]）○花島 慎弥[1,2]・安田 智一[1]・樺山 一哉[1]・廣澤 幸一朗[3]・鈴木 健一[3]

Modification of membrane properties of small extracellular vesicle exosomes using lipid exchange (*[1]Graduate School of Science, Osaka University, [2]Department of Engineering, Tottori University, [3]iGCORE, Gifu University*) ○Shinya Hanashima,[1,2] Tomokazu Yasuda,[1] Kazuya Kabayama,[1] Koichiro M. Hirosawa,[3] Kenichi G. N. Suzuki[3]

Exosomes are small extracellular vesicles involved in distal cell−cell communication and cancer migration by transferring functional cargo molecules. By using fluorescence spectroscopy, we revealed that the exosome membranes involve lipid raft-like regions approximately half of the entire membrane surface and the asymmetry of the bilayer is maintained to some extent.[1] We further focused on cholesterol in exosome membranes and semi-artificial exosomes with low or high cholesterol content were prepared through a lipid exchange reaction mediated by methylated cyclodextrin, and cellular uptake was examined. In PC-3 cell-derived exosomes, cellular uptake increased with increasing membrane cholesterol content, whereas bovine milk exosomes showed the opposite dependency. These results not only reveal the fundamental roles of cholesterol in exosome membranes for cellular uptake but may also open a door for the application of these cholesterol-tuned exosomes to strengthen delivery of the cargo molecule. *Keywords: exosomes; membranes; lipid raft*

微小な細胞外小胞であるエクソソームは、特定の積み荷分子を標的細胞に届けることで、細胞間の情報伝達を担うとともにガンの転移に関与する。 われわれは蛍光分光法を用いて、エクソソーム膜の約半分は脂質ラフト様の領域で占められており、脂質二重層の非対称性がある程度維持されていることを明らかにした[1)]。今回、エクソソーム膜に豊富に含まれるコレステロール分子に着目し、メチル化シクロデキストリン(MCD)を介した脂質交換反応を利用してコレステロールを除去または追加した半人工エクソソームを調製して、細胞への取り込みを調べた。 その結果、PC-3 細胞由来のエクソソームでは、膜コレステロール含有量の増加に伴い細胞取り込みが増加しましたが、牛乳エクソソームは逆の依存性を示した。 これらの結果は、エクソソーム膜のコレステロールが細胞取り込みに重要であることを明らかにするとともに、コレステロール含量が調整されたエクソソームが積み荷分子の送達効率や選択性を高めることができる可能性を示した。

1) T. Yasuda, H. Watanabe, K. M. Hirosawa, K. G. N. Suzuki, K. Suga, S. Hanashima, *Langmuir* in press.

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Development of Cancer-targeting Agents Based on Near-infrared-absorbing Diradical-platinum Complexes toward Photothermal Therapy

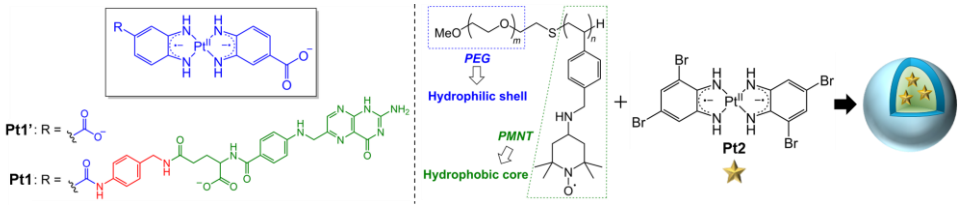
([1]*Grad. Sch. Env. Stud., Tohoku Univ.*, [2]*Grad. Sch. Sci. Tech. Innov., Yamaguchi Univ.*, [3]*Grad. Sch. Pure Appl. Sci., Univ. of Tsukuba*) ○Ryota Sawamura,[1] Atsuko Masuya-Suzuki,[2] Hao Thi Tran,[3] Long Binh Vong,[3] Yukio Nagasaki,[3] Nobuhiko Iki[1]

Keywords: Near-infrared absorption; Diradical-platinum complexes; Photothermal therapy; Drug delivery system

Photothermal therapy utilizes agents that can convert the energy of near-infrared (NIR) light into heat to kill cancer cells. Diradical-platinum complexes consisting of Pt(II) and two *o*-phenylenediamine ligands show strong near-infrared (NIR) absorption and generate heat.[1] This implies that they have the potential to act as agents of cancer photothermal therapy. If they can be delivered to the tumor selectively, the side effects will be reduced by locally heating the lesioned area. Here we studied the design of novel therapeutic agents using these complexes based on two strategies: active targeting of cancer cells and passive targeting of tumors.

Firstly, aiming for the delivery to folate receptors on the surface of cancer cells, we synthesized the complex **Pt1** conjugated to folic acid via the diamine linker.[2] **Pt1** was internalized into human breast cancer MCF-7 cells *ca.* 11 times as much as non-conjugated complex **Pt1'** and exhibited NIR absorption in the cells.[2] We are planning to investigate the detailed cellular uptake mechanism and photothermal conversion-based cell-killing of **Pt1**.

Secondly, we prepared the complex-loading polymeric micelles by using the amphiphilic copolymer PEG-*b*-PMNT, which possesses ROS scavenging character[3] for tumor-selective delivery. Our idea was to suppress the oxidative activation of tumor cells via the activation of inflammatory components such as nuclear factor, NF-κB. The average particle size of the micelles was 20–30 nm, assuming excellent accumulation into the tumor by the enhanced permeability and retention effects. Especially, the micelles loading hydrophobic complex **Pt2** showed strong NIR absorption in human osteosarcoma MG63 cells. A study on the photothermal conversion properties of **Pt2**-loading micelles is now ongoing.



1) R. Sawamura, M. Sato, A. Masuya-Suzuki, N. Iki, *RSC Adv.* **2020**, *10*, 6460. 2) R. Sawamura, A. Masuya-Suzuki, N. Iki, *Chem. Lett.* **2022**, *51*, 1157. 3) T. Yoshitomi, D. Miyamoto, Y. Nagasaki, *Biomacromolecules* **2009**, *10*, 596.

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表皮再生能を期待した貼付型薬剤担持ナノラッピング材の創製と機能評価

（東海大院工[1]・東海大医[2]・東海大マイクロ・ナノ研[3]）○芝 燿汰[1]・谷神 紘太[1]・布山 忠裕[1]・住吉 秀明[2]・稲垣 豊[2]・岡村 陽介[1,3]

Fabrication of Evaluation of Drug-Wrapped Adhesive Nanomaterials with Epidermal Regeneration Ability ([1]*Graduate School of Engineering, Tokai University,* [2]*Tokai University School of Medicine,* [3]*Micro/Nano Technology Center, Tokai University*) ○Yota Shiba[1], Genta Yagami[1], Tadahiro Fuyama[1], Hideaki Sumiyoshi[2], Yutaka Inagaki[2], Yosuke Okamura[1,3]

Collagen sponge has been clinically used to treat skin defects as artificial dermis[1]. However, its porous surface makes it difficult for epidermal regeneration, requiring epidermal grafts from other sites. Recently, moon jellyfish collagen has been found to have excellent epidermal regeneration ability[2]. On the other hand, nanosheets with the thickness of nanometer scale have been found to exhibit high adhesive properties that allow to be attached to various interfaces by only physical adsorption[3]. In this study, we propose a fabrication method of a collagen-wrapped nanomaterial composed of biodegradable poly(lactic acid) (PLA) nanosheet for promoting the epidermal regeneration ability. An aqueous solution of sodium polystyrene sulfonate (PSS) as a sacrificial layer was spin-coated on SiO_2 substrate (50 × 50 mm^2). A toluene solution of PLA was then spin-coated on the PSS-coated substrate. When the substrate was immersed in water, the freestanding PLA nanosheet was peeled off while maintaining the shape of the substrate. The PLA nanosheet was recovered on a non-woven fabric. Another PLA nanosheet (25 × 25 mm^2) was pressed onto the recovered PLA nanosheet. An aqueous solution of Moon jellyfish collagen was dropped and dried on the PLA nanosheets. Finally, the PLA nanosheet adhered on nonwoven fabric was folded and wrapped the jellyfish collagen. The detailed results on epidermal regeneration ability in diabetic mice will be released on the 103rd CSJ annual meeting.

Keywords : polymer nanosheet, drug wrapping, moon jellyfish collagen, wound healing

現在、皮膚欠損創の治療には、人工真皮が使用されている[1]。しかし、その最表面が多孔質のため、表皮が進展しにくく、他部位からの表皮移植を要する。他方、ミズクラゲのコラーゲンは優れた表皮再生能を有することが見出されている[2]。また、膜厚がナノメートルサイズのナノシートは、物理吸着のみで様々な界面に貼付可能となる高接着性が発現することが見出されている[3]。本研究は、生分解性高分子であるポリ乳酸 (PLA) からなるナノシートでミズクラゲコラーゲンをラッピングしたコラーゲンラッピング材の創製法を提案し、さらなる表皮再生能の向上を狙う。

SiO_2 基板 (50 × 50 mm^2) 上にポリスチレンスルホン酸ナトリウム水溶液にてスピンコートして犠牲層とした。続いて、PLA のトルエン溶液にてスピンコートした。次に、水中にて基板ごと浸漬させたところ、基板の形状を維持した状態で PLA ナノシートを剥離できた。不織布上に回収した PLA ナノシートの上に別途調製した PLA ナノシート (25 × 25 mm^2) を押し当て、転写した。また、転写した PLA ナノシート上にミズクラゲコラーゲン水溶液を滴下後、乾燥させた。最後に、PLA ナノシート (50 × 50 mm^2) を不織布ごと折りたたみ、ミズクラゲコラーゲンをラッピングする手法を確立した。現在、糖尿病モデルマウスを使用した表皮再生能評価を進めており、当日併せて報告する。

1) Koide M. *et al. J. Bio. Mater. Res*. **27**, 79-87 (1993), 2) Sumiyoshi H. *et al. Regen. Ther.* **18**, 223-230 (2021), 3) Okamura Y. *et al. Adv. Mater*. **21**, 4388-4392 (2009).

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生体高分子の高効率封入を可能にする光応答性膜変形技術と *in vivo* ファージディスプレイ法への応用

（東農工大院工[1]、慶大理工[2]、東大院工[3]、KISTEC[4]）○内田紀之[1]・笠勇之助[1]・松原輝彦[2]・佐藤智典[2]・安楽泰孝[3]・村岡貴博[1,4]

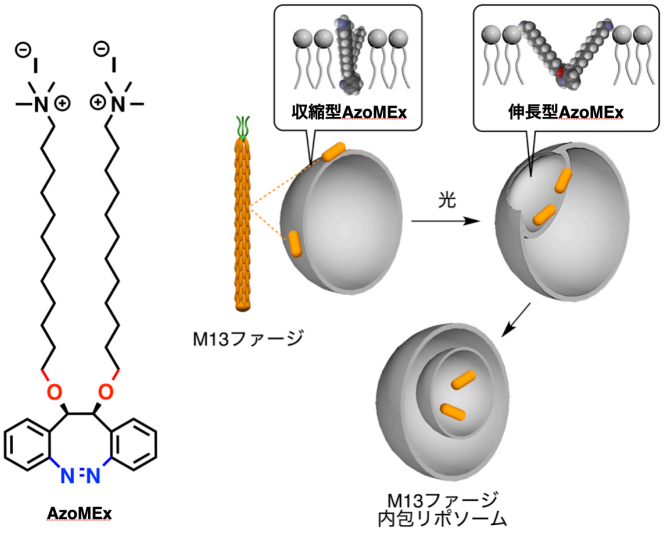
Photoresponsive Membrane Deformation for Highly Efficient Encapsulation of Biomacromolecules and Its Application to *in vivo* Phage Display Method ([1]*Tokyo University of Agriculture and Technology*, [2]*Keio University*, [3]*The University of Tokyo*, [4]*KISTEC*)

○Noriyuki Uchida[1], Yunosuke Ryu[1], Teruhiko Matsubara[2], Toshinori Sato[2], Yasutaka Anraku[3], Takahiro Muraoka[1,4]

Endocytosis is a membrane deformation phenomenon that allows the direct uptake of solutions containing macromolecules. In this study, we designed a light-responsive membrane stretching molecular machine and found that an endocytosis of phospholipid vesicles containing the molecular machine, was induced. Furthermore, we successfully incorporated micro-meter scale M13 bacteriophage into the vesicles by the endocytosis by which *in vivo* stability of M13 phage in blood vessels was improved.

Keywords: Phospholipid Bilayers; Photoresponsiveness; Molecular Machine; Phage Display; Endocytosis

エンドサイトーシスに代表されるベシクルの内部への分裂はマイクロスケールの生体高分子を含む溶液を直接取り込むことが可能な膜変形現象である。しかしながら、これまで膜変形における物理的な制約から、人工的に実現するのが困難とされてきた。最近、演者は可視光照射によって構造が直線状から扇状へと変化する、アゾベンゼン骨格を有する光応答性膜伸長分子機械（AzoMEx:図 A）の合成に成功した。さらに、AzoMEx を導入した DOPC ベシクル（DOPC/AzoMEx ベシクル）に対して可視光を照射したところ、リン脂質ベシクルのエンドサイトーシスが起こること見出した[1)]。この人工エンドサイトーシスを利用することで、マイクロスケールの M13 バクテリオファージをベシクル内に取り込み、保護することで、*in vivo* における血中内での安定性を向上させることができる（図 B）。本講演ではこのエンドサイトーシス様の分裂を起こすベシクルの材料設計、および応用の詳細に関して報告する。



1）特願 2021-077870

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超分子らせんファイバーを形成するペプチドの開発と生体接着性光制御

（東農工大院工[1]・東医歯大 CBIR[2]・KISTEC[3]）
○矢口 敦也[1]・内田 紀之[1]・味岡 逸樹[2,3]・村岡 貴博[1,3]

Development of an Amphiphilic Peptide that Self-assembles into Helical Fibers and Controlling of Bioadhesion Properties by Light

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Center for Brain Integration Research, Tokyo Medical and Dental University*, [3]*Kanagawa Institute of Industrial Science and Technology*)
○Atsuya Yaguchi,[1] Noriyuki Uchida,[1] Itsuki Ajioka,[2,3] Takahiro Muraoka[1,3]

Bioadhesion plays an important role in many biological activities such as environmental recognition and enzymatic reactions. In particular, the helical structure of biopolymers regulates adhesion to biomaterials[1]. However, the interactions with artificial polymers are mainly dominated by the molecular structures of the polymers such as electrical charge. Thus, the development of artificial adhesive materials derived from the formation of higher-order helical structures has been difficult. Here, we developed a self-assembling peptide **AzoRADA** with azobenzene introduced into the side chain as a basis for the new material that controls adhesion to biomolecules by forming the helical structure. By changing the sequence order of the self-assembling peptides, it is possible to control the shape of the aggregation while maintaining the types and quantity ratios of the constituent amino acids. In fact, **AzoRADA** changed its assembly shape depending on the position of azobenzene introduction, and especially the peptide with azobenzene at their ends gelled in water by forming helical fibers (Fig. 1a, 1b). This gel was transformed into sol by isomerization of the azobenzene from trans to cis upon light irradiation (Fig. 1d). In addition, the helical fiber was more hydrophilic compared to non-helical fibers, which enabled bioapplications to tuning adhesiveness (Fig. 1c).

Keywords: Peptide; Self-Assembly; Hydrogel; Higher-Order Structure; Photoisomerization

生体における接着は、特定のアミノ酸配列認識の他、らせんなどの高次構造認識に由来するものも見られ[1]、高度な情報処理プロセスの１つと捉えられる。一方で、人工高分子と物質との相互作用は主に電荷などの分子構造で説明されるため、高次のらせん構造形成に由来する人工接着材料の開発は未開拓領域であった。

本研究では、生体分子との接着をらせん構造形成により制御する新規材料の基盤として、アゾベンゼンを側鎖に導入した自己集合性ペプチド **AzoRADA** を開発した。自己集合性ペプチドは、アミノ酸配列の順序を入れ替えることで、構成されるアミノ酸の種類や量比を保持しながら集積形状を制御できる。実際に **AzoRADA** は、アゾベンゼンの導入位置により集積形状が変化し、末端側へ導入した場合に超分子らせんファイバーが得られた(Fig. 1a, 1b)。この分子レベルの集積構造の違いは、マクロな表面特性を変化させ、生体物質に対する接着性を大きく向上させた(Fig. 1c)。さらに、アゾベンゼンのトランス−シス異性化を利用し、**AzoRADA** を塗布したガラス基盤への接着制御を実現した(Fig. 1d)。

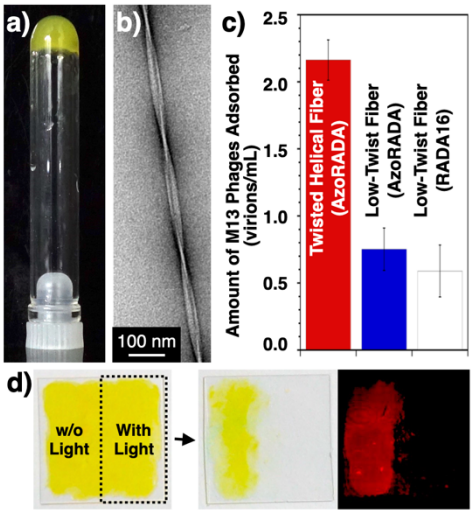


Fig. 1 a) Photograph of AzoRADA hydrogel. b) TEM images of the helical fiber of AzoRADA. c) The amount of M13 phages adhered onto AzoRADA fiber-coated substrates as calculated by the plaque assay. d) Photograph and fluorescence image (647 nm) of photo-selective detachment of fluorescent phage-Cy5 from AzoRADA fiber-coated glass substrate.

1) T. Schwartz *et al. Science* **1999**, *284*, 1841-1845.

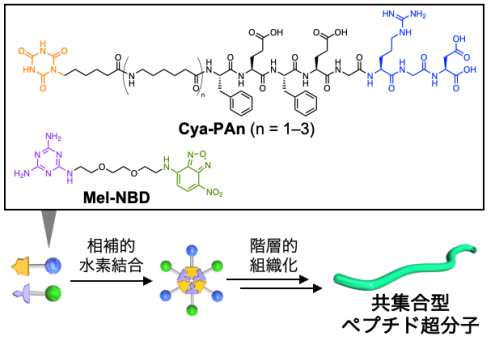
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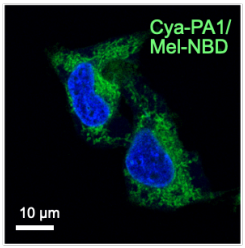
共集合型ペプチド超分子の相移行性

(九大院工[1]) ○若林 里衣[1]・大林 洋貴[1]・神谷 典穂[1]・後藤 雅宏[1]
Phase transfer of co-assembled peptide supramolecules ([1]*Graduate School of Engineering, Kyushu University*) ○Rie Wakabayashi,[1] Hiroki Obayashi,[1] Noriho Kamiya,[1] Masahiro Goto[1]

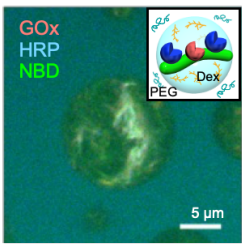
We have developed peptide supramolecules formed through a complementary hydrogen bond interaction between peptide amphiphiles (Cya-PAs) and fluorescent small molecule (Mel-NBD). The size of these peptide supramolecules were shown to be depending on the lengths of alkyl chains of Cya-PAs, which further affects the intracellular delivery of the supramolecules. In this presentation, we will report about phase transfer of the supramolecules through membranes or without membranes and the relationship between the transfer and supramolecular designs. The use of these supramolecule for the control over protein localization and cascade reactions will also be introduced.
Keywords：Supramolecule; Peptide; Co-assembly; Phase transfer; Membrane

我々はこれまでに相補的水素結合部位を導入した両親媒性ペプチド (Cya-PA) と蛍光小分子 (Mel-NBD) が共集合することにより形成する超分子を開発した。本ペプチド超分子は、Cya-PA に導入したアルキル鎖長に応じ長軸方向のサイズが変化する。またそのサイズ依存的に細胞内移行することが示されている。本講演では、これらの共集合型ペプチド超分子の膜を介した[1)]、あるいは膜を介さない[2)]相間移行性ついて、超分子のデザインとの相関について報告する。また、後者についてはタンパク質の局在制御とカスケード反応への利用可能性についても紹介する。





細胞内移行



液滴選択性＆タンパク局在

1) R. Wakabayashi, H. Obayashi, R. Hashimoto, N. Kamiya, M. Goto, *Chem. Commun.* **2019**, *55*, 6997.
2) H. Obayashi, R. Wakabayashi, N. Kamiya, M. Goto, *Chem. Commun.* **2023**, *59*, 414.

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[E1661-2am] 17. Biofunctional Chemistry, Biotechnology

Chair: Tomohiro Doura, Tomonori Tamura

Thu. Mar 23, 2023 9:00 AM - 11:30 AM E1661 (1611, Bldg. 16 [1F])

[E1661-2am-01] Development of fast blinking fluorophores for real-time single-molecule super-resolution imaging

○Bochao Li[1], Toshiyuki Kowada[1], Takahiro Fujiwara[2], Shin Mizukami[1] （1. Tohoku Univ., 2. Kyoto Univ.）

9:00 AM - 9:20 AM

[E1661-2am-02] Optical regulation of intracellular protein localization using photochromic protein dimerizers

○Toshizo Sato[1], Toshiyuki Kowada[1,2], Satoshi Hamaguchi[1], Toshitaka Matsui[1,2], Shin Mizukami[1,2] （1. Graduate School of Life Sciences, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University）

9:20 AM - 9:40 AM

[E1661-2am-03] pH-Responsive and Peptide Sequence-Specific Dynamic Covalent Bond Chemistry

○Yuto Ohno[1], Alexander Vinogradov[1], Hiroaki Suga[1] （1. The University of Tokyo）

9:40 AM - 10:00 AM

[E1661-2am-04] Discovery of CFA-type Covalent Inhibitors that Modulate Activity of Beta Oxidation Pathway Based on FBDD Approach

○ruikang Yin[1], Kazuya Inoue[1], Shohei Uchinomiya[1], Akio Ojida[1] （1. kyushu Universitity）

10:00 AM - 10:20 AM

[E1661-2am-05] Development of second generation NASA warhead for covalent inhibitors

○Masaharu Kawano[1], Shunsuke Murakawa[1], Tomonori Tamura[1], Itaru Hamachi[1,2] （1. Graduate School of Engineering, Kyoto University, 2. ERATO JST）

10:30 AM - 10:50 AM

[E1661-2am-06] New developments in *FixEL* method incorporating chemical sensors

○Takeharu Mino[1], Hiroshi Nonaka[1,2], Seiji Sakamoto[2], Mamoru Ishikawa[2], Itaru Hamachi[1,2] （1. Graduate School of Engineering, Kyoto University, 2. JST ERATO）

10:50 AM - 11:10 AM

[E1661-2am-07] Chemogenetic regulation of adenosine A_{2A} receptor focusing on subtype selectivity of the antagonists

○Yuma Matsuoka[1], Tomohiro Doura[1], Shigeki Kiyonaka[1] （1. Nagoya University）

11:10 AM - 11:30 AM

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Development of fast blinking fluorophores for real-time single-molecule super-resolution imaging

([1]*Graduate School of Life Sciences, Tohoku University,* [2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,* [3]*Institute for Integrated Cell-Material Sciences, Kyoto University*) ○Bochao Li,[1] Toshiyuki Kowada,[1,2] Takahiro Fujiwara,[3] Shin Mizukami[1,2]
Keywords: Single-molecule localization microscopy; Fluorescent probe

Single-molecule localization microscopy (SMLM) is one of the promising approaches to achieve super-resolution imaging by switching fluorophores between on and off states. Currently, direct Stochastic Optical Reconstruction Microscopy (dSTORM) is one of the widely used SMLM methods that use strong laser intensity accompanied with cytotoxic additives to trigger reversible stochastic switching of fluorophores between fluorescent and dark states (blinking). Because of these harsh imaging conditions, dSTORM is often incompatible with live cells. One way to solve this problem is the use of spontaneous blinking fluorophores. Some of the xanthene fluorophores show the intramolecular spirocyclization reaction interconverting the fluorescent open form and the non-fluorescent closed form in the ground state (**Fig 1a**). Spontaneous blinking simplifies the imaging process, allowing live-cell SMLM imaging with low laser intensity and no additive. However, relatively low blinking kinetics of the reported fluorophore, HMSiR (**Fig 1a**),[1] only allows minute-scale imaging and is not suitable for imaging fast cellular dynamics in second scale.

Although AMSiR (**Fig 1a**) is not suitable for SMLM imaging due to low population of the open forms, the amino group of AMSiR can induce much faster blinking kinetics than the hydroxy group of HMSiR.[1] Taking this into account, we developed a series of fast blinking fluorophores for real-time SMLM imaging by inducing the steric and electronic effects at the adjacent position of the ring-closing part on AMSiR (**Fig 1b**). The new fluorophores showed several times faster blinking kinetics than HMSiR, and the temporal resolution for an image acquisition was improved to be as short as seconds under high-rate camera.

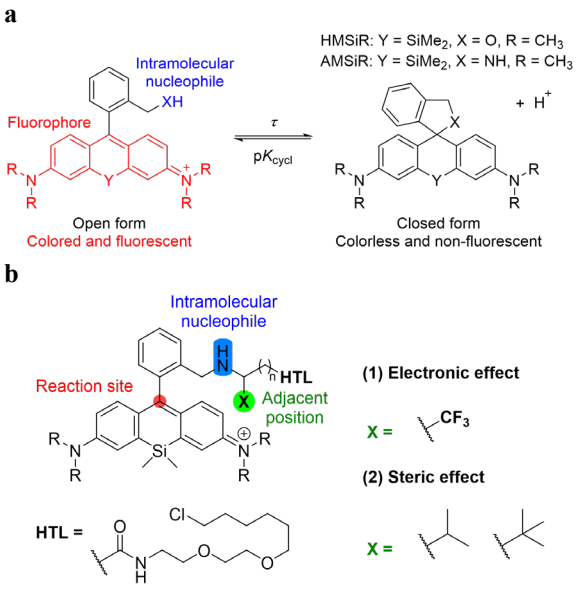


Fig 1. (a) Thermal equilibrium of intramolecular spirocyclization of rhodamines between the fluorescent open form and the non-fluorescent closed form.[1] (b) Design strategies of AMSiR-based fast-blinking fluorophores.

(1) Uno, S.-n., *et al. Nat. Chem.* **2014**, *6*, 681–689.

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フォトクロミック蛋白質二量化剤を用いた生細胞内蛋白質局在の光制御

○佐藤 歳三[1]、小和田 俊行[1,2]、濱口 聡志[1]、松井 敏高[1,2]、水上 進[1,2] (1. 東北大院生命、2. 東北大多元研)
Optical regulation of intracellular protein localization using photochromic protein dimerizers ([1]*Graduate School of Life Sciences, Tohoku University*, [2] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○Toshizo Sato[1], Toshiyuki Kowada[1,2], Satoshi Hamaguchi[1], Toshitaka Matsui[1,2], Shin Mizukami[1,2]

Protein functions in cells are regulated by their intermolecular interactions and localization changes, and their dysfunction causes various diseases. We have therefore developed a method for photo-reversible regulation of intracellular protein localization using light-responsive small molecules to artificially regulate protein-protein interactions and to elucidate the regulatory mechanism of protein functions. azoMTX is a photochromic ligand developed by incorporating an azo moiety into methotrexate (MTX), an inhibitor for *Escherichia coli* dihydrofolate reductase (eDHFR). The affinity of azoMTX for eDHFR can be modulated by photo-isomerization, that is, its binding and dissociation to eDHFR can be photo-reversibly controlled.[1] We also have developed a photochromic protein dimerizer, pcDH, by combining azoMTX with a HaloTag ligand.[2] However, pcDH does not completely photoisomerize from the *cis* to *trans* isomer with lower affinity to eDHFR. Slight amount of the eDHFR–pcDH–HaloTag complex formation was also observed even after green light illumination. In this presentation, we will report a novel photochromic protein dimerizer with an arylazopyrazole structure that can be almost completely isomerized to the *trans* isomer and its application in photo-reversible control of protein dimerization in living cells.
Keywords : optical regulation; protein dimerizer; dihydrofolate reductase

細胞内蛋白質の機能は分子間相互作用や局在変化によって調節されており、その異常は様々な疾患の原因となる。我々は、光応答性小分子を用いて細胞内での蛋白質局在を光可逆的に制御する手法を開発し、蛋白質間相互作用の人為的な制御や蛋白質機能の調節機構の解明に取り組んできた。azoMTX は、大腸菌ジヒドロ葉酸還元酵素（eDHFR）の阻害剤であるメトトレキセート（MTX）にアゾベンゼン骨格を導入したフォトクロミックリガンドであり、光異性化に伴う親和性の変化によって eDHFR に対する結合・解離を光可逆的に制御可能であった[1]。さらに、azoMTX と共有結合性タグ蛋白質 HaloTag のリガンドを組み合わせることでフォトクロミック蛋白質二量化剤 pcDH を開発した[2]。しかし、pcDH は親和性の低いトランス体への完全な光異性化が困難であり、緑色光照射時でも eDHFR と HaloTag の複合体がわずかに形成されることが課題であった。本発表では、アリールアゾピラゾール骨格の導入によりほぼ完全な *trans* 体への光異性化を実現した新規フォトクロミック蛋白質二量化剤の開発、ならびに、それを用いた生細胞内蛋白質の光二量化制御について報告する。

1） Mashita, T.; Kowada, T.; Takahashi, H.; Matsui, T.; Mizukami, S. *ChemBioChem* **2019**, *20*, 1382.
2） Mashita, T.; Kowada, T.; Yamamoto, H.; Hamaguchi, S.; Matsui, T.; Mizukami, S. *ChemRxiv*. **2022**.

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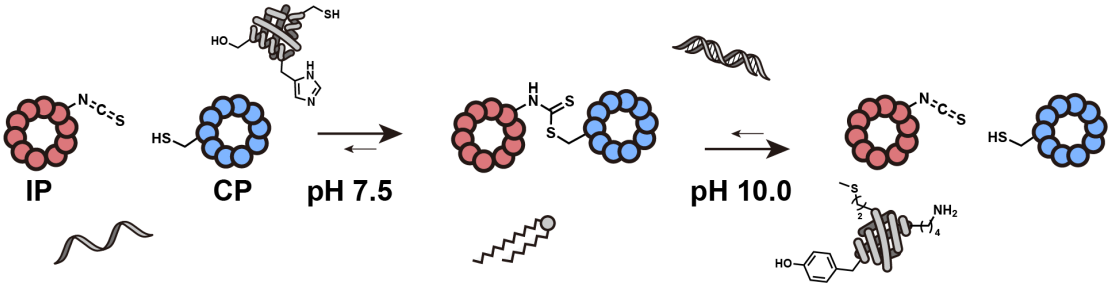
pH-Responsive and Peptide Sequence-Specific Dynamic Covalent Bond Chemistry

([1]*Graduate School of Science, The University of Tokyo*) ○ Yuto Ohno,[1] Alexander Vinogradov,[1] Hiroaki Suga[1]

Keywords: peptide; mRNA display; dynamic covalent bond chemistry; dithiocarbamate; bioconjugation

Site-selective protein modification, i.e., chemo- and regioselective labeling of a single amino acid on a protein surface, remains a major challenge in chemical biology. Multiple recent studies[1] report the development of oligopeptide tags and/or conjugation reagents to realize irreversible site-selective modification. In contrast, *reversible* labeling using dynamic covalent chemistry (DCC)[2] remains much less developed. DCC can be uniquely leveraged in a variety of contexts, e.g., for affinity protein purification, target pulldown from complex biological mixtures or to mask reactive functionalities on a protein surface. Here, we disclose the development of a pair of cyclic peptides which react selectively with each other and form stable conjugates that can be dissociated at high pH.

The RaPID system[3], a peptide discovery platform, was leveraged to discover a pair of mutually reactive cyclic peptides in a two-step process. First, a cysteine-containing peptide (CP) which reacts selectively with an isothiocyanate-containing (ITC) substrate at neutral pH was selected. Next, an ITC-containing peptide (IP) was selected against the CP obtained in the first step. At neutral pH, the pair of peptides quickly (k_2 > 100 $M^{-1}s^{-1}$) reacts to form a stable dithiocarbamate, which can be rapidly dissociated under basic conditions (pH > 10). The developed IP can selectively recover CP from complex biological media such as cell lysates with minimal background. This presentation will focus on the discovery of the reactive peptide pair as well as the analysis of reaction kinetics, mechanism, and some practical applications.



1) G. J. L. Bernardes et al. *Nat. Rev. Chem.* **2019**, 3, 147. 2) a) E. V. Anslyn et al. *Nat. Chem.* **2016**, 8, 968. b) T. Weil et al. *Bioconjugate Chem.* **2018**, 29, 2665. 3) H. Suga et al. *Chem. Commun.* **2017**, 53, 1931.

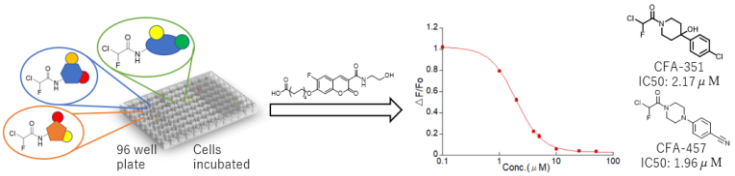
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FBDD 戦略に基づくβ酸化を制御するコバレント阻害剤の探索

（九大薬 [1]）○YIN RUIKANG[1]・井上和哉 [1]・内之宮祥平 [1]・王子田彰夫 [1]
Discovery of Covalent inhibitors that Modulate Activity of Beta Oxidation Pathway Based on FBDD Approach ([1]Graduate School of Pharmacy, Kyushu University) ○YIN RUIKANG[1], Kazuya Inoue[1], Shohei Uchinomiya[1], Akio Ojida[1]

Beta oxidation pathway plays a vital role in organism as one of energy metabolism pathways. Aberrant pattern of beta oxidation is deeply associated with various diseases including heart failure, obesity, and cancer. Therefore, it weighs heavily with human health and diseases therapy to find chemical modulators for beta oxidation activity. FBDD is known as an efficient approach for drug development. Recently, covalent fragments which inhibit target proteins by forming covalent bond have been paid much attention thanks to their strong effect and prolonged residence time. While chloroacetamide group (CA group) and acrylamide group have been widely used as prevalent warheads, their relatively high reactivity might cause significant side-effects due to non-specific reaction with off-target proteins. Our group have recently developed chlorofluoroacetamide group (CFA group) which shows high target selectivity thanks to its mild reactivity (1). In this presentation, we report a construction of CFA covalent fragment library and its application to inhibitor discovery for beta oxidation activity. We carried out screening of covalent fragments in live cells with a fluorescent probe for beta-oxidation and found that two covalent compounds, named as CFA-351 and CFA-457, effectively inhibit the activity of beta oxidation. We also conducted protein target identification of CFA-351 and CFA-457 by chemical proteomics analysis.
Key words: covalent inhibitor, fragment library, warhead

β 酸化は、生体内の主要なエネルギー生産経路の一つであり、β 酸化活性異常は、狭心症、肥満、がんと深く関連している。そのため、β酸化活性を制御する化合物は、疾患治療に有用である。創薬研究における有用な戦略として、低分子フラグメントライブラリーを用いた FBDD が挙げられる。特に最近、標的タンパク質と共有結合形成によって強い薬効が期待できるコバレントフラグメントライブラリーが注目されている。これまで本手法での共有結合形成のための反応基としてクロロアセトアミドやマイケルアクセプターが用いられてきたが、反応性が高いため off-taget との非特異的な反応が問題となっていた。一方、我々の研究室では穏やかな反応性を有するクロロフルオロアセトアミド (CFA)を、標的タンパク質選択性の高い新しい反応基として開発した(1)。今回我々は、CFA 基を有するコバレントフラグメントライブラリーを新しく構築し、β酸化阻害剤の探索に応用した。我々の研究室で開発したβ酸化活性を検出可能な蛍光プローブを用いて、生細胞でのスクリーニングを行った結果、β酸化活性を強く阻害する 2 つの低分子化合物(CFA351, CFA457)を見出した。さらに、ケミカルプロテオミクスによって CFA351, CFA457 の標的タンパク質を同定したので報告する。



(1). Naoya S. et al. Selective and reversible modification of kinase cysteines with chlorofluoroacetamides. *Nature Chemical Biology* , **15,** 250–258, (2019)

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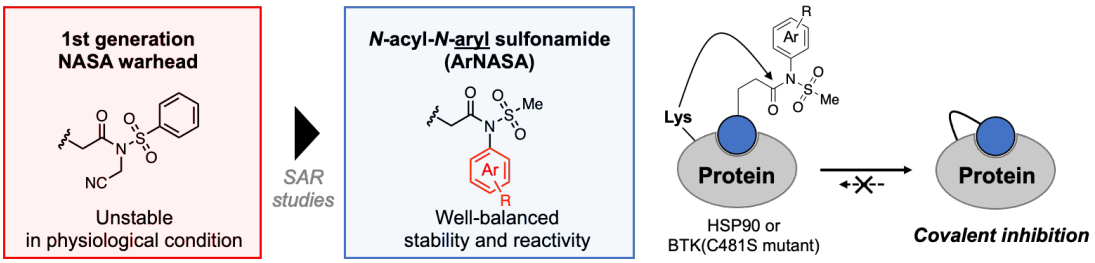
Development of second generation NASA warhead for covalent inhibitors

([1]*Graduate School of Engineering, Kyoto University*, [2]*ERATO JST*) ○Masaharu Kawano,[1] Shunsuke Murakawa,[1] Tomonori Tamura,[1] Itaru Hamachi[1, 2]

Keywords: Covalent inhibitors; *N*-acyl-*N*-aryl sulfonamide; HSP90; BTK

Covalent inhibition of a target protein function has gained widespread attention in the field of drug discovery. Covalent inhibitors are typically designed by incorporating an electrophilic warhead into a ligand of the target protein, allowing for its irreversible inhibition through the formation of a covalent bond. Although most of the current approaches utilize the unique reactivity of cysteines to generate the covalent linkage, there is a growing need for warheads that can target non-cysteine residues to expand the range of covalent-druggable proteins. In this context, we have recently showed that *N*-acyl-*N*-alkyl sulfonamide (**NASA**) warhead is applicable to covalent inhibitors targeting lysine or tyrosine residues.[1, 2] Nevertheless, NASA-type covalent inhibitors suffered from instability in serum-containing medium due to their high intrinsic reactivity, which hinders their *in vivo* applications to date.

To address this challenge, we sought to optimize the structure of NASA warhead and found that *N*-acyl-*N*-aryl sulfonamide (**ArNASA**) is promising for covalent inhibition strategy. Our structure-activity relationship studies indicated that the reactivity of ArNASA warheads can be precisely controlled by substituents on the aromatic ring. Importantly, optimized ArNASA derivatives exhibited significantly greater stability than the conventional NASA warhead, whereas they showed excellent reaction efficiency comparable to that of the conventional NASA warhead in covalent inhibition of Heat shock protein 90 (HSP90). This exceptional reaction property enabled covalent inhibition of HSP90 in living cells even in the presence of fetal bovine serum (FBS). We will also report on the development of covalent inhibitors for drug-resistant Bruton's tyrosine kinase (BTK) mutant based on ArNASA warheads.



1) T. Tamura *et al.*, *Nat. Commun.*, 2018, 9, 1870. 2) T. Ueda *et al.*, *J. Am. Chem. Soc.*, 2021, 143(12), 4766-4774.

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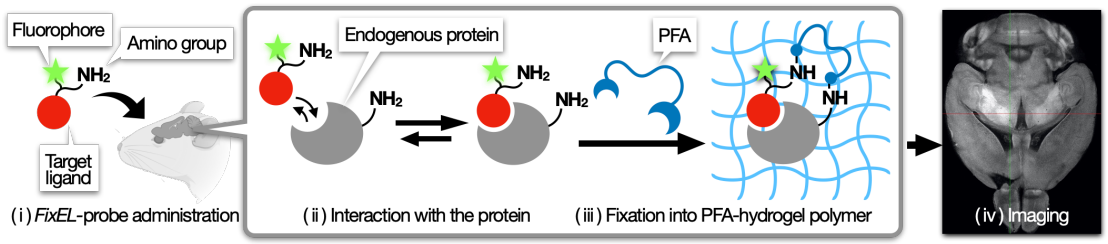
ケミカルセンサーを組み込んだ *FixEL* 法の新展開

（京大院工[1]・JST ERATO[2]）○美野 丈晴[1]・野中 洋[1,2]・坂本 清志[2]・石川 守[2]・浜地 格[1,2]

New developments in *FixEL* method incorporating chemical sensors ([1]*Graduate School of Engineering, Kyoto University*, [2]*JST ERATO*) ○Takeharu Mino,[1] Hiroshi Nonaka,[1,2] Seiji Sakamoto,[2] Mamoru Ishikawa,[2] Itaru Hamachi[1,2]

Various small molecules are used as functional probes in live animals. To optimize the *in vivo* use of such small molecules, their spatial distribution in tissues and diffusion and efflux rates are important. However, there are limited methods to study such parameters. Recently, we have developed *FixEL*, a method for imaging the small molecule distribution in the mouse brain.[1)] In *FixEL*, the target small molecule is modified with amine and fluorescent dye. After this molecule is administered to mice, the whole mouse body was treated with PFA. PFA treatment causes tissue fixation and crosslinking between the amino groups on the small molecule and surrounding proteins. This allows the distribution of small molecules at a certain moment to be fixed on the tissue and observed with fluorescence microscopy. In addition, we also attempted to develop a new type of chemical sensor that can be used *in vivo* by focusing on the reaction between amino groups and PFA. *Keywords : Ligand-protein interaction, in vivo Imaging, Chemical sensor probes, Neuroscience, Hydrogel-tissue chemistry (HTC)*

様々な小分子が機能性プローブとして基礎研究から医療診断まで幅広く用いられている。機能性小分子の生体内での利用を最適化するためには、分子の組織内空間分布や、標的への結合選択性、拡散・排出速度を詳細に知ることが望ましい。しかし小分子の組織内分布や動態を調べる方法は限られている。そこで最近我々はマウス脳内での小分子分布をイメージング解析可能とする新たな手法として *FixEL* 法を開発した[1)]。*FixEL* 法では標的とする小分子に対し事前にアミノ基と蛍光色素を導入したプローブを用いる。本プローブをマウスへ投与したのち、灌流法によって迅速な PFA 全身処理を行うと、組織固定が進行すると同時に、小分子上のアミノ基と PFA との結合が瞬時に形成される。これにより、ある瞬間の小分子の生体内分布を組織上に固定し、蛍光顕微鏡レベルの分解能で観察可能となる。さらに、今回新たに、*FixEL* 法の原理を発展させることで、*in vivo* 利用可能な生体環境応答性ケミカルセンサーの構築も試みた。



1) H. Nonaka, T. Mino et al, *Chem.* **2023**, in press. DOI: 10.1016/j.chempr.2022.11.005

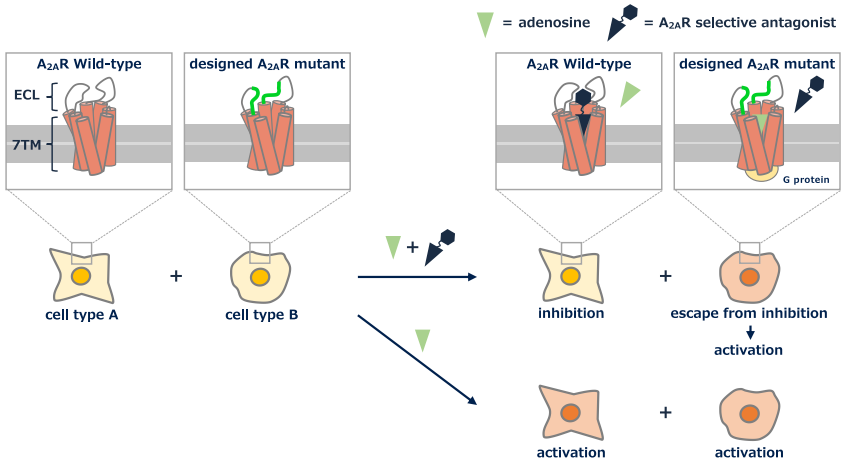
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拮抗剤のサブタイプ選択性に着目したアデノシン A_{2A} 受容体のケモジェネティクス制御

（名大院工）○松岡 佑真・堂浦 智裕・清中 茂樹
Chemogenetic regulation of adenosine A_{2A} receptor focusing on subtype selectivity of the antagonists (*Graduate School of Engineering, Nagoya University*) ○Yuma Matsuoka, Tomohiro Doura, Shigeki Kiyonaka

G protein-coupled receptors (GPCRs) regulate a wide range of physiological processes. However, due to the broad distribution of GPCRs in various cells or tissues, their roles in each cell-type remain unclear. We here describe a novel method termed eLEC (extracellular-loop engineered chemogenetics), which allows regulation of defined GPCRs in target cells. In this presentation, we report the regulation of adenosine A_{2A} receptor ($A_{2A}R$) by eLEC, focusing on the action mechanisms of the subtype selective antagonists. By swapping extracellular loops between $A_{2A}R$ and other adenosine receptors, $A_{2A}R$ mutants escaped from inhibition by $A_{2A}R$-selective antagonists without affecting original receptor function. Notably, this strategy has been applied to primary astrocytes endogenously expressing $A_{2A}R$.
Keywords: GPCR, adenosine A_{2A} receptor, subtype selectivity, chemogenetics, primary astrocyte

G タンパク質共役型受容体（GPCR）は生体内に広く発現し多様な生理学的プロセスに関与する。しかし、同種の GPCR であっても発現細胞種によって異なる機能を持つため、詳細な機能は未解明であった。そこで我々は細胞種選択的に特定 GPCR の活性を制御可能な手法として extracellular-Loop Engineered Chemogenetics (eLEC)を提唱している。この手法では、多くの GPCR において内在リガンドが結合する 7 回膜貫通(7TM)ドメインから離れた細胞外ループ(ECL)にアミノ酸変異を導入し、変異体選択的な制御を行う。我々は class A GPCR に属するアデノシン A_{2A} 受容体（$A_{2A}R$）へ eLEC を適用することで、内在リガンドへの親和性に影響を与えずに、ECL と相互作用し $A_{2A}R$ へ高い選択性を持つ拮抗薬の親和性を変化できると期待した。実際に $A_{2A}R$ 以外のアデノシン受容体サブタイプの ECL を $A_{2A}R$ へ導入し作製した変異受容体では、$A_{2A}R$ 選択的拮抗剤の阻害能が 500 倍以上低下することを見出した。さらに、$A_{2A}R$ の発現が知られる初代アストロサイトにおいても本戦略が適用できることを確認したため、本年会で報告する。



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[E1662-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Satoshi Abe, Takahiro Muraoka

Thu. Mar 23, 2023 1:10 PM - 3:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-2pm-01] Modulation of the activity of enzyme assembled on DNA scaffold

○Peng Lin[1], Tomohiko Hayashi[2], Huyen Dinh[3], Eiji Nakata[1], Masahiro Kinoshita [1,4], Takashi Morii[1] （1. Kyoto University, 2. Niigata University, 3. Humboldt University of Berlin, 4. Chiba University）

1:10 PM - 1:30 PM

[E1662-2pm-02] Effect of charge around thiol group on promoting disulfide bonds-containing protein native structure formation

○Mai Kitamura[1], Takahiro Muraoka[1,2] （1. Tokyo University of Agriculture and Technology, 2. KISTEC）

1:30 PM - 1:50 PM

[E1662-2pm-03] Development of high-active protein folding promotors like enzyme

○Shunsuke Okada[1], Masaki Okumura[2], Takahiro Muraoka[1,3] （1. Tokyo Univ. of Agr. and Tech., 2. Tohoku Univ., 3. KISTEC）

1:50 PM - 2:10 PM

[E1662-2pm-04] In-cell protein crystal engineering for structure determination of intrinsically disordered protein

○Mariko Kojima[1], Satoshi Abe[1], Takafumi Ueno[1] （1. Tokyo Institute of Technology）

2:10 PM - 2:30 PM

[E1662-2pm-05] Crystallization of ferritin directly from E. Coli cell lysate and structure determination.

○BASUDEV MAITY[1], Koki Date[1], Satoshi Abe[1], Takafumi Ueno[1] （1. TOKYO INSTITUTE OF TECHNOLOGY）

2:40 PM - 3:00 PM

[E1662-2pm-06] Engineering of in-cell protein crystals for the construction of solid materials

○Satoshi Abe[1], Junko Tanaka[1], Yuto Nakasuji[1], Takafumi Ueno[1] （1. Tokyo Institute of Technology）

3:00 PM - 3:20 PM

[E1662-2pm-07] *In-Cell* Engineering of Protein Crystals into Hybrid Solid Catalysts for Artificial Photosynthesis

○Tiezheng Pan[1], Basudev Maity[1], Satoshi Abe[1], Takafumi Ueno[1] （1. Tokyo Institute of Technology）

3:20 PM - 3:40 PM

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Modulation of the activity of enzyme assembled on DNA scaffold

([1]*Institute of Advanced Energy, Kyoto University,* [2]*Niigata University,* [3]*Humboldt University of Berlin,* [4]*Chiba University*) ○Peng Lin,[1] Tomohiko Hayashi,[2] Huyen Dinh,[3] Eiji Nakata,[1] Masahiro Kinoshita,[1,4] Takashi Morii[1]

Keywords: DNA Scaffold; Enzyme Reactions; Catalytic Enhancement; Chemical Mechanisms

Assembling enzymes of interest on the surface of carrier provides a simple yet useful method for practical enzyme applications.[1] With the advantages of accurate addressability and structural programmability, DNA scaffolds provide the ideal platforms for the spatial arrangement of enzymes.[2] The enhanced activity of enzyme assembled on the DNA scaffold has been widely observed, however, the mechanism behind this phenomenon is still controvertial.[3] In this study, we evaluated possible effects of the DNA scaffold on enzymatic reactions from various aspects.

Upon being assembled on the DNA scaffold, xylose reductase (XR) or xylitol dehydrogenase (XDH) displayed significant catalytic enhancements over the respective free enzyme. The different optimal pH profiles of XR (pH 6.0) and XDH (pH 8.0), the neutral and net negative charge of their substrates and cofactors, respectively, indicated that neither the local pH change near the surface of DNA scaffold nor the electrostatic interaction between the substrate or cofactor and the scaffold accounted for the accelerated enzyme reaction. We showed that the reduced adsorption of scaffolded enzymes on the reaction vessels could partly contribute to the catalytic enhancement,[4] however, the critical characteristics of the DNA scaffold affecting the scaffolded enzyme reactions remain to be elucidated.

We hypothesized that the high-density water layer formed near the DNA scaffold surface played an essential role in the acceleration of enzyme reaction by modulating the local concentration of the substrates. This hypothesis was systematically tested by using hydrophilic or hydrophobic substrates of XR and carbonic anhydrase (CA), which would be discussed in detail. Our study provides the novel insight into the origins of the catalytic enhancement of enzymes assembled on the DNA scaffold.

1) R. A. Sheldon, *Adv. Synth. Catal.* **2007**, *349*, 1289-1307. 2) F. Hong, F. Zhang, Y. Liu, H. Yan, *Chem. Rev.* **2017**, *117*, 12584-12640. 3) P. Lin, H. Yang, E. Nakata, T. Morii, *Molecules* **2021**, *57*, 3925. 4) P. Lin, H. Dinh, E. Nakata, T. Morii, *Chem. Commun.* **2021,** *57*, 3925.

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チオール基近傍の電荷がジスルフィド結合を含むタンパク質の天然構造形成促進へ与える影響

（東京農工大院工[1]・KISTEC[2]）○喜多村 真衣[1]・村岡 貴博[1,2]

Effect of charge around thiol group on folding promotion of disulfide bonds-containing proteins

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2] *Kanagawa Institute of Industrial Science and Technology*)
○Mai Kitamura,[1] Takahiro Muraoka[1,2]

Proteins express their biological functions only after folding into their native structures. Since proteins are essential materials for drugs, protein folding promotion is an important subject in science as well as industry. Many of the therapeutic proteins possess multiple disulfide bonds. The disulfide bond-containing proteins fold into the native structures through not only the hydrophobic interactions but also disulfide bond formation, therefore their overall folding processes are generally complicated. In this study, we attempt to develop synthetic compounds that promote folding of disulfide bond-containing proteins.

For that purpose, we designed the compounds by mimicking the structure seen in the active sites of protein disulfide isomerase (PDI). PDI is an enzyme that promotes protein folding in a cell. In the active sites, charged units are conjugated near the thiol group in a cysteine residue. The synthesized thiol compound bearing positively charged ammonium group showed folding acceleration of model disulfide bond-containing proteins, ribonuclease A and bovine pancreatic trypsin inhibitor.

Keywords：oxidative protein folding; disulfide bonds; nucleophile; ammonium groups; thiol

タンパク質は、天然構造を形成することでその生物学的機能を発現する。近年、タンパク質は医薬品としても注目され、天然構造への効率的なタンパク質フォールディング制御を可能にする技術は、産業面でも重要である。医薬品として用いられるタンパク質の多くは、ジスルフィド結合を有する。ジスルフィド結合を有するタンパク質のフォールディング過程は、疎水性相互作用に加えてジスルフィド結合形成が大きく関与するため、一般に複雑である。このような背景から、本研究では、分子内にジスルフィド結合を有するタンパク質をターゲットとし、そのフォールディングを促進する低分子化合物の開発を目的とした。

その開発に向け、本研究では、生体内でジスルフィド結合形成を伴うタンパク質のフォールディング促進に関与する酵素 Protein Disulfide Isomerase (PDI)に着目した。特に、PDI の活性中心チオール基の近傍に電荷を有するアミノ酸残基が配置されている点に注目し、同様の構造を持つ低分子化合物として、電荷を近傍に配置したチオール化合物を合成した。分子内に複数本のジスルフィド結合を有するタンパク質であるリボヌクレアーゼ A とウシ膵臓トリプシン阻害剤を用いて、合成化合物のタンパク質フォールディング促進効果を評価した。その結果、正電荷を帯びているアンモニウム基を近傍に配置したチオール化合物が、高いフォールディング促進効果を有することが示された。

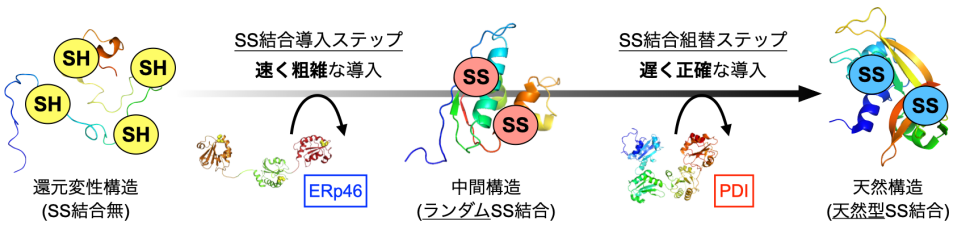
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酵素匹敵活性を持つタンパク質フォールディング促進剤の開発

（東京農工大[1]・東北大[2]・KISTEC[2]）○岡田 隼輔[1]・奥村 正樹[1]・村岡 貴博[3]
Development of high-active protein folding promotors like enzyme ([1]*Tokyo University of Agr. and Tech.*, [2]*Tohoku Univ., KISTEC*) ○ Shunsuke Okada,[1] Masaki Okumura,[2] Takahiro Muraoka[1,3]

Proteins are functional molecules for materials science and pharmaceutical applications. They form the native conformations by folding of the polypeptide chains, which allows performing their inherent functions. In the case of protein synthesis using *E. coli*, misfolding and the following precipitation is one of the critical technical problems that lower the yield of the target protein in the active form, thus promotion of protein folding is an important technique for biological study and applications. To design synthetic folding promotors, we focused on the formation of disulfide bonds that closely relate to oxidative protein folding. In the folding process in our body, A polypeptide chain synthesized from ribosome is folded via disulfide bonds formation, and the folding process is assisted by multiple enzymes, such as protein disulfide isomerase (PDI) and ERp46 to furnish the native proteins efficiently. In this study, we developed novel synthetic folding promotors as the enzyme mimics for the promotion of folding. We successfully demonstrated the significant folding promotion by stepwise addition of these molecules under condensed mixture.
Keywords : Oxidative Protein Folding; Disulfide Bonds; Thiol; PDI; ERp46

タンパク質は、機能性材料や薬剤などとして近年注目を集める重要な物質群である。その生物学的機能や薬効の発現には、天然構造へのフォールディングが不可欠である。我々は、タンパク質のジスルフィド(SS)結合形成に着目し、天然型 SS 結合形成を促し、フォールディングを進めるチオール化合物の開発を行なっている[1)]。細胞内では、複数酵素が段階的に作用し、翻訳タンパク質のフォールディングを効率的に進めることが近年報告された[2)]。我々は、酵素多段階反応の生物学的意義がタンパク質濃縮環境でのフォールディング促進にあると考え、本研究では、これら酵素の促進活性に匹敵する低分子チオール化合物を開発した。これら開発分子を段階的に加えることで、疎水的な還元変性構造の凝集体形成を抑えつつ、天然構造へのフォールディングを進め、濃縮条件下での顕著なフォールディング促進を実証した。



1) S. Okada, M. Matsusaki, K. Arai, Y. Hidaka, K. Inaba, M. Okumura, T. Muraoka, *Chem. Commun.* **2019**, *55*, 759–762.
2) R. Kojima, M. Okumura, S. Masui, S. Kanemura, M. Inoue, M. Saiki, H. Yamaguchi, T. Hikima, M Suzuki, S. Akiyama, K. Inaba, *Structure* **2014**, *22*, 431–443.

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In-cell protein crystal engineering for structure determination of intrinsically disordered protein

([1]*School of Life Science and Technology, Tokyo Institute of Technology*)
○Mariko Kojima,[1] Satoshi Abe,[1] Takafumi Ueno[1]
Keywords: Protein crystal engineering; Intrinsically disordered protein; In-cell protein crystal; X-ray crystallography

In X-ray crystallography of proteins, fusion with tags is one of the most effective methods to obtain crystals of the peptide and protein that are difficult to crystallize with a high diffraction quality.[1] These tags, called 'crystallization tags,' promote crystallization by creating the interface between target peptides/proteins and tags. In-cell crystallizing proteins are expected to be crystallization tags due to their high crystallization ability and easy synthesis process utilizing the cell environment.[2] However, due to limitations in the rapidity of synthesis and molecular design strategy, rational crystal design based on the feedback of X-ray crystallographic analysis has not been realized. This study established a high-throughput screening system combining cell-free protein crystallization and computational protein design (Figure 1). Finally, we succeeded in the structure determination of intrinsically disordered proteins (IDPs). We previously reported that polyhedra crystal (PhC), known to form spontaneously in insect cells, is also obtained by wheat germ cell-free expression of polyhedrin monomer (PhM) within 24 hours.[3] The structure was determined at high resolution. We designed fusion proteins composed of PhM as crystallization tags and small organic molecule binding sites of c-Myc (c-Myc$_{402\text{-}412}$) as the target protein.[4] Screenings were performed three times; 1st screening for selecting fusion sites of PhM for crystallization of c-Myc$_{402\text{-}412}$, 2nd screening for optimization of insert positions, and 3rd screening for replacement with other IDPs. Further structure analysis is ongoing. Our study will develop the protein crystal engineering methods enhancing the structure determination and control of target molecules.

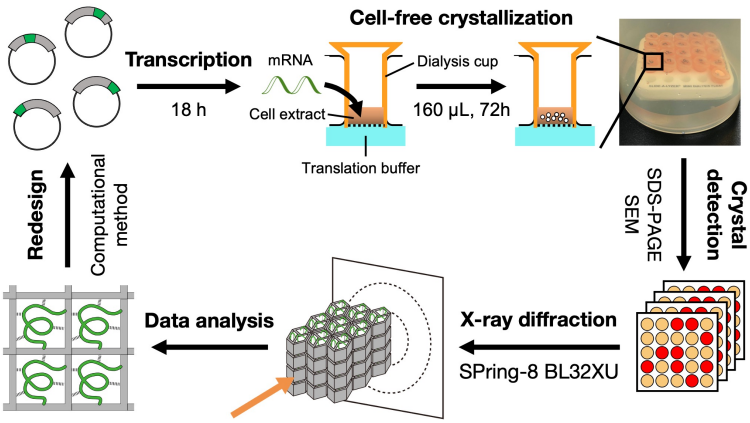


Figure 1. Scheme of high-throughput screening of X-ray crystallography for proteins.

1) B. Kobe, *et al., Acta Cryst,* **2015**, *71*, 861. 2) M. Kojima, *et al., Biomater. Sci.* **2023.** 3) S. Abe, J. Tanaka, M. Kojima, *et al., Sci Rep*, **2022**, *12*, 16031. 4) A. V. Follis, *et al., Chem. Biol.* **2008**, *15*, 1149.

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Crystallization of ferritin directly from E. Coli cell lysate and structure determination

([1]*School of Life Science and Technology, Tokyo Institute of Technology.*)
○Basudev Maity,[1] Date Koki,[1] Satoshi Abe,[1] Takafumi Ueno[1]
Keywords: Ferritin cage; Cell lysate; Crystallization; High-speed AFM; Structure analysis.

Protein crystallography is a powerful method to determine high resolution structures of biomacromolecules. Recently, they found various applications as solid materials in catalysis, enzyme storage, biotechnology etc. Therefore, method of bulk crystallization is necessary. However, purification and crystallization are the challenges in many proteins. Recently, in-cell protein crystallization has attracted attention as it does not require any purification steps.[2] Despite many promises, such crystallization is very specific and limited to only a few proteins (<10). Since the mechanism of in-cell crystallization is unclear, applications to new recombinant proteins become unsuccessful. Similarly, the newly developed cell-free crystallization method is also limited to few proteins.[3] Therefore, establishing an alternate crystallization method directly from cells would be interesting. This presentation will describe a methodology to crystallize ferritin cage as a model protein directly from E. Coli cell lysate without any purification (Fig. 1). We achieved X-ray diffractable microcrystals (~10 μm) within half day and determined the structure at 2.8 Å resolution using microfocus synchrotron beamline. Using high-speed AFM, we visualized the orientation of ferritins on the crystal surface. Thus, our demonstration provides an important message on protein crystallization for next generation structural biology.

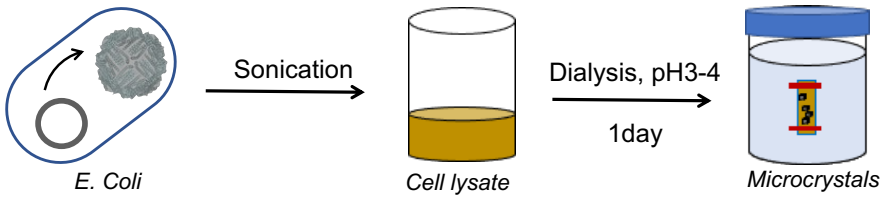


Figure 1: Method of ferritin crystallization directly from E. Coli cell lysate.

1) A. McPherson and J. A. Gavira. *Acta Cryst.* **2014**, F70, 2-20. 2) R. Schönherr, J. M. Rudolph and L. Redecke. *Biol. Chem.* **2018**, 399, 751–772. 3) S. Abe, J. Tanaka, M. Kojma, S. Kanamaru, K. Hirata, K. Yamashita, A. Kobayashi, and T. Ueno. *Sci. Rep.*, **2022**, 12, 16031.

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Engineering of in-cell Protein Crystals for the Construction of Solid Materials

(*School of Life Science and Technology, Tokyo Institute of Technology*) ○Satoshi Abe, Junko Tanaka, Yuto Nakasuji, Takafumi Ueno

Keywords: Protein crystals, In-cell crystals, Crystal structure analysis

Protein crystals formed in living cells have several natural functions, such as storing viruses and toxins, immune activation, and solid catalysts.[1] We have previously reported the construction of solid functional materials by in-cell crystal engineering, including synthesizing enzyme-encapsulated and porous crystals by amino acid deletion and constructing supramolecular assemblies by cross-linking.[2] However, the types of in-cell protein crystals used as solid materials are limited, and new scaffold crystals are desired. We focused on crystalline inclusion proteins A and B (CipA and CipB), which spontaneously crystalize in *P. luminescens*. To crystallize these proteins more efficiently, we developed a new method using cell-free protein synthesis. We successfully determined the structure of CipA by adding a twin inhibitor to the reaction mixture.[3] CipA was found to form crystals by accumulating tetramers as a building block. In this study, we analyze the assembly structures of CipB and crystallizing target proteins using CipA as a template for creating solid materials. Structure determination of CipB formed by cell-free crystallization or in *E.coli* has been analyzed at SPring-8. However, the structure has not yet been determined. Then, we identified the assembly structure of dissolved CipB crystals synthesized in *E.coli* (Figure 1). As a result, we found that CipB is formed by a 24-mer cage structure with a 5 nm cavity as a building block. We are currently analyzing the structure of CipB by recrystallizing dissolved CipB protein assembly. We are also developing a method for the crystallization and structure determination of exogenous proteins and peptides using CipA.

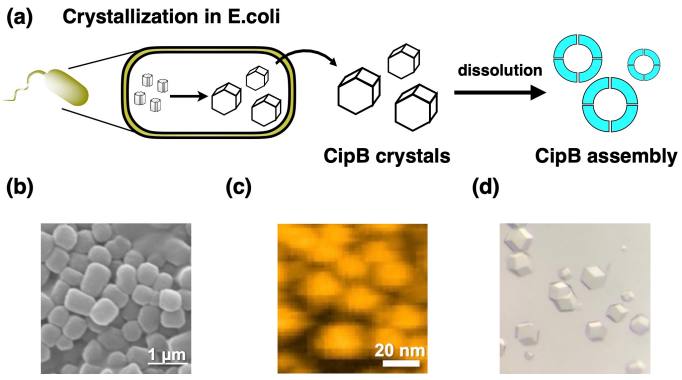


Figure 1. (a) Identification of the assembly structures of CipB. (b) SEM image of CipB. (c) AFM image of dissolved structure of CipB. (d) Crystal of recrystallized CipB assembly structure

(1) M. Kojima *et al.*, *Biomaterials Sci.* **2022**, 10, 354. (2) T. Nguyen *et al., ACS Appl. Nano Mater.* **2021**, 4, 1672., S. Abe *et al., Angew. Chem. Int. Ed.* **2021**, 60, 12341. (3) S. Abe *et al.*, *Sci. Rep.* **2022**, 12, 16031.

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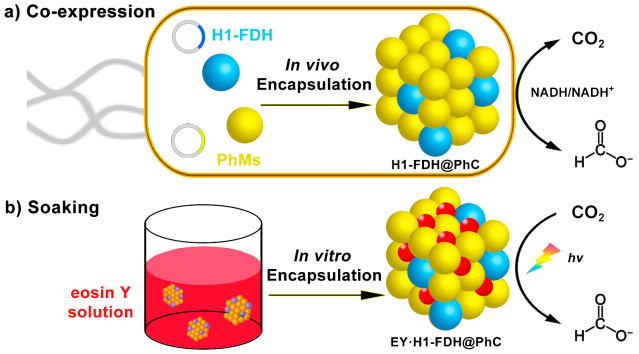
In-Cell Engineering of Protein Crystals into Hybrid Solid Catalysts for Artificial Photosynthesis

([1]*Tokyo Institute of Technology*) ○Tiezheng Pan,[1] Basudev Maity,[1] Satoshi Abe,[1] Takafumi Ueno[1]

Keywords: Protein Crystal; Enzyme Immobilization; Solid Catalyst; Polyhedra Crystal; Photosynthesis

The periodically aligned amino acid residues of protein crystals allow for comprehensive structural analysis and site-specific modification, which are essential features in the research of protein immobilization, solid catalysts, X-ray crystallography, and hybrid materials.[1] Even though the engineering of protein crystals has been studied via physicochemical and genetic routes,[2] the current encapsulation systems of protein crystals are limited to either exogenous small molecules or monomeric proteins. Thus, the potential of protein crystals to contain both natural enzymes and synthetic functional molecules has not been fully explored, and these "hybrid" protein crystals could offer great opportunities for promoting complicated reactions involving multiple modules such as photosynthesis.

In this study, we constructed an enzyme-coupled artificial photosynthesis system based on hybrid protein crystals. First, the internal space and electrostatic potential of polyhedra crystal (PhC) were engineered to encapsulate both the enzyme and the small guest molecule. Second, formate dehydrogenase from *Candida boidinii* (cbFDH) and the photosensitizer eosin Y (EY) were incorporated in PhC by in-cell co-assembly and soaking methods, respectively. Eventually, the engineered protein crystals maintained the *in-cell* self-assembly capacity, and the hybridization of natural enzyme and synthetic photosensitizer yielded competing photosynthesis activity and thermal stability. This immobilization method greatly simplifies the purification of FDH and maintains 94.4% catalytic activity compared to the free enzyme. Moreover, the recyclable and thermal stable features of the solid catalyst would lower the cost of NADH-dependent productions.



1) Huber, T. R.; Hartje, L. F.; McPherson, E. C.; Kowalski, A. E.; Snow, C. D. Programmed Assembly of Host–Guest Protein Crystals. *Small* **2017**, *13*, 1602703. 2) Kojima, M.; Abe, S.; Ueno, T. *Biomater. Sci.* **2022**, *10*, 354–367.

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[E1661-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Shuntaro Takahashi, Fumitaka Hashiya

Thu. Mar 23, 2023 1:10 PM - 3:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-2pm-01] Genome scale DNA assembly using modified primers

○Fumitaka Hashiya[1,6], Kaoru Onda[2], Kohei Nomura[2], Gao Yiuno[2], Hirotaka Murase[2], Kosuke Nakamoto[2], Masahito Inagaki[2], Haruka Hiraoka[2], Naoko Abe[2], Yasuaki Kimura[2], Natsuhisa Oka[3,4,6], Goro Terai[5,6], Kiyoshi Asai[5,6], Hiroshi Abe[1,2,6,7] (1. Nagoya University, Research Center for Materials Science, 2. Graduate School of Science, Nagoya University, 3. Department of Chemistry and Biomolecular Science, Gifu University, 4. Institute for Glyco-core Research (iGCORE), Gifu University, 5. Department of Computational Biology and Medical Sciences, University of Tokyo, 6. CREST, Japan Science and Technology Agency, 7. Institute for Glyco-core Research (iGCORE), Nagoya University)

1:10 PM - 1:30 PM

[E1661-2pm-02] Development of a DNA assembly technology using modified nucleic acids

○Mikiya Kase[1], Masahito Inagaki[1], Haruka Hiraoka[1], Humitaka Hashiya[1], Naoko Abe[1], Yasuaki Kimura[1], Hiroshi Abe[1] (1. The Univ. of Nagoya)

1:30 PM - 1:50 PM

[E1661-2pm-03] Light-triggered control of rolling circle transcription aiming for RNA interference inside cells

○Yusuke Yonamine[1], Wei Jie Cheah[2], Hideyuki Mitomo[1], Kuniharu Ijiro[1] (1. RIES, Hokkaido Univ., 2. Grad. Sch. Life Sci., Hokkaido Univ.)

1:50 PM - 2:10 PM

[E1661-2pm-04] Improvement of chemical pseudo-primer extension reaction of L-*a* TNA based on reaction mechanism analysis

○Hikari Okita[1], Keiji Murayama[1], Hiroyuki Asanuma[1] (1. Nagoya Univ.)

2:10 PM - 2:30 PM

[E1661-2pm-05] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (87) : Prediction of ligand binding by hydration analysis of guanine quadruplex using high pressure

○Shuntaro Takahashi[1], Saki Matsumoto[1], Tatsuya Ohyama[1], Sudipta Bhowmik[2,3], Naoki Sugimoto[1,4] (1. Konan Univ. FIBER, 2. Calcutta Univ., 3. SBV Univ. MGMARI, 4. Konan Univ. FIRST)

2:40 PM - 3:00 PM

[E1661-2pm-06] Development of methods for the efficient ligation of staple nicks in DNA origami

○Arivazhagan Rajendran[1], Kirankumar Krishnamurthy[1], Eiji Nakata[1], Takashi Morii[1] (1. Kyoto University)

3:00 PM - 3:20 PM

[E1661-2pm-07] Photocatalytic profiling of G4 DNA-interacting proteins

○Ahmed Mostafa Abdelhady[1,2], Kazumitsu Onizuka[1,2], Tatsuki Masuzawa[3], Shinichi Sato[4], Keita Nakane[4], Takanori Oyoshi[3], Fumi Nagatsugi[1,2] (1. Graduate School of

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Science, Tohoku University, 2. IMRAM, Tohoku University, 3. Graduate School of Science and Technology, Shizuoka University, 4. FRIS, Tohoku University)
3:20 PM - 3:40 PM

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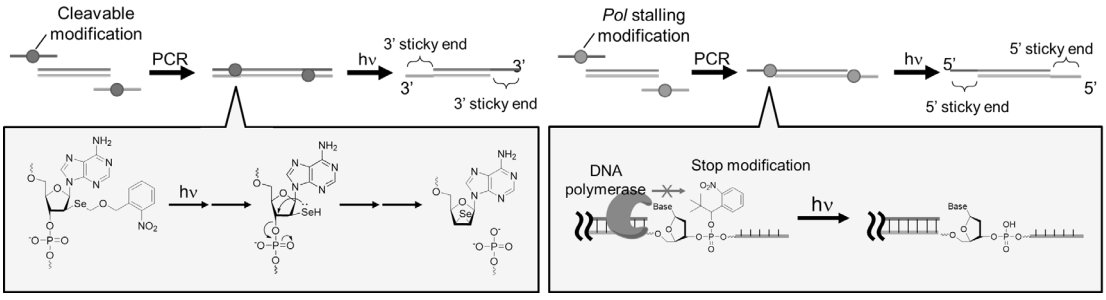
Genome scale DNA assembly using modified primers

(*[1]Nagoya University, Research Center for Materials Science, [2]Graduate School of Science, Nagoya University, [3]Department of Chemistry and Biomolecular Science, Gifu University, [4]Institute for Glyco-core Research (iGCORE), Gifu University, [5]Department of Computational Biology and Medical Sciences, University of Tokyo, [6]CREST, Japan Science and Technology Agency, [7]Institute for Glyco-core Research (iGCORE), Nagoya University*) ○Fumitaka Hashiya[1,6], Kaoru Onda[2], Kohei Nomura[2], Gao Yiuno[2], Hirotaka Murase[2], Kosuke Nakamoto[2], Masahito Inagaki[2], Haruka Hiraoka[2], Naoko Abe[2], Yasuaki Kimura[2], Natsuhisa Oka[3,4,6], Goro Terai[5,6], Kiyoshi Asai[5,6], Hiroshi Abe[1,2,6,7]

Keywords: Polymerase chain reaction; Sticky end; Polymerase stall; Photo cleavage; DNA hybridization

Sticky end generation on DNA is an essential technique to perform DNA assembly. Restriction enzyme digestion is a simple and effective method to prepare sticky end, but it requires a specific sequence on target DNA. Additionally, most restriction enzyme generates four nucleotide overhang which is not enough to achieve efficient hybridization. It has been reported that PCR amplification with chemically modified primer and subsequent treatment can generate arbitrary length and sequence sticky end[1,2]. However, these methods deposit the modification on base moiety and limit sequence design.

In the present work, we have developed two modified primers that possess modification on sugar or phosphate moiety so that any sequence designs are available. Post cleavable primer with selenyl group on 2’ position can cause strand cleavage on PCR product to generate 3’ overhang sticky end. Stop primer which possesses photo-caging groups on phosphate can stall polymerase elongation to generate 5’ overhang sticky end. The sticky end prepared by these primers could perform efficient DNA assembly. We also achieved genome-scale DNA assembly which is difficult with conventional methods.



1) N. Nemoto, *ACS. Comb. Sci.* **2020,** 22, 4, 165.
2) M. Komiyama, *Molecules,* **2012,** 17, 328.

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・Development of a DNA assembly technology using modified nucleic acids

([1]*Graduate School of Science, Nagoya University*, [2]R*esearch Center for Materials Science, Nagoya University*, [3]*JST-CREST*, [4]*iGCORE*) ○ Mikiya Kase[1], Masahito Inagaki[1], Haruka Hiraoka[1], Fumitaka Hashiya[2], Naoko Abe[1], Yasuaki Kimura[1], Hiroshi Abe[1,3,4]

Keywords: *Modified nucleic acids, 3'-S-Phosphorothiolate Oligonucleotides, Silver Nanoparticles, Oligonucleotide Strand Cleavage, DNA Assembly Methods*

In recent years, with the development of genome editing technology represented by CRISPR-Cas9, research on the synthesis of genomic DNA has attracted much attention. To synthesize long genomic DNA (more than several hundred thousand base pairs), it is important to develop novel DNA assembly technologies that can accurately and efficiently ligate short DNA fragments amplified by polymerase chain reaction (PCR). The golden gate assembly is a typical enzymatic method. The restriction enzymes are used for the DNA cleavage to produce the sticky ends, therefore the cleavage sequence specificity is high, but the lack of sequence flexibility considering the ligation of multiple DNA fragments[1]. In addition, the length of the overhang region of the sticky ends that can be prepared by restriction enzyme treatment is limited to four bases, making the DNA fragments ligation efficiency dependent on the activity of the ligase and making it difficult to control. To overcome the drawbacks, we focus on the development of a new method to prepare sticky ends for the efficient ligation of DNA fragments to achieve the construction of genome-scale DNA based on the chemical approach. In this study, we have developed a novel chemical oligonucleotide strand cleavage method that can be applied to genome-size DNA synthesis. We have been interested in the property of 3'-*S*-phosphorothiolate modification in which the 3'-oxygen atom of the natural phosphodiester linkage is replaced by a sulfur atom[2]. It is considered that some Lewis acids can activate the sulfur-phosphorous linkage of the 3'-*S*-phosphorothiolate to induce oligonucleotide strand cleavage. We found out the 3'-*S*-phosphorothiolate linkage of DNA could be specifically cleaved by the silver nanoparticles, and the cleavage activity depends on the size and surface properties of the nanoparticles. We optimized the 3'-*S*-phosphorothiolate DNA cleavage condition by the silver nanoparticles and successfully applied it to prepare the sticky ends. Also, we demonstrated the T4 DNA ligase-mediated ligation of chemically prepared sticky end DNA fragments to synthesize several >800-bp DNA. In this presentation, we will discuss the synthesis of 3'-*S*-phosphorothiolate DNA, oligonucleotide strand cleavage by silver nanoparticles, and its application for long DNA assembly.

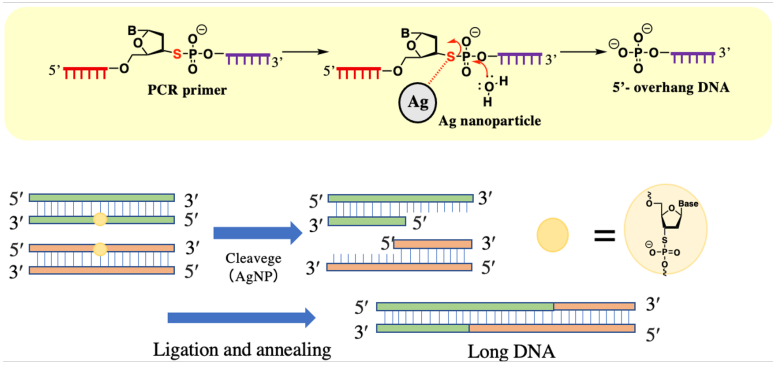


Fig1. DNA Assembly Method Based on Silver Nanoparticle Strand Cleavage

1) S. Marillonnet, *et al., PLoS ONE*, **2008**, *3*(11), e3647. 2) (a) J. S. Vyle, *et al, Biochemistry*, **1992**, *31*, 3012; (b) G. Sabbagh, *et al., Nucleic Acids Res.*, **2004**, *32*(2), 495.

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細胞内 RNA 干渉を目指した光照射によるローリングサークル転写制御

（北大電子研[1]・北大院生命[2]）○与那嶺 雄介[1]・ウェイジエ チア[2]・三友 秀之[1]・居城 邦治[1]

Light-triggered control of rolling circle transcription aiming for RNA interference inside cells

(*[1]RIES, Hokkaido University., [2]Grad. Sch. Life Sci., Hokkaido University*)
○Yusuke Yonamine,[1] Wei Jie Cheah,[2] Hideyuki Mitomo,[1] Kuniharu Ijiro[1]

RNA interference therapeutics are hindered due to instability of siRNA and lack of spatiotemporal control. In this study, light triggered amplification of siRNA inside cells by rolling circle transcription (RCT) is being developed using a highly active T7 RNA polymerase (RNAP) and a circle DNA coding a siRNA sequence, which are delivered into cells to amplify the siRNA utilizing intracellular rNTPs. First, RCT condition *in vitro* was optimized. Second, photo-cleavable biotin was introduced into the DNA template, and then, incubated with streptavidin (SAv) to control RCT activity. The result revealed bulkiness of SAv was insufficient to repress the RCT completely, whereas the repression was abrogated by inducing dissociation of SAv with UV-irradiation. Third, inhibition of RCT was investigated with a bulkier gold nanorod modified with a cationic ligand, which can bind to the negatively charged DNA template. As the result, RCT was completely repressed. In future, by incorporating a thermo-cleavable linker into the ligand, dissociation of circle DNA by photothermal effect of the gold nanorod with light irradiation will be induced, which triggers RCT.
Keywords : Rolling circle transcription, RNA polymerase, RNA interference

RNA 干渉による医薬品は、siRNA の不安定性や、時空間的な制御が困難であるために開発が妨げられている。本研究では、活性の高い T7 RNA 合成酵素（RNAP）と、siRNA の配列をコードした環状 DNA を細胞内に送達し、細胞質内の RNA モノマー（rNTP）を用いたローリングサークル転写（RCT）による siRNA 増幅（Fig. 1a）の光制御を目指す。まず、in vitro での RCT 条件を最適化した。続いて、UV 光で切断されるビオチン基を鋳型 DNA に導入し、ストレプトアビジン（SAv）と結合させ、SAvの嵩高さによる転写活性の ON/OFF を検討した。その結果、SAvの嵩高さは RNAP の接近を妨げるには不充分であったが、部分的に RCT が抑制され、UV 光照射による SAvの解離でこの抑制が解除された。最後に、より嵩高いロッド状金ナノ粒子をカチオン性リガンドで修飾し、鋳型 DNA と結合させた所、転写を完全に停止できた（Fig. 1b）。今後、熱切断リンカーをリガンドに導入し、金ナノ粒子の光熱変換による加熱で鋳型 DNA を遊離させ、RCT を開始する機構を検討予定である。

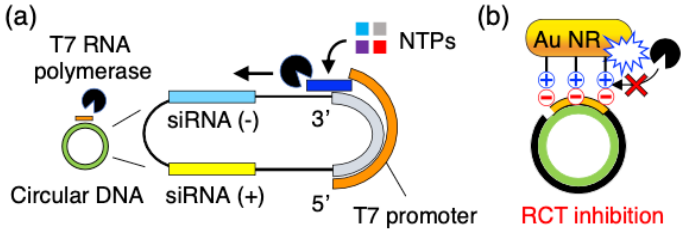


Figure 1. (a) Amplification of siRNA by rolling circle transcription with T7 RNA polymerase. (b) Repression of RCT with a cationic gold nanorod.

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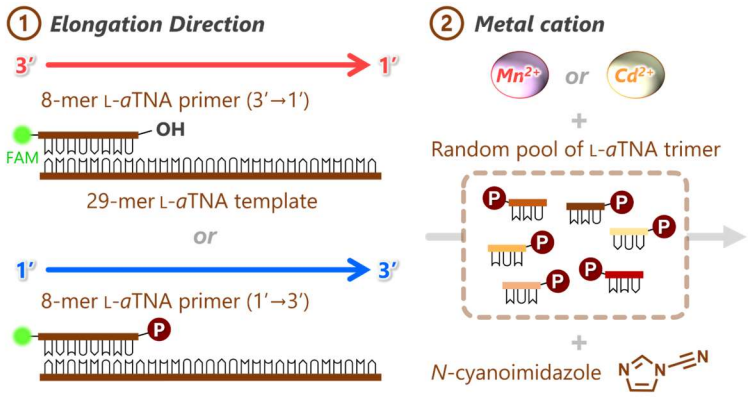
反応メカニズム解析に基づく人工核酸 L-*a*TNA の化学的な鎖伸長反応の高効率化

（名大院工）〇沖田 ひかり・村山 恵司・浅沼 浩之
Improvement of Chemical Pseudo-Primer Extension Reaction of L-*a*TNA Based on Reaction Mechanism Analysis (*Graduate School of Engineering, Nagoya University*) 〇Hikari Okita, Keiji Murayama, Hiroyuki Asanuma

We have developed *acyclic* artificial nucleic acids that do not involve deoxyribose backbone and demonstrated their high durability against enzymatic degradation. Among them, *acyclic* L-threoninol nucleic acid (L-*a*TNA) can form highly stable duplex with complementary L-*a*TNA, DNA, and RNA strands. However since useful enzymes like polymerase did not recognize L-*a*TNA scaffold, L-*a*TNA cannot be replicated or transcribed enzymatically. To solve this problem, we have established chemical replication system of 17-mer L-*a*TNA by nonenzymatic ligation with a condensing reagent, *N*-cyanoimidazole and Mn^{2+} ion. In this study, we succeeded in long-chain, 29-mer L-*a*TNA replication system with a random pool of L-*a*TNA trimers by changing elongation direction and divalent metal cation through reaction mechanism analysis.

Keywords : Chemical Ligation; Artificial Nucleic Acid; Template-Directed Synthesis; DNA

当研究室では DNA のリボース骨格を鎖状骨格に改変することで非環状型の人工核酸を創出しており、いずれも極めて高い酵素分解耐性を有している。その中でも L-threoninol を主鎖に持つ L-*a*TNA は相補的な L-*a*TNA 鎖だけでなく、天然核酸の DNA や RNA とも安定な二重鎖を形成できる [1]。しかしながら、有用な酵素が L-*a*TNA を認識できないため、配列複製や転写反応などの酵素反応に応用することが困難であった。この問題を解決するために、酵素の代わりに縮合剤である *N*-cyanoimidazole とマンガンイオンを用いた化学連結法によって 3-mer L-*a*TNA のランダム配列プールの中から配列特異的に目的の 17-mer L-*a*TNA 鎖を合成する配列複製法をすでに確立している [2]。本研究では、鎖伸長反応におけるメカニズム解析を通して伸長方向と二価金属イオンに注目することで、さらに長鎖の 29-mer L-*a*TNA の非酵素的な配列複製に成功したので、本発表ではその結果について報告する。



1) K. Murayama, H. Kashida, H. Asanuma, *Chem. Commun.* **2015**, *51*, 6500.
2) K. Murayama, H. Okita, T. Kuriki, H. Asanuma, *Nat. Commun*. **2021**, *12*, 804.

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Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (87) : Prediction of ligand binding by hydration analysis of guanine quadruplex using high pressure

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○Shuntaro Takahashi[1], Saki Matsumoto[1], Tatsuya Ohyama[1], Sudipta Bhowmik[2,3], Naoki Sugimoto[1,4]

Keywords: High pressure; Volume; G-quadruplex; Hydration; Ligand

Hydration around nucleic acids such as DNA and RNA is an important factor not only for the stability of nucleic acids but also for their interaction with binding molecules. Thus, it is necessary to quantitatively elucidate the hydration properties of nucleic acids around their certain structures. Pressure was used to analyze the partial molar volume of the biopolymer, which can be calculated by the sum of the molecular volume of the biopolymer and the solvation volume. High pressure is a physical tool that allows quantitative analysis of volume changes in polymers.[1,2] As non-canonical structures like G-quadruplexes (G4s) dynamically fold and unfold in cells with hydration changes, high pressure is useful to study the dynamics of G4 formation and ligand binding on G4.

In this study, we employed high pressure to quantitatively analyze the volume change of G4 formations.[3] By systematically changing the number of stacked G-quartets, we examined the volume change of G4 in layer-structured units and found that the core quadruplex region showed more volume increase than the edge regions including the terminus and loops. Analysis of each volume component indicated that there is significant dehydration from the core region with the formation of the quadruplex (Figure 1). This result indicates that the hydration state of the core region is less affected than that of the peripheral region, even in a molecular crowding environment where the hydration environment changes. This allows us to predict the binding of the ligand to the guanine quadruplex depending on the chemical structure of the ligand and the solution environment. In fact, it was confirmed that ligand molecules such as netropsin, which bind to the core region, were not affected by the molecular crowding environment. Thus, the volume parameters determined by high pressure were shown to be useful for predicting the behavior of ligand molecules on guanine quadruplexes in an intracellular molecular crowding environment.

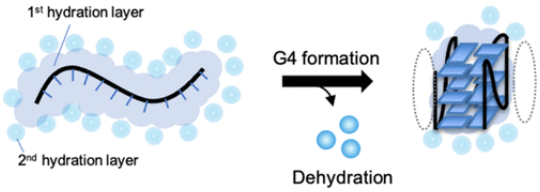


Figure 1. Schematic image of hydration upon G4 formation.

1) S. Takahashi, N. Sugimoto, *Angew. Chem. Int. Ed.,* **2013**, *52*, 13774. 2) S. Takahashi, S. Bhowmik, N. Sugimoto, *J. Inorg. Biochem.*, **2017**, *166*, 199. 3) S. Matsumoto, S. Takahashi, S. Bhowmik, T. Ohyama, N. Sugimoto, *Anal. Chem.*, **2022**, *94*, 7400.

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Development of methods for the efficient ligation of staple nicks in DNA origami

(*Institute of Advanced Energy, Kyoto University*) ○Arivazhagan Rajendran, Kirankumar Krishnamurthy, Eiji Nakata, Takashi Morii

Keywords: DNA ligation; DNA origami; Origami stability; Nuclease; Cell lysate

During the past one and a half decades, structural DNA nanotechnology has seen enormous growth due to the introduction of the scaffolded DNA origami method,[1] which enabled the synthesis of nanostructures with ~100 nm in diameter. These structures have been used for the nanopatterning of various nanoparticles and quantum dots, attachment of carbon nanotubes, immobilization of biomolecules, carriers of drugs, and the analysis of single molecular reactions and processes.[2] Despite the proof-of-concept demonstrations of the applications, the real-life utilization of the origami materials is limited due to their unsatisfactory stability. There have been limited efforts to stabilize the DNA origami against thermal, mechanical, chemical, and biological modifications/environments. We have recently performed a detailed characterization of the enzymatic ligation of two-dimensional (2D) DNA origami to establish suitable conditions.[3-4] Under the optimized conditions, up to 10 staples ligation with a maximum ligation efficiency of ~55% was achieved. Also, the ligation is found to increase the thermal stability of the origami from as low as 5°C to as high as 20°C, depending on the structure. Besides our initial demonstration, due to the tightly packed anti-parallelly oriented arrangement of multiple duplexes in the origami and the difficulties in the accessibility of the nicks by ligase, enzymatic ligation was only partly successful. Therefore, it is necessary to develop methods to enhance ligation efficiency.

Here, we demonstrate a cosolvent-based method for the efficient backbone ligation of the nicks in origami. The reaction conditions are optimized to attain the maximum possible ligation efficiency. This method achieved near quantitative ligation of the nicks in 2D origami. The cosolvent-assisted enzymatic ligation required overnight for the completion of the reaction. In addition, the cosolvent enhances the reaction rate of the enzymatic reaction, reduces the amount of enzyme needed, and enhances ligation efficiency. Compared to non-ligated origami, the ligated origami exhibited improved stability against thermal treatments, during electrophoresis, against nuclease, and cell lysate. Though the cosolvent-assisted enzymatic ligation was successful for 2D origami, it failed to result in quantitative ligation for 3D origami. Therefore, an alternative method of chemical ligation was developed for the efficient ligation of 3D origami.

1) P. W. K. Rothemund, *Nature* **2006,** *440*, 297. 2) A. Rajendran, E. Nakata, S. Nakano, and T. Morii, *ChemBioChem* **2017,** *18*, 696. 3) A. Rajendran, K. Krishnamurthy, A. Giridasappa, E. Nakata, and T. Morii, *Nucleic Acids Res.* **2021,** *49*, 7884. 4) A. Rajendran, K. Krishnamurthy, S. Park, E. Nakata, Y. Kwon, T. Morii, *Chem. Eur. J.* **2022**, e202200108.

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Photocatalytic profiling of G4 DNA-interacting proteins

([1] IMRAM, Tohoku Univ., [2] Graduate School of Science, Tohoku Univ., [3] Graduate School of Science and Technology, Shizuoka Univ., [4] FRIS, Tohoku Univ.) ○Ahmed Mostafa Abdelhady[1,2], Kazumitsu Onizuka[1,2], Tatsuki Masuzawa[3], Shinichi Sato[4], Keita Nakane[4], Takanori Oyoshi[3], Fumi Nagatsugi[1,2]

Keywords: G4-binding proteins, Protein photo-labeling, DNA G4, LC-MS/MS-coupled Proteomics.

Interactions between nucleic acids and proteins are vital in regulating numerous cellular processes, such as gene expression, DNA replication, and DNA repair. Many methods have been developed to identify these interactions. However, robust approaches to interrogate transient and weak interaction networks are limited. DNA G-quadruplexes (G4s) are observed in the telomeres and the promoter region of an oncogene and are found to play a critical role in fundamental biological events. It is suggested that G4s homeostasis and functions may be intricately linked to their interacting proteins. Previously photocatalyst-mediated selective histidine proximity labeling with 1-methyl-4-aryl-urazole (MAUra) has been reported.[1,2] In this study, we report a photocatalytic proximity labeling approach for the investigation of DNA G4-interacting proteins (G4IPs) (Figure 1). We tested the G4-binding protein (UP1) selective labeling in a mixture of UP1 and BSA. We applied our approach to label G4IPs in nuclear extract proteins. The proteins labeled with MAUra-desthiobiotin (DTB) were identified by a quantitative nano-LC-MS/MS-based proteomics analysis, and numerous unknown G4IP candidates have been enriched.

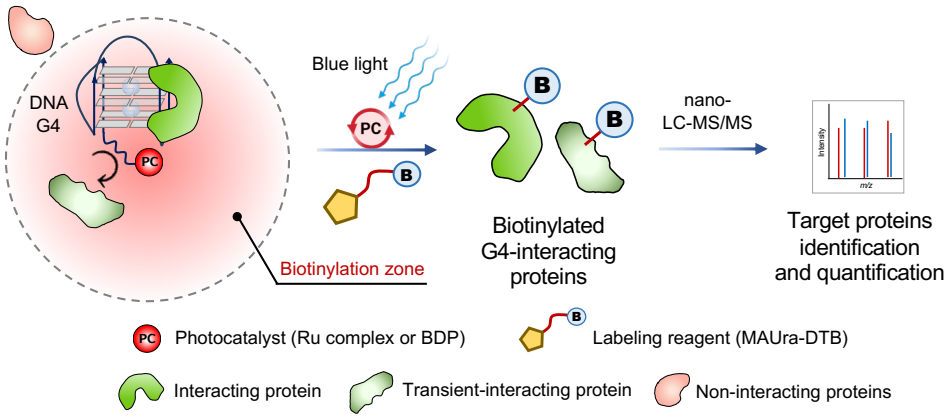


Figure 1. Schematic for the labeling approach.

1) Sato, S., Nakamura, H., *et al., Chem. Commun.* **2018**, *54*, 5871-5874.
2) Nakane, K., Sato, S., Nakamura, H., *et al., J. Am. Chem. Soc.* **2021,** *143*, 7726-7731.

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[E1661-2vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Takafumi Furuhata, Tomoshige Fujino

Thu. Mar 23, 2023 4:10 PM - 6:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-2vn-01] Intracellular artificial construction of droplets based on an amphiphilic YK peptide tag and client protein enrichment

○Masahiro Hashimoto[1], Takayuki Miki[1], Hiroki Takahashi[1], Sae Nakayama[1], Hisakazu Mihara[1] (1. Tokyo Institute of Technology, School of Life Science and Technology)

4:10 PM - 4:30 PM

[E1661-2vn-02] Pattern enrichment analysis for efficient peptide ligands selection from a phage library

○Takayuki Miki[1], Keigo Namii[1], Kenta Seko[1], Shota Kakehi[1], Hisakazu Mihara[1] (1. School of Life Science and Technology, Tokyo Instituite of Technology)

4:30 PM - 4:50 PM

[E1661-2vn-03] Improvement of the diversity of monobody and macrocyclic peptide libraries in mRNA display technology

○Shun Umemoto[1], Taishi Kondo[1], Tomoshige Fujino[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Nagoya University, 2. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)

4:50 PM - 5:10 PM

[E1661-2vn-04] Anti-azobenzene artificial antibodies for photocontrollable binding

○Tomoshige Fujino[1], Mamoru Funane[1], Naoya Murata[1], Tatsuyuki Yoshii[2], Gosuke Hayashi[1], Shinya Tsukiji[2], Hiroshi Murakami[1,3] (1. Graduate School of Engineering, Nagoya University, 2. Graduate School of Engineering, Nagoya Institute of Technology, 3. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)

5:10 PM - 5:30 PM

[E1661-2vn-05] A machine learning guided thiopeptide library design for the discovery of de novo thiopeptide binders

○Jun Shi Chang[1], Alexander Vinogradov[1], Yuki Goto[1], Hiroaki Suga[1] (1. Tokyo Univeristy)

5:40 PM - 6:00 PM

[E1661-2vn-06] Enzyme mediated one-pot synthesis of branched polyubiquitin (K48/K63) chain via photo-induced stepwise synthesis

○Phebee Angeline Devadasan Racheal[1], Takafumi Furuhata[1], Iori Murayama[1], Usano Toyoda[1], Akimitsu Okamato[1] (1. The Univ. of Tokyo)

6:00 PM - 6:20 PM

[E1661-2vn-07] Regulation of enzyme activity by perturbation to conformational change process using antibody mimetic "monobody"

○Ibuki Nakamura[1], Hiroshi Amesaka[2], Mizuho Hara[2], Kento Yonezawa[1], Hironari Kamikubo[1], Shun-ichi Tanaka[2], Shun Hirota[1], Takashi Matsuo[1] (1. Division of Materials Science, Nara Inst. Sci. Tech., 2. Department of Biomolecular Chemistry, Kyoto Prefectural University)

6:20 PM - 6:40 PM

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Intracellular artificial construction of droplets based on an amphiphilic YK peptide tag and client protein enrichment

(*School of Life Science and Technology, Tokyo Institute of Technology*) ○Masahiro Hashimoto, Takayuki Miki, Hiroki Takahashi, Sae Nakayama, Hisakazu Mihara

Keywords: Self-assembling peptide, liquid-liquid phase separation, Protein-protein interaction analysis, Living cells

In living cells, proteins and nucleic acids form droplets via liquid-liquid phase separation. The droplets regulate various biological phenomena, such as signal transduction and gene expression. The droplet formation process is thought to be triggered by the nucleation of scaffold proteins, followed by the enrichment of client proteins. Most previous studies on droplets focus on the identification and characterization of scaffolding domain/protein by introducing mutations or deletions. However, detail investigations of client recruitment steps in situ are required to understand their fundamental biological functions. For this purpose, the artificial construction of droplets in living cells is essential. Previously, we developed a Y15 peptide tag (YEYKYEYKYEYKYEY) which can assemble proteins in the cells[1,2]. However, due to the irreversible interaction between Y15 peptides, Y15-tagged proteins formed gel-like aggregates without fluidity, which is different from liquid droplets.

Here, we designed an amphiphilic YK13 peptide tag (YKYKYKYKYKYKY). YK13 peptide self-assembles into thioflavin-T positive structures in response to polyanionic species such as ATP. Upon addition of ATPase, YK13 assemblies started to dissociate as ATP degradation. The reversible interaction makes droplets formation feasible in living cells. YK-tagged sfGFPs were observed as granules, and the FRAP analysis revealed that the granule had high fluidity. The fluidity decreased in a peptide chain length-dependent manner, indicating the importance of peptide-peptide interactions. In addition, we tagged various scaffold proteins with the YK peptide, resulting in droplet formation in living cells. Besides, we also observed the client protein enrichments. Taken together, we consider that YK peptide tag is a valuable tool to investigate the droplet formation and client proteins recruitment.

[1] T. Miki, T. Nakai, M. Hashimoto, K. Kajiwara, H. Tsutsumi, H. Mihara, *Nat.Commun.*, **2021**, 12, 3412 [2] T. Miki, M. Hashimoto, T. Nakai, H. Mihara, *Chem. Commun.*, **2021**, 57, 11338

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Phage Display 法による効率的なペプチドリガンド探索を実現する Pattern Enrichment 解析

（東工大生命理工 [1]）○三木　卓幸 [1]・浪井　啓吾 [1]・瀬古　健太 [1]・筧　翔太 [1]・三原　久和 [1]

Pattern enrichment analysis for efficient peptide ligands selection from a phage library ([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Takayuki Miki,[1] Keigo Namii,[1] Kenta Seko,[1] Shota Kakehi,[1] Hisakazu Mihara[1]

Phage display is the most widely used technique to discover de novo peptides ligands. However, the inevitable problems such as compositional bias tremendously reduce the success rate of the peptide library screening. In this study, we devised a 'Pattern Enrichment Analysis'[1] (Fig. 1). Firstly, we prepared two samples (one obtained by affinity selection, the other simply amplified without selection), and reads the two sequence datasets on next-generation sequencer. These sequences are compared to find the three-residue pattern most enriched in the selected sample. This enables to compare two sequence datasets with high coverage and identify the peptide ligand and the key residues for binding.

Keywords : Phage Display; Helical Peptide; Next Generation Sequencing; Pattern Enrichment

ファージディスプレイ法は、標的蛋白質と結合するペプチドリガンドを探索する汎用的な技術である。しかし、ライブラリのペプチドは均一でなく、また増幅過程においてバイアスが生じることから、標的と親和性のあるペプチドを得ることは容易ではない。これらの影響を軽減するため、我々は「Pattern Enrichment 解析」を考案した [1]（図１）。まず、標的蛋白質に対してセレクションを行ったサンプルと、単に増幅したサンプルの２つを用意し、それぞれの配列群を次世代シーケンサーで読む。次に、これらの配列を比較し、セレクションを行ったサンプルに最も濃縮されている 3 残基のパターンを見つける方法である。これにより、2 サンプル間でペプチド配列を高いカバレージで比較できる。さらに、ペプチドと蛋白質との結合において、重要な残基（いわゆるホットスポット）の同定が容易になる。

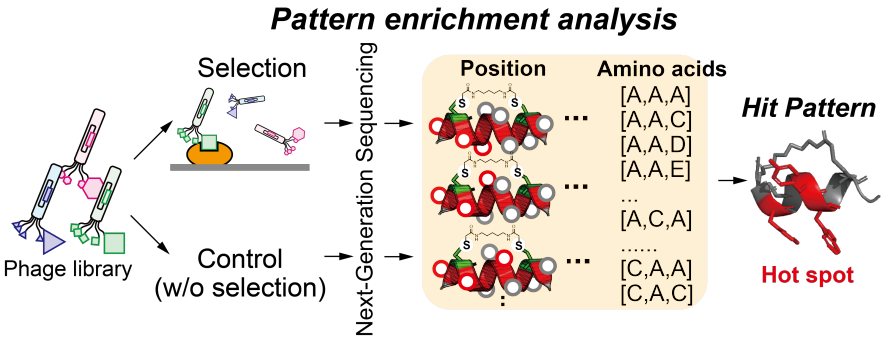


図 1. Pattern Enrichment 解析による効率的なペプチドリガンドの探索

1) Pattern enrichment analysis for phage selection of stapled peptide ligands. T. Miki, K. Namii, K. Seko, S. Kakehi, G. Moro and H. Mihara, *Chem. Sci.* **13**, 12634–12642 (2022) **Front Cover, ChemSci Pick**

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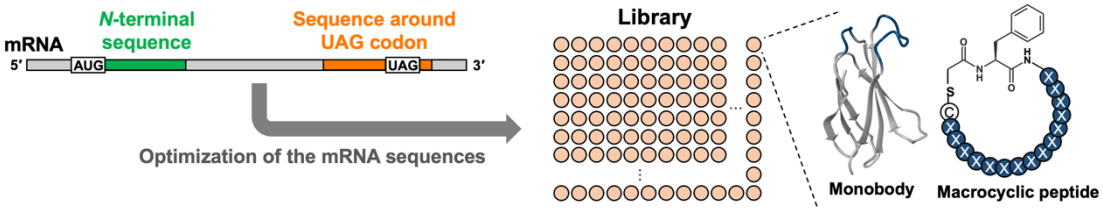
mRNA 提示法における人工抗体・環状ペプチドライブラリの多様性の最大化

(名大院工[1]、名大ナノライフ[2]) ○梅本 駿[1]・近藤 太志[1]・藤野 公茂[1]・林 剛介[1]・村上 裕[1,2]

Improvement of the diversity of monobody and macrocyclic peptide libraries in mRNA display technology ([1]*Graduate School of Engineering, Nagoya University,* [2]*Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University*) ○Shun Umemoto,[1] Taishi Kondo,[1] Tomoshige Fujino,[1] Gosuke Hayashi,[1] Hiroshi Murakami[1,2]

mRNA display technology is a powerful tool for selecting functional peptides and proteins. In this technology, the greater the diversity of the library produced, the easier it is to obtain better molecules. In this study, we comprehensively analyzed the effects of mRNA sequences to increase the library diversity in the mRNA display. First, mRNA libraries with three random codons immediately following the start codon were used to evaluate the effect of *N*-terminal sequence. Next, mRNA libraries with two random codons immediately before and one random base immediately after the UAG codon were used to evaluate the effect of the sequences around the UAG codon. Finally, using the promising sequences from the above analyses, we constructed highly diverse monobody and macrocyclic peptide libraries (1.2×10^{14} /mL). This work will accelerate the development of functional peptides and proteins in the future.
Keywords : mRNA display; Directed evolution; Library diversity; Monobody; Cyclic peptide

mRNA 提示法[1,2]は、機能性ペプチドやタンパク質を選択するための強力な手法である。この手法では、作製されるライブラリの多様性が大きいほど、より優れた分子が取得しやすくなる。本研究では、mRNA 提示法におけるライブラリ多様性を高めるために、mRNA 配列の違いが及ぼす影響を網羅的に解析した。まず、開始コドンの直後に 3 つのランダムコドンを持つ mRNA ライブラリ（計 32,768 配列）を用いて、*N* 末端配列がどのように影響するかを評価した。次に、UAG コドンの直前に 2 つのランダムコドンを持ち、UAG コドンの直後に 1 つのランダム塩基を持つ mRNA ライブラリ（計 6,480 配列）を用いて、UAG コドン周辺の配列がどのような影響するかを評価した。最後に上記の解析結果で有望であった配列を用いて、1.2×10^{14} という大きなライブラリ多様性を持つ人工抗体モノボディライブラリと大環状ペプチドライブラリを構築することに成功した。今回の成果は、mRNA 提示法を用いた機能性ペプチド・タンパク質の開発に今後役立つことが期待される。



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2) N. Nemoto, E. MiyamotoSato, Y. Husimi, H. Yanagawa, *FEBS Lett.* **1997**, 414, 405-408.

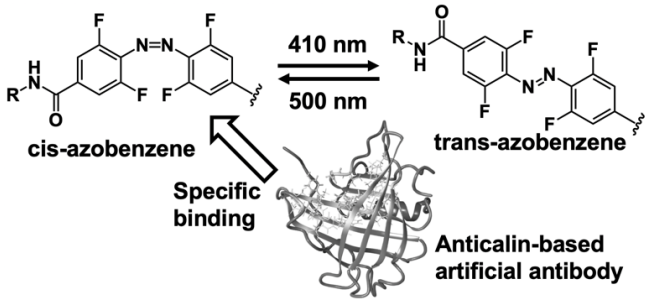
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光制御を目指した抗アゾベンゼン人工抗体の創製

(名大院工[1]・名工大院工[2]・名大未来ナノ[3]) ○藤野公茂[1]・舟根守[1]・村田直哉[1]・吉井達之[2]・林剛介[1]・築地真也[2]・村上裕[1,3]
Anti-azobenzene artificial antibodies for photocontrollable binding ([1]*Graduate School of Engineering, Nagoya University,* [2]*Graduate School of Engineering, Nagoya Institute of Technology,* [3]*Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University*) ○Tomoshige Fujino,[1] Mamoru Funane,[1] Naoya Murata,[1] Tatsuyuki Yoshii,[2] Gosuke Hayashi,[1] Shinya Tsukiji,[2] and Hiroshi Murakami[1,3]

In this study, we selected anticalin-based artificial antibodies[1] against cis-azobenzene for developing small molecule–artificial antibody pairs, whose interactions are photocontrollable in living cells (Figure). We constructed an artificial antibody library using TRAP display[2] by introducing random mutations into 21 amino acid residues inside the barrel structure of the anticalin molecule. We then selected artificial antibodies against cis-azobenzene as the target molecule and irradiated cis-azobenzene with 410-nm light to change its conformation to trans to recover the antibodies selective to the cis-form of azobenzene. Then, we performed affinity maturation of two clones that were functional in living cells. We divided the 21 amino acids randomly mutated in the first selection into three parts and reconstructed the libraries using saturation mutagenesis. From these libraries, we successfully obtained artificial antibodies with high selectivity to cis-azobenzene.
Keywords : Directed evolution, Artificial antibody, Anticalin, Azobenzene, Photoisomerization

本研究では、光照射により細胞内での結合のオン/オフを切り替え可能な小分子と人工抗体のペアを確立するため、cis-アゾベンゼンに特異的に結合するアンティカリン[1]骨格人工抗体の選択を行なった（図)。人工抗体ライブラリは TRAP 提示法[2]により構築し、アンティカリンのバレル構造の内側に位置する 21 アミノ酸をランダム化した。まず、cis-アゾベンゼンを標的として人工抗体の選択を行なった。その後、410 nm の光照射により cis-アゾベンゼンを trans 型に変換し、標的から乖離した人工抗体を回収することで、cis-アゾベンゼンに特異的な人工抗体を選択した。さらに、細胞内で結合を光制御できた 2 種のクローンを元に、親和性成熟を行なった。具体的には、最初の選択でランダム化した 21 アミノ酸を 3 グループに分け、それぞれに飽和変異を導入したライブラリを再構築した。ここから cis-アゾベンゼンへの選択を再度行うことで、cis 体への特異性が高い人工抗体クローンの取得に成功した。なお、取得した人工抗体の細胞内での機能評価は、本年会で宮崎らが発表する。



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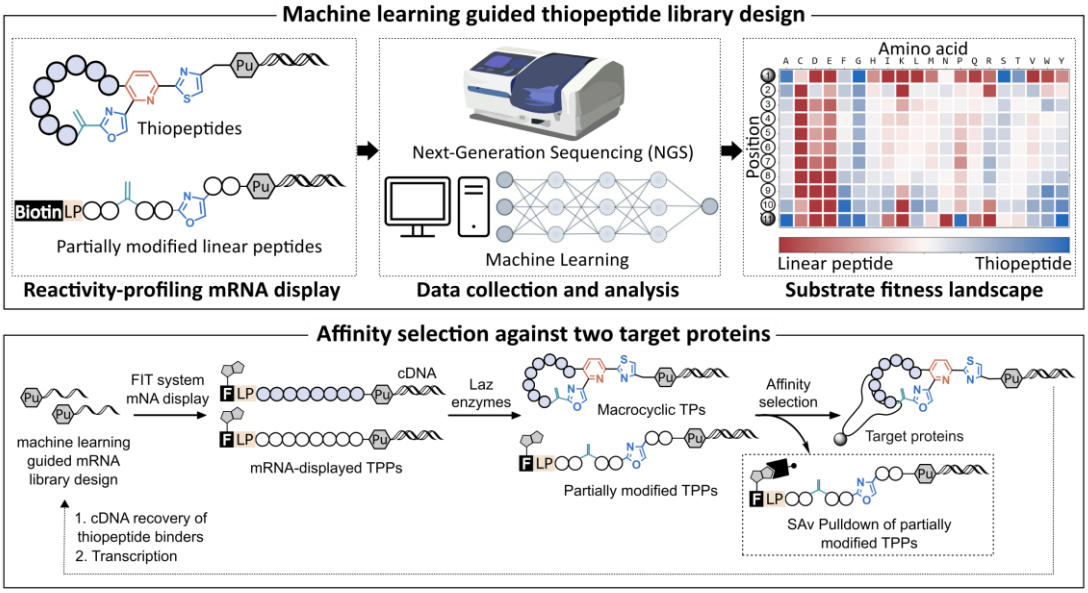
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A machine learning guided thiopeptide library design for the discovery of de novo thiopeptide binders

([1]*Graduate School of Science, Tokyo University*) ○Jun Shi Chang,[1] Alexander Vinogradov,[1] Yuki Goto,[1] Hiroaki Suga[1]

Keywords: *thiopeptide, lactazole, biosynthesis, machine learning, mRNA display*

mRNA display has enabled the identification of a multitude of pseudo-natural thiopeptides with new biological activities. Recently, we have reported a platform for the discovery of functional thiopeptides based on re-engineered biosynthesis of lactazole A, a natural product assembled by five biosynthetic Laz enzymes.[1] However, the screening library size was limited because larger macrocycles usually jeopardize the thiopeptide conversion efficiency. Herein, we utilized a combination of reactivity-profiling mRNA display as an ultrahigh throughput technique for data acquisition and machine learning for data analysis as an integrated tool to accurately profile the substrate preference for the entire lactazole biosynthetic pathway. With the substrate fitness landscape, we designed a screening library with up to 7 different macrocycle ring sizes and performed *in vitro* selection against two target proteins. Out of the 14 synthesized compounds, 10 had high binding affinity for the target protein (best K_D = 1.3 nM). The most potent compound inhibited the NF-kB signaling in THP-1 cells and was also shown to internalize to the cytosol of HEK293T cells. Altogether, we demonstrated that this platform is robust in selecting biologically active thiopeptide candidates with high binding affinity against any selected target protein.



1) A. A. Vinogradov, Y. Zhang, K. Hamada, J. S. Chang, C. Okada, H. Nishimura, N. Terasaka, Y. Goto, K. Ogata, T. Sengoku, H. Onaka, H. Suga, *J. Am. Chem. Soc*. **2022**, *144*, 20332–20341.

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Enzyme mediated one-pot synthesis of branched polyubiquitin (K48/K63) chain via photo-induced stepwise synthesis

([1]*Graduate School of Engineering, University of Tokyo)* ○ Phebee Angeline Devadasan Racheal,[1] Takafumi Furuhata,[1] Iori Murayama,[1] Usano Toyoda,[1] Akimitsu Okamoto[1]

Keywords: Ubiquitin; Enzymatic assembly; Photo-irradiation; heterotypic chain; One-pot synthesis

Ubiquitination is an essential post-translational modification involved in various cellular processes[1]. In mammalian cells, the Lys48 and Lys63 linked chains were found to be prevalent. The signal diversity arises from the monoubiquitylation to poly-ubiquitin chains of either homotypic or heterotypic chain. However, the study related to structure to function role on complex structures are highly limited[2,3]. Here we devised a one-pot enzymatic synthesis method for the structure defined poly-ubiquitin chains.

To this aim, we designed and synthesized ubiquitin whose lysine (Lys) of interest is protected by a photo-labile NVOC group which is readily deprotected by UV irradiation without perturbing the reaction condition suitable for enzymatic assembly. The successive round of NVOC deprotection via UV irradiation and enzymatic ubiquitin assembly has enabled stepwise chain elongation and site-specific introduction of branch point in respective polyubiquitin chains. The photo-controlled elongation of polyubiquitin chains led to the one-pot construction of K63 triubiquitin chains and a K48/K63 tetraubiquitin chains with defined branch positions. We will discuss synthesis, characterization, and applicability of structure-defined polyubiquitin chains in this presentation.

1) Boughton A.J, *Structure.* **2019**, *28(1)*, 29-43. 2) Ohtake, F, *Molecular cell,* **2016**, *64(2), 251-266*. 3) Richard Y. Nature Cell Biology, **2016** volume 18, pages 579–586.

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抗体様タンパク質「モノボディ」を用いた構造変化過程への摂動による酵素活性制御

(奈良先端大 物質創成[1]・京都府立大院 生命環境[2]) ○中村 伊武輝[1]、雨坂 心人[2]、原 瑞穂[2]、米澤 健人[1]、上久保 裕生[1]、田中 俊一[2]、廣田 俊[1]、松尾 貴史[1]
Regulation of enzyme activity by perturbation to conformational change process using antibody mimetic "monobody" ([1]*Division of Materials Science, Nara Inst. Sci. Tech*, [2]*Department of Biomolecular Chemistry, Kyoto Prefectural University*) ○Ibuki Nakamura,[1] Hiroshi Amesaka,[2] Mizuho Hara,[2] Kento Yonezawa,[1] Hironari Kamikubo,[1] Shun-ichi Tanaka,[2] Shun Hirota[1], Takashi Matsuo[1]

For structurally flexible proteins, the perturbation to the conformational change process will be a useful strategy to control their functions. To examine the utility of the “conformational-change trap strategy” for regulating the functions of flexible proteins, we investigated the regulation of an adenylate kinase mutant (Adk_{tm}) with antibody-mimetics “monobodies” that specifically recognize distinct conformational states of a targeted protein. As a result, two OPEN-form-specific clones (OP-2 and OP-4) were found to clearly inhibit the kinase activity of Adk_{tm}. SEC-SAXS analysis for the Adk_{tm}/OP-4 complex proved that OP-4 binds to the hinge side of Adk_{tm} without hindering the substrate-binding pathway. The titration of pyrene-conjugated Adk_{tm} with Ca^{2+}·ADP showed that OP-4 surely interferes in the domain closure to form the CLOSED-form (an active form) without influence to the substrate-binding. Our experimental findings demonstrate that the functions of flexible proteins can be regulated through conformational-change trapping with conformational state-specific monobodies.
Keywords : Antibody mimetic, Activity regulation, Conformational change, Protein-protein interaction, Adenylate kinase

タンパク質の機能を制御する最も有効な戦略は、活性部位に対する摂動であるが、大きな構造変化を伴いながら機能を発揮する柔軟なタンパク質では、構造変化過程への摂動も有用であると考えられる。そこで、OPEN⇔CLOSED の構造変化を伴って ATP/ADP/AMP 間のリン酸基転移を触媒するアデニル酸キナーゼ三変異体（Adk_{tm}）に対して、Adk_{tm} の立体構造状態を特異的に認識する抗体様タンパク質「モノボディ」を用いて、タンパク質の機能を制御する「構造変化トラップ」戦略の有用性を検討した。ファージディスプレイシステムにより、Adk_{tm} の各構造状態を選択的に捉えるモノボディのうち、OPEN 型を認識する OP-2 と OP-4 の２つのモノボディは、Adk_{tm} のキナーゼ活性を明確に阻害することが分かった。また、Adk_{tm}/OP-4 複合体の SEC-SAXS 解析により、OP-4 は Adk_{tm} の基質結合経路を阻害することなく、Adk_{tm} の活性部位の遥か外側に結合することが証明された（Fig. 1）。さらに、Ca^{2+}•ADP による滴定実験によって、基質結合サイトが空いているにもかかわらず、CLOSED 型への構造変化が阻害されていることがわかった。これらの結果は、構造状態特異的なモノボディを用いた構造変化トラップによって、柔軟なタンパク質の機能を制御できることを示している。

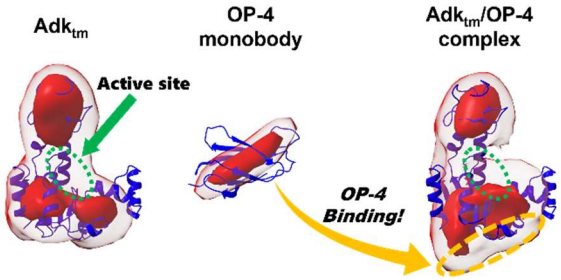


Fig. 1. The shape of Adk_{tm}/OP-4 complex calculated by SEC-SAXS measurements.

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Academic Program [Oral B] | 18. Polymer | Oral B

[K304-2am] 18. Polymer

Chair: Shohei Saito, Yusuke Tsutsui

Thu. Mar 23, 2023 9:00 AM - 11:20 AM K304 (K304, Lecture Hall Bldg. [3F])

[K304-2am-01] Self-assembly of 2D Conjugated Covalent Organic Framework into 1D Electronically Conductive Nanotubes

○zhuowei LI[1], Takahiro Tsuneyuki[1], Samrat Ghosh[1], Takumi Nakazato[2], Masahiro Odawara[2], Wakana Matsuda[1], Masaki Nobuoka[1], Bin Chen[1], Rajendra Prasad Paitandi[1], Yusuke Tsutsui[1], Takayuki Tanaka[1], Masayuki Suda[1], Yoshihiro Miyake[2], Hiroshi Shinokubo[2], Shu Seki[1] （1. Kyoto University, 2. Nagoya University）

9:00 AM - 9:20 AM

[K304-2am-02] Fluorescent probe showing a two-step spectral change in response to polymer chain tension and strain-induced crystallization

○Kensuke Suga[1], Mitsuo Hara[2], Takuya Yamakado[1], Shohei Saito[1] （1. Grad. Sch. of Sci., Kyoto Univ., 2. Grad. Sch. of Eng., Nagoya Univ.）

9:20 AM - 9:40 AM

[K304-2am-03] Induction and Memory of Macromolecular Helicity: Kinetic Analysis Based on Helix Inversion Model

○Takaya Fujie[1], Takeshi Yamamoto[1], Michinori Suginome[1] （1. Kyoto University ）

9:40 AM - 10:00 AM

[K304-2am-04] The Effects of Dehydration Temperature and Monomer Chirality on Primitive Polyester Synthesis and Microdroplet Assembly

Rehana Afrin[1], Chen Chen[1], Davide Sarpa[2], Mahendran Sithamparam[3], Ruiqin Yi[1], Chaitanya Giri[4], Irena Mamajanov[1], H James Cleaves[1,5,6], Kuhan Chandru[3], ○Tony Z Jia[1,5] （1. Earth-Life Science Institute, Tokyo Institute of Technology, 2. The University of Southampton, 3. Space Science Centre (ANGKASA), Institute of Climate Change, National University of Malaysia, 4. Research and Information System for Developing Countries (RIS), 5. Blue Marble Space Institute of Science, 6. Earth and Planets Laboratory, Carnegie Institution of Washington）

10:00 AM - 10:20 AM

[K304-2am-05] Excessive molecular structure and properties determination of different types of Alkyl sulfonated polyimide (ASPI) with universal neural network potential (uNNP)

○Attila Taborosi[1], Michihisa Koyama[1], Yuki Nagao[2], Nobuyuki Zettsu[1] （1. Shinshu University, 2. Japan Advance Institute of Science and Technology）

10:20 AM - 10:40 AM

[K304-2am-06] Formation of latex films with high toughness

○Yuma Sasaki[1], Yuichiro Nishizawa[1], Hayato Suzuki[1], Takuma Kureha[3], Kazuya Uenishi[4], Kazuko Nakazono[5], Toshikazu Takata[6], Daisuke Suzuki[1,2] （1. Grad. Sch. of Textile Sci. &Tech., Shinshu Univ., 2. RISM, Shinshu Univ., 3. Grad. Sch. of Sci. and Tech., Hirosaki Univ., 4. Yokohama Rubber Co., Ltd., 5. Dept. of Chemical Sci. and Engineering, Tokyo Tech, 6. Grad. Sch. of Advanced Sci. and Engineering, Hiroshima Univ.）

10:40 AM - 11:00 AM

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[K304-2am-07] Ultrahighly Refractive and Degradable Thiourea Polymers with Dense and Multiple Intermolecular Hydrogen Bonds

○Seigo Watanabe[1], Kenichi Oyaizu[1] （1. Waseda Univ.）

11:00 AM - 11:20 AM

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2D 共役共有結合有機骨格(COF)の自己組織化による 1D 電子伝導性ナノチューブへの in-situ 変換

（京大院工 [1]・名大院工 [2]・兵庫県大院理 [3]）○Zhuowei Li[1]・常行 恭弘 [1]・Samrat Ghosh[1]・仲里 巧 [2]・小田原 正浩 [2]・松田 若菜 [1]・信岡 正樹 [1]・Bin Chen[1]・Rajendra Prasad Paitandi[1]・筒井 祐介 [1]・田中 隆行 [1]・須田 理行 [1]・三宅 由寛 [2]・忍久保 洋 [2]・関 修平 [1]

Self-assembly of 2D Conjugated Covalent Organic Framework into 1D Electronically Conductive Nanotubes ([1]*Graduate School of Engineering, Kyoto University*, [2]*Graduate School of Engineering, Nagoya University,* [3]*Graduate School of Science, University of Hyogo*) ○ Zhuowei Li [1], Takahiro Tsuneyuki1, Samrat Ghosh[1], Takumi Nakazato[2], Masahiro Odawara[2], Wakana Matsuda1, Masaki Nobuoka[1], Bin Chen[1], Rajendra Prasad Paitandi[1], Yusuke Tsutsui1, Takayuki Tanaka[1], Masayuki Suda[1], Yoshihiro Miyake[3], Hiroshi Shinokubo[2], Shu Seki[1]

In-situ transformation of two-dimensional conjugated covalent organic framework (COF) sheets was achieved by a simple "roll-to-sheet" self-assembly protocol, mimicking interconvertible carbon allotropes of two-dimensional (2D) graphene and one-dimensional (1D) carbon nanotubes. An use of azapyrene instead of pyrene as a building block of the COF was the key to achieve the transformation, leading to COF nanotubes with uniform cross-sectional diameters. Substituting the 2,7 carbons in pyrene with nitrogens gave contrasting optical and electronic properties reflecting the coiled structure of the conjugated 2D sheet. The nanotubes exhibited semiconducting properties and provided stable conductive pathways along the tubular axes under ambient conditions.

Keywords :　Covalent organic framework, Nanotubes

2 次元 (2D) グラフェンと 1 次元(1D)カーボンナノチューブの相互関係を模し、本研究では溶媒界面における 2D 共役共有結合有機骨格（COF)シートを「ロール」させ、簡便に 1D ナノチューブ構造へ in-situ 変換する方法について報告する。ピレン COF の２，７位の炭素を窒素で置換したアザピレンを用いると、2 次元重合過程において、断面直径が均一な同軸ナノチューブを与える。この 1D ナノチューブの物性はロール状構造を反映し、ピレン COF 結晶とは対照的な光学的および電子特性を示した。空気中で安定した電子伝導経路を持つ半導体性を示し、アザピレンの窒素中心を利用した安定な電荷キャリアドーピングにより、高い伝導性を付与できることが明らかとなった。

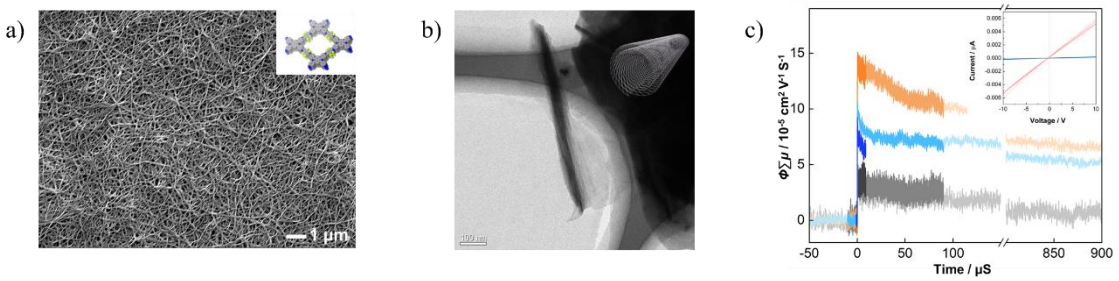


Figure 1. a) SEM/schematic of Aza-1PF COF tubular film, b) TEM/schematic morphology of Aza-1PF COF tubule, and c) Transient/static electronic conductivity of Aza-1PF film and Aza-1PF film with the dopant.

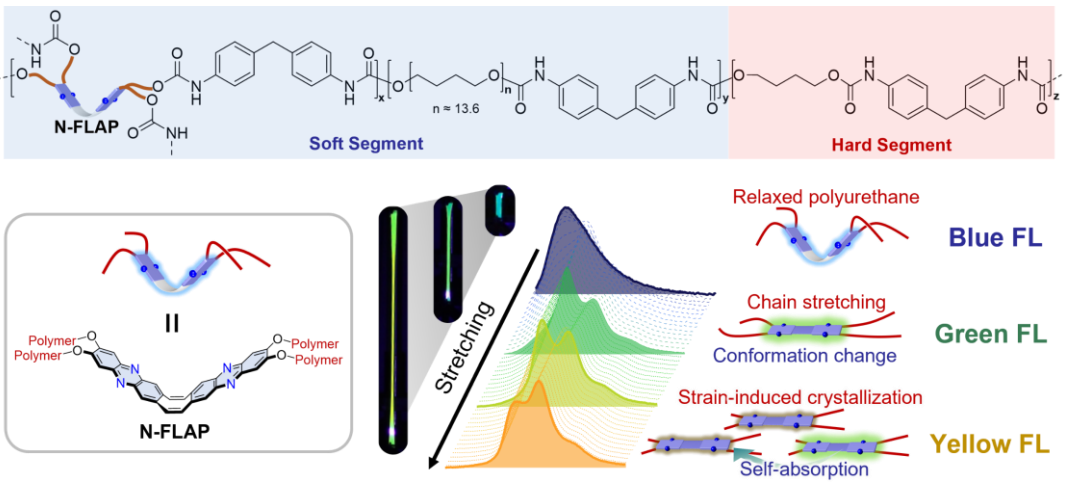
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Fluorescent probe showing a two-step spectral change in response to polymer chain tension and strain-induced crystallization

([1]*Kyoto University*, [2]*Nagoya University*)
Kensuke Suga,[1] Mitsuo Hara,[2] Takuya Yamakado,[1] Shohei Saito[1]
Keywords: Fluorescence, Force Probe, Polyurethane, Strain-Induced Crystallization, FLAP

Strain-induced crystallization (SIC) is significantly related to the mechanical properties of polymers. There are many reports on the relationship between SIC and the resultant hardness.[1,2] However, the relationship between tension applied to the polymer chain and SIC has yet to be understood in detail. On the other hand, flapping molecules (FLAP) can be used as a force probe to quantify nanoscale tension in the entangled polymer chains.[3,4] In this study, we developed a novel approach to observe how the nanoscale tension causes the SIC of polymers using a FLAP fluorescent probe.

A nitrogen-embedded FLAP (**N-FLAP**)[5] was incorporated into segmented polyurethanes (PU) with high **N-FLAP** concentration (0.65 wt%), and their fluorescence response under external stress was investigated. Upon stretching the specimens, a blue fluorescence band was turned into a green fluorescence band in the low-stress region. The fluorescence color change can be explained as a V-shape-to-planar structural change of **N-FLAP** caused by the nanoscale tension in the polymer chain. Furthermore, a new yellow fluorescent band appeared as higher stress was applied to the PU. Detailed absorption and fluorescence analysis during stretching revealed that the second-step fluorescence color change was caused by self-absorption of the green fluorescence triggered by the SIC of the PU. As a result, polymer chain tension and SIC under external stress were both tracked by the two-step fluorescence spectral change.



1) C. Liu, K. Mayumi, K. Ito, *et al. Science* **2021**, *372*, 1078. 2) R. Osumi, K. Urayama, *et al. ACS Macro Lett.* **2022**, *11*, 747. 3) R. Kotani, H. Yabu, S. Saito, *et al. Nature Commun.* **2022**, *13*, 303. 4) T. Yamakado, S. Saito, *J. Am. Chem. Soc.* **2022**, *144*, 2804. 5) Y. Goto, S. Omagari, R. Sato, T. Yamakado, R. Achiwa, N. Dey, K. Suga, M. Vacha, S. Saito, *J. Am. Chem. Soc.* **2021**, *143*, 14306.

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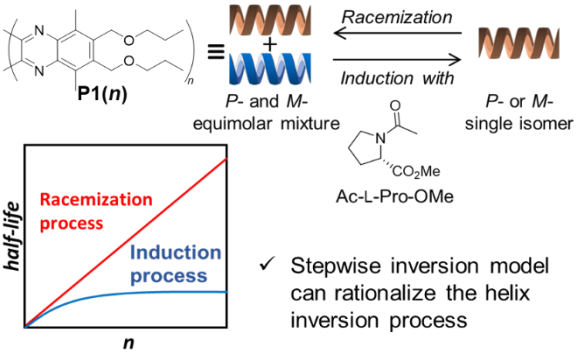
高分子らせん不斉の誘起と記憶：らせん反転伝播モデルに基づいた速度論的解析

（京大院工）○藤江 峻也・山本 武司・杉野目 道紀
Induction and Memory of Macromolecular Helicity: Kinetic Analysis Based on Helix Inversion Model (*Graduate School of Engineering, Kyoto University*) ○ Takaya Fujie, Takeshi Yamamoto, Michinori Suginome

Rate of screw-sense inversion of poly(quinoxaline-2,3-diyl) (PQX) bearing achiral ether side chains was measured by using an L-proline derivative as a nonbonding chiral additive. The rate of screw-sense induction process was found to be faster than that of racemization process. In addition, the rate of induction process was essentially independent of the degree of polymerization, while the rate of the racemization process was monotonously decreased with increase of the degree of polymerization. The difference in the rates of helix inversion between the induction and racemization processes was successfully explained by the helix reversal mechanism in which the helix inversion starts from the polymer terminus and propagate in different manners depending on the inversion conditions.
Keywords : Polyquinoxaline; Circular Dichroism; Half-Life; Degree of Polymerization; Racemization

新たなキラル機能性材料の開発を目指し、外部刺激に応じて主鎖のらせん不斉を制御できる動的らせん高分子の開発が進められている[1]。しかしながら、らせん反転挙動の速度論的解析はこれまでほとんど検討されておらず、高分子構造がらせん反転速度に与える影響は明らかにされていなかった。本研究では、動的らせん構造を有するポリ（キノキサリン-2,3-ジイル）（PQX）のらせん反転挙動の速度論的解析をラセミ化条件と不斉誘起条件においておこなうことで、その重合度依存性を解明した。

L-プロリン誘導体をキラル添加剤とするアキラル PQX のらせん不斉誘起条件[2]における CD スペクトル強度の経時変化を測定したところ、らせん反転挙動は一次の反応速度式で近似することができ、らせん不斉の誘起は、L-プロリン誘導体によって誘起した左巻きらせんを高希釈によってラセミ化させる条件下に比べ迅速に進行した。また、ラセミ化条件における半減期が重合度に比例して増加したのに対し、不斉誘起条件における半減期は重合度が増加するに従いほぼ一定となった。これまでの知見から、PQX のらせん反転は高分子末端で発生したらせん反転構造がもう一方の末端へと伝播することで進行するものと想定される。このモデルをもとに速度論的解析を行ったところ、最初にらせん反転構造が発生する際のエネルギー障壁はらせん不斉誘起とラセミ化のいずれの条件においてもほぼ同等であることが示された。また、右巻きと左巻きが同一エネルギーとなるラセミ化条件下では、重合度の増加に伴いらせん反転構造伝播の途中で巻き戻りが生じる確率が向上し、見かけのらせん反転速度が低下していることが示唆された。



1) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116*, 13752.
2) S. Ikeda, R. Takeda, T. Fujie, N. Ariki, Y. Nagata, M. Suginome, *Chem. Sci.* **2021**, *12*, 8811.

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The Effects of Dehydration Temperature and Monomer Chirality on Primitive Polyester Synthesis and Microdroplet Assembly

([1]Earth-Life Science Institute, Tokyo Institute of Technology, [2]The University of Southampton, [3]Space Science Centre (ANGKASA), Institute of Climate Change, National University of Malaysia, [4]Research and Information System for Developing Countries (RIS), [5]Blue Marble Space Institute of Science, [6]Earth and Planets Laboratory, Carnegie Institution of Washington
Rehana Afrin[1], Chen Chen[1], Davide Sarpa[2], Mahendran Sithamparam[3], Ruiqin Yi[1], Chaitanya Giri[4], Irena Mamajanov[1], H. James Cleaves II[1,5,6], Kuhan Chandru[3], ○Tony Z. Jia[1,5]
Keywords: *Origins of Life, Prebiotic Chemistry, Polyesters, Protocells, Liquid-Liquid Phase Separation*

Synthesis of polyester gels via dehydration of α-hydroxy acids (αHAs) is a plausible route to form primitive functional polymers. αHApolyester gels assemble into membraneless droplets upon rehydration in aqueous media that can segregate and compartmentalize early biomolecules. However, conditions for polyester synthesis and microdroplet assembly have yet to be broadly explored. Thus, the effects of heat and monomer chirality on dehydration synthesis and assembly of homopolyester microdroplets are investigated using microscopy and mass spectrometry. Lower dehydration temperatures (≤80 °C) are observed to result in shorter polyesters than higher temperatures (up to 150 °C). After rehydration of polyester products, droplet assembly propensity correlates with longer polymer length. Low temperature (40 °C) dehydration yields only short polyesters and nearly no droplet formation. Finally, polyesters derived from dehydration/rehydration synthesis of homochiral lactic acid and phenyllactic acid monomers are of equal length and with a similar propensity for droplet assembly as those derived from racemic starting materials. These results suggest that polyesters and microdroplets derived from them can form under a wide variety of temperatures and from different monomer chiralities, enabling many possibilities for such systems to have played a role in systemic self-organization during the origins of life.

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Excessive molecular structure and properties determination of different types of alkyl sulfonated polyimide (ASPI) with universal neural network potential (UNNP)

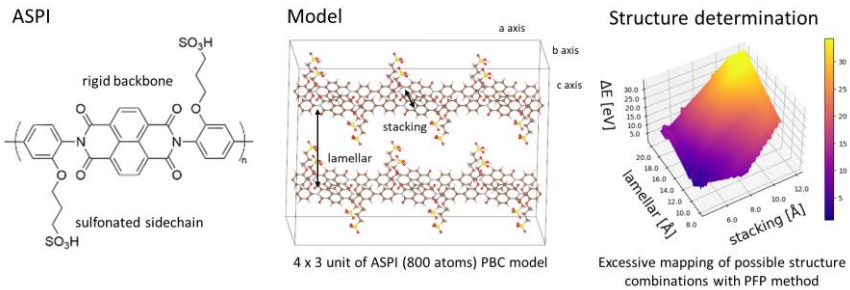
([1]*Research Initiative for Supra-Materials, Shinshu University*, [2]*School of Material Science, Japan Advanced Institute of Science and Technology*) ○Attila Taborosi,[1] Michihisa Koyama,[1] Yuki Nagao,[2] Nobuyuki Zettsu[1]

Keywords: Alkyl sulfonated polyimide; Molecular structure determination; Universal neural network potential; Computational chemistry simulation; Lyotropic liquid crystal

Alkyl sulfonated polyimide (ASPI) with rigid aromatic backbones and sulfonated alkyl side chains show promising proton conductivity especially with water uptake[1], and possible application as ion channels in Li-ion batteries. However, the role of backbone rigidity and side chain contribution for the lyotropic liquid crystal properties remains unclear.

Neural Network Potentials (NNP) are rapidly gaining attention due to the powerful combination of neural networks with large-scale datasets. Furthermore, the so-called Universal Neural Network Potentials (UNNP) have been developed, which enables to handle many combinations of different elements on the periodic table and supporting the material discovery, determination of unknown/new structures and extend the limitation of quantum mechanics.

The UNNP called as PreFerred Potential[2] (PFP) was used to determine the molecular structure of different types of ASPI with an excessive mapping of possible structure combinations. The characterization and elucidation of molecular properties and investigation of molecular level solvation of these different ASPI types can aid the understanding of lyotropic liquid crystal formation and the further design of ASPI types, and the usage of them as coating/ion channel material in Li-ion batteries.



1) a) Y. Ono *et al.*, *Macromolecules* **2018**, *51*, 3351. b) Y. Nagao, Sci. Technol. Adv. Mater. **2020**, *21*, 79 2) S. Takamoto *et al.*, *Nat. Commun.* **2022**, *13*, 2991.

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Formation of latex films with high toughness

([1] *Graduate School of Textile Science & Technology, Shinshu University,* [2]*Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University,* [3]*Graduate School of Science and Technology, Hirosaki University,* [4]*Yokohama Rubber Co., Ltd.,* [5]*Department of Chemical Science and Engineering, Tokyo Institute of Technology,* [6]*Graduate School of Advanced Science and Engineering, Hiroshima University*)
○Yuma Sasaki,[1] Yuichiro Nishizawa,[1] Hayato Suzuki,[1] Takuma Kureha,[3] Kazuya Uenishi,[4] Kazuko Nakazano,[5] Toshikazu Takata,[6] Daisuke Suzuki,[1,2]
Keywords: Elastomer; Colloid; Rotaxane; Mechanical properties; Crack propagation

Polymeric materials are lighter, softer, and processable than other materials such as metals and ceramics due to their low density and the modulus, and are applied as components in automobiles, aircraft, and building materials. In various polymer material applications, there is a need to ensure long-term durability for safe and reliable use, and there is growing interest in the preparation of tough polymer materials and the elucidation of their fracture mechanisms. Against this background, our group have achieved toughening of latex film by introducing rotaxane crosslinker (RC) into microparticles.[1] The results show that the introduction of RCs improves the mechanical properties of polymer microparticles and is also important in strengthening the particle interface without additives. Furthermore, understanding the fracture behavior of latex films when various defects such as cracks and scratches are introduced is highly important as a strategy for tough polymeric materials in terms of green chemistry. In this study, we investigated the effect of RC in microparticles on the fracture of the film interface.

Tear tests showed that the cracks propagated horizontally in films with non-crosslinked or chemically crosslinked particles, while cracks propagated in an irregular direction when RC was introduced (**Fig.(a,b)**). The fact that the crack growth occurred at a sufficiently slow rate suggests that the RC in the microparticles is effective in dissipating stresses at the boundary of microparticles in various directions in the film.

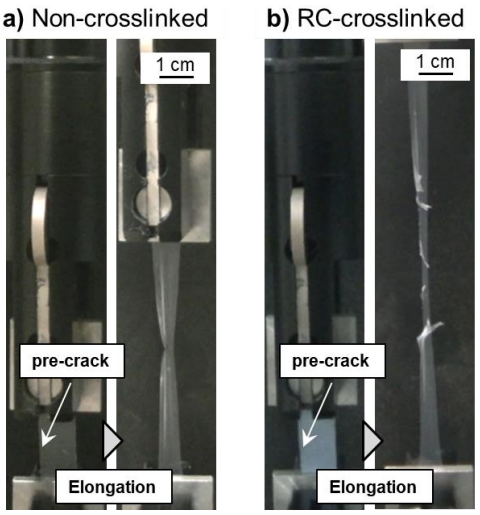


Figure. Photographs of before/after elongation notched **(a)** Non-crosslinked, **(b)** RC-crosslinked latex films.

1) a) S. Hiroshige *et al.*, *Chem. Eur. J.* **2017**, *23*, 8405. b) T. Kureha *et al.*, *Langmuir* **2020**, *36*, 4855. c) S. Hiroshige *et al.*, *J. Soc. Rheology, Jpn.* **2019**, *47*, 51.

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Ultrahighly Refractive and Degradable Thiourea Polymers with Dense and Multiple Intermolecular Hydrogen Bonds

(*Dept. of Applied Chem., Waseda Univ.*) ○Seigo Watanabe, Kenichi Oyaizu
Keywords: Thiourea; High Refractive Index; Hydrogen Bonds: Degradability

High-refractive-index polymers (HRIPs) are attractive for preparing high-performance and flexible optical devices, and the required value of the refractive index (RI) has been getting higher up to over 1.8.[1] Although there has been much effort on enhancing the RI of polymers such as sulfur-rich molecular design[2] and introducing heavy chalcogenide atoms,[3] few HRIPs satisfying both RI over 1.8 and visible transparency have been reported. As a solution, we recently reported hydrogen-bond-incorporated poly(phenylene sulfide)s representing ultrahigh RI (n_D = 1.85 in maximum) which was ascribed to the free volume reduction induced by intermolecular H-bonds.[4]

In this study, we report ultrahighly refractive aromatic thiourea polymers as an expanded version of our strategy (Figure 1a). High-molecular-weight thiourea polymers were easily prepared via polyaddition or polycondensation (Figure 1b). As thiourea form randomly distributed hydrogen bonds,[5] the polymer films were flexible and transparent despite the presence of dense hydrogen bonding networks (Figure 1c). The polymers showed high refractive indices of n_D ~ 1.7-1.8 owing to the dual contribution of high polarizability and dense multiple hydrogen bonds. We also demonstrated that these polymers were degradable under the presence of excess diamine owing to the dynamic properties of thiourea units.

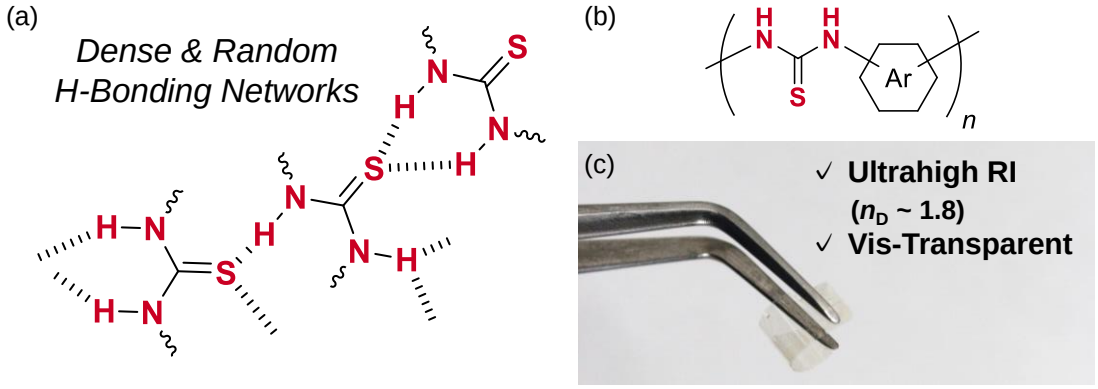


Figure 1. Features of thiourea polymers in this study: (a) Schematic representation of hydrogen bonding networks by thiourea. (b) Molecular design of the thiourea polymers. (c) Photograph of flexible thiourea film with ultrahigh RI and visible transparency.

1) T. Higashihara, M. Ueda, *Macromolecules* **2015**, *48*, 1915. 2) J. Pyun *et al.*, *ACS Macro Lett.* **2020**, *9*, 245. 3) J. Zhu *et al.*, *Polym. Chem.* **2019**, *10*, 4279. 4) S. Watanabe, K. Oyaizu *et al.*, *Macromolecules* **2022**, *55*, 2252.; *ACS Polym. Au* **2022**, *2*, 458. 5) T. Aida *et al.*, *Science* **2018**, *359*, 72.

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[B445-2am] 19. Colloid and Interface Chemistry

Chair: Hirokazu Kobayashi, Kenshi Matsumoto

Thu. Mar 23, 2023 9:00 AM - 11:30 AM B445 (445, Bldg. 4 [4F])

[B445-2am-01] Flow Synthesis of 15 Elements Alloy Nanoparticles and Their Alcohol Electrooxidation Properties

○Hiroki Minamihara Minamihara[1], Kohei Kusada[1,2], Tomokazu Yamamoto[3], Takaaki Toriyama[3], Syo Matsumura[3], Osami Sakata[4], Shogo Kawaguchi[4], Yoshiki Kubota[5], Hiroshi Kitagawa[1] （1. Kyoto University, 2. JST PRESTO, 3. Kyusyu University, 4. JASRI/SPring-8, 5. Osaka Metropolitan University）

9:00 AM - 9:20 AM

[B445-2am-02] Monitor the Growth of ZnTe Microspheres in a PVP-contained Polyol System

○Yuen-ting Rachel Chau[1], Mai Thanh Nguyen[1], Tetsu Yonezawa[1] （1. Hokkaido University）

9:20 AM - 9:40 AM

[B445-2am-03] Quasi-Reversible Photoinduced Displacement of Perylenebisimide Derivatives from the Surface of ZnS Nanocrystals

○Daisuke Yoshioka[1], Yusuke Yoneda[2], I-Ya Chang[3], Hikaru Kuramochi[2], Kim Hyeon-Deuk[3], Yoichi Kobayashi[1,4] （1. Ritsumeikan Univ., 2. Inst. Mol. Sci., 3. Kyoto Univ., 4. PRESTO JST）

9:40 AM - 10:00 AM

[B445-2am-04] Colloidal Synthesis of Ag_8GeS_6 Quantum Dots Showing an Intense Near-IR Photoluminescence

○Nurmanita Rismaningsih[1], Junya Kubo[1], Tatsuya Kameyama[1], Norikazu Fujihira[2], Tsukasa Torimoto[1] （1. Graduate School of Engineering, Nagoya University, 2. Murata Manufacturing Co., Ltd.）

10:00 AM - 10:20 AM

[B445-2am-05] Au@Pd core-shell nanoparticles as high electrocatalyst for ethanol oxidation

○Jianhui Yang[1], Shinya Maenosono[1] （1. Japan Advanced Institute of Science and Technology）

10:30 AM - 10:50 AM

[B445-2am-06] Exploration of highly active multi-element nanoalloy catalyst and analysis of their structures by statistical method

○Yuto Maruta[1], Kohei Kusada[1], Okkyun Seo[3], Osami Sakata[3], Shogo Kawaguchi[3], Yoshiki Kubota[5], Hiromasa Kaneko[4], Takaaki Toriyama[2], Tomokazu Yamamoto[2], Yasukazu Murakami[2], Hiroshi Kitagawa[1] （1. Fac. of Science, Kyoto Univ., 2. Kyushu Univ., 3. JASRI, 4. Meiji Univ., 5. Osaka Metro. Univ.）

10:50 AM - 11:10 AM

[B445-2am-07] Element-Selective Observation of Dynamics in High-Entropy Alloy Nanoparticles with XAFS

○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Yoshiki Kubota[5], Shogo

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Kawaguchi[6], Toshiaki Ina[6], Kazuo Kato[6], Hiroshi Kitagawa[1] （1. Grad. Sch. Sci., Kyoto Univ., 2. Hakubi Center, Kyoto Univ., 3. URC, Kyushu Univ., 4. Grad. Sch. Eng., Kyushu Univ., 5. Grad. Sch. Sci., Osaka Metro. Univ., 6. JASRI/SPring-8）
11:10 AM - 11:30 AM

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Flow Synthesis of 15 Elements Alloy Nanoparticles and Their Alcohol Electrooxidation Properties

([1]Grad. Sch. Sci., Kyoto Univ., [2]Hakubi Cent. Adv. Res., [3]JST PRESTO, Kyoto Univ., [4]URC, Kyushu Univ., [5]Natl. Inst. Tech., Kurume Col., [6]JASRI/SPring-8, [7]Grad. Sch. Sci., Osaka Metro. Univ.)

○ Hiroki Minamihara[1], Kohei Kusada[1,2,3], Tomokazu Yamamoto[4], Takaaki Toriyama[4], Syo Matsumura[5], Yasukazu Murakami[4], Osami Sakata[6], Shogo Kawaguchi[6], Yoshiki Kubota[7], Hiroshi Kitagawa[1]

Keywords: Nanoparticles, Multi-element alloy, Electrocatalyst, Alcohol oxidation reaction, Flow sythesis

Multi-element alloy nanoparticles (MEA NPs) have widely attracted attention because of their superior catalytic activities[1]. Recently, many synthesis methods of MEA NPs have been developed. For example, AuCoCuFeNiPdPtSn and IrPtRhRuPd MEA NPs were synthesized by carbothermal method[2] and wet-chemistry method[3]. However, there are few examples of the MEA NPs composed of more than ten elements due to the difficulty to mix various elements having different properties in a particle. In this study, we first synthesized BiCoCuFeGaInIrNiPdPtRhRuSbSnTi NPs (Fig.) by a liquid-phase reduction method using an originally developed continuous-flow reactor which is specialized for synthesis of ultra MEA NPs. The obtained NPs were characterized by scanning transmission electron microscopy (STEM) and powder X-ray diffraction (PXRD). Elemental analyses suggested the successful mixing of all the elements. By PXRD, we identified the obtained NPs have an amorphous structure because each element has different atomic radius and structure. Moreover, we investigated their electronic structure and electrocatalytic activity for alcohol oxidation reactions in 1M KOH solution. In the presentation, we also discuss the catalytic properties and electronic structure of the obtained MEA NPs.

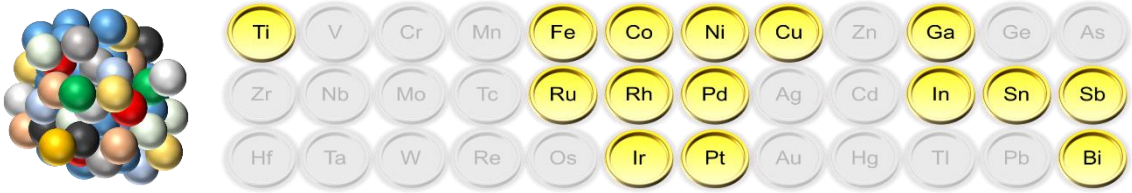


Fig. 15 elements MEA NP and the periodic table

[1] H. Minamihara et al., *J. Am. Chem. Soc.,* **2022**, 144, 26, 11525. [2] Y. Yao et al., *Science*, 359, 1489 (**2018**). [3] D. Wu et al., *Chem. Sci.*, **2020**, 11, 12731–12736.

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Monitor the Growth of ZnTe Microspheres in a PVP-contained Polyol System

(*Graduate School of Engineering, Hokkaido University*) ○Yuen-ting Rachel Chau, Mai Thanh Nguyen, Tetsu Yonezawa

Keywords: ZnTe microspheres; Hot injection method; Formation mechanism

Solvothermal method is conventionally used to synthesize ZnTe microspheres.[1-2] The method involves reaction at higher temperature than the boiling point of the solvent and under elevated pressure in sealed vessel. This brings difficulties in sequentially tracing the formation of ZnTe microspheres.[2] In this study, a hot injection method is conducted under open pressure. This method used to trace the formation of zincblende structured ZnTe microspheres. A mixture of 0.20 mmol of zinc chloride ($ZnCl_2$), 0.16 mmol of sodium tellurite (Na_2TeO_3), 0.64 mL of ethylenediamine and 3 mL of ethylene glycol (EG) as the precursor solution was injected into a 200 °C-preheated 15 mL-EG that contained 0, 259, 518 and 1036 mg of PVP, respectively. Formation of ZnTe microspheres was traced from 0.2 h to 48 h. Te rods were the major products at reaction time of 0.2 h and 0.5 h. ZnTe microspheres grew at both tips and sides of Te rods when PVP was not involved, whereas they grew only at the tips of Te rods when PVP was used. Further proceeding the reaction from 0.5 h to 48 h, more ZnTe microspheres and less Te rods were obtained. Therefore, Te rods were the sacrificial template for the growth of ZnTe microspheres at longer time. Voids were observed in ZnTe microspheres (Figure 1a), that possibly due to the dissolution of small ZnTe crystals to large crystals during the growth. Sizes of ZnTe microspheres were determined by the nucleation and growth rate of Te rods at the initial stage of the reaction, which were affected by amount of PVP used. Homogeneous, 0.6 μm-sized ZnTe microspheres were obtained using 518 mg of PVP in the synthesis (Figure 1b). Reaction temperature, amount of Na_2TeO_3, selection of zinc salts, and amount of ethylenediamine also alternate the growth rate of ZnTe microspheres.

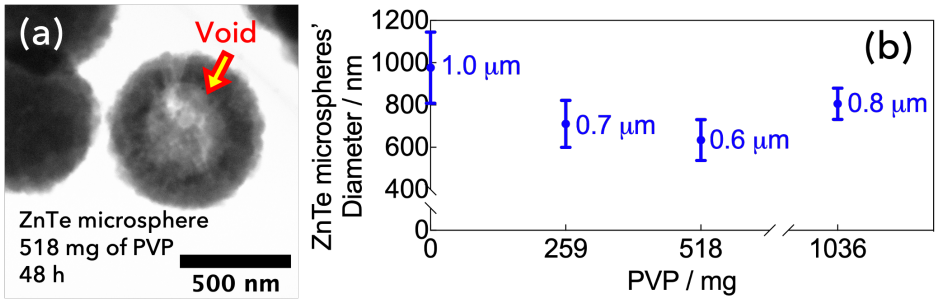


Figure 1. (a) TEM images of samples synthesized at 48 h with 518 mg of PVP. (b) Average diameter of ZnTe microspheres obtained against amount of PVP.

1) M.F. Ehsan, *RSC Adv.* **2015**, *5*, 6186. 2) S. Li, *New J. Chem*. **2022**, *46*, 3777.

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Quasi-Reversible Photoinduced Displacement of Perylenebisimide Derivatives from the Surface of ZnS Nanocrystals

([1]*College of Life Sciences, Ritsumeikan University*, [2]*Institute for Molecular Science*, [3]*Graduate School of Science., Kyoto University*, [4]*PRESTO JST*) ○Daisuke Yosioka,[1] Yusuke Yoneda,[2] I-Ya Chang,[3] Hikaru Kuramochi,[2] Kim Hyeon-Deuk,[3,4] Yoichi Kobayashi,[1,4]

Keywords: Semiconductor nanocrystals; Charge separation; Time-resolved spectroscopy; Ligands; Radical anion

Organic-inorganic nanohybrids using semiconductor nanocrystals (NCs) coordinated with aromatic organic molecules have been widely studied in the fields of optoelectronic materials, such as solar cells, photocatalysis, and photon upconversion. In these materials, coordination bonds of ligand molecules are usually assumed to be stable during optical processes. However, this assumption is not always valid.

In this study, we demonstrate that the coordination bonds between ligand molecules and NCs by carboxyl groups are displaced quasi-reversibly by light irradiation using zinc sulfide (ZnS) NCs coordinated with perylenebisimide (PBI, Figure 1b inset) as a model system (Figure 1a). Time-resolved spectroscopy over a wide time range from tens-of femtosecond to second timescales and density functional theory calculations show that the photoinduced ligand displacement is driven by ultrafast hole transfer from PBI to ZnS NCs. Interestingly, the PBI is released from NCs surface as a radical anion after light irradiation, and the PBI radical anion survives over the second timescale (Figure 1b). Moreover, the long-lived charge-separated state can be generated repeatedly without any degradations. Density functional theory calculations suggest that the ligand is displaced with the neighboring Zn atom as a metal complex.

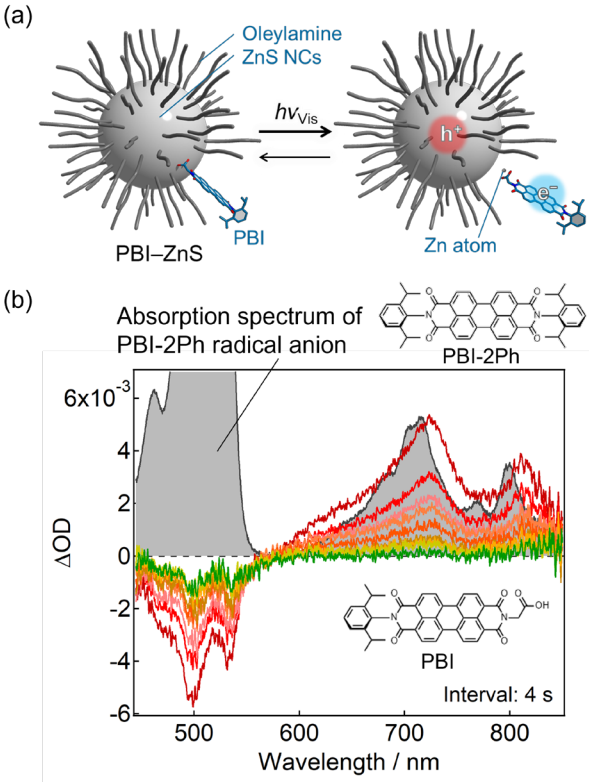


Fig. 1 (a) Schematic of the quasi-reversible photoinduced displacement of PBI-coordinated ZnS NCs and (b) the absorption spectrum of a PBI derivative (PBI-2Ph) under the constant voltage at −1.0 V (vs ferrocene/ferrocenium) and the transient absorption spectra of PBI-ZnS (PBI/ZnS = 6.8) in chloroform.

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Colloidal Synthesis of Ag_8GeS_6 Quantum Dots Showing an Intense Near-IR Photoluminescence

([1]*Graduate School of Engineering, Nagoya University*, [2]*Murata Manufacturing Co., Ltd.*)
○Nurmanita Rismaningsih,[1] Junya Kubo,[1] Tatsuya Kameyama,[1] Norikazu Fujihira,[2] and Tsukasa Torimoto[1]

Keywords: Quantum Dots, Photoluminescence, I-IV-VI Group Semiconductor, Near-IR Responsive Materials, Band-edge Photoluminescence.

Semiconductor quantum dots (QDs) have engaged considerable attention for wide-ranged applications, because of their excellent photochemical properties. To date, since available near-infrared responsive QDs such as CdTe and PbS contained highly toxic Cd and Pb elements, Cd- and Pb-free multinary quantum dots are preferred. On the other hand, Ag_2ZnSnS_4, Ag_8SnS_6, and Ag_8GeS_6, have attracted consideration because of their less toxicity and light absorption property in visible and near-IR region. However, only a few reports have focused on preparing these size-quantized nanocrystals for tailoring their photochemical properties. In this study, we report the preparation of Ag_8GeS_6 core and Ag_8GeS_6@ZnS core/shell QDs using a feasible liquid-phase chemical synthesis method.

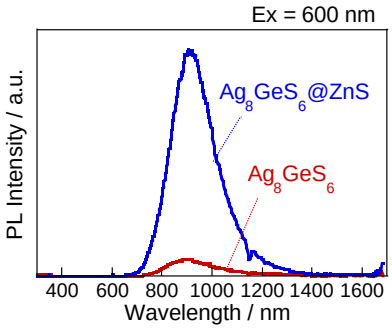


Fig. 1 PL spectra of Ag_8GeS_6 and Ag_8GeS_6@ZnS QDs in chloroform.

Ag_8GeS_6 were prepared by solution-phase synthesis, reacting a mixture of metal precursors in organic solvents. Thus-obtained QDs were surface-coated with ZnS to improve their optical properties. The QDs were dispersed in aqueous solutions by the ligand exchange with hydrophilic molecules.

The XRD analysis showed that the obtained nanocrystals had an orthorhombic Ag_8GeS_6 crystal structure. TEM measurements revealed that the prepared Ag_8GeS_6 QDs had an average particle size of 4.53 nm, while that of Ag_8GeS_6@ZnS was 5.15 nm, with estimated ZnS shell thickness of 0.31 nm. The onset wavelengths in the absorption spectra of Ag_8GeS_6 and Ag_8GeS_6@ZnS were observed at 850 nm and 830 nm, respectively. The energy gap of Ag_8GeS_6 QDs was slightly decreased from 1.45 eV to 1.37 eV with an increase in Ge/(Ge+Ag) ratio. Ag_8GeS_6 QDs with Ge/(Ge+Ag) = 0.82 exhibited a broad photoluminescence (PL) peak at 880 nm with the PL QY of about 20% (**Fig. 1**). The ZnS coating of Ag_8GeS_6 QDs enlarged the PL QY to 60%, which was considerably high in comparison to those of near-IR-emissive multinary QDs in our previous studies, such as Ag–In–Ga–Se and Ag–In–Ga–S–Se QDs [1,2]. Therefore, we conclude that the present Ag_8GeS_6@ZnS QDs are a promising probe for bio-imaging with near-IR photoluminescence.

[1] T. Kameyama, *et al*., *ACS Appl. Nano Mater*, **3**, 3275-3287 (2020).
[2] N. Rismaningsih, *et al.*, *J. Mater. Chem. C*, **9**, 12791-12801 (2021).

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Au@Pd Core-Shell Nanoparticles as Highly Active Electrocatalyst for Ethanol Oxidation

([1]*School of Materials Science, JAIST, Japan*, [2]*College of Chemistry & Materials Science, Northwest University, P. R. China*)
○Jianhui Yang,[1,2] Junfang Hao,[1,2] Shinya Maenosono[1]

Keywords: *Noble Metal, Seed Growth Method, Core-Shell Nanoparticles, Electrocatalyst*

Palladium (Pd)-based nanomaterials exhibit highly catalytic activities in a wide variety of organic coupling reactions, hydrogenation, ethanol oxidation reactions.[1-3] Among them, bimetallic Au-Pd nanoparticles (NPs) have received increasing interest due to their unique plasmonic and catalytic properties which are distinguish from that of their corresponding monometallic counterparts. Au@Pd core-shell NPs exhibit higher activity and better stability in ethanol electooxidation than those of Au-Pd alloy NPs.[4] Au was selected as the core mainly because of its several advantages, such as surface plasmon resonance, chemical stability, simple and controllable synthesis. In addition, the strain effect caused by lattice mismatch between the Au core and Pd shell may result in significant alteration on the adsorption energy, and thus enhance the surface catalytic activity.[3] Therefore, it is important to construct Au@Pd core-shell NPs with a rough and porous shell, which provide many highly active sites on their surfaces, and allow for effective use of the inner surface in core-shell NPs.

In this study, Au@Pd core-shell NPs (Fig. 1a) were synthesized by a seed mediated growth method in the presence cetyltrimethylammonium chloride. The effects of pH, surfactant, and reaction temperature on the morphologies of the resulting Au@Pd core-shell NPs were systematically studied. The size of Au@Pd core-shell NPs can be easily controlled by simply adjusting the volume of Au seed. The enhanced catalytic activity of Au@Pd core-shell NPs (Fig. 1b) is presumably related to the lattice strain created between Au core and Pd shell and the abundant surface defects on the Pd shells. The size and structure of Au@Pd core-shell NPs was optimized to maximize their highly electrocatalytic activity for ethanol oxidation reaction.

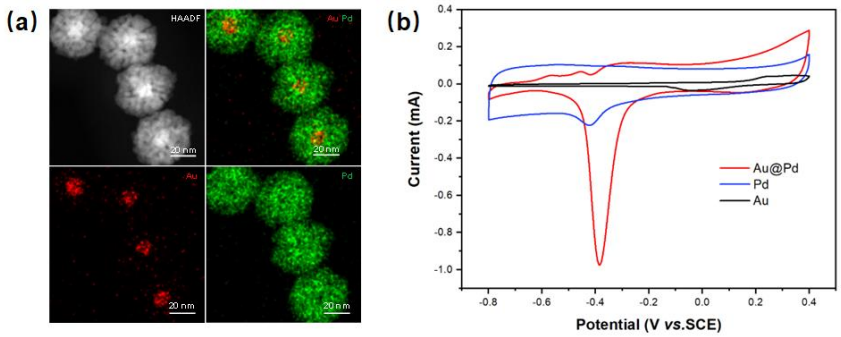


Fig. 1. (a) Transmission electron microscopy images of Au@Pd core-shell NPs. (b) Cyclic voltammograms of the Au, Pd, and Au@Pd core-shell NPs in 0.1 M KOH + 0.5 M ethanol.

(1) J.-W. Hu, J.-F. Li, B. Ren, D.-Y. Wu, S.-G. Sun, Z.-Q. Tian, *J. Phys. Chem. C* **2007**, *111*, 1105; (2) J. Xu, A. R. Wilson, A. R. Rathmell, J. Howe, M. Chi, B. J. Wiley, *ACS Nano*, **2011**, *5*, 6119; (3) L. Zhang, Z. Xie, J. Gong, *Chem. Soc. Rev.* **2016**, *45*, 3916; (4) S.-C. Hsu, Y.-C. Chuang, B. T. Sneed, D. A. Cullen, T.-W. Chiu, C.-H. Kuo, *Nano Lett.* **2016**, *16*, 5514.

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Exploration of highly active multi-element nanoalloy catalysts and analysis of their structures by statistical method

([1]Grad. Sch. Sci., Kyoto Univ., [2]Hakubi Center, Kyoto Univ., [3]JST-PRESTO, [4]URC, Kyushu Univ.,[5]Grad. Sch. Eng., Kyushu Univ, [6]*Japan Synchrotron Radiation Research Institute* [7]Grad. Sch. Sci., Osaka Pref. Univ. [8]Grad. Sch. Tech., Meiji Univ.) ○Yuto Maruta[1], Kohei Kusada[1, 2, 3], Tomokazu Yamamoto[4], Takaaki Toriyama[4], Yasukazu Murakami[4, 5], Okkyun Seo[6], Shogo Kawaguchi[6], Osami Sakata[6], Yoshiki Kubota[7], Hiromasa Kaneko[8], Hiroshi Kitagawa[1]

Keywords: Nanoparticles, Multi-element alloys, Platinum-group metals, Statistical analysis, Catalysts of hydrogen evolution reaction

Recently, multi-element nanoalloy catalysts have attracted much attention due to their high stabilities and activities. For example, equimolar platinum-group metal (PGM) quinary alloy nanoparticles (NPs) show an extremely high catalytic activity for hydrogen evolution reaction (HER)[1]. It was also found that PGM quinary alloy NPs with Pt-rich composition show a higher activity than equimolar one[2]. However, it is quite difficult to find their optimized compositions because of their compositional complexities. One possible way to overcome this difficulty is to use statistical methods.

Here, we first synthesized PGM quinary alloy NPs with more than 70 different compositions directly supported on carbon. X-ray fluorescence (XRF) analysis showed that the compositions of all the samples are consistent with nominal ratios. Their crystal structures were characterized by powder X-ray diffraction (PXRD). The lattice constant was calculated by Rietveld refinement of the XRD patterns, and their lattice constants follow Vegard's law. These results showed that PGM quinary alloy NPs were successfully synthesized with different compositions. The catalytic activity of HER was investigated by a three-electrode electrochemical measurement. Turnover frequency (TOF) which shows an activity normalized by electrochemically active surface area was used as a target variable, and the TOF was explained by a partial least square (PLS) model with only the compositional descriptors including square and cross terms (Figure A). By using the obtained statistical model, we performed virtual experiments with 50,000 compositional patterns of the quinary alloy and found the optimized composition in PdPt-rich region. Moreover, to explore an additional element for a highly active catalyst, PLS model using the descriptors of elemental features was constructed. The used averages and variances of elemental features were obtained from XenonPy, a Python open-source platform for materials informatics. This model suggested new chemical compositions of multi-element nanoalloy catalysts for HER. This result indicates that learning the elemental features of the multi-elements materials would enable an extrapolative search for other alloy systems.

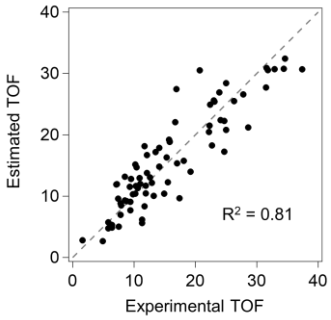


Figure A. Experimental TOF vs. estimated TOF

1) D. Wu et al., *Chem. Sci.*, 2020,11, 12731-12736. 2) Y. Maruta et al., *Chem Commun.*, 2022, 58, 6421-6424.

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Element-Selective Observation of Dynamics in High-Entropy Alloy Nanoparticles with XAFS

([1]*Grad. Sch. Sci., Kyoto Univ.*, [2]*Hakubi Center, Kyoto Univ.*, [3]*URC, Kyushu Univ.*, [4]*Grad. Sch. Eng., Kyushu Univ.*, [5]*Grad. Sch. Sci., Osaka Metro. Univ.*, [6]*JASRI/SPring-8*)
○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Yoshiki Kubota[5], Shogo Kawaguchi[6], Toshiaki Ina[6], Kazuo Kato[6], Hiroshi Kitagawa[1]
Keywords: High-Entropy Alloy; Nanoparticles; EXAFS; Debye–Waller Factor; Liquid Metal

High-entropy alloy (HEA) is multi-principal element alloy characterized by its large configurational entropy.[1] Recent studies have demonstrated that HEA nanoparticles (HEA NPs) show characteristic catalytic activities which cannot be explained in the context of conventional alloys.[2] Although the origin of their unconventional properties remains unrevealed, the variety of local coordination environment in these multiple element alloys would have a significant importance. However, due to the difficulty in analyzing the structure of these complicated and nano-sized materials, their structure, especially dynamic structure, has been poorly understood.

Our purpose of this study is to investigate the local dynamics in HEA NPs and associate it with the intrinsic nature of constituent elements. As prospective target materials, we synthesized the HEA NPs composed of liquid metal elements (Ga, In and Sn) and platinum group metal (PGM) elements (**Fig.**), which have totally different thermodynamic properties such as melting points. To discuss the dynamics, we focused on Debye–Waller factor (DWF) accessible with X-ray spectroscopies, and performed X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements under variable-temperature conditions. Notably, the element-selective analysis based on EXAFS DWF[3] illustrated that local dynamics varies with involved elements even in the same alloy. Our results support the idea of the variety in local coordination environment in HEA NPs, and moreover offer new methodology to investigate the dynamics in multiple element materials.

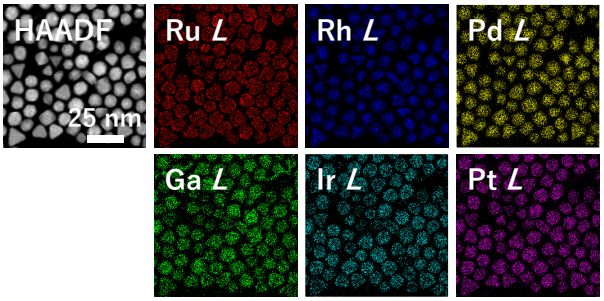


Fig. HAADF-STEM image of the Ga–PGM HEA NPs and the corresponding EDX maps.

1) B. S. Murty *et al.*, "High-Entropy Alloys", Elsevier, **2014**. 2) D. Wu *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 13833-13838. 3) P. Fornasini *et al.*, *J. Synchrotron Rad.*, **2015**, *22*, 1242-1257.

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[B444-2pm] 19. Colloid and Interface Chemistry

Chair: Toshiki Sawada, Yukikazu Takeoka

Thu. Mar 23, 2023 1:30 PM - 3:40 PM B444 (444, Bldg. 4 [4F])

[B444-2pm-01] *In situ* structural analysis of liquid crystalline photo-alignment films at the interface of low-molecular-mass liquid crystals

○Chikara Kawakami[1], Mitsuo Hara[1], Shusaku Nagano[2], takahiro Seki[3] (1. Graduate School of Engineering, Nagoya University, 2. Department of Chemistry, Rikkyo University, 3. Emeritus Professor of Nagoya University)

1:30 PM - 1:50 PM

[B444-2pm-02] Thermo-responsive Gold nanorods reversible assembly flexible control with uniform orientation using DNA brushes

○JINGYAN YANG[1], Hideyuki Mitomo[2], Yu Sekizawa[1], Yusuke Yonamine[2], Kuniharu Ijiro[2] (1. Grad. Sch. Life Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ.)

1:50 PM - 2:10 PM

[B444-2pm-03] Vesicle adhesion induced by molecular recognition mimicking tissue formation

○Tomoya Kojima[1], Koichi Terasaka[1], Kouichi Asakura[1], Taisuke Banno[1] (1. Keio University)

2:10 PM - 2:30 PM

[B444-2pm-04] A Strategy to Make Commodity Plastics Self-Healable

○Yuta Fujisawa[1], Pier-luc Champagne[1], Yoshimitsu Itoh[1,2], Takuzo Aida[1,3] (1. The University of Tokyo, 2. JST PRESTO, 3. RIKEN CEMS)

2:40 PM - 3:00 PM

[B444-2pm-05] Supramolecular hydrogel capable of showing autonomous gel-to-sol-to-gel transition in response to oxidation

○Yuki Shintani[1], Hiroshi Katagiri[2], Masato Ikeda[1,3,4] (1. The United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University, 2. Graduate School of Organic Materials Science, Yamagata University., 3. Faculty of Engineering, Gifu University., 4. Institute for Glyco-core Research (iGCORE), Gifu University)

3:00 PM - 3:20 PM

[B444-2pm-06] High thermoelectric voltage of thermocell achieved by thermo-responsive dissolution of hydrogen bond donor

○Hirotaka Inoue[1], Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

3:20 PM - 3:40 PM

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低分子液晶存在下における液晶性光配向膜の *in situ* 構造解析

(名大院工[1]・立教大理[2]・名大名誉[3]) ○河上知良[1]・原　光生[1]・永野修作[2]・関　隆広[3]

In situ structural analysis of liquid crystalline photo-alignment films at the interface of low-molecular-mass liquid crystals ([1]*Graduate School of Engineering, Nagoya University*, [2]*Department of Chemistry, Rikkyo University,* [3]*Emeritus Professor of Nagoya University*) ○ Chikara Kawakami,[1] Mitsuo Hara,[1] Shusaku Nagano,[2] Takahiro Seki[3]

Many methods have been proposed to control the orientation of liquid crystalline (LC) phases from the interface, including photo-alignment technology that utilizes surfaces with photo-alignment switching ability[1]. Photo-alignment technology for LCs has been applied to thin displays. Recently, new findings on the orientation behavior of LC molecules in the vicinity of photo-responsive surfaces have been discovered, and it remains interesting[2].

In this study, we have injected low-molecular-mass LCs into a LC cell consisting of a substrate coated with a film of side-chain LC azobenzene polymer, which is a photo-responsive surface, and evaluated the structure inside the LC cell. As a result, it was found that a hybrid LC phase formed by both mesogens was newly induced, and its order was higher than that of the LC phase formed by each mesogen alone. The time-course change of the hybrid LC phase and light responsivity will also be reported in the presentation.

Keywords : Liquid crystal; Interface; Self-assembly; Photo-responsibility; Small-angle X-ray scattering

液晶相の界面からの配向制御法はこれまでに数多く提案されている。光配向スイッチング能をもつ表面を利用した光配向技術もその一例であり[1]、薄型ディスプレイ用途で社会実装もされてきた。最近においても、光応答表面近傍の液晶分子の配向挙動に関する新たな知見が見いだされるなど、依然として興味の対象である[2]。本研究では、光応答性表面である側鎖型液晶性アゾベンゼン高分子薄膜を塗布した基板からなる液晶セルに低分子液晶を注入し、セル内部構造を評価した。その結果、両メソゲンからなるハイブリッド液晶相が新たに形成され、その秩序が各メソゲンの単独液晶相よりも高いことを見いだした。当日は、ハイブリッド液晶相構造の経時変化や光応答性を検証した結果についても併せて報告する。

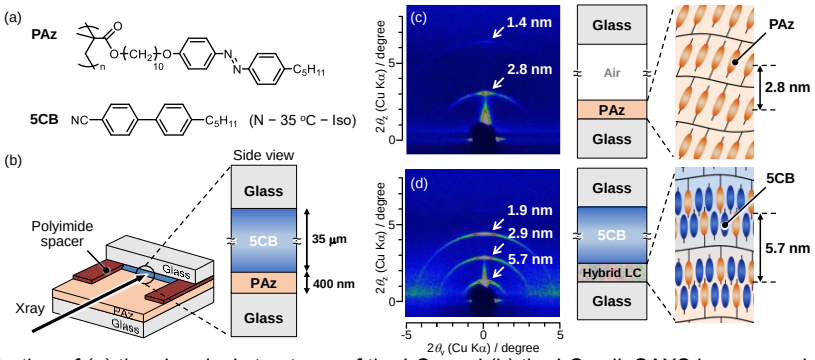


Figure Illustration of (a) the chemical structures of the LCs and (b) the LC cell. SAXS images and structural models at 50 °C (c) before and (d) after injection of 5CB into the LC cells.

1) K. Ichimura *et al.*, *Langmuir* **1988**, 4, 1214, T. Seki *et al.*, *Langmuir* **1993**, 9, 211, K. Fukuhara, *et al.*, *Nat. Commun.* **2014,** 5, 3320.
2) S. Aya *et al.*, *Langmuir* **2016**, 32, 10545, S. Aya *et al.*, *Phys. Rev. E* **2018**, 98, 052701.

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Thermo-responsive Gold nanorods reversibly assemble flexible control with uniform orientation using DNA brushes

([1]*Graduate School of Life Science, Hokkaido University*, [2]*Research Institute for Electronic Science, Hokkaido University*) ○ Jingyan YANG[1], Hideyuki MITOMO[2], Yu SEKIZAWA[1], Yusuke YONAMINE[2], and Kuniharu IJIRO[2]

Keywords: gold nanorods; assembly/disassembly; thermo-responsive; DNA brush

Rod-shaped gold nanoparticles (GNRs) have two localized surface plasmon resonance (LSPR) modes. The major axis provides a characteristic and strong plasmon mode (L-LSPR). This L-LSPR in GNRs depends on the oscillation direction of light, and also is sensitive to their configuration, such as assembly/disassembly, due to the plasmon coupling effects. Thus, it is expected that the realization of flexible control of gold nanorod orientation and assembly leads to application to optical devices with new functions. In our previous study, we found that the oligo ethylene glycol ligand modified GNRs show thermo-responsive properties, which enabled reversible assembly/disassembly in response to temperature changes in solution. Although the temperature change is useful stimuli for devices, the loss of GNRs due to precipitation and variation of GNR orientation even after side-by-side assembly limit the application of this system in optical devices. On the other hand, our group also found cationic ligand modified GNRs can be attached in a DNA brush with uniform orientation. This DNA brush system can prevent GNR precipitation and provide a flexible move for GNRs. In this study, we investigated the thermo-responsive assembly of gold nanorods with uniform orientation in DNA brushes (Figure 1).

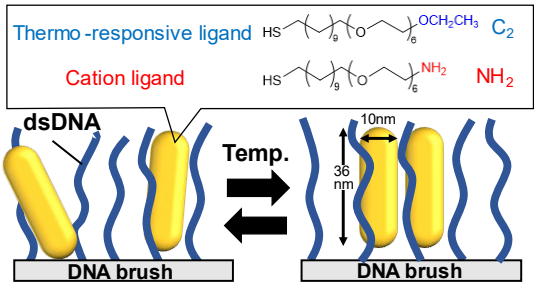


Figure 1 Schematic image of this study

Double-stranded (ds-)DNA brushes (148bp) were prepared according to our previous report. The GNR surface was modified with a mixture of hexa (ethylene glycol)-undecane thiol derivatives with ethyl and NH_2 terminus. Cationic GNRs were adsorbed on the DNA brush via electrostatic interactions and their configuration was evaluated by spectral analysis at various temperatures. The L-LSPR peak of the GNRs attached in the ds-DNA brush showed lower intensity than T-LSPR, indicating that the GNR is almost vertical to the substrate (Figure 2). Bule shifts with low intensity on L-LSPR were observed upon heating, indicating the GNRs formed side-by-side assembly with vertical orientation. These spectra were returned to the original upon cooling. These results show that thermo-responsive GNRs in DNA brushes can be a reversibly controllable plasmonic array with uniform orientation responding to temperature changes.

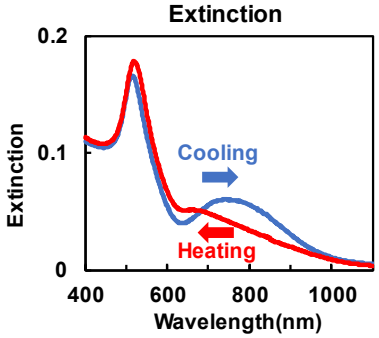


Figure 2 Extinction spectra of GNRs in a DNA brush

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Vesicle adhesion induced by molecular recognition mimicking tissue formation

([1]*Faculty of Science and Technology, Keio University*) ○ Tomoya Kojima,[1] Koichi Terasaka,[1] Kouichi Asakura,[1] Taisuke Banno[1]

Keywords: Vesicles; Molecular Recognition; Artificial Cells

In multicellular organisms, there are hierarchical organization; the levels of the organization arranged from the simplest to most complex are cells, tissues, organs, and organisms. Focusing on the functions of organs, dynamic motion such as pulsation of hearts and contraction/relaxation of muscles emerge due to the assembly of multiple cells and their cooperative behavior. Thus far, macroscopic dynamics mimicking the behavior of only one cell, such as self-reproduction[1] and taxis,[2] have been reported using vesicles. However, there are only a few reports on dynamics of artificial tissues. Herein, towards the emergence of such dynamics, we investigated adhesions of two different vesicles to form tissue structures mediated by a molecular recognition.

Focusing on salt-bridge[3] as a molecular recognition, which is a combination of ionic bonding and hydrogen bonding, several salt-bridge combinations such as guanidium, ammonium, and carboxylate ions were used comprehensively to induce vesicle adhesions. Among the tested compounds, it was revealed that adhesions between vesicles occurred efficiently when adding long-chain amine or carboxylic acid to vesicles, respectively. The ζ potential of each vesicle was opposite, suggesting the Coulombic attraction between two different vesicles. In addition, the peak shift in IR and ^{1}H NMR spectra implied that hydrogen bonding was formed between amine and carboxylic acid. To investigate the degree of mixing of lipids by the adhesions, fluorescence resonance energy transfer (FRET) was evaluated to reveal that FRET did not occur between fluorescent lipids, indicating that almost no mixing of lipids occurred. Thus, vesicle adhesions without no mixing of vesicle components were achieved by salt-bridge interactions.

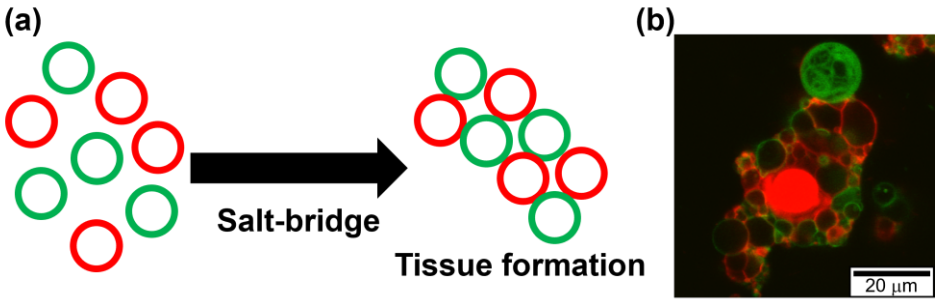


Fig. 1 (a) Schematic representation and (b) microscopic image of vesicle adhesion.

1) I. Budin *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 751−753. 2) A. Joseph *et al.*, *Sci. Adv.* **2017**, *3*, e1700362. 3) R. Mogaki *et al.*, *Chem. Soc. Rev.* **2017**, *46*, 6480−6491.

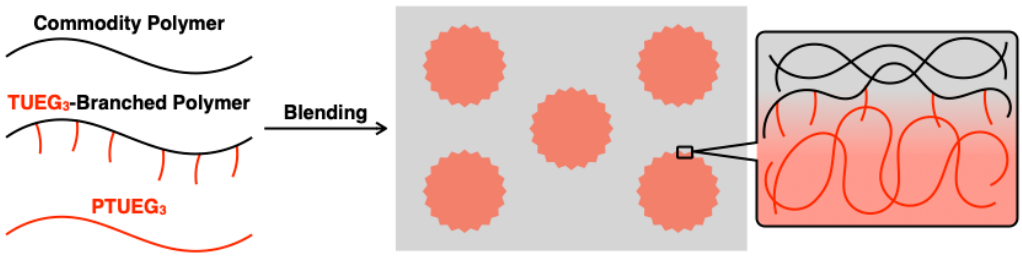
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A Strategy to Make Commodity Plastics Self-Healable

([1]*The University of Tokyo*, [2]*JST PRESTO,* [3]*RIKEN CEMS*)
○Yuta Fujisawa,[1] Pier-luc Champagne,[1] Yoshimitsu Itoh,[1,2] Takuzo Aida,[1,3]
Keywords: Self-Healing Materials; Commodity Plastics; Polymer Blends; Copolymers; Nanophase Separation

Plastic materials are indispensable for our daily life. However, plastic waste has caused a serious environmental issue. Self-healing polymers that can spontaneously repair damage would be promising for suppressing the issue of plastic waste and realizing a sustainable future. Recently, we reported that nonhealable poly(octamethylene thiourea) ($PTUC_8$) can be made to be self-healable by simply blending with a small amount of self-healable poly(ether thiourea) ($PTUEG_3$).[1] Since the polymer blends were nanophase-separated into $PTUEG_3$-rich and $PTUC_8$-rich domains, they successfully carried self-healing properties at ambient temperatures derived from $PTUEG_3$[2] while maintaining the intrinsic properties such as non-hygroscopic nature of $PTUC_8$.

If the above blending strategy can be applied to commodity plastics, self-healing plastics which would directly contribute to reducing plastic waste can be easily produced. However, even upon blending, polymers are usually immiscible with each other and end up with a macroscopic phase separation. To overcome this problem, we designed polymers with an ether thiourea ($TUEG_3$) branch and the same backbone as a target commodity polymer. The newly designed polymers can work as self-healable guests or surfactants to reduce interfacial energy and between a commodity polymer and $PTUEG_3$ and increase the miscibility between them.



1) Y. Fujisawa, Y. Nan, A. Asano, Y. Yanagisawa, K. Yano, Y. Itoh, T. Aida, *Angew. Chem., Int. Ed.* **2023**, e202214444.
2) Y. Yanagisawa, Y. Nan, K. Okuro, T. Aida, *Science* **2018**, *359*, 72.

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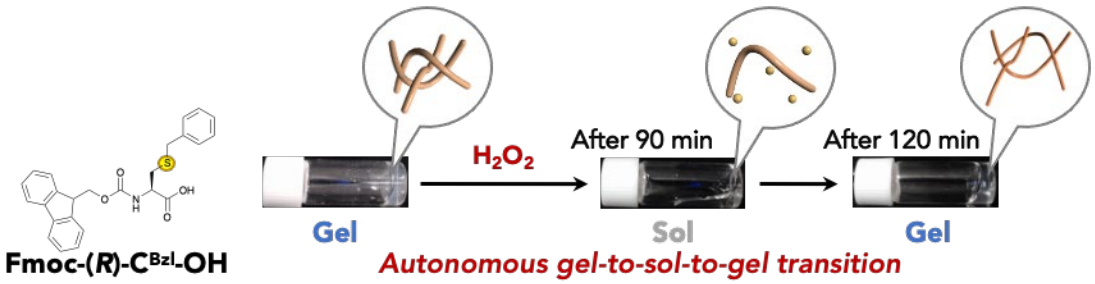
Supramolecular hydrogel capable of showing autonomous gel-to-sol-to-gel transition in response to oxidation

([1]*The United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University,* [2]*Graduate School of Organic Materials Science, Yamagata University*, [3] *Faculty of Engineering, Gifu University*, [4]*Institute for Glyco-core Research (iGCORE)*, *Gifu University*) ○Yuki Shintani,[1] Hiroshi Katagiri,[2] Masato Ikeda[1,3,4]

Keywords: Supramolecular; hydrogel; Self-assembly; Oxidation-responsiveness; Gel-sol-gel transition; Sulfide

Peptide and amino acid derivatives are considered as one of the ideal building blocks for stimulus-responsive supramolecular (bio)materials[1] because of their excellent biocompatibility and straightforward synthesis. Reactive oxygen species (ROS) are reported to be overexpressed at the sites of disease and inflammation, and thus the development of supramolecular materials including hydrogels capable of responding ROS will lead to the development of disease-oriented intelligent supramolecular biomaterials.[2] To date, ROS-responsive supramolecular nanostructures have been developed by incorporating ROS-responsive moieties (*e.g.*, sulfides, selenoether, ferrocene, thioketal, phenylboronate ester) into self-assembling molecules.

In this study, we found that a supramolecular hydrogel constructed from a cysteine derivative shows gel-to-sol macroscopic transition in response to hydrogen peroxide (H_2O_2) while back to gel state autonomously depending on the conditions (*e.g*, equivalent of H_2O_2). These unique macroscopic transitions should be related to the oxidation behavior of the sulfide moiety, and the formation of sulfoxides was indeed confirmed by HPLC and MS. Furthermore, we found that the chirality of the sulfoxide moieties has strong influence on the morphology of the supramolecular structures, which were elucidated by means of spectroscopic analysis and microscopic observations.



1) X. Du, J. Zhou, J. Shi, B. Xu, *Chem. Rev.*, **2015**, 115, 13165–13307. 2) B. Hu, Z. Lian, Z. Zhou, L. Shi, A. Yu., *ACS Appl. Bio Mater.,* **2020**, 3, 5529–5551.

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High Thermoelectric Voltage of Thermocell Achieved by Thermo-Responsive Dissolution of Hydrogen Bond Donor

([1]*The University of Tokyo*) ○Hirotaka Inoue,[1]Hongyao Zhou,[1] Teppei Yamada
Keywords: Thermocell; Hydrogen bond; Benzoquinone

Thermocell is a thermoelectric conversion device using a redox equilibrium shift by temperature change. The voltage per unit of a temperature difference (Seebeck coefficient, S_e) is a critical parameter for improving the power output and efficiency of the thermocell. S_e value of the thermocell can be boosted by the thermo-induced concentration difference between oxidized and reduced forms. For example, α-cyclodextrin captures I_3^- anion on the cold side and releases it on the hot side, which enhances the S_e value to 1.5 mV K^{-1}.[1] A higher S_e value of 3.7 mV K^{-1} was achieved by the crystallization of $Fe(CN)_6^{4-}$ with guanidinium cation.[2] This method causes the higher concentration difference between $Fe(CN)_6^{3-/4-}$, though the crystal containing the redox-active molecules impedes their diffusion and decreases the power output.[3] Here, we show the new strategy utilizing the concentration difference of a hydrogen bond donor (Figure a). Chloranil (CA) is an organic redox compound that has a couple of reduction states. Two-electron reduced form (CA^{2-}) is a stronger hydrogen bond acceptor compared with one-electron reduced form ($CA^{\bullet-}$), and Uno et al. reported the positive potential shift of $CA^{\bullet-/2-}$ with increasing hydrogen bond donor.[4] Thus, the thermo-responsive dissolution of the hydrogen bond donor can induce a significant S_e value.

We take advantage of 1,12-dodecanediol as a hydrogen bond donor. The donor solubility in acetonitrile gradually increases with elevating temperature below 50 °C and steeply rises above 50 °C. We conducted the thermoelectric measurement for the electrolyte of $CA^{\bullet-/2-}$ with 1,12-dodecanediol. The S_e value is 0.2 mV K^{-1} below 35 °C at the hot side (T_H), increases to 3.3 mV K^{-1} at 35-52 °C of T_H, and reaches 8.3 mV K^{-1} above 52 °C of T_H (Figure b). The positive S_e value, in contrast to the original negative S_e value, is attributed to the positive potential shift by increasing donor concentration at the hot side. We will discuss the mechanism in terms of the association of the donor with CA^{2-}.

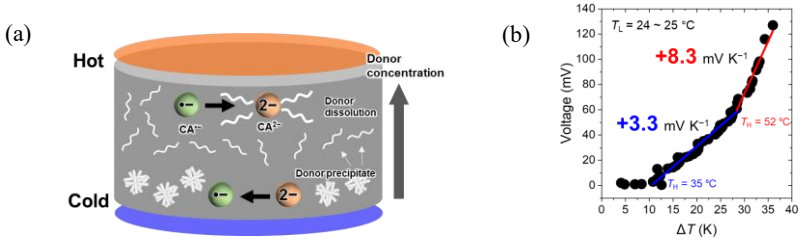


Figure (a) Schematic illustration of our thermocell. (b) Thermoelectric voltage as a function of a temperature difference between hot and cold sides.

[1] H. Zhou et al., *J Am Chem Soc* **2016**, *138*, 10502–10507. [2] J. Zhou et al., *Science (1979)* **2020**, *370*, 342–346. [3] L. Jiang et al., *ACS Appl Mater Interfaces* **2022**, *14*, 22921–22928. [4] B. Uno et al., *Journal of Organic Chemistry* **2000**, *65*, 1448–1455.

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Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B

[K206-2am] 20. Materials Chemistry -Basic and Application-

Chair: Naoki Tanaka, Yutaka Ie

Thu. Mar 23, 2023 9:00 AM - 11:30 AM K206 (K206, Lecture Hall Bldg. [2F])

[K206-2am-01] Optically tunable organic microdroplet lasers

○Hiroshi Yamagishi Yamagishi[1], Keitaro Fujita[1], Yohei Yamamoto[1] (1. University of Tsukuba)

9:00 AM - 9:20 AM

[K206-2am-02] Alkyl-π Liquid Electrets for Stretchable Mechanoelectric Generators

○Takashi Nakanishi[1], Akira Shinohara[1], Ravindra Kumar Gupta[1] (1. NIMS)

9:20 AM - 9:40 AM

[K206-2am-03] Bulk photovoltaic effect of ferroelectric liquid crystals based on extended π-conjugated units bearing lactic dimer units

○Masahiro Funahashi[1,2] (1. Kagawa Univ., 2. National Institute of Advanced Industrial Science and Technology)

9:40 AM - 10:00 AM

[K206-2am-04] Development of Functional Dye Films for Visualizing Volatile Organic Halogenated Compounds

○Kumpei Kozuka[1], Keiichi Imato[1], Yousuke Ooyama[1] (1. Hiroshima University)

10:00 AM - 10:20 AM

[K206-2am-05] Polymorphism and Mechanochromic Luminescence from Mesogenic Gold(I) Complex

○Andriani Furoida[1], Osamu Tsutsumi[1] (1. Ritsumeikan University)

10:30 AM - 10:50 AM

[K206-2am-06] Nonvolatile and highly-condensed π– gels based on alkyl–π functional molecular liquids

○Akito Tateyama[1,2], Masamichi Yamanaka[3], Takashi Nakanishi[1,2] (1. Hokkaido Univ., 2. NIMS, 3. Meiji Pharmaceutical Univ.)

10:50 AM - 11:10 AM

[K206-2am-07] Fabrication and analysis of periodic polymer structures induced by photopolymerization using scanning light

○Hirona Nakamura[1], Takuto Ishiyama[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology, 2. PRESTO, JST)

11:10 AM - 11:30 AM

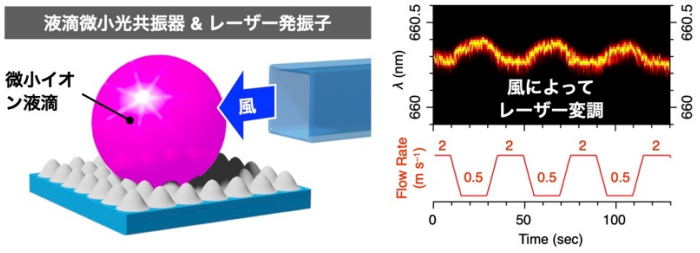
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微小有機液滴レーザーの開発と変調

（筑波大数理[1]）○山岸 洋[1]・藤田 圭太郎[1]・山本 洋平[1]
Optically tunable organic microdroplet lasers ([1]*Faculty of Pure and Applied Sciences, University of Tsukuba*) ○Hiroshi Yamagishi,[1] Keitaro Fujita,[1] Yohei Yamamoto[1]

An optical resonator is a minute object that can confine light within its body. Resonators are essential for a series of optical devices including spectrometers and laser oscillators. Since the optical properties of the resonators depend largely on their morphology and the distribution of refractive index, resonators are typically manufactured by using sophisticated methods such as photolithography, vapor deposition, and polishing. Here, we report a facile method to produce highly robust droplet resonators from a non-volatile organic liquid.[1] The droplet works as an efficient optical resonator and laser emitter when doped with an organic dye and when excited with a pulse laser. The droplet is morphologically flexible and deforms upon applying external force via air convection, which lead to the tuning of its lasing property.
Keywords :　Laser Oscillator; Droplet; Tunable Laser; Organic Liquid

光共振器は、その内部に光を閉じ込めることができる微細な素子である。光共振器は光の干渉や増幅を起こす優れた素子であり、分光器やレーザー光源といった様々な光デバイスの重要な構成要素として利用されている。これらの光共振器の光学的特性を決定しているのは、その形状と屈折率の空間分布であり、通常これらの特性はフォトリソグラフィーや真空蒸着、研磨などの技術を利用することで極めて精密に調整されている。一方、今回我々は、不揮発性の有機液体が基板上で自発的に球状の形態をとり、優れた光共振器およびレーザー発振器として働くことを見出した。[1] この手法には精密な形状・屈折率の制御が不要で、簡単に実施することができる。得られた液滴レーザーは液体で構成されていることから極めて柔軟で、気体の対流による僅かな力場に応答して形状が僅かに歪む。また、この形状の歪みによってレーザー発光特性を変調することができる。



1) H. Yamagishi, K. Fujita, Y. Yamamoto *et al.*, *under review*.

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アルキルーπ液体エレクトレットの創成と伸縮性振動発電素子への応用

（物材機構）○中西 尚志・篠原 英・GUPTA Ravindra Kumar
Alkyl-π Liquid Electrets for Stretchable Mechanoelectric Generators (*International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS)*) ○Takashi Nakanishi, Akira Shinohara, Ravindra Kumar Gupta

Energy harvesting systems with light weight, good stretchability, as well as large and stable power generation would be ideal wearable soft electronic devices applicable for healthcare and robotics applications. For these demands, “liquid electrets” which possess deformability and maintain trapped charges in the molecules can be the potential substances.[1] We have developed liquid electrets in which π-conjugated molecules such as porphyrins[2] or π-conjugated polymers[3] are wrapped with bulky yet flexible branched-alkyl chains and electrostatic charges are trapped and retained in the liquid. Stretchable and deformable mechanoelectric generators (MEGs) capable to be stretched up to 300% were constructed with those liquid electrets (Fig. 1a, b). The MEGs can respond to various frequencies below 50 Hz (Fig. 1c), in particular, known to occur in human body movement.

Keywords : Functional molecular liquids, Liquid electrets, Stretchable Mechanoelectric Generators, Energy harvesting, π-Conjugated molecules

軽量、優れた伸縮性および高安定出力発電可能な環境発電システムは、医療およびロボット応用に適用可能な理想的なウェアラブル電子素子として期待されている。自由変形可能で且つ分子内に静電荷を安定保持できる液体エレクトレットは、同目的に最適な分子材料となり得る可能性を秘めている[1]。

本研究では、ポルフィリン[2]や共役ポリマー[3]を基材に、嵩高く柔軟性に富む分岐アルキル鎖の導入により、静電荷を安定保持可能な液体エレクトレットを開発した。これら液体エレクトレットを用いた、最大 300%伸張、自由変形可能な振動発電素子は、体動領域の 50 Hz 以下の周波数において効率的な発電を示した（Fig. 1）。

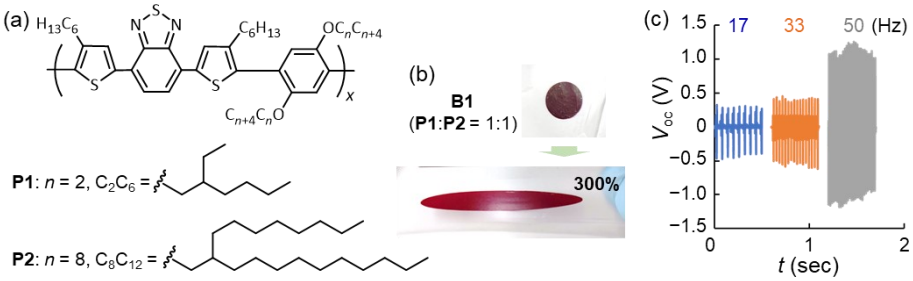


Fig. 1. (a) Chemical structure of alkylated π-conjugated polymers (**P1** and **P2**), (b) photos for equality blend film of **B1** (= **P1** + **P2**) and its stretchability up to 300%, and (c) its MEG results.

1) Z. Guo et al., *Mol. Syst. Des. Eng.* **2022**, *7*, 537. 1) A. Ghosh et al., *Nature Commun.* **2019**, *10*, 4210.
2) A. Shinohara et al., *Polym. J.* **2023**, in press, doi:10.1038/s41428-022-00725-w.

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側鎖に乳酸ダイマーを導入した拡張π共役強誘電性液晶のバルク光起電力効果

（香川大創造工[1]・産総研健康[2]）○舟橋正浩[1,2]
Bulk photovoltaic effect of ferroelectric liquid crystals based on extended π-conjugated units bearing lactic dimer units ([1]*Faculty of Engineering and Design, Kagawa University*, [2]*Health and Medical Research Institute, AIST*) ○Masahiro Funahashi[1,2]

Ferroelectric liquid crystals based on an extended π-conjugated unit exhibit spontaneous polarization and carrier transport properties. By coupling of a polarization field with the carrier transport, the ferroelectric liquid crystals exhibit a bulk photovoltaic effect in the polarized smectic crystal phases. However, the photovoltaic effect could not be retained for long time because of the dielectric relaxation. In this study, ferroelectric liquid crystals based on extended π-conjugated units bearing lactic ester dimer units were synthesized and the mesomorphic properties, ferroelectricity, carrier transport, and photovoltaic effect were investigated.
Keywords : ferroelectric liquid crystal, bulk photovoltaic effect, extended π-conjugated unit, oligothiophene, organic electronics

拡張π電子共役系を有する強誘電性液晶は、分極したスメクティッククリスタル相で自発分極と電荷輸送性を示す。分極電界と電荷輸送がカップリングすることによりバルク光起電力効果を示すことが見出されているが、分極状態が緩和するため、光起電力を長期間保持できなかった。本講演では、乳酸ダイマーを側鎖に導入した拡張π電子共役強誘電性液晶 **1** を合成した（Fig. 1 (a)）。化合物 **1** は 105℃以下で強誘電性スメクティック相を示す。二枚の ITO 電極からなる厚さ 2 μm のセルに化合物 **1** を注入し、直流電圧を印加しながら等方相から冷却すると分極したスメクティック相が出現する。白色光（2.4 mWcm^{-2}）を照射すると、バルク光起電力効果による光電流が観測された（Fig. 1 (b)）。開放電圧は 1.0 V、短絡電流は 12 μAcm^{-2} であった。PCBM を添加すると、光電流は約一桁増大した（Fig. 1 (c)）。PCBM を添加した試料での開放電圧は 0.95 V、短絡電流は 75 μAcm^{-2} であった。分極状態は 1 週間以上保持された。側鎖部位に複数の極性官能基を導入したため、側鎖の運動性が低下したためと考えられる。

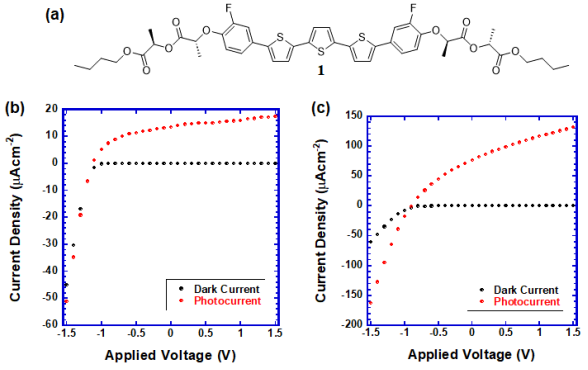


Fig. 1 (a) Molecular structure of compound **1**. Current-voltage characteristics in the polarized smectic crystal phase of (b) pure compound **1** and (c) PCBM-doped compound **1** for white light illumination (20 mWcm^{-2})

1) M. Funahashi, High open-circuit voltage in the bulk photovoltaic effect for the chiral smectic crystal phase of a double chiral ferroelectric liquid crystal doped with a fullerene derivative, *Mater. Chem. Front.*, **5**, 8265–8274 (2021).

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揮発性有機ハロゲン化合物を可視化する機能性色素フィルムの開発

（広大院先進理工[1]）○小塚 訓平・今任 景一・大山 陽介

Development of Functional Dye Films for Visualizing Volatile Organic Halogenated Compounds (*Graduate School of Advanced Science and Engineering, Hiroshima University*)

○Kumpei Kozuka, Keiichi Imato, Yousuke Ooyama

Solvatochromism is the phenomenon that the shift of the photoabsorption band due to the difference of solvent polarity. Meanwhile, we found that a D-π-A pyridinium dye exhibits a specific solvatochromism in halogenated solvents, that is, organohalogenochromism (OHC). Indeed, photoabsorption bands of the D-π-A pyridinium dye in halogenated solvents show a bathochromic shift compared with those in the non-halogenated solvents. In this work, in order to develop functional dye materials for visualizing volatile organic halogenated compounds (VOHCs), we prepared the copolymer of the D-π-A pyridinium dye with styrene. This polymer expresses OHC in halogenated solvents as with D-π-A pyridinium dye. In this presentation, we will report the optical sensing properties of the copolymer films to VOHCs.

Keywords : Pyridinium Dye; Volatile Organic Halogenated Compounds; Organohalogenochromism; Photoabsorption Wavelength; Polymer

ソルバトクロミズムとは溶媒の極性の変化によって色素の光吸収帯がシフトする現象のことである。一方で、当研究室では新規に合成した D-π-A 型ピリジニウム色素 **OD2**（**Fig. 1**）の光吸収帯が、溶媒の極性に依存せず、ハロゲン溶媒中において特異的に長波長シフトするオルガノハロゲノクロミズム（OHC）特性を有することを見出している[1, 2]。本 OHC は、色素-ハロゲン溶媒分子間相互作用やハロゲン溶媒中における色素分子の電荷の非局在化に起因していることが示唆されているが、OHC の詳細なメカニズムは明らかになっていない。そこで本研究では、色素-ハロゲン溶媒分子間相互作用から OHC を解明すること、および機能性材料化を図ることを目的として、OHC 色素骨格を含有するポリマー**poly(OD2-*co*-styrene)**を合成した（**Fig. 1**）。得られたポリマーの光吸収帯はハロゲン溶媒中において長波長シフトしており、OHC 特性を有することを確認した（**Fig. 2**）。本発表では、ポリマーフィルムの揮発性有機ハロゲン化合物曝露（VOHCs）に伴う光吸収スペクトル測定を試みた結果について報告する。

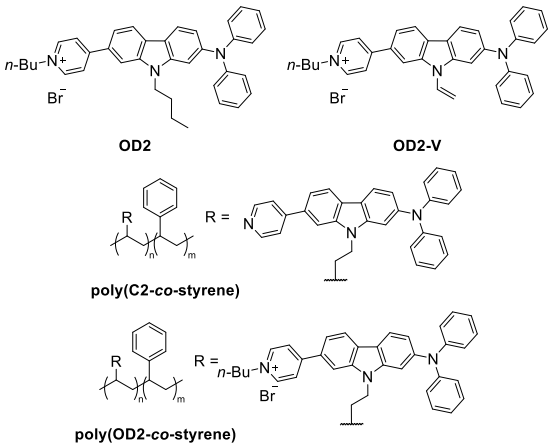


Fig. 1 Chemical structures of **OD2**, **OD2-V**, **poly(C3-*co*-styrene)** and **poly(OD2-*co*-styrene)**.

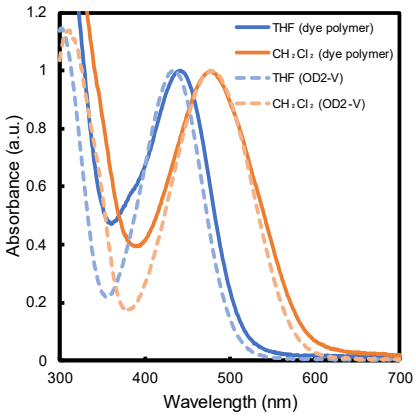


Fig. 2 UV-vis spectra of **poly(OD2-*co*-styrene)** (solid lines) and **OD2-V** (dotted lines) in THF and CH_2Cl_2.

1) Y. Ooyama, Y. Oda, T. Mizumo and J. Ohshita, *Tetrahedron,* **2013**, *69*, 1755-1760.
2) T. Higashino and Y. Ooyama, *Chem. Lett.*, **2021**, *50*, 1530-1533.

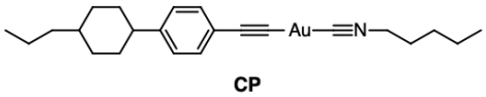
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Polymorphism and Mechanochromic Luminescence from Mesogenic Gold(I) Complex

([1]*Graduate School of Life Sciences, Ritsumeikan University*) ○Andriani Furoida,[1] Osamu Tsutsumi[1]

Keywords: Aggregation-Induced Emission; Polymorphism; Mechanochromic Luminescence; Gold Complex

The development of organic molecules with aggregation-induced emission (AIE) behavior is of great importance in the field of organic optoelectronics. In recent years, there has been growing interest in materials that can show distinct solid-state luminescence from one chromophore by making use of polymorphism behavior. Polymorphic materials possess more than one crystalline phase, where each phase shows different emission color. Mechanochromic luminescence (MCL) is another useful feature in which mechanical stimuli (e.g., grinding and stretching) enable emission color tuning which correlates with the change in aggregated structure. Organic materials with such properties have wide possible applicability in sensors, probes, and memory devices.[1] In particular, gold complex is an attractive material to induce both strong luminescence in condensed phase and stimuli-responsive luminescence behavior owing to the unique Au–Au (aurophilic) system.[2]



CP

Figure 1. Molecular structures of synthesized gold complex.

In this study, we designed and synthesized cyclohexylphenylacetylide gold(I) complex bearing isocyanide ligands (Figure 1). This type of rod-shaped gold complex having ligands with less steric hindrance around Au atoms is favorable to manifest aurophilic interaction. Photophysical behaviors of the gold complex in various states were discussed based on not only its primary structure but also aggregated structure. Interestingly, **CP** exhibited intriguing stimuli-responsive luminescence by having both polymorphism and MCL properties. Distinct emission color was observed in **CP** under different recrystallization conditions (Figure 2). Such emission color-dependent is likely to attribute to the change in the aggregated structure between crystal polymorphs as well as the ground crystal.

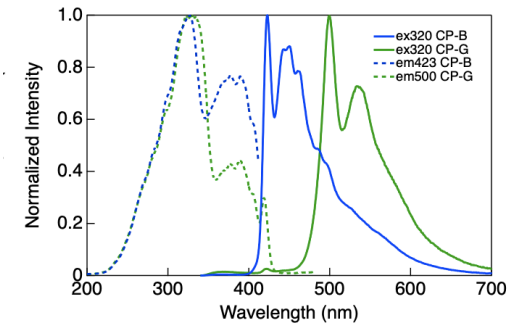


Figure 2. Emission and excitation spectra of **CP** crystal polymorphs.

1) Y. Sagara and T. Kato, *Angew. Chem., Int. Ed.*, **2008**, 47, 5175.
2) K. Fujisawa, N. Kawakami, Y. Onishi, Y. Izumi, S. Tamai, N. Sugimoto and O. Tsutsumi, *J. Mater. Chem. C*, **2013**, 1, 5359.

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Nonvolatile and highly-condensed π-gels based on alkyl-π functional molecular liquids

([1]*Graduate School of Life Science, Hokkaido University*, [2]*Internatinal Center for Materials Nanoarchitectonics, National Institute for Materials Science*, [3]*Meiji Pharmaceutical University*) ○Akito Tateyama,[1,2] Masamichi Yamanaka,[3] Takashi Nakanishi[1,2]
Keywords: π-Gels; Functional Molecular Liquids; Low Molecular Weight Gelator

In developing soft electronics and soft robotics, functional soft materials are realized as one of the crucial key components. By modifying a functional π-conjugated unit with bulky yet flexible branched alkyl chains, solvent-free functional liquids (alkyl-π liquids) have been developed[1]. Such alkyl-π liquids have the advantages of deformability and ease of molding and processing, however, they require strict encapsulation to prevent leakage and support materials for device fabrication.

Herein, we have attempted to gelate alkyl-π liquids with a low molecular weight gelator. Since conventional π-gels have functional π-units introduced in the gelator molecule, the content of π-units is only a few wt%. In addition, the π-gels are degraded over time because of the volatilization of the solvent. In contrast, alkyl-π liquid gels can contain π-units up to 59 wt% and are nonvolatile.

In this presentation, we mainly utilize a liquid naphthalene (**1**) possessing a branched alkoxy chain (Fig. 1a) as a gel medium, and a gelator containing a unit for intermolecular hydrogen bonding (**2**)[2] (Fig. 1b). Although compound **1** exhibits low viscous fluid (Fig. 2a), it produced a gel state by the addition of 1 wt% of gelator **2** (Fig. 2b). Measurements of UV absorption and fluorescence spectra showed that the optical properties of the aboriginal naphthalene liquid were maintained in the gel state. Besides, we demonstrate gel formation of the other alkyl-π liquids containing a carbazole or a pyrene and wax gels with linear alkanes. Those instances exhibit the breadth of possible applications of these alkyl-π liquid based π-gels.

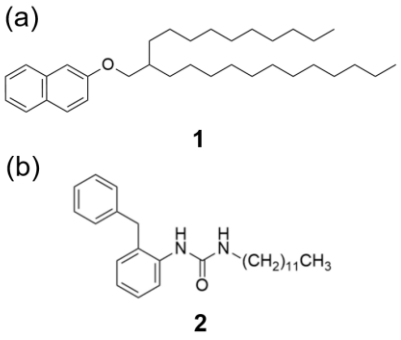


Fig.1 Molecular structures of (a) a liquid naphthalene **1**, and (b) a gelator **2**.

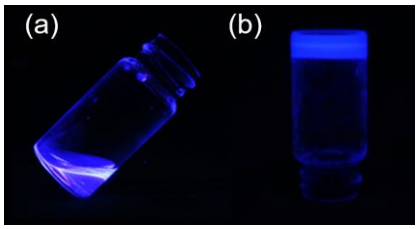


Fig.2 Images of (a) neat liquid **1**, and (b) gel formed from liquid **1** with 1 wt% gelator **2**, under 365 nm UV irradiation.

1) T. Machida, et al., *J. Mater. Chem. C*, **2021**, *9*, 10661-10667. 2) T. Komiyama, et al., *Chem. Asian. J.*, **2021**, *16*, 1750-1755.

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Fabrication and Analysis of Periodic Polymer Structures Induced by Photopolymerization Using Scanning Light

([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*, [2]*PRESTO, JST*)
○Hirona Nakamura,[1] Takuto Ishiyama,[1] Miho Aizawa,[1,2] Kyohei Hisano,[1] Shoichi Kubo,[1] Atsushi Shishido[1]

Keywords: Phase Separation; Periodic Structure; Photopolymerization; Liquid Crystal

Control of phase-separated structures has been studied for many years as a method for designing highly functional materials due to the close relationship between material properties and phase-separated structures.[1–3] Nevertheless, controlling the mesoscopic orientation of phase-separated structures is still a challenge. Recently, we discovered the spontaneous formation of periodically aligned phase-separated structures during photopolymerization with a scanned slit light;[4] however, the formation mechanism remains unclear. In this study, optical analyses of the periodic structures fabricated under various photopolymerization conditions were conducted to explore the formation mechanism towards the arbitrary control of the periodic structures.

A mixture consisting of an anisotropic monomer A6CB, a crosslinker HDDMA, and a photoinitiator Irgacure651 was prepared (**Figure 1**). The mixture was injected into a handmade glass cell with a thickness of 3 μm at its isotropic temperature (150 °C), and photopolymerized by scanning a slit UV light to fabricate a polymer film. Subsequently, the film was cooled down to room temperature at a cooling rate of 1 °C/min.

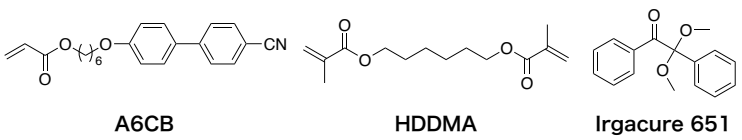


Figure 1. Chemical structures used for photopolymerization.

The observation of the film with a polarized optical microscope revealed that a micrometer-sized periodic structure formed in the polymer film. When a He-Ne laser beam (λ = 633 nm) was incident on the obtained film, the diffracted light appeared along the light scanning direction. The diffraction efficiency depended on the photopolymerization conditions, such as temperature, light intensity, and light scanning rate. This result indicates that the photopolymerization condition affects the morphology of the periodic structure. Furthermore, we performed an *in-situ* observation of the photopolymerization process using a polarized optical microscope equipped with a digital UV light processor, and analyzed the relationship between the photopolymerization process and the formation of periodic structures.

1) K. Yamanaka, T. Inoue, *Polymer* **1989**, *30*, 662. 2) Y. Yamashita, K. Komori, T. Murata, H. Nakanishi, T. Norisuye, T. Yamao, Q. Tran-Cong-Miyata, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **2018**, *9*, 015009. 3) S. Biria, F. H. Chen, S. Pathreeker, I. D. Hosein, *Adv. Mater.* **2018**, *30,* 1705382. 4) M. Aizawa, K. Hisano, A. Shishido, *The 97th Annual Meeting of CSJ* **2017**, 1E7-15.

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[K206-2pm] 20. Materials Chemistry -Basic and Application-

Chair: Hajime Shigemitsu, Takashi Nakanishi

Thu. Mar 23, 2023 1:10 PM - 3:40 PM K206 (K206, Lecture Hall Bldg. [2F])

[K206-2pm-01] Amine and CO_2 Responsiveness of Ring-Perfluorinated Dye and Its Optical Properties

○Ryunosuke Kani[1], Yasuhiro Kubota[1], Toshiyasu Inuzuka[1], Kazumasa Funabiki[1] (1. Gifu University)

1:10 PM - 1:30 PM

[K206-2pm-02] Control of Molecular Alignment in Liquid-Crystalline Polymer Particles Synthesized by Dispersion Polymerization

○Tomoki Shigeyama[1], Kyohei Hisano[1], Osamu Tsutsumi[1] (1. Ritsumeikan Univ.)

1:30 PM - 1:50 PM

[K206-2pm-03] Development of Ladder-Type Fused pi-Conjugated Units Bearing Spirocyclopentadithiophenes for Non-Fullerene Acceptors in Organic Solar Cells

○Kai Wang[1], Takuji Seo[1], Hajime Nitta[1], Seihou Jinnai[1,2], Yutaka Ie[1,2] (1. Osaka Univ., 2. ICS-OTRI, Osaka Univ.)

1:50 PM - 2:10 PM

[K206-2pm-04] Effect of the tether length of reagents with two reactive sites on the band gap of single-walled carbon nanotubes

○Yui Konno[1], Rina Morooka[1], Tatsunari Morishita[1], Pei Zhao[2], Daiki Uchida[1], Michio Yamada[1], Masahiro Ehara[2], Yutaka Maeda[1] (1. Tokyo Gakugei University, 2. Institute for molecular science)

2:10 PM - 2:30 PM

[K206-2pm-05] Biomolecular Machines as Functional Building Blocks in Programmed Nanostructures

○Kiyoshi Morishita[1,2], PK Hashim[1], Haruaki Yanagisawa[1], Masahide Kikkawa[1], Hideki Taguchi[3], Takuzo Aida[1,2] (1. The University of Tokyo, 2. RIKEN CEMS, 3. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

[K206-2pm-06] Regulation of reversible self-assembly ability by substitution and deletion of amino acid residues of elastin peptide $(FPGVG)_n$ analogs

○Keitaro Suyama[1], Shogo Sumiyoshi[2], Marin Shimizu[2], Naoki Tanaka[2], Keisuke Tomohara[1], Suguru Taniguchi[3], Iori Maeda[4], Takeru Nose[1,2] (1. Faculty of Arts and Science, Kyushu University, 2. Department of Chemistry, Faculty and Graduate School of Science, Kyushu University, 3. Division of Biomedical Sciences, Fukuoka Dental College, 4. Department of Physics and Information Technology, Kyushu Institute of Technology)

3:00 PM - 3:20 PM

[K206-2pm-07] Characterization of Artificial Protein Nanocage-Cross-Linked-hydrogels

○Nasu Erika[1], Norifumi Kawakami[1], Ryoichi Arai[2], Kenji Miyamoto[1] (1. Keio University, 2. Shinshu University)

3:20 PM - 3:40 PM

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Amine and CO_2 Responsiveness of Ring-Perfluorinated Dye and Its Optical Properties

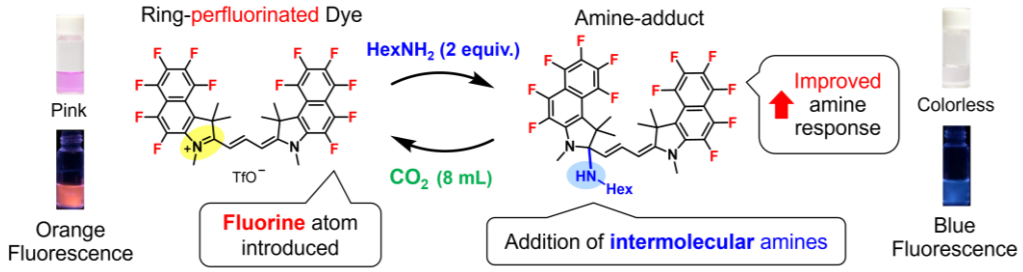
([1]*Graduate School of Engineering, Gifu University,* [2]*Faculty of Engineering, Gifu University,* [3]*Life Science Research Center Division of Instrumental Analysis, Gifu University.*) ○ Ryunosuke Kani,[1] Toshiyasu Inuzuka,[3] Yasuhiro Kubota,[2] Kazumasa Funabiki [2]

Keywords: Functional organic dyes, Fluorine chemistry, Amine-responsive materials, CO_2-responsive materials

Among organic dyes, polymethine cyanine dyes are one of the promising motifs for stimuli-responsive dyes because of their good optical properties and the ability to easily adjust absorption and fluorescence wavelengths by changing the length of the methine chains.[1]

Cyanine dyes have been reported to react with a cyanide ion[2] and intramolecular amino group[3] that add to the iminium moiety. However, there have been no reports of cyanine dyes responding to intermolecular amines or CO_2, because cyanine dyes have poor reactivity, and the optical properties are not readily changed by intermolecular amines or CO_2.

In this work, the introduction of a number of fluorine atoms into the aromatic rings of cyanine dye increases the reactivity of the amine more than 3000-fold compared to the dye without fluorine atoms, and the addition reaction is completed by adding only two equivalents of intermolecular amine. At this time, this solution changed from pink to colorless and from orange fluorescence to blue fluorescence.[4] Furthermore, we also discovered that bubbling CO_2 into the solution can recover absorption and fluorescence to over 90% of the original dye, and the solution turned pink and orange fluorescence was observed. This work is the first example of an intermolecular amine- and CO_2-responsive cyanine dye.



1) X. Peng et al., *Chem Rev* **2016**, *116*, 7768-7817. 2) J. Cheng et al., *Tetrahedron Lett.* **2009**, *50*, 6668−6671 etc. 3) K. Miki et al., *Chem. Commun.* **2017**, *53*, 7792-7795 etc. 4) R. Kani et al., *RSC Adv.*, **2022**, *12*, 25587-25592.

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Control of Molecular Alignment in Liquid-Crystalline Polymer Particles Synthesized by Dispersion Polymerization

(*Collage of Life Sciences, Ritsumeikan University*) ○Tomoki Shigeyama, Kyohei Hisano, Osamu Tsutsumi

Keywords: Liquid-Crystalline Polymer; Dispersion Polymerization; Polymeric Particles

Liquid crystal polymers (LCPs) show advanced optical and mechanical functionalities depending on their molecular alignment. The molecular alignment can be reversibly controlled by external stimuli, so LCPs can be used as soft-sensors and actuators. Since these functionalities appear when the liquid crystals are aligned over a relatively long range (> 1 μm), the development of alignment control methods is important for the application of LCPs. In general, low-molecular-weight liquid crystals can be easily aligned over a long range. On the other hand, LCPs easily form very small domains (~ 100 nm) because the alignment is inhibited by the main chain. Therefore, to achieve alignment control of LCPs, a polymerization of aligned liquid crystalline monomers have been employed. In this method, the monomers must exhibit liquid crystalline phase. Thus, it is difficult to fabricate an aligned LCPs from monomers that exhibit liquid crystalline phase only after polymerization. Thus, a versatile method to control molecular alignment in LCPs is required.

In this study, we achieved to control molecular alignment in LCPs by dispersion polymerization which is a versatile and simple method to synthesize the polymer particles. In the dispersion polymerization, monomers, a stabilizer, and an initiator are dissolved in the poor solvent for the produced polymer. As a result, the produced polymer precipitates and micro-sized particles can be obtained. We fabricated monodispersed chiral-nematic LCP particles with the size of 2.6 ± 0.1 μm (Figure 1a). Transmission electron microscopy (TEM) observation of the cross-section revealed stripe pattern arising from helical molecular alignment of chiral-nematic LCP (Figure 1b). From the uniform stripe pattern, we concluded that LCP was aligned over a long range during dispersion polymerization. We expect that this alignment was formed during the nucleation-growth process of LCP precipitation. Actually, the growth of molecular alignment can be observed by tracing the particle growth process during dispersion polymerization. This method can be applied to wide range of monomers as long as they are soluble in a polymerization solvent. We expect this method will be a versatile control method of molecular alignment in LCPs.

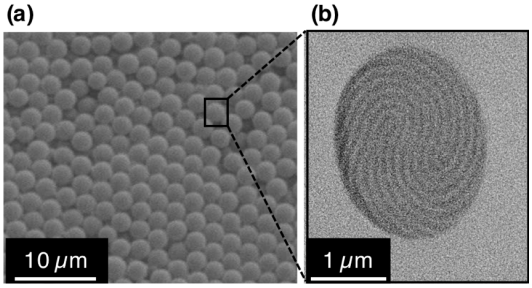


Figure 1. (a) Scanning electron microscope image and (b) TEM image of a chiral-nematic LCP particle of this study.

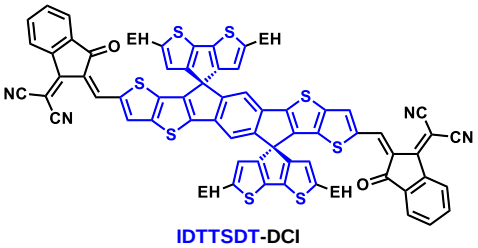
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Development of Ladder-Type Fused π-Conjugated Units Bearing Spirocyclopentadithiophenes for Non-Fullerene Acceptors in Organic Solar Cells

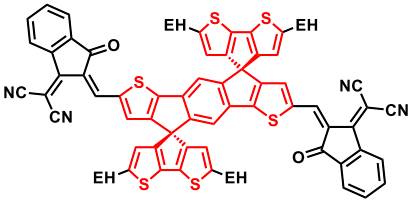
([1]*SANKEN, Osaka University*, [2]*ICS-OTRI, Osaka University*) ○Wang Kai,[1] Takuji Seo,[1] Hajime Nitta,[1] Seihou Jinnai,[1,2] Yutaka Ie[1,2]

Keywords: Organic Solar Cells, n-Type Organic Semiconductors, π-Conjugated Systems, Electron Acceptors, Non-fullerene Acceptors

Fused polycyclic aromatic compounds are attracted attention as π-conjugated units for organic donor and acceptor materials for organic solar cells (OSCs) because of their unique optical and electronic functions derived from the rigid π-conjugated plane. Recently, we have reported that cyclopentene annelated thiophene with spiro-substituted alkylfluorene was effective for the rigidification of the π-conjugated framework and exhibited good OSC characteristics as non-fused non-fullerene acceptors.[1] In this study, we designed and synthesized rigid π-conjugated skeletons **IDTTSDT** and **IDTSDT** by introducing spiro-substituted dithiophenes into fully fused ladder-type π-conjugated skeleton, and developed **IDTTSDT**- and **IDTSDT**-based non-fullerene acceptors (**IDTTSDT-DCI** and **IDTSDT-DCI**).



IDTTSDT-DCI



IDTSDT-DCI

On UV-vis absorption spectra in chloroform, **IDTTSDT-DCI** and **IDTSDT-DCI** showed the maximum absorbance peak at 692 nm and 678 nm, respectively. Differential pulse voltammetry measurements showed the first reduction peaks with the potentials of –0.81 and –0.78 V vs. Fc/Fc^+, respectively. Based on these values, the lowest unoccupied molecular orbital energy levels of **IDTTSDT-DCI** and **IDTSDT-DCI** were estimated to be –3.85 and –3.82 eV, respectively. The OSC devices using **IDTTSDT-DCI** and **IDTSDT-DCI** as acceptor materials, and PBDB-T (CAS No. 1415929-80-4) as a donor material showed good OSC characteristics (Figure 1). It will be discussed the effect of extended π-conjugation on the physical properties and OSC performances.

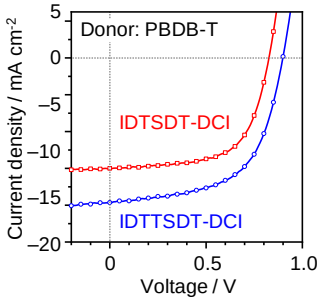


Figure 1. *J–V* curves of OSC device.

1) S. Jinnai, K. Murayama, K. Nagai, M. Mineshita, K. Kato, A. Muraoka, A. Yamakata, A. Saeki, Y. Kobori, Y. Ie, *J. Mater. Chem. A* **2022**, *10*, 20035.

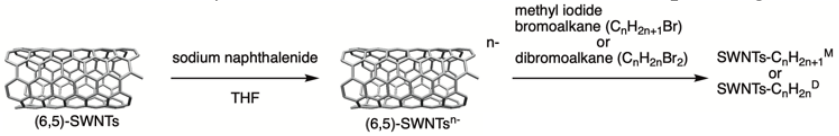
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Effect of the tether length of reagents with two reactive sites on the band gap of single-walled carbon nanotubes

([1] *Department of Chemistry, Tokyo Gakugei University,* [2] *Research Center for Computational Science, Institute for Molecular Science*)
○ Yui Konno[1], Rina Morooka[1], Tatsunari Morishita[1], Pei Zhao[2], Daiki Uchida[1], Michio Yamada[1], Masahiro Ehara[2], Yutaka Maeda[1]
Keywords: Carbon nanotube, Photoluminescence, wavelength control, chirality separation

The structure of single-walled carbon nanotubes (SWNTs) can be defined by the chiral indices, (n,m), which specify its perimeter vector. Semiconducting SWNTs show characteristic photoluminescence (PL) peaks in the near-infrared region, with excitation and emission wavelengths dependent on the chiral index.[1] Recently, it has been revealed that the functionalization of SWNTs is effective to introduce quantum defects that emerge new PL in the red-shifted region. For instance, butylation of (6,5) SWNTs emerges PL at ~1100 nm (E_{11}^{*}) and ~1230 nm (E_{11}^{**}).[2] Additionally, (6,5) SWNTs functionalized using 1,2-bis(bromomethyl)benzene, which is structurally restricted to cycloadditions, resulted in the highly selective emergence of an E_{11}^{**} PL peak at 1231 nm. Recently, the reductive alkylation, as shown in the following scheme, SWNTs by using dibromoalkane ($C_nH_{2n}Br$, n = 3–5) showed a dominant peak in the range of 1215–1231 nm depending on the alkyl chain length of the dibromoalkane used.[3] These results suggested the cycloaddition to SWNTs by using dibromoalkanes.

Here, extending the previous scope in cyclization addition of SWNTs, SWNTs were reductively alkylated with a series of bromoalkanes ($C_nH_{2n+1}Br$, n = 1–4, 8) and dibromoalkanes ($C_nH_{2n}Br_2$, n = 3–8) to evaluate the effect of the length and bulkiness of the alkyl chain on the PL properties. The functionalization of SWNTs with dibromoalkanes ($C_nH_{2n}Br$, n = 3–5) exhibits a single E_{11}^{**} PL peak, whereas functionalization with dibromoalkanes with n = 6–8 emerged two new PL peaks (E_{11}^{*} and E_{11}^{**}PL), similar PL property with corresponding bromoalkanes. In addition, separation of functionalized SWNTs based on the chirality was conducted to reveal the effect of the functionalization on the PL properties in various SWNTs.[4,5] To gain insight into the origin of new PL peaks depending on the alkyl chain lengths of dibromoalkanes, the thermodynamic stabilities and transition energies of expected cyclization products were estimated by theoretical calculations for the corresponding model compound.



Scheme. Reductive alkylation of SWNTs.

1) D. Janas, *Chem. Soc. Rev.* **2002**, *7*, 2860. 2) Y. Maeda et al. *Nanoscale* **2016**, *8*, 16916. 3) Y. Maeda et al. *RSC Adv*. **2019**, *9*, 13998. 4) H. Kataura et al. *Carbon* **2018**, *132*, 1. 5) Y. Maeda et al. *J. Phys. Chem. C* **2020**, *124*, 21886.

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Biomolecular Machines as Functional Building Blocks in Programmed Nanostructures

([1]*The University of Tokyo*, [2]*RIKEN Center for Emergent Matter Science*, [3]*Tokyo Institute of Technology,*) ○ Kiyoshi Morishita,[1,2] P.K. Hashim,[1] Haruaki Yanagisawa,[1] Masahide Kikkawa,[1] Hideki Taguchi,[3] Takuzo Aida[1,2]

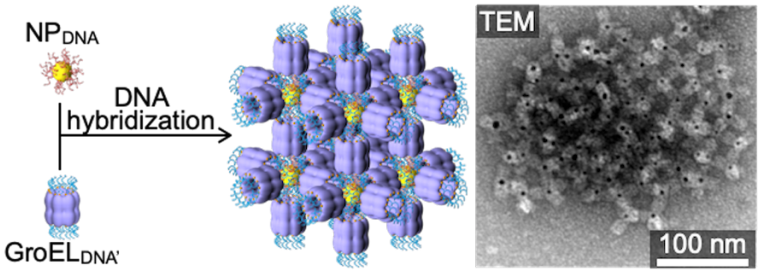
Keywords: Supramolecular chemistry; Biomolecular machines; GroEL; Nanomaterials; Self-assembly

Biomolecular assembly is a requisite to the emergence and diversification of life on earth. However, considering the wide diversity of biomolecule structures and functions, relatively little has been applied to synthetic systems.[1]

Here we employ the biomolecular machine GroEL[2] as a supramolecular linker between nanoparticles to construct porous 3D clusters. GroEL is a large (800 kDa, 14.6 × 13.7 nm) barrel-shaped chaperonin protein that, in nature, assists in the refolding of denatured proteins with its hydrophobic cavities and ATP-dependant conformational motions.

We append DNA strands to the apical domains of GroEL[3] ($GroEL_{DNA}$) and complementary strands to 5-nm-diameter gold nanoparticles ($NP_{DNA'}$). The annealed mixture affords porous clusters with a single homeotropically-aligned GroEL unit linking NPs, as confirmed by TEM, cryoEM and cryoEM tomography. The small NPs accommodate a maximum of 6 $GroEL_{DNA}$ units, resulting in a 3D network with a NP-NP center-to-center distance of 33 nm. The large pores of the clusters, which are an order of magnitude larger than those of conventional supramolecular porous materials, permits the exploration of an expanded view of host-guest chemistry. The loading of a series of poly(ethylene glycol) (PEG)-appended GroELs as ultra large macromolecular guests is evaluated, showing a size-based guest selectivity on the order of several tens of nanometers.

Cluster growth could be monitored by dynamic light scattering (DLS) and manipulated in-situ by heating or adding either of the monomer species. Further, the GroEL units in the assembled state retain their ATPase activity, highlighting the dynamic nature of the clusters. Finally, the versatility of GroEL as a building block is demonstrated though the construction of porous clusters having 3 $GroEL_{DNA}$ units linking adjacent $NP_{DNA'}$.



1) J. Zhu, et al., *Chem. Rev.* **2021**, *121*, 13701. 2) S. Sim, T. Aida, *Acc. Chem. Res.* **2017**, *50*, 492. 3) D. Kashiwagi, et al., *J. Am. Chem. Soc.* **2018**, *140*, 26.

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Regulation of reversible self-assembly ability by substitution and deletion of amino acid residues of elastin peptide $(FPGVG)_n$ analogs

(*[1]Faculty of Arts and Science, Kyushu University, [2]Department of Chemistry, Faculty and Graduate School of Science, Kyushu University, [3]Division of Biomedical Sciences, Fukuoka Dental College, [4]Department of Physics and Information Technology, Kyushu Institute of Technology*) ○Keitaro Suyama[1], Shogo Sumiyoshi[2], Marin Shimizu[2], Naoki Tanaka[2], Keisuke Tomohara[1], Suguru Taniguchi[3], Iori Maeda[4], Takeru Nose[1,2]

Keywords: Elastin-like Peptide; Thermoresponsive Material; Reversible Self-assembly

Elastin-like peptides (ELPs) are temperature-responsive molecules derived from repetitive sequences of elastin. ELPs exhibit temperature-dependent reversible phase transition under physiological conditions. Owing to their reversible self-assembly ability, ELPs are expected to be applied in various applications as biomaterials with a low environmental impact. It has been revealed that self-assembly ability of ELPs is enhanced with increasing peptide chain length, peptide concentration, and hydrophobicity of peptide sequences, respectively. Previously, we have developed a phenylalanine-containing ELP, $(FPGVG)_n$,[1] which exhibited strong coacervation ability at a significantly low number of repetitions (n = 5) and low concentration in water. In this study, we investigated whether the self-assembly ability of synthetic short-chain ELP, $(FPGVG)_5$, (F5) could be controlled by substitution of a single amino acid residue or deletion of residue(s) in its sequence.

F5, used as the standard ELP, and a series of F5-F1X analogs, which substituted the *N*-terminal Phe residue of F5 with various amino acids, were synthesized by the conventional solid-phase method using the Fmoc strategy. In addition, another series of short ELP analogs, $(FPGV)_n$ (n = 2–5; deletion of Gly from the repeating sequence, FPGVG) were also synthesized. The self-assembly ability of the synthesized ELP analogs was evaluated by determining the phase transition temperature (T_t) of the peptides in a phosphate buffer solution with turbidity measurements. In this study, the T_t of F5 was determined to be 27.8°C at the concentration of 10 mg/mL. When the *N*-terminal Phe residue was substituted with Tyr and Trp, self-assembly ability of the peptides was improved; the T_t values of F5-F1Y and F5-F1W were 24.4°C and 7.8°C, respectively. In contrast, most F5 analogs substituted the *N*-terminal residue with a non-aromatic amino acid did not show phase transition at the same concentration (10 mg/mL). In addition, $(FPGV)_n$ analogs showed stronger self-assembly ability compared to F5. For example, the T_t value of $(FPGV)_5$ was 17.9°C at the concentration of 2.0 mg/mL. These results showed that it was possible to design thermoresponsive short ELPs with appropriate T_t value.

1) I. Maeda, S. Taniguchi, N. Watanabe, A. Inoue, Y. Yamasaki, T. Nose, *Protein Pept. Lett*. **2015**, *22*, 934.

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人工タンパク質ナノケージを架橋したハイドロゲルの機能解析

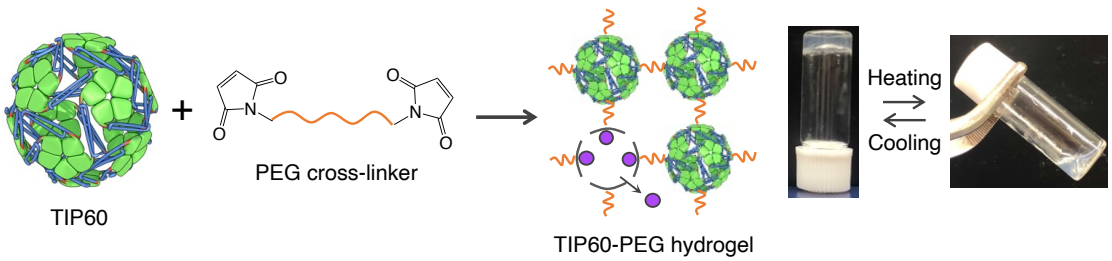
(慶應義塾大学[1]・信州大学[2]) ○那須 英里圭[1]・川上 了史[1]・新井 亮一[2]・宮本 憲二[1]

Characterization of Artificial Protein Nanocage-Cross-Linked-hydrogels ([1]*Keio University,* [2]*Shinshu University*) ○Erika Nasu,[1] Norifumi Kawakami,[1] Ryoichi Arai[2], Kenji Miyamoto[1]

An artificial protein nanocage, TIP60, is a spherical nanoparticle assembled from 60 of fusion proteins. TIP60 can incorporate small molecules in the inner cavity through pores on the surface. In this study, we constructed hydrogels by cross-linking TIP60 nanocages with polyethylene glycol (PEG). We assumed that the disassembly of TIP60s within the hydrogel upon heating was expected to result in a transition from gel to sol state. As a result, the hydrogel showed thermoresponsive sol-gel transition by heating and cooling cycle through the melting temperature of TIP60. The result of the small-angle X-ray scattering measurement suggested that the spherical structure of TIP60 disappeared after heating and returned after cooling. We also investigated molecular incorporation and controlled release by TIP60 nanocages in the hydrogel.

Keywords : Artificial protein nanocages; Thermoresponsive hydrogels; Controlled release

人工タンパク質ナノケージ TIP60 は、60 分子のモノマーが会合してできるサッカーボール型の粒子である[1,2]。TIP60 は中空な粒子であり、その表面に存在する孔から入った小分子化合物を内包することができる。また、変異導入によりシステイン残基を導入することで、TIP60 の内外表面を化学修飾により機能化することも可能である[3]。本研究では、TIP60 の外側表面に導入したシステインをポリエチレングリコール（PEG）リンカーで架橋することによりハイドロゲルを構築し、その性質を調べた。本ハイドロゲルは、TIP60 が PEG ネットワーク構造の架橋点となる設計であり、TIP60 の 60 量体構造がゲル構造の維持に重要であると考えられる。そこで、TIP60 の変性温度以上で加熱するとゲルは流動性を示し、冷却後に再びゲル化することが観察された。このゾルゲル転移が TIP60 の構造変化に起因する現象か、小角 X 線散乱(SAXS)測定を行ったところ、加熱により TIP60 の粒子構造が消失し、冷却後に再び粒子構造が回復することを示唆する結果を得た。また、TIP60 の内外両方にシステインを導入した二重変異体の PEG 架橋により調製したゲルを用いて、ゲル中での TIP60 による小分子化合物の内包・放出も検討した。



1) N. Kawakami *et al.*, *Angew. Chem. Int. Ed.,* 2018, 57, 12400 2) J. Obata *et al.*, *Chem. Commun.*, 2021, 57, 10226 3) E. Nasu *et al.*, *ACS Appl. Nano Mater.* 2021, 4, 2434

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[K303-2am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Akira Yamakata, Masayuki Yagi
Thu. Mar 23, 2023 9:00 AM - 11:30 AM K303 (K303, Lecture Hall Bldg. [3F])

[K303-2am-01] Temperature control of nanowire/hexagonal prismatic WO_3 structure with a high performance for photoelectrochemical water oxidation

○Tomohiro Katsuki[1], Debraj Chandra[1], Yuta Tsubonouchi[1], Norihisa Hoshino[1], Zaki Zahran[1], Masayuki Yagi[1] （1. Grad. School of Sci. and Tech., Niigata Univ）

9:00 AM - 9:20 AM

[K303-2am-02] Development of Visible-Light Photomeltable Azobenzenes and Their Application as Solar Thermal Fuels

○Dennis Kwaria[1,2], Keegan McGehee[1,2], Suyi Liu[1,2], Yoshihiro Kikkawa[2], Shotaro Ito[3], Yasuo Norikane[2,1] （1. Graduate School of Pure and Applied Science, University of Tsukuba, 2. Research Institute for Advanced Electronics and Photonics, National Institute of Advanced Industrial Science and Technology (AIST), 3. Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)）

9:20 AM - 9:40 AM

[K303-2am-03] Near-infrared Light Induced Mechanical Motions of Organic Crystals Coated with Photothermal Conversion Materials

○Yuki Hagiwara[1], Dong Wook Kim[2], Shodai Hasebe[1], Mingchao Zhang[2], Toru Asahi[1], Hideko Koshima[1], Metin Sitti[2] （1. Waseda University, 2. Max Planck Institute for Intelligent Systems）

9:40 AM - 10:00 AM

[K303-2am-04] Quantitative description to stabilize local pH shift in a solar-driven water splitting device and demonstration of coupled reductive upgrading of biomass feedstock

○Keisuke Obata[1,2], Michael Schwarze[3], Roel van de Krol[2,3], Reinhard Schomäcker[3], Fatwa firdaus Abdi[2] （1. The Univ. of Tokyo, 2. Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 3. Technische Universität Berlin）

10:10 AM - 10:30 AM

[K303-2am-05] n Type Carbon Nanotubes with Extremely High Thermal Stability in Air Produced by Doping with Organic Superbases

○Shohei Horike[1,2,3,4], Qingshuo Wei[3], Kouki Akaike[3], Kazuhiro Kirihara[3], Masakazu Mukaida[3], Yasuko Koshiba[1,2], Kenji Ishida[1,2] （1. Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University, 3. National Institute of Advanced Industrial Science and Technology (AIST), 4. PRESTO, Japan Science and Technology Agency）

10:30 AM - 10:50 AM

[K303-2am-06] Development of Paleo-redox indicators for paleocean surface using chlorophyll-derived substances

○Kenta Asahina[1], Satoshi Takahashi[2], Ryosuke Saito[3], Kunio Kaiho[4], Yasuhiro Oba[5] （1.

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National Institute of Advanced Industrial Science and Technology, 2. Nagoya University, 3. Yamaguchi University, 4. Tohoku University, 5. Hokkaido University）

10:50 AM - 11:10 AM

[K303-2am-07] Atmospheric ozone as an indicator of earthquake generation

○Hiroshi Sakugawa[1] （1. Hiroshima University）

11:10 AM - 11:30 AM

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Temperature control of nanowire/hexagonal prismatic WO_3 structure with a high performance for photoelectrochemical water oxidation

(*Grad. School of Sci. and Tech., Niigata Univ.*) ○Tomohiro Katsuki, Debraj Chandra, Yuta Tsubonouchi, Norihisa Hoshino, Zaki Zahran, Masayuki Yagi

Keywords: Semiconductor; Water oxidation; Tungsten oxide; Temperature control; Anisotropic growth

A photoanode capable of efficiently promoting water oxidation is a key essence for realizing a photoelectrochemical (PEC) water splitting cell for hydrogen production. WO_3 is a promising photoanode for PEC water oxidation due to its high oxidation potential. WO_3 photoanodes with specific nanostructures have been actively studied to improve PEC performance for water oxidation, and there are various ways to control the nanostructure. Recently, we reported efficient visible-light-driven water oxidation on an in situ N_2-intercalated WO_3 nanorod photoanode using hydrazine (N_2H_4).[1] In this report, we demonstrate that nanowire (NW) and hexagonal prismatic (HP) WO_3 photoanodes can be easily produced by controlling the synthesis temperature during the synthesis of WO_3 powder using N_2H_4.

N_2H_4 derived WO_3 ($(N_2H_4)WO_3$) precursor was synthesized by adding tungstic acid to water at controlled temperatures of 20~45°C and adding $N_2H_4 \cdot H_2O$ dropwise with stirring. The $(N_2H_4)WO_3$ precursor synthesized at 20°C had a nanowire structure, which transitioned to a hexagonal prismatic structure (45°C) as the synthesis temperature was increased (Fig. 1A). The NW-WO_3 and HP-WO_3 photoanodes were prepared by adding the NW- or HP- $(N_2H_4)WO_3$ precursor to a methanol solution dissolved in polyethylene glycol, coating it on an ITO substrate, and sintering it at 550°C under an oxygen atmosphere. Interestingly, the WO_3 morphology was maintained after calcination. IPCE at 420 nm (47%) was 3.1 times higher than that of the NW-WO_3 photoanode (15%) (Fig. 1B). Electrochemical impedance spectra and X-ray diffraction revealed that the high PEC performance of the HP-WO_3 electrode was attributed to the crystal structure of the HP-WO_3 particle surface.

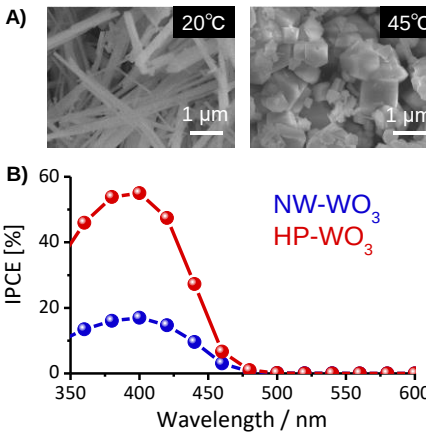


Fig. 1 A) SEM images of precursor (left; 20°C, right; 45°C), B) IPCE curves of NW-WO_3 (blue) and HP-WO_3 (red) in $HClO_4$ (pH 0) at 1.23 V vs. RHE under light irradiation.

1) D. Chandra, D. Li, T. Sato, Y. Tanahashi, T. Togashi, M. Ishizaki, M. Kurihara, E. A. Mohamed, Y. Tsubonouchi, Z. N. Zahran, K. Saito, T. Yui, M. Yagi, *ACS Sustainable Chem. Eng.* **2019**, *7*, 17896-17906.

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Development of Visible-Light Photomeltable Azobenzenes and Their Application as Solar Thermal Fuels

([1]*Graduate School Science and Technology, University of Tsukuba*, [2]*National Institute of Advanced Industrial Science and Technology (AIST)*) ○Dennis Kwaria[1,2], Keegan McGehee[1,2], Suyi Liu[1,2], Yoshihiro Kikkawa[2], Shotaro Ito[2], Yasuo Norikane[2,1]

Keywords: Azobenzene; Solar thermal fuel; Photoswitch; Photochromism

Photomelting (photochemically-induced isothermal solid-liquid transition) is a chemical process during which photochemical reaction on solid material results in product that have liquid phase. Azobenzene is a versatile photoswitch that can undergo reversible trans to cis isomerization upon irradiation, some of its derivatives exhibit photomelting behavior. Recently, photomeltable materials gain attention from solar thermal fuel (STF, Fig. 1b) field. In addition to eliminating the needs for solvent, photomeltable materials have another advantage to be used as STF, as energy released during discharging state is a combination between isomerization enthalpy and recrystallization latent heat (Fig. 1a)[1,2]. However, ultraviolet (UV) light is still mostly used to induce photomelting.[3] This limits the usability of photomelting-driven materials, because UV only makes a small fraction of the sunlight spectrum. Here we wish to report novel visible-light driven photomeltable azobenzenes with potential application as STF.

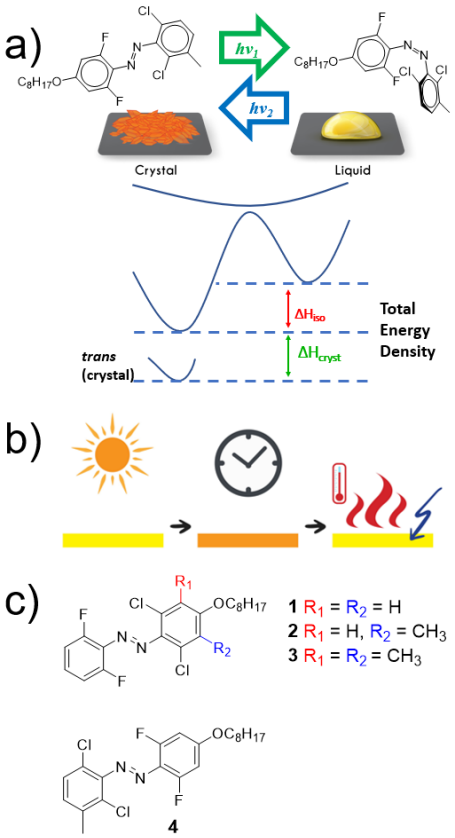


Fig. 1 (a) Schematic diagram of an azobenzene derivative photomelting and photoisomerization energy landscape. (b) Conceptual image of STF (c) Molecular structure of discussed compounds

We synthesized several visible-light responsive azobenzene derivatives **1-4** (Fig. 1c) with two *ortho*-fluorine and two *ortho*-chlorine at different rings bearing *para*-octyloxy chain and they are confirmed to photomelt. All the compounds have a relatively stable *cis* isomer, with lifetime at 30°C ranging from 43.0-117.2 days, making them potentially suitable for STF application.

1) K. Ishiba, M. Morikawa, C. Chikara, T. Yamada, K. Iwase, M. Kawakita, and N. Kimizuka, *Angew. Chem. Int. Ed.* **2015**, 54, 1532. 2) Z. Y. Zhang, Y. He, Z. Wang, J. Xu, M. Xie, P. Tao, D. Ji, K. Moth-Poulsen, T. Li, *J. Am. Chem. Soc.* **2020**, 142, 12256. 3) T. Yamamoto, Y. Norikane, and H. Akiyama, *Polym. J.* **2018**, 50, 551.

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Near-infrared Light Induced Mechanical Motions of Organic Crystals Coated with Photothermal Conversion Materials

(*[1] Waseda University, [2] Max Planck Institute for Intelligent Systems*) ○Yuki Hagiwara,[1] Dong Wook Kim,[2] Shodai Hasebe,[1] Mingchao Zhang,[2] Toru Asahi,[1] Hideko Koshima,[1] Metin Sitti[2]

Keywords: Mechanical Motions, Salicylideneaniline Crystals, Photothermal Conversion Materials, Titanium Carbide, Near-infrared Light

Mechanically responsive crystals are expected to be applicable to actuators and soft robots.[1,2] In the past two decades, many photomechanical crystals have been developed based on photoisomerization[3] and the photothermal effect.[4] However, previously reported crystal motions were mostly driven by ultraviolet (UV) and visible light irradiation,[2] and near-infrared (NIR) light-induced crystal actuation has not been reported. Here we have achieved that the *p*-chlorosalicylideneaniline (enol-**1**) crystals[5] exhibit bending behavior using UV, visible, and NIR light, by coating the photothermal conversion material $Ti_3C_2T_x$.[6]

$Ti_3C_2T_x$ was coated only on the top surface of crystals by $Ti_3C_2T_x$ solution drop-casting (Fig. 1a). Comparing to the pristine enol-**1** crystal absorption spectrum (blue, Fig. 1b), the fully $Ti_3C_2T_x$-coated crystal had the large and broad absorption in visible and NIR region (red, Fig. 1b). Upon UV (365 nm), blue (455 nm), red (660 nm) and NIR (810 nm) light irradiation to the top surface of the fully $Ti_3C_2T_x$-coated crystal (7560 × 914 × 256 μm^3) at the same intensity (200 mW cm^{-2}), all the wavelengths could induce bend-down motion by the photothermal effect, reaching 0.8°, 0.6°, 0.7° and 0.8° in 10 s, respectively (Fig. 1c). Surprisingly, when the crystal was flipped over, the crystal exhibited the bend-up motion by red and NIR light irradiation (Fig. 1d). Finally, the difference of bending behavior among four wavelengths was successfully simulated in both non-flipped and flipped states.

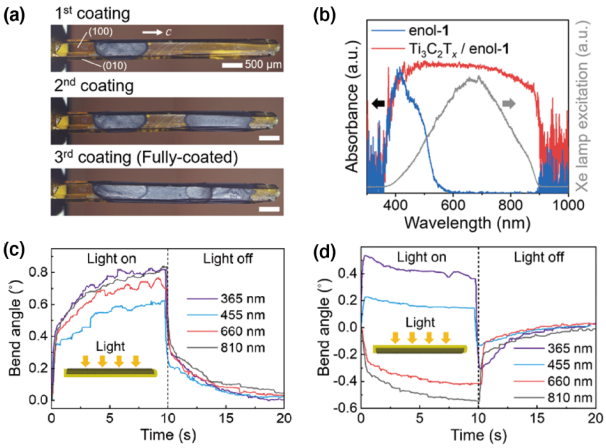


Fig. 1 (a) The coating process of the Ti3C2Tx on the enol-**1** crystal by three-step $Ti_3C_2T_x$ nanosheet solution drop-casting. (b) Absorption spectra of the pristine enol-**1** crystal and the $Ti_3C_2T_x$-coated enol-**1** crystal under excitation with Xenon (Xe) lamp light. (c, d) Time profiles of bend angles of the $Ti_3C_2T_x$-coated enol-**1** crystal in non-flipped (c) and flipped (d) states.

[1] Koshima, H. ed. *Mechanically responsive materials for soft robotics* (Weinheim: Wiley-VCH, 2020). [2] Koshima, H., Hasebe, S., Hagiwara, Y. & Asahi, T. *Isr. J. Chem.* **61**, 683–696 (2021). [3] Koshima, H., Ojima, N. & Uchimoto, H. *J. Am. Chem. Soc.* **131**, 6890–6891 (2009). [4] Hasebe, S. et al. *J. Am. Chem. Soc.* **143**, 8866–8877 (2021). [5] Hasebe, S., Hagiwara, Y., Hirata, K., Asahi, T. & Koshima, H. *Mater. Adv.* **3**, 7098–7106 (2022). [6] Li, R., Zhang, L., Shi, L. & Wang, P. *ACS Nano* **11**, 3752–3759 (2017).

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Quantitative description to stabilize local pH shift in a solar-driven water splitting device and demonstration of coupled reductive upgrading of biomass feedstock

([1]*Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH*, [2]*Graduate School of Engineering, The University of Tokyo,* [3]*Department of Chemistry, Technische Universität Berlin*) ○Keisuke Obata,[1,2] Michael Schwarze,[3] Roel van de Krol,[1,3] Reinhard Schomäcker,[3] Fatwa F. Abdi[1]

Keywords: Electrochemistry; Multiphysics Modeling; Water Splitting; Biomass Feedstock

Neutral pH buffer electrolyte is an attractive media to safely perform solar-driven water splitting in a wide area. However, local pH shifts close to the electrodes lead to concentration overpotentials.[1] In this study, a pH-sensitive fluorescence sensor foil was introduced between Pt model electrodes to *in situ* observe the local pH during water splitting, which successfully captured a pH shift of ca. 1 unit in 0.1 M potassium phosphate solution even at 1 mA cm^{-2} (Fig. 1a).[2] The observed shift was reproduced by multiphysics simulations containing electrochemistry, mass-transport, and fluid dynamics. The simulations revealed that the buoyancy effect due to the concentration change generates a convection close to the electrode, which partly helps to stabilize the pH shift.

Production of value-added products is a promising way for deep implementation of photoelectrochemical technique. This study further investigates hydrogenation of itaconic acid (IA), one of the major biomass feedstocks, to methylsuccinic acid (MSA) using (photo)electrochemically *in situ* generated H_2 and Rh based homogeneous catalyst. Although Pt can heterogeneously reduce IA to MSA, its production rate dropped within one hour most likely due to the passivation of the active sites (Fig. 1b). In the presence of Rh catalyst, MSA was continuously produced highlighting the great advantage of the present coupled catalytic approach. Solar-driven upgrading from IA to MSA has been successfully demonstrated using either $BiVO_4$ photoanode or GaInP/GaAs/Si tandem photovoltaic cell.

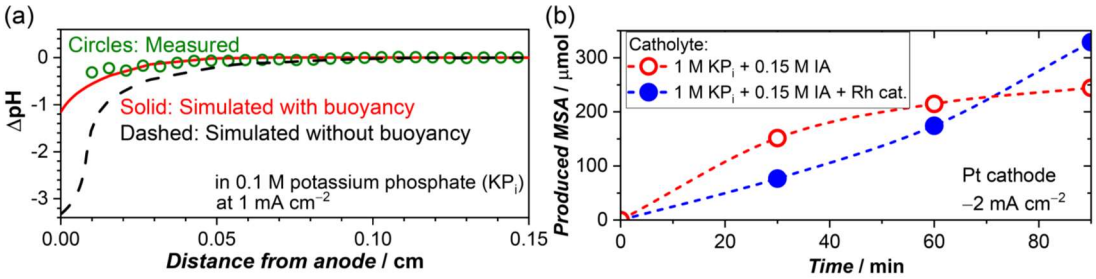


Figure 1 (a) Measured and simulated pH profile close to the anode. (b) Time course of MSA production during chronopotentiometry using Pt cathode.

1) M. R. Singh, et al., *Energy Environ. Sci.* **2015**, *8*, 2760. 2) K. Obata, *et al.*, *Energy Environ. Sci.* **2020**, *13*, 5104.

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n-Type Carbon Nanotubes with Extremely High Thermal Stability in Air Produced by Doping with Organic Superbases

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Keywords: Carbon Nanotube; n-Type Doping; Charge Transfer; Organic Superbase; Thermoelectrics

Carbon nanotubes (CNTs) have the potential to be used as future component of electronic and energy devices such as thin-film transistors and thermoelectric generators. These devices use both p- and n-type materials to create p/n junctions. While CNTs accept autoxidation in air so that they show p-type polarity,[1] the development of stable n-type CNTs is still challenging. As devices are inescapably heated during operation, it is crucial to preserve not only the stability near room temperature but also the thermal stability.

Here, we demonstrate that organic superbases (Fig. 1a) can be used as n-type inducers for CNTs *via* electron transfer from the bases to the CNTs. Doping of CNTs could be performed by facile immersing process into the dopant solution (Fig. 1b). Thermoelectric measurement of the CNT films revealed that the Seebeck coefficient (thermopower) of CNTs changes from positive to negative upon doping, by which electron injection into CNTs and p- to n-type polarity switching could be confirmed. Importantly, the negative Seebeck coefficient doped with TBD and Me-TBD could be retained for more than 6 months during incubation at 100 °C in air (Fig. 1c). To highlight the potential capability of stable n-type CNTs, a thermoelectric device was constructed using the CNT p/n junctions, which exhibits a power output of ~4.7 μW from a temperature difference of 40 K.[2]

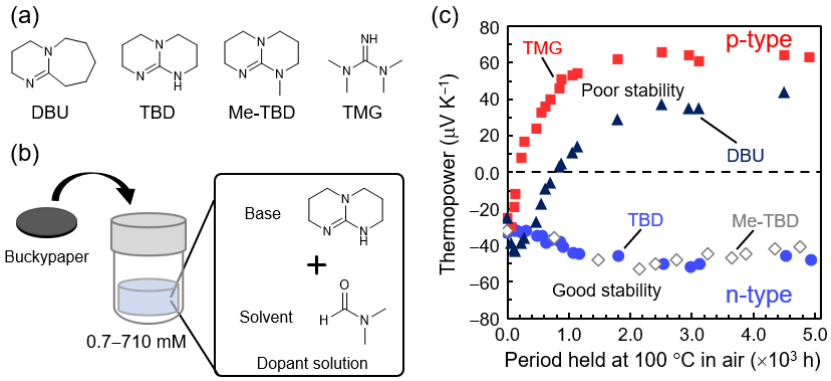


Fig. 1 (a) Chemical structures of organic superbases used as dopant for CNT. (b) Schematic of doping process. (c) Long-term stability of doped state of CNTs at 100 °C in air.

1) Kang *et al.*, *Nanotechnology* **2005**, *16*, 1048. 2) Horike *et al.*, *Nat. Commun.* **2022**, *13*, 3517.

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クロロフィル由来物質を用いた古海洋表層の酸化還元指標の開発

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Development of Paleo-redox indicators for paleocean surface using chlorophyll-derived substances ([1]*Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology,* [2]*Department of Earth and Environmental Sciences, Nagoya University,* [3]*Department of Geosphere Sciences, Yamaguchi University,* [4]*Department of Earth Science, Tohoku University,* [5]*Institute of Low Temperature Science, Hokkaido University*) ○Kenta Asahina,[1] Satoshi Takahashi,[2] Ryosuke Saito,[3] Kunio Kaiho,[4] Yasuhiro Oba[5]

The sedimentary rocks contained porphyrins, which are thought to have originated from chlorophylls possessed by photosynthetic organisms that lived in the past. Green sulfur bacteria that live in anaerobic environments have bacteriochlorophyll. The analysis of bacteriochlorophyll-derived materials in sedimentary rocks could indicate that the ocean surface layer was an anoxic environment in the past. We developed an analytical method for bacteriochlorophyll-derived substances in sedimentary rocks. The analytical results of bacteriochlorophyll-derived substances were consistent with those of carotenoid-derived substances from green sulfur bacteria. This presentation proposes an indicator that the past ocean surface layer was an anoxic environment using chlorophyll-derived substances in sedimentary rocks. This research is expected to be useful for estimating past global environmental changes and the environments that caused mass extinctions of organisms.

Keywords : Porphyrin; Chlorophyll; Maleimide; Chromic acid oxidation; Paleo-redox index

堆積岩中には、ポルフィリン類が含まれており、それらは過去に生息していた光合成生物のクロロフィル類が起源とされている。光合成生物の種類によって保有するクロロフィル類が異なるため、堆積岩中に保存されたポルフィリン類は、過去の光合成生物組成を反映する指標となる。嫌気環境でのみ生息可能な緑色硫黄細菌は、バクテリオクロロフィルを有している。すなわち、堆積岩中のバクテリオクロロフィル由来物質を検出することができれば、過去の海洋表層が無酸素環境であったことを示す証拠となる。しかしながら、堆積岩中のクロロフィル由来物質は、ケロジェンと呼ばれる不溶性高分子に結合しているため、直接分析することができない。本研究では、堆積岩をクロム酸酸化することでケロジェンに結合したポルフィリンのピロール部位を切り出し、ピロール部位の組成比から過去のクロロフィル組成 (光合成生物組成)を解析する手法を開発した。本手法で全クロロフィルが持つピロールとバクテリオクロロフィル特有のピロールの組成比と、緑色硫黄細菌が保有するカロテノイド由来物質の分析結果を比較した結果、調和的な結果を示した。本講演では、堆積岩中のクロロフィル由来物質であるピロール部位の組成比を用いて、過去の海洋表層が無酸素環境であったことを示す指標を提案する。本研究の成果は、地球環境変動や生物の大量絶滅の原因となった環境の推定に役立つことが期待される。

Reference; Asahina, K., Takahashi, S., Saito, R., Kaiho, K., Oba, Y., *RSC Adv.* **2022**, *12*, 31061.

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地震発生の指標としての大気中オゾン

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Atmospheric ozone as an indicator of earthquake generation

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Relationship between atmospheric ozone and earthquake generation was examined in this study. The data of surface-level ozone (tropospheric ozone, so-called "photochemical oxidant") were obtained from the Atmospheric Environmental Regional Observation System, managed by the Ministry of Environment, Japan. About 2000 monitoring sites are located from Hokkaido to Okinawa, Japan. There was a good correlation between the increase of atmospheric ozone concentration and the generation of earthquake (Magnitude >4.0) happened during 2010-2022 in Japan. Atmospheric ozone concentration started to increase in a couple days before earthquake generation, reached a maximum within 24 hr before or after the earthquake generation, and then decreased/disappeared within a couple days after the generation. Ozone concentration increased at a max. 5~30 ppb during the earthquake events, compared with before and after the earthquake events. The increase rate of ozone concentration was a maximum at a place near epicenter and high magnitude earthquakes tended to make appear the ozone at a place far from the epicenter (>a few hundred km). Atmospheric ozone may be an indicator of earthquake generation.

Keywords : Atmospheric ozone, Tropospheric ozone, Photochemical oxidant, Earthquake

本研究において大気中オゾンと地震発生との関連性について調べた。地表面レベルオゾン（対流圏オゾン、通称“光化学オキシダント”）の濃度データは、環境省大気汚染物質広域監視システムから入手した。この大気汚染監視システムは、北海道から沖縄まで全国で約 2000 の測定局を有する。その結果、2010 年～2022 年の 13 年間で日本で発生した地震（マグニチュード 4 以上）と大気中オゾンとの間に良い相関があることが示された。大気中オゾン濃度は地震発生の数日前から増加し、発生の 24 時間前後でピークに達し、その後数日以内に減少した。増加濃度は最大で 5～30ppb であった。震源付近で増加濃度が最も高く、マグニチュードが大きい地震ほど遠く離れた場所（数百 km 以上）でもオゾンの増加が見られた。大気中オゾンは、地震発生の指標として用いることができる可能性がある。

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