Fri. Mar 25, 2022

D201

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

[D201-3pm] 01. Education and History of Chemistry

Chair: Osamu Kamei, Tomonori NOMOTO
2:00 PM - 3:40 PM D201 (Online Meeting)

[D201-3pm-01] Analysis with the Systematized Survey on the History of Technology: Frozen Ground Eng., E.P. Assisted Bicycle, Telephone Set, Jet engine for Commercial Aircraft, FDD, and Related technologies

○Osamu KAMEI[1] (1. National Museum of Nature and Science)

2:00 PM - 2:20 PM

[D201-3pm-02] A simple spectroscope using a consumer digital camera for live spectroscopic demonstrations

○Tomonori NOMOTO[1] (1. Chiba University)

2:20 PM - 2:40 PM

[D201-3pm-03] Development of Microscale Experiments for Physically Challenged Students

○Kazuyuki Yamada[1], Kazuko Ogino[2] (1. Kirigaoka School for the Physically Challenged, University of Tsukuba, 2. Graduate School of Science, Tohoku University)

2:40 PM - 3:00 PM

[D201-3pm-04] Improvement of "Copper into Gold: The Alchemist's Dream" Using Surfactant and Aluminum Foil

○Takahiro Suzuki[1] (1. Otsuma Ranzan Junior and Senior High School)

3:00 PM - 3:20 PM

F203

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

[F203-3am] 04. Physical Chemistry -Properties-

Chair: Yuta Takano, Tetsuro Kusamoto
9:00 AM - 11:40 AM F203 (Online Meeting)

[F203-3am-01] Theoretical Study on Vibronic Couplings of Excited States Contributing to Singlet Fission Process

○Takayoshi Tonami[1], Kenji Okada[1], Hajime Miyamoto[1], Ryohei Kishi[1,2,5], Yasutaka Kitagawa[1,2,3,5], Masayoshi Nakano[1,2,3,4,5] (1. Graduate School of Engineering Science, Osaka University, 2. QIQB, Osaka University, 3. CSRN, Osaka University, 4. ICS-OTRI, Osaka Universit, 5. RCSEC, Osaka University)

9:00 AM - 9:20 AM

[F203-3am-02] Theoretical Study on Singlet Fission Dynamics in One-dimensional Aggregates Composed of Bowl-Shaped Molecules

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

9:20 AM - 9:40 AM

[F203-3am-03] Theoretical Study on Singlet Fission Dynamics in Pentacene Multi-ring Aggregate Models

○Hajime Miyamoto[1], Kenji Okada[1], Kazuaki Tokuyama[1], Kishi Ryohei[1,2,3], Yasutaka Kitagawa[1,2,3,4], Nakano Masayoshi[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. Center for Spintronics Research Network, Osaka University, 5. Innovative Catalysis Science Devision, Institute for Open and Transdisciplinary Research Initiatives, Osaka University)

9:40 AM - 10:00 AM

[F203-3am-04] Environmental Degradation of PbS and CdSe Quantum dots and the Related Toxicity

○Jeladhara Sobhanan[1], Yuta Takano[1], Vasudevanpillai Biju[1] (1. Hokkaido University)

10:00 AM - 10:20 AM

[F203-3am-05] Optimizing single-crystal perovskite sizes, shapes, and their roles on electroluminescence blinking

○Dong Zhang[1], Takuya Okamoto[2], VasudevanPillai Biju[1,2] （1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University）

10:20 AM - 10:40 AM

[F203-3am-06] Ligand Effects on Precisely Synthesized Gold Clusters in the Ultrafast Carrier Dynamics

○Daichi Eguchi[1], Eisuke Kawashima[2], Takahito Nakajima[2], Naoto Tamai[1] （1. Kwansei Gakuin University, 2. RIKEN Center for Computational Science）

10:40 AM - 11:00 AM

[F203-3am-07] Highly efficient emission of Eu(III) complex doped host-guest films by triplet sensitization

○Shiori Miyazaki[1], Kiyoshi Miyata[1], Pedro Paulo Ferreira da Rosa[2], Fumiya Suzue[2], Yuichi Kitagawa[2,3], Kenichi Goushi[4], Chihaya Adachi[4], Yasuchika Hasegawa[2,3], Ken Onda[1] （1. Kyushu Univ., 2. Hokkaido Univ., 3. Hokkaido Univ., WPI-ICReDD, 4. Kyushu Univ., OPERA）

11:00 AM - 11:20 AM

[F203-3am-08] Observation of single-molecule magnetoluminescence from stable luminescent radicals

○Ryota Matsuoka[1], Shojiro Kimura[2], Tetsuro Kusamoto[1] （1. LCCMS, IMS, 2. IMR, Tohoku Univ.）

11:20 AM - 11:40 AM

F102

Academic Program [Oral B] | 05. Physical Chemistry -Chemical Kinetics and Dynamics- | Oral B

[F102-3am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Keiichi Inoue, Wataru Kashihara
9:00 AM - 11:20 AM F102 (Online Meeting)

[F102-3am-01] Study on the dynamics of channel opening and closing of cation channel rhodopsin, C1C2

○Keiichi Inoue[1], Keisei Shibata[1], Kazumasa Oda[1], Tomohiro Nishizawa[1], Yuji Hazama[1], Ryohei Ono[1,2], Osamu Nureki[1], Hidefumi Akiyama[1] （1. The Univ. of Tokyo, 2. Gunma Univ.）

9:00 AM - 9:20 AM

[F102-3am-02] Photochemical Reaction of Ketoprofen with Twenty Kinds of Proteinogenic Amino Acids

○Wataru Kashihara[1], Kazuyoshi Ueda[1,2], Tadashi Suzuki[1] （1. Aoyama Gakuin University, 2. Yokohama National University）

9:20 AM - 9:40 AM

[F102-3am-03] Kinetic analyses of photoinduced protein folding and interaction with molecular chaperone SecB

○Yusuke Nakasone[1], Ikuya Nakaoka[1], Honoka Ohta[3], Soichiro Kawagoe[2], Koichiro Ishimori[3], Tomohide Saio[2], Masahide Terazima[1] （1. Kyoto University, 2. Tokushima University, 3. Hokkaido University）

9:40 AM - 10:00 AM

[F102-3am-04] Polarization dependence of the carrier dynamics in a lead halide perovskite crystal observed by femtosecond transient absorption microscopy

○Tetsuro Katayama[1], Yuma Fujita[1], Akira Yamamoto[1], Yuichiro Akagi[1], Akihiro Furube[1] （1. Tokushima University）

10:00 AM - 10:20 AM

[F102-3am-05] Ultrafast Ring-Opening Reaction of 1,3-Cyclohexadiene: Identification of Non-Adiabatic Transition Pathway via Doubly Excited State and Product Coherence

○Shutaro Karashima[1], Alexander Humeniuk[2], Ryuta Uenishi[1], Takuya Horio[1], Manabu Kanno[3], Tetsuro Ohta[1], Junichi NIshitani[1], Roland Mitric[2], Toshinori Suzuki[1] （1. Kyoto University, 2. Universität Würzburg, 3. Tohoku University）

10:20 AM - 10:40 AM

[F102-3am-06] Super-reaction: the Collective Enhancement of a Reaction Rate by Molecular Polaritons in the Presence of Energy Fluctuations

○Nguyen Thanh Phuc[1] （1. Kyoto University）

10:40 AM - 11:00 AM

[F102-3am-07] Reaction Mechanism of Isotopic Hydrogen Evolution Reaction at Nano-Structured Metal Electrodes

○Hiro Minamimoto[1], Mizuho Homma[1], Kei Murakoshi[1] （1. Hokkaido University）

11:00 AM - 11:20 AM

J401

Academic Program [Oral B] | 07. Inorganic Chemistry | Oral B

[J401-3pm] 07. Inorganic Chemistry

Chair: Takane Imaoka, Sayaka Uchida
1:00 PM - 3:40 PM J401 (Online Meeting)

[J401-3pm-01] Syntheses and polymorphic transformations of ionic crystals based on mononuclear bismuth(III) complexes and polyoxometalates

○Tsukasa Iwano[1], Daiki Akutsu[1], Zhewei Weng[1], Naoki Ogiwara[1], Sayaka Uchida[1] （1. Grad. Sch. Arts and Sci., The Univ. of Tokyo）

1:00 PM - 1:20 PM

[J401-3pm-02] The Formation of $Al_{28}V_4$ Polycation in Porous Ionic Crystal for Acetalization Reaction

○Wei Zhou[1], Naoki OGIWARA[1], Sayaka UCHIDA[1] （1. School of Arts and Sciences,The university of Tokyo）

1:20 PM - 1:40 PM

[J401-3pm-03] Non-humidified intermediate-temperature proton conductors based on a Dawson-type polyoxometalate and poly(ethylene glycol) derivatives

○Naoki Ogiwara[1], Masahiro Tomoda[1], Shotaro Miyazaki[1], Zhewei Weng[1], Sayaka Uchida[1] （1. School of Arts and Sciences, The University of Tokyo ）

1:40 PM - 2:00 PM

[J401-3pm-04] Degradation of Polymers by Polyoxometalate Photocatalysts

○Chifeng Li[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] （1. The Univ. of Tokyo）

2:00 PM - 2:20 PM

[J401-3pm-05] Precise Synthesis and CO_2 Hydrogenation Catalysis of Early-Transition Metal Clusters

○Augie Atqa[1], Masanori Wakizaka[2], Wang-Jae Chun[3], Takane Imaoka[1], Kimihisa Yamamoto[1] （1. Tokyo Institute of Technology, 2. Tohoku University, 3. International Christian University）

2:20 PM - 2:40 PM

[J401-3pm-06] Synthesis and properties of heterogeneous elemental blended Sn clusters using dendrimer template synthesis method

○Hisanori Muramatsu[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2,3], Reina Hosono[1], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] （1. Tokyo Tech., Lab. Chem. Life Sci., 2. JST-ERATO, 3. JST-PRESTO）

2:40 PM - 3:00 PM

[J401-3pm-07] Atomic Behaviors of Quantum Dots and NaCl Crystal Nucleus Revealed by Single-molecule Analyses

○Takayuki Nakamuro[1], Olivier Chevalier[1], Masaya Sakakibara[1], Rui Shang[1], Eiichi Nakamura[1] （1. The University of Tokyo）

3:00 PM - 3:20 PM

[J401-3pm-08] Cleavage of molecular hydrogen and catalysis over molecular hybrids of silver nanoclusters and polyoxometalates

○Kentaro Yonesato[1], Daiki Yanai[1], Seiji Yamazoe[2], Daisuke Yanai[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] （1. The Univ. of Tokyo, 2. Tokyo Metro. Univ.）

3:20 PM - 3:40 PM

B204

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

[B204-3pm] 08. Catalysts and Catalysis

Chair: Tamao Ishida, Hidehiro Sakurai
1:20 PM - 3:40 PM B204 (Online Meeting)

[B204-3pm-01] Dehydrogenative coupling of alkane and benzene catalyzed by supported metal-solid acid catalyst system

○Moe Takabatake[1], Satoshi Misaki[1], Masayuki Nambo[2], Wang-Jae Chun[3], Yuichi Manaka[1,4], Ken Motokura[1,2] （1. Tokyo Tech, 2. Yokohama National Univ., 3. ICU, 4. AIST）

1:20 PM - 1:40 PM

[B204-3pm-02] Selective Synthesis of Primary Anilines Using NH_3 as a Nitrogen Source via Acceptorless Dehydrogenative

Aromatization

○Hui Li[1], Takafumi Yatabe[1], Satoshi Takayama[1], Kazuya Yamaguchi[1] （1. The Univ. of Tokyo）

1:40 PM - 2:00 PM

[B204-3pm-03] CeO_2 Supported Au− Pd Alloy Nanoparticle Catalyst for Heterogeneously Catalyzed Decarbonylation of 1,2-Diketones

○Takehiro Matsuyama[1], Takafumi Yatabe[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] （1. The University of Tokyo）

2:00 PM - 2:20 PM

[B204-3pm-04] Elucidation of active site and reaction mechanism of Pd/Au/CeO_2-catalyzed dehydrogenation of ketones

○Daisuke Takei[1], Takafumi Yatabe[1], Tomohiro Yabe[1], Ray Miyazaki[2], Jun-ya Hasegawa[2], Kazuya Yamaguchi[1] （1. The University of Tokyo, 2. Hokkaido University）

2:20 PM - 2:40 PM

[B204-3pm-05] Atomically Precise Synthesis of Au_{25} Cluster Catalyst on Double Metal Hydroxide by Long-term Oxidative Aging of $Au_{25}(SR)_{18}$

○Shinya Masuda[1], Shinjiro Takano[1], Seiji Yamazoe[2,3,4], Tatsuya Tsukuda[1,4] （1. The Univ. of Tokyo, 2. Tokyo Metropolitan Univ., 3. JST, PRESTO, 4. ESICB, Kyoto Univ.）

2:40 PM - 3:00 PM

[B204-3pm-06] Synthesis of Murdochite-type Oxide Mg_6MnO_8 Nanoparticles and the Catalytic Oxidation Properties

○Eri Hayashi[1], Takatoshi Tamura, Takeshi Aihara[1], Keigo Kamata[1], Michikazu Hara[1] （1. Tokyo Institute of Technology）

3:00 PM - 3:20 PM

[B204-3pm-07] Enhancement of Catalytic 1,4-Arylation Activity by N-Heterocyclic Carbene Ligand Decoration on Cr and Rh-incorporated Ceria Catalysts

○Satoru Ikemoto[1], Satoshi Muratsugu[1], Yuta Tsuji[2], Kazunari Yoshizawa[2], Mizuki Tada[1,3] （1. Dept. Chem., Nagoya Univ., 2. IMCE, Kyushu Univ., 3. RCMS, Nagoya Univ.）

3:20 PM - 3:40 PM

J403

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

[J403-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Minoru Mitsumi, Yumi Yakiyama

1:00 PM - 3:40 PM J403 (Online Meeting)

[J403-3pm-01] Role of intramolecular hydrogen bonding in the redox chemistry of hydroxybenzoate-bridged paddlewheel diruthenium (II,II) complexes

○Wataru Kosaka[1,2], Yudai Watanabe[2], Hitoshi Miyasaka[1,2] （1. IMR, Tohoku Univ., 2. Sch. of Sci., Tohoku Univ.）

1:00 PM - 1:20 PM

[J403-3pm-02] Helical Inversion Dynamics in a Metal–Peptide Framework

○Wei Yuan[1], Hiroshi Sato[2,3], Takuzo Aida[1,2] （1. The Univ. of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. Japan Science and Technology Agency (JST), Precursory Research for Embryonic Science and Technology (PRESTO)）

1:20 PM - 1:40 PM

[J403-3pm-03] Syntheses and Physical Properties of Robust Porous Molecular Conductors with 1,2,4-Triazole Group

○Hiroaki Iguchi[1], Mengxing Cui[1], Yongbing Shen[1], Shohei Koyama[1], Shinya Takaishi[1] （1. Tohoku University）

1:40 PM - 2:00 PM

[J403-3pm-04] Accumulated Lattice Strain as an Internal Trigger for Spontaneous Pathway Selection

○Hubiao Huang[1] （1. Riken）

2:00 PM - 2:20 PM

[J403-3pm-05] Synthesis, Crystal Strucutre and Photophysical Properties of Acceptor-Encapsulated Porous Zinc Porphyrin Dimers

○Mitsuyuki Oshiro[1], Minoru Mitusmi[1], Chiasa Uragami[2], Hideki Hashimoto[2] （1. Okayama Univ. of Sci., 2. Kwansei Gakuin Univ. ）

2:20 PM - 2:40 PM

[J403-3pm-06] Sensing Behavior of Sumanene Functionalized Bis(terpyridine)

Ruthenium(II) Complexes

○Junyi Han[1], Yumi Yakiyama[1,2], Yuta Uetake[1,2], Hidehiro Sakurai[1,2] (1. Graduate School of Engineering, Osaka Univ., 2. ICS-OTRI, Osaka Univ.)

2:40 PM - 3:00 PM

[J403-3pm-07] Kinetic analysis for optimizing the Zn-catalyzed transesterification conditions of MA and MMA with diols to maximize monoesterified products

○Taito KATO[1,2], Haruki NAGAE[1], Kazushi MASHIMA[1] (1. Osaka University, 2. Nippon Shokubai)

3:00 PM - 3:20 PM

[J403-3pm-08] Synthesis of Antimony Porphycene and Catalytic Hydrogen Evolution Driven by Ligand-Centered Reduction

○Taro Koide[1], Zhi Zhang[1], Taro Fujioka[1], Yoshio Yano[1], Toshikazu Ono[1,2], Yoshio Hisaeda[1,2] (1. Graduate School of Engineering, Kyushu University, 2. Center for Molecular Systems (CMS), Kyushu University)

3:20 PM - 3:40 PM

J402

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

[J402-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryo Ohtani, Koji Oohora
1:00 PM - 3:40 PM J402 (Online Meeting)

[J402-3pm-01] Spin crossover and second harmonic generation of cyanido-bridged metal assemblies

○Koji Nakabayashi[1], Shintaro Kawabata[1], Takefumi Kanno[1], Kenta Imoto[1], Stephen Klimke[2], Franz Renz[2], Shin-ichi Ohkoshi[1] (1. The University of Tokyo, 2. Leibniz University Hannover)

1:00 PM - 1:20 PM

[J402-3pm-02] Synthesis of cyanide-bridged metal complex clusters with polar structures

○Junichi Yanagisawa[1], Ryo Ohtani[1], Masaaki Ohba[1] (1. Kyushu Univ.)

1:20 PM - 1:40 PM

[J402-3pm-03] Guest-dependent Magnetic and Structural Variations in a Magnetically-bistable 2-D Hollow-Sheet-type Coordination Polymer

○Haruka Yoshino[1,2], Wataru Kosaka[1], Hitoshi Miyasaka[1], Masaaki Ohba[2] (1. Institute for Materials Research, Tohoku University, 2. Department of Chemistry, Faculty of Science, Kyushu University)

1:40 PM - 2:00 PM

[J402-3pm-04] A pentacyanidonitrosylmetallate-based assembly exhibiting switchable nonlinear optical functionalities

○Kenta Imoto[1], Masaya Komine[1], Marie Yoshikiyo[1], Asuka Namai[1], Shin-ichi Ohkoshi[1] (1. Department of Chemistry, School of Science, The University of Tokyo)

2:00 PM - 2:20 PM

[J402-3pm-05] Reversible Polarity Switching Based on Solvent Ligand Exchange Reaction Triggered by Solvent Vapor

○Fumiya Kobayashi[1], Misato Gemba[1], Makoto Tadokoro[1] (1. Tokyo University of Science)

2:20 PM - 2:40 PM

[J402-3pm-06] Metallo-supramolecular Polymer Synthesis Driven by Data-science

○DINES CHANDRA SANTRA[1], Rizwangul Ibrahim[1], Ritsuko Nagahata[2], Kenji Nagahata[1], Masahiko Demura[1], Masayoshi Higuchi[1] (1. National Institute for Materials Science (NIMS), 2. National Institute of Advanced Industrial Science and Technology (AIST))

2:40 PM - 3:00 PM

[J402-3pm-07] Low-Valent First-Row Transition Metal Complexes Featuring Vanadocene or Chromocene Bisamide ligands

○Hinano Kusunose[1], Tsubasa Hatanaka[1], Hiroyuki Kawaguchi[2], Yasuhiro Funahashi[1] (1. Osaka Univ., 2. TITech)

3:00 PM - 3:20 PM

[J402-3pm-08] C– H bond amination catalyzed by engineered hemoprotein containing iron porphycene as an artificial cofactor

○Yoshiyuki Kagawa[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka Univ.)

3:20 PM - 3:40 PM

D202

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

[D202-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takuya Kochi, Koji Kubota
1:00 PM - 3:40 PM D202 (Online Meeting)

[D202-3pm-01] Palladium-Catalyzed Remote Arylative Substitution of Various Terminal Alkenes

○Kazuma Muto[1], Fumitoshi Kakiuchi[1], Takuya Kochi[1] (1. Keio University)

1:00 PM - 1:20 PM

[D202-3pm-02] Photoinduced Copper-Catalyzed Asymmetric Acylation of Allylic Phosphates with Acylsilanes

○Yusuke Ueda[1], Yusuke Masuda[1,2], Tomohiro Iwai[4], Imaeda Keisuke[1], Takeuchi Hiroki[1], Ueno Kosei[1], Min Gao[3], Jun-ya Hasegawa[3,2], Masaya Sawamura[1,2] (1. Hokkaido Universuty Faculty of Science, 2. WPI-ICReDD, 3. Hokkaido Universuty Institute for Catalysis, 4. The University of Tokyo,Graduate School of Art and Sciences)

1:20 PM - 1:40 PM

[D202-3pm-03] Quantum Chemical Study of Asymmetric Propargylic Substitution Reactions Catalyzed by Optically Active Thiolate-Bridged Diruthenium Complexes

○Ken Sakata[1], Yui Goto[1], Takeshi Yoshikawa[1], Yoshiaki Nishibayashi[2] (1. Toho University, 2. University of Tokyo)

1:40 PM - 2:00 PM

[D202-3pm-04] Palladium-Catalyzed Remote Diborylative Cyclization of Various 1,n-Dienes with Diborons

○Shota Kanno[1], Kakiuchi Fumitoshi[1], Kochi Takuya[1] (1. Faculty of Science and Technology, Keio University)

2:00 PM - 2:20 PM

[D202-3pm-05] Hydroxycarbonylation of alkenes using formic acid catalyzed by rhodium (III) hydride diiodide complex without using any additives

○Masaki Okada[1,2,3,4], Katsuhiko Takeuchi[1], Kazuhiro Matsumoto[1], Tomoharu Oku[4], Choi Jun-Chul[1,2] (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba, 3. Research Association of High-Throughput Design and Development for Advanced Functional Materials, 4. NIPPON SHOKUBAI CO., LTD.)

2:20 PM - 2:40 PM

[D202-3pm-06] Palladium-Catalyzed C-H Arylation of Benzophospholes

○Shibo Xu[1], Kazutoshi Nishimura[1], Koji Hirano[1], Masahiro Miura[1] (1. Osaka University)

2:40 PM - 3:00 PM

[D202-3pm-07] Development of new ligands for mechanochemical cross-coupling reactions

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

3:00 PM - 3:20 PM

[D202-3pm-08] Auto-tandem copper catalysed carboxylation of undirected alkenyl C– H bonds with CO_2

○HAREKRISHNA SAHOO[1], Liang Zhang[1], Zhaomin Hou[1] (1. RIKEN)

3:20 PM - 3:40 PM

D203

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

[D203-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kosuke Higashida, Yasunori Minami
1:20 PM - 3:40 PM D203 (Online Meeting)

[D203-3pm-01] A Boron-Transfer Mechanism Mediating the Thermally Induced Revival of Frustrated Carbene– Borane Pairs from their Shelf-Stable Adducts

○Mahiro Sakuraba[1], Yoichi Hoshimoto[1], Jyunya Hasegawa[2], Sensuke Ogoshi[1] (1. Graduate School of Engineering, Osaka Univ. , 2. Institute for Catalysis, Hokkaido Univ.)

1:20 PM - 1:40 PM

[D203-3pm-02] Regiodivergent and Stereoselective Intermolecular [2+2] Cycloaddition of

Amino-functionalized Alkenes and Allenes by Rare-Earth Catalysts

○Wenxuan Xu[1,2], Xuefeng Cong[1], Kun An[1], Shaojie Lou[1], Zhenghua Li[1], Masayoshi Nishiura[1], Tetsuro Murahashi[2], Zhaomin Hou[1,2] (1. RIKEN, 2. Tokyo Institute of Technology)

1:40 PM - 2:00 PM

[D203-3pm-03] Advancement of a cooling system for solution XAS experiment and in situ local structure analysis of boryl copper species by XAS measurements

○Yuta Uetake[1,2], Yu Ozawa[3], Kazuki Matsumoto[4], Tetsuo Honma[5], Koji Kubota[3,6], Hajime Ito[3,6] (1. Grad. Sch. Eng., Osaka Univ., 2. ICS-OTRI, Osaka Univ., 3. Grad. Sch. Eng., Hokkaido Univ., 4. DFC Co., Ltd., 5. JASRI, 6. WPI-ICReDD, Hokkaido Univ.)

2:00 PM - 2:20 PM

[D203-3pm-04] Nucleophilic Addition of Carboxylic Acids and Phenols toward Non-activated Alkynes Catalyzed by Gold-Zinc Bimetallic Complexes Including Imidazo[1,5-*a*]pyridine-3-ylidene Ligands

○Vishal Kumar Rawat[2], Kosuke Higashida[1,2], Masaya Sawamura[1,2] (1. WPI-ICReDD, Hokkaido University, 2. Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

[D203-3pm-05] Regio- and Diastereoselective [3 + 2] Annulation of Aliphatic Aldimines with Alkenes via beta-C(sp3)– H Activation by Scandium Catalysts

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

2:40 PM - 3:00 PM

[D203-3pm-06] Chromium-catalyzed *syn*-Stereoselective Ring-opening Arylation of 7-Oxabenzonorbornadienes

○Kohei Nishi[1], Hayato Tsurugi[1], Kazushi Mashima[1] (1. Osaka Univ.)

3:00 PM - 3:20 PM

[D203-3pm-07] Yttrium-Catalyzed Reagioselective Alumination and Subsequent Functionalization of Benzylic C– H Bonds of 2-Alkylpyridines

○Masanori Takimoto[1,2], Masayoshi Nishiura[1,2], Zhaomin Hou[1,2] (1. RIKEN CPR, 2. RIKEN CSRS)

3:20 PM - 3:40 PM

H301

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

[H301-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Yasunori Matsui, Yosuke Tani
1:00 PM - 3:40 PM H301 (Online Meeting)

[H301-3pm-01] Through-space Charge-transfer Photoluminescence of the Nonconjugated Electron Donor–Acceptor Dyad

○Takuya Ogaki[1,2], Yutaro Kuramoto[1], Ryohei Takayasu[3], Yasunori Matsui[1,2], Eisuke Ohta[1,2], Hiroshi Ikeda[1,2] (1. Grad. Sch. Eng., Osaka Pref. Univ., 2. RIMED, Osaka Pref. Univ., 3. Col. Eng., Osaka Pref. Univ.)

1:00 PM - 1:20 PM

[H301-3pm-02] Copper(I)-pyrazolate clusters as solid-state phosphors: Tunable emissions via a remote steric effect

○Yuichiro Watanabe[1], Benjamin M Waher[1], Matthias Zeller[1], Sergei Savikhin[1], Lyudmila V Slipchenko[1], Alexander Wei[1] (1. Purdue University)

1:20 PM - 1:40 PM

[H301-3pm-03] Design of Solid-State Photoluminescence Materials Based on Stacked π-Planes Assisted by Carborane

○Junki Ochi[1], Kazuo Tanaka[1] (1. Kyoto University)

1:40 PM - 2:00 PM

[H301-3pm-04] Photo-induced crystal– liquid phase transition of heteroaromatic diketones probed by phosphorescence

○Mao komura[1], Takuji Ogawa[1], Hikaru Sotome[2], Hiroshi Miyasaka[2], Yosuke Tani[1] (1. Grad. Sch. Sci., Osaka Univ. , 2. Grad. Sch. Eng. Sci., Osaka Univ.)

2:00 PM - 2:20 PM

[H301-3pm-05] Highly Efficient and Robust Phosphorescence of Thienyl Diketone Derivative

○Yosuke Tani[1], Yuya Oshima[1], Takuji Ogawa[1]
（1. Osaka Univ.）
2:20 PM - 2:40 PM

[H301-3pm-06] Development of boronate self-assembly as photocatalysts for hydrogen production
○Ryohei Hasegawa[1,2], Yuji Kubo[1,2]（1. Tokyo metropolitan university Graduate School of Urban Environmental Sciences, 2. Tokyo metropolitan university Research Center for Hydrogen Energy-based Society）
2:40 PM - 3:00 PM

[H301-3pm-07] Drastic changes in the mechanical properties of long alkyl-chained organic crystals depending on recrystallizing solvent
○Sotaro Kusumoto[1], Yoshihiro Koide[1], Shinya Hayami[2]（1. Kanagawa Univ., 2. Kumamoto Univ.）
3:00 PM - 3:20 PM

[H301-3pm-08] Repeated elongation and decomposition of supramolecular fibers induced by surfactant addition
○Shogo Torigoe[1], Ryou Kubota[1], Kazutoshi Nagao, Itaru Hamachi[1]（1. The Univ. of Kyoto）
3:20 PM - 3:40 PM

H201

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

[H201-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Yoshimitsu Itoh, Masahiro Yamashina
1:20 PM - 3:40 PM H201 (Online Meeting)

[H201-3pm-01] Structural chemistry and stimuli-responsive phase transition of *N,N'*-dialkylimidazolium nonafluorobutanesulfonate ionic liquids
○Tomoyuki Takeyama[1,2], Yuuki Inoue[2], Kenji Chayama[2], Satoshi Iwatsuki[2], Koichiro Takao[1]
（1. Tokyo Institute of Technology, 2. Konan University）
1:20 PM - 1:40 PM

[H201-3pm-02] Anthracene-based molecular tweezers: construction of self-assembled cyclic hexamer through complementary interactions
○Yuta SAWANAKA[1], Masahiro YAMASHINA[1], Shinji TOYOTA[1]（1. Tokyo Tech）
1:40 PM - 2:00 PM

[H201-3pm-03] Structural control of sheet-like diketopyrrolopyrrole aggregates by seeded polymerization and their excited-state dynamics
○Soichiro Ogi[1], Natsumi Fukaya[1], Hikaru Sotome[2], Kazuhiro Fujimoto[3], Takeshi Yanai[1,3], Hiroshi Miyasaka[2], Shigehiro Yamaguchi[1,3]（1. Graduate School of Science, Nagoya University, 2. Graduate School of Engineering Science, Osaka University, 3. Institute of Transformative Bio-Molecules, Nagoya University）
2:00 PM - 2:20 PM

[H201-3pm-04] Nanoscale Twinning of Molecular Self-Assembled Networks
Kyohei Yamagata[1], Matsuhiro Maeda[1], Zeno Tessari[2], Kunal S. Mali[2], Steven De Feyter[2], ○Kazukuni Tahara[3]（1. Graduate School of Science and Technology, Meiji University, 2. Department of Chemistry, KU Leuven, 3. School of Science and Technology, Meiji University）
2:20 PM - 2:40 PM

[H201-3pm-05] Transformation of highly hydrophobic organophosphorus compounds into supramolecular amphiphiles through the Staudinger reaction
○Masahiro Yamashina Yamashina[1], Hayate Suzuki[1], Shinji Toyota[1]（1. Tokyo Tech.）
2:40 PM - 3:00 PM

[H201-3pm-06] Supramolecular Polymerization of Photo-Aromatizable Thiophene-Fused Chiral [4*n*]Annulene: Photofunctions and Chiral Superstructures
○Tsubasa Aoki[1], Michihisa Ueda[1], Takuzo Aida[1,2], Yoshimitsu Itoh[1,3]（1. Grad. Sch. Eng., The Univ. of Tokyo, 2. RIKEN CEMS, 3. PRESTO, JST）
3:00 PM - 3:20 PM

[H201-3pm-07] 'Spontaneous' Pathway Selection in Stereochemical Supramolecular

Copolymerization: Metal– Organic Nanotubes Assembled with a Planar Chiral Monomer

○Yingluo Zhao[1,2], Hiroko Kawano, Hiroshi Yamagishi[3], Saya Otake[1], Yoshimitsu Itoh[1], Nobutaka Shimizu[4], Hubiao Huang[2], Takuzo Aida[1,2] （1. The University of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. Tsukuba University, 4. High Energy Accelerator Research Organization）

3:20 PM - 3:40 PM

K2

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

[K2-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Okano Kentaro, Yuji Nishii
2:00 PM - 3:40 PM K2 (Online Meeting)

[K2-3pm-01] Synthesis of Bisbenzofuropyrazines by Pd-catalyzed Intramolecular Double Cyclization and Their Room Temperature Phosphorescence Properties

○Shotaro Nakamura[1], Madoka Tsuboi[1], Taisei Taniguchi[1], Yuji Nishii[1], Norimitsu Tohnai[1], Masahiro Miura[2] （1. Osaka Univ., 2. ICS-OTRI, Osaka Univ.）

2:00 PM - 2:20 PM

[K2-3pm-02] Decaazapentacenes appended with electron-rich triphenylamine and phenanthrene units - their redox-coupled photophysical and self-assembling properties.

○Gary James Richards[1], Majid Tamboli[1], Keita Aoki[1], Jonathan P. Hill[2], Akiko Hori[1] （1. Shibaura Institute of Technology, 2. National Institute for Materials Science）

2:20 PM - 2:40 PM

[K2-3pm-03] 3-Position-selective Trifluoromethylation of Pyridine Rings Using Nucleophilic Activation based on 1,4-Reduction

○Ryuhei Muta[2], Takeru Torigoe[1,2], Yoichiro Kuninobu[1,2] （1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University）

2:40 PM - 3:00 PM

[K2-3pm-04] Design, Synthesis, Properties of TEtraQuinoline (TEQ) and its Application as Zinc(II) Ion Fluorescence Sensor

○Wei Xu[1], Naoya Kumagai[1,2] （1. Keio University, 2. Institute of Microbial Chemistry）

3:00 PM - 3:20 PM

[K2-3pm-05] In Situ Transmetalation and Lewis Acid-Catalyzed Halogen Dance of *N*-Heteroaryllithiums

○Kengo Inoue[1], Yuxuan Feng[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）

3:20 PM - 3:40 PM

K4

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

[K4-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Takashi Niwa, Takuya Kodama
2:20 PM - 3:40 PM K4 (Online Meeting)

[K4-3pm-02] Phosphine-Catalyzed Three-Component Coupling of Acyl Fluorides, Alkynes, and Silyl Nucleophiles

○Hayato Fujimoto[1], Momoka Kusano[1], Shisato Yamamura[1], Takuya Kodama[1], Mamoru Tobisu[1] （1. Osaka Univ.）

2:40 PM - 3:00 PM

[K4-3pm-03] Synthesis and Isolation of Phosphine-Stabilized Phosphenium Complexes with a [2]Ferrocenophane Framework

○Tianqing Zhang[1], Vladimir Ya. Lee[2], Shinobu Aoyagi[1], Takahiro Sasamori[2] （1. Graduate School of Science, Nagoya City University, 2. Faculty of Pure and Applied Sciences, University of Tsukuba）

3:00 PM - 3:20 PM

[K4-3pm-04] NUCLEOPHILIC SUBSTITUTION OF 2,2-BIS(ARYLTHIO)-4,4,6,6-TETRACHLOROCYCLOTRIPHOSPHAZENE WITH

AMMONIA, PHENOXIDE, AND THIOPHENOXIDE

○Manabu KUROBOSHI[1], Hideo TANAKA[1], Ayako UENO[1], Ayane Kawano[1] (1. Okayama University)

3:20 PM - 3:40 PM

K307

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

[K307-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Yoshitaka Aramaki, Yasuhiro Yamashita, Takeshi Nanjo
1:00 PM - 3:40 PM K307 (Online Meeting)

[K307-3pm-01] Asymmetric Preparation of β-Amino-α-ketoacids by the Highly Stereoselective Mannich-type Addition for the Peptide Synthesis

○Yusuke Tokuhiro[1], Kosuke Yoshikawa[1], Sei Murayama[1], Takeshi Nanjo[1], Yoshiji Takemoto[1] (1. Grad. Sch. Pharm. Sci., Kyoto Univ.)

1:00 PM - 1:20 PM

[K307-3pm-02] Elucidation of the Stereocontrol Mechanism in Chiral Borate Catalysis toward Data-Driven Catalyst Design

○Fumito Ueoka[1], Shigeru Yamaguchi[2], Daisuke Uraguchi[3], Takashi Ooi[1] (1. Nagoya University, 2. RIKEN, 3. Hokkaido University)

1:20 PM - 1:40 PM

[K307-3pm-03] Development of Addition Reactions of Ketones with Alkenes through Photo-Induced Activation of Their Enolates

○Tsubasa Hirata[1], Yoshihiro Ogasawara[1], Yasuhiro Yamashita[1], Shu Kobayashi[1] (1. The University of Tokyo)

1:40 PM - 2:00 PM

[K307-3pm-04] Development of Catalytic Enantioselective Mannich Reactions of Esters and Effective Transformations of the Mannich Adducts toward Asymmetric Synthesis of β-Lactams

○Seiya Fushimi[1], Tomoya Kimura[1], Yasuhiro Yamashita[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

2:00 PM - 2:20 PM

[K307-3pm-05] Development of Bifunctional Cyclooctene Catalysts

○Tagui NAGANO[1], Keisuke ASANO[1], Seijiro MATSUBARA[1] (1. Kyoto Univ.)

2:20 PM - 2:40 PM

[K307-3pm-06] Tandem Enantioselective [3+2] and [4+2] Cycloaddition Reactions of *in situ*-generated *N*-allenoylpyrazoles induced by Chiral π – Cu(II) Catalyst

○Weiwei Guo[1], Masahiro Hori[1], Yoshihiro Ogura[1], Kazuki Nishimura[1] (1. Nagoya Univ.)

2:40 PM - 3:00 PM

[K307-3pm-07] Parallel kinetic resolution via bromocyclization reaction enabled by Lewis/Brø nsted base concerted catalysis of chiral bisphosphine oxide

○Ryo Hirokawa[1], Mamoru Ichikawa[1], Tatsunari Hisanaga[1], Yuji Kawato[1], Ryo Takita[2], Kohei Watanabe[2], Kenji Yamashita[1], Yoshitaka Hamashima[1] (1. School of Pharmaceutical Sciences, The Univ. of Shizuoka, 2. Graduate School of Pharmaceutical Sciences, The Univ. of Tokyo)

3:00 PM - 3:20 PM

[K307-3pm-08] 9-Fluorenol-Catalyzed Denitrative Radical Generation from Nitroalkanes

○Myuto Kashihara[1], Kohei Kosaka[1], Naoki Matsushita[1], Shunta Notsu[1], Ayumi Osawa[1], Yoshiaki Nakao[1] (1. Kyoto University)

3:20 PM - 3:40 PM

B104

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

[B104-3am] 16. Natural Products Chemistry, Chemical Biology

Chair: Taiki Kuribara, Takefumi Kuranaga
9:00 AM - 11:20 AM B104 (Online Meeting)

[B104-3am-01] Synthetic Study on Ellagitannins Using Stereocontrol of Sugar Conformations

○Shintaro Matsumoto[1], Kei Murakami[1], Shinnosuke Wakamori[2] (1. Kwansei Gakuin Univ., 2. Tokyo Univ. of Agriculture)

9:00 AM - 9:20 AM

[B104-3am-02] Synthetic Study of High-mannose-type Glycan Library Using Dendritic

Glycosylation Strategy

○Ruchio Usui[1], Megumi Kabasawa[1], Tatsuya Hirukawa[1], Taiki Kuribara[1], Kiichiro Totani[1] (1. Seikei University)

9:20 AM - 9:40 AM

[B104-3am-03] Development of fluorescent-labeled glycan probe towards CRT

○Taiki Kuribara[1], Taiga Kojima[1], Keita Shibayama[1], Yoichi Takeda[2], Kiichiro Totani[1] (1. Seikei University, 2. Ritsumeikan University)

9:40 AM - 10:00 AM

[B104-3am-04] Design and evaluation of derivatives of a measles virus inhibitor peptide that inhibits conformational change of measles virus fusion protein

○Ziwei Gao[1], Jumpei Morimoto[1], Jiei Sasaki[2], Tateki Suzuki[2], Takao Hashiguchi[2], Shinsuke Sando[1] (1. Graduate School of Engineering, The University of Tokyo, 2. Institute for Frontier Life and Medical Sciences, Kyoto University)

10:00 AM - 10:20 AM

[B104-3am-05] Development of Macrocyclic Peptide Heterodimer as PPI Inhibitor against Immune Checkpoint CD47- SIRPα

○Jinxuan ZHAO[1], Yoji Murata[2], Naohiro Terasaka[1], Takashi Matozaki[2], Suga Hiroaki[1] (1. the University of Tokyo, 2. Kobe University)

10:20 AM - 10:40 AM

[B104-3am-06] *In vitro* selection of antibiotic peptides that inhibit the bacterial ribosome

○Rei Takahashi[1], Takayuki Katoh[1], Axel Innis[2], Hiroaki Suga[1] (1. The University of Tokyo Graduate School of Science Department of Chemistry, 2. Institut Européen de Chimie et Biologie (IECB))

10:40 AM - 11:00 AM

[B104-3am-07] Total synthesis of acremoxanthone A, a naturally occurring heptacyclic aromatic polyketide

○Hiroshi Nakakohara[1], Yoichi Hirano, Hiroshi Takikawa[2], Keisuke Suzuki[3], Ken Ohmori[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Graduate School of Pharmaceutical Sciences, Kyoto University, 3. Institute of Innovative Research, Tokyo Institute of Technology)

11:00 AM - 11:20 AM

G301

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

[G301-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Takayuki Miki, Takashi Hayashi
1:00 PM - 3:40 PM G301 (Online Meeting)

[G301-3pm-01] Development of peptide tags self-assembling in cells 1: Protein-protein interaction analysis accompanied by cluster formation

○Masahiro Hashimoto[1], Takayuki Miki[1], Taichi Nakai[1], Tatsuya Niwa[1,2], Hisakazu Mihara[1] (1. Tokyo Institute of Technology, School of Life Science and Technology, 2. Tokyo Institute of Technology, Institute of Innovative Research)

1:00 PM - 1:20 PM

[G301-3pm-02] Development of peptide tags self-assembling in cells 2: Design and construction of highly-ordered protein assemblies

○Takayuki Miki[1], Hiroki Takahashi[1], Masahiro Hashimoto[1], Keigo Kajiwara[1], Sae Nakayama[1], Hisakazu Mihara[1] (1. Tokyo Institute of Technology)

1:20 PM - 1:40 PM

[G301-3pm-03] Energy Transfer in a Disulfide Bond-Mediated Heterodimer Consisting of a Fluorescent Protein and a Hemoprotein

○Julian Wong Soon[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka University)

1:40 PM - 2:00 PM

[G301-3pm-04] Directed Evolution of Myoglobin Reconstituted with an Iron Corrole Complex Using a New High-throughput Screening Platform Based on an Affinity Purification System

○Koki Takeuchi[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Graduate School of Engineering, Osaka University)

2:00 PM - 2:20 PM

[G301-3pm-05] Development of a Protein Purification

System using MBP-tagged Streptavidin and its Application for the Construction of Reconstituted Heme Protein Library

○Motonao Iwaki[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Osaka University)

2:20 PM - 2:40 PM

[G301-3pm-06] Millisecond absorption change and its molecular origin of blue light sensor BLUF protein

○Shunrou Tokonami[1], Morihiko Onose[1], Yusuke Nakasone[1], Masahide Terazima[1] (1. Kyoto University)

2:40 PM - 3:00 PM

[G301-3pm-07] Enhancing the signal response of the auto-fluorescent protein-based NO biosensor

○Shunsuke Tajima[1], Eiji Nakata[1], Reiko Sakaguchi[2], Masayuki Saimura[1], Yasuo Mori[3], Takashi Morii[1] (1. Institute of Advanced Energy, Kyoto University, 2. School of Medicine, University of Occupational and Environmental Health, 3. Graduate School of Engineering, Kyoto University)

3:00 PM - 3:20 PM

[G301-3pm-08] Genetically encoded biosensors for L-lactate

○Yusuke Nasu[1], Saaya Hario[1], Robert E Campbell[1] (1. The University of Tokyo)

3:20 PM - 3:40 PM

G201

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

[G201-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Tatsuya Nishihara, Tomonori Tamura
1:00 PM - 3:40 PM G201 (Online Meeting)

[G201-3pm-01] Prototype Screening and Optimization of HaloTag-based Chemigenetic Fluorescent Indicators

○Dazhou CHENG[1], Wenchao ZHU[1], Takuya TERAI[1], Yusuke NASU[1], Robert Earl CAMPBELL[1,2] (1. Department of Chemistry, Graduate School of Science, The University of Tokyo, 2. Department of Chemistry, University of Alberta)

1:00 PM - 1:20 PM

[G201-3pm-02] Orthogonal activation of GPCR-type glutamate receptor via coordination-based chemogenetics

○Akinobu Senoo[1], Yamada Yutaro[1], Ojima Kento[1,2], Doura Tomohiro[1], Kiyonaka Shigeki[1] (1. Nagoya Univ., 2. Kyoto Univ.)

1:20 PM - 1:40 PM

[G201-3pm-03] Comprehensive imaging of hypoxic cells by fluorescent probes with azide group

○Hiroki Makanai[1], Miei Kanda, Tatsuya Nishihara[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

1:40 PM - 2:00 PM

[G201-3pm-04] *FixEL*: a new method for visualizing ligand dynamics in the brain by reframing the PFA fixation chemistry.

○Takeharu Mino[1], Hiroshi Nonaka[1,2], Seiji Sakamoto[1], Jae Hoon Oh[2], Yu Watanabe[1], Mamoru Ishikawa[2], Akihiro Tsushima[1], Kazuma Amaike[1], Shigeki Kiyonaka[2,3], Tomonori Tamura[1,2], Radu Aricescu[4,5], Wataru Kakegawa[2,6], Eriko Miura[6], Michisuke Yuzaki[6], Itaru Hamachi[1,2] (1. Graduate School of Engineering, Kyoto University, 2. JST ERATO, 3. Graduate School of Engineering, Nagoya University, 4. Division of Structural Biology, University of Oxford, 5. Neurobiology Division, MRC Laboratory of Molecular Biology, 6. Keio University School of Medicine)

2:00 PM - 2:20 PM

[G201-3pm-05] Mapping a glutamate receptor interactome in living mice by photoactivated proximity labeling

○Mikiko Takato[1], Hayata Utsunomiya[1], Tomonori Tamura[1], Itaru Hamachi[1,2] (1. Kyoto University, 2. JST ERATO)

2:20 PM - 2:40 PM

[G201-3pm-06] Fluorogenic labeling of lipid droplets via intralipid click reaction

○Hiro Shiotani[1], Junwei Wang[1], Masayasu Taki[1], Shigehiro Yamaguchi[1] (1. Nagoya university)

2:40 PM - 3:00 PM

[G201-3pm-07] Fluorescence Imaging of Fatty Acid Beta Oxidation Pathway in Tissue Samples

Using An Activity-Based Probe

○Shohei Uchinomiya[1], Tomoki Nagaura[1], Naoya Matsunaga[1], Akito Tsuruta[1], Kazuya Inoue[1], Shigehiro Ohdo[1], Akio Ojida[1] (1. pharmaceutical science, Kyushu University)

3:00 PM - 3:20 PM

[G201-3pm-08] Substituted *meso*-Vinyl-BODIPY as Thiol-Selective Fluorogenic Probes for Sensing Unfolded Proteins in Living Cells

○HUIYING MU[1], Koji Miki[1], Kouichi Ohe[1] (1. Kyoto University)

3:20 PM - 3:40 PM

G101

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

[G101-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Yuichiro Aiba, Yasuaki Kimura
1:00 PM - 3:40 PM G101 (Online Meeting)

[G101-3pm-01] Color-changing fluorescent barcode based on strand displacement reaction for multiplexed imaging of biomolecules

○Koki Makino[1], Hiroyuki Asanuma[1], Hiromu Kashida[1] (1. Graduate School of Engineering, Nagoya University)

1:00 PM - 1:20 PM

[G101-3pm-02] Nucleic Binding Selectivity of RGG Domain in TLS/FUS Regulated by Arginine Methylation

○Tatsuki Masuzawa[1], Ryota Yagi[2], Shinnosuke Kawai[2], Takanori Oyoshi[2] (1. Graduate school of Science and Technology, Shizuoka University, 2. Graduate school of Integrated Science and Technology, Shizuoka University)

1:20 PM - 1:40 PM

[G101-3pm-03] NMR study on the binding of naphthyridine dimer to d(CGG) triad

○Shuhei Sakurabayashi[1,2], Kyoko Furuita[1], Takeshi Yamada[2], Toshimichi Fujiwara[1], Kazuhiko Nakatani[2], Chojiro Kojima[1,3] (1. SANKEN, Osaka University, 2. Institute for Protein Research, Osaka University, 3. Yokohama National University)

1:40 PM - 2:00 PM

[G101-3pm-04] Recognition of double-stranded DNA by using parallel-stranded PNAs

○Masanari Shibata[1], Yuichiro Aiba[1], Masaki Hibino[1], Hiroshi Sugimoto[2], Osami Shoji[1] (1. Nagoya University, 2. Riken/SPring-8)

2:00 PM - 2:20 PM

[G101-3pm-05] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (78) : Analysis of structural dynamics of *c-Myc* G-quadruplex DNA using high pressure

○Shuntaro Takahashi[1], Tatsuya Ohyama[1], Shuo-Bin Chen[2], Jia-Heng Tan[2], Naoki Sugimoto[1,3] (1. Konan Univ. FIBER, 2. Sun Yat-sen Univ., 3. Konan Univ. FIRST)

2:20 PM - 2:40 PM

[G101-3pm-06] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (75): Development of RNA-ligand pairs for multicolor RNA imaging in cells

○Tamaki Endoh[1], Jia-Heng Tan[2], Shuo-Bin Chen[2], Naoki Sugimoto[1,3] (1. FIBER, Konan University, 2. Sun Yat-sen Universsity, 3. FIRST, Konan University)

2:40 PM - 3:00 PM

[G101-3pm-07] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (73):Effect of G-quadruplex stability change on transcriptional repression in cancer cells

○Hisae Tateishi-Karimata[1], Keiko Kawauchi[2], Tatsuya Ohyama[1], Hirano Masaki[3], Atsushi Natsume[4], Naoki Sugimoto[1,2] (1. Frontier Institute for Biomolecular Engineering Research (FIBER) Konan University, 2. Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Ko-nan University, 3. Division of Molecular Oncology, Aichi Cancer Center Research Institute, 4. Nagoya University, The Institute of Innovation for Future Society)

3:00 PM - 3:20 PM

[G101-3pm-08] Membrane permeable oligonucleotide (MPON) modified with disulfide units induces efficient exon skipping through enhanced membrane permeability and nucleus internalization

○Haruka Hiraoka[1], Zhaoma Shu[1], Bao Tri Le[2], Keiko Masuda[3], Kosuke Nakamoto[1], Kotaro

Hayashi[4], Naoko Abe[1], Yasuaki Kimura[1], Rakesh N. Veedu[2], Yoshihiro Shimizu[3], Satoshi Uchida[5], Hiroshi Abe[1,3,6] (1. Nagoya Univ., 2. Murduch Univ., 3. RIKEN, 4. iCONM, 5. Kyoto Pref. Univ. of Med., 6. iGCORE)

3:20 PM - 3:40 PM

G202

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

[G202-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Ryo Okamoto, Shinya Hanashima
1:00 PM - 3:40 PM G202 (Online Meeting)

[G202-3pm-01] Elucidation of dynamic behavior of exosome membranes involved in intracellular uptake efficiency

○Tomokazu Yasuda[1], Koichiro M Hirosawa[2], Kenichi G.N. Suzuki[2], Kazuya Kabayama[1], Michio Murata[1], Shinya Hanashima [1] (1. The University of Osaka, 2. Institute for Glyco-core Research (iGCORE), Gifu University)

1:00 PM - 1:20 PM

[G202-3pm-02] Membrane Deformations by Designed Molecules: Endocytosis-like Vesicle Fission Induced by a Photoreactive Amphiphilic Molecule

Noriyuki Uchida[1], ○Takahiro Muraoka[1] (1. Tokyo Univ. of Agriculture and Technology)

1:20 PM - 1:40 PM

[G202-3pm-03] Control of molecular localization in artificial cells using chemical inputs

○Keita Tsutsui[1], Masaru Yoshikawa[1], Tomoaki Matsuura[2], Shinya Tsukiji[1] (1. Grad. Sch. of Eng. Nagoya Inst. of Tech., 2. Tokyo Inst. of Tech. ELSI)

1:40 PM - 2:00 PM

[G202-3pm-04] Asymmetric lipid-protein vesicles facilitate function of membrane proteins and construction of cell fission model

○Masato Suzuki[1], Koki Kamiya[1] (1. Gunma Univ)

2:00 PM - 2:20 PM

[G202-3pm-05] Preparation and functional analysis of single chain antibodies bound to sialyl Tn antigen sugar chains

○Mitsuki Hashiguchi[1], Komi Yoshimatsu[1], Yumi Matsubayashi[1], Kaito Hashiguchi[1], Nana Masunaga[1], Hiroyuki Shinchi[1], Masahiro Wakao[1], Yuji Ito[1], Yasuo Suda[1] (1. The Univ. of Kagoshima)

2:20 PM - 2:40 PM

[G202-3pm-06] One Pot-Chemical Synthesis of Glycoproteins and Their Specific Glycan-Hydration Effect

○Hiroyuki Shibata[1], Yuya Tanaka[1], Donglin Zhao[1], Yuta Maki[1,2], Yasuhiro Kajihara[1,2], Ryo Okamoto[1,2] (1. Dept. Chem., Grad. Sch. Sci., Osaka Univ., 2. PRC,Grad. Sch. Sci., Osaka Univ.)

2:40 PM - 3:00 PM

[G202-3pm-07] Synthesis of *N*-glycolylneuraminic acid derivatives (IV)
~Investigation of the glycosylation reaction~

○Jianhong Zhang[1], Tetsuo Koyama[1], Takahiro Matsushita[1,2], Ken Hatano[1,2], Koji Matsuoka[1,2] (1. graduate school of science and engineering, saitama university, 2. advanced institute of innovative technology, saitama university)

3:00 PM - 3:20 PM

[G202-3pm-08] Orientation of the Ganglioside GM3 Glycan in Lipid Bilayers as Elucidated by Solid-State NMR

○Katsuaki Sasaki[1], Yuichi Umegawa[1], Michio Murata[1], Shinya Hanashima[1] (1. Grad. Sch. Sci., Osaka Univ.)

3:20 PM - 3:40 PM

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

[G202-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Takafumi Ueno, Osami Shoji
4:10 PM - 6:50 PM G202 (Online Meeting)

[G202-3vn-01] Analysis of activation mechanisms of P450BM3 by decoy molecules

○Kai Yonemura[1], Shinya Ariyasu[1], Hiroshi Sugimoto[2], Shigeru Matsuoka[3], Osami Shoji[1] (1. Nagoya University, 2. RIKEN/SPring-8, 3. Oita University)

4:10 PM - 4:30 PM

[G202-3vn-02] Structural investigations of a semi-clathrate hydrate formation using porous ferritin crystal
○Jiaxin Tian[1], Basudev Maity[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)
4:30 PM - 4:50 PM

[G202-3vn-03] Structural analysis by engineering cell-free protein crystals
○Junko Tanaka[1], Satoshi Abe[1], Shuji Kanamaru[1], Takafumi Ueno[1] (1. The Univ. of Tokyo Institute of Technology)
4:50 PM - 5:10 PM

[G202-3vn-04] In-cell crystal engineering for the development of solid biomaterials
○Satoshi Abe[1], Mariko Kojima[1], Junko Tanaka[1], Yuto Nakasuji[1], Takafumi Ueno[1] (1. Tokyo Tech)
5:10 PM - 5:30 PM

[G202-3vn-05] Dynamics structural analysis of miniprotein by in-cell crystal engineering
○Mariko Kojima[1], Yuki Hishikawa[1], Satoshi Abe[1], Tadaomi Furuta[1], Duy Phuoc Tran[1], Akio Kitao[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)
5:30 PM - 5:50 PM

[G202-3vn-06] Experimental and theoretical study on converting myoglobin into a stable domain-swapped dimer by utilizing a tight hydrogen bond network at the hinge region
○Cheng Xie[1], Hiromitsu Shimoyama[2], Masaru Yamanaka[1], Satoshi Nagao[1], Hirofumi Komori[4], Naoki Shibata[3], Yoshiki Higuchi[3], Yasuteru Shigeta[2], Shun Hirota[1] (1. Nara Inst. Sci. Tech. (NAIST), 2. Univ. of Tsukuba, 3. Univ. of Hyogo, 4. Kagawa Univ.)
5:50 PM - 6:10 PM

[G202-3vn-07] Re-design of an artificial protein nanocage TIP60: structural analysis of a mutant assembled by responding to metal ions
○Naoya Ohara[1], Norifumi Kawakami[1], Ryoichi Arai[2], Naruhiko Adachi[3], Toshio Moriya[3], Masato Kawasaki[3], Toshiya Senda[3], Kenji Miyamoto[1] (1. Keio University, 2. Shinshu University, 3. High Energy Accelerator Research Organization)
6:10 PM - 6:30 PM

[G202-3vn-08] Construction of hydrogel containing an engineered hexameric hemoprotein and evaluation of its redox-responsive mechanical properties
○Kazuki Kageyama[1], Koji Oohora[1], Hayashi Takashi[1] (1. Osaka univ.)
6:30 PM - 6:50 PM

G201

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

[G201-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Takahiro Muraoka, Kazuma Amaike
4:10 PM - 5:50 PM G201 (Online Meeting)

[G201-3vn-01] Design, synthesis, and chiroptical properties of macrocyclic oligomers composed of bispyrrolidinoindoline scaffold
○Tasuku honda[1], Daiji Ogata[2], Junpei Yuasa[2], Takahiro Muraoka[3], Hiroki Oguri[1] (1. The University of Tokyo, 2. Tokyo University of Science, 3. Tokyo University of Agriculture and Technology)
4:10 PM - 4:30 PM

[G201-3vn-02] Development of functional oligonucleotide for target metabolite analysis
○Tatsuya Nishihara[1], Shuhei Moritani[1], Yuto Motohashi[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)
4:30 PM - 4:50 PM

[G201-3vn-03] Identification and molecular control of diapause-inducing signal in silkworm
○Hayato Yamada[1], Kazuma Amaike[1], Kenichiro Itami[1] (1. Nagoya University)
4:50 PM - 5:10 PM

[G201-3vn-04] Development of Nanocarbon Molecules Accelerating Nucleic Acid Transport
○Erika Kato[1], Zetschok Dominik[1], Kazuma Amaike[1], Kenichiro Itami[1,2] (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University)
5:10 PM - 5:30 PM

[G201-3vn-05] Development of a novel stomatal opening inhibitor and its mechanistic study

○Ayaka Ueda[1], Yusuke Aihara[1], Hiroyuki Kitano[1], Shigeo Toh[3], Kazuma Amaike[1], Hideto Ito[1], Shinya Hagihara[4], Toshinori Kinoshita[1,2], Kenichiro Itami[1,2] （1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University, 3. Faculty of Agriculture, Meijo University, 4. CSRS）

5:30 PM - 5:50 PM

C203

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

[C203-3pm] 18. Polymer

Chair: Akifumi Kawamura, Rintaro Takahashi
1:40 PM - 3:40 PM C203 (Online Meeting)

[C203-3pm-01] Development of Poly(Ester– Carbonate)s Comprising Aromatic Mesogens and Aliphatic Oligocarbonates with Hydrophilic Side-Chains

○Yuya Watanabe[1], Riki Kato[1], Kazuki Fukushima[1], Takashi Kato[1] （1. Sch. of Eng., The Univ. of Tokyo）

1:40 PM - 2:00 PM

[C203-3pm-02] Relationship between viscoelastic properties and molecular behavior of physical gels with ideal network cross-linked by duplex DNA

○Masashi Ohira[1], Katashima Takuya[1], Naito Mitsuru[1], Aoki Daisuke[2], Sakai Takamasa[1], Shibayama Mitsuhiro[3], Xiang Li[4] （1. The Univ. of Tokyo, 2. Tokyo Tech., 3. CROSS, 4. Hokkaido Univ.）

2:00 PM - 2:20 PM

[C203-3pm-03] Design and Synthesis of Amphiphilic Alternating Peptides with LCST Behaviors

Namiki Komuro[1], Noriyuki Nakajima[1], Masahiro Hamada[1], ○Yasuhito Koyama[1] （1. Toyama Pref. Univ.）

2:20 PM - 2:40 PM

[C203-3pm-04] Synthesis of Zwitterionic Polymers with 4-Armed Structures and Their Photo-gelation

○Takashi Miyata[1], Kurumi Fukao[1], Akifumi Kawamura[1] （1. Kansai Univ.）

2:40 PM - 3:00 PM

[C203-3pm-05] Nanostructure formation on fiber surfaces of filter paper via hydrolysis and self-assembly of cellulose

○Yuuki Hata[1], Sumiyo Hiruma[1], Hiromi Miyazaki[1], Shingo Nakamura[1] （1. Nat'l Def. Med. Coll.）

3:00 PM - 3:20 PM

[C203-3pm-06] Construction of a Novel System for Cancer Cell-specific Delivery Utilizing MMP-9 Activity IV: Effect of Polymer Structure upon MMP Responsibility and Cellular Uptake Efficiency

Nagisa Kanazawa[1], Ryota Azuma[1], Yuka Matsuhashi[1], Ikuhiko Nakase[2], Tsuyoshi Yamamoto[3], Masaki Nishijima[1], Yasuyuki Araki[1], Asako Yamayoshi[3], ○Takehiko WADA[1] （1. Tohoku Univ., 2. Osaka Prefecture Univ., 3. Nagasaki Univ.）

3:20 PM - 3:40 PM

A202

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

[A202-3pm] 19. Colloid and Interface Chemistry

Chair: Tsuyoshi Akiyama, Toshiki Sawada
1:40 PM - 3:40 PM A202 (Online Meeting)

[A202-3pm-01] Formation of Spherical Colloidal Clusters with Icosahedral Structure: Dependence on Colloidal Particle Size

○Ryosuke Ohnuki[1], Yukikazu Takeoka[2], Yoshioka Shinya[1] （1. Tokyo University of Science, 2. Nagoya University）

1:40 PM - 2:00 PM

[A202-3pm-02] Synthesis and Solution Properties of Amino Acid-Sugar Hybrid Surfactants Using Glycine and Maltose

○Yumi Nagahama[1], Ayami Kobayashi[1], Yohsuke Hada[2], Shigetoyo Sawaki[2], Shiho Yada[1], Tomokazu Yoshimura[1] （1. Grad. Sch. Human. Sci., Nara Women's Univ., 2. Technoble Co., Ltd.）

2:00 PM - 2:20 PM

[A202-3pm-03] Guest-responsive supramolecular hydrogels expressing selective sol– gel

transition for sulfated glycosaminoglycans
○Shun-ichi Tamaru[1], Naofumi Kuroda[1] (1. Sojo University)
2:20 PM - 2:40 PM

[A202-3pm-04] Correlation between Liquid Crystalline and Gelation Properties with Ionic Liquid Gels Formed by Fluorine-Containing Phenyl Benzoate Derivatives That Exhibits Liquid Crystallinity
Tatsuya Tomarino[1], ○Kenta Matsumoto[1], Yuta Kawamoto[1], Junya Yamaguchi[1], Kotaro Kanetada[1], Masashi Akiyama[2], Yuki Morita[3], Hiroaki Okamoto[1] (1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University, 3. Advanced Technology Institute, Yamaguchi University)
2:40 PM - 3:00 PM

[A202-3pm-05] Construction of covalent cluster framework by using the reactivities of surface ligands
Yuki Saito[1], Yukatsu Shichibu[1,2], ○Katsuaki KONISHI[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)
3:00 PM - 3:20 PM

[A202-3pm-06] Coherent Motion of Billions of Nanosheets for Generating Propagating Wave
○Koki Sano[1,2,3], Ebina Yasuo[4], Takayoshi Sasaki[4], Yasuhiro Ishida[3] (1. Shinshu Univ., 2. JST PRESTO, 3. RIKEN, 4. NIMS)
3:20 PM - 3:40 PM

C204

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

[C204-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Mihoko Yamada, Naoki Tanaka
1:00 PM - 3:40 PM C204 (Online Meeting)

[C204-3pm-01] Electron doping of single-walled carbon nanotubes starting from diborane compounds
○Naoki Tanaka[1,2], Aoi Hamasuna[1], Koichiro Kato[1,2,3], Tsuyohiko Fujigaya[1,2,3] (1. Department of Applied Chemistry, Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)
1:00 PM - 1:20 PM

[C204-3pm-02] Near Infrared Photoluminescence Modulation of Biotin-functionalized Single-walled Carbon Nanotubes Based on Avidin Binding
○Yoshiaki Niidome[1], Rie Wakabayashi[1], Masahiro Goto[1,2], Tsuyohiko Fujigaya[1,3,4], Tomohiro Shiraki[1,3] (1. Graduate School of Engineering, Kyushu Univ., 2. CFC, Kyushu Univ., 3. WPI-I2CNER, Kyushu Univ., 4. CMS, Kyushu Univ.)
1:20 PM - 1:40 PM

[C204-3pm-03] Near Infrared Emission Property Variation of Chemically Functionalized Single-walled Carbon Nanotubes Based on Structures of Chemical Modifiers
○Tomohiro Shiraki[1,2], Haruka Aoki[1], Keita Hayashi[1], Tsuyohiko Fujigaya[1,2,3] (1. Department of Applied Chemistry, Kyushu University, 2. I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)
1:40 PM - 2:00 PM

[C204-3pm-04] Preparation and characterization of carbon nanotube dispersions exhibiting liquid crystal phase
○Keiko Kojima[1,2], Miho Aizawa[2,3], Takahiro Yamamoto[2], Kazufumi Kobashi[2], Toshiya Okazaki[2,1] (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST), 3. JST PRESTO)
2:00 PM - 2:20 PM

[C204-3pm-05] Control of near-infrared photoluminescence of single-walled carbon nanotube by chemical functionalization with dendron and its end group conversion
○Yui Konno[1], Michio Yamada[1], Yutaka Maeda[1] (1. Tokyo Gakugei University)
2:20 PM - 2:40 PM

[C204-3pm-06] Precise synthesis of graphene nanoribbon

in metal-organic framework

○Takashi Kitao[1,2], Kazuki Nakata[1], Takashi Uemura[1] （1. The Univ. of Tokyo, 2. JST-PRESTO）

2:40 PM - 3:00 PM

[C204-3pm-07] Carbon-doped Graphitic Carbon Nitride Based Films as New Functional Materials

○Niannian Wu[1,2], Nobuhiko Mitoma[2], Takuzo Aida[1,2] （1. University of Tokyo, 2. Riken）

3:00 PM - 3:20 PM

[C204-3pm-08] Syntheses of new photochromic tetrathienylcorannulenes with a curved aromatic skeleton and their optical properties

○Mihoko Yamada[1], Tomoya Sawazaki[1], Mae Fujita[1], Tomoki Fujitani[1], Tsuyoshi Kawai[1] （1. NAIST）

3:20 PM - 3:40 PM

C205

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

[C205-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Toshihiro Okamoto, Shinya Takaishi
1:20 PM - 3:40 PM C205 (Online Meeting)

[C205-3pm-01] Chromatography separation of hydrogen isotopes at room temperature using dihydrogen complexes

○Shinya Takaishi[1], Tamon Yamauchi[1], Kaiji Uchida[1], Shin-ichiro Noro[2], Naoki Kishimoto[1] （1. Tohoku University, 2. Hokkaido University）

1:20 PM - 1:40 PM

[C205-3pm-02] Semi-Rational Molecular Design for Achieving Ferroelastic Properties

○Chi Feng[1], Mingoo Jin[2], Tomohiro Seki[3], Satoshi Takamizawa[4], Hajime Ito[1,2] （1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. Faculty of Science, Shizuoka University, 4. Graduate School of Nanobioscience, Yokohama City University）

1:40 PM - 2:00 PM

[C205-3pm-03] Aggregated structures and single-crystal n-type transistor properties of N-doped perylene diimides with cyclohexyl-type substituents

○Shohei Kumagai[1], Yutaro Arai[1], Craig P. Yu[1], Naotaka Kasuya[1], Hiroyuki Ishii[2], Go Watanabe[3], Shun Watanabe[1], Jun Takeya[1], Toshihiro Okamoto[1,4,5] （1. The Univ. of Tokyo, 2. Univ. of Tsukuba, 3. Kitasato Univ., 4. PRESTO, JST, 5. CREST, JST）

2:00 PM - 2:20 PM

[C205-3pm-04] A fundamental look at the lab-to-fab transition of a new permanent magnet

○T. Thuy Trinh[1], Ryota Sato[1], Toshiharu Teranishi[1] （1. Kyoto University）

2:20 PM - 2:40 PM

[C205-3pm-05] Diradical character of near-infrared absorbing polymethine dyes consisting of oxocarbon residues

○Taishi Oka[1], Takeshi Maeda[1], Daisuke Sakamaki[2], Hideki Fujiwara[2], Shigeyuki Yagi[1], Tatsuki Konishi[4], Kenji Kamada[3] （1. Graduate School of Engineering, Osaka Prefecture University, 2. Graduate School of Science, Osaka Prefecture University, 3. National Institute of Advanced Industrial Science and Technology, 4. Graduate School of Science and Technology, Kwansei Gakuin University）

2:40 PM - 3:00 PM

[C205-3pm-06] Effect of heavier element on the ultra-low frequency phonons in Nd(III) based luminescent nanomagnets

○KUNAL KUMAR[1], Olaf Stefanczyk[1], Koji Nakabayashi[1], Yuuki Mineo[1], Shin-ichi Ohkoshi[1] （1. University of Tokyo）

3:00 PM - 3:20 PM

[C205-3pm-07] Nanoscale local structural analysis of organic crystal by micro electron diffraction

○Hikaru Sakamoto[1], Masataka Ohtani[1] （1. Kochi university of technology）

3:20 PM - 3:40 PM

D103

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

[D103-3am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Takaya Kubo, Masayuki Yagi
9:00 AM - 11:40 AM D103 (Online Meeting)

[D103-3am-01] Substituents effects of spirobifluorene-based dopant-free hole-transporting materials for perovskite solar cells
○Daisuke Tsuchiya[1], Shinichi Inoue[1], Toshiya Ueno[1], Nobuko Onozawa-Komatsuzaki[2], Atsushi Kogo[2], Takashi Funaki[2], Masayuki Chikamatsu[2], Takurou N. Murakami[2] (1. Nippon Fine Chemical Co., Ltd., 2. National Institute of Advanced Industrial Science and Technology (AIST))
9:00 AM - 9:20 AM

[D103-3am-02] Dopant-free cyano-substituted spiro-type hole-transporting materials for perovskite solar cells
○Nobuko Onozawa-Komatsuzaki[1], Atsushi Kogo[1], Takashi Funaki[1], Masayuki Chikamatsu[1], Takurou Murakami[1], Daisuke Tsuchiya[2], Shinichi Inoue[2], Toshiya Ueno[2] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Nippon Fine Chemical Co., Ltd.)
9:20 AM - 9:40 AM

[D103-3am-03] The effect of ligand coverage on nanocrystals on the carrier collection efficiency of $AgBiS_2$ nanocrystal-based solar cells
○Yun Xiao[1], Haibin Wang[1], Fumiyasu Awai[1], Naoyoki Shibayama[2], Takaya Kubo[1], Hiroshi Segawa[1] (1. The University of Tokyo, 2. Toin University of Yokohama)
9:40 AM - 10:00 AM

[D103-3am-04] Solvent engineering of liquid-phase ligand exchanged PbS quantum dot inks for infrared photovoltaics
○Haibin Wang[1], Yun Xiao[2], Jotaro Nakazaki[2], Takaya Kubo[2], Hiroshi Segawa[1,2] (1. Grad. Sch. Arts and Sci. The Univ. of Tokyo, 2. RCAST, The Univ. of Tokyo)
10:00 AM - 10:20 AM

[D103-3am-05] Solution-phase synthesis of Ag-Bi-S quantum dots for the application to photovoltaics
○Kazutaka Akiyoshi[1], Wentao Zhang[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)
10:20 AM - 10:40 AM

[D103-3am-06] Efficient water oxidation on N-doped $CuWO_4$ photoanodes by immobilization of iron complexes.
○Tomohiro Katsuki[1], Yuta Tsubonouchi[1], Zaki Zahran[1], Masayuki Yagi[1] (1. Grad. School of Sci. Tech., Niigata Univ.)
10:40 AM - 11:00 AM

[D103-3am-07] Investigation of isotopic selectivity on plasmon-induced photoconversion system
○Daiki Sato[1], Hiro Minamimoto[2], Kei Murakoshi[2] (1. Hokkaido University Graduate School of Chemical Sciences and Engineering, 2. Hokkaido University Faculty of Science)
11:00 AM - 11:20 AM

[D103-3am-08] Formate production from CO_2 and water using a $1m^2$-sized artificial photosynthetic cell with a solar-to-chemical conversion efficiency of 10.5%
○Naohiko Kato[1], Yasuhiko Takeda[1], Yasuaki Kawai[1], Natsumi Nojiri[1], Masahito Shiozawa[1], Shintaro Mizuno[1], Ken-ichi Yamanaka,[1], Takeshi Morikawa,[1], Tsuyoshi Hamaguchi[1] (1. Toyota Central R&D Labs., Inc.)
11:20 AM - 11:40 AM

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

[D201-3pm] 01. Education and History of Chemistry

Chair: Osamu Kamei, Tomonori NOMOTO

Fri. Mar 25, 2022 2:00 PM - 3:40 PM D201 (Online Meeting)

[D201-3pm-01] Analysis with the Systematized Survey on the History of Technology: Frozen Ground Eng., E.P. Assisted Bicycle, Telephone Set, Jet engine for Commercial Aircraft, FDD, and Related technologies

○Osamu KAMEI[1] （1. National Museum of Nature and Science）

2:00 PM - 2:20 PM

[D201-3pm-02] A simple spectroscope using a consumer digital camera for live spectroscopic demonstrations

○Tomonori NOMOTO[1] （1. Chiba University）

2:20 PM - 2:40 PM

[D201-3pm-03] Development of Microscale Experiments for Physically Challenged Students

○Kazuyuki Yamada[1], Kazuko Ogino[2] （1. Kirigaoka School for the Physically Challenged, University of Tsukuba, 2. Graduate School of Science, Tohoku University）

2:40 PM - 3:00 PM

[D201-3pm-04] Improvement of "Copper into Gold: The Alchemist's Dream" Using Surfactant and Aluminum Foil

○Takahiro Suzuki[1] （1. Otsuma Ranzan Junior and Senior High School）

3:00 PM - 3:20 PM

技術の系統化調査による分析：凍土工学，電動アシスト自転車，電話機，民間航空機用ジェットエンジン及びフロッピーディスクとドライブの技術開発を中心に

（独立行政法人 国立科学博物館）○亀井 修

Analysis with the Systematized Survey on the History of Technology: Frozen Ground Eng., E.P. Assisted Bicycle., Telephone Set, Jet engine for Commercial Aircraft, FDD, and Related technologies

（*National Museum of Nature and Science, Japan*）○KAMEI, Osamu

The Center of the History of Japanese Industrial Technology (CHJI) with the National Museum of Nature and Science, Japan (NMNS) has been studying the systematized survey on the history of industrial technology which also include the viewpoints of the sustainable development in the Anthropocene. At this time, the analysis of the development tendency with following issues is described; Frozen Ground Engineering, Electric Power Assisted Bicycle, Telephone Set, Jet Engine for Commercial Aircraft, Floppy Disk Drive, and related technologies. The followings are confirmed; technological development starting with product import model, technology development led by the world of ideas and important technology model, suspended flows model, and the difference between "technological innovation" and "innovation".

Keywords : History of Industrial technology; Technological innovation; Innovation; Anthropocene; Sustainable Development

国立科学博物館・産業技術史資料情報センターでは，持続可能な開発や人新世[1)]等の視点も導入し，企業や学協会等の協力や実際の技術開発の現場に携わった専門家による日本の技術開発の歴史を系統的に記録・調査・公開してきている[2)]。本報告では，凍土工学[3)]，電動アシスト自転車[4)]，電話機[5)]，民間航空機用大型ジェットエンジン[6)]，フロッピーディスクとドライブ[7)]の各分野の技術開発の系統化調査に基づく分析を行った。その結果，従前の検討[8) 9)]と同様な「完成品輸入→模倣・ノックダウン・技術導入→国産化→改善・独自技術の開発→世界をリードするトップランナー」といった形の進展や，発想や重要技術が海外に先行あるいは並行して開発，ステップ・アップされた形の進展，途中で伸び悩んだ形となった技術分野があること，「技術革新」と「イノベーション」の違いを確認した。

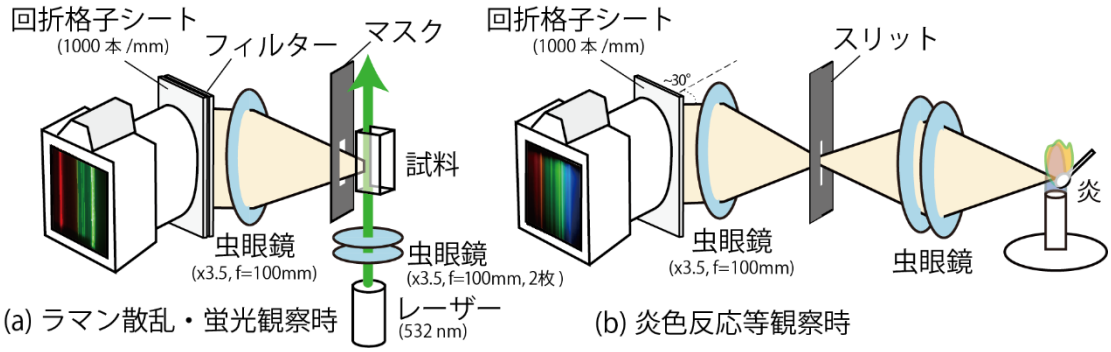
1) Museums in the Anthropocene - Toward the History of Humankind within Biosphere & Technosphere -, Edited by Osamu KAMEI and *et al.*, 国立科学博物館, **2016**. (http://sts.kahaku.go.jp/english/diversity/document/symposium/system/pdf/104_e.pdf)
2) 国立科学博物館産業技術史資料情報センター, http://sts.kahaku.go.jp, (2021/12/01). 各報告書の PDF 版を掲出.
3) 赤川敏，*技術の系統化調査報告*，国立科学博物館, **2021**, *30*, 1−101.
4) 明田久稔, *ibid.*, 103−225.
5) 大賀寿郎, *ibid.*, 227−339.
6) 勝又一郎, *ibid.*, 341−434.
7) 嘉本秀年，*技術の系統化調査報告 共同研究編*，国立科学博物館・北九州産業技術保存継承センター, **2021**, *14*, 1−108.
8) 科学技術白書に見る「技術革新」の意味合いの変遷，有賀 暢迪; 亀井 修, *Bull. Natl. Mus. Nat. Sci., Ser. E*, **2014**, *37*, 1-17.
9) 日本の技術革新とイノベーション―国立科学博物館の技術の系統化調査と科学技術白書を中心に―，亀井 修，有賀 暢迪, *JASC 研究会（150830）予稿集*, **2015**, 7-8.

デジタル一眼カメラを使った分光実験ライブ演示用簡易分光器

（千葉大院工）〇野本 知理
A simple spectroscope using a consumer digital camera for live spectroscopic demonstrations
(*Graduate School of Engineering, Chiba University*) 〇Tomonori Nomoto

Simple spectroscopic setups for observing colored spectral images from lamp spectra to weaker light sources such as flame reaction, fluorescence and Raman scattering are introduced by simply adding low-cost components (a transmission diffraction grating sheet, a magnifying glass, etc.) to a consumer digital camera. As actual demonstrations, live-streamed spectroscopic demonstrations were performed as museum events. The specification of the spectroscope and actual demonstration methods are also introduced.
Keywords : Chemical Education, Spectroscope, Raman Spectroscopy, Flame reaction, Demonstration

化学において，分光学は物質の同定・定量や化学反応の解析のために必要不可欠なツールとして利用されている．一方，分光実験で得られるスペクトルは目では判別できない微弱光になることも多いため，化学教育において演示実験として利用できる分光実験は感度面の制約もあり多くない．そこで今回，近年広く普及しているデジタル一眼カメラに回折格子シート・虫眼鏡等安価な光学素子を使った簡単な光学系（下図）を追加することで、微弱光を伴う現象のスペクトルも撮影可能な演示用簡易分光器を構築した。これにより，ランプ等の明るい光源だけでなく，炎色反応や蛍光、さらにはラマン散乱[1]のような微弱なスペクトルまで色のついたスペクトル画像を示すことが可能になった。また科学館イベントの一環として，製作した分光器を用いた分光実験演示のライブ配信も行った[2,3]. 本講演ではデジタル一眼カメラを使った簡易分光器の構築，性能評価，および各スペクトルの取得・演示方法について紹介する。



図：デジタル一眼カメラを使った(a)ラマン散乱・蛍光用 (b)炎色反応等観察用簡易分光器の構成例

1) T. Nomoto, “Color-Observable Simple Raman Spectroscope for Live Exhibitions Using a Consumer Digital Camera”, J. Chem. Educ., **2021**, *98*, 3356.
2) 科学ライブショー「ユニバース」 on YouTube Live
https://youtube.com/playlist?list=PL9qOCchwv1O_WvhoXRkfaIhSCSmcQbpI7
3) 分光実験@科学ライブショー「ユニバース」
https://youtube.com/playlist?list=PLeglKUCHsH6NVmY6Djcb4LbBrQvdGy-Q2

肢体不自由生徒のためのマイクロスケール実験の開発と実践

（筑波大学附属桐が丘特別支援学校[1]・東北大学大学院理学研究科[2]）
○山田 一幸[1]・荻野和子[2]

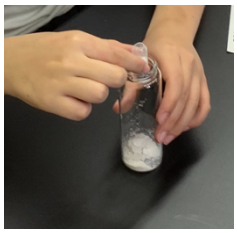
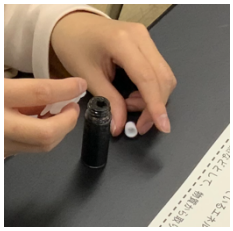
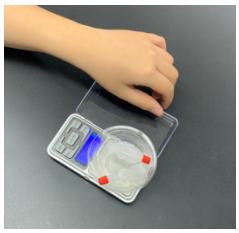
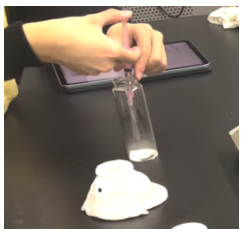
Development of Microscale Experiments for Physically Challenged Students

([1] *Kirigaoka School for the Physically Challenged, University of Tsukuba*, [2] *Graduate School of Science, Tohoku University*) ○Kazuyuki Yamada[1], Kazuko Ogino[2]

The physically challenged students have difficulty in practical work in science classes, especially in handling some tools and apparatus. Teachers must take special care for the safety of students who have difficulty in walking and moving. In many special schools for physically challenged students, science classes are given mainly by lectures and demonstrations: Students rarely have opportunity to carry out experiments by themselves. When students carry out experiments, big laboratory equipment is used to make it easier and to observe. Recently, microscale chemistry (MC) is becoming popular in regular schools nationwide. However, the practice of MC experiments in special schools has not been reported. In this paper, we report the development and practice of several microscale experiments suitable for physically challenged students in junior and senior high schools.

Keywords : *microscale experiment(MC); physical challenged; reasonable accommodation; universal design*

肢体不自由生徒には、運動や動作に困難がある。そのため、理科の観察や実験の学習活動において、器具操作に対する難しさを生じさせてしまう。また、実験の安全性にも十分配慮しなければならない。肢体不自由生徒が所属する特別支援学校における理科の実験は、教師による演示実験や観察を中心とした内容が多い。生徒が実験する際、見えにくさや扱いにくさを解消すべく、目盛りを見やすくし、大きめの実験器具を使用して、生徒が実験しやすい配慮を施している[1)]。また、全国の通常校でマイクロスケール実験を取り入れている学校も増えているが、特別支援学校での MC 実験の実践は報告されていない。本研究では、操作が簡単で安全性の高い MC 実験の特色に着目して、肢体不自由生徒に配慮した実験器具を用いた中高生レベルの MC の開発と実践を報告する。（写真は中学２年化学分野と高校化学基礎の実験）

1) 教科指導における障害特性を踏まえた指導・支援のコツ(4)観察・実験を中心とした理科の授業における学習上の困難と指導の工夫, 小山 信博, 肢体不自由教育 : 手足の不自由な子どもたち : 日本肢体不自由教育研究会機関誌 (233), 44-51, 2018-01

界面活性剤とアルミ箔を用いた「錬金術師の夢」実験の改良

（大妻嵐山高[1]）○鈴木　崇広[1]
Improvement of "Copper into Gold: The Alchemist's Dream" using surfactant and aluminum foil ([1]*Otsuma Ranzan Junior and Senior High School*)○Takahiro Suzuki[1]

In a well-known brass plating experiment, a Cu coupon is subjected to Zn plating and heating with a Bunsen burner. Currently, aqueous 6 mol/L NaOH or 6 mol/L $ZnCl_2$ is typically used as the plating solution, however, the use of a strong acid or base provides operational risks. Herein, we introduce a modified method that uses aqueous 2 mol/L $ZnCl_2$, sodium dodecyl sulfate and aluminum foil as the plating solution. This method reduces operational risks and deposits silver-white Zn on Cu coupons more evenly than the $ZnCl_2$ method, which uses 3-times the concentration. When the Zn-plated Cu coupon was heated, it changed to brass plating.
Keywords : Oxidation/Reduction, Electrochemistry, Plating, Metals

銅板に銀色の亜鉛めっきを施し，さらに加熱することで金色の黄銅めっきにすることが「錬金術師の夢」実験として知られている[1)]。従来の方法では Zn 粉末と 6 mol /L NaOH 水溶液[1)]（pH 14 以上）または 6 mol /L $ZnCl_2$ 水溶液[2)]（pH 1 以下）が用いられるが，使用後の Zn 粉末は活性が高く，ろ過後に空気中の酸素と反応して酸化発熱による蓄熱の結果，発火する事故例が報告されている。また，従来の強塩基性条件は，高濃度の NaOH 水溶液の突沸や飛散などの危険がある。一方で強酸性条件では Zn が不均一に析出し，美しいめっき面が得られない。

本研究では，アルミ箔と 2.0 mol /L $ZnCl_2$ 水溶液に陰イオン界面活性剤であるドデシル硫酸ナトリウム（SDS）を添加しためっき液（pH 4）を用いて，銅板に従来法の強塩基または強酸性条件より安全に，均一な亜鉛めっきを施し，黄銅めっきに誘導できることを明らかにした（Fig.1,2）。

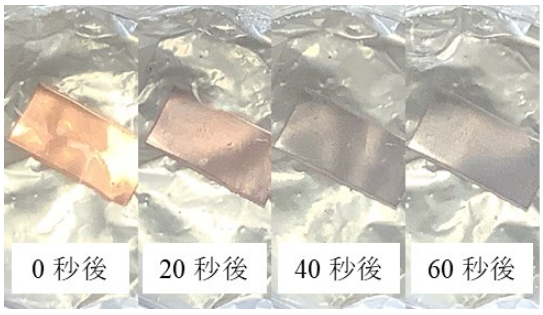


Fig.1　加熱中の銅板の変化の様子

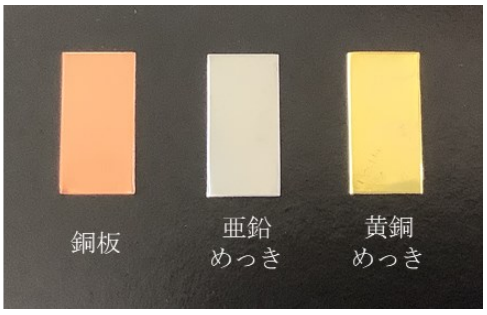


Fig.2　銅板と作製しためっき

1) LeeR. Summerlin, James L. Ealy, Jr. *Chemical Demonstrations: A Sourcebook for Teachers*, 1st ed., American Chemical Society, **1985**, Vol.1, p.104 .
2) 吉田　工，化学と教育 **2001**，*49*，791.

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

[F203-3am] 04. Physical Chemistry -Properties-

Chair: Yuta Takano, Tetsuro Kusamoto

Fri. Mar 25, 2022 9:00 AM - 11:40 AM F203 (Online Meeting)

[F203-3am-01] Theoretical Study on Vibronic Couplings of Excited States Contributing to Singlet Fission Process

○Takayoshi Tonami[1], Kenji Okada[1], Hajime Miyamoto[1], Ryohei Kishi[1,2,5], Yasutaka Kitagawa[1,2,3,5], Masayoshi Nakano[1,2,3,4,5] （1. Graduate School of Engineering Science, Osaka University, 2. QIQB, Osaka University, 3. CSRN, Osaka University, 4. ICS-OTRI, Osaka Universit, 5. RCSEC, Osaka University）

9:00 AM - 9:20 AM

[F203-3am-02] Theoretical Study on Singlet Fission Dynamics in One-dimensional Aggregates Composed of Bowl-Shaped Molecules

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

9:20 AM - 9:40 AM

[F203-3am-03] Theoretical Study on Singlet Fission Dynamics in Pentacene Multi-ring Aggregate Models

○Hajime Miyamoto[1], Kenji Okada[1], Kazuaki Tokuyama[1], Kishi Ryohei[1,2,3], Yasutaka Kitagawa[1,2,3,4], Nakano Masayoshi[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. Center for Spintronics Research Network, Osaka University, 5. Innovative Catalysis Science Devision, Institute for Open and Transdisciplinary Research Initiatives, Osaka University）

9:40 AM - 10:00 AM

[F203-3am-04] Environmental Degradation of PbS and CdSe Quantum dots and the Related Toxicity

○Jeladhara Sobhanan[1], Yuta Takano[1], Vasudevanpillai Biju[1] （1. Hokkaido University）

10:00 AM - 10:20 AM

[F203-3am-05] Optimizing single-crystal perovskite sizes, shapes, and their roles on electroluminescence blinking

○Dong Zhang[1], Takuya Okamoto[2], VasudevanPillai Biju[1,2] （1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University）

10:20 AM - 10:40 AM

[F203-3am-06] Ligand Effects on Precisely Synthesized Gold Clusters in the Ultrafast Carrier Dynamics

○Daichi Eguchi[1], Eisuke Kawashima[2], Takahito Nakajima[2], Naoto Tamai[1] （1. Kwansei Gakuin University, 2. RIKEN Center for Computational Science）

10:40 AM - 11:00 AM

[F203-3am-07] Highly efficient emission of Eu(III) complex doped host-guest films by triplet sensitization

○Shiori Miyazaki[1], Kiyoshi Miyata[1], Pedro Paulo Ferreira da Rosa[2], Fumiya Suzue[2], Yuichi Kitagawa[2,3], Kenichi Goushi[4], Chihaya Adachi[4], Yasuchika Hasegawa[2,3], Ken Onda[1] （1. Kyushu Univ., 2. Hokkaido Univ., 3. Hokkaido Univ., WPI-ICReDD, 4. Kyushu Univ., OPERA）

11:00 AM - 11:20 AM

[F203-3am-08] Observation of single-molecule magnetoluminescence from stable luminescent radicals

○Ryota Matsuoka[1], Shojiro Kimura[2], Tetsuro Kusamoto[1] （1. LCCMS, IMS, 2. IMR, Tohoku Univ.）

11:20 AM - 11:40 AM

一重項分裂過程に寄与する励起状態の振電相互作用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 CSRN[4]・阪大 ICS[5]）○當波 孝凱[1], 岡田 健治[1], 宮本 孟[1], 岸 亮平[1,2,3,4,5], 北河康隆[1,2,3,4,5], 中野雅由[1,2,3,4,5]
Aziridination of Styrene Derivatives Using Iminoiodinane Catalyzed by Iodine and Ammonium Iodide (*[1]Graduate School of Engineering Science, Osaka University, [2]RCSEC, Osaka University [3]CSRN, Osaka University, [4]QIQB, Osaka University, [5]ICS-OTRI, Osaka University*) ○Takayoshi Tonami,[1] Kenji Okada,[1] Hajime Miyamoto,[1] Ryohei Kishi,[1,2,3,4] Yasutaka Kitagawa,[1,2,3,4] Masayoshi Nakano[1,2,3,4,5]

Singlet fission (SF) is a photophysical process where a singlet exciton is converted into a correlated triplet pair. The important factors governing SF dynamics are: (i) excitation energies (or diradical characters) of monomer, (ii) intermolecular electronic coupling, and (iii) vibronic coupling (VC). VC is one of the factors that are expected to affect the SF efficiency. For efficient SF materials design, constructing realistic models and establishing calculation methods for analysis of VC are needed. In this study, we investigate VCs in the excited states contributing to SF process by quantum chemical calculations.
Keywords : Singlet Fission; Vibronic Coupling; Pentacene Crystal; Excited State; Quantum Chemical Calculation

一重項分裂(SF)は光照射により生成した 1 つの一重項励起子(S_1S_0)から相関三重項対(TT)を生成する光物理化学過程であり、太陽電池等への応用が期待されている [1)]。このような応用の実現には、TT を高速かつ高収率に生成することができる分子や集合系の設計が必要であり、(i)励起状態のエネルギー準位、(ii)分子間の π 軌道の重なりによる相互作用(電子カップリング)、(iii)分子振動と励起状態間の相互作用(振電相互作用, VC)が重要な要素として考えられている [1,2)]。本研究では、(iii)に関して、SF 過程に関係する励起状態(Fig. 1)の VC を量子化学計算により検討する。VC が励起子ダイナミクスに影響することは多くの実験・理論研究で報告されており [3)]、SF に寄与し得る VC が大きければ、他の無輻射失活パスの抑制に繋がり、SF 速度の向上が期待できる。そのため、SF 材料設計には、実在系に近いモデルの構築や VC の計算法を確立することが必要である。当日は、代表的な SF 分子であるペンタセンの結晶構造を用いて計算した VC の結果について議論する。

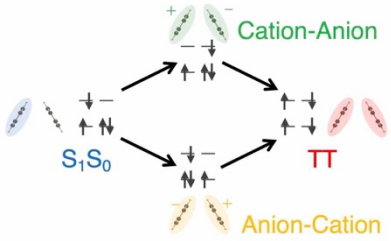


Figure 1. Excited states in SF process

1) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891. 2) (a)T. Minami, M. Nakano, *J. Phys. Chem. Lett.* **2012**, *3*, 145.; S. Ito et al., *J. Photochem. Photobiol. C: Photochem. Rev.* **2018**, *34*, 85., (b) Nagami et al., *J. Chem. Phys.,* **2020**, *153*, 134302. 3) K. Miyata et al., *Nat. Chem.* **2017**, *9*, 983., A. A. Bakulin et al., *Nat. Chem.* **2016**, *8*, 16., T. C. Berkelbach et al., *J. Chem. Phys.* **2013**, *138*, 114102.

ボウル型分子の一次元集合系におけるシングレットフィッションダイナミクスに関する理論研究

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

Theoretical Study on Singlet Fission Dynamics in One-dimensional Aggregates Composed of Bowl-Shaped Molecules (*[1]Graduate School of Engineering Science, Osaka University, [2]Quantum Information and Quantum Biology Division (QIQB), Osaka University, [3]Research Center for Solar Energy Chemistry (RCSEC), Osaka University, [4]Center for Spintronics Research Network (CSRN), Osaka University, [5]Innovative Catalysis Science Division (ICS), Osaka University)* ○ Kenji Okada,[1] Kazuaki Tokuyama,[1] Ryohei Kishi,[1,2,3] Yasutaka Kitagawa,[1,2,3,4] Masayoshi Nakano[1,2,3,4,5]

Singlet fission (SF) is a photophysical process, where a singlet exciton splits into two triplet excitons. In recent years, SF has attracted a great deal of attention due to its potential to improve the photoelectric conversion efficiency of organic solar cells. In order to improve the SF efficiency, it is essential to tune the energies of S_1, T_1 and charge transfer (CT) states, and further improve the electronic couplings. In this study, we investigate the SF dynamics in columnar stacked one-dimensional aggregate models composed of bowl-shaped SF molecules (Fig. 1). It is found that the structural symmetry in aggregate is one of the important factors to determine the SF efficiency.

Keywords : Singlet Fission, Quantum Chemical Calculation, Exciton Dynamics, Curved π-System

シングレットフィッション(SF)は 1 つの一重項励起子が 2 つの三重項励起子に分裂する光物理化学過程であり、高効率有機太陽電池への応用が期待されている[1)]。高効率な SF 材料のためには、エネルギー整合条件 $E(S_1) \geq 2E(T_1)$や、電荷移動(CT)状態のエネルギー・分子間の分子軌道の電子的な相互作用(電子カップリング)などの多くの要素を包括的に考慮した分子設計が求められる。本研究では、湾曲 π 共役分子の一次元的な分子集合系における SF の機構の理論的解明と新たな分子設計指針構築を目指し、ボウル型のペロピレン類縁体をモデルとした一次元集合系(Fig. 1)の SF ダイナミクスについてシミュレーションにより検討を行った。その結果、回転対称性を有する分子が対称軸を共有するような多量体構造においては、特定の電子カップリングが消失するため SF に適さないことがわかった。この課題に対しては非対称的に化学修飾を施すことが有効に働くことが確認された。

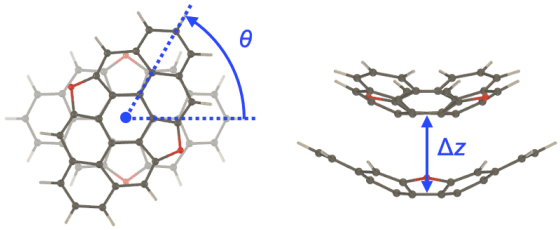


Figure 1. An example of dimer unit in columnar stacked bowl-shaped peropyrene model.

1) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891; *Annu. Rev. Phys. Chem.* **2013**, *64*, 361–386.

ペンタセンマルチリング分子集合系モデルにおけるシングレットフィッションダイナミクスに関する理論研究

（阪大院基礎工[1]・阪大 QIQB[2]・阪大 RCSEC[3]・阪大 CSRN[4]・阪大 ICS-OTRI[5]）○宮本 孟[1]・岡田 健治[1]・徳山 和明[1]・岸亮平[1,2,3]・北河康隆[1,2,3,4]・中野雅由[1,2,3,4,5]

Theoretical Study on Singlet Fission Dynamics in Pentacene Multi-ring aggregate Models

([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]*Center for Spintronics Research Network, Osaka University,* [5]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives, Osaka University*) ○Hajime Miyamoto,[1] Kenji Okada,[1] Kazuaki Tokuyama,[1] Ryohei Kishi,[1,2,3] Yasutaka Kitagawa,[1,2,3,4] Masayoshi Nakano[1,2,3,4,5]

Singlet Fission (SF) is a photophysical process in which one singlet exciton S_1 splits into two triplet excitons in organic molecular aggregates. SF is expected to improve the photoelectric conversion efficiency in organic solar cells. In this study, we have investigated the SF dynamics in pentacene multi-ring aggregate systems shown in Figure 1 by using quantum master equation approach. We focused on the aggregate configuration dependences (represented by inter-ring and intra-ring relative configuration) of site selectivity of correlated-double triplets pair (TT) generated by SF process.

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

シングレットフィッション（SF）は、光励起によって生じた一重項励起子 S_1 が、隣接分子間のπ軌道重なりによる相互作用により二つの三重項励起子に分裂する現象であり、有機太陽電池の光電変換効率向上への応用の観点から盛んに研究が行われている[1]。SF は二分子以上で起こる現象であるため、効率的な SF 材料の設計には単分子レベルから分子集合系レベルでの構造−SF 特性相関に関する知見の蓄積が不可欠である。本研究では、分子集合系のトポロジーが SF 特性に与える影響を明らかにするために、図 1 のような分子間隔の異なる二種類の J 型環状 3 量体[2]を並列したマルチリング集合系モデルにおける SF ダイナミクスを量子マスター方程式法に基づき計算した。本モデルでは主に、Ring2 内およびリング間の分子間距離 d_1, d_2 [Å]をパラメータとして、TT 生成の位置選択性の制御について議論した。

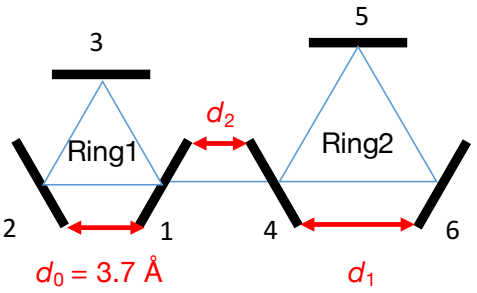


図 1. ペンタセン J 型環状 3 量体を並列したマルチリング集合系モデル

1) (a) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891. (b) S. Ito, T. Nagami, M. Nakano, *J. Photochem. Photobiol. C: Photochem. Rev.* **2018**, *34*, 85. (c) M. Nakano et al. *J. Comput. Chem.* **2019**, *40*, 89. 2) H. Miyamoto, M. Nakano, *ChemPhotoChem* **2020**, *4*, 5249.

Environmental Degradation of PbS and CdSe Quantum Dots and the Related Toxicity

([1]*Graduate School of Environmental Science,* [2]*Research Institute for Electronic Science, Hokkaido University*) ○Jeladhara Sobhanan,[1] Yuta Takano,[1,2] Vasudevanpillai Biju[1,2]
Keywords: quantum dots; engineered nanomaterials; cytotoxicity; genotoxicity

The growing interest in the field of engineered nanomaterials for various applications such as energy harvesting, optoelectronics, bioanalysis, nanomedicine, and cosmetics raises concerns over their toxicity and safety.[1] Lead halide perovskite and heavy metal chalcogenide nanocrystals attract attention due to their strong quantum confinement, large exciton Bohr radius, and the size-dependent tunable band gaps in the visible to near-infrared regions.[2] These nanomaterials are photoactive, and potentially could be transformed by photoetching resulting in the release of heavy metals into the environment,[3] which are generally associated with neurotoxicity, hepatotoxicity, and nephrotoxicity.[4] Here, with the help of cytotoxicity and comet assays, we conduct studies on various cultured cells treated with PbS or CuS quantum dots. We reveal significant proliferation and DNA damage to the cells exposed to cadmium or lead ions released from these quantum dots.

This study reveals higher levels of cell proliferation and DNA damage to PC12 cells than H1650 cells exposed to metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}). We find that the genotoxicity of Pb^{2+} to H1650 cells is lower than H1650 cells treated with Cd^{2+}. This result also suggests the neurotoxicity of lead due to not only a downregulation of glutathione, elevated levels of reactive oxygen and nitrogen species, and a calcium influx but also the proactivation of activator protein 1 that is correlated with protein kinase c. This research underscores the significance of cell and molecular biology studies to understand the health and environmental costs of nanomaterials.

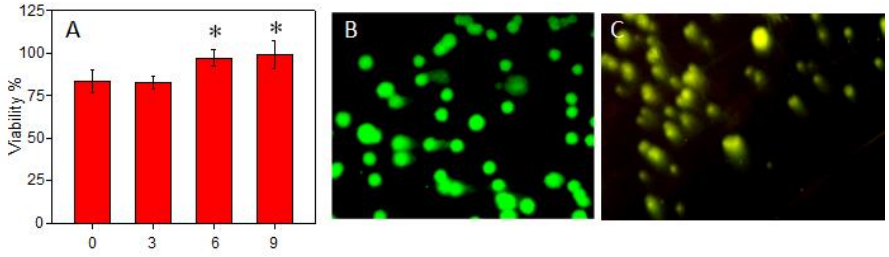


Figure 1. Cell viability histograms and comet images of H1650 cells (A) treated with photoactivated PbS quantum dots for 72 h and (B) Pb^{2+} for 72 h. (C) Comet images of PC12 cells treated with 0.1 μM Pb^{2+} for 72 h.

1) Y. Zhu, et al, *Environ. Res*., **2019**, 174, 54. 2) M. Zhong, Y. Liang, J. Zhang, Z. Wei, Q. Li and D. Xu, *J. Mater. Chem. A*, **2019**, 7, 6659. 3) Y. T. Shen, D. Lei and W. Feng, *J. Mater. Chem. C*, **2013**, 1, 1926. 4) Q. Jia, X. Ha, Z. Yang, L. Hui and X. Yang, *Toxicol. Mech. Methods*, **2012**, 22, 705.

Optimizing single crystal-perovskite sizes, shapes, and their roles on electroluminescence blinking

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Reasearch Institute for Electronic Science, Hokkaido University*) Dong Zhang,[1] Takuya Okamoto,[2] Vasudevanpillai Biju[1,2]

Keywords: Halide Perovskite; electroluminescence; photoluminescence; microcrystals; blinking

Photoluminescence (PL) and electroluminescence (EL) blinking are common phenomena in nano-size semiconductors, which negatively impact the properties and optical/photovoltaic applications of these materials. Blinking is the random fluctuations of the PL or EL intensity. The intensity levels during the fluctuation switch between the ON, Grey, and OFF states.[1]

In this study, two types of $MAPbBr_3$ microcrystals (MCs) are synthesized by the Inverse Temperature Crystallization (ITC) and Room Temperature Crystallization (RTC) methods. We demonstrate that the crystal size and EL properties vary considerably with the synthesis method. The PL spectra show the single crystals prepared by the RTC method have a bright narrow emission peak at 534 nm (Figure 2c). The optical properties of these MCs are measured by the time-resolved fluorescence microscopy. We find that the single crystal prepared by the RTC method has a short PL lifetime (τ_1=1.23 ns, τ_2=1.32 ns; Figure 2d). The EL blinking is measured by sandwiching $MAPbBr_3$ MCs between two ITO electrodes. The crystals prepared by the RTC method show bright EL with blinking. This can be explained by the charging-discharging or trapping-de-trapping processes. Additionally, the suppression of blinking is investigated by halide vacancy filling.

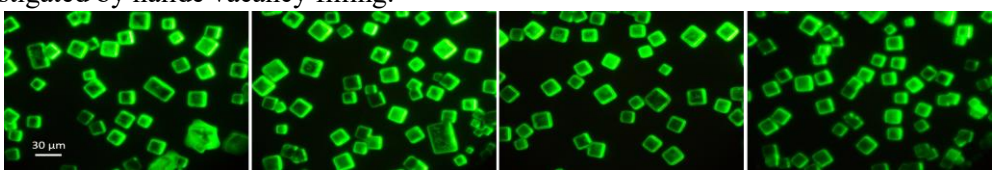


Figure 1. PL images of $MAPbBr_3$ MCs.

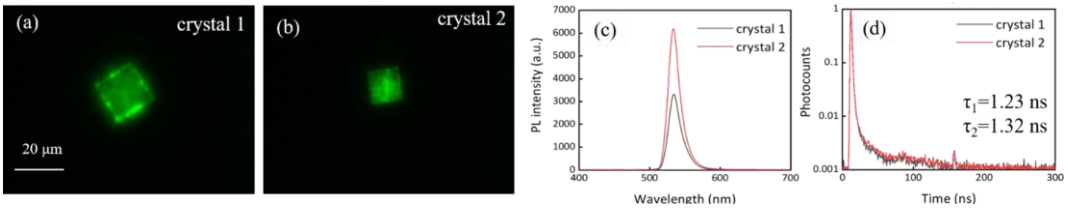


Figure 2. (a,b) PL images, (c) PL spectra, and (d) PL decay profiles of $MAPbBr_3$ MCs.

1) Y. Tian, A. Merdasa, M. Peter, M. Abdellah, K. Zheng, C. S. Ponseca, Jr., T. Pullerits, A. Yartsev, V. Sundstrom and I. G. Scheblykin, *Nano Lett*. **2015**, 15, 1603-1608.

精密合成された金クラスターの超高速キャリアダイナミクスにおける配位子効果

(関学院理[1]・理化学研究所計算科学研究センター[2]) ○江口 大地[1]・川嶋 英佑[2]・中嶋 隆人[2]・玉井 尚登[1]

Ligand Effects on Precisely Synthesized Gold Clusters in the Ultrafast Carrier Dynamics

([1] *Graduate School of Science, Kwansei Gakuin University*, [2] *RIKEN Center for Computational Science*) ○Daichi Eguchi,[1] Eisuke Kawashima,[2] Takahito Nakajima,[2] Naoto Tamai[1]

Gold clusters (AuCs) defined by their molecular formulas exhibit composition- and geometric structure-dependent properties, which are not observed in the bulk and the nanoparticles. Gold core in AuCs plays an important role in the physicochemical properties of AuCs. It is well known that the properties are perturbed by organic ligands, however, the ligand effects on the carrier relaxation processes upon photoexcitation are still unclear. In this study, we examined the effects of various ligands in the carrier dynamics of AuCs by using ultrafast pump-probe spectroscopy and TDDFT calculations, which were carried out using NTChem.

Keywords : Gold Cluster; Ligand Effects; Ultrafast Spectroscopy

金クラスターは、その組成を分子式で定義することができ、その電子構造は組成により制御可能であることから光電変換材料への応用が期待されている。金クラスターの物性は金核が担っており、その物性は有機配位子により摂動を受けることが知られているが [1]、光励起後のキャリアの緩和過程に及ぼす影響は未解明な点が残されている。本研究では、有機配位子が金クラスターのキャリアダイナミクスに与える影響を超高速分光測定で調査を行った。

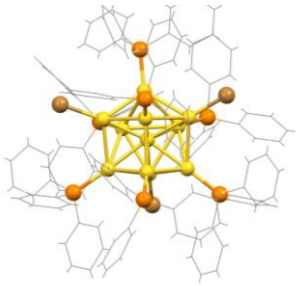


Figure 1. Crystal structure of TPP-H/Au_{11}. Hydrogen atoms and solvent molecules are omitted for clarify.

置換基の性質が異なるトリフェニルホスフィン誘導体 (TPP-R, R: CN, CF_3, F, H, CH_3, OMe) 存在下で金前駆体を還元することで金クラスターを合成した (TPP-R/Au_{11})。単結晶 X 線構造解析の結果から、TPP-R/Au_{11} の核は金原子が 11 原子より構成されており、その表面に臭素原子が 3 原子、TPP-R が 7 分子配位している構造であることが分かった (Figure 1)。励起波長 400 nm でフェムト秒過渡吸収分光測定を行ったところ、励起直後から 1 ns までのすべての時間領域でブリーチ信号 (定常光の吸収スペクトル測定の極大吸収波長に対応) と可視領域全体にかけて観測される正の吸収を足し合わせたスペクトル形状であった。この正の信号のダイナミクスに着目すると、電子吸引性置換基を有する配位子で保護されたクラスターでは緩和が早いことが分かった。分子科学計算ソフトウェアである NTChem を用いて TDDFT 計算を行ったところ、上記の結果は HOMO と LUMO の重なりの度合いに由来することが分かった。

1) D. Eguchi, M. Sakamoto, T. Teranishi, *Chem. Sci.,* **2018**, *9*, 261.

Highly Efficient Emission of Eu(III) Complex Doped Host-Guest Films by Triplet Sensitization

([1]*Department of Chemistry, Kyushu University*, [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University,* [3]*Faculty of Engineering, Hokkaido University,* [4]*WPI-ICReDD, Hokkaido University,* [5]*OPERA, Kyushu University*) ○Shiori Miyazaki,[1] Kiyoshi Miyata,[1] Pedro Paulo Ferreira da Rosa,[2] Fumiya Suzue,[2] Yuichi Kitagawa,[3,4] Kenichi Goushi,[5] Chihaya Adachi,[5] Yasuchika Hasegawa,[3,4] Ken Onda[1]

Keywords: Eu Complex; Lanthanide; Time-resolved Spectroscopy; Energy Transfer

Trivalent europium (Eu(III)) complexes are expected to be used as electroluminescence devices because of their high color purity emission[1]. The complexes utilize intramolecular energy transfer from ligands to a metal center. In an emitting layer of EL devices, guest molecules are doped in host molecules, and energy transfer occurs between guest molecules and host molecules. To date, the emission mechanism is unclear, and the design strategies of the complex have not been established. To elucidate the emission mechanism in host-guest films, we investigated the Eu(III)-complex-doped host-guest films using time-resolved photoluminescence spectroscopy (TR-PL) and transient absorption spectroscopy (TAS).

The 10 wt% $Eu(hfa)_3(TPPO)_2$ (hfa: hexafluoroacetylacetonate, TPPO: triphenylphosphineoxide) (Figure 1a) doped host-guest films were fabricated. We discovered that the photoluminescent quantum yield (PLQY) of the host-guest film depends on a choice of host molecule. Here, we focus on the most luminescent host-guest film which employed T2T (T2T: 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine) (Figure 1b) as the host molecule. The PLQY of this film (80%) is higher than those of solutions (59%)[2]. By measuring its excitation spectra, we discovered the intermolecular energy transfer from T2T to Eu(III) complex. To elucidate the emission mechanism in detail, we tracked the energy transfer processes of the various host-guest films after T2T excitation. By TR-PL and TAS measurements, we found quick and high quantum yield intersystem crossing of T2T. After the intersystem crossing, efficient energy transfer occurs from the T_1 state of the T2T to the T_1 state of ligands (Figure 2). The energy transfer mechanism we revealed here is able to sensitize the highly efficient luminescence of the Eu(III).

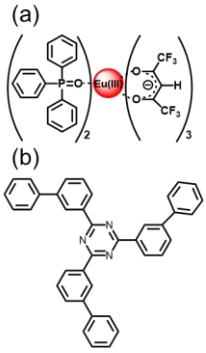


Figure 1. chemical structures (a) $Eu(hfa)_3(TPPO)_2$ (b) T2T.

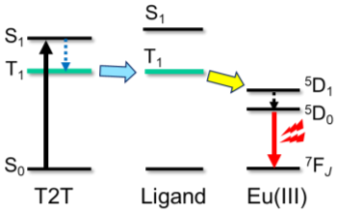


Figure 2. Energy transfer mechanism in the host-guest film.

This work is supported by JSPS Core-to-Core Program, (grant number: JPJSCCA20180005).

1) L. Wang, *et al.*, *Adv. Optical Mater.* **2019**, *7*, 1801256. 2) Y. Kitagawa, *et al.*, *Dalton Trans.* **2018**, *47*, 7327. 3) S. Miyazaki, *et al.*, *J. Phys. Chem. A.* **2020**, *124*, 6601.

安定発光ラジカルが示す単分子マグネトルミネッセンスの観測

（分子研生命錯体[1]・東北大金研[2]）○松岡 亮太[1]・木村 尚次郎[2]・草本 哲郎[1]
Observation of single-molecule magnetoluminescence from stable luminescent radicals ([1]*LCCMS, Institute for Molecular Science*, [2]*Institute for Materials Research, Tohoku University*) ○Ryota Matsuoka,[1] Shojiro Kimura,[2] Tetsuro Kusamoto[1]

Luminescent organic radicals have attracted much attention because they exhibit interesting luminescent properties different from those of closed-shell molecules due to their open-shell electronic structures. In particular, magnetoluminescence, a change in the emission spectrum of molecules by magnetic fields, is a unique property of luminescent radicals. However, the conditions under which magnetoluminescence occurs and the detailed mechanism remain largely unexplored. In this study, we have succeeded in observing magnetoluminescence as a single-molecular property of radicals for the first time. The details and the mechanism of its occurrence will be presented.
Keywords : Radical; Luminescence; Magnetic field

発光性有機ラジカルはその開殻電子状態に由来した閉殻分子とは異なる興味深い発光特性を示すことから注目を集めている。中でも発光性有機ラジカルが示す磁場による発光スペクトル変化（マグネトルミネッセンス）は、スピンと発光が協奏したラジカルならではのユニークな物性である。これまでに我々は、発光ラジカルを非磁性前駆体結晶中にランダムドープした試料[1,2]、または発光ラジカルを構成要素とした配位高分子結晶[3]において、顕著なマグネトルミネッセンスを観測してきた。しかしこれらの系は相互作用する発光ラジカルの数や距離、相対配置を完全に制御できないという本質的問題を抱えており、その結果マグネトルミネッセンスの発現条件や詳細なメカニズムには未解明の部分が多く残っている。今回、新規安定発光ラジカルを有機化学的な分子設計に基づき合成し、マグネトルミネッセンスをラジカルの単分子物性としてはじめて観測することに成功したので、その詳細や発現メカニズムについて発表する。

1) Kimura, S.; Kusamoto, T.; Kimura, S.; Kato, K.; Teki, Y.; Nishihara, H. *Angew. Chem. Int. Ed.* **2018**, *57*, 12711–12715.

2) Kimura, S.; Kimura, S.; Nishihara, H.; Kusamoto, T. *Chem. Commun.* **2020**, *56*, 11195–11198.

3) Kimura, S.; Matsuoka, R.; Kimura, S.; Nishihara, H.; Kusamoto, T. *J. Am. Chem. Soc.* **2021**, *143*, 5610–5615.

Academic Program [Oral B] | 05. Physical Chemistry -Chemical Kinetics and Dynamics- | Oral B

[F102-3am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Keiichi Inoue, Wataru Kashihara

Fri. Mar 25, 2022 9:00 AM - 11:20 AM F102 (Online Meeting)

[F102-3am-01] Study on the dynamics of channel opening and closing of cation channel rhodopsin, C1C2

○Keiichi Inoue[1], Keisei Shibata[1], Kazumasa Oda[1], Tomohiro Nishizawa[1], Yuji Hazama[1], Ryohei Ono[1,2], Osamu Nureki[1], Hidefumi Akiyama[1] （1. The Univ. of Tokyo, 2. Gunma Univ.）

9:00 AM - 9:20 AM

[F102-3am-02] Photochemical Reaction of Ketoprofen with Twenty Kinds of Proteinogenic Amino Acids

○Wataru Kashihara[1], Kazuyoshi Ueda[1,2], Tadashi Suzuki[1] （1. Aoyama Gakuin University, 2. Yokohama National University）

9:20 AM - 9:40 AM

[F102-3am-03] Kinetic analyses of photoinduced protein folding and interaction with molecular chaperone SecB

○Yusuke Nakasone[1], Ikuya Nakaoka[1], Honoka Ohta[3], Soichiro Kawagoe[2], Koichiro Ishimori[3], Tomohide Saio[2], Masahide Terazima[1] （1. Kyoto University, 2. Tokushima University, 3. Hokkaido University）

9:40 AM - 10:00 AM

[F102-3am-04] Polarization dependence of the carrier dynamics in a lead halide perovskite crystal observed by femtosecond transient absorption microscopy

○Tetsuro Katayama[1], Yuma Fujita[1], Akira Yamamoto[1], Yuichiro Akagi[1], Akihiro Furube[1] （1. Tokushima University）

10:00 AM - 10:20 AM

[F102-3am-05] Ultrafast Ring-Opening Reaction of 1,3-Cyclohexadiene: Identification of Non-Adiabatic Transition Pathway via Doubly Excited State and Product Coherence

○Shutaro Karashima[1], Alexander Humeniuk[2], Ryuta Uenishi[1], Takuya Horio[1], Manabu Kanno[3], Tetsuro Ohta[1], Junichi NIshitani[1], Roland Mitric[2], Toshinori Suzuki[1] （1. Kyoto University, 2. Universität Würzburg, 3. Tohoku University）

10:20 AM - 10:40 AM

[F102-3am-06] Super-reaction: the Collective Enhancement of a Reaction Rate by Molecular Polaritons in the Presence of Energy Fluctuations

○Nguyen Thanh Phuc[1] （1. Kyoto University）

10:40 AM - 11:00 AM

[F102-3am-07] Reaction Mechanism of Isotopic Hydrogen Evolution Reaction at Nano-Structured Metal Electrodes

○Hiro Minamimoto[1], Mizuho Homma[1], Kei Murakoshi[1] （1. Hokkaido University）

11:00 AM - 11:20 AM

Study on the dynamics of channel opening and closing of cation channelrhodopsin, C1C2

([1]*The Institute for Solid State Physics, The University of Tokyo*, [2]*Graduate School of Science, The University of Tokyo,* [3]*Graduate School of Science and Technology, Gunma University*)
○Keiichi Inoue[1], Keisei Shibata[1], Kazumasa Oda[2], Tomohiro Nishizawa[2], Yuji Hazama[1], Ryohei Ono[1,3], Shunki Takaramoto[1], Reza Bagherzadeh[1], Hiromu Yawo[1], Osamu Nureki[2], Hidefumi Akiyama[1]

Keywords: Channelrhodopsin, Retinal, Resonance Raman spectroscopy, Flash photolysis

Channelrhodopsins (ChR) are light-gated cation channels that non-specifically transport Na^+, H^+, Ca^{2+}, and other cations. ChR consists of heptahelical transmembrane helices covalently binding retinal Schiff base chromophore at a lysine residue in the seventh helix. Despite its extensive application in optogenetics, the detail of the mechanism of channel opening and closing of ChR remains unclear. Recently, it was proposed by high-level QM/MM calculation[1] and time-resolved serial femtosecond crystallography[2] that twisting and lateral movement toward TM3 of the retinal occur in the pre-open state.

To obtain the structural information about the retinal in the open state of ChR and to clarify the role played by the retinal governing the channel opening and closing, we conducted the time-resolved resonance Raman spectroscopy, a measurement of kinetic isotope effect (KIE) by the laser flash photolysis spectroscopy, and the laser patch-clamp for ChR C1C2. As the result, a gradual increase in Raman bands of hydrogen-out-of-plane modes, indicating enhancement of retinal twisting was observed after photo-excitation and it was maximized in the open state (P_{2b}) (Fig. 1). Furthermore, while the channel opening exhibited no KIE between in H_2O and D_2O, the channel closing of C1C2 became about 3-fold slower, indicating the channel closing is regulated by a proton transfer to the retinal from the protein moiety.

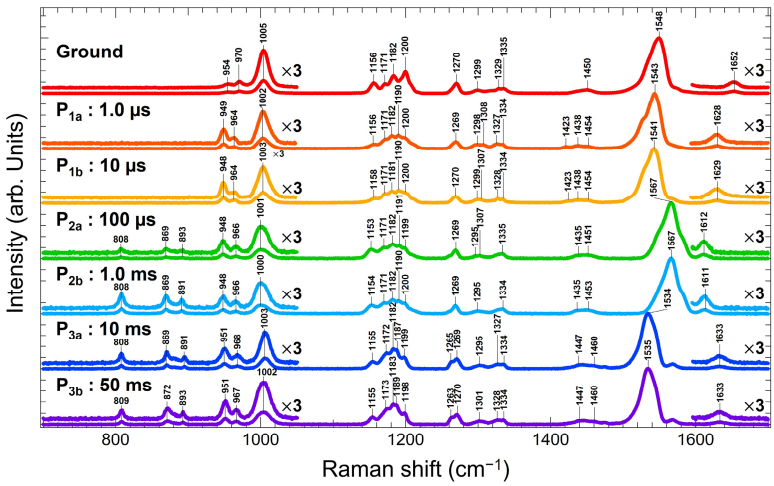


Figure 1. Resonance Raman spectra of C1C2

1) C. Cheng, *Biophys. J.* **2018**, *115*, 1281. 2) K. Oda, *eLife*. **2021**, *10*, e62389.

Photochemical Reaction of Ketoprofen with Twenty Kinds of Proteinogenic Amino Acids

([1]*College of Science and Engineering, Aoyama Gakuin University*, [2]*Graduate School of Engineering, Yokohama National University*) ○ Wataru Kashihara,[1] Kazuyoshi Ueda,[1,2] Tadashi Suzuki [1]

Keywords: *Ketoprofen*; *Nonsteroidal anti-inflammatory drug; Transient absorption spectroscopy; Human serum albumin*

Ketoprofen (KP) is one of the most popular nonsteroidal anti-inflammatory drugs, however, drug-induced photosensitivity of KP has been reported as a serious side effect. KP is incorporated into a protein, and a covalent bond is formed between KP and a protein via the generation of free radicals by irradiation of UV light, which leads to production of an allergen [1)]. The photochemistry of KP with twenty kinds of proteinogenic amino acids in the phosphate buffer solution at pH 7.4 was studied by transient absorption spectroscopy. KP carboxylate anion (KP^-) gave rise to a carbanion via a decarboxylation within a nanosecond, and the carbanion yielded 3-ethylbenzophenone ketyl biradical (3-EBPH) through a proton transfer reaction [2)]. Twelve kinds of proteinogenic amino acids obviously accelerated the reaction. The reaction rate constant to form 3-EBPH with each amino acid was successfully determined. In addition, structural information on the complexes of KP^- docked in a human serum albumin (HSA) was obtained by molecular mechanics (MM) and molecular dynamics (MD) calculations. From the reactivity of the KP carbanion with proteinogenic amino acids and the stable structures for the complexes of KP^- docked in a HSA, the initial processes of photochemical reaction of KP^- in a HSA were discussed. The approach in this work would be the effective for understanding of the mechanism for drug-induced photosensitivity of other NSAIDs.

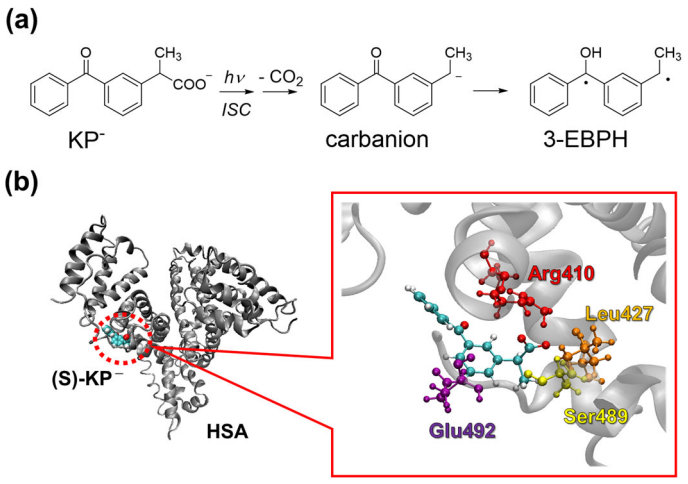


Fig. 1 (a) Reaction scheme of KP carboxylate anion (KP^-) with UV irradiation. (b) Most stable structure of complex of (S)-KP^- docked in a HSA.

1) K. Atarashi, M. Takano, S. Kato, H. Kuma, M. Nakanishi, Y. Tokura, *J. Photochem. Photobiol. B* **2012**, *113*, 56. 2) M. Shinoda, T. Isozaki, T. Suzuki, *Photochem. Photobiol.* **2014**, *90*, 92.

光誘起フォールディング反応および分子シャペロン SecB との相互作用ダイナミクス

（京大院理[1]・北大院総合化学[2]・徳大院医[3]）○中曽根 祐介[1]・中岡 育也[1]・大田 帆香[2]・川越 聡一郎[3]・石森 浩一郎[2]・齋尾 智英[3]・寺嶋 正秀[1]
Kinetic analyses of photoinduced protein folding and interaction with molecular chaperone SecB ([1]*Graduate School of Science, Kyoto University*, [2]*Graduate School of Chemical Science and Engineering, Kyoto University,* [3]*Faculty of Medicine, Tokushima University*,) ○Yusuke Nakasone, Ikuya Nakaoka[1], Honoka Ohta[2], Soichiro Kawagoe[3], Koichiro Ishimori[2], Tomohide Saio[3], Masahide Terazima[1]

To understand molecular mechanisms of protein folding, we have investigated the light-induced structural change of AzoGB1, a B1 domain of protein G containing an azobenzene molecule in its helical structure. Utilizing the photoisomerization of azobenzene, folding and unfolding of AzoGB1 can be triggered by light reversibly. In this study, we investigated the conformation changes of AzoGB1 and intermolecular interaction changes with a molecular chaperon SecB by the transient grating (TG) method. We detected the reversible photoreaction of AzoGB1 in the absence and presence of SecB as changes in the diffusion coefficient (*D*) and determined the kinetic parameters of intra- and intermolecular reactions. For example, we found that *D* of AzoGB1 increased with a time constant of 1 ms upon photoexcitation by blue pulse, which is attributed to the folding reaction. In the presence of SecB, *D* changed in two phases (slight decrease (200 μs) and significant increase (17 ms)). It has been suggested that SecB binds unfolded peptide to prevent the aggregation and the folding requires the dissociation from SecB. The slow component (17 ms) may be the dissociation process of SecB, which is a rate determining step of the folding.
Keywords : protein folding; chaperon; azobenzene; diffusion; transient grating;

Gタンパク質B1ドメインのヘリックス構造にアゾベンゼンを導入した人工タンパク質 AzoGB1 は、アゾベンゼンの光異性化反応を利用して、高次構造の形成・崩壊を光可逆的に制御できる。本研究では、フォールディング制御機構の速度論的理解に向けて、AzoGB1 の構造変化および分子シャペロン SecB との相互作用ダイナミクスを過渡回折格子法により時間分解検出した。励起光の波長を切り替えることで、構造形成・崩壊反応を個別に捉えることに成功し、AzoGB1 単体では、構造形成が 1 ms, 崩壊が 400 μs で起こることがわかった。続いて SecB 共存下での測定を行ったところ、顕著な拡散係数変化として分子間反応が観測され、シャペロン存在下でのフォールディング反応や、光でアンフォールドした状態に SecB が会合する過程を時間分解で明らかにした。SecB 共存下でのフォールディング速度は 17ms と見積もられ、AzoGB1 単体の場合に比べて顕著に遅くなることがわかった。SecB はほどけたペプチド鎖に結合して凝集を抑える働きがあるが、高次構造形成を促す際には解離する必要がある。17ms の時定数で拡散係数の顕著な増大が起こるため、このステップで解離反応が起こり、同時にフォールディングが完了することが示唆された。

フェムト秒顕微過渡吸収分光法を用いたハロゲン化鉛ペロブスカイト結晶中のキャリアダイナミクスの偏光依存性

（徳大院理工 [1]）○片山 哲郎 [1]・藤田 優真 [1]・山本 輝 [1]・赤木 裕一郎 [1]・古部 昭広 [1]

Polarization Dependence of the Carrier Dynamics in a Lead Halide Perovskite Crystal Observed by Femtosecond Transient Absorption Microscopy

([1]*Graduate School of Science and Technology, Tokushima University*) Tetsuro Katayama,[1] Yuma Fujita,[1] Akira Yamamoto,[1] Yuichiro Akagi,[1] Akihiro Furube[1]

Recently, lead halide perovskite ($CH_3NH_3PbX_3$, X=Cl, Br, I) is attracting attention as a nano-laser material because of its low threshold lasing behavior and wavelength-tunable emission. However, the initial stage of lasing process in a microcrystal is unknown because of the limitation of time and spatial resolution. In this study, we measured the carrier dynamics in a $CH_3NH_3PbBr_3$ microcrystal by using a femtosecond transient absorption microscopy. We discuss the pump/probe polarization dependence of the carrier dynamics in a $CH_3NH_3PbBr_3$ microcrystal.

Keywords : Carrier Dynamics, Polariton, organic-inorganic lead halide perovskite, transient absorption microscopy

光励起に続く誘導放出を利用した光増幅現象は、光化学分野における光と物質の相互作用を理解するという基礎的な観点からだけでなく、近年発展しつつある光コンピューティング、光エレクトロニクス分野における光源の微小化、省電力化の実現という応用的な観点からも重要な現象である。その中でハロゲン化鉛ペロブスカイト($CH_3NH_3PbX_3$,X=Cl,Br,I)微結晶系は室温において低閾値光学発振(レージング)が報告されており、さらにその発光波長がハロゲン化物の混合比率により容易に制御可能であるため次世代ナノレーザー媒体として期待されている。しかしながらこの試料系の共振器内の光と励起子の相互作用状態(励起子-ポラリトン)は未解明な点が多い。そこで本研究ではフェムト秒顕微過渡吸収測定装置を用いてペロブスカイト単一微結晶に対して、キャリアダイナミクスの偏光依存性を計測し、光学発振初期過程を観測した。その結果、Fig.1 に示すように観測光の偏光によって異なる過渡吸収スペクトルが得られ、結晶の長軸に対して平行な偏光方向の時のみ 550 nm 付近に強い誘導放出信号が得られることを見出した。発表ではこれら偏光依存性の詳細を議論する。

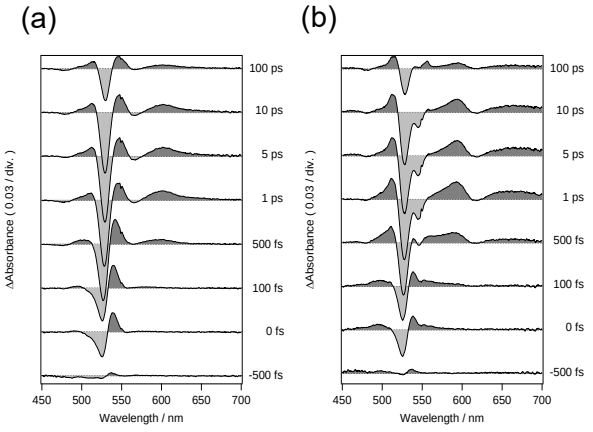


Fig.1 Femtosecond transient absorption spectra of a $CH_3NH_3PbBr_3$ microcrystal with perpendicular (a) and parallel (b) polarization monitoring to the long axis of a crystal (Ex. 400 nm, 4.7 μJ /cm^2).

1,3-シクロヘキサジエンの超高速開環反応：二電子励起状態を経た非断熱遷移と生成物コヒーレンス

（京都大院・理[1]，ビュルツブルク大[2]，東北大院・理[3]）○唐島 秀太郎[1]・Humeniuk Alexander[2]・上西 隆太[1]・堀尾 琢哉[1]・菅野 学[3]・太田 哲郎[1]・西谷 純一[1]・Mitrić Roland[2]・鈴木 俊法[1]

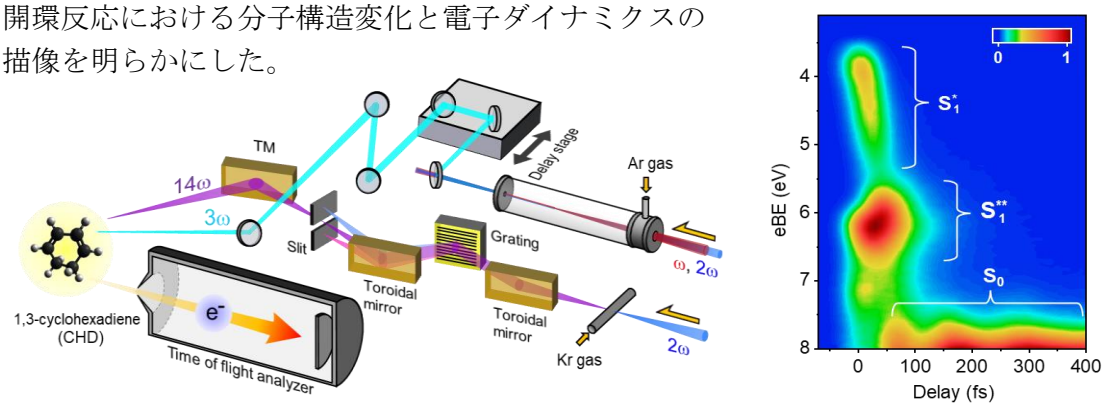
Ultrafast Ring-Opening Reaction of 1,3-Cyclohexadiene: Identification of Non-Adiabatic Pathway via Doubly Excited State and Product Coherence

(*Department of Chemistry, Kyoto University[1], Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Germany[2] Department of Chemistry, Tohoku University, Japan[3]*) ○Shutaro Karashima[1], Alexander Humeniuk[2], Ryuta Uenishi[1], Takuya Horio[1], Manabu Kanno[3], Tetsuro Ohta[1], Junichi Nishitani[1], Roland Mitric[2], Toshinori Suzuki[1]

The photoinduced ring-opening reaction of 1,3-cyclohexadiene (CHD) to produce 1,3,5-hexatriene (HT) is a well-known example of electrocyclic chemical reactions and follows the Woodward−Hoffmann rule. However, the photoexcited $S_1^*(\pi,\pi^*)$ state of CHD is not electronically correlated with the ground state (S_0) of HT, and the reaction must proceed via nonadiabatic transitions. In the present study, we have clearly observed the nonadiabatic reaction pathway via the doubly excited state (S_1^{**}) of CHD using ultrafast extreme UV photoelectron spectroscopy. The results indicate that the reaction occurs in only 68 fs and creates product vibrational coherence. Computational simulations and experimental results provide deeper insights into the electronic dynamics in this paradigmatic electrocyclic ring-opening reaction.

Keywords : 1,3-Cyclohexadiene; Ring-opening Photoreaction; Photoelectron Spectroscopy

1,3-cyclohexadiene (CHD)から 1,3,5-hexatriene(HT)への光異性化反応は電子開環反応の代表例であり Woodward-Hoffmann 則に従って反応が進行する。しかし、CHD の $S_1^*(\pi,\pi^*)$状態は HT の S_0 状態と電子的に相関しないため、非断熱遷移を経る必要がある。本研究では極端紫外極短パルスレーザーを用いた時間分解光電子分光法を開発し、光励起された CHD が二電子励起状態(S_1^{**})を経た非断熱過程によって 68 fs という極短時間に開環反応を起こし、生成物の振動コヒーレンスを発生することを明確にし、開環反応における分子構造変化と電子ダイナミクスの描像を明らかにした。



(左) 実験装置概略図、(右) 実験で測定された光電子スペクトルの時間発展図

Superreaction: the Collective Enhancement of a Reaction Rate by Molecular Polaritons in the Presence of Energy Fluctuations

Nguyen Thanh Phuc
Kyoto University

The last decade has witnessed the emergence of a new field of study around *molecular polaritons* [1]. Polaritons modify the physical and chemical properties of molecular systems significantly through the *strong coupling* of electronic or vibrational molecular excitations to an optical cavity. This coupling leads to the formation of a *hybrid state* of light and matter, resulting in various interesting phenomena. Important applications have been proposed and demonstrated, including the manipulation of chemical landscapes, the modification of chemical reactivity by molecular-vibration polaritons, cavity-enhanced energy transfer and conductivity in organic media. Further applications include polariton lasing and Bose-Einstein condensates, and nonlinear optical properties with applications in optoelectronic devices.

In this talk, I will show that by exploiting the inherent collective character of molecular polaritons in conjunction with the effect of polaron decoupling, a *superreaction* can be realized, involving a *collective enhancement* of charge of excitation-energy transfer reaction rate in a system of donors all coupled to a common acceptor (Fig. 1) [2]. This effect is analogous to the phenomenon of *superradiation*. The underlying mechanism is shown to be the protection of *quantum coherence* between different molecules as the light-matter interaction becomes stronger. It is the demonstration of the *polaron decoupling* effect, i.e., the suppression of environmental influence on the polariton, in a *dynamic* context, as opposed to its static manifestation in optical spectroscopy [3].

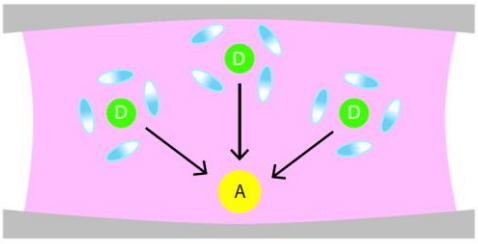


Figure 1: Schematic illustration of a superreaction, involving the collective enhancement of the electron or exciton transfer reaction rate in a system of donors (green) coupled to a common acceptor (yellow), all located inside an optical cavity (light magenta).

[1] T. W. Ebbesen, *Acc. Chem. Res.*, **49**, 2403 (2016).
[2] N. T. Phuc, J. Chem. Phys. **155**, 014308 (2021) (2021 JCP Emerging Investigators Special Collection).
[3] F. C. Spano, *J. Chem. Phys.* **142**, 184707 (2015); N. T. Phuc and A. Ishizaki, *Phys. Rev. Research* **1**, 033019 (2019); S. Takahashi and K. Watanabe, J. Phys. Chem. Lett. **11**, 1349 (2020).

Functionalization of Isotopic Hydrogen Evolution Reactions using Nano-Structured Electrodes

([1]*Department of Chemistry, Faculty of Science, and* [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*)
○Hiro Minamimoto,[1] Mizuho Homma,[2] Ryo Osaka,[2] and Kei Murakoshi[1]
Keywords: Hydrogen Evolution Reaction; Isotopic Molecular Selectivity; Metal Nano-Electrode; Electrochemical Mass Spectroscopy

The isotopic selectivity of the hydrogen evolution reactions (HER) is quite complicated process. It has been reported that the isotopic selectivity strongly depended on the various factors, such as the electrode potential, solution temperature, or the concentration of D_2O.[1] Although various approaches have been conducted, the arbitrary tuning of the isotopic selectivity is a key issue for the chemists. By contrast, the surface process at the nanostructured interface can be modulated due to the confined electric field. Recently, we have successfully found the change in the isotopic selectivity depending on the morphology of the electrode surface.[2] In addition, the unique isotopic selective molecular condensation was observed at the specific nanostructured interface using electrochemical spectroscopic method. From those backgrounds, in this study, we have constructed the various nano-structured metal electrodes to examine the isotopic reaction selectivity of the HER for the functionalization of the isotopic HER process.

The nano-structured electrodes, we have prepared the well-defined Ag structures by using the polystyrene-based template methods (Ag-NSL) on the glassy-carbon (GC) electrodes. For the detail discussion about the isotopic reaction selectivity on the nano-structured electrode, the electrochemical mass spectroscopy system has been applied.[2] Figure shows the separation factor (S_D) values which can be used as the indication for the isotopic selectivity for each electrode. As indicated in the figure, it was found that the unique isotopic selectivity can be seen on the nano-structured Ag-electrode compared to the normal Ag electrode. From the theoretical kinetic simulations, it was found that the specific surface process was selectively accelerated on the nano-structured electrode. In addition, it was also found that the tuning the metal species or morphologies allowed us to switch the H_2 to D_2 generations. Through all attempts, we have successfully achieved the functionalization of isotopic selectivity on HER for the first time.

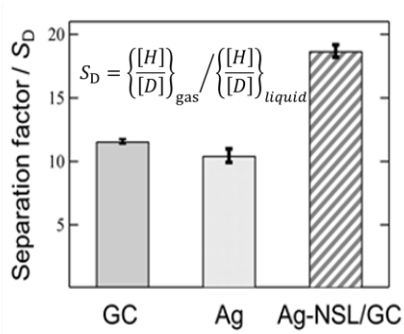


Fig. Estimated S_D values for GC, Ag and Ag-NSL/GC electrodes. Each value was obtained from mass spectra by using GC, Ag, and Ag-NSL/GC electrodes. The electrolyte solution was 0.5 M Na_2SO_4 aq. solution containing 90 mol% D_2O.

1) J. O'M. Bockris, and D. B. Matthews, *J. Chem. Phys.*, **1996**, *44*, 298.
2) H. Minamimoto, and K. Murakoshi, *Electrochim. Acta* **2019**, *304*, 87.

Academic Program [Oral B] | 07. Inorganic Chemistry | Oral B

[J401-3pm] 07. Inorganic Chemistry

Chair: Takane Imaoka, Sayaka Uchida

Fri. Mar 25, 2022 1:00 PM - 3:40 PM J401 (Online Meeting)

[J401-3pm-01] Syntheses and polymorphic transformations of ionic crystals based on mononuclear bismuth(III) complexes and polyoxometalates

○Tsukasa Iwano[1], Daiki Akutsu[1], Zhewei Weng[1], Naoki Ogiwara[1], Sayaka Uchida[1] （1. Grad. Sch. Arts and Sci., The Univ. of Tokyo）

1:00 PM - 1:20 PM

[J401-3pm-02] The Formation of $Al_{28}V_4$ Polycation in Porous Ionic Crystal for Acetalization Reaction

○Wei Zhou[1], Naoki OGIWARA[1], Sayaka UCHIDA[1] （1. School of Arts and Sciences,The university of Tokyo）

1:20 PM - 1:40 PM

[J401-3pm-03] Non-humidified intermediate-temperature proton conductors based on a Dawson-type polyoxometalate and poly(ethylene glycol) derivatives

○Naoki Ogiwara[1], Masahiro Tomoda[1], Shotaro Miyazaki[1], Zhewei Weng[1], Sayaka Uchida[1] （1. School of Arts and Sciences, The University of Tokyo ）

1:40 PM - 2:00 PM

[J401-3pm-04] Degradation of Polymers by Polyoxometalate Photocatalysts

○Chifeng Li[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] （1. The Univ. of Tokyo）

2:00 PM - 2:20 PM

[J401-3pm-05] Precise Synthesis and CO_2 Hydrogenation Catalysis of Early-Transition Metal Clusters

○Augie Atqa[1], Masanori Wakizaka[2], Wang-Jae Chun[3], Takane Imaoka[1], Kimihisa Yamamoto[1] （1. Tokyo Institute of Technology, 2. Tohoku University, 3. International Christian University）

2:20 PM - 2:40 PM

[J401-3pm-06] Synthesis and properties of heterogeneous elemental blended Sn clusters using dendrimer template synthesis method

○Hisanori Muramatsu[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2,3], Reina Hosono[1], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] （1. Tokyo Tech., Lab. Chem. Life Sci., 2. JST-ERATO, 3. JST-PRESTO）

2:40 PM - 3:00 PM

[J401-3pm-07] Atomic Behaviors of Quantum Dots and NaCl Crystal Nucleus Revealed by Single-molecule Analyses

○Takayuki Nakamuro[1], Olivier Chevalier[1], Masaya Sakakibara[1], Rui Shang[1], Eiichi Nakamura[1] （1. The University of Tokyo）

3:00 PM - 3:20 PM

[J401-3pm-08] Cleavage of molecular hydrogen and catalysis over molecular hybrids of silver nanoclusters and polyoxometalates

○Kentaro Yonesato[1], Daiki Yanai[1], Seiji Yamazoe[2], Daisuke Yanai[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] （1. The Univ. of Tokyo, 2. Tokyo Metro. Univ.）

3:20 PM - 3:40 PM

Syntheses and polymorphic transformations of ionic crystals based on mononuclear bismuth(III) complexes and polyoxometalates

([1]*Graduate School of Arts and Sciences, The University of Tokyo*)
○Tsukasa Iwano,[1] Daiki Akutsu,[1] Zhewei Weng,[1] Naoki Ogiwara,[1] Sayaka Uchida [1]
Keywords: ionic crystal; polymorphism; bismuth ion; polyoxometalate; proton transport

The controlled assembly of molecules, ions, and ligands as building blocks based on crystal engineering leads to various functional crystalline solids. In particular, polyoxometalates (POMs), which are anionic metal oxide clusters, have been a popular motif in crystal engineering[1)]. To revisit simple mononuclear metal complexes as counter cations of POMs, seven ionic crystals based on Keggin- or Dawson-type POMs with mononuclear bismuth(III) complexes[2),3)] as counter cations were synthesized (Fig. 1). The bismuth(III) center exhibited triangular dodecahedron, square antiprism, or pseudo-cubic eight-coordination geometries, with dimethyl sulfoxide or *N*,*N*-dimethylformamide as ligands. The ionic crystals showed polymorphic transformation depending on the synthetic or recrystallization conditions. As a method for exploring functionality, proton conductivities of the ionic crystals were measured under humidified conditions. The ionic crystals with high porosity, tertiary amine moieties, or coordination water exhibited high proton conductivities, and large activation energies indicate that protons are transferred mainly with water molecules via vehicle mechanism[4)].

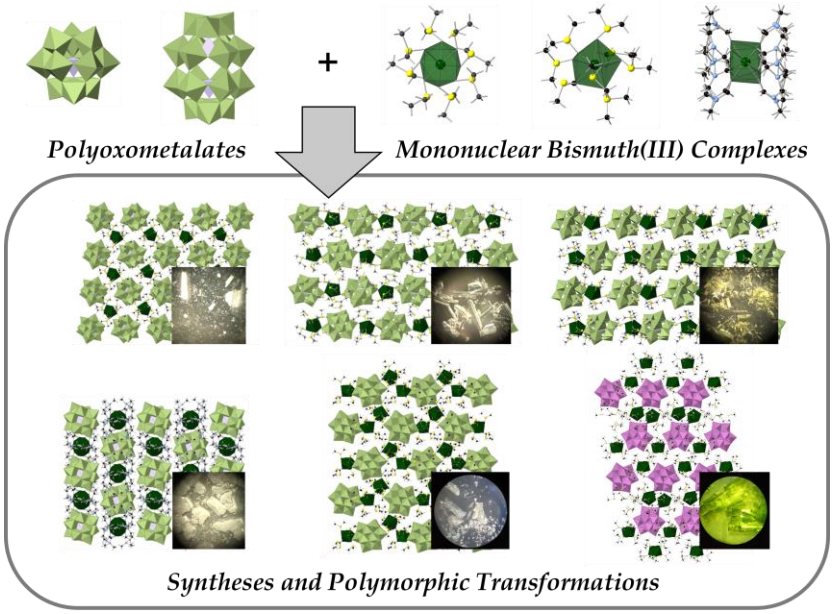


Fig. 1 Ionic crystals based on polyoxometalates and mononuclear bismuth(III) complexes

1) C. P. Pradeep *et al*., *Dalton Trans.*, **2010**, 39, 9443. 2) E. G. Gumbris *et al*., *Russ. J. Inorg. Chem.*, **2012**, 57, 337. 3) A. A. Mukhacheva *et al.*, *Polyhedron*, **2018**, 141, 393. 4) K. D. Kreuer, *Chem. Mater.*, **1996**, 8, 610.

The Formation of $Al_{28}V_4$ Polycation in Porous Ionic Crystal for Acetalization Reaction

([1]*Department of Basic Science, School of Arts and Sciences, The University of Tokyo*) ○ Wei ZHOU[1], Naoki OGIWARA[1], Sayaka UCHIDA[1]

Keywords: Aluminum Polyoxocation; Polyoxometalates; Ionic Crystal

A rapid growth of interest in investigating the hydrolysis of aluminum salts in water produces an array of polyoxoaluminum clusters with various sizes, shapes, and compositions, which are widely used in catalysis, water treatment, and as pillaring agents.[1, 2] Among those 1−2-nm-sized polyoxoaluminum clusters, Keggin-type $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (**Al_{13}**) is the most classic one. Particularly, **δ-Al_{13}** isomer is utilized as the building block linked through octahedral AlO_6 sites to construct larger polyoxoaluminum clusters, such as **Al_{26}**, **Al_{30}** and **Al_{32}**.[3] The heteroatom substitutions of those larger polyoxoaluminum clusters can fulfill the diversity of structural topologies of polyaluminum species. Herein, we demonstrate the first case of heteroatom substitutions of V^{5+} in aluminum Polyoxocation (**$Al_{28}V_4$**) isolated in the solid state from aqueous solution with polyoxometalate (POM) anions, $[\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]^{6-}$. The present study describes the synthesis and structural characterization of this all-inorganic porous ionic crystal (PIC) of $[V_4Al_{28}O_{22}(OH)_{48}(H_2O)_{24}][\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]_2\cdot 45H_2O$ [**I**].

In a typical synthesis, ***δ*-Al_{13}** solution was mixed with an aquous solution of $[\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]^{6-}$ by using a hydrothermal method to obtain **I**. Single crystal X-ray diffraction analysis reveals that **I** crystallized in the orthorhombic *Cmce* space group (#64), in which the **$Al_{28}V_4$** cations (Figure 1a) are arranged in a herringbone manner to form an extended 2D network structure in the *bc*-plane and the 2D network are alternately arranged along the *a*-axis to construct a 3D assembled structure. $[\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]^{6-}$ anions (Figure 1b) are located between the 2D networks of **$Al_{28}V_4$** cations and stabilized by electrostatic interactions and hydrogen bonds (Figure 1c). Further, **I** is applicable in acid-catalyzed acetalization of benzaldehyde and shows higher catalysis activity than **Al_{13}** based PICs.

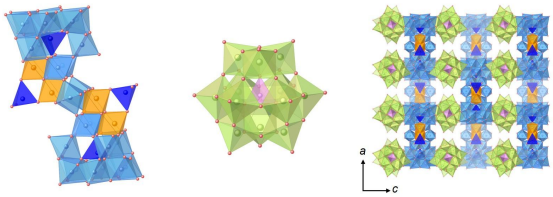


Figure 1. The crystal structure of (a) **$Al_{28}V_4$** (b) $\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}^{6-}$ and (c) **I** along *b*-axis

1)W. H. Casey, *Chem. Rev.* **2006**, 106, 1, 1−16. 2) W. Zhou, N. Ogiwara, Z.W. Weng, N. Tamai, C. C. Zhao, L. K. Yan and S. Uchida, *Chem. Commun.*, **2021**, 57, 8893−8896. 3) J. Rowsell and L. F. Nazar, *J. Am. Chem. Soc*. **2000**, 122, 3777−3778.

Dawson 型 POM とポリエチレングリコール誘導体を基盤とした中温領域作動のプロトン伝導体

（東大院総合 [1]）○荻原 直希 [1]・友田 雅大 [1]・宮崎 翔太郎 [1]・翁 哲偉 [1]・内田 さやか [1]
Non-humidified intermediate-temperature proton conductors based on a Dawson-type polyoxometalate and poly(ethylene glycol) derivatives ([1]*School of Arts and Sciences, The University of Tokyo*) ○ Naoki Ogiwara,[1] Masahiro Tomoda,[1] Shotaro Miyazaki,[1] Zhewei Weng,[1] Sayaka Uchida[1]

We demonstrate a new strategy to synthesize Polyoxometalate (POM)–polymer composites exhibiting fast proton conduction under non-humidified intermediate-temperature conditions. Specifically, a molecular design approach utilizing poly(ethylene glycol)s (PEGs) of different terminal groups or chain lengths controls the proton carrier density, and a crystal engineering approach using a large Dawson-type POM ($[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$) with an anisotropic molecular shape and alkali metal ions as counter cations fine-tunes the mobility of the confined PEGs as proton carriers. By integrating these approaches, proton conductivity over 10^{-4} S cm^{-1} at 150 °C, comparable to the well-known highly proton-conductive solid-state materials, is achieved. The proton conduction mechanism is discussed with alternative current impedance spectroscopy and solid-state NMR spectroscopy.
Keywords : Polyoxometalate; Proton Conduction; Crystal Engineering

固体中のプロトン伝導は燃料電池の固体電解質やセンサーにおいて重要な役割を果たす。特に Pt 触媒の CO 被毒への耐性の観点から、非加湿条件下・中温領域作動のプロトン伝導体の開発が急務である。これまでに我々は Keggin 型ポリ酸($[PW_{12}O_{40}]^{3-}$)とポリエチレングリコール(PEG)からなる複合体は、中温領域でも安定にプロトン伝導性を発現することを報告した。[1] しかしながら、その伝導度は 2.0×10^{-6} S cm^{-1} (150 °C, 非加湿）に留まっており、伝導性向上のための分子設計が必要である。

本研究では Keggin 型ポリ酸よりもサイズの大きな Dawson 型ポリ酸($[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$)に着目し、[2] PEG 及び対カチオンとなる Cs^+、K^+と反応させることにより新規複合体の合成を行った（図）。交流インピーダンス法により、得られた複合体の伝導性を評価したところ、1.3×10^{-4} S cm^{-1} (150 °C, 非加湿）であり、Keggin 型複合体を凌駕する伝導度を示すことがわかった。これは、Dawson 型複合体では、ポリ酸で囲まれたナノチャネル口径が Keggin 型複合体と比べて拡張されており、チャネル中に閉じ込められた PEG の運動性が向上したためだと示唆された。[3]

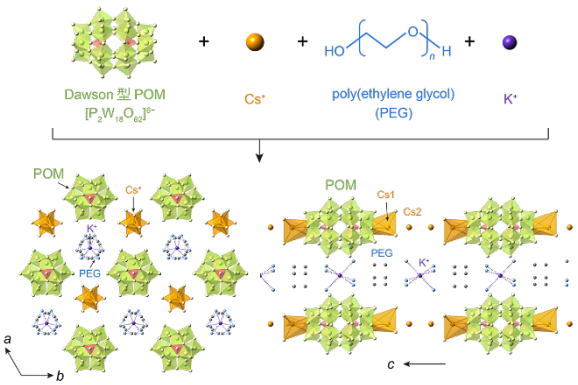


図. 複合体の合成と結晶構造。

1) *J. Solid State Chem.*, **2016**, *234*, 92.
2) *Inorg. Chem.*, **2008**, *47*, 3679.
3) *Nanoscale*, **2021**, *13*, 8049.

Degradation of Polymers by Polyoxometalate Photocatalysts

(*School of Engineering, The University of Tokyo*) ○Chifeng Li, Kosuke Suzuki, Kazuya Yamaguchi

Keywords: Polyoxometalate; Degradation of Polymer; Polymer; Photocatalyst

Plastic waste problem has grown into one of the top environmental problems of the world, and the degradable polymers are gaining attention as a means for tackling this problem. Although various strategies for degradation of polymers have been developed, they often require large loading of transition metal catalysts, suffered from slow degradation rate, and are limited to specific polymers, such as polyolefins.[1] On the other hand, the catalytic degradation of more environmentally friendly polymers, such as polyesters and polyethers, are less studied. Polyoxometalates (POMs) are structurally well-defined nanometer-sized metal oxide clusters. Compared with the common photocatalysts such as organometallic complexes or organic dyes, they possess several advantages, for example, the strong light absorption, the high thermal and redox stability, the ability to activate molecular oxygen, the structure diversity, and the tunability of their properties through changing structures, constituent elements and counter cations.[2]

In this work, we report the degradation of polymers by using polyoxometalates as photocatalysts. GPC analysis was used for the investigation of the change of molecular weights of the polymers during the reactions. In the presence of a small amount of polyoxometalate catalysts, this system can efficiently promote the photodegradation of various polyesters and polyethers. The details of the system will be discussed in the presentation.

Figure 1. Schematics of the photodegradation of polyesters and polyethers by polyoxometalates photocatalysis.

1) I. E. Napper, R. C. Thompson, *Environ. Sci. Technol*. **2019**, *53*, 4775. 2) a) K. Suzuki, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2018**, *8*, 10809; b) C. Li, K. Suzuki, N. Mizuno, K. Yamaguchi, *Chem. Commun.* **2018**, *54*, 7127; c) C. Li, N. Mizuno, K. Murata, K. Ishii, T. Suenobu, K. Yamaguchi, K. Suzuki, *Green Chem.* **2020**, *22*, 3896.

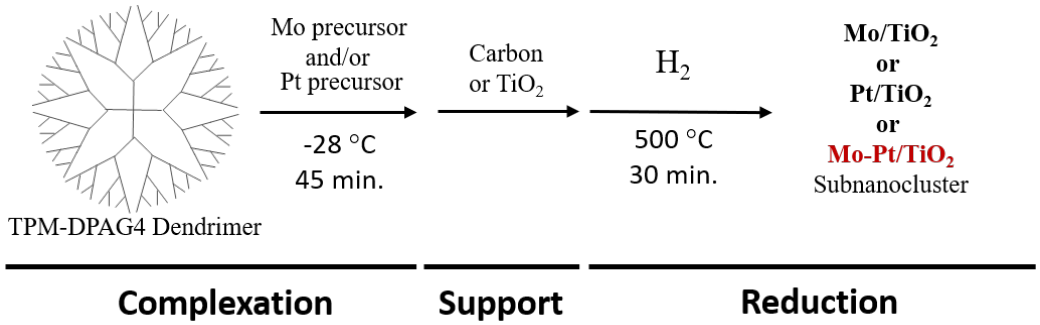
Precise Synthesis and CO_2 Hydrogenation Catalysis of Early-Transition Metal Clusters

([1]*Tokyo Institute of Technology*, [2]*Tohoku University*, [3]*International Christian University*)
○ Augie Atqa,[1] Masanori Wakizaka,[2] Wang-Jae Chun,[3] Takane Imaoka,[1] Kimihisa Yamamoto[1]
Keywords: Subnanocluster; Molybdenum; Phenylazomethine Dendrimer; Carbon Dioxide Hydrogenation

Ultra-small subnanoclusters exhibit unique properties compared to their nanoparticles and metal bulks, such as high catalytic activity. In this context, ultra-small precious metal clusters like Platinum have been extensively investigated.[1-3] This research targeted early-transition metals such as Molybdenum. We have succeeded in precisely synthesizing Mo clusters on carbon and TiO_2 support using the carbothermal hydrogen reduction (CHR) method at 500 ºC by employing a phenylazomethine dendrimer as a template. By utilizing the potential gradient within the dendrimer molecule, we have also succeeded in precisely synthesizing the Mo-Pt bimetallic subnanocluster supported on TiO_2.

The formation and characteristics of clusters were confirmed using X-ray photoelectron spectroscopy (XPS), high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray absorption fine structure (XAFS) studies. We found that Mo clusters with less than 1.3 nm formed oxycarbides, and Mo nanoparticles larger than 1.3 nm formed carbides on a carbon support. It indicates a size-dependent phase transformation, what we called subnano-transformation.[4]

We have evaluated the catalytic activity of Mo-based clusters, including Mo-Pt/TiO_2 bimetallic subnanocluster, on the CO_2 hydrogenation under mild temperature (T =150 ºC). It revealed that alloying and subnano-ization of Mo-Pt particles resulted in a high turnover number of CO_2 compared to Mo-only and Pt-only subnanoclusters and nanoparticles.



1) Imaoka *et al*, *J. Am. Chem. Soc.* **2013**, 135(35), 13089-13095. 2) Imaoka *et al*, *Angew. Chem. Int. Ed* **2015**., 54(34), 9810-9815. 3) Huda *et al*, *Angew. Chem. Int. Ed.* **2019**, 58(4), 1002-1006. 4) Atqa *et al*, *Nanoscale* **2020**, 12(29), 15814-15822.

Synthesis and properties of heterogeneous elemental blended Sn clusters using dendrimer template synthesis method

([1] *Lab. Chem. Life Sci., Tokyo Tech.*, [2]*JST-ERATO*, [3]*JST-PRESTO*)
○Hisanori Muramatsu[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2,3], Reina Hosono[1], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2]

Keywords: cluster, sub-nano particle, iron, tin, magnetic property

Metal clusters are known to exhibit unique properties different from those of the bulk. Some of these can mimic elemental atoms[1)], and are expected for elemental substitutions based on their peculiar properties. However, such clusters are only synthesized in small amounts in the gas phase or in stable clusters with a magic number in the liquid phase. Therefore, the preparation method to control atoms in the clusters are expected. In our laboratory, cluster synthesis using dendrimers has been developed for tuning the constituting atoms. The dendrimers have an electron density gradient enabling coordination of metal salts from the inner imines. By using this method, we have synthesized various metal clusters and revealed the properties depending on the number of constituent atoms and composition[2,3)]. In this study, we synthesized $FeSn_{12}$ as a Fe-Sn alloy cluster and develop its functions.

$FeCl_3$ and $SnCl_2$ were integrated into a fourth-generation dendrimer (pyTPM-DPA G4). 9-isoabsorption points were observed in the UV-Vis spectrum, indicating a stepwise complexation from the pyridine in the inner layer to the imine in the outer layer (**Fig. 1a, b**). Therefore, we synthesized clusters using pyTPM-DPA G4 as a template (**Fig. 1c**) and investigated their properties. The magnetic moment of $FeSn_{12}$ is larger than that of other Fe clusters synthesized in the same way.

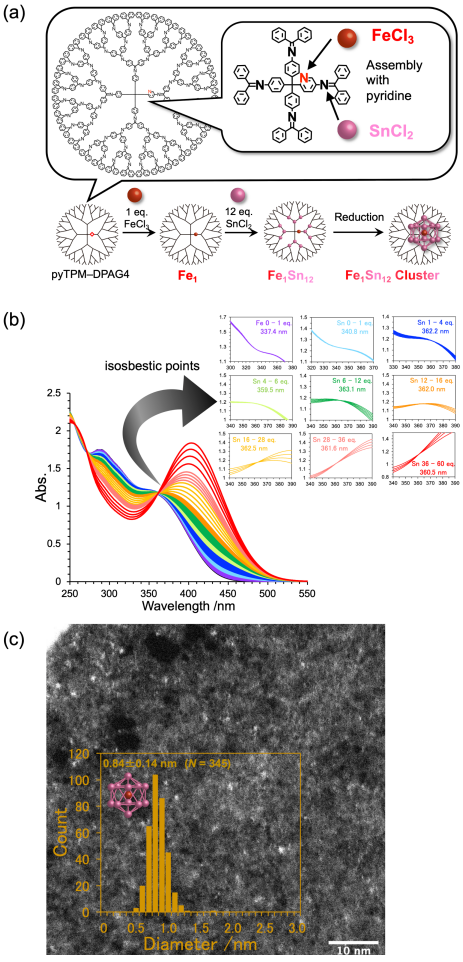


Fig. 1 (a) Images of this study, (b) UV-vis tightening of $FeCl_3/SnCl_2$ vs. pyTPM-DPA G4, (c) STEM image and size distribution of $FeSn_{12}$.

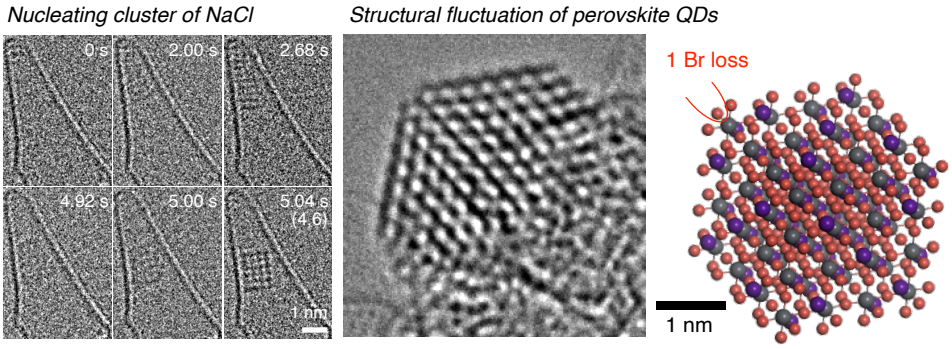
1) D. E. Bergeron *et al.*, *Science*, **2004**, *304*, 84. 2) K. Yamamoto *et al.*, *Nature*, **2002**, *415*, 509. 3) K. Yamamoto *et al.*, *Acc. Chem. Res.*, **2014**, *47*, 1127.

Atomic Behaviors of Quantum Dots and NaCl Crystal Nucleus Revealed by Single-Molecule Analyses

(*Department of Chemistry, The University of Tokyo*) ○Takayuki Nakamuro, Olivier Chevalier, Masaya Sakakibara, Shang Rui, Eiichi Nakamura
Keywords: Perovskite Quantum Dot; Crystal Nucleus; Transmission Electron Microscope; Atomic resolution; Single Molecule Analysis

The acquisition of structural information is of paramount importance in nanostructured materials such as quantum dots (QDs) since the structure of the material is directly related to its optical and material properties. We have developed a method to utilize the inner space of carbon nanotubes (CNTs) as the nano-observation fields, and a method to chemically modify molecules on CNTs surface for single-molecule atomic-resolution time-resolved electron microscopic (SMART-EM) observations. In this study, we report on SMART-EM observations of crystal nuclei, which consist of tens to hundreds of atoms, to reveal their dynamic behaviors.

The fluctuation of nucleating clusters in nucleation was analyzed in detail by using NaCl as a model and observing the crystallization phenomenon continuously for 152 seconds.[1] SMART-EM observations have revealed features of NaCl nucleating clusters fluctuating between disordered and ordered structures, and a similar result has been reported for the nucleation process of gold.[2] A newly synthesized blue light-emitting perovskite QDs that emits at 463 nm with quantitative photoluminescence quantum yield show only one bromine defect at the corner Pb atom and no defect at the edges of the cubic structure, as suggested by the chemical composition derived from the SEM-EDX analysis and optical properties. We also detected the dynamic structural fluctuation of QDs through SMART-EM observations.



1) T. Nakamuro, M. Sakakibara, H. Nada, K. Harano, E. Nakamura, *J. Am. Chem. Soc.* **2021**, *143*, 1763. 2) S. Jeon *et al*., *Science* **2021**, *371*, 498.

銀ナノクラスター-ポリオキソメタレート複合分子の水素解離特性と触媒特性

（東大院工[1]・都立大院理[2]・東大院総文[3]）○米里 健太郎[1]・屋内 大輝[1]・山添 誠司[2]・横川 大輔[1]・鈴木 康介[1]・山口 和也[1]

Cleavage of Molecular Hydrogen and Catalysis over Molecular Hybrids of Silver Nanoclusters and Polyoxometalates ([1]*School of Engineering, The University of Tokyo*, [2]*School of Engineering, Tokyo Metropolitan University*, [3]*School of Arts and Science, The University of Tokyo*) ○Kentaro Yonesato[1], Daiki Yanai[1], Seiji Yamazoe[2], Daisuke Yokogawa[3], Kosuke Suzuki[1], Kazuya Yamaguchi[1]

Silver nanoclusters have widely attracted great interest owing to their unique properties that depend on structures and electronic states. We have recently developed the synthesis of atomically precise silver nanoclusters using polyoxometalate as inorganic ligands, which exhibit high stability and absorption bands in visible light region assignable to charge transfer between silver nanoclusters and polyoxometalates. Herein, we revealed that the molecular hybrids exhibited unique reactivity to cleave molecular hydrogen into protons and electrons (i.e., $H_2 \rightarrow 2H^+ + 2e^-$) under mild conditions, in which generated protons and electrons were stored polyoxometalates and silver nanoclusters. Additionally, these molecular hybrids exhibited catalysis based on the hydrogen cleavage properties.

Keywords : Inorganic synthesis, Silver nanoclusters, Polyoxometalates, Reduction catalyst

銀ナノクラスターは、その構造や電子状態に依存した特異な物理化学特性を有し、幅広い応用が期待される。当研究室では、ポリオキソメタレートを無機配位子として有する銀ナノクラスターの精密合成を実現し、この複合分子が極めて高い安定性を示すことや、銀ナノクラスターとポリオキソメタレートの電荷移動遷移に由来する可視光吸収帯を有することなどを明らかにしてきた。[1] 本研究では、銀ナノクラスターとポリオキソメタレートからなる複合分子が、温和な条件下で分子状水素の解離特性を有し、生成したプロトンと電子がそれぞれポリオキソメタレート骨格と銀ナノクラスターに貯蔵されることを明らかにした（図 1）。また、これらの複合分子が水素解離特性を利用した触媒作用を示すことを見出した。

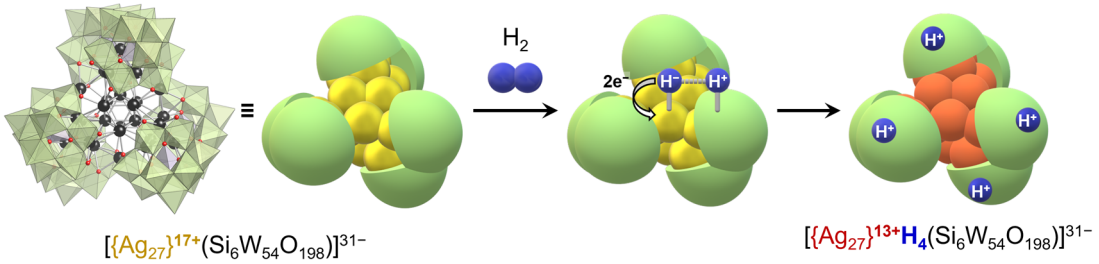


Figure 1. 銀ナノクラスター–ポリオキソメタレート複合分子の水素解離特性

1) K. Yonesato, H. Ito, H. Itakura, D. Yokogawa, T. Kikuchi, N. Mizuno, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2019**, *141*, 19550.
2) K. Yonesato, S. Yamazoe, D. Yokogawa, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2021**, *60*, 16994.

[B204-3pm] 08. Catalysts and Catalysis

Chair: Tamao Ishida, Hidehiro Sakurai

Fri. Mar 25, 2022 1:20 PM - 3:40 PM B204 (Online Meeting)

[B204-3pm-01] Dehydrogenative coupling of alkane and benzene catalyzed by supported metal-solid acid catalyst system

○Moe Takabatake[1], Satoshi Misaki[1], Masayuki Nambo[2], Wang-Jae Chun[3], Yuichi Manaka[1,4], Ken Motokura[1,2] (1. Tokyo Tech, 2. Yokohama National Univ., 3. ICU, 4. AIST)

1:20 PM - 1:40 PM

[B204-3pm-02] Selective Synthesis of Primary Anilines Using NH_3 as a Nitrogen Source via Acceptorless Dehydrogenative Aromatization

○Hui Li[1], Takafumi Yatabe[1], Satoshi Takayama[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

1:40 PM - 2:00 PM

[B204-3pm-03] CeO_2 Supported Au– Pd Alloy Nanoparticle Catalyst for Heterogeneously Catalyzed Decarbonylation of 1,2-Diketones

○Takehiro Matsuyama[1], Takafumi Yatabe[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

2:00 PM - 2:20 PM

[B204-3pm-04] Elucidation of active site and reaction mechanism of Pd/Au/CeO_2-catalyzed dehydrogenation of ketones

○Daisuke Takei[1], Takafumi Yatabe[1], Tomohiro Yabe[1], Ray Miyazaki[2], Jun-ya Hasegawa[2], Kazuya Yamaguchi[1] (1. The University of Tokyo, 2. Hokkaido University)

2:20 PM - 2:40 PM

[B204-3pm-05] Atomically Precise Synthesis of Au_{25} Cluster Catalyst on Double Metal Hydroxide by Long-term Oxidative Aging of $Au_{25}(SR)_{18}$

○Shinya Masuda[1], Shinjiro Takano[1], Seiji Yamazoe[2,3,4], Tatsuya Tsukuda[1,4] (1. The Univ. of Tokyo, 2. Tokyo Metropolitan Univ., 3. JST, PRESTO, 4. ESICB, Kyoto Univ.)

2:40 PM - 3:00 PM

[B204-3pm-06] Synthesis of Murdochite-type Oxide Mg_6MnO_8 Nanoparticles and the Catalytic Oxidation Properties

○Eri Hayashi[1], Takatoshi Tamura, Takeshi Aihara[1], Keigo Kamata[1], Michikazu Hara[1] (1. Tokyo Institute of Technology)

3:00 PM - 3:20 PM

[B204-3pm-07] Enhancement of Catalytic 1,4-Arylation Activity by N-Heterocyclic Carbene Ligand Decoration on Cr and Rh-incorporated Ceria Catalysts

○Satoru Ikemoto[1], Satoshi Muratsugu[1], Yuta Tsuji[2], Kazunari Yoshizawa[2], Mizuki Tada[1,3] (1. Dept. Chem., Nagoya Univ., 2. IMCE, Kyushu Univ., 3. RCMS, Nagoya Univ.)

3:20 PM - 3:40 PM

担持金属-固体酸混合触媒系によるアルカンとベンゼンの脱水素カップリング反応

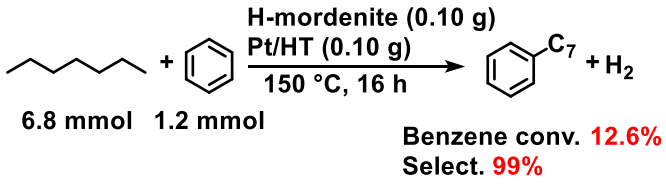
（東工大物質理工[1]・横国大理工[2]・国際基督教大[3]・産総研再エネ[4]）○高畠 萌[1]・美崎 慧[1]・南保 雅之[2]・田 旺帝[3]・眞中 雄一[1,4]・本倉 健[1,2]
Dehydrogenative coupling of alkane and benzene catalyzed by supported metal-solid acid catalyst system ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Department of Chemistry and Life Science, Yokohama National University,* [3]*International Christian University*, [4]*Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology*) ○Moe Takabatake[1], Satoshi Misaki[1], Masayuki Nambo[2], Wang-Jae Chun[3], Yuichi Manaka[1,4], Ken Motokura[1,2]

The dehydrogenative coupling reaction of alkanes with benzene is a useful reaction that can directly convert inexpensive and abundant alkanes into raw materials for chemical products. The reaction of alkanes and benzenes catalyzed by Pt or Pd supported on solid acids has been reported, but it requires high temperature[1)].

In our group, we found that a catalyst mixture of hydrotalcite-supported Pd and montmorillonite, a solid acid, promoted the reaction of *n*-heptane and benzene at 150 °C[2)]. In addition, we found that the catalytic activity was improved by using hydrotalcite-supported Pt instead of supported Pd. In the supported Pt system, product selectivity changed significantly by changing the type of solid acid: a 99% selectivity toward the alkylation product was achieved by using H-mordenite in the reaction of *n*-heptane and benzene.
Keywords : Pt; Solid Acid; Dehydrogenative Coupling; Alkane; Benzene

アルカンとベンゼンの脱水素カップリング反応は、安価で豊富なアルカンを直接化成品原料へと転換できる有用な反応である。これまでに固体酸に Pt や Pd を担持した触媒によるアルカンとベンゼンの反応が報告されているが、200 °C 以上の高温を必要としている [1)]。

当研究室では、ハイドロタルサイト担持 Pd と固体酸であるモンモリロナイトの混合触媒が 150 °C における *n*-ヘプタンとベンゼンの反応を円滑に進行させることを見出した [2)]。さらに、担持 Pd に代わって担持 Pt を用いることで触媒活性が向上することを見出した。また、固体酸の種類が生成物の選択性に影響することを利用し、*n*-ヘプタンとベンゼンの反応に H-mordenite を用いるとベンゼン転化率 12.6%、目的生成物である炭素鎖 7 のアルキル化生成物（Ph-C7）への選択率 99% を達成した（Scheme 1）。触媒の構造解析や基質展開結果も報告する。



Scheme 1

1) N. Danilina, E. L. Payrer, J. A. van Bokhoven, *Chem. Commun.,* **2010**, *46*, 1509-1510.
2) M. Takabatake, A. Hashimoto, W.-J. Chun, M. Nambo, Y. Manaka, K. Motokura, *JACS Au*, **2021**, *1*, 119-123.

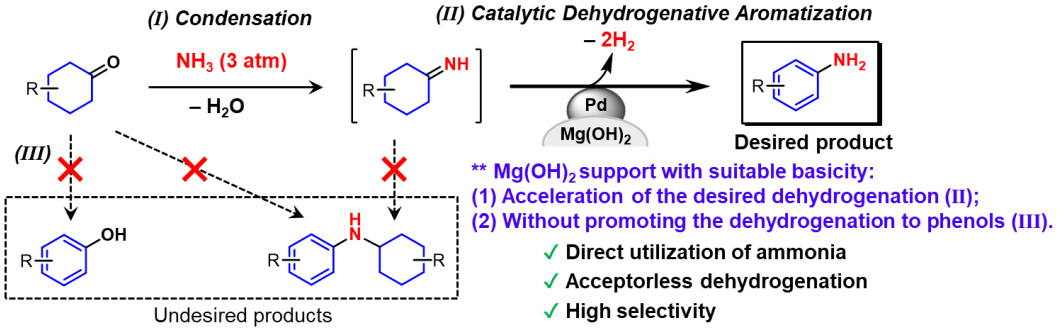
Selective Synthesis of Primary Anilines Using NH_3 as a Nitrogen Source *via* Acceptorless Dehydrogenative Aromatization

([1]*School of Engineering, The University of Tokyo*) ○Hui Li,[1] Takafumi Yatabe,[1] Satoshi Takayama,[1] Kazuya Yamaguchi[1]

Keywords: Primary anilines; Ammonia; Acceptorless dehydrogenative aromatization; Heterogeneous catalysis; Basic support

Although synthetic methods of primary anilines including reduction of nitrobenzenes, aromatic substitution, and cross-coupling reactions were reported, there are still several disadvantages such as the multi-step synthesis which does not directly utilize NH_3, inevitable pre-functionalization of substrates, and/or the limitation of specific *ortho/meta/para* selectivity in those processes. Moreover, the cross-coupling reactions require a stoichiometric amount of base and produce halogen-containing byproducts.[1] Recently, a new method, phenol-to-aniline amination, was also reported, yet it tolerates a narrow substrate scope.[2] On the other hand, our group has successfully developed a process for the synthesis of primary anilines from a variety of cyclohexanones using NH_3 as a direct nitrogen source *via* Pd nanoparticle-catalyzed dehydrogenative aromatization.[3] However, this reaction requires a stoichiometric amount of styrene as the hydrogen acceptor. Overall, as far as we know, there is virtually no general and efficient heterogeneous catalytic system for this conversion without using any acceptor.

In this study, we have developed a novel method for the selective synthesis of primary anilines in high yields from cyclohexanones by utilizing NH_3 as the nitrogen source directly *via* acceptorless dehydrogenative aromatization in the presence of an $Mg(OH)_2$-supported Pd nanoparticle catalyst. Various experimental results suggested that the basic sites on $Mg(OH)_2$ could effectively accelerate the desired dehydrogenation of cyclohexylimine intermediates formed by the condensation of cyclohexanones and NH_3, which suppressed the formation of the undesired *N*-cyclohexylanilines. In addition, the undesirable formation of phenols by direct cyclohexanone dehydrogenation hardly proceeded because of the suitable basicity of $Mg(OH)_2$.



1) J. Schranck, A. Tlili, *ACS Catal.,* **2018**, *8*, 405. 2) T. Cuypers, P. Tomkins, D. E. De Vos, *Catal. Sci. Technol.,* **2018**, *8*, 2519. 3) Y. Koizumi, X. Jin, T. Yatabe, R. Miyazaki, J. Hasegawa, K. Nozaki, N. Mizuno, K. Yamaguchi, *Angew. Chem. Int. Ed.,* **2019**, *58*, 10893.

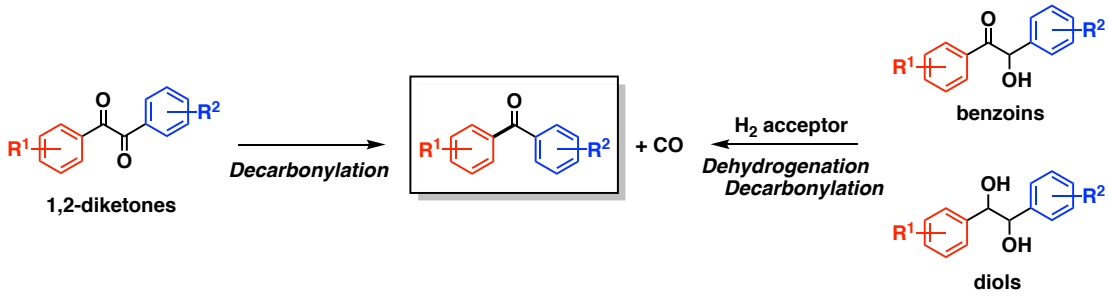
CeO_2 Supported Au–Pd Alloy Nanoparticle Catalyst for Heterogeneously Catalyzed Decarbonylation of 1,2-Diketones

([1]*School of Engineering, The University of Tokyo*) ○Takehiro Matsuyama,[1] Takafumi Yatabe,[1] Tomohiro Yabe,[1] Kazuya Yamaguchi[1]

Keywords: Au−Pd Alloy; Decarbonylation; 1,2-Diketones; Heterogeneous Catalysts; Cerium Oxide

Ketone is an essential moiety in the synthesis of pharmaceuticals, agrochemicals, and natural products, and various synthetic methods of ketones, including Friedel–Crafts acylation, have been developed to date. A new approach to ketone synthesis via 1,2-diketones has been paid attention to due to the possibility of utilizing various starting materials such as alkynes, alkenes, and aldehydes. However, reported decarbonylation of 1,2-diketones to ketones mostly depended on a kind of benzilic acid rearrangement utilizing a stoichiometric amount of base and anilines,[1)] and a few reports of 1,2-diketones decarbonylation involving oxidative addition demonstrated limited substrate scopes such as aliphatic diketones[2)] or alkynyl 1,2-diketones.[3)] To the best of our knowledge, no report of decarbonylation of diaryl 1,2-diketones involving oxidative addition has been reported.

In this study, we have developed heterogeneously catalyzed decarbonylation of 1,2-diketones to ketones involving oxidative addition using a CeO_2-supported Au–Pd alloy nanoparticle catalyst (Au−Pd/CeO_2), which demonstrates a wide substrate scope and functional group tolerance. In addition, we have also reported tandem reactions starting from benzoins or diols to synthesize diaryl ketones using the catalyst with a hydrogen acceptor. Au−Pd/CeO_2 was confirmed to function as a heterogeneous catalyst by hot filtration and ICP-AES analysis of the filtrate, and the catalyst can be recycled. In this presentation, we will discuss the alloy effect and the support effect in detail based on the thorough catalyst characterization, kinetic analysis, and control experiments.



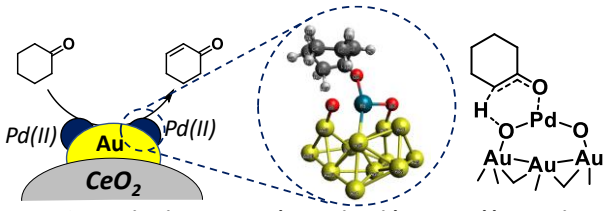
1) L. Gu, H. Zhang, *RSC Adv.* **2015**, *5*, 690. 2) K. Kaneda, H. Azuma, M. Wayaku, S. Tehanishi, *Chem. Lett*. **1974**, *3*, 215. 3) R. E. Whittaker, G. Dong. *Org. Lett*. **2015**, *17*, 5504.

Elucidation of active site and reaction mechanism of Pd/Au/CeO_2-catalyzed α,β-dehydrogenation of ketones

([1]*School of Engineering, The University of Tokyo*, [2]*Institute for Catalysis, Hokkaido University*)
○Daisuke Takei,[1] Takafumi Yatabe,[1] Tomohiro Yabe,[1] Ray Miyazaki,[2] Jun-ya Hasegawa,[2] Kazuya Yamaguchi[1]
Keywords: C–H bond activation; Heterogeneous catalyst; Aerobic oxidative dehydrogenation; DFT calculation; XAFS

Aerobic α,β-dehydrogenation of ketones to α,β-unsaturated ketones, which are present in bioactive substances and versatile organic synthetic intermediates, is an attractive transformation. Recently, we have reported heterogeneously catalyzed aerobic α,β-dehydrogenation of ketones including cyclohexanones via α-C–H activation for the first time using a Pd–Au bimetallic nanoparticle catalyst supported on CeO_2 (Pd/Au/CeO_2).[1] This catalytic system was truly heterogeneous, but it showed much higher catalytic activity for α,β-dehydrogenation of cyclohexanone than previously reported homogeneous catalysts.[2]

In this study, we experimentally and computationally elucidated the active site and mechanism of Pd/Au/CeO_2-catalyzed α,β-dehydrogenation of cyclohexanone via efficient C–H bond activation.[3] Detailed characterization of the catalyst revealed that bimetallic nanoparticles are formed on the CeO_2 support with an average size of about 2.5 nm and comprising an Au nanoparticle core and PdO nanospecies dispersed on the core. Activity tests and detailed characterizations demonstrated that the dehydrogenation activity increased with the coordination numbers of Pd–O species in the presence of Au(0) species. Such experimental evidence suggests that a Pd(II)–(μ-O)–Au(0) structure is the true active site for this reaction. Density functional theory (DFT) calculations using a suitable $Pd_1O_2Au_{12}$ cluster model with the Pd(II)–(μ-O)–Au(0) structure proposed a C–H bond activation mechanism via concerted catalysis in which the Pd atom acts as a Lewis acid and the adjacent μ-oxo species acts as a Brønsted base simultaneously. The calculated results reproduced various experimental results for the selective formation of 2-cyclohexen-1-one from cyclohexanone without forming phenol, the regioselectivity of the reaction, the turnover-limiting step, and the activation energy.



New C–H activation strategy by Lewis acid-Brønsted base pair of Pd(II)–(μ-O)–Au(0) structure

1) D. Takei, T. Yatabe, X. Jin, T. Yabe, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2020**, *10*, 5057.
2) T. Diao, S. S. Stahl, *J. Am. Chem. Soc.* **2011**, *133*, 14566.
3) D. Takei, T. Yatabe, T. Yabe, R. Miyazaki, J. Hasegawa, K. Yamaguchi, *JACS Au in press*.

Atomically Precise Synthesis of Au_{25} Cluster Catalyst on Double Metal Hydroxide by Long-term Oxidative Aging of $Au_{25}(SR)_{18}$

([1]*Graduate School of Science, The University of Tokyo*, [2]*Graduate School of Science, Tokyo Metropolitan University,* [3]*JST-PRESTO,* [4]*Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University*) ○Shinya Masuda,[1] Shinjiro Takano,[1] Seiji Yamazoe,[2,3,4] Tatsuya Tsukuda[1, 4]

Keywords: Gold cluster catalyst, Ligand protected gold cluster, Atomically precise synthesis, Oxidation catalysis, Oxidative aging

One of the promising approaches for atomically precise synthesis of heterogeneous Au cluster catalysts is to activate ligand-protected Au clusters by pretreatment on a solid support. The most conventional pretreatment is removal of the ligands by calcination at >250 °C in vacuum,[1] but it also induced aggregation of the clusters. Another pretreatment method reported so far includes aging at a low temperature (~150 °C) in the presence of oxygen. However, much less is known about the structural change of the clusters during oxidative aging. In the present work, we focused on the structural change of $Au_{25}(BaET)_{18}$ (BaET: 2-(Boc-amino)ethanethiolate) during long-term oxidative aging at low temperature on double metal hydroxide (DMH) support composed of Co and Ce (Co_3Ce).

The structural change of $Au_{25}(BaET)_{18}$ on Co_3Ce during the aging was studied by Au L_3-edge X-ray absorption fine structure (XAFS) measurement. Time course of coordination numbers (*CN*s) determined by curve-fitting analyses of extended XAFS are plotted in Fig. 1. Firstly, the $CN_{Au–S}$ values monotonically reduced by aging for ≤8 h and became ~0 by aging for ≥12 h, suggesting the ligands were completely removed. Secondly, the $CN_{Au–Au}$ values became 4–5 after aging for 12 h. Such small *CN* values suggest that Au_{25} clusters take a flattened structure since the $CN_{Au–Au}$ for a hemisphere structure is estimated to be ~6 and that for monolayer of (111) plane in face-centered cubic structure is estimated to be 4.2. This structure was stabilized owing to the strong anchoring of gold by oxygen atoms on this support since $CN_{Au–O}$ was appeared after aging.

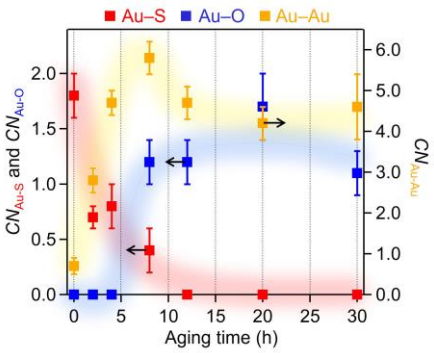


Fig. 1. Time course of coordination numbers (*CN*s) of Au–S, Au–O, and Au–Au bonds during the aging.

Finally, obtained Au_{25}/Co_3Ce catalyst exhibited quite high activity in the benzyl alcohol oxidation to benzoic acid under mild condition.[2]

1) S. Yamazoe, T. Yoskamtorn, S. Takano, S. Yadnum, J. Limtrakul, T. Tsukuda, *Chem. Rec.* **2016**, *16*, 2338. 2) S. Masuda, S. Takano, S. Yamazoe, T. Tsukuda, *Nanoscale,* in press.

ムルドカイト型酸化物 Mg_6MnO_8 ナノ粒子の合成と酸化触媒特性

（東工大フロンティア材料研）○林 愛理・相原 健司・田村 高敏・鎌田 慶吾・原 亨和

Synthesis of Murdochite-type Oxide Mg_6MnO_8 Nanoparticles and the Catalytic Oxidation Properties

(*Laboratory for Materials and Structures, Tokyo Institute of Technology*) ○Eri Hayashi, Takatoshi Tamura, Takeshi Aihara, Keigo Kamata, Michikazu Hara

Selective oxidation of hydrocarbons to oxygen-containing compounds is a key technology in the chemical industry. Molecular oxygen (O_2) economically and environmentally outperforms other oxidants. Therefore, catalytic oxidative C–H functionalization with O_2 as the sole oxidant has received much attention. The structure of Mg_6MnO_8 consisting of isolated tetravalent manganese species located in basic oxide MgO would be effective for the liquid phase oxidation due to the presence of both basicity and oxidizing ability. To date, Mg_6MnO_8 has been synthesized by sol−gel, impregnation, and solid-state methods; however, the surface areas are still low and the catalytic applications have been limited to gas-phase reactions. Herein, we report the synthesis and characterization of Mg_6MnO_8 nanoparticles with high surface area (108 $m^2\ g^{-1}$) by the sol-gel method using malic acid, and their catalytic application to the selective oxidation of alkylarenes with O_2.[1)] Mg_6MnO_8 nanoparticles exhibited much higher catalytic activity for the oxidation of fluorene than other manganese oxides.

Keywords : High Surface Area; Selective Oxidation; Murdochite-type Oxide

選択酸化反応は、C-H 結合を活性化し炭化水素原料を工業的に有用な含酸素化合物に変換する重要な反応であり、分子状酸素（O_2）は、資源的に豊富、低環境負荷などの利点を有する最も理想的な酸化剤である。そのため、O_2 のみを酸化剤とし選択酸化反応を高効率かつ温和な条件で進行させることは重要である。ムルドカイト型酸化物 Mg_6MnO_8 はマンガン 4 価が塩基性固体 MgO 中に孤立して存在しており、塩基性と酸化能を併せもつことから液相酸化反応への応用が期待される。これまでに様々な合成法が報告されているが、低表面積かつ応用例は気相反応のみとなっている。本研究では、リンゴ酸を用いたゾルゲル法による高表面積 Mg_6MnO_8 の合成・キャラクタリゼーションと種々の基質の酸素酸化反応への触媒応用について検討を行った。合成した Mg_6MnO_8 の XRD パターンは、ムルドカイト型構造と良い一致を示した（Figure 1）。比表面積は 108 $m^2\ g^{-1}$ であり、これまでの報告値（2–15 $m^2\ g^{-1}$）よりも 7 倍以上大きな値であった。種々のマンガン酸化物を触媒とし、フルオレンの酸化反応により活性評価を行ったところ、Mg_6MnO_8 は他のマンガン酸化物よりも高い活性を示した。本講演では Mg_6MnO_8 の基質適用性や反応メカニズムについても議論する。

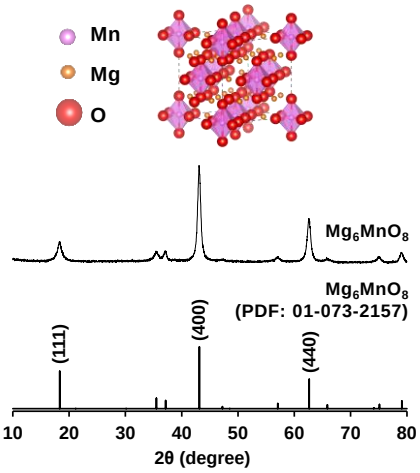


Figure 1. Structure of cubic Mg_6MnO_8 and XRD patterns for Mg_6MnO_8 (upper) and cubic Mg_6MnO_8 (JCPDS 01-073-2157, lower).

1) E. Hayashi, T. Tamura, T. Aihara, K. Kamata, M. Hara, *ACS Appl. Mater. Interfaces* in revision.

Enhancement of Catalytic 1,4-Arylation Activity by N-Heterocyclic Carbene Ligand Decoration on Cr and Rh-incorporated Ceria Catalysts

([1]*Graduate School of Science, Nagoya University*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*, [3]*Research Center for Materials Science, Nagoya University*)
○Satoru Ikemoto,[1] Satoshi Muratsugu,[1] Yuta Tsuji,[2] Kazunari Yoshizawa,[2] Mizuki Tada[1,3]
Keywords: *Mixed Metal Oxide, NHC Ligand, Rhodium, Ceria, 1,4-Arylation*

Decoration of organic ligands onto heterogeneous catalysts is one of the effective strategies to functionalize heterogeneous catalysis; for examples, catalytic activity enhancement[1] and chemoselectivity tuning[2] by the decoration of N-heterocyclic carbene (NHC) ligands on the supported metal nanoparticle. We have succeeded in functionalizing a Cr- and Rh-incorporated ceria catalyst[3] with a NHC ligand (1,3-dicyclohexylimidazol-2-ylidene (ICy)) (denoted as ICy-$Cr_{0.19}Rh_{0.06}CeO_z$) and found that catalytic 1,4-arylation activity of cyclohexenone and phenylboronic acid was newly emerged on ICy-$Cr_{0.19}Rh_{0.06}CeO_z$ (Figure 1(A)).[4] The active sites and the catalytic activity enhancement by the NHC decoration were investigated.

Rh *K*-edge EXAFS of ICy-$Cr_{0.19}Rh_{0.06}CeO_z$ (ICy: 0.8 wt%) showed similar Rh-Rh bonds (coordination number = 2.8±0.4) to H_2-reduced $Cr_{0.19}Rh_{0.06}CeO_z$, indicating that small Rh nanoclusters remained after the NHC decoration. N 1s XPS of ICy-$Cr_{0.19}Rh_{0.06}CeO_z$ at 400.6 eV (Figure 1(B)) and the photoluminescence spectral analyses strongly suggested that the decorated ICy "carbene" was interacted with the active Rh nanoclusters on the catalyst surface.

DFT calculation suggested the influence of NHC coordination onto the active Rh cluster. Phenyl group (from phenylboronic acid) was adsorbed at a bridge site of a modelled tetrahedral Rh_4 cluster on CeO_2 (Rh_4/CeO_2) (Figure 1(C-a)). On the other hand, phenyl group was adsorbed on a top site of ICy-decorated Rh_4/CeO_2, which was closer to cyclohexenone (Figure 1(C-b)). DFT results suggested that ICy controlled the adsorption site of a phenyl group closer to cyclohexenone on the Rh clusters, resulting in facilitation of C-C bond formation.

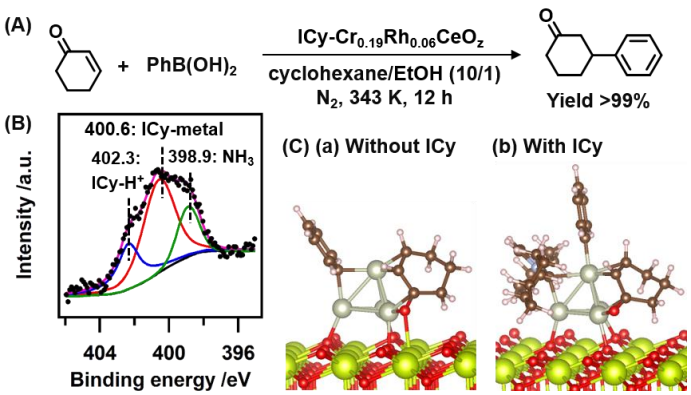


Figure 1. (A) 1,4-Arylation of cyclohexenone with phenylboronic acid. (B) N 1s XPS of ICy-$Cr_{0.19}Rh_{0.06}CeO_z$. (C) DFT optimized structure of Rh_4/CeO_2 (a) without ICy and (b) with ICy coordinated with phenyl group and cyclohexenone.

1) Ernst, J. B. *et al. J. Am. Chem. Soc.* **2017**, *139*, 9144. 2) Ernst, J. B. *et al. J. Am. Chem. Soc.* **2016**, *138*, 10718. 3) Ikemoto, S. *et al. Phys. Chem. Chem. Phys.* **2019**, *21*, 20868. 4) Ikemoto, S. The 101st CSJ Annual Meeting, **2021**, A07-2am-10.

[J403-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Minoru Mitsumi, Yumi Yakiyama

Fri. Mar 25, 2022 1:00 PM - 3:40 PM J403 (Online Meeting)

[J403-3pm-01] Role of intramolecular hydrogen bonding in the redox chemistry of hydroxybenzoate-bridged paddlewheel diruthenium (II,II) complexes

○Wataru Kosaka[1,2], Yudai Watanabe[2], Hitoshi Miyasaka[1,2] （1. IMR, Tohoku Univ., 2. Sch. of Sci., Tohoku Univ.）

1:00 PM - 1:20 PM

[J403-3pm-02] Helical Inversion Dynamics in a Metal– Peptide Framework

○Wei Yuan[1], Hiroshi Sato[2,3], Takuzo Aida[1,2] （1. The Univ. of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. Japan Science and Technology Agency (JST), Precursory Research for Embryonic Science and Technology (PRESTO)）

1:20 PM - 1:40 PM

[J403-3pm-03] Syntheses and Physical Properties of Robust Porous Molecular Conductors with 1,2,4-Triazole Group

○Hiroaki Iguchi[1], Mengxing Cui[1], Yongbing Shen[1], Shohei Koyama[1], Shinya Takaishi[1] （1. Tohoku University）

1:40 PM - 2:00 PM

[J403-3pm-04] Accumulated Lattice Strain as an Internal Trigger for Spontaneous Pathway Selection

○Hubiao Huang[1] （1. Riken）

2:00 PM - 2:20 PM

[J403-3pm-05] Synthesis, Crystal Strucutre and Photophysical Properties of Acceptor-Encapsulated Porous Zinc Porphyrin Dimers

○Mitsuyuki Oshiro[1], Minoru Mitusmi[1], Chiasa Uragami[2], Hideki Hashimoto[2] （1. Okayama Univ. of Sci., 2. Kwansei Gakuin Univ. ）

2:20 PM - 2:40 PM

[J403-3pm-06] Sensing Behavior of Sumanene Functionalized Bis(terpyridine) Ruthenium(II) Complexes

○Junyi Han[1], Yumi Yakiyama[1,2], Yuta Uetake[1,2], Hidehiro Sakurai[1,2] （1. Graduate School of Engineering, Osaka Univ., 2. ICS-OTRI, Osaka Univ.）

2:40 PM - 3:00 PM

[J403-3pm-07] Kinetic analysis for optimizing the Zn-catalyzed transesterification conditions of MA and MMA with diols to maximize monoesterified products

○Taito KATO[1,2], Haruki NAGAE[1], Kazushi MASHIMA[1] （1. Osaka University, 2. Nippon Shokubai）

3:00 PM - 3:20 PM

[J403-3pm-08] Synthesis of Antimony Porphycene and Catalytic Hydrogen Evolution Driven by Ligand-Centered Reduction

○Taro Koide[1], Zhi Zhang[1], Taro Fujioka[1], Yoshio Yano[1], Toshikazu Ono[1,2], Yoshio Hisaeda[1,2] （1. Graduate School of Engineering, Kyushu University, 2. Center for Molecular

Systems (CMS), Kyushu University)
3:20 PM - 3:40 PM

Role of intramolecular hydrogen bonding in the redox chemistry of hydroxybenzoate-bridged paddlewheel diruthenium (II,II) complexes

([1]*Institute for Materials Research, Tohoku University*, [2]*Graduate School of Science, Tohoku University*) ○Wataru Kosaka,[1,2] Yudai Watanabe,[2] Hitoshi Miyasaka[1,2]

Keywords: Redox property; Paddlewheel-type diruthenium complexes; Intramolecular hydrogen bonding

Carboxylate bridged paddlewheel diruthenium complexes ([Ru_2]) have attracted attention for the use as functional modules such as redox-active component in metal-organic frameworks. For this purpose, tuning the electronic properties of [Ru_2] unit has become key. Our groups have already demonstrated systematic tunability of the electronic properties in a series of F- or Cl-substituted benzoate-bridged [$Ru_2^{II,II}$] complexes.[1,2] Meanwhile, a phenolic OH group has electron-donating ability, in contrast to the electron-withdrawing abilities of F/Cl substituents. In particular, it often acts as a proton-donor for hydrogen bonding. Hence, the synthesis of an OH-substituted [$Ru_2^{II,II}$] series was desirable, but has rarely been reported because of the difficulty of isolation in crystalline form.

In this study, a series of trans-heteroleptic [$Ru_2^{II,II}$] complexes[3] with various OH-substituted benzoate ligands, [$Ru_2((OH)_xPhCO_2)_2(2,6\text{-}(CF_3)_2PhCO_2)_2(THF)_2$] were synthesized (Fig. 1a). The characterization of these compounds allowed a systematic analysis of the electronic property dependency on the OH substituent.[4] In this heteroleptic series, the redox potential ($E_{1/2}$) of the [$Ru_2^{II,II}$]/[$Ru_2^{II,III}$]$^+$ couple in THF varies over a wide range, from −18 mV (vs. Ag/Ag^+) for ***p*-OH** to 432 mV for **2,6-(OH)$_2$**. The redox properties are linearly dependent on the acidity (pK_a) of the OH-substituted benzoic acids. The value of the Hammett constant σ_o for the *o*-OH substituent was determined to be 0.667, indicating a strongly electron-withdrawing character, contrary to the expectation of electron-donating character for an OH group. The redox properties of the compounds were well explained in a framework of Hammett analyses (Fig. 1b) and were also consistent with their HOMO energy levels evaluated by DFT calculations based on the atomic coordinates. The unexpected electron-withdrawing character of the *o*-OH groups could be attributed to the direct effect of intramolecular hydrogen bonding on the charge density on the carboxylate.

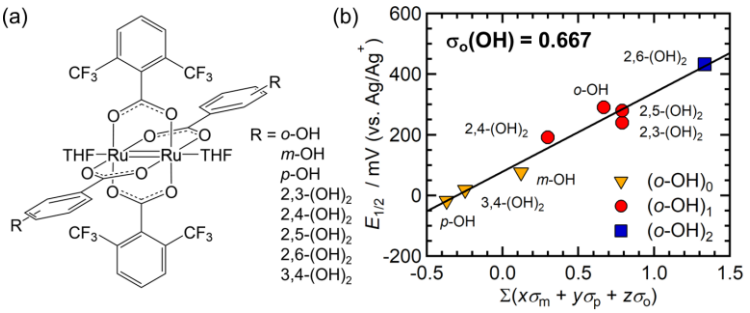


Fig. 1 (a) Scheme of molecular structure. (b) Plots of $E_{1/2}$ vs Hammett constant.

1) H. Miyasaka et al. *Dalton Trans*. **2011**, *40*, 673. 2) W. Kosaka et al. *Dalton Trans*. **2015**, *44*, 8156. 3) Y. Sekine et al. *Chem*. *Lett*. **2018**, *47*, 693. 4) W. Kosaka et al. *Dalton Trans*. **2022**, *51*, 85.

Helical Inversion Dynamics in a Metal–Peptide Framework

([1]*School of Engineering, The University of Tokyo*, [2]*RIKEN Center for Emergent Matter Science*, [3]*JST-PRESTO*) ○Wei Yuan,[1] Hiroshi Sato,[2,3] Takuzo Aida[1,2]

Keywords: Peptide Helix; Dynamic Helix; Helical Inversion; Metal–Organic Frameworks

Helix is a unique structural motif in nature and its structurally dynamic behavior plays a crucial role in various events such as chiral sensing. Inspired by the helical structures in nature, a great interest has been paid to the design of artificial systems with helical motifs that exhibit dynamic behaviors.[1] Peptides containing achiral amino acids such as 2-aminoisobutyric acid (Aib) that adopt stable hydrogen-bonded helical conformations can undergo helix inversion between right-handed (*P*) and left-handed (*M*) helices by external stimuli.[2] However, helix inversion processes have been exclusively investigated in solution (Fig. 1a), while there are only few studies in solid, especially in the crystalline state where molecular motions are greatly restricted (Fig. 1b).

We designed ^{Aib}**L** composed of an Aib hexamer with terminally appended pyridyl groups (Fig. 1b). ^{Aib}**MOF**, [Zn_2(^{Zn}Por)(^{Aib}**L**)], was synthesized by the reaction of ^{Aib}**L**, $Zn(NO_3)_2{\cdot}6H_2O$, and tetrakis(4-carboxyphenyl)porphyrin ($^{2H}PorH_4$) in a mixture of DMF/EtOH. Single-crystal X-ray analysis revealed that ^{Aib}**MOF** consists of stacked 2D double layers. Each double layer contains two porphyrin sheets pillared by 3_{10}-helical ^{Aib}**L**. A racemic mixture of *P* and *M* helices are present in the crystal due to a 2-fold disorder.

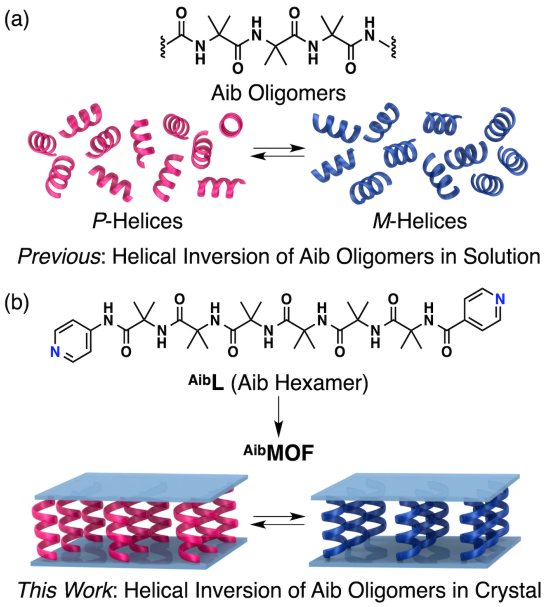


Figure 1 (a) Helix inversion of Aib oligomers in solution. (b) Molecular structure of ^{Aib}**L** composed of an Aib hexamer modified with terminal pyridyl groups and schematic representation of ^{Aib}**MOF** to realize helical inversion even in the crystalline state.

^{13}C-labeled ^{Aib}**L** was synthesized as an NMR helicity detector, and ^{Aib}**MOF** prepared from the ^{13}C-labeled ligand was subjected to variable temperature solid state ^{13}C NMR spectroscopy. The spectra showed that the signals assigned to *P* and *M* helical structures reversibly coalesce and split with a coalescence temperature (T_c) of 333 K, indicating that the helices are dynamically inverting even in the crystalline state as a function of temperature. It is noteworthy that such dynamic motion of ^{Aib}**L** in ^{Aib}**MOF** do not deteriorate the crystalline framework of ^{Aib}**MOF**. This is accomplished by the intrinsic porosity of ^{Aib}**MOF**, allowing the space required for the inversion motion.

1) J. Clayden *et al.*, *Chem. Commun*. **2016**, *52*, 4852. 2) T. Aida *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 716.

Syntheses and Physical Properties of Robust Porous Molecular Conductors with 1,2,4-Triazole Group

([1]*Graduate School of Science, Tohoku University*) ○Hiroaki Iguchi,[1] Mengxing Cui,[1] Yongbing Shen,[1] Shohei Koyama,[1] Shinya Takaishi[1]

Keywords: Molecular Conductor; Porous Coordination Polymer, Naphthalenediimide; Interpenetration

Molecular conductors with one-dimensional (1D) electron system are very promising as switching materials, because they can change their conducting, magnetic and optical properties by external stimuli such as light, pressure and temperature. However, chemical stimuli such as molecular desorption/adsorption have rarely been applied to these materials, because the dense molecular packing disturbs the response to the chemical stimuli. To solve this problem, we recently proposed porous molecular conductors (PMCs) as the fusion of metal-organic frameworks (MOFs) and molecular conductors. The reported PMCs consist of 1D coordination polymer with π-stacking columns among them.[1,2)] Thus, the framework was fragile and the removal of solvent molecules in the pores gave irreversible structural change.

In this work, we chose *N*,*N'*-bis-(1,2,4-triazolyl)naphthalenediimide (NDI-trz) as the organic linker, because terminal 1,2,4-triazolyl group was used to construct three-dimensional (3D) MOFs compatible with the periodicity of π-stacking array.[3)] The solvothermal reaction with $CdCl_2$ afforded the complicated mixture, whereas we found tiny black single crystals therein. The X-ray structure analysis exhibited that two 3D frameworks were interpenetrated with forming infinite π-stacking columns (Fig. 1). The pure polycrystalline compounds was obtained by electrocrystallization. This PMC was more robust than the previously reported PMCs due to the 3D framework. The electrical conductivity of the single crystal was 2×10^{-4} S cm^{-1} at 300 K. The semiconducting behavior was observed in the temperature-dependence conductivity measurement.

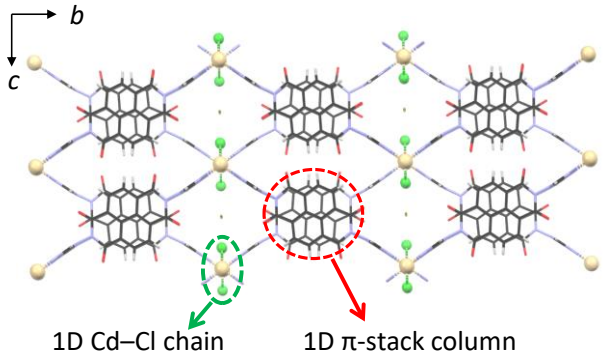


Fig. 1 Crystal structure of the new PMC with interpenetrated 3D frameworks

1) L. Qu, H. Iguchi, M. Yamashita et al., *J. Am. Chem. Soc.* **2019**, *141*, 6802. 2) S. Koyama, H. Iguchi et al., *Chem. Commun.* **2020**, *56*, 13109. 3) G. Huang, T.-F. Liu, R. Cao et al., *Angew. Chem., Int. Ed.* **2020**, *59*, 4385.

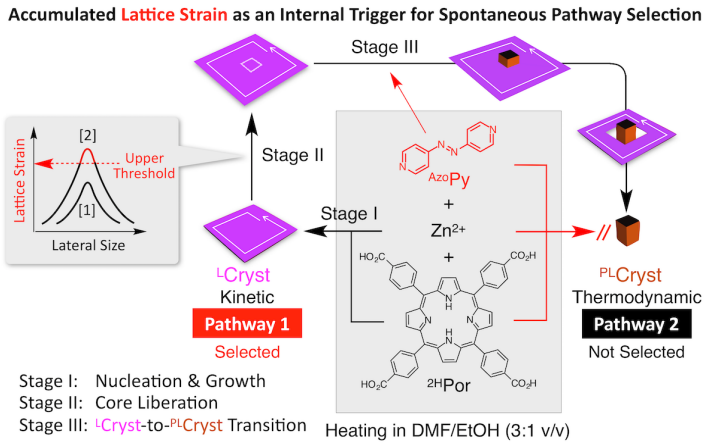
Accumulated Lattice Strain as an Internal Trigger for Spontaneous Pathway Selection

(*Center for Emergent Matter Science (CEMS), Riken*) ○Hubiao Huang

Keywords: Screw Dislocation; Spontaneous Crystal Transition; Lattice Strain; Pathway Selection.

Biological systems are in a far-from-equilibrium state, where a diverse range of components with various lifespans emerge and interact in different pathways before they disappear.[1] Usually, such multiple biological events proceed, in order, because of the timely selection of appropriate pathways. The concept of path-way complexity is highly important, not only in biology but also in other systems including multicomponent assembly and crystallization,[2] and raises the question of how pathway selection can be executed. In a well-designed biological process, a key component that can internally trigger pathway selection may be produced according to a designated timeline.[1] Although a new strategy to mimic biological pathway selection using in-situ produced "internal triggers" has been reported,[3] nonbiological processes have generally been considered to require physical or chemical external triggers for pathway selection.[4]

Here we report an unprecedented finding that a lattice strain accumulated with the growth of a crystal serves as an "internal trigger" for pathway selection in multicomponent crystallization. We discovered a "spontaneous" crystal transition, where the kinetically preferred layered crystal, initially formed by excluding the pillar component, carries a single dislocation at its geometrical center. This crystal "spontaneous-ly" liberates a core region to relieve the accumulated lattice strain around the dislocation. Consequently, the liberated part becomes dy-namic and enables the pillar ligand to invade the crystalline lattice, thereby transforming into a thermodynamically preferred pillared-layer crystal.



Reference: 1. *Nat. Rev. Mol. Cell Biol.* **2008**, *9*, 255; 2. *Science* ***2020***, *368*, 642; 3. *Science* **2015**, *349*, 1075; 4. *Nature* **2012**, *481*, 491.

アクセプター内包多孔性亜鉛ポルフィリンダイマーの合成，結晶構造，光物性

（岡山理大理[1]・関学大生命環境[2]）○大城実之[1]・満身稔[1]・浦上千藍紗[2]・橋本秀樹[2]

Synthesis, Crystal Structures and Photophysical Properties of Accptor-Encapsulated Porous Zinc Porphyrin Dimers

([1]*Okayama University of science*, [2] *Kwansei Gakuin University*)
○Mitsuyuki Oshiro,[1] Minoru Mitsumi,[1] Chiasa Uragami,[2] Hideki Hashimoto[2]

To construct a photo charge-separation system with a long lifetime based on a porous metal complex, we are developing porous metal porphyrins in which an acceptor is encapsulated in its pores. This study focused on zinc porphyrin dimers, and two different types of zinc porphyrin dimers **ZnPD_222** and **ZnPD_121** were synthesized. We report synthesis and X-ray crystal structures of two kinds of crystals, **ZnPD_222•C_{60}** and **ZnPD_121•C_{60}**, with different sheet structures obtained by co-crystallization of each ZnPD with C_{60}.

Keywords : Metal-Organic Framework (MOF), Zinc porphyrin

当研究では，多孔性金属錯体に基づく長寿命の光電荷分離システムの開発を目指し、細孔内にアクセプターを内包したアクセプター内包多孔性亜鉛ポルフィリン錯体の合成を行なっている。これまでに、亜鉛ポルフィリンモノマーを用い、細孔内にアクセプターとしてC_{60}を導入したフラーレン内包多孔性亜鉛ポルフィリン錯体の結晶化とX線結晶構造解析に成功するとともに、その電荷分離寿命が0.25nsであることを明らかにしている[1)]。本研究では、さらなる電荷分離状態の長寿命化を目指し、自己集合により不飽和な配位サイトを有する二次元四角格子を形成することが可能であり，ピリジル基を繋ぐアセチレン数を変えた二種類の亜鉛ポルフィリンダイマー**ZnPD_222**及び**ZnPD_121**を合成し、フラーレンとの共結晶化を行なった（図1）。各ポルフィリンダイマーにおいて二種類の異なるシート構造を持つ結晶構造が得られた（図2）。本発表では、二種類の亜鉛ポルフィリンダイマーの合成とともに、フラーレン内包多孔性亜鉛ポルフィリンダイマーの結晶構造、光物性評価について報告する。

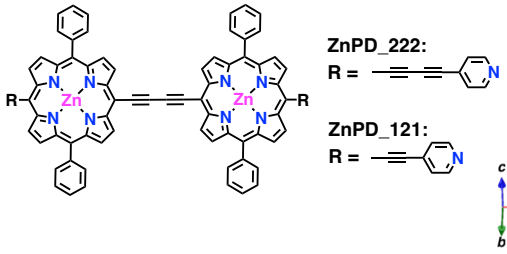


図１．亜鉛ポルフィリンダイマー**ZnPD**.

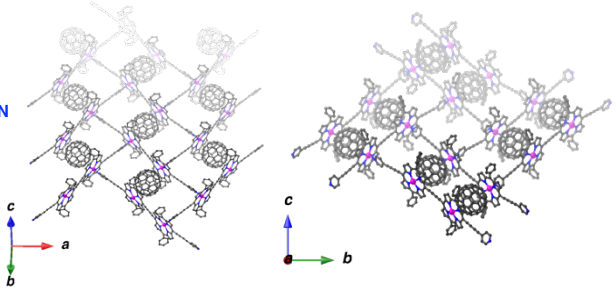


図２．**ZnPD_222**·C_{60}の結晶構造.

1) 堀内ら，錯体化学討論会第65回討論会, 3Fa-03, **2015**.

Sensing behavior of sumanene-functionalized bis(terpyridine) Ruthenium(II) complexes

([1]*Grad. Sch. Eng., Osaka Univ.*, [2]*ICS-OTRI, Osaka Univ.*)
○Junyi Han,[1] Yumi Yakiyama,[1,2] Yuta Uetake,[1,2] Hidehiro Sakurai [1,2]
Keywords: Sumanene; Terpyridine; Ruthenium complexes; Fluorescence; Ion trapping.

$Ru(terpy)_2^{2+}$ (terpy = 2,2':6',2"-terpyridine) has gained much attention as functional templates in supramolecular chemistry. Addition of the ion sensing units on the terpyridine unit will change the whole physical property and bring the opportunity to be utilized as a photosensor system. In this context, we introduced sumanene, a bowl-shaped π-conjugated molecule,[1] which recently reported to show significant and selective interaction to Cs^+,[2] as an ion trapping site to the ruthenium complex.

Four kinds of terpyridiyl ligands **L1-L4** (Fig. 1a) were synthesized by Kröhnke reaction and Suzuki-Miyaura coupling reaction from formylsumanene, bromosumanene and benzaldehyde. Complexation of the ligands with $RuCl_2(DMSO)_4$ or $RuCl_3$ in $EtOH/CHCl_3$ followed by the counterion exchange with NH_4PF_6 yielded the symmetric disumanenyl complexes (**C1**, **C2**), and unsymmetrical ones (**C3**, **C4**). The absorption spectra of all the complexes showed two intense bands at around 300 nm corresponding to the ligand-centered (LC) state. Their emission spectra were also studied at room temperature to find that all the complexes exhibited one broad emission band at 400–500 nm under the excitation wavelength of 300 nm. Noteworthy is that unsymmetrical complexes showed another emission peak at 530 nm (Fig. 1b). We further focused on their cation recognition property in $MeCN/H_2O$ solution to find their Li^+ sensing ability and the effect of counter anion. (Fig. 1c).

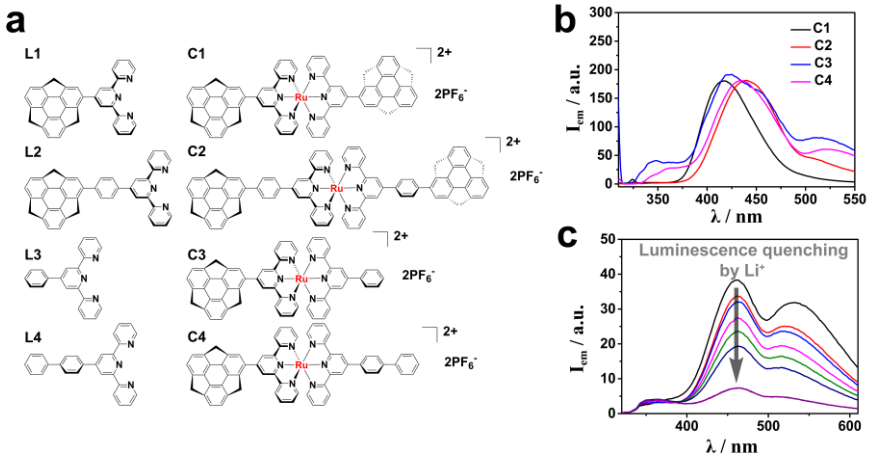


Figure 1. a) Structure of **L1-L4** and **C1-C4**. b) PL spectra of **C1-C4**. c) Li^+ titration study with **C4**.

1) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878. 2) a) A. Kasprzak, H. Sakurai, *Dalton Trans*. **2019**, *48*, 17147; b) A. Kasprzak, A. Kowalczyk, A. Jagielska, B. Wagner, A. M. Nowicka, H. Sakurai, *Dalton Trans*. **2020**, *49*, 9965; c) A. Kasprzak, H. Sakurai, *Chem. Commun*. **2021**, *57*, 343.

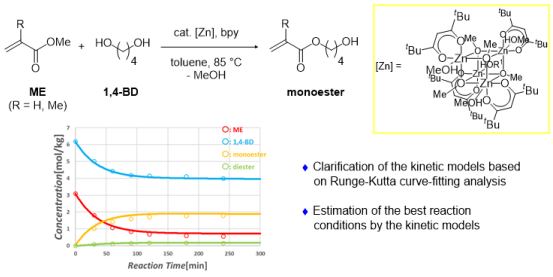
Kinetic analysis for optimizing the Zn-catalyzed transesterification conditions of MA and MMA with diols to maximize monoesterified products

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Innovation and Business Development Division, Nippon Shokubai Co., LTD.*) ○Taito KATO,[1,2] Haruki NAGAE,[1] Kazushi MASHIMA[1]

Keywords: (Meth)acrylates; Diols; Transesterification; Kinetic analysis; Cluster complexes

(Meth)acrylate is widely used in industrial products, and terminal hydroxylated (meth)acrylates are monomers directly produced by diols and methyl (meth)acrylate, but catalytic transesterification, which is an equilibrium reaction that selectively and highly converts mono-esterification, requires well-optimized reaction conditions. Catalytic transesterification, however, involves several obstacles that must be overcome, such as (1) a long reaction time to proceed to transesterification, (2) a statistical mixture of terminal hydroxylated monomers and diol bis(meth)acrylates, and (3) contamination by undesired side reactions, such as Michael addition and polymerization of vinyl monomers.

In this study, we demonstrated that a unique alkoxy-bridged tetranuclear zinc complex $[Zn(tmhd)(OMe)(MeOH)]_4$ worked as an appropriate catalyst for the transesterification of methyl (meth)acrylate with a variety of diols such as 1,4-butanediol, briefly leading to an equilibrium state of a statistical mixture of the terminal hydroxylated monomers and diol bis(meth)acrylates.[1] The zinc complex also minimized an undesired influence of side reactions such as Michael addition and polymerization in the case of methyl acrylate. We also report that the yield of terminal hydroxylated monomers was maximized on the basis of an in-depth kinetic study based on the Runge-Kutta method curve-fitting analysis using Mathcad software. DFT calculations of the reaction mechanism of methyl acrylate and 1,4-butanediol suggested that the transesterification was preferentially catalyzed by a mononuclear zinc catalyst compared with a dinuclear zinc species, and the activation energy of the first step of the transesterification precisely matched the result of the curve fitting analysis.



1) T. Kato, S. Akebi, H. Nagae, K. Yonehara, T. Oku, K. Mashima, *Catal. Sci. Technol.*, **2021**, *11*, 6975–6986.

アンチモンポルフィセンの合成と配位子還元による触媒的水素発生

（九大院工[1]・九大 CMS[2]）○小出 太郎[1]、張 智[1]、藤岡 太郎[1]、矢野 嘉男[1]、小野 利和[1,2]、久枝 良雄[1,2] (1. 九大院工、2. 九大 CMS)

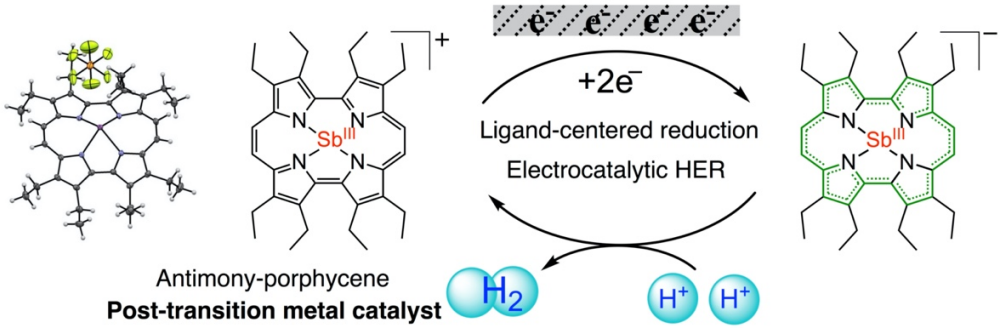
Synthesis of Antimony Porphycene and Catalytic Hydrogen Evolution Driven by Ligand-Centered Reduction

([1]*Graduate School of Engineering, Kyushu University*, [2]*Center for Molecular Systems, Kyushu University*) ○Taro Koide,[1] Zhi Zhang,[1] Taro Fujioka[1], Yoshio Yano[1], Toshikazu Ono[1,2], Yoshio Hisaeda[1,2]

β-Octaethylporphycene antimony(III) complex (**Sb(III)OEPo**) and antimony(V) complex (**Sb(V)OEPo-Br$_2$**) were synthesized and characterized by spectroscopic measurements and single crystal X-ray diffraction analysis. The redox behavior of these complexes was clarified by the Cyclic voltammetry (CV) and electro-spectro measurements. The catalytic reactivity of **Sb(III)OEPo** and **Sb(V)OEPo-Br$_2$** for hydrogen evolution reaction (HER) was demonstrated by the CV and bulk electrolysis under reductive conditions with TFA. The hydrogen production was driven by the ligand-centered reduction of antimony porphycenes, suggesting that the redox feature of the porphycene enables the utilization of main-group element as a central element of the complex and anodically shifted potentials for HER.[1]

Keywords : porphycene, antimony complex, hydrogen evolution, catalyst, redox-active ligand

β-オクタエチルポルフィセンアンチモン(III)錯体（**Sb(III)OEPo**）およびアンチモン(V)錯体（**Sb(V)OEPo-Br$_2$**）を合成し、各種スペクトル測定と単結晶 X 線結晶構造解析によって同定した。サイクリックボルタンメトリー（CV）および電解スペクトル測定から、それら錯体の電気化学挙動を明らかにした。還元条件下、TFA 存在下での水素発生反応（HER）についても検討し、CV およびバルク電解によって、**Sb(III)OEPo** と **Sb(V)OEPo-Br$_2$** が触媒活性を示した。アンチモンポルフィセンの配位子中心還元によって触媒的に水素発生が進行することが示され、ポルフィセンの酸化還元特性を利用することで、中心元素として典型元素を導入した錯体の利用が可能となり、水素発生反応をより正側の電位で行えることが明らかとなった[1]。



1) Z. Zhang, T. Fujioka, T. Koide, Y. Yano, T. Ono, Y. Hisaeda, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2048–2053.

[J402-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryo Ohtani, Koji Oohora

Fri. Mar 25, 2022 1:00 PM - 3:40 PM J402 (Online Meeting)

[J402-3pm-01] Spin crossover and second harmonic generation of cyanido-bridged metal assemblies

○Koji Nakabayashi[1], Shintaro Kawabata[1], Takefumi Kanno[1], Kenta Imoto[1], Stephen Klimke[2], Franz Renz[2], Shin-ichi Ohkoshi[1] （1. The University of Tokyo, 2. Leibniz University Hannover）

1:00 PM - 1:20 PM

[J402-3pm-02] Synthesis of cyanide-bridged metal complex clusters with polar structures

○Junichi Yanagisawa[1], Ryo Ohtani[1], Masaaki Ohba[1] （1. Kyushu Univ.）

1:20 PM - 1:40 PM

[J402-3pm-03] Guest-dependent Magnetic and Structural Variations in a Magnetically-bistable 2-D Hollow-Sheet-type Coordination Polymer

○Haruka Yoshino[1,2], Wataru Kosaka[1], Hitoshi Miyasaka[1], Masaaki Ohba[2] （1. Institute for Materials Research, Tohoku University, 2. Department of Chemistry, Faculty of Science, Kyushu University）

1:40 PM - 2:00 PM

[J402-3pm-04] A pentacyanidonitrosylmetallate-based assembly exhibiting switchable nonlinear optical functionalities

○Kenta Imoto[1], Masaya Komine[1], Marie Yoshikiyo[1], Asuka Namai[1], Shin-ichi Ohkoshi[1] （1. Department of Chemistry, School of Science, The University of Tokyo）

2:00 PM - 2:20 PM

[J402-3pm-05] Reversible Polarity Switching Based on Solvent Ligand Exchange Reaction Triggered by Solvent Vapor

○Fumiya Kobayashi[1], Misato Gemba[1], Makoto Tadokoro[1] （1. Tokyo University of Science）

2:20 PM - 2:40 PM

[J402-3pm-06] Metallo-supramolecular Polymer Synthesis Driven by Data-science

○DINES CHANDRA SANTRA[1], Rizwangul Ibrahim[1], Ritsuko Nagahata[2], Kenji Nagahata[1], Masahiko Demura[1], Masayoshi Higuchi[1] （1. National Institute for Materials Science (NIMS), 2. National Institute of Advanced Industrial Science and Technology (AIST)）

2:40 PM - 3:00 PM

[J402-3pm-07] Low-Valent First-Row Transition Metal Complexes Featuring Vanadocene or Chromocene Bisamide ligands

○Hinano Kusunose[1], Tsubasa Hatanaka[1], Hiroyuki Kawaguchi[2], Yasuhiro Funahashi[1] （1. Osaka Univ., 2. TITech）

3:00 PM - 3:20 PM

[J402-3pm-08] C– H bond amination catalyzed by engineered hemoprotein containing iron porphycene as an artificial cofactor

○Yoshiyuki Kagawa[1], Koji Oohora[1], Takashi Hayashi[1] （1. Osaka Univ.）

3:20 PM - 3:40 PM

Spin crossover and second harmonic generation of cyanido-bridged metal assemblies

([1]*The University of Tokyo*, [2]*Leibniz University Hannover*) ○Koji Nakabayashi,[1] Shintaro Kawabata,[1] Takefumi Kanno,[1] Kenta Imoto,[1] Stephen Klimke,[1] Franz Renz,[2] Shin-ichi Ohkoshi[1]

Keywords: *Magnetic complexes, Spin crossover, Second harmonic generation*

Cyanido-bridged metal assemblies are attractive magnetic compounds for which magnetic properties and functionalities can be designed by elaborate selection of building blocks.[1] In the cyanido-bridged assemblies, spin crossover is a fundamental magnetic property as well as long-range magnetic ordering. Various functional spin crossover systems have been reported since spin crossover was observed at a Prussian blue analogue.[2] Herein, we present spin crossover compounds based on cyanido-bridged Fe-Nb assemblies and their optical properties like second harmonic generation. The chiral and achiral Fe-Nb complexes, $Fe^{II}_2[Nb^{IV}(CN)_8](L)_8 \cdot 6H_2O$ (L = *R*-1-(3-pyridyl)ethanol: ***R*-FeNb**; *S*-1-(3-pyridyl)ethanol: ***S*-FeNb**; *rac*-1-(3-pyridyl)ethanol: ***rac*-FeNb**), were synthesized.[3] All complexes have an identical 3D cyanido-bridged coordination network in which the Fe^{II} site are coordinated to two cyanides and four pyridylethanol molecules (Figure 1a), and show a gradual incomplete spin crossover. For the chiral compounds of ***R*-FeNb** and ***S*-FeNb**, second harmonic generation was observed, and the intensity of the second harmonic (SH) light was modulated by the spin crossover (Figure 1b).

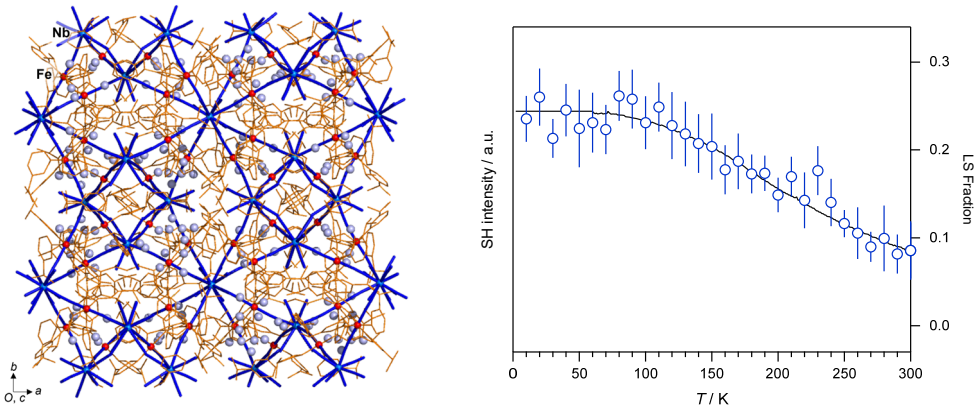


Figure 1. (a) Crystal structure of ***R*-FeNb**, (b) Temperature dependency of the SH light intensity (blue circles) for ***R*-FeNb** with the fraction change of the low spin (LS) state estimated from the magnetic susceptibilities.

1) M. Reczyński, D. Pinkowicz, K. Nakabayashi, C. Näther, J. Stanek, M. Kozieł, J. Kalinowska-Tłuścik, B. Sieklucka, S. Ohkoshi, B. Nowicka, *Angew. Chem. Int. Ed.*, **2021**, *60*, 2330. 2) W. Kosaka, K. Nomura, K. Hashimoto, S. Ohkoshi, *J. Am. Chem. Soc.* **2005**, *127*, 8590. 3) S. Kawabata, K. Nakabayashi, K. Imoto, S. Klimke, F. Renz, S. Ohkoshi, *Dalton Trans.*, **2021**, *50*, 8524.

Synthesis of cyanide-bridged metal complex clusters with polar structures

([1]*Department of Chemistry, Graduate School of Science, Kyushu University*) ○Junichi Yanagisawa,[1] Ryo Ohtani,[1] Masaaki Ohba[1]

Keywords: Polarity; Cyanide-bridged; Phase transition

Cyanide-based organic inorganic hybrid materials (OIHM) have attracted much attention due to their functionalities such as phonon, optical, magnetic and ferroelectric properties.[1] They forms mainly double metal ion type with the general formula of $A_2MM'(CN)_6$, where A = organic cation; M = alkali metal cation and M' = transition metal ion. However, such cyanide-based OIHM have been synthesized by using highly symmetric cyanide metal complex units. In this study, we focused on asymmetric metal complex $[MnN(CN)_4]^{2-}$ for constructing new polar cyanide-anion based OIHM.

Herein, we synthesized $(NEt_4)_{1.75}Rb_{0.25}[MnN(CN)_4]$ (**1**) Single crystal X-ray structural analysis for **1** at 100 K shows that **1** consists of cyanide-bridged tetranuclear clusters by self-clustering of $[MnN(CN)_4]^{2-}$ units (**Fig 1**). The tetranuclear clusters incorporate one Rb cation, thereby they have a unique Janus-type anisotropic structure. The anisotropic clusters arrange same directions in **1** to form polar crystal (Space group: *P*4). In order to investigate the phase transition behavior, we carried out differential scanning calorimetry (DSC) measurement. DSC curves for **1** show several anomalies involving solid-solid phase transition (**Fig 2**). Furthermore, other alkali metal cations such as Na^+, K^+ and Cs^+ have also been used to synthesize the cyanide-based OIHM to investigate their assembled structures.

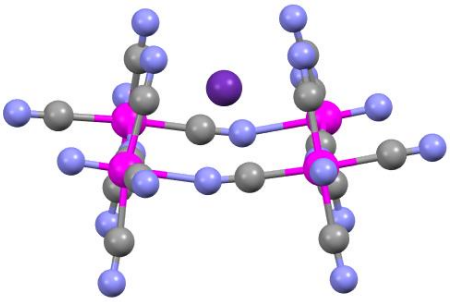


Fig 1. The structure of a polar cluster in **1**

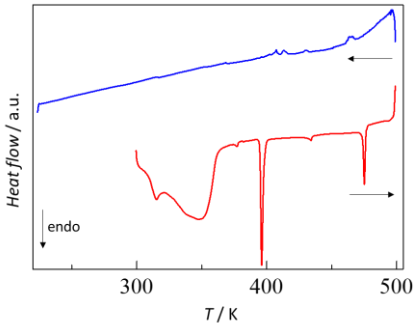


Fig 2. DSC curves of **1**

1) M. Ptak, *et al., Coord. Chem. Rev.* **2021**, *448*, 214180. 2) K. Wieghardt, *et al*., *Inorg. Chem.* **1998**, *37*, 1767-1775.

Guest-dependent Magnetic and Structural Variations in a Magnetically-bistable 2-D Hollow-Sheet-type Coordination Polymer

([1]*Institute for Materials Research, Tohoku University*, [2]*Graduate School of Science, Kyushu University*) ○Haruka Yoshino,[1,2] Wataru Kosaka,[1] Hitoshi Miyasaka,[1] Masaaki Ohba[2]

Keywords: Coordination polymer; Spin crossover; Dimensional structural change; Guest adsorption

Coordination polymers (CPs) and metal-organic frameworks (MOFs) consisting of metal ions and organic ligands are expected to be chemo-responsive materials, interlocking porous functions and physical properties of the framework.

Here, we prepared a novel CP $\{Fe^{II}(pz)(H_2O)_2[Au^{III}(CN)_4]_2 \cdot H_2O\}$ (pz = pyrazine; **FeAu-H$_2$O**), which formed a 1-D chain-type structure based on cyanide-bridged Au-Fe-Au trinuclear units and pz that bridged between the Fe^{II} sites. **FeAu-H$_2$O** exhibited a dimensional structural conversion to 2-D hollow sheet-type structure of $\{Fe^{II}(pz)[Au^{III}(CN)_4]_2\}$ (**FeAu**) with forming additional Au-CN-Fe bridges accompanying elimination of the coordinated H_2O on the Fe site by dehydration treatment (Fig. 1(a), (b)). The reversible structural change between **FeAu-H$_2$O** and **FeAu** was confirmed by *in situ* PXRD, IR and H_2O adsorption measurements. Furthermore, **FeAu-H$_2$O** and **FeAu** exhibited paramagnetic and cooperative spin transition (ST) behavior, respectively. Thus, H_2O molecules adsorbed in the pore work as a significant factor to break Au-CN-Fe bonds, resulting in the reversible magnetic and structural switching between **FeAu-H$_2$O** and **FeAu**.

We also investigated alcohols (R-OH; R = Me, Et) responsivity for **FeAu**. Rietveld analyses of **FeAu-R-OH** revealed that these compounds maintained the 2-D hollow sheet-type structure with rotation of pillar ligand after uptaking alcohols (Fig.1(c)). Correlation between ST behavior and structural changes were discussed based on the results of temperature dependences of *in situ* magnetic and synchrotron PXRD measurements.

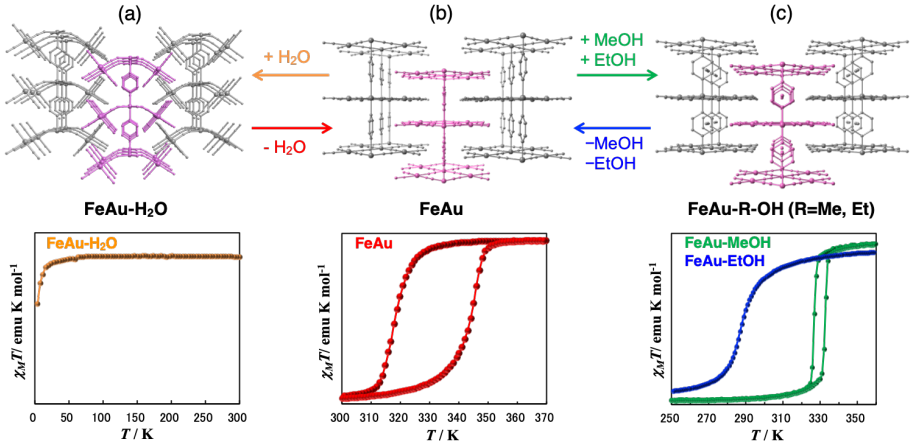


Fig.1 Guest-dependent magnetic and structural change of **FeAu**

A pentacyanidonitrosylmetallate-based assembly exhibiting switchable nonlinear optical functionalities

([1]*Graduate School of Science, The University of Tokyo*) ○Kenta Imoto,[1] Masaya Komine,[1] Marie Yoshikiyo,[1] Asuka Namai,[1] Shin-ichi Ohkoshi[1]

Keywords: nonlinear optical effect; metal assembled complex; optical switching

Noncentrosymmetric materials are extensively studied due to their unique optical properties and we have investigated noncentrosymmetric cyanido-bridged bimetal assemblies with second harmonic generation (SHG).[1,2] In this work, we prepared a Dy-$[Fe(CN)_5(NO)]$ one-dimensional metal assembly, $[Dy(phen)_2(NO_3)(H_2O)][Fe(CN)_5(NO)]\cdot 3H_2O$ (phen = 1,10-phenanthroline), and investigated the crystal structure, physical and nonlinear optical features, and their photoswitching effect.[3]

The target compound was obtained by reacting an aqueous solution of $Na_2[Fe(CN)_5(NO)]$ and $Dy(NO_3)_3$ with a methanolic solution of phen, and possesses an orthorhombic structure with a polar $Pna2_1$ space group composed of a cyanide bridged one dimensional chain structure (Figure 1a). The NO ligands direct along the crystallographic *c*-axis, resulting in spontaneous electric polarization along *c*-axis. The UV-vis spectrum contains metal-to-ligand charge transfer (MLCT) bands from 3d orbitals of Fe to π^* orbitals of NO, and f–f transitions of Dy^{III}. SHG measurements of a single crystal using a femtosecond pulsed laser (wavelength: 1040 nm) showed that the detected 520-nm light intensity is quadratically proportional to the fundamental light power, supporting that the observed signal is due to SHG. The analyzer angle versus SH intensity shows that the output SH light is polarized along the crystallographic *c*-axis direction, and the SH intensity increased 5 times as large as the intensity before irradiation by irradiating 473-nm laser at 100 K. Successive irradiating with 804-nm light reduces the SH intensity. The observed photoswitching of SHG is caused by the photoinduced linkage isomerization of the iron nitrosyl sites, i.e., Fe–NO ↔ Fe–ON, confirmed by the photoirradiation experiment of IR spectrum.

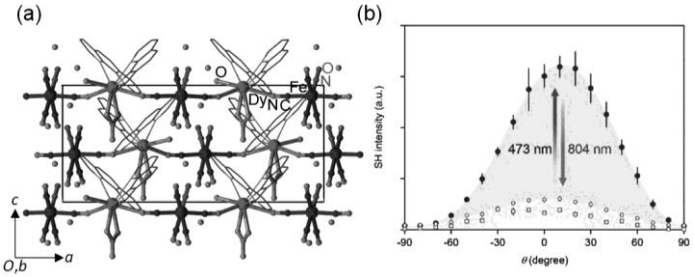


Figure 1. (a) Crystal structure viewed from *b*-axis. (b) The analyzer angle versus SH intensity before irradiation (open circles), after 473-nm irradiation (closed circles), and after 804-nm irradiation (open squares).

1) S. Ohkoshi, K. Nakagawa, K. Imoto, H. Tokoro, Y. Shibata, K. Okamoto, Y. Miyamoto, M. Komine, M. Yoshikiyo, A. Namai, ***Nat. Chem.*** 12, 338 (2020). 2) M. Komine, K. Imoto, Y. Miyamoto, K. Nakabayashi, S. Ohkoshi, ***Eur. J. Inorg. Chem.*** 1367 (2018). 3) M. Komine, K. Imoto, A. Namai, M. Yoshikiyo, S. Ohkoshi, ***Inorg. Chem.*** 60, 2097 (2021).

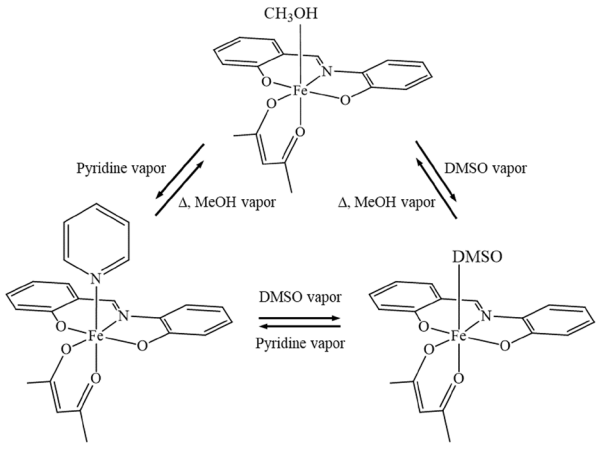
Reversible Polarity Switching Based on Solvent Ligand Exchange Reaction Triggered by Solvent Vapor

(*Department of Chemistry, Faculty of Science, Tokyo University of Science*) ○Fumiya Kobayashi, Misato Gemba, Makoto Tadokoro

Keywords: *Soft Crystal*; *Solvent Vapor*; *Polar*; *Second Harmonic Generation (SHG)*

The development of functional switching molecules that exhibit bistability with respect to ferroelectric, ferromagnetic and spin crossover (SCO) properties have attracted considerable interest for use in new functional devices that include memory devices and sensors. However, reports describing the switching of polarity are extremely limited compared to those describing the switching of magnetic properties. While such a functional switching system induced by absorption/desorption of guest molecules is an attractive candidate for use in the construction of molecular devices, the synthesis of new systems of this type clearly remains challenging.

In the present study, we have focused on investigating mononuclear complexes of type [M(sap)(acac)(sol)] (M = Fe^{III}, Al^{III}; H_2sap = 2-salicylideneaminophenol; acac = acetylacetate) incorporating a substitution-prone coordination site. In this context it is well established that six-coordinated octahedral metal complexes in which a coordination site is occupied by a solvent molecule show a propensity for solvent ligand exchange with a second solvent having a higher coordination ability, giving rise to the prospect that polarity-dependent solvatochromism may occur. Herein, we demonstrated a solvent vapor-induced polarity switching involving mononuclear iron(III) complexes of type [Fe^{III}(sap)(acac)(sol)] (sol = MeOH (**1**), DMSO (**2**), pyridine (**3**)) and aluminum(III) complexes of type [Al^{III}(sap)(acac)(sol)] (sol = MeOH (**4**), EtOH (**5**), DMSO (**6**)): in each of these the coordinated solvent corresponds to a substitution prone coordination site.



1) F. Kobayashi, R. Akiyoshi, D. Kosumi, M. Nakamura, L. F. Lindoy, S. Hayami, *Chem. Commun.*, **2020**, *56*, 10509–10512.

Metallo-Supramolecular Polymer Synthesis Driven by Data-Science

([1] *National Institute for Materials Science,* [2] *National Institute of Advanced Industrial Science and Technology*) ○Dines Chandra Santra[1], Rizwangul Ibrahim[1], Ritsuko Nagahata[2], Kenji Nagahata[1], Masahiko Demura[1], Masayoshi Higuchi[1]

Keywords: coloration efficiency; MSPs; electrochromism; 3D-structure; data-science

Materials informatics has received much attention recently as a powerful tool to develop materials. In general polymer materials are composed of monomers and the selection of the monomers decides the chemical and physical properties of the polymers. In addition, the degree of polymerization is also an important factor to influence the properties of the polymers. If materials informatics is successfully introduced to the polymer design, polymers with desired properties will be synthesized efficiently. In this presentation we report our recent approach on the search of electrochromic (EC) metallo-supramolecular polymers (MSPs) with the help of materials informatics.

MSPs are synthesized by complexation of metal ions and multitopic organic ligands. The obtained polymer chains are composed of successive metal complex moieties, which often have a metal-to-ligand charge-transfer (MLCT) absorption. We revealed the reversible switching of the disappearance/appearance of the MLCT absorption triggered by the electrochemical redox of the metal ions.[1] The EC properties were evaluated from viewpoints of the wavelength of the MLCT absorption and the redox potential, the contrast, the switching speed, and the coloration efficiency (CE) etc. To improve the EC properties, the polymer components should be suitably selected. However, the present research to find better EC polymers is based on our experience and serendipity, because the number of the components is too many to synthesize all the polymers with the combination of the components. To overcome the issue, materials informatics was introduced.

Four components were selected among many components of MSPs such as the metal species, the counter anions, and the ligand structures, and several variations on the chemical structures were chosen regarding each component. Among all the combination of the variations, the selected number of the corresponding MSPs according to an orthogonal table were synthesized. The obtained polymers showed significantly different EC properties and it was found that this method with statistics was useful to find the polymers with better EC properties quickly. The detailed information on the selected components, the structural variations, and the combinations in the polymer synthesis, and the measurement results on the EC properties will be explained in this presentation.

References.

1) M. Higuchi, *J. Mater. Chem. C*, **2014**, 2, 9331 (Feature article).

Low-Valent First-Row Transition Metal Complexes Featuring Vanadocene or Chromocene Bisamide ligands

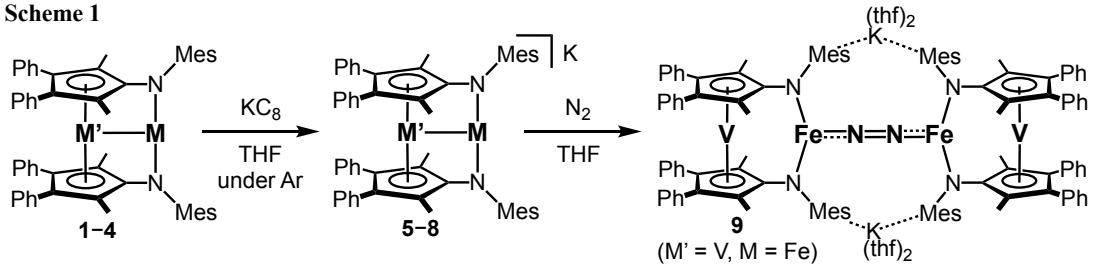
([1]*Graduate School of Science, Osaka University*, [2]*Graduate School of Science, Tokyo Institute of Technology*) ○Hinano Kusunose,[1] Tsubasa Hatanaka,[1] Hiroyuki Kawaguchi,[2] Yasuhiro Funahashi[1]

Keywords: dinitrogen activation; arylamide ligands; metallocene; low-valent complexes

A number of dinitrogen complexes of iron have been thus far prepared while only a few research groups have reported significant N-N bond weakening of dinitrogen moiety. As a representative example, Holland group has achieved reduction of iron *β*-diketiminate complexes to provide dinitrogen complexes with N-N bond lengths of 1.215(6)-1.257(8) Å[1]. To achieve more effective activation of dinitrogen, we employed metallocene bisamide ligands, in which 1) the amide groups make the metal center electron-rich and 2) metallocene units would slightly stabilize a reduced state of the metal center through a metal-metal interaction. We report synthesis and reductions of iron and cobalt complexes derived from 1,1'-bis(arylamide)vanadocene and chromocene ligands. Reduction of the vanadium-iron complex was found to result in formation of a three-coordinate dinitrogen complex, where the N-N bond length lies in the longest category of the reported values[2].

Metallocene bisamide ligands were prepared from the reactions of M'Cl_2 (M' = V, Cr) and N-(cyclopentadienyl)amide. Treatment of the metallocene ligands with MCl_2 (M = Fe, Co) led to the formation of VFe, VCo, CrFe, and CrCo complexes **1**-**4** (Scheme 1). X-ray crystallography showed that the complexes possess short M'-M distances, indicative of bonding interactions between two metal centers. Addition of KC_8 to the complexes **1**-**4** under argon atmosphere was found to provide Fe(I) and Co(I) products **5**-**8**, respectively. Surprisingly, under 1 atm of N_2, the complex **5** was converted to the complex **9**, where two iron centers bind to the molecular dinitrogen in end-on fashion. The N-N bond distance of 1.208(5) Å is considerably elongated, compared to free N_2 (1.098 Å), comparable to the reported values for N=N double bonds.

Scheme 1



[1] P. L. Holland *et al.*, *Inorg. Chem.* **2016**, *55*, 2960-2968; *J. Am. Chem. Soc.* **2006**, *128*, 756-769; *J. Am. Chem. Soc.* **2001**, *123*, 9222-9223.

[2] T. Hatanaka, H. Kusunose, H. Kawaguchi, Y. Funahashi, *Eur. J. Inorg. Chem.* **2020**, 1449-1455.

C–H Bond Amination Catalyzed by Engineered Hemoprotein Containing Iron Porphycene as an Artificial Cofactor

(*Graduate School of Engineering, Osaka University*) ○Yoshiyuki Kagawa, Koji Oohora, Takashi Hayashi

Keywords: Iron Porphycene; Artificial Metalloenzyme; Hemoprotein; C–H Bond Amination; Metal Nitrene Species

Insertion of metal nitrene into a C–H bond is a powerful transformation to directly form a new C–N bond. Recently, artificial metalloenzymes based on hemoproteins have been reported as promising biocatalysts for nitrene transfer reactions.[1] Our group has previously reported C–H bond hydroxylation[2] and olefin cyclopropanation[3] catalyzed by myoglobin reconstituted with metal complexes of porphycene, a constitutional isomer of porphyrin. In this work, we demonstrate myoglobin containing iron porphycene as an artificial cofactor catalyzes C–H bond amination (Fig. 1).

We initially evaluated the intramolecular amination of 2,4,6-triisopropylbenzenesulfonyl azide catalyzed by reconstituted myoglobin with iron porphycene (rMb-FePc), native myoglobin (nMb) and iron porphycene (FePc). rMb-FePc exhibits higher turnover number (TON = 318) compared to nMb (TON = 255) and FePc (TON = 256). Interestingly, rMb-FePc yields the product by C–H bond amination with higher selectivity (96%) against competitive reduction of the azide substrate relative to nMb (80%). In addition, TON by rMb-FePc reached to 5.7 x 10^4 in the presence of a large excess of substrate. Kinetic experiments revealed that k_{cat}/K_m value of rMb-FePc (59 $mM^{-1} \cdot s^{-1}$) is 5-fold higher than that of nMb (12 $mM^{-1} \cdot s^{-1}$). This obvious difference of the k_{cat}/K_m values is derived from the k_{cat} values: k_{cat} of rMb-FePc and nMb are 55 s^{-1} and 14 s^{-1}, respectively. Furthermore, several rMb-FePc mutants were prepared and the catalytic reaction for 2,4,6-triethylbenzenesulfonyl azide was evaluated. The H64A mutant promotes the reaction with TON of 25 with 28%*ee*, whereas rMb-FePc and nMb show lower activities (TON = 6 and 2, respectively) with no enantioselectivity. This work represents that the incorporation of a suitable cofactor into protein matrices will be a useful strategy to develop new biocatalysts. Further investigations using other hemoproteins with FePc toward the C–H bond amination is now in progress.

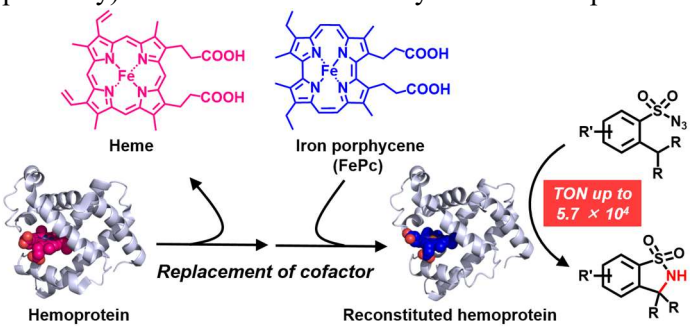


Fig. 1. Catalytic C–H bond amination by reconstituted hemoprotein.

1) a) F. H. Arnold *et al.*, *Nat. Chem.* **2017**, *9*, 629. b) J. F. Hartwig *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 1750. 2) K. Oohora, T. Hayashi *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 17282. 3) K. Oohora, T. Hayashi *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 18460.

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

[D202-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takuya Kochi, Koji Kubota

Fri. Mar 25, 2022 1:00 PM - 3:40 PM D202 (Online Meeting)

[D202-3pm-01] Palladium-Catalyzed Remote Arylative Substitution of Various Terminal Alkenes

○Kazuma Muto[1], Fumitoshi Kakiuchi[1], Takuya Kochi[1] (1. Keio University)

1:00 PM - 1:20 PM

[D202-3pm-02] Photoinduced Copper-Catalyzed Asymmetric Acylation of Allylic Phosphates with Acylsilanes

○Yusuke Ueda[1], Yusuke Masuda[1,2], Tomohiro Iwai[4], Imaeda Keisuke[1], Takeuchi Hiroki[1], Ueno Kosei[1], Min Gao[3], Jun-ya Hasegawa[3,2], Masaya Sawamura[1,2] (1. Hokkaido Universuty Faculty of Science, 2. WPI-ICReDD, 3. Hokkaido Universuty Institute for Catalysis, 4. The University of Tokyo,Graduate School of Art and Sciences)

1:20 PM - 1:40 PM

[D202-3pm-03] Quantum Chemical Study of Asymmetric Propargylic Substitution Reactions Catalyzed by Optically Active Thiolate-Bridged Diruthenium Complexes

○Ken Sakata[1], Yui Goto[1], Takeshi Yoshikawa[1], Yoshiaki Nishibayashi[2] (1. Toho University, 2. University of Tokyo)

1:40 PM - 2:00 PM

[D202-3pm-04] Palladium-Catalyzed Remote Diborylative Cyclization of Various 1,n-Dienes with Diborons

○Shota Kanno[1], Kakiuchi Fumitoshi[1], Kochi Takuya[1] (1. Faculty of Science and Technology, Keio University)

2:00 PM - 2:20 PM

[D202-3pm-05] Hydroxycarbonylation of alkenes using formic acid catalyzed by rhodium (III) hydride diiodide complex without using any additives

○Masaki Okada[1,2,3,4], Katsuhiko Takeuchi[1], Kazuhiro Matsumoto[1], Tomoharu Oku[4], Choi Jun-Chul[1,2] (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba, 3. Research Association of High-Throughput Design and Development for Advanced Functional Materials, 4. NIPPON SHOKUBAI CO., LTD.)

2:20 PM - 2:40 PM

[D202-3pm-06] Palladium-Catalyzed C-H Arylation of Benzophospholes

○Shibo Xu[1], Kazutoshi Nishimura[1], Koji Hirano[1], Masahiro Miura[1] (1. Osaka University)

2:40 PM - 3:00 PM

[D202-3pm-07] Development of new ligands for mechanochemical cross-coupling reactions

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

3:00 PM - 3:20 PM

[D202-3pm-08] Auto-tandem copper catalysed carboxylation of undirected alkenyl C– H bonds with CO_2

○HAREKRISHNA SAHOO[1], Liang Zhang[1], Zhaomin Hou[1] （1. RIKEN）

3:20 PM - 3:40 PM

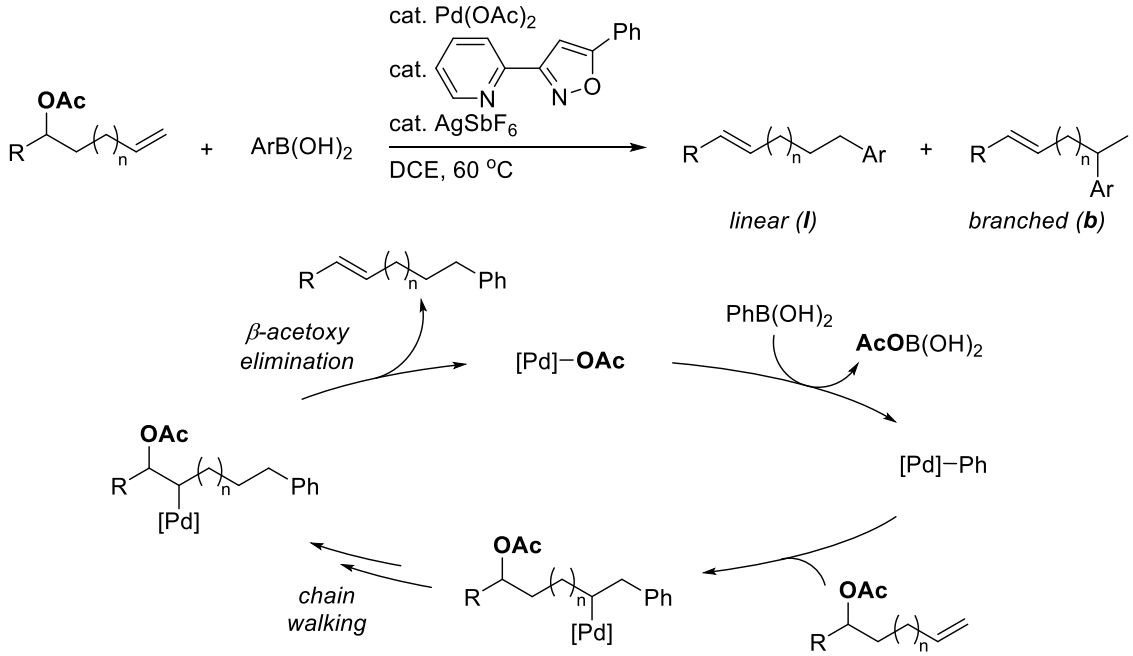
Palladium-Catalyzed Remote Arylative Substitution of Various Terminal Alkenes

(*Faculty of Science and Technology, Keio University*) ○Kazuma Muto, Fumitoshi Kakiuchi, Takuya Kochi

Keywords: Palladium Catalyst, Remote Substitution, Chain Walking, Arylation

While catalytic allylic substitution has become one of the most powerful classes of transition-metal-catalyzed reactions, the corresponding remote substitution has rarely been explored. In this context, we envisioned that the incorporation of a chain-walking process into catalytic cycles of allylic substitution reactions would realize the remote substitution reactions.[1] Here we report a palladium-catalyzed remote arylative substitution of alkenes bearing a distant acetoxy group via chain walking and β-acetoxy elimination.[2]

The reaction of a terminal alkene having a remote acetoxy group with phenylboronic acid using a 1,10-phenanthroline palladium catalyst provided the remote arylation product with ca. 2:1 regioselectivity. Ligand screening was then conducted to improve the linear/branched regioisomer ratio, and a pyridine-isoxazole ligand was found to give the product with ca. 4:1 regioselectivity. The reaction is applicable to various terminal alkenes having a distant acetoxy group containing 1 to 7 methylenes and arylboronic acids possessing a variety of functional groups. The remote arylative substitution is considered to proceed via transmetalation between an acetoxypalladium species with arylboronic acid, alkene insertion, chain walking, and β-acetoxy elimination.



(1) Ohmiya, H.; Makida, Y.; Tanaka, T.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 17276-17277.
(2) Muto, K.; Kumagai, T.; Kakiuchi, F.; Kochi, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 24500-24504.

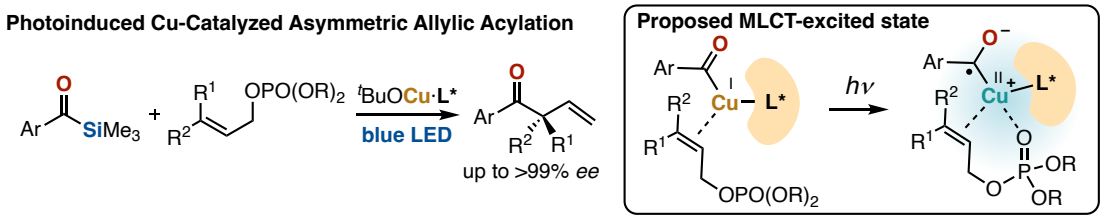
Photoinduced Copper-Catalyzed Asymmetric Acylation of Allylic Phosphates with Acylsilanes

(1. Hokkaido University Faculty of Science, 2. WPI-ICReDD, 3. Hokkaido University Institute for Catalysis, 4. The University of Tokyo, Graduate School of Art and Sciences)
○Yusuke Ueda[1], Yusuke Masuda[1,2], Tomohiro Iwai[4], Imaeda Keisuke[1], Takeuchi Hiroki[1], Ueno Kosei[1], Min Gao[3], Jun-ya Hasegawa[3,2], Masaya Sawamura[1,2]

Keywords: *Acylation, Asymmetric Synthesis, Copper Catalyst, Photoinduced reaction, MLCT*

Photoinduced catalysis enables novel molecular transformations for organic synthesis complementary to thermal catalytic reactions. In particular, photoinduced transition-metal-catalyzed reactions in which the metal plays a dual role as a photoabsorbent and a center for chemical bond cleavage/formation are distinct from the more broadly investigated reactions with external photoredox catalysts, offering advantages of simplicity of the reaction system and cost-effectiveness by avoiding the use of expensive external substances.[1] In addition, the better reaction control by metal-bound ligands is an attractive feature of this methodology as evidenced by the growing number of reports in this regard, some of which detail highly enantioselective reactions by the use of chiral ligands.[2]

Here, we report a visible-light-induced copper-catalyzed highly enantioselective umpolung allylic acylation reaction with acylsilanes as acyl anion equivalents.[3] Triplet-quenching experiments and DFT calculations suggested the reaction mechanism involving copper-to-acyl metal-to-ligand charge transfer (MLCT) photoexcitation that generates a charge-separated triplet state as a highly reactive intermediate. According to the calculations, the allylic phosphate substrate in the excited state undergoes novel molecular activation into an allylic radical weakly bound to the copper complex. The allyl radical fragment undergoes copper mediated regio- and stereocontrolled coupling with the acyl group under the influence of the chiral N-heterocyclic carbene ligand.



1) (a) Parasram, M.; Gevorgyan, V. *Chem. Soc. Rev*. **2017**, *46*, 6227−6240. (b) Hossain, A.; Bhattacharyya, A.; Reiser, O. *Science* **2019**, *364*, eaav9713. (c) Cheng, W.-M.; Shang, R. *ACS Catal.* **2020**, *10*, 9170−9196.
2) (a) Lipp, A.; Badir, S. O.; Molander, G. A. *Angew. Chem., Int. Ed*. **2021**, *60*, 1714−1726. (b) Genzink, M. J.; Kidd, J. B.; Swords, W. B.; Yoon, T. P. *Chem. Rev.* **2021**, DOI: 10.1021/acs.chemrev.1c00467.
3) Ueda, Y.; Masuda, Y.; Iwai, T.; Imaeda, K.; Takeuchi, H.; Ueno, K.; Gao, M.; Hasegawa, J.; Sawamura, M. *J. Am. Chem. Soc.* **2022**, *in press.* DOI: 10.1021/jacs.1c11526

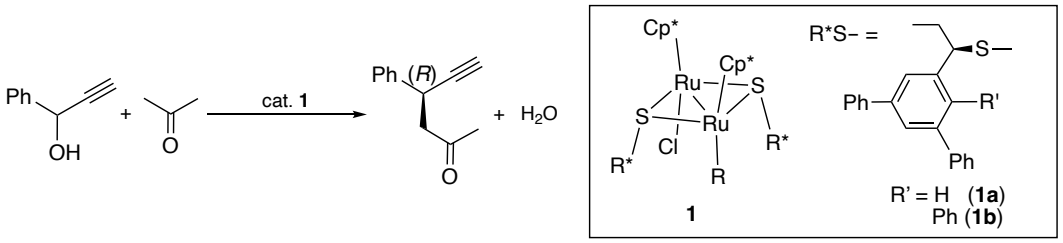
光学活性硫黄架橋二核ルテニウム触媒を用いた不斉プロパルギル位置換反応に関する量子化学的研究

（東邦大薬[1]・東大院工[2]）○坂田 健[1]・後藤 優衣[1]・吉川 武司[1]・西林 仁昭[2]
Quantum Chemical Study of Asymmetric Propargylic Substitution Reactions Catalyzed by Optically Active Thiolate-Bridged Diruthenium Complexes ([1]*Faculty of Pharmaceutical Sciences, Toho University*, [2]*Graduate School of Engineering, The University of Tokyo*) ○Ken Sakata,[1] Yui Goto,[1] Takeshi Yoshikawa,[1] Yoshiaki Nishibayashi[2]

The enantioselectivity in the propargylic substitution reactions of propargylic alcohols with acetone catalyzed by optically active thiolate-bridged diruthenium complexes was examined by using ωB97D-X level DFT calculations. Among the transition-state structures with lower energies, the number of structures leading to the major (*R*) product was found to be larger than that of structures leading to the minor (*S*) product, providing enantioselectivity in terms of probability distributions.
Keywords : DFT calculations; Asymmetric Propargylic Substitution Reactions; Diruthenium Complex

西林らは, 架橋硫黄上に光学活性な配位子を導入した硫黄架橋二核ルテニウム錯体を触媒として用いることで，プロパルギル位置換反応の不斉化に成功している [1]。そこで本研究では，光学活性硫黄架橋二核ルテニウム錯体 (**1**) を触媒として用いたプロパルギルアルコールとアセトンの不斉プロパルギル位アルキル化反応 [2] に注目し, 不斉発現のメカニズムに関して量子化学計算による検討をおこなった (**Scheme 1**)。先行研究 [3] に基づき，プロパルギルアルコールと **1a** から中間体として生成するアレニリデン錯体に対してエノールが求核攻撃する過程における様々な遷移状態構造を ωB97X-D レベルの DFT 計算によって探索した。プロパルギル位炭素原子の絶対配置が *R* の主生成物に至る遷移状態構造を 28 種類，および絶対配置が *S* の生成物に至る遷移状態構造 28 種類の計 56 個の遷移状態構造を見出した。それぞれの構造に対して得られたボルツマン分布をもとに，エナンチオマー過剰率は 27 % ee と見積もられた。得られた結果は，実験結果 (43 % ee) をよく再現していることがわかった。

Scheme 1



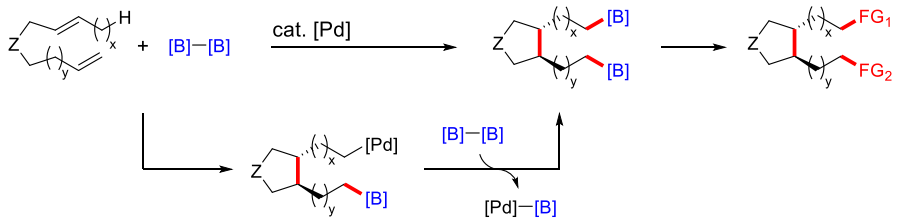
1) Nishibayashi, Y. *Chem. Lett.* **2021**, *50*, 1282−1288.
2) Inada, Y.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7715−7717.
3) Sakata, K.; Miyake, Y.; Nishibayashi, Y. *Chem. Asian J.* **2009**, *4*, 81−88.
4) Sakata, K.; Goto, Y.; Yoshikawa, T.; Nishibayashi, Y. *Chem. Asian J.* **2021**, *16*, 3760−3766.

Palladium-Catalyzed Remote Diborylative Cyclization of Various 1,n-Dienes with Diborons

(*Faculty of Science and Technology, Keio University*) ○Shota Kanno, Fumitoshi Kakiuchi, Takuya Kochi

Keywords: Palladium Catalyst; Chain Walking; Remote Functionalization; Borylation; Cyclization

Remote functionalization of alkenes has attracted growing interest because it allows for transformations at the positions which are difficult to functionalize selectively.[1] However, the examples of catalytic reactions of alkene substrates to form bonds at positions remote from each other, namely remote difunctionalization, are still limited.[2] Previously, we achieved intramolecular remote difunctionalization for a palladium-catalyzed hydrosilylation/cyclization of 1,n-dienes by using chain walking.[3] In the course of the study, we recently found a reaction of 1,n-dienes with diborons to furnish five-membered carbocycles as well as two carbon-boron bonds which are distant from each other as the first example of remote bismetalation of alkene substrates by addition of dimetal reagents. Here we report the detail of the reaction development, as well as its application and the mechanistic studies.[4] A variety of dienes and diborons can be used to form cyclopentane derivatives with two boryl groups at remote positions. Especially, the reaction of 1,n-dienes ($n \geq 7$) achieved the catalytic formation of three distant bonds between non-hydrogen atoms in one sequence for the first time. By transforming boron functional groups, we also achieved formal remote difunctionalizations that have not been reported so far. Furthermore, mechanistic studies revealed that the reaction is considered to proceed via regioselective conversion of an unactivated sp^3 C–H bond to a C–B bond by a rare process, formal σ-bond metathesis between a C–Pd and B–B bonds.



(1) A review: H. Sommer, F. Juliá-Hernández, R. Martin, I, Marek. *ACS Cent. Sci*. **2018**, *4*, 153.
(2) Selected examples: (a) R. C. Larock, Y. D. Lu, A. C. Bain, C. E. Russell, *J. Org. Chem*. **1991**, *56*, 4589. (b) W, Li, J. K. Boon, Y. Zhao, *Chem. Sci*. **2018**, *9*, 600. (c) P. Yu, J.-S. Lin, L. Li, S.-C. Zheng, Y.-P. Xiong, L.-J. Zhao, B. Tan, X.-Y. Liu, *Angew. Chem., Int. Ed*. **2014**, *53*, 11890.
(3) T. Kochi, K. Ichinose, M. Shigekane, T. Hamasaki, F. Kakiuchi, *Angew. Chem. Int. Ed*. **2019**, *58*, 5261.
(4) S. Kanno F. Kakiuchi, T. Kochi, *J. Am. Chem. Soc*. **2021**, *143*, 19275.

ロジウム(III)ヒドリドジヨージド錯体を触媒とした添加剤不要なギ酸によるアルケンのヒドロキシカルボニル化反応

（産総研[1]・筑波大[2]・ADMAT[3]・日本触媒[4]）○岡田 雅希[1,2,3,4]・竹内 勝彦[1]・松本 和弘[1]・奥 智治[4]・崔 準哲[1,2]

Hydroxycarbonylation of alkenes using formic acid catalyzed by Rhodium (III) hydride diiodide complex without using any additives ([1]*AIST* [2]*University of Tsukuba,* [3]ADMAT, [4]*Nippon Shokubai*) ○ Masaki Okada,[1,2,3,4] Katsuhiko Takeuchi,[1] Kazuhiro Matsumoto,[1] Tomoharu Oku,[4] Jun-Chul Choi[1,2]

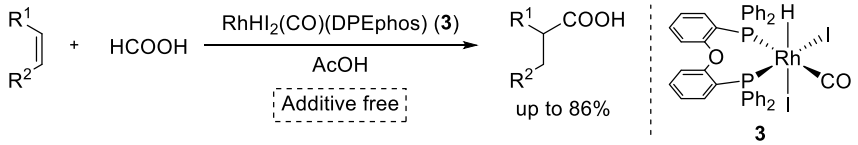
The hydroxycarbonylation of alkenes with formic acid is one of the ideal methods for the synthesis of carboxylic acids with 100% atomic efficiency. Although reaction systems using Rh(I) complex catalysts have been reported, the use of methyl iodide and excess amounts of phosphine ligands as additives has been a problem. In this study, we report the development of an environmentally friendly reaction system using new Rh(III) hydride diiodide complexes, $RhHI_2(CO)(PPh_3)_2$ (**2**) and $RhHI_2(CO)$(DPEphos) (**3**), which achieve high selectivity and high yields without the need for any additives.

Keywords : Hydroxycarbonylation; Carboxylic Acids; Formic Acid; Rhodium; Bidentate Phosphine Ligands

ギ酸を使用したアルケンのヒドロキシカルボニル化は原子効率が 100%の理想的なカルボン酸合成法の一つである。これまで Rh(I)錯体を触媒とした反応が報告されていたが、添加剤として CH_3I や過剰量の PPh_3 が必要な点が課題であった [1,2]。本研究では、新たに合成した Rh(III)ヒドリドジヨージド錯体を用いることで、添加剤不要かつ高収率・高選択的な環境調和性に優れた反応系を開発したことを報告する [3]。

まず、既報の反応を参考に Rh(I)錯体および添加剤の検討を行ったところ、Rh(I)ヨード錯体 $RhI(CO)(PPh_3)_2$ (**1**)に添加剤として Me_4NI と *p*-TsOH·H_2O を加えた反応系が有効であることを見出した。そして、錯体 **1** に Me_4NI および *p*-TsOH·H_2O を作用させることで、Rh(III)ヒドリドジヨージド錯体 $RhHI_2(CO)(PPh_3)_2$ (**2**)が反応中間体として生成することを見出した。さらに、別途合成した **2** を触媒とすることで、添加剤を用いないギ酸によるアルケンのヒドロキシカルボニル化を実現した。最後に配位子の探索を行った結果、二座ホスフィン配位子の DPEphos を有する $RhHI_2(CO)$(DPEphos) (**3**)が本反応に最も高い活性を示すことを明らかにした。

謝辞 : 本成果は国立研究開発法人新エネルギー・産業技術総合開発機構(NEDO) の委託業務(JPNP16010)で得られた成果です。



1) J.-P. Simonato, *J. Mol. Catal. A Chem.*, **2003**, *197*, 61.
2) T. Oku, M. Okada, M. Puripat, M. Hatanaka, K. Morokuma, J.-C. Choi, *J. CO_2 Util.* **2018**, *25*, 1.
3) M. Okada, K. Takeuchi, K. Matsumoto, T. Oku, J.-C. Choi, *Org. Biomol. Chem.* **2021**, *19*, 8727.

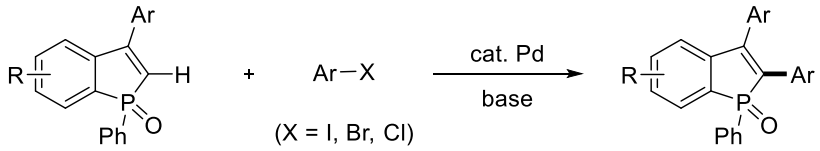
Palladium-Catalyzed C-H Arylation of Benzophospholes

(*[1]Institute for Open and Transdisciplinary Research Initiatives, Osaka University*, *[2]Graduate School of Engineering, Osaka University)* ○XU, Shibo;[1] NISHIMURA, Kazutoshi;[2] HIRANO, Koji;[2] MIURA, Masahiro[1]

Keywords: Palladium Catalysts; Benzophospholes; C-H Arylation; Arylated Benzophospholes

Due to its better step and atom economy, transition-metal-promoted C-H functionalization has been an incredible strategy in the conversion of simple starting materials to the diverse and value-added molecules. Among them, the direct and regioselective C-H transformation of five-membered heterocycles has received particular attention in the formation of aryl-heteroaryl linkages, which are ubiquitous in pharmaceuticals and functional organic materials.[1] As identically important structure motifs, benzophosphole derivatives[2] have been explored in their synthetic approaches,[3] however, the C-H functionalization of such critical skeleton has been untapped over the past 40 years, to the best of our knowledge.

Herein, we report the first example of Pd-catalyzed regioselective C2-H arylation of benzophospholes with aryl halides. This protocol provides a concise and complementary access to the arylated benzophospholes. The starting benzophospholes could be readily prepared from 1,1-diarylethylenes and phenylphosphinic acid via our previously developed phosphenium dication-based strategy.[4] Additionally, the reaction features the broad scope of aryl halides, thus enabling the flexible installation of various electron-donor groups at the C2 position. Moreover, the consecutive C-C coupling of benzophosphole with dihaloarenes is also possible to furnish the highly π-conjugated framework of great interest in material chemistry. Investigation of luminescence properties of the obtained products will also be included in this presentation.



1) a) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200. b) Stepek, I. A.; Itami, K. *ACS Materials Lett.* **2020**, *2*, 951. c) Li, B.; Ali, A. I.M.; Ge, H. *Chem.* **2020**, *6*, 2591. d) Huang, H.-Y.; Benzai, A.; Shi, X.; Doucet, H. *Chem. Rec.* **2021**, *21*, 343.

2) Yamaguchi, S.; Fukazawa, A.; Taki, M. *Yuki Gosei Kagaku Kyokaishi* **2017**, *75*, 1179.

3) a) Unoh, Y.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 12975. b) Chen, Y.; Duan, W. *J. Am. Chem. Soc.* **2013**, *135*, 16754. c) Nishimura, K.; Unoh, Y.; Hirano, K.; Miura M. *Chem. Eur. J.* **2018**, *24*, 13089.

4) Nishimura, K.; Hirano, K.; Miura. M. *Org. Lett.* **2020**, *22*, 3185.

メカノケミカルクロスカップリング反応において高活性を示す新規配位子の開発

（北海道大学大学院工学研究院[1]・北海道大学 WPI-ICReDD[2]）
○瀬尾 珠恵[1]・久保田 浩司[1,2]・伊藤 肇[1,2]

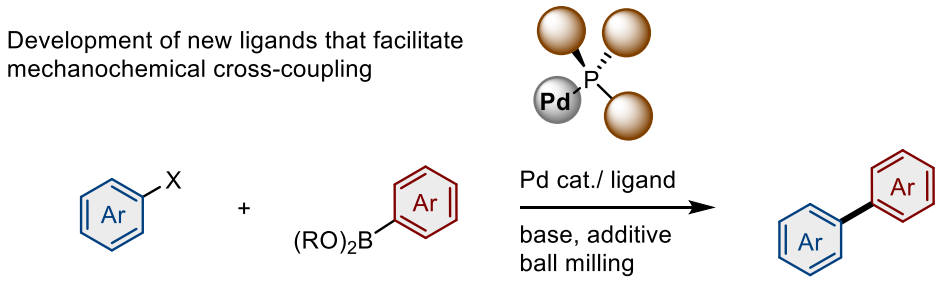
Development of new ligands for mechanochemical cross-coupling reactions

([1]*Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*)
○Tamae Seo,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Solvent-less mechanochemical cross-coupling reactions catalyzed by palladium have provided a solution to the many issues associated with conventional solution-based conditions.[1-4] Currently, palladium-based catalysts, which were originally developed for solution-based reactions, have been diverted to mechanochemical conditions. To further improve the efficiency and generality of mechanochemical cross-coupling, the development of a new ligand specifically designed for mechanochemical conditions is highly desired. In this study, we discovered new air-stable and easily prepared phosphine ligands that facilitate the mechanochemical Suzuki-Miyaura cross-coupling of poorly soluble polyaromatic halides with arylboronic acids at near room temperature. These new ligands realized significantly better efficiency than that of conventional privileged ligands for cross-coupling reactions.

Keywords : Mechanochemistry; Suzuki-Miyaura Cross-Coupling; Ball Mill; Palladium; Phosphine Ligand

パラジウム触媒を用いたメカノケミカルクロスカップリング反応は、従来の溶媒を用いる溶液系の様々な合成的課題を解決する新しい手法として注目されている[1-4]。現状、溶液系を志向して開発されたパラジウム触媒用の配位子を流用している形となっているが、更なる活性向上のためにボールミル条件に特化した配位子の開発が求められている。本研究では、空気下で取り扱いのでき容易に合成可能な新規ホスフィン配位子が、メカノケミカル鈴木-宮浦クロスカップリング反応において高活性を示すことを見出した。この配位子は、従来の溶液系クロスカップリング反応に用いられている配位子よりも非常に高い活性を示した。

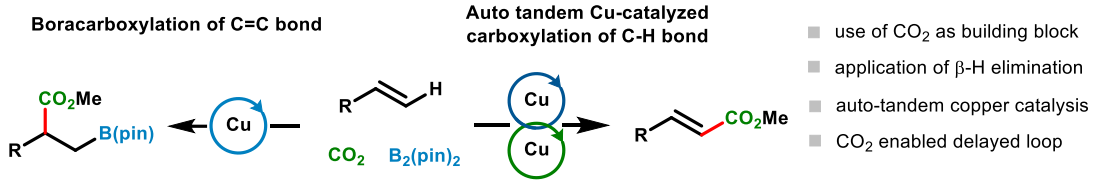


1) Seo, T.; Toyoshima, N.; Kubota, K.; Ito, H. *J. Am. Chem. Soc.* **2021**, *143*, 6165.
2) Takahashi, R.; Seo, T.; Kubota, K.; Ito, H. *ACS Catal.* **2021**, *11*, 14803.
3) Seo, T.; Kubota, K.; Ito, H. *J. Am. Chem. Soc.* **2020**, *142*, 9884.
4) Seo, T.; Ishiyama, T.; Kubota, K.; Ito, H. *Chem. Soc.* **2019**, *10*, 8202.

Auto-tandem copper-catalysed carboxylation of undirected alkenyl C–H bonds with CO_2

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science,* [2]*Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research*)
○ Harekrishna Sahoo,[1] Liang Zhang,[1,2] and Zhaomin Hou[1,2]
Keywords: Auto-tandem catalysis, β-hydride elimination, CO_2 delay loop, Copper, Carboxylation

Development of new catalytic reactions enabling control of the selectivities of chemical processes for the divergent synthesis of value-added compounds lies at the heart of modern organometallic chemistry and catalysis. *β*-Hydride elimination is one of the most fundamental reactions in organometallic chemistry. However, the incorporation of a *β*-hydride elimination process into productive *auto-tandem catalysis* is highly challenging because of the instability of the in-situ generated metal hydride species, which often results in catalyst deactivation. The development of a straightforward approach to overcome this problem is of utmost importance because it will greatly extend the potential of *β*-hydride elimination in organometallic catalysis and synthetic applications. Carbon dioxide (CO_2) is an attractive one-carbon (C1) building block for the assembly of important chemicals because it is abundant, readily available, cheap, and renewable. Our group has been working on CO_2 fixation with a wide range of organic substrates using copper catalysts.[1] In this presentation, we would like to present an auto-tandem copper-catalyzed carboxylation of undirected alkenyl C–H bonds with CO_2. This unprecedented transformation has been achieved through the *β*-hydride elimination of an alkyl copper species to give a copper hydride, which then undergoes a delayed loop with insertion of CO_2 to form an active catalyst to promote two mechanistically distinct catalytic cycles. On the other hand, by suppressing the *β*-hydride elimination process, the boracarboxylation of the alkene C=C unit has been exclusively achieved.



1) a) Zhang, L.; Hou, Z. *Chem. Sci*. **2013**, *4*, 3395. b) Li, Z.; Zhang, L. Nishiura, M.; Luo, G.; Luo, Y.; Hou, Z. *J. Am. Chem. Soc*. **2020**, *142*, 1966. c) Carry, B.; Zhang, L.; Nishiura, M.; Hou, Z. *Angew. Chem. Int. Ed*. **2016**, *55*, 6257. d) Zhang, L.; Cheng, J.; Carry, B.; Hou, Z. *J. Am. Chem. Soc*. **2012**, *134*, 14314. e) Ohishi, T.; Zhang, L.; Nishiura, M.; Hou, Z. *Angew. Chem. Int. Ed*. **2011**, *50*, 8114. f) Zhang, L.; Cheng, J.; Ohishi, T.; Hou, Z. *Angew. Chem. Int. Ed*. **2010**, *49*, 8670. g) Ohishi, T.; Nishiura, M.; Hou, Z. *Angew. Chem. Int. Ed*. **2008**, *47*, 5792.

[D203-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kosuke Higashida, Yasunori Minami

Fri. Mar 25, 2022 1:20 PM - 3:40 PM D203 (Online Meeting)

[D203-3pm-01] A Boron-Transfer Mechanism Mediating the Thermally Induced Revival of Frustrated Carbene– Borane Pairs from their Shelf-Stable Adducts

○Mahiro Sakuraba[1], Yoichi Hoshimoto[1], Jyunya Hasegawa[2], Sensuke Ogoshi[1] （1. Graduate School of Engineering, Osaka Univ. , 2. Institute for Catalysis, Hokkaido Univ.）

1:20 PM - 1:40 PM

[D203-3pm-02] Regiodivergent and Stereoselective Intermolecular [2+2] Cycloaddition of Amino-functionalized Alkenes and Allenes by Rare-Earth Catalysts

○Wenxuan Xu[1,2], Xuefeng Cong[1], Kun An[1], Shaojie Lou[1], Zhenghua Li[1], Masayoshi Nishiura[1], Tetsuro Murahashi[2], Zhaomin Hou[1,2] （1. RIKEN, 2. Tokyo Institute of Technology）

1:40 PM - 2:00 PM

[D203-3pm-03] Advancement of a cooling system for solution XAS experiment and in situ local structure analysis of boryl copper species by XAS measurements

○Yuta Uetake[1,2], Yu Ozawa[3], Kazuki Matsumoto[4], Tetsuo Honma[5], Koji Kubota[3,6], Hajime Ito[3,6] （1. Grad. Sch. Eng., Osaka Univ., 2. ICS-OTRI, Osaka Univ., 3. Grad. Sch. Eng., Hokkaido Univ., 4. DFC Co., Ltd., 5. JASRI, 6. WPI-ICReDD, Hokkaido Univ.）

2:00 PM - 2:20 PM

[D203-3pm-04] Nucleophilic Addition of Carboxylic Acids and Phenols toward Non-activated Alkynes Catalyzed by Gold-Zinc Bimetallic Complexes Including Imidazo[1,5-*a*]pyridine-3-ylidene Ligands

○Vishal Kumar Rawat[2], Kosuke Higashida[1,2], Masaya Sawamura[1,2] （1. WPI-ICReDD, Hokkaido University, 2. Faculty of Science, Hokkaido University）

2:20 PM - 2:40 PM

[D203-3pm-05] Regio- and Diastereoselective [3 + 2] Annulation of Aliphatic Aldimines with Alkenes via beta-C(sp3)– H Activation by Scandium Catalysts

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

2:40 PM - 3:00 PM

[D203-3pm-06] Chromium-catalyzed *syn*-Stereoselective Ring-opening Arylation of 7-Oxabenzonorbornadienes

○Kohei Nishi[1], Hayato Tsurugi[1], Kazushi Mashima[1] （1. Osaka Univ.）

3:00 PM - 3:20 PM

[D203-3pm-07] Yttrium-Catalyzed Reagioselective Alumination and Subsequent Functionalization of Benzylic C– H Bonds of 2-Alkylpyridines

○Masanori Takimoto[1,2], Masayoshi Nishiura[1,2], Zhaomin Hou[1,2] （1. RIKEN CPR, 2. RIKEN CSRS）

3:20 PM - 3:40 PM

A Boron-Transfer Mechanism Mediating the Thermally Induced Revival of Frustrated Carbene–Borane Pairs from their Shelf-Stable Adducts

([1]*Department of Applied Chemistry, Faculty of Engineering, Osaka University*; [2]*Institute for Catalysis, Hokkaido University*) ○ Mahiro Sakuraba,[1] Yoichi Hoshimoto,[1] Jun-ya Hasegawa,[2] Sensuke Ogoshi[1]

Keywords: Frustrated Lewis Pairs; H_2 Activation; Carbene; Triaryl Borane

Recent developments on chemistry of frustrated Lewis pairs (FLPs) are noteworthy, as illustrated by the heterolytic cleavage of H_2 mediated by the main-group elements.[1)] In 2015, we demonstrated a strategy to generate FLPs from shelf-stable classical Lewis adducts (CLAs) comprising *N*-phosphine-oxide-substituted imidazolylidenes (PoxIms) and $B(C_6F_5)_3$;[2)] however, the revival mechanism was not fully clarified. Herein, we report the reaction mechanism on this revival process based on a combination of experimental and theoretical studies.[3)]

Treatment of CLA **1** with H_2 resulted in the formation of **4** via the regeneration of FLP species (Figure 1). A transfer of the borane moiety from the carbene carbon atom to the *N*-phosphinoyl oxygen atom (from **1** to **2**) was identified as a key step for the heterolytic cleavage of H_2 by the regenerated FLP species. The molecular structure of **3** including the *N*-phosphinoyl oxygen−boron bond was confirmed by the single-crystal X-ray diffraction analysis. The mechanism showed in Figure 1 was also supported by kinetics and DFT studies.

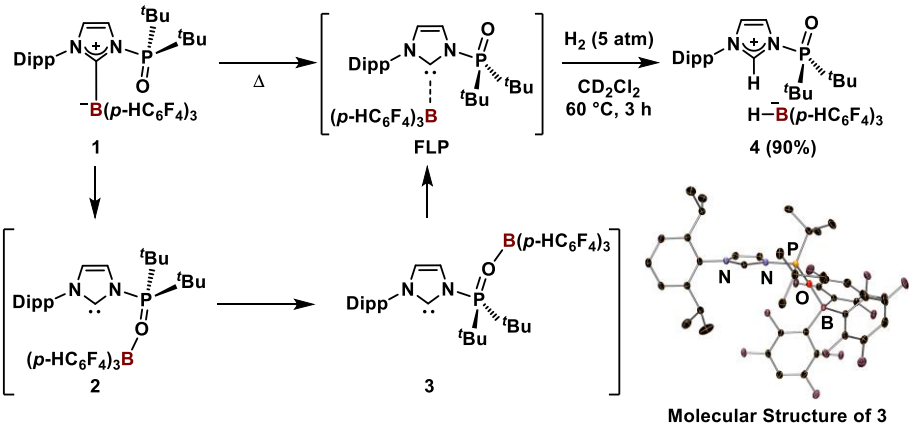


Figure 1. Revival of FLP from **1** and its reaction with H_2.

1) A. R. Jupp, D. W. Stephan, *Trends Chem.* **2019**, *1*, 35. 2) Y. Hoshimoto, T. Kinoshita, M. Ohashi, S. Ogoshi, *Angew. Chem. Int. Ed.* **2015**, *54*, 11666. 3) Y. Hoshimoto, M. Sakuraba, T. Kinoshita, M. Ohbo, M. Ratanasak, J. Hasegawa, S. Ogoshi, *Commun. Chem.* **2021**, *4*, 137.

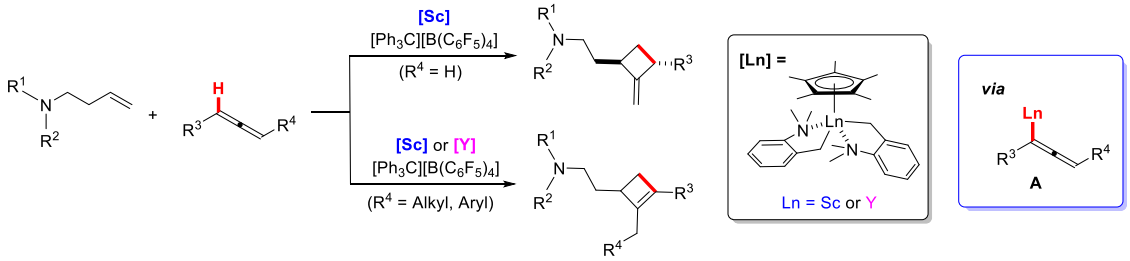
Regiodivergent and Stereoselective Intermolecular [2 + 2] Cycloaddition of Amino-functionalized Alkenes and Allenes by Rare-Earth Catalysts

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science*, [2]*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*)○ Wenxuan Xu[1,2], Xuefeng Cong[1], Kun An[1], Shaojie Lou[1], Zhenghua Li[1], Masayoshi Nishiura[1], Tetsuro Murahashi[1,2], Zhaomin Hou[1,2]

Keywords: alkenes; allenes; rare-earth catalysts; cycloaddition; C−H activation

The catalytic [2 + 2] cycloaddition of allenes and alkenes is, in principle, the most atom-efficient and straightforward route for the construction of cyclobutane or cyclobutene skeletons, which are important structural motifs in many natural products and bioactive compounds as well as useful building blocks in organic synthesis. However, most of the [2 + 2] cycloaddition reactions of allenes and alkenes reported previously were intramolecular reactions, while the analogous intermolecular reactions were limited to electronically biased allenes or alkenes. The involvement of allene C−H activation in the cycloaddition reactions has not been reported previously. Here we report the unprecedented regio- and stereoselective intermolecular [2 + 2] cycloaddition reactions of amino-functionalized alkenes with a wide range of allenes via rare-earth-catalyzed allene C−H activation.

The reaction of amino-functionalized alkenes with monosubstituted allenes in the presence of a half-sandwich scandium catalyst afforded the methylenecyclobutane products in high yields with excellent regio- and stereoselectivity (see scheme shown below). In contrast, the reaction with 1,3-disubstituted allenes exclusively yielded the cyclobutene products. In these transformations, an allenyl rare earth species like **A** formed by allene C−H activation acted as a true catalyst species. Both steric and electronic factors played an important role in determining the regio- and stereoselectivity.

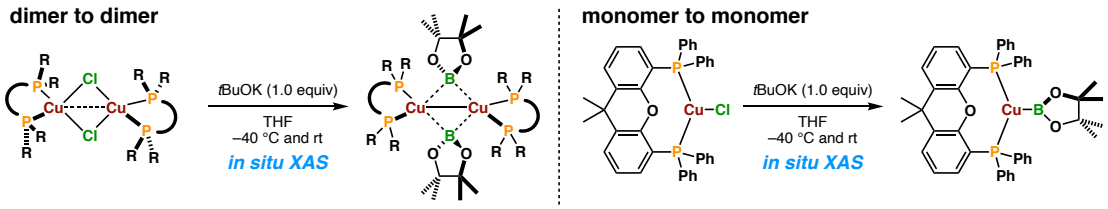


溶液 XAS 実験のための低温計測システムの高度化と in situ XAS 計測によるボリル銅種の局所構造解析

(阪大院工[1]・阪大 ICS-OTRI[2]・北大院工[3]・(株)DFC[4]・JASRI[5]・北大 WPI-ICReDD[6])
○植竹 裕太[1,2]・小澤 友[3]・松本 一希[4]・本間 徹生[5]・久保田 浩司[3,6]・伊藤 肇[3,6]
Advancement of a cooling system for solution XAS experiment and in situ local structure analysis of boryl copper species by XAS measurements ([1]Grad. Sch. Eng., Osaka Univ., [2]ICS-OTRI, Osaka Univ., [3]Grad. Sch. Eng., Hokkaido Univ., [4]DFC Co., Ltd., [5]JASRI, [6]WPI-ICReDD, Hokkaido Univ.) ○Yuta Uetake[1,2], Yu Ozawa[3], Kazuki Matsumoto[4], Tetsuo Honma[5], Koji Kubota[3,6], Hajime Ito[3,6]

The local structure of boryl copper intermediates in solution were investigated by in situ solution X-ray absorption spectroscopy (XAS) experiments. As a result, it was found that the structure of boryl copper species varied depending on the ligands used. In addition, we developed a cooling system for XAS experiments in organic solvents, and installed it at SPring-8 BL14B2 beamline. Using this apparatus, the variable-temperature in situ XAS experiments were performed, and it was found that boryl copper dimer was generated even at –40 °C, and thus-prepared dimeric structure was retained even when the temperature was raised to room temperature under the reaction conditions.
Keywords : Boryl copper; X-ray absorption spectroscopy; Low-temperature XAS measurement; Device development; DFT calculation

銅触媒を用いるホウ素化反応は、不活性結合の切断やアルケンへの付加といった多様な反応形式で基質にホウ素を導入できるため、合成化学的に有用であり広く研究されてきた[1]。一方で、反応系中で発生しているボリル銅中間体の構造に関する検討は限定的である[2,3]。今回我々は、ボリル銅種の溶液中での構造を詳細に検討するため、X 線吸収スペクトル（XAS）を中心とした in situ 構造解析を実施した。その結果、配位子として dppbz および QuinoxP*を用いた場合にはダイマー体が、xantphos を用いた場合にはモノマー体が優先して生成していることが示唆され、中間体構造の配位子依存性を見出した。また、溶液系の温度可変 in situ XAS 実験に対応したクライオ装置を開発し、SPring-8 BL14B2 ビームラインに実装した。それを用いて温度可変 in situ XAS 実験を–40 °C および室温で行ない、温度変化による構造変化を追跡した。



1) D. Hemming, R. Fritzemeier, S. A. Westcott, W. L. Santos, P. G. Steel, *Chem. Soc. Rev.* **2018**, *47*, 7477.
2) C. Borner, L. Anders, K. Brandhorst, C. Kleeberg, *Organometallics* **2017**, *36*, 4687.
3) H. Iwamoto, Y. Ozawa, Y. Takenouchi, T. Imamoto, H. Ito, *J. Am. Chem. Soc.* **2021**, *143*, 6413.

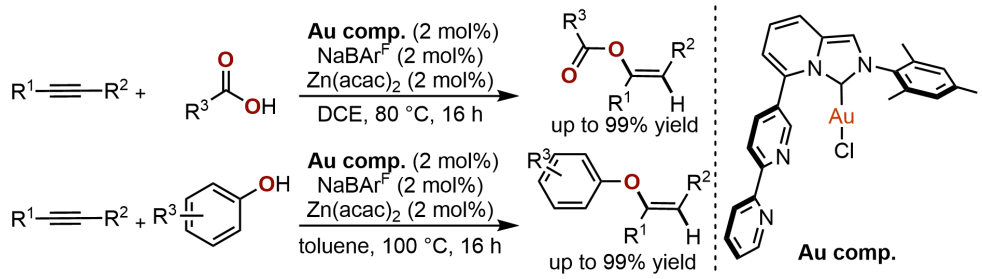
Nucleophilic Addition of Carboxylic Acids and Phenols towards Non-activated Alkynes Catalyzed by Gold-Zinc Bimetallic Complexes Including [1,5-*a*]pyridine-3-ylidene Ligands

([1]*Faculty of Science, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*) ○Vishal Kumar Rawat,[1] Kosuke Higashida,[1,2] Masaya Sawamura[1,2]

Keywords: Gold Catalyst; *N*-Heterocyclic Carbene; Cooperative Catalysis; Nucleophilic Addition

Imidazo[1,5-*a*]pyridin-3-ylidene[1] is an attractive *N*-heterocyclic carbene (NHC) platform for designing organometallic catalysts, since the substituent at the C5-position impacts the catalytic environment of metal atom bound to carbene at the C3-position. In fact, we reported that 5-imidazolyl-imidazo[1,5-*a*]pyridin-3-ylidene silver cationic complexes served as a highly active catalyst toward cyclization of alkyne-tethered carboxylic acids through acid-base cooperative actions.[2] This contribution will report the development of gold complexes bearing imidazo[1,5-*a*]pyridin-3-ylidene including coordinative *N*-heteroaromatics at the C5-position, in which *N*-heteroaromatics served as a ligand for constructing hetero-bimetallic complexes with hard metal salts.

For evaluating the catalytic activity of the gold complexes, we attempted hydrocarboxylation and hydrophenoxylation of non-activated alkynes by the use of the hetero-bimetallic complexes generated through pre-mixing the gold complex with non-coordinative anion sources and metal salts. These nucleophilic addition was plausibly accelerated through cooperative action of the Lewis acidic gold atom for activating alkynes and the basic metal for increasing nucleophilicity of carboxylic acids or phenols through deprotonation of acidic protons.[3] We found that the gold-zinc hetero-bimetallic complexes showed highly catalytic performance toward hydrocarboxylation and hydrophenoxylation of non-activated alkynes, and these catalyst showed wide substrate scope and functional group tolerances.



1) Siguenza, J. L.; Izquierdo, C.; Diez, E.; Fernandez, R.; Lassaletta, J. M. *Dalton Trans.* **2016**, *45*, 10113-10117.

2) Rawat, V. K.; Higashida, K.; Sawamura, M. *Adv. Synth. Catal.* **2021**, *363*, 1631-1637.

3) (a) Oonishi, Y.; Gómez-Suárez, A.; Martin, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 9767-9771. (b) Dupuy, S.; Gasperini, D.; Nolan, S. P. *ACS Catal.* **2015**, *5*, 6918-6921.

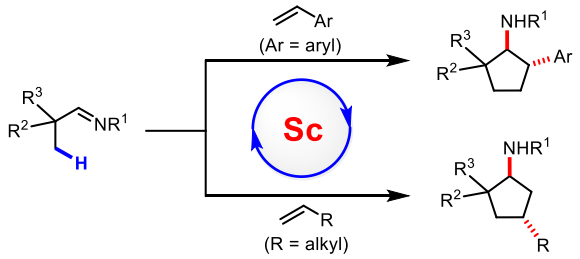
Regio- and Diastereoselective [3 + 2] Annulation of Aliphatic Aldimines with Alkenes via β-C(sp^3)−H Activation by Scandium Catalysts

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science,* [2]*Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako, Saitama 351-0198*) ○Xuefeng Cong,[1] Masayoshi Nishiura,[1,2] Zhaomin Hou[1,2]

Keywords: Aminocyclopentane; Scandium; [3+2] Annulation; C(sp^3)−H activation; Aliphatic Aldimine

The catalytic [3 + 2] annulation of aliphatic aldimines with alkenes via β-C(sp^3)−H activation is of much interest and importance for the synthesis of multi-substituted aminocyclopentanes, which are important components in many natural products, bioactive molecules and pharmaceuticals. However, such transformation has remained a challenge to date because of the lack of suitable catalysts.[1-3] Here we report for the first time the regio- and diastereoselective [3 + 2] annulation of a wide range of aliphatic aldimines with alkenes via the activation of an unactivated β-C(sp^3)−H bond by half-sandwich scandium catalysts.

This protocol offers a straightforward and atom-efficient route for the synthesis of a new family of multi-substituted aminocyclopentane derivatives from easily accessible aliphatic aldimines and alkenes. The annulation of aldimines with styrenes exclusively afforded the corresponding 5-aryl-*trans*-substituted 1-aminocyclopentane derivatives with excellent diastereoselectivity (d.r. > 19:1) through the 2,1-insertion of a styrene unit. In the annulation of aldimines with aliphatic alkenes, the alkene insertion took place in a 1,2-fashion, selectively affording the corresponding 4-alkyl-*trans*-substituted 1-aminocyclopentane products. The addition of a catalytic amount of an appropriate amine such as adamantylamine (AdH_2) or dibenzylamine (Bn_2NH) showed significant effects on the catalyst activity and stereoselectivity. Some key reaction intermediates were isolated to elucidate the reaction mechanism.



1) M. Font, M. Gulías, J. Luis Mascareñas, *Angew. Chem. Int. Ed.* **2021**, DOI: 10.1002/anie.202112848. 2) J. R. Hummel, J. A. Boerth, J. A. Ellman, *Chem. Rev.* **2017**, *117*, 9163. 3) X. Cong, G. Zhan, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2020**, *142*, 5531.

Chromium-catalyzed *syn*-Stereoselective Ring-opening Arylation of 7-Oxabenzonorbornadienes

(*Graduate School of Engineering Science, Osaka University*) ○Kohei Nishi, Hayato Tsurugi, Kazushi Mashima

Keywords: Chromium catalyst; Aryl Grignard reagent; 7-Oxabenzonorbornadiene; Ring-opening; C-C bond formation

Stereoselective synthesis of multi-functionalized 1,2-dihydronaphthalenols has attracted interest due to their usability as building blocks for synthesizing biologically active compounds.[1] Ring-opening and arylation of 7-oxabenonorbornadienes with organometallic reagents is a straightforward method to derivatize to the 1,2-dihydronaphthalenol motif[2] since the easy accessibility of 7-oxabenzonorbornadienes from furan derivatives and benzyne precursors *via* [4 + 2]-cycloaddition reaction.[3] Among the organometallic reagents used in this reaction, Grignard reagents are the most readily available carbon nucleophiles from the corresponding aryl halides and magnesium powders; however, they were less applicable due to the lower tolerance to the functional groups due to the high reactivity of the Grignard reagents.[2c] Herein, we report that chromium complexes served as catalysts for *syn*-stereoselective ring-opening arylation of 7-oxabenzonorbornadienes with aryl Grignard reagents, giving *syn*-2-aryl-1,2-dihydronaphthalen-1-ols. Chromium complexes exhibited extremely high catalytic activity, reaching to the turn-over number up to 25,000 as the highest turn-over number among the chromium-catalyzed C-C bond formation reactions. In this reaction, we demonstrated a versatility of a rather simple protocol of successive *in situ*-aryl Grignard formation followed by chromium-catalyzed reactions; aryl Grignard reagents bearing various reactive functional groups were applicable to the chromium-catalyzed ring-opening arylation at -20 °C, giving *syn*-2-aryl-1,2-dihydronaphthalen-1-ols with the corresponding functionality.[4] Substrate scope and the reaction mechanism are disclosed in this presentation.

【References】

(1) a) Snyder, S. E.; Aviles-Garay, F. A.; Chakraborti, R.; Nichols, D. E.; Watts, V. J.; Mailman, R. B. *J. Med. Chem.* **1995**, *38*, 2395－2409. b) Lautens, M.; Rovis, T. *J. Org. Chem.* **1997**, *62*, 5246－5247. (2) a) Kumar, S. V.; Yen, A.; Lautens, M.; Guiry, P. J. *Chem. Soc. Rev.*, **2021**, *50*, 3013－3093. b) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48. c) Nakamura, M.; Matsuo, K.; Inoue, T.; Nakamura, E. *Org. Lett.* **2003**, *5*, 1373－1375. (3) Sanz, R. *Org. Prep. Proced. Int.*, **2008**, *40*, 215－291. (4) Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 3333－3336.

イットリウム触媒による 2-アルキルピリジンのベンジル位選択的 C−H アルミ化と変換

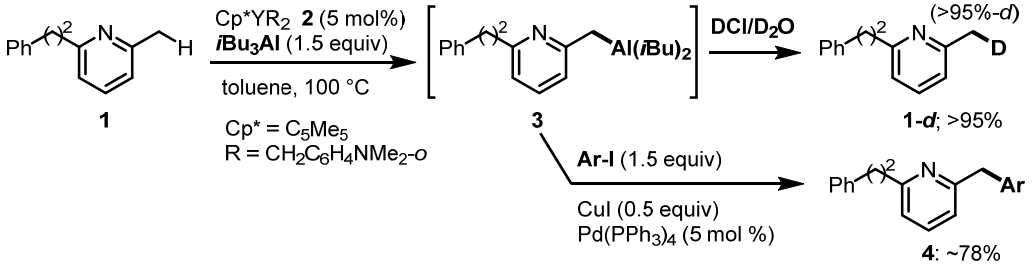
（理研 CPR[1]・理研 CSRS[2]）○瀧本 真徳[1,2]・西浦 正芳[1,2]・侯 召民[1,2]

Yttrium-Catalyzed Reagioselective Alumination and Subsequent Functionalization of Benzylic C−H Bonds of 2-Alkylpyridines ([1]*Organometallic Chemistry Laboratory, RIKEN CPR*, [2]*Advanced Catalysis Research Group, RIKEN CSRS*) ○Masanori Takimoto,[1,2] Masayoshi Nishiura,[1,2] Zhaomin Hou[1,2]

Alkylpyridines are important nitrogen-containing organic components frequently found in numerous valuable functional organic compounds. One of the most efficient synthetic methods for alkylpyridines is the benzylic C-H bond functionalization of readily available alkylpyridines with a relatively simple structure.[1)] We have recently found that a half-sandwich yttrium-bis(alkyl) complex **2** could readily catalyze the reaction of a benzylic C−H bond of 2,6-dialkylpyridines, such as **1**, with triisobutylaluminum in which the benzylic C−H bond is transformed to C−Al bond. The C−H alumination of **1** occurs selectively at the sterically least hindered benzylic position in a regioselective manner to form organoaluminum species **3**, and deuterated product **1-*d*** was obtained by treating **3** with DCl. The C−Al bond of the generated organoaluminum species **3** could be further functionalized. For instance, arylation of **3** with various aryl iodides could be performed in the presence of CuI and a Pd-catalyst to afford **4** in good yields.

Keywords: C−H activation, pyridines, rare-earth metal catalysts, organoaluminums, metalation

アルキルピリジンは、様々な有用有機化合物の基本骨格として重要な化合物である。様々な構造のアルキルピリジンの効率的合成手法の一つとして、より単純な構造を持つアルキルピリジン類に対し、ベンジル位 C−H 結合変換反応を適用することが挙げられる [1)]。我々は、2,6-位にアルキル基を有するピリジンに、触媒量のハーフサンドイッチ型イットリウムジアルキル錯体 **2** の存在下、トリイソブチルアルミニウムを反応させると、立体的に最も空いたベンジル位の C−H 結合が選択的に C−Al 結合へと変換される、ベンジル位 C−H アルミ化反応が進行することを見出した。例えば、2-メチル-6-フェネチルピリジン **1** を 5 mol%のイットリウム錯体 **2** の存在下、トリイソブチルアルミニウムとトルエン中反応させると、2-位メチル基上で選択的 C−H アルミ化反応が進行してアルミ化体 **3** が生成し、**3** は重塩酸処理することで重水素化体 **1-*d*** を与えた。**3** はさらに化学変換が可能であり、例えば、CuI と Pd 触媒の存在下、種々のヨウ化アリールと反応させることで、アリール化体 **4** が収率良く得られた。



1) We previously reported a yttrium-catalyzed C−H alkylation of 2,6-alkylpyridines with alkenes; B.-T. Guan, B. Wang, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2013**, *52*, 4428.

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

[H301-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Yasunori Matsui, Yosuke Tani
Fri. Mar 25, 2022 1:00 PM - 3:40 PM H301 (Online Meeting)

[H301-3pm-01] Through-space Charge-transfer Photoluminescence of the Nonconjugated Electron Donor– Acceptor Dyad

○Takuya Ogaki[1,2], Yutaro Kuramoto[1], Ryohei Takayasu[3], Yasunori Matsui[1,2], Eisuke Ohta[1,2], Hiroshi Ikeda[1,2] （1. Grad. Sch. Eng., Osaka Pref. Univ., 2. RIMED, Osaka Pref. Univ., 3. Col. Eng., Osaka Pref. Univ.）

1:00 PM - 1:20 PM

[H301-3pm-02] Copper(I)-pyrazolate clusters as solid-state phosphors: Tunable emissions via a remote steric effect

○Yuichiro Watanabe[1], Benjamin M Waher[1], Matthias Zeller[1], Sergei Savikhin[1], Lyudmila V Slipchenko[1], Alexander Wei[1] （1. Purdue University）

1:20 PM - 1:40 PM

[H301-3pm-03] Design of Solid-State Photoluminescence Materials Based on Stacked π-Planes Assisted by Carborane

○Junki Ochi[1], Kazuo Tanaka[1] （1. Kyoto University）

1:40 PM - 2:00 PM

[H301-3pm-04] Photo-induced crystal– liquid phase transition of heteroaromatic diketones probed by phosphorescence

○Mao komura[1], Takuji Ogawa[1], Hikaru Sotome[2], Hiroshi Miyasaka[2], Yosuke Tani[1] （1. Grad. Sch. Sci., Osaka Univ. , 2. Grad. Sch. Eng. Sci., Osaka Univ. ）

2:00 PM - 2:20 PM

[H301-3pm-05] Highly Efficient and Robust Phosphorescence of Thienyl Diketone Derivative

○Yosuke Tani[1], Yuya Oshima[1], Takuji Ogawa[1] （1. Osaka Univ.）

2:20 PM - 2:40 PM

[H301-3pm-06] Development of boronate self-assembly as photocatalysts for hydrogen production

○Ryohei Hasegawa[1,2], Yuji Kubo[1,2] （1. Tokyo metropolitan university Graduate School of Urban Environmental Sciences, 2. Tokyo metropolitan university Research Center for Hydrogen Energy-based Society）

2:40 PM - 3:00 PM

[H301-3pm-07] Drastic changes in the mechanical properties of long alkyl-chained organic crystals depending on recrystallizing solvent

○Sotaro Kusumoto[1], Yoshihiro Koide[1], Shinya Hayami[2] （1. Kanagawa Univ., 2. Kumamoto Univ.）

3:00 PM - 3:20 PM

[H301-3pm-08] Repeated elongation and decomposition of supramolecular fibers induced by surfactant addition

○Shogo Torigoe[1], Ryou Kubota[1], Kazutoshi Nagao, Itaru Hamachi[1] （1. The Univ. of Kyoto）

3:20 PM - 3:40 PM

日本化学会 第102春季年会 (2022)

非共役電子ドナーアクセプターダイアドのスルースペース電荷移動発光

（阪府大院工[1]・阪府大 RIMED[2]・阪府大工[3]）○大垣拓也[1,2]・倉本悠太郎[1]・高安凌平[3]・松井康哲[1,2]・太田英輔[1,2]・池田　浩[1,2]

Through-space Charge-transfer Photoluminescence of the Nonconjugated Electron Donor–Acceptor Dyad ([1]*Grad. Sch. Eng., Osaka Pref. Univ.,* [2]*RIMED, Osaka Pref. Univ.,* [3]*Col. Eng., Osaka Pref. Univ.*) ○ Takuya Ogaki,[1,2] Yutaro Kuramoto,[1] Ryohei Takayasu,[3] Yasunori Matsui,[1,2] Eisuke Ohta,[1,2] Hiroshi Ikeda[1,2]

We previously reported that an electron donor (D)–acceptor (A) dyad **1** (Fig. a) possessing a cage skeleton as a nonconjugated linker displays solvatofluorochromism, in which the photoluminescence color changes from blue to orange depending on the solvent polarity.[1] To develop red-emissive materials, in this work, we synthesized a new nonconjugated D–A dyad **2** with a more electron-deficient dicyanomethylene moiety. In toluene, the dyad **2** showed orange photoluminescence with a maximum (λ_{PL}) at 625 nm (Fig. b). Crystallization of **2** from chloroform–methanol afforded two crystal polymorphs, **2O** and **2R**, which exhibited orange (λ_{PL} = 630 nm) and red (652 nm) photoluminescence, respectively. The X-ray crystallographic analysis (Fig. c) revealed that the intramolecular D–A distance in **2R** is shorter than that in **2O**, indicating that the red photoluminescence of **2R** is derived from intramolecular through-space charge transfer excited state.

Keywords : Through-space Charge Transfer, Photoluminescence, X-ray Crystallographic Analysis, Crystal Polymorphs, Intermolecular Interaction

我々は以前，かご骨格を非共役リンカーとする電子ドナー（D）–アクセプター（A）ダイアド **1**（Fig. a）が，溶媒極性によって青色から薄橙色発光へと変化するソルバトフルオロクロミズムを示すことを報告した [1]．本研究では，新たな赤色系発光材料を開発するため，より電子不足なジシアノメチレン部をもつ新規非共役 D–A ダイアド **2** を合成した．トルエン中において，**2** は発光極大（λ_{PL}）を 625 nm にもつ橙色発光を示した（Fig. b）．クロロホルム–メタノールから **2** を結晶化させると，2 種類の結晶多形 **2O** および **2R** が得られ，それぞれ橙色（λ_{PL} = 630 nm）および赤色発光（652 nm）を示した．X 線結晶構造解析の結果（Fig. c），**2O** に比べ，**2R** における分子内 D–A 間距離が短いことから，**2R** の赤色発光は分子内スルースペース電荷移動励起状態に由来することが示唆された．

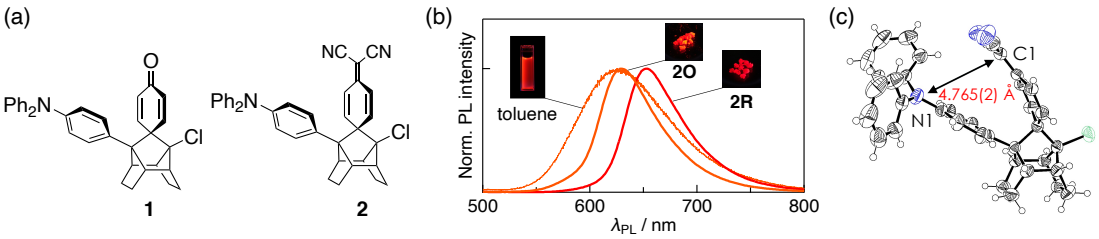


Fig. (a) Structures of D–A dyads **1** and **2**. (b) Photoluminescence spectra of **2**. (c) ORTEP drawing of **2R**.

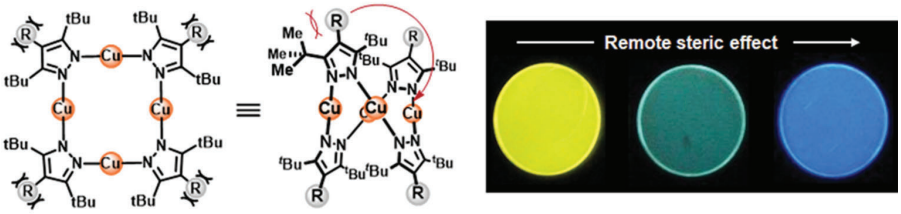
1) Kuramoto, Y.; Nakagiri, T.; Ikeda, H. *et al. Photochem. Photobiol. Sci.* **2018**, *17*, 1157–1168.

Copper(I)-pyrazolate clusters as solid-state phosphors: Tunable emissions via a remote steric effect

([1]*Department of Chemistry, Purdue University*) ○Yuichiro Watanabe,[1] Benjamin M. Washer,[1] Matthias Zeller,[1] Sergei Savikhin,[1] Lyudmila V. Slipchenko,[1] Alexander Wei[1]

Keywords: Solid-state Phosphorescence; Cluster Complexes; Steric Effect; Rigidochromism; Conformation Analysis

Optoelectronics depends on luminophores that emit brightly at red, green, and blue, but access to the latter is hindered by the limited availability of phosphors that can produce blue emissions in the solid state. Here, we describe a novel manifestation of rigidochromic behavior in a series of tetranuclear Cu(I)–pyrazolate (Cu_4pz_4) macrocycles, with implications for solid-state luminescence at deep-blue wavelengths (λ_{em} < 460 nm). The Cu_4pz_4 emissions are remarkably sensitive to structural effects far from the luminescent core: When 3,5-di-*tert*-butylpyrazoles are used as bridging ligands, adding a C4 substituent can induce a blueshift of more than 100 nm. We focus on a series of 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. This long-range steric effect can influence the conformational behavior of adjacent *tert*-butyl groups, with a subsequent impact on the global conformation of the Cu_4pz_4 complex. Emissions are mediated primarily through a cluster-centered triplet (^{3}CC) state; compression of the Cu_4 cluster into a nearly close-packed geometry prevents reorganization of its excited-state structure, and preserves the ^{3}CC energy at a high level. The remote steric effect may thus offer alternative strategies toward the design of blue phosphors with rigid excited-state geometries.



1) A. Maspero, S. Brenna, S. Galli, A. Penoni, *J. Organomet. Chem.* **2003,** *672* (1), 123–129. 2) K. Fujisawa, Y. Ishikawa, Y. Miyashita, K. -I. Okamoto, *Chem. Lett.* **2004**, *33* (1), 66–67. 3) K. Fujisawa, Y. Ishikawa, Y. Miyashita, K. -I. Okamoto, *Inorg. Chimica Acta* **2010**, *363* (12), 2977–2989.

Design of Solid-State Photoluminescence Materials Based on Stacked π-Planes Assisted by Carborane

(*Graduate School of Engineering, Kyoto University*)
○Junki Ochi, Kazuo Tanaka
Keywords: Carborane; Solid-state emission; Electrostatic interaction

o-Carborane is an icosahedral cluster composed of ten boron and two carbon atoms with three-center two-electron (3c2e) bonds. Its three-dimensionally delocalized skeletal electrons through 3c2e bonds can be an origin of various unique luminescent properties.[1] Moreover, the electronically polarized structure has the potential to form electrostatic interactions and therefore to be a versatile scaffold to develop functional materials (Fig. 1).

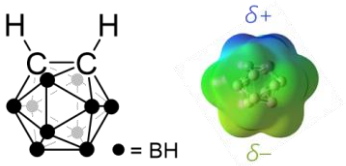


Fig. 1 (left) Chemical structure of *o*-carborane. (right) Electrostatic potential map of *o*-carborane.

In this research, we synthesized five types of acridine-modified compounds (Fig. 2, left).[2] There are two types of classification: spacer units and methylation degree. First, **E1**, **E2**, and **M1** contain various spacer units with different conjugation length. Second, **M1**, **M1-Me$_2$**, and **M1-Me$_8$** have the same methylene spacer but different carborane skeletons with partial methylation. Interestingly, these five compounds showed a wide range of photoluminescence in the crystalline state from light blue to orange. After the series of measurements under various conditions, we attributed those broad emission bands to solid-state excimer emission derived from the π-stacking in the crystalline state. From single-crystal X-ray analyses, it was revealed that all compounds formed a dimer structure assisted by CH···N interactions, and efficient π–π interaction was formed (Fig. 2, right). It can be concluded that a slight change of π–π interaction by chemical modifications drastically influenced the photoluminescence from the crystalline samples.

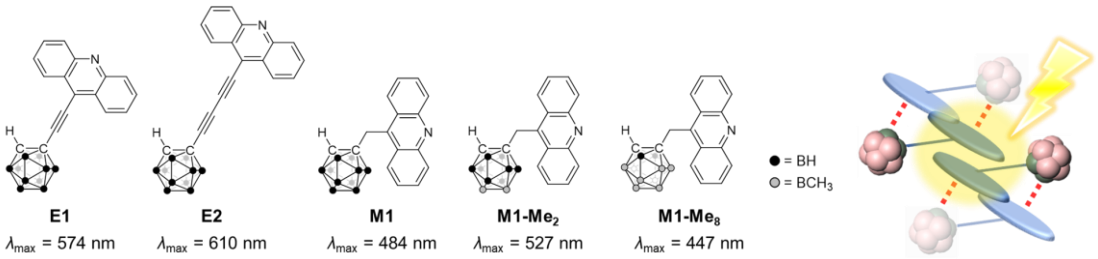


Fig. 2 (left) The synthesized compounds. (right) Dimer structure assisted by CH···N interactions.

1) J. Ochi, K. Tanaka, Y. Chujo. *Angew. Chem. Int. Ed.*, **2019**, *59*, 9841–9855.
2) For **E1** and **E2**: J. Ochi, K. Tanaka, Y. Chujo. *Inorg. Chem.*, **2021**, *60*, 8990–8997.

Photo-induced crystal-liquid phase transition of heteroaromatic diketones probed by phosphorescence

([1]*Graduate School of Science, Osaka University*, [2]*Graduate School of Engineering Science, Osaka University*) ○Mao komura,[1] Takuji Ogawa,[1] Hikaru Sotome,[2] Hiroshi Miyasaka,[2] Yosuke Tani [1]

Keywords: Room-temperature phosphorescence; Solvent-free liquid; Phase transition; 1,2-diketone; photoresponse

Previously, we demonstrated that heteroaromatic diketone **1** exhibits room-temperature phosphorescence in solvent-free liquid state but is virtually non-emissive in crystalline state due to a difference in the molecular conformation (Figures 1a).[1] Here we report our unexpected finding that irradiating UV light to the non-emissive crystal **1** induces melting, the progress of which is probed by the stepwise change in RTP properties (Figure 1b, c).

We irradiated UV light to a single crystal while monitoring the time-course of PL spectra. Prior to the visibly discernible melting, the drastic change of the PL spectra was observed within the initial two seconds. Then, the same RTP as in the solvent-free liquid state gradually increased in intensity (Figure 1c, green and blue line). The trans planar conformer generated by UV irradiation contributes to the melting transition. Our work represents the first example of a photo-induced RTP of organic compounds accompanied by solid-liquid phase transition, which promotes understanding of the phase transition phenomenon at the molecular level.

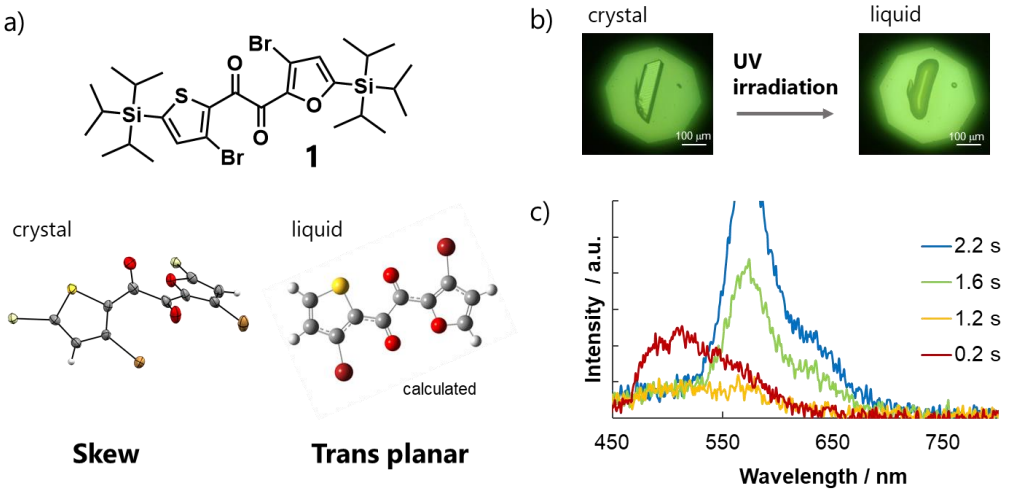


Figure 1. a) Chemical structure and conformations of **1**. b) Optical microscope images of crystal **1** before and after UV irradiation. c) Time course of the PL spectra of **1**.

1) M. Komura, T. Ogawa and Y. Tani, *Chem. Sci.*, **2021**, *12*, 14363–14368.

機械刺激に強い高効率りん光を示すチエニルジケトン誘導体

（阪大院理）○谷 洋介・大島 祐也・小川 琢治
Highly Efficient and Robust Phosphorescence of Thienyl Diketone Derivative (*Graduate School of Science, Osaka University*) ○Yosuke Tani, Yuya Oshima, Takuji Ogawa

Room-temperature phosphorescence (RTP) of metal-free organic molecules is challenging owing to their intrinsically small phosphorescence rate constant (k_p). Although some organic crystals are reported to exhibit efficient RTP, the RTP properties, such as efficiency and color, depend on the crystallinity and are prone to deteriorate significantly upon applying mechanical stimulation. Recently, we found that thienyl diketone derivatives exhibit highly efficient RTP owing to large k_p; however, their crystals exhibit moderate RTP with efficiency of up to 4% because they crystallize in a less emissive conformation.[1)] Herein, we report a highly efficient RTP that is robust to mechanical stimulation. The newly developed diketone derivative has a highly emissive conformation in the crystal.

Keywords : Room-Temperature Phosphorescence; Organic Crystal; Amorphous; Crystal Engineering; Metal-Free

りん光は、スピン反転を伴う禁制発光である。イリジウムなどの金属を含まない有機分子は本質的にりん光速度定数 k_p が小さく、高効率な室温りん光(RTP)を実現するのは容易でない。近年、結晶化により無輻射失活を抑制し、有機分子の RTP を得る例が盛んに報告されている。しかし k_p が小さいため発光特性は結晶の質に依存し、その多くは、結晶性が損なわれると発光効率の著しい低下や発光色の変化が起きる。一方、我々は最近、チエニルジケトン骨格が平面配座において極めて大きな k_p を示すことを見出した。ただしこの配座は準安定配座であるため、ほとんどの誘導体は最安定なねじれ配座で結晶化し、結晶状態における RTP の量子収率は高々4%であった [1)]。

本研究ではチエニルジケトンの置換基を種々検討し、トリ（*n*-ブチル）シリル基を有する誘導体 **TBS-BrTn** が結晶中で平面配座をとることを見出した（図 1）。その量子収率は室温大気下で最大 50%と極めて高く、機械刺激を加えてアモルファス化したあとでも 30%以上と高効率であった。また、発光スペクトルにも顕著な変化はなかった。発表では、種々の状態における配座と発光特性の関連を含め詳細に議論する。

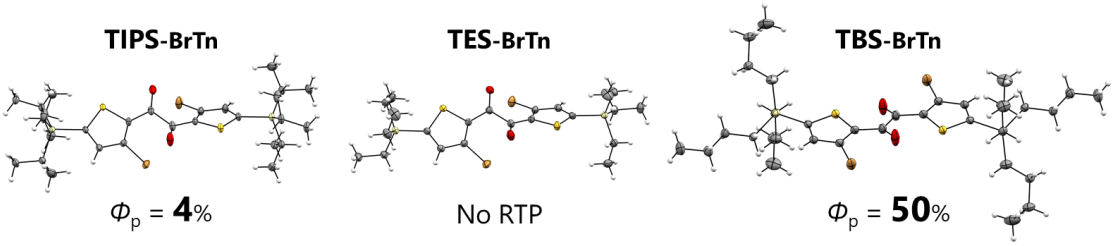


Fig. 1 Crystal structures and phosphorescence quantum yields of thienyl diketone derivatives.

1) a) Y. Tani, M. Terasaki, M. Komura, T. Ogawa, *J. Mater. Chem. C* **2019**, *7*, 11926.; b) Y. Tani, M. Komura, T. Ogawa, *Chem. Commun.* **2020**, *56*, 6810.

ボロネート自己組織体を用いた水素発生用光触媒系の開発

（都立大院都市環境[1]・都立大 ReHES[2]）○長谷川椋平[1]・久保由治[1,2]

Development of boronate self-assembly as photocatalysts for hydrogen production

([1]*Graduate School of Urban Environmental Science, Tokyo Metropolitan University*, [2]*Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University,*)
○Ryohei Hasegawa[1], Yuji Kubo[1,2]

Considering an ideal energy carrier as a sustainable energy source, the use of solar energy to produce hydrogen from water is desirable and profitable method. Although metal oxides semiconductors such as TiO_2 have been extensively studied toward this end, drawback of low light harvesting properties and low water-compatibility has been pointed out. In this study, new photocatalytic systems based on boronate self-assembles (**BP**) as the platform have been developed, where porphyrin-based sensitizer and Pt co-cocatalyst were embedded on the surface with polyethyleneimine. The hydrogen production using the resultant system is discussed.

Keywords : Boronic acid; Self-assembly; Support material; Photocatalyst; Polyethyleneimine

再生可能エネルギー由来の水素製造が、新たな社会システムを支えるグリーンエネルギーとして注目されている。酸化チタンに代表される酸化物半導体を利用した水の直接光分解は低コスト水素製造技術として盛んに検討されている。しかしながら、大きなバンドギャップ（～3.2 eV）に加えて水との親和性が低い欠点が指摘されている [1]。本研究では、超分子化学的アプローチから水分散性自己組織体を基体とする光触媒系を構築し、諸物性を評価することを目的とした (Fig. 1)。

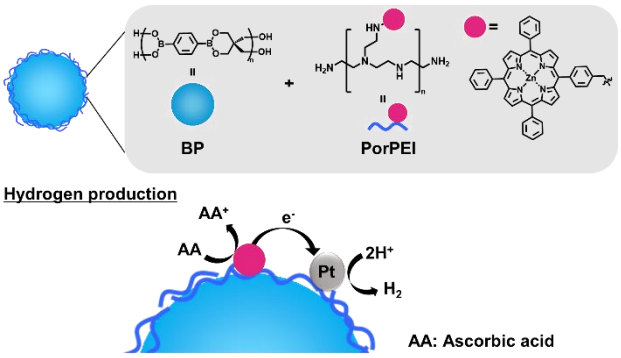


Fig. 1 Schematic view of **PorPEI/Pt @BP** as a photocatalyst.

当研究室で開発したボロネート自己組織体 (**BP**) は、ベンゼン-1,4-ジボロン酸とペンタエリスリトールの逐次的脱水反応から合成され、その構成成分末端のヒドロキシ基に基づく水分散性とポリエチレンイミン (PEI) との親和性をもつ [2]。そこで、増感機能が期待される亜鉛ポルフィリンで誘導した PEI (**PorPEI**)と Pt ナノ粒子（助触媒）を **BP** 表面に担持させた。得られた分子系 (**PorPEI/Pt @BP**) は、アスコルビン酸を添加したリン酸緩衝液 (pH = 3.7) に分散させ、Xe ランプ ($\lambda > 400$ nm, 100 mW cm^{-2})照射下で水素発生の評価をおこなった。その結果、0.304 mmol g^{-1} h^{-1} の水素が観測され、光触媒としての機能を見出した。本発表では、得られた光触媒の性質について議論する。

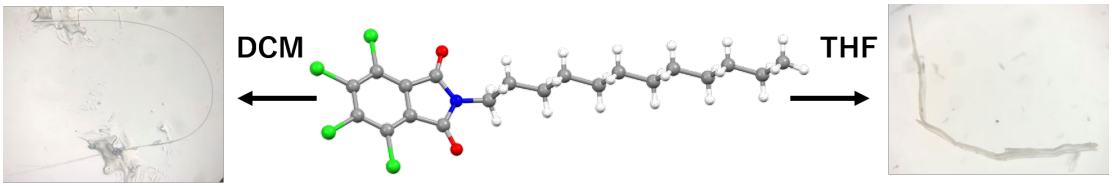
1) S. Y. Park, *et al.*, *J. Phys. Chem.* C, **2020**, *124*, 6971−6978.
2) Y. Kubo, R. Nishiyabu, T. D. James, *Chem. Commun.*, **2015**, *51*, 2005−2020.

Drastic changes in the mechanical properties of long alkyl-chained organic crystals depending on recrystallizing solvent

([1]*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University*, [2]*Department of Chemistry, Graduate School of Science and Technology, Kumamoto University*)
○Sotaro Kusumoto,[1] Yoshihiro Koide,[1] Shinya Hayami[2]
Keywords: Organic Crystal; Elastic Crystal; Plastic Crystal; Solvent dependence

Organic and inorganic crystals can cause reversible (elasticity) or irreversible deformation (plasticity) by external stimuli such as mechanical force, pressure, heat, etc.[1], and molecular crystals responding to them have recently attracted much attention[2] in the area of crystal engineering, supramolecular chemistry and material science with applications in artificial muscles, pharmaceuticals, mechanosensors, smart materials, actuators, etc. However, since most crystals display hard properties because of their dense and highly ordered arrangement and are able to be brittle and crack by mechanical stresses, as well as irreversibly deformed after being damaged, they are curbed in their applicability as materials for flexible devices.

The choice of solvent and/or evaporation rate for single crystal growth by evaporation technique may influence on a factor such as the introduction of solvent molecules in the crystal lattice, the formation of polymorphs, or the change of crystal face, as well as the production of "elastic and brittle"[3] or "plastic and brittle"[4] crystals, and thus a suitable solvent may be an important factor for the preparation of flexibly bendable crystals. Different crystallizations of the same compound to "elastic" or "plastic bending" are very rare, and according to our knowledge, coumarin is the only organic crystal that reveals such behaviour. The variations into such deformations depending on recrystallization solvents is still an unexplored area, and we firstly report in detail the formation of solvent-dependent crystals and their mechanical properties as well as their characterizations.



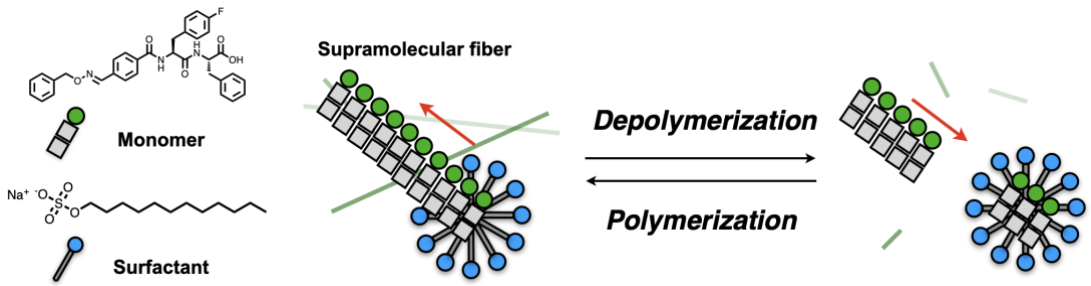
1) A. Hasija and D. Chopra, *CrystEngComm*, 2021, **23**, 5711–5730. 2) S. Kusumoto, A. Sugimoto, D. Kosumi, Y. Kim, Y. Sekine, M. Nakamura and S. Hayami, *CrystEngComm*, 2021, **23**, 5560–5563. 3) S. Kusumoto, A. Sugimoto, Y. Zhang, Y. Kim, M. Nakamura and S. Hayami, *Inorg. Chem.* 2021, **60**, 3, 1294–1298. 4) S. Kusumoto, A. Saso, H. Ohmagari, M. Hasegawa, Y. Kim, M. Nakamura, L. F. Lindoy and S. Hayami, *ChemPlusChem,* 2020, **85**, 1692-1696.

界面活性剤添加により伸長と収縮を繰り返す超分子ファイバー

（京大院工[1], JST-ERATO[2]）○鳥越 祥吾[1]・窪田 亮[1]・長尾 和俊[1]・浜地 格[1,2]
Repeated elongation and decomposition of supramolecular fibers induced by surfactant adiition
([1]*Graduate School of Engineering, Kyoto University,* [2]*JST-ERATO*) ○Shogo Torigoe,[1] Ryou Kubota,[1] Kazutoshi Nagao,[1] Itaru Hamachi[1,2]

In living cells, formation and decomposition of biological self-assemblies like cytoskeleton are precisely controlled by enzymatic reactions and protein-protein interactions to exhibit functions such as cell motility and transport. However, it is still difficult to develop an artificial molecular system that spontaneously repeats assembly and disassembly and observe it in real-time. To date, we have succeeded in real-time imaging of the formation of supramolecular fibers composed of diphenylalanine derivatives. Here, we found that the addition of a surfactant, SDS, induced repeated elongation /decomposition of supramolecular nanofibers, confirmed by real-time CLSM imaging. The decomposition of the fibers did not occur at lower SDS concentrations than CMC, indicating that the interaction between the supramolecular fiber and the surfactant micelle is essential for the repetition of the elongation and decomposition. In this presentation, we report these results and the possible mechanism in detail.
Keywords : Supramolecular, Surfactant, Out-of-equilibrium, Real-time imaging

細胞では、細胞骨格に代表される自己集合体の離合集散が酵素反応やタンパク質間相互作用によって制御され、細胞運動や物質輸送などの機能を発現している。しかし、人工系において離合集散を自発的に繰り返す分子システムの構築およびそのリアルタイム観察は未だ困難な課題である。一方、我々はこれまでにジフェニルアラニン誘導体をモノマーとする超分子ファイバーの構築、ならびに共焦点レーザー顕微鏡によるファイバー形成のその場観察技術を開発してきた[1]。本研究では超分子ファイバーの収縮と伸長が、界面活性剤である硫酸ドデシルナトリウム（SDS）の添加によって、繰り返し起こることを顕微鏡によるリアルタイム観察で発見した。臨界ミセル化濃度以下の SDS 添加では脱重合が進行しなかったことから、超分子ファイバーと SDS ミセルの相互作用が伸長・収縮の動的挙動に重要であることが明らかとなった。本発表ではこれらの結果とメカニズムについて詳細を述べる。



1) S. Onogi, I. Hamachi, *et.al.*, *Nat. Chem.* **2016**, *8*, 743.

[H201-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Yoshimitsu Itoh, Masahiro Yamashina
Fri. Mar 25, 2022 1:20 PM - 3:40 PM H201 (Online Meeting)

[H201-3pm-01] Structural chemistry and stimuli-responsive phase transition of *N,N'*-dialkylimidazolium nonafluorobutanesulfonate ionic liquids

○Tomoyuki Takeyama[1,2], Yuuki Inoue[2], Kenji Chayama[2], Satoshi Iwatsuki[2], Koichiro Takao[1] (1. Tokyo Institute of Technology, 2. Konan University)

1:20 PM - 1:40 PM

[H201-3pm-02] Anthracene-based molecular tweezers: construction of self-assembled cyclic hexamer through complementary interactions

○Yuta SAWANAKA[1], Masahiro YAMASHINA[1], Shinji TOYOTA[1] (1. Tokyo Tech)

1:40 PM - 2:00 PM

[H201-3pm-03] Structural control of sheet-like diketopyrrolopyrrole aggregates by seeded polymerization and their excited-state dynamics

○Soichiro Ogi[1], Natsumi Fukaya[1], Hikaru Sotome[2], Kazuhiro Fujimoto[3], Takeshi Yanai[1,3], Hiroshi Miyasaka[2], Shigehiro Yamaguchi[1,3] (1. Graduate School of Science, Nagoya University, 2. Graduate School of Engineering Science, Osaka University, 3. Institute of Transformative Bio-Molecules, Nagoya University)

2:00 PM - 2:20 PM

[H201-3pm-04] Nanoscale Twinning of Molecular Self-Assembled Networks

Kyohei Yamagata[1], Matsuhiro Maeda[1], Zeno Tessari[2], Kunal S. Mali[2], Steven De Feyter[2], ○Kazukuni Tahara[3] (1. Graduate School of Science and Technology, Meiji University, 2. Department of Chemistry, KU Leuven, 3. School of Science and Technology, Meiji University)

2:20 PM - 2:40 PM

[H201-3pm-05] Transformation of highly hydrophobic organophosphorus compounds into supramolecular amphiphiles through the Staudinger reaction

○Masahiro Yamashina Yamashina[1], Hayate Suzuki[1], Shinji Toyota[1] (1. Tokyo Tech.)

2:40 PM - 3:00 PM

[H201-3pm-06] Supramolecular Polymerization of Photo-Aromatizable Thiophene-Fused Chiral [4*n*]Annulene: Photofunctions and Chiral Superstructures

○Tsubasa Aoki[1], Michihisa Ueda[1], Takuzo Aida[1,2], Yoshimitsu Itoh[1,3] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. RIKEN CEMS, 3. PRESTO, JST)

3:00 PM - 3:20 PM

[H201-3pm-07] 'Spontaneous' Pathway Selection in Stereochemical Supramolecular Copolymerization: Metal– Organic Nanotubes Assembled with a Planar Chiral Monomer

○Yingluo Zhao[1,2], Hiroko Kawano, Hiroshi Yamagishi[3], Saya Otake[1], Yoshimitsu Itoh[1], Nobutaka Shimizu[4], Hubiao Huang[2], Takuzo Aida[1,2] (1. The University of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. Tsukuba University, 4. High Energy

Accelerator Research Organization)
3:20 PM - 3:40 PM

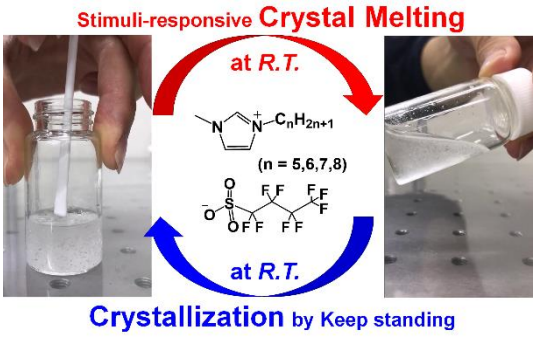
Structural chemistry and stimuli-responsive phase transition of *N*,*N'*-dialkylimidazolium nonafluorobutanesulfonate ionic liquids

([1] *Laboratory for Zero-Carbon Energy, Tokyo Institute of Technology*, [2]*Depertment of Chemistry, Konan University*) ○Tomoyuki Takeyama[1,2], Yuuki Inoue[2], Kenji Chayama[2], Satoshi Iwatsuki[2], Koichiro Takao[1]

Keywords: Ionic Liquid; Crystal Structure; Phase Transition; Stimuli-responsive; Imidazolium Salt

Ionic liquids (ILs) are composed of organic cations and anions, and exhibit low melting points (mp, below 100ºC). Although a melting point seems to strongly correlate with the molecular structure of IL, its precise structure and arrangement are usually quite difficult to be determined because of its liquefaction tendency.[1] If the structure of IL in a crystalline phase is revealed, we can discuss more about melting behavior of ILs from the structural aspects.

Here, we synthesized a series of *N*,*N'*-dialkylimidazolium room temperature ionic liquids (RTILs) with nonafluorobutanesulfonate ([$C_n$mim][NFBS] n = 5–8), and characterized them by elemental analysis, NMR, SCXRD and DSC. Although any [$C_n$mim][NFBS] studied here were viscous "ILs" right after the preparation, they have crystallized after standing at room temperature for several hours or days. Mechanical stimuli like agitation with a spatula onto the crystalline [$C_n$mim][NFBS] (n = 5–7) resulted in unexpected melting of these salts, while such a behavior was not observed for [C_8mim][NFBS]. The DSC analyses clarified that [$C_n$mim][NFBS] (n = 5–7) exhibit multiple phase transitions from 268 K to 303 K including several pre-melting stages probably due to molecular motions of the alkyl or perfluoroalkyl chains. Furthermore, any of [$C_n$mim][NFBS] studied here exhibit negative dP/dT slopes in a pressure dependency of the melting point. Such a characteristic thermal behavior would be ascribed to the C–H···O and C–H···F hydrogen bond networks to form hydrophilic and hydrophobic domains in the crystal lattices and also to give loosely packed crystal structures.[2]



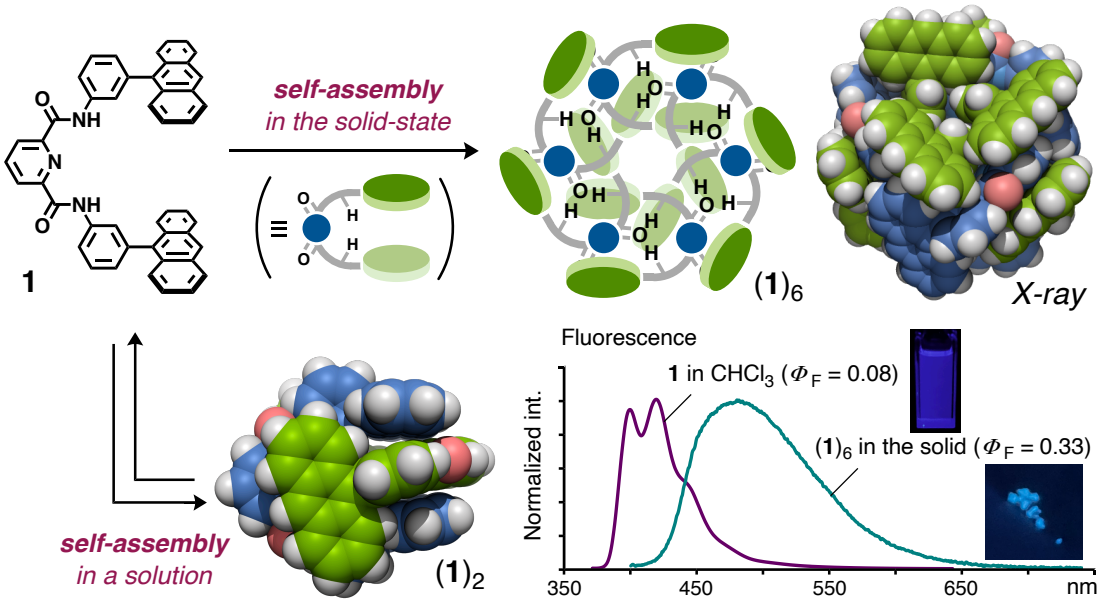
1) A. R. Choudhury, *et al.*, *J. Am. Chem. Soc.* **2005**, *127*, 16792−16793; 2) T. Takeyama, *et al.*, *Cryst. Growth Des.* **2021**, *21*, 617–624.

Anthracene-based Molecular Tweezers: Construction of Self-assembled Cyclic Hexamer through Complementary Interactions

(*School of Science, Tokyo Institute of Technology*)
○Yuta Sawanaka, Masahiro Yamashina, Shinji Toyota

Keywords: anthracene, molecular tweezers, complementary interactions, supramolecular assembly

Numerous well-defined supramolecules based on intrinsic noncovalent interactions (e.g., hydrogen bonds[1] and π interactions[2]) have been reported. However, the construction of supramolecules using the host-guest systems is still a formidable challenge.[3] Here we report the formation of self-assembled cyclic hexamer $(\mathbf{1})_6$ from anthracene-based molecular tweezers **1** through complementary interactions. X-ray analysis revealed that cyclic hexamer $(\mathbf{1})_6$ was exclusively assembled by complementary interactions including π-π stackings and hydrogen bonds among six units of **1**. In contrast, **1** formed a *head*-to-*head* dimeric assembly $(\mathbf{1})_2$ in a chloroform solution (K_D = 460 M^{-1}). Owing to tight packing of six tweezers **1**, hexamer $(\mathbf{1})_6$ showed a strong blue emission in the solid state (Φ_F = 0.33) compared to a weak violet emission of **1** in the solution (Φ_F = 0.08). Further structural details and physical properties will be discussed in this presentation.



References

1) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997,** *97*, 1647.
2) S. Hiraoka, K. Harano, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2008**, *130*, 14368.
3) J. Rotzlera, M. Mayor, *Chem. Soc. Rev.* **2013**, *42*, 44.

種重合によるシート状ジケトピロロピロール集合体の構造制御と励起状態ダイナミクス

（名大院理[1]・阪大院基礎工[2]・名大 ITbM[3]）○大城宗一郎[1]・深谷菜摘[1]・五月女光[2]・藤本和宏[3]・柳井毅[1,3]・宮坂博[2]・山口茂弘[1,3]

Structural Control of Sheet-like Diketopyrrolopyrrole Aggregates by Seeded Polymerization and Their Excited-state Dynamics ([1]*Graduate School of Science, Nagoya University,* [2]*Graduate School of Engineering Science, Osaka University,* [3]*Institute of Transformative Bio-Molecules, Nagoya University*) ○Soichiro Ogi,[1] Natsumi Fukaya,[1] Hikaru Sotome,[2] Kazuhiro Fujimoto,[3] Takeshi Yanai,[1,3] Hiroshi Miyasaka,[2] Shigehiro Yamaguchi[1,3]

We have continued to study on thermodynamic and kinetic controls of supramolecular nanostructures composed of amphiphilic π-conjugated molecules in aqueous media and elucidation of their optical properties. For this purpose, we designed and synthesized amide-functionalized diketopyrrolopyrrole (DPP) derivatives bearing varied hydrophilic and hydrophobic groups. Experimental and computational studies revealed the effects of side chains on the self-assembly pathway and the π-stacking mode in the aggregated state. In addition, a transient absorption spectroscopy was applied to seeded-grown DPP aggregates with different sizes to elucidate their excited-state dynamics upon photo irradiation.
Keywords : Amphiphile; Diketopyrrolopyrrole; Seeded polymerization; Quantum chemical calculation; Excited-state dynamics

我々は，一重項分裂特性を示すジチエニルジケトピロロピロール (TDPP)集合体に着目し，水媒体中における TDPP 集合体の種（たね）重合と機能開拓に取り組んでいる[1]．本研究では，異なる親水性オリゴエチレングリコール（OEG）と疎水性アルキル鎖を導入した両新媒性 TDPP 色素について水媒体中における自己集合特性を評価した (Figure 1a).

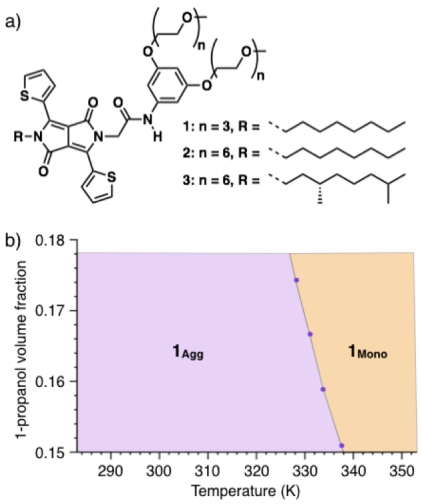


Figure 1. (a) Molecular structures of **1**, **2**, and **3**. (b) A phase diagram of **1** with the relationship between 1-propanol volume fraction and temperature.

スペクトル測定および顕微鏡観察により，オクチル基を有する **1**，**2** はシート状の J 会合体を形成することがわかった．一方，**3** はナノ粒子状集合体を形成した．これらのアルキル側鎖が分子配列様式に与える影響を，分子動力学計算と TD-DFT 計算を組み合わせた解析により明らかにした．溶媒および温度を変えて集合特性を評価した結果，**1** では会合状態 (**1**$_{Agg}$)から単分散状態 (**1**$_{Mono}$)へ直接転移したのに対し，長い OEG 側鎖を有する **2** では途中でナノ粒子状集合体の形成が確認された (Figure 1b)．この状態を速度論的かつ選択的に調製する条件を見出し，得られた準安定状態を利用する種重合法によりナノシートのサイズ制御を達成した．また，得られたナノシートの過渡吸収分光測定を行い，光励起ダイナミクスを評価した．

1) S. Ogi, N. Fukaya, Arifin, Y. Hijikata, S. Yamaguchi, *Chem. Eur. J.* **2019**, *25*, 7303.

二次元分子集合ネットワークにおけるナノスケール双晶

（明大院理工[1]・ルーバン大化[2]・明大理工[3]）山形 恭平[1]・前田 松祐[1]・Zeno Tessari[2]・Kunal S. Mali[2]・Steven De Feyter[2]・○田原 一邦[3]
Nanoscale Twinning of Molecular Self-Assembled Networks ([1]*Graduate School of Science and Technology, Meiji University*, [2]*Department of Chemistry, KU Leuven,* [3]*School of Science and Technology, Meiji University*) Kyohei Yamagata,[1] Matsuhiro Maeda,[1] Zeno Tessari,[2] Kunal S. Mali,[2] Steven De Feyter,[2] ○Kazukuni Tahara[3]

Twinning is often seen in three-dimensional crystals. In contrast, it has been observed on solid surfaces only in single-atomic layered, inorganic sheet materials and colloidal crystals. No observation exists on the twinning of molecular self-assembled networks formed at the solid surfaces. We herein report that an isosceles triangular molecule having four long alkoxy chains shows nanoscale conglomerate formation at the liquid/graphite interface, in which opposite chiral domains are continuously connected through coherent gray boundaries, as revealed by scanning tunneling microscopy. The crucial elements for the twinning in surface-confined molecular self-assemblies are also discussed.
Keywords : Two-dimensional Self-assembly; Scanning Tunneling Microscopy; Twining; Liquid/solid Interface; Two-dimensional Chirality

双晶は三次元結晶系では頻繁に見られるが、二次元の固体表面では単原子層無機シート材料やコロイド結晶での観察例に限られている。分子が形成する自己集合ネットワークでの双晶の観測はこれまでに報告されていない。双晶では、配向の異なる二つ以上の結晶が、ある結晶方位において軸または平面で接合されており、それらはキラルな関係となる。

今回我々は、有機溶媒とグラファイトとの界面での走査型トンネル顕微鏡（STM）観測にもとづき、長鎖アルコキシ基を四つ置換した二等辺三角形のデヒドロベンゾ[14]アヌレン誘導体が約 10 数 nm 幅のキラルなドメインを形成すること、このキラルなドメインはその対をなすキラルなドメインと不整合なく接合されて連続的に配置されることを明らかにした（図）。このようにキラリティーの異なるドメインが連続して接合された分子集合体の観測は我々の知る限り無く、このことは双晶との関連からも興味深い。この結果にもとづき、表面での分子性双晶の成因について考察した。

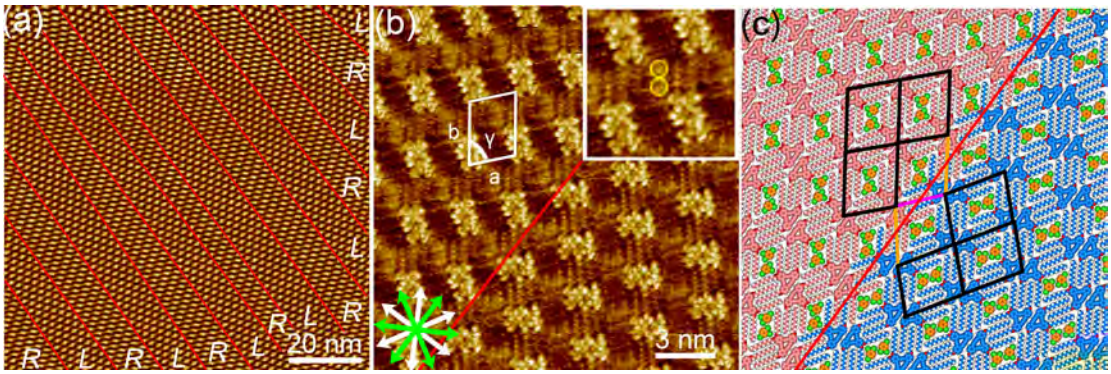


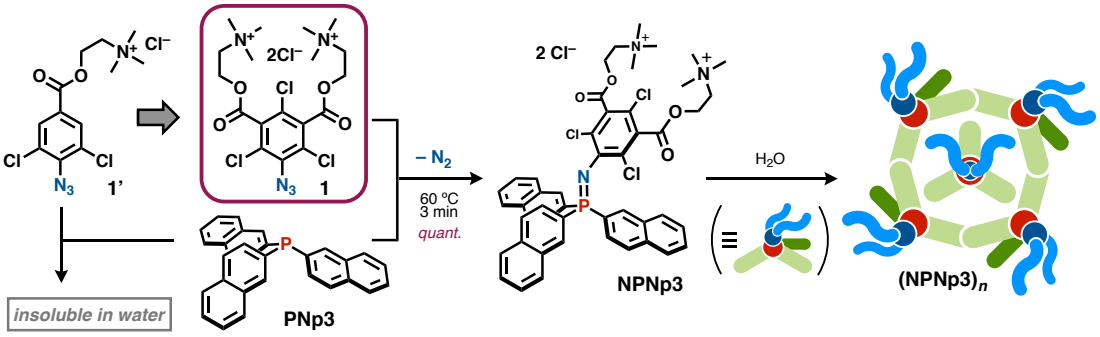
図. (a,b) キラルな二つのドメインから構成される構造の STM 画像。(c) ネットワークのモデル。キラリティーの異なるドメインを構成する分子を赤と青で示す。

シュタウディンガー反応を活用した高疎水性リン化合物の両親媒性分子化

（東工大理）○山科 雅裕・鈴木 颯・豊田 真司
Transformation of highly hydrophobic organophosphorus compounds into supramolecular amphiphiles through the Staudinger reaction (*School of Science, Tokyo Institute of Technology*) ○Masahiro Yamashina, Hayate Suzuki, Shinji Toyota

We previously reported the click-type synthetic method of amphiphiles through the Staudinger reaction[1] of hydrophilic azide and hydrophobic organophosphorous compounds.[2] Here we report the highly hydrophilic azide, which can transform highly hydrophobic organophosphorous compounds into supramolecular amphiphiles by simple mixing in organic solvent. The obtained amphiphiles were highly water-soluble and formed micelle-liked aggregates in water. Furthermore, hydrophobic dyes were encapsulated within spherical aggregates in water.
Keywords : amphiphile; Staudinger reaction; click chemistry; host-guest

我々はこれまでにシュタウディンガー反応[1]を活用し、親水性アジド **1'**と有機リン化合物の直接連結から、簡便に両親媒性分子を合成する手法を開発した[2]。しかしながら、**1'**は高疎水性のリン化合物を両親媒性分子に変換できない課題があった。本研究では高親水性アジド **1** を用い、様々な高疎水性リン化合物の両親媒性分子化を達成したので報告する。２つの親水基を有する **1** とトリナフチルホスフィン（**PNp3**）を有機溶媒中で加熱撹拌すると、両親媒性のアザイリド（**NPNp3**）が定量的に生成した。得られた **NPNp3** は高い水溶性と加水分解耐性を示し、水中で球状ミセルを形成することが判明した。さらに、水中で疎水性色素（Nilered）の内包にも成功し、その内包量は先行研究例と比較して 50 倍以上も向上することがわかった。同様に、4-*tert*-ブチルフェニルやビフェニルを含むリン化合物の両親媒性分子化も達成した。



References

[1] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635–646.
[2] M. Yamashina, H. Suzuki, N. Kishida, M. Yoshizawa, S. Toyota, *Angew. Chem. Int. Ed.* **2021**, *60*, 17915-17919.

Supramolecular Polymerization of Photo-Aromatizable Thiophene-Fused Chiral [4*n*]Annulene: Photofunctions and Chiral Superstructures

([1]*Grad. Sch. of Eng., The Univ. of Tokyo,* [2]*RIKEN CEMS,* [3]*PRESTO, JST*) ○Tsubasa Aoki,[1] Michihisa Ueda,[1] Takuzo Aida,[1,2] Yoshimitsu Itoh[1,3]

Keywords: Chirality; Supramolecular Polymers; Excited-State Aromaticity; [4*n*]Annulene, Thiophene

One of the long-standing challenges for polymer scientists is to control the polymerization reaction remotely. Historically, modulating the activity of polymer growing ends was employed to realize the remote control by light[1] or electric field.[2] On the other hand, activating/deactivating monomers themselves has been focused in supramolecular polymerization, where the polymerization capability of monomers is switched by a large conformational change of photochromic molecules upon photoirradiation.[3]

Here we report the conceptually new monomer to realize the first example of photo-suspendable supramolecular polymerization.[4] Such an unprecedented control of supramolecular polymerization was achieved by using a monomer comprising thiophene-fused chiral [4*n*]annulene derivative (**COT**), which exhibits high-speed flapping motion in their excited-states.[5,6] Detailed analyses based on absorption spectroscopy, theoretical model fitting, and DFT calculation revealed that the ring-inversion speed of each monomer during photoirradiation was accelerated in four orders of magnitude to suspend the nucleation-elongation process of polymerization. In the presentation, we will discuss the mechanism of the novel photo-suspendable behavior of this supramolecular polymer and its superstructures with anomalous optical activity.

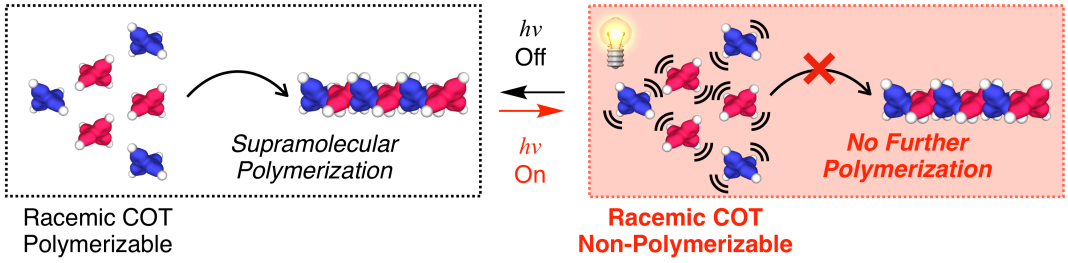


Fig. Photo-Suspendable Supramolecular Polymerization

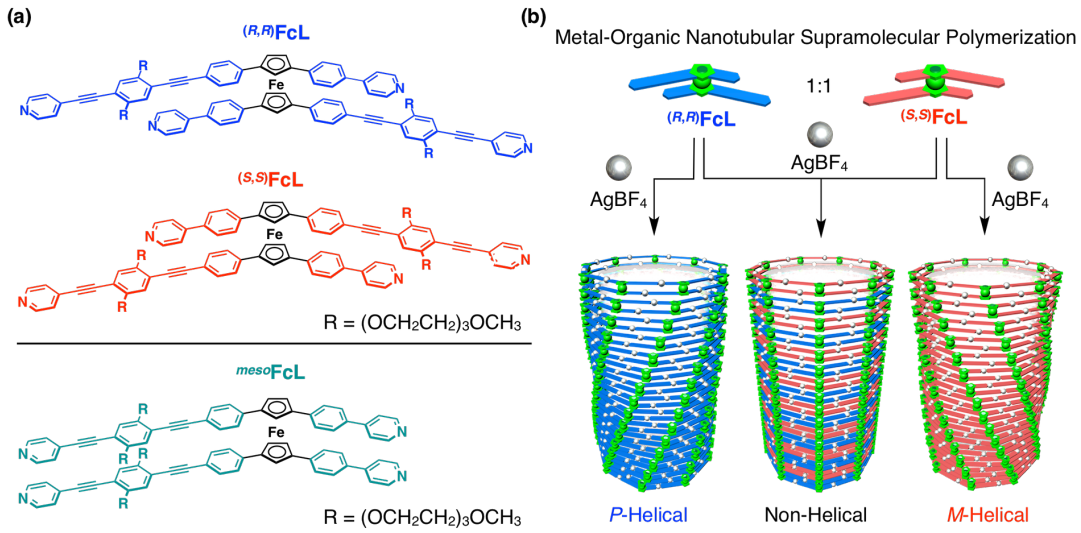
1) M. Kuroki *et al*., *JACS* **1987**, *109*, 4738. 2) A. Magenau *et al*., *Science* **2011**, *332*, 81. 3) a) M. Endo *et al*., *JACS* **2016**, *138*, 14347. b) S. Shin *et al*., *JACS* **2018**, *140*, 6088. 4) T. Aoki *et al*., *submitted*. 5) M. Ueda *et al*., *Nature Commun*. **2017**, *8*, 346. 6) M. Ueda, T. Aoki *et al*., *JACS* **2021**, *143*, 5121.

‘Spontaneous’ Pathway Selection in Stereochemical Supramolecular Copolymerization: Metal–Organic Nanotubes Assembled with a Planar Chiral Monomer

(1. The University of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. Tsukuba University, 4. High Energy Accelerator Research Organization) ○Yingluo Zhao[1,2], Hiroko Kawano, Hiroshi Yamagishi[3], Saya Otake[1], Yoshimitsu Itoh[1], Nobutaka Shimizu[4], Hubiao Huang[2], Takuzo Aida[1,2]

Keywords: Supramolecular Polymerization, Chiral Assembly, Metal–Organic Nanotubes

Helical metal–organic nanotubes have the potential of chiral separation and asymmetric synthesis.[1] However, the channel dimensions of the metal–organic nanotubes so far reported are not large enough to accommodate functional organic guests.[2] Here we report a one-handed helical (homochiral) metal–organic nanotube with an unprecedentedly large diameter of 9.1 nm by Ag^{+}-mediated supramolecular polymerization of **FcL**, a planar-chiral ferrocene-cored tetratopic pyridyl monomer. When its enantiomers $^{(R,R)}$**FcL** and $^{(S,S)}$**FcL** were allowed to copolymerize, we found an unusual dependency of the chiroptical feature of the produced copolymer on the enantiomeric excess of employed **FcL**. Furthermore, the obtained metal–organic nanotubes showed a large heterogeneity in diameter. Detailed investigations suggested the occurrence of a spontaneous pathway selection in the supramolecular copolymerization due to a non-monotonic consumption of the chiral monomer as a consequence of the preferential occurrence of a heterochiral chain growth.



1)E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116,* 13752.
2) J. Jia, L. Zheng, *Coord. Chem. Rev.* **2020**, *403*, 213083.

[K2-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Okano Kentaro, Yuji Nishii

Fri. Mar 25, 2022 2:00 PM - 3:40 PM K2 (Online Meeting)

[K2-3pm-01] Synthesis of Bisbenzofuropyrazines by Pd-catalyzed Intramolecular Double Cyclization and Their Room Temperature Phosphorescence Properties

○Shotaro Nakamura[1], Madoka Tsuboi[1], Taisei Taniguchi[1], Yuji Nishii[1], Norimitsu Tohnai[1], Masahiro Miura[2] (1. Osaka Univ., 2. ICS-OTRI, Osaka Univ.)

2:00 PM - 2:20 PM

[K2-3pm-02] Decaazapentacenes appended with electron-rich triphenylamine and phenanthrene units - their redox-coupled photophysical and self-assembling properties.

○Gary James Richards[1], Majid Tamboli[1], Keita Aoki[1], Jonathan P. Hill[2], Akiko Hori[1] (1. Shibaura Institute of Technology, 2. National Institute for Materials Science)

2:20 PM - 2:40 PM

[K2-3pm-03] 3-Position-selective Trifluoromethylation of Pyridine Rings Using Nucleophilic Activation based on 1,4-Reduction

○Ryuhei Muta[2], Takeru Torigoe[1,2], Yoichiro Kuninobu[1,2] (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

2:40 PM - 3:00 PM

[K2-3pm-04] Design, Synthesis, Properties of TEtraQuinoline (TEQ) and its Application as Zinc(II) Ion Fluorescence Sensor

○Wei Xu[1], Naoya Kumagai[1,2] (1. Keio University, 2. Institute of Microbial Chemistry)

3:00 PM - 3:20 PM

[K2-3pm-05] In Situ Transmetalation and Lewis Acid-Catalyzed Halogen Dance of *N*-Heteroaryllithiums

○Kengo Inoue[1], Yuxuan Feng[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)

3:20 PM - 3:40 PM

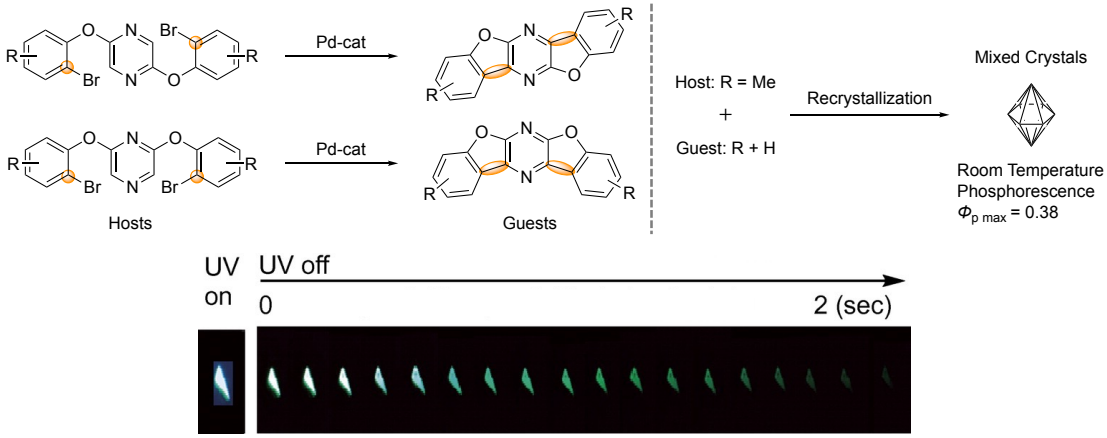
Synthesis of Bisbenzofuropyrazines by Pd-catalyzed Intramolecular Double Cyclization and Their Room Temperature Phosphorescence Properties

([1]*Graduate School of Engineering, Osaka University*, [2]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University*)
○Shotaro Nakamura,[1] Madoka Tsuboi,[1] Taisei Taniguchi,[1] Yuji Nishii,[1] Norimitsu Tohnai,[1] Masahiro Miura[2]

Keywords: Palladium Catalyst; C-H Activation; Room Temperature Phosphorescence; Mixed Crystal

Polycyclic heteroaromatic compounds have attracted much research interest because of their fundamentally interesting and even practically useful electrochemical and photophysical properties. In particular, luminescent materials have been actively studied for the application in bioimaging techniques, optoelectronic devices, etc. Recently, transition-metal-catalyzed intramolecular direct coupling reaction has been one of the effective methods for the construction of polycyclic heteroaromatic compounds. Based on this concept, we developed the synthetic method of linear-shaped bisbenzofuropyrazine derivatives and investigated their fluorescence as well as mechanochromic characteristics.[1)]

In this work, we have synthesized a series of linear-shaped and bent-shaped bisbenzofuropyrazine derivatives by palladium-catalyzed intramolecular double cyclization. Mixed crystals involving the coupling products (guest) and the corresponding uncyclized starting materials (host) were found to exhibit not only fluorescence, but also phosphorescence even under ambient conditions.[2)] Detailed effects of the mother skeletons and the substituents on their photoluminescent properties will be reported.



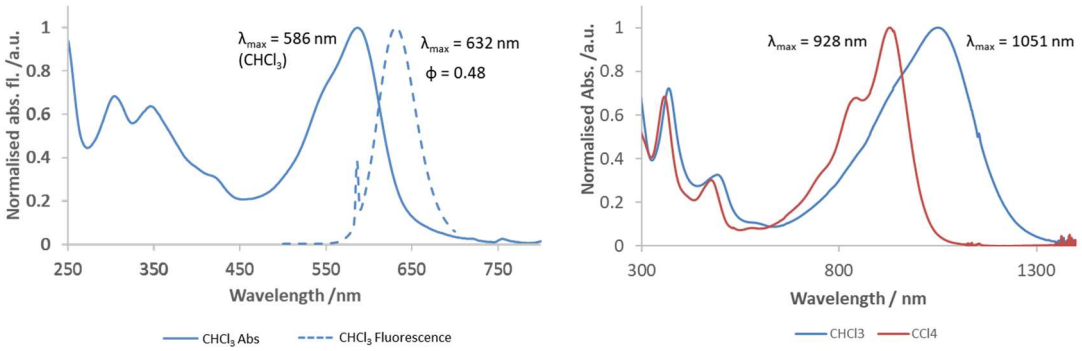
1) S. Nakamura, N. Tohnai, Y. Nishii, T. Hinoue, M. Miura, *ChemPhotoChem* **2019**, *3*, 46.
2) S. Nakamura, M. Tsuboi, T. Taniguchi, Y. Nishii, N. Tohnai, M. Miura, *Chem. Lett*. **2020**, *49*, 921.

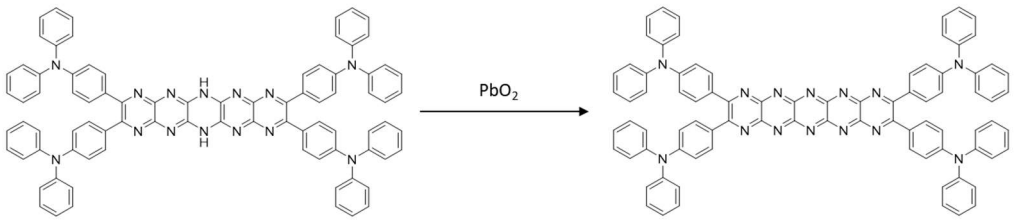
Decaazapentacenes Appended with Electron-Rich Triphenylamine and Phenanthrene Units - Their Redox-Coupled Photophysical and Self-Assembling Properties

([1]Department of Applied Chemistry, Shibaura Institute of Technology, [2]International Center for Materials Nanoarchitectonics, National Institute for Materials Science) ○ Gary James Richards[1], Majid Tamboli[1], Keita Aoki[1], Jonathan P. Hill[2], Akiko Hori[1]

Keywords: Pyrazinacenes, NIR Absorption, Redox, Photoluminescence

Pyrazinacenes[1] are analogues of classic acenes with apical CH groups replaced with nitrogen atoms. These stable compounds are currently being investigated for a variety of applications based on their photophysical and electronic propeties.[2,3] Here we describe decaazapentacenes appended with electron rich triphenylamine (TPA) or phenanthrene units. For TPA appended molecules a large shift in absorption from 586 nm in the reduced form to 1050 nm when oxidized is observed in chloroform solution. In this presentation, we will discuss the photophysical properties of these compounds including absorption and fluorescence properties of both oxidized and reduces species as well as their self-assembling behaviours.





1) a) G. J. Richards, J. P. Hill, *Acc. Chem. Res.* **2021**, *54*, 16, 3228-3240. b) G. J. Richards, J. P. Hill, N. K. Subbaiyan, F. D'Souza, P. A. Karr, M. R. J. Elsegood, S. J. Teat, T. Mori, K. Ariga, *J. Org. Chem.* **2009**, *74*, 8914-8923. 2) G. J. Richards, A. Cador, S. Yamada, A. Middleton, W. A. Webre, J. Labuta, P. A. Karr, K. Ariga, F. D'Souza, S. Kahlal, J.-F. Halet, J. P. Hill, *J. Am. Chem. Soc.* **2019**, *141*, 50, 19570-19574. 3) G. J. Richards, S. Ishihara, J. Labuta, D. Miklík, T. Mori, S. Yamada, K. Ariga, J. P. Hill, *J. Mater. Chem. C.* **2016**, *4*, 11514-11523.

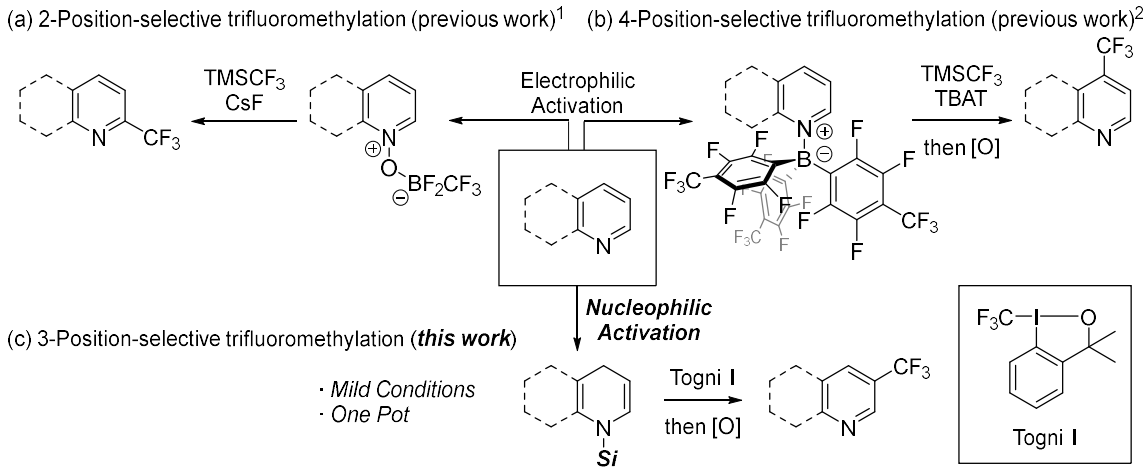
3-Position-selective Trifluoromethylation of Pyridine Rings Using Nucleophilic Activation based on 1,4-Reduction

([1]*Institute for Materials Chemistry and Engineering, Kyushu University*, [2]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Ryuhei Muta,[2] Takeru Torigoe,[1,2] Yoichiro Kuninobu[1,2]

Keywords: Trifluoromethylation; *N*-containing Heteroaromatic Compound; Regioselective; C-H Functionalization; Pyridine

Trifluoromethyl group plays an important role in drugs, agrochemicals, and organic functional materials. Therefore, the development of regioselective C(sp^2)-H trifluoromethylation is one of the most important research subjects in synthetic organic chemistry. In the case of pyridine derivatives, regioselective C(sp^2)-H trifluoromethylation at the electrophilic 2- and 4-positions has been developed.[1,2] On the other hand, the example of trifluoromethylation at the 3-position is still rare, and a new methodology to achieve 3-position-selective C(sp^2)-H trifluoromethylation of pyridines is highly desirable. We report herein an efficient method for 3-position-selective introduction of a trifluoromethyl group into pyridine rings via the conversion of the C(sp^2)-H bonds.

To achieve 3-position-selective trifluoromethylation, we focused on the reaction of electron-rich *N*-silyl enamine intermediates, which can be derived from pyridine rings and a hydrosilane, with Togni reagent and subsequent oxidation. As a result, 3-position-selective trifluoromethylated pyridine derivatives were obtained in good yields.



1) T. Nishida, H. Ida, Y. Kuninobu, M. Kanai, *Nat. Commun.* **2014**, *5*, 3387. 2) M. Nagase, Y. Kuninobu, M. Kanai, *J. Am. Chem. Soc.* **2016**, *138*, 6103-6106.

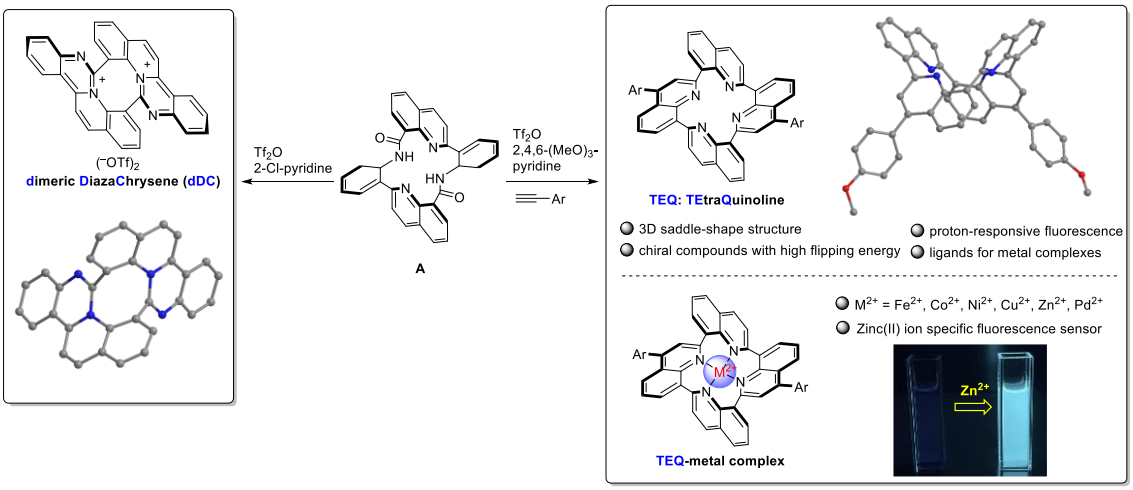
Design, Synthesis, Properties of TEtraQuinoline (TEQ) and Its Application as Zinc(II) Ion Fluorescence Sensor

(*Keio University*) ○Wei Xu, Naoya Kumagai

Keywords: Heterocyclic compounds, Fluorescence sensor, Quinoline, Metal complex

Quinoline is a nitrogen-embedded 10π aromatic planar unit which can be potentially used to build higher order functional molecular architectures. Based on our previous work of TriQuinoline (TQ), a novel quasi-flat head-to-tail quinoline trimer which showed unusual physical and chemical properties, we anticipated to construct a new and non-flat quinoline tetramer. Herein, we report the synthesis of TEtraQuinoline (TEQ) from quinoline containing diamide **A** and alkyne in the presence of Tf_2O/pyridine derivatives and its applications as a new tetradentate ligand as well as Zn^{2+} fluorescence sensor. The synthesis of dimeric DiazaChrysene (dDC) from **A** in the absence of alkyne will also be discussed.

C_2 symmetric substituted TEtraQuinoline (TEQ) has a unique saddle-shape structure and high flipping energy barrier to secure stereochemical integrity, which was experimentally supported by no erosion of enantiomeric excess even at 240 °C. In addition, TEtraQuinoline (TEQ) can be coordinated with various kinds of transition metal cations (e.g. Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, $Zn^{2+}$and Pd^{2+}) to form corresponding metal complexes, which were confirmed by X-ray crystallography. It also displays intriguing chemical and physical properties e.g. proton-responsive fluorescence and selective Zn^{2+} responsive fluorescence.



1) S. Adachi, M. Shibasaki, N. Kumagai, *Nat. Commun.* **2019**, *10*, 3820.

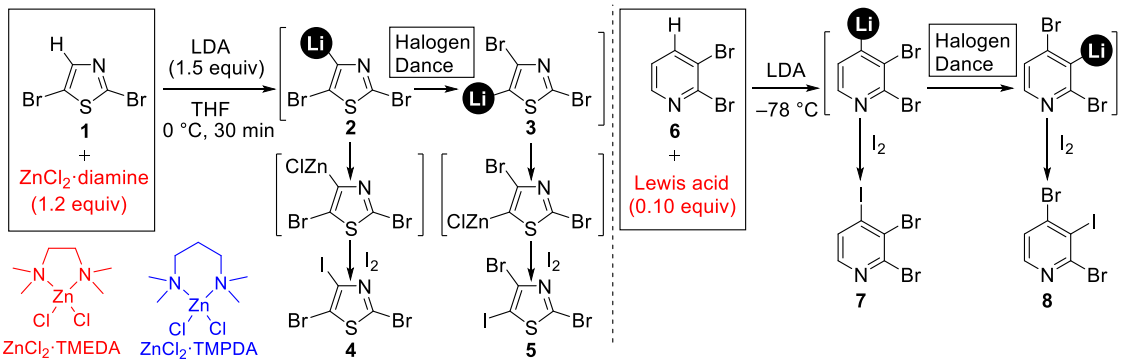
In Situ Transmetalation and Lewis Acid-Catalyzed Halogen Dance of *N*-Heteroaryllithiums

([1]*Department of Chemical Science and Engineering, Kobe University*, [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Kengo Inoue,[1] Yuxuan Feng,[1] Kentaro Okano,[1] Atsunori Mori[1,2]

Keywords: Azole; Pyridine; Halogen dance; In situ transmetalation; Lewis acid

Selective syntheses of multiple structural isomers are of importance to expand a chemical space. We have developed a new in situ transmetalation,[1] which enables selective trapping of unexplored *N*-heteroaryllithiums in halogen dance[2] to synthesize multiple structural isomers.

We achieved a method to use unexplored *N*-heteroaryllithiums by trapping transient azolyllithiums or facilitating halogen dance of pyridyllithiums. We focused on deprotolithiation of 2,5-dibromothiazole (**1**) with LDA which provided complex mixture at 0 °C. These results indicated that the possible organolithiums **2** and **3** were transient species. After screening of zinc halide diamine complexes to trap these organolithiums, $ZnCl_2$·TMEDA proved effective for the selective trapping of the first generated organolithium **2**, providing thiazole **4** in 89% yield after iodination. The use of $ZnCl_2$·TMPDA gave thiazole **5** in 72% yield, exclusively. The contrasting result was realized by a slower transmetalation of $ZnCl_2$·TMPDA. In contrast, halogen dance of lithiated pyridine **6** was sluggish, and subsequent iodination provided iodopyridines **7** and **8** in 53% and 12% yields, respectively. After optimization, a catalytic amount (0.10 equiv) of BF_3·OEt_2 drastically promoted halogen dance to afford pyridine **8** in 71% yield, whereas $B(C_6F_5)_3$ was less effective. We will discuss mechanistic insight into each reaction and the difference between bromoazoles and bromopyridines in halogen dance.



$ZnCl_2$·diamine	**4** [%][a]	**5** [%][a]
none	–[b]	–[b]
$ZnCl_2$·TMEDA	89[c]	–[b]
$ZnCl_2$·TMPDA	–[b]	72[c]

[a] ^{1}H NMR yield. [b] Not observed. [c] Isolated yield.

Lewis acid	**7** [%][a]	**8** [%][a]
none	53	12
BF_3·OEt_2	–[b]	71[c]
$B(C_6F_5)_3$	–[b]	31

[a] ^{1}H NMR yield. [b] Not observed. [c] Isolated yield.

1) a) Inoue, K.; Feng, Y.; Mori, A.; Okano, K. *Chem. Eur. J.* **2021**, *27*, 10267. b) Frischmuth, A.; Fernández, M.; Barl, N. M.; Achrainer, F.; Zipse, H.; Berionni, G.; Mayr, H.; Karaghiosoff, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2014**, *53*, 7928.
2) Schnürch, M.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046.

[K4-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Takashi Niwa, Takuya Kodama

Fri. Mar 25, 2022 2:20 PM - 3:40 PM K4 (Online Meeting)

[K4-3pm-02] Phosphine-Catalyzed Three-Component Coupling of Acyl Fluorides, Alkynes, and Silyl Nucleophiles

○Hayato Fujimoto[1], Momoka Kusano[1], Shisato Yamamura[1], Takuya Kodama[1], Mamoru Tobisu[1] （1. Osaka Univ.）

2:40 PM - 3:00 PM

[K4-3pm-03] Synthesis and Isolation of Phosphine-Stabilized Phosphenium Complexes with a [2]Ferrocenophane Framework

○Tianqing Zhang[1], Vladimir Ya. Lee[2], Shinobu Aoyagi[1], Takahiro Sasamori[2] （1. Graduate School of Science, Nagoya City University, 2. Faculty of Pure and Applied Sciences, University of Tsukuba）

3:00 PM - 3:20 PM

[K4-3pm-04] NUCLEOPHILIC SUBSTITUTION OF 2,2-BIS(ARYLTHIO)-4,4,6,6-TETRACHLOROCYCLOTRIPHOSPHAZENE WITH AMMONIA, PHENOXIDE, AND THIOPHENOXIDE

○Manabu KUROBOSHI[1], Hideo TANAKA[1], Ayako UENO[1], Ayane Kawano[1] （1. Okayama University）

3:20 PM - 3:40 PM

Phosphine-Catalyzed Three-Component Coupling of Acyl Fluorides, Alkynes, and Silyl Nucleophiles

(*Graduate School of Engineering, Osaka University*) ○Hayato Fujimoto, Momoka Kusano, Shisato Yamamura, Takuya Kodama, Mamoru Tobisu

Keywords: Phosphine-Catalyst; Acyl Fluoride; Silyl Nucleophile; Three-Component Coupling

Catalysis by late transition metal complexes is enabled by their facile reversible redox reactivity based on their partially filled d-orbitals. The realization of such redox catalysis by p-block elements is a challenging but rewarding research subject for the advancement in both fundamental main group chemistry and sustainable catalytic technology.[1] In this context, a P(III)/P(V) redox cycle that involves pentacoordinate phosphorane is a competent manifold for applications to catalytic reactions via a formal oxidative addition/transmetalation/reductive elimination sequence. Despite the promising stoichiometric redox reactivity of pentacoordinate organophosphorus compounds,[2] their use in catalytic processes have been primarily limited to oxygen transfer reactions that involve the interconversion between phosphines and phosphine oxides, except for relatively simple, prototypical transformation, such as hydrogenation[3] and reduction of allyl bromides.[4] In this presentation, we report on the phosphine-catalyzed three-component coupling of acyl fluorides, alkynes, and silyl nucleophiles.[5] The key to the success of the reaction is the formal transmetalation between pentacoordinate P(V) species (i.e., fluorophosphorane) and a silyl nucleophile.

1) a) T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608. b) C. Weetman, S. Inoue, *ChemCatChem* **2018**, *10*, 4213. c) R. L. Melen, *Science* **2019**, *363*, 479.

2) a) M. C. Hilton, X. Zhang, B. T. Boyle, J. V. Alegre-Requena, R. S. Paton, A. McNally, *Science* **2018**, *362*, 799. b) S. Lim, A. T. Radosevich, *J. Am. Chem. Soc.* **2020**, *142*, 16188.

3) N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330.

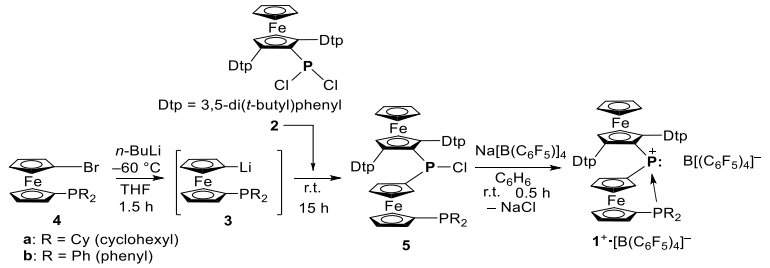
4) K. D. Reichl, N. L. Dunn, N. J. Fastuca, A. T. Radosevich, *J. Am. Chem. Soc.* **2015**, *137*, 5292.

5) H. Fujimoto, M. Kusano, T. Kodama, M. Tobisu, *J. Am. Chem. Soc.* **2021**, *143*, 18394.

Synthesis and Isolation of the Phosphine-Stabilized Phosphenium Complexes with a [2]Ferrocenophane Framework Compounds

([1]*Graduate School of Science, Nagoya City University*, [2]*Faculty of Pure and Applied Sciences, University of Tsukuba*)
○Tianqing Zhang,[1] Vladimir Ya. Lee,[2] Shinobu Aoyagi,[1] Takahiro Sasamori,[2]
Keywords: Phosphenium Ion; Ferrocenyl; [2]Ferrocenophane; Intramolecular Coordination; Low-coordinated Phosphorus Species

Recent studies on the low-coordinate species of the heavier main group elements, such as silylenes and germylenes, have shown that they can behave similarly to the transition metal complexes.[1] Phosphenium ions, derivatives of divalent phosphorus R_2P^+ that are isoelectronic to silylenes, are intrinsically highly reactive. In the most isolable phosphenium ions, the phosphorus center is thermodynamically stabilized by electron-donating substituents, which results in its electronic perturbation and decrease in the reactivity.[2] Moreover, phosphenium ion species can be stabilized kinetically by steric protection with bulky substituents.[3] Therefore, we used a bulky ferrocenyl group which can kinetically stabilize phosphenium ion towards self-oligomerization due to its high redox activity. As the second substituent at the phosphenium center, another ferrocenyl group containing stabilizing intramolecular-donor PR_2 substituent (R = cyclohexyl or phenyl) was applied to ensure the reversible thermodynamic stabilization. The bis(ferrocenyl)chlorophosphine precursor **5** was synthesized by the reaction of (ferrocenyl)dichlorophospine **2**[4] and ferrocenyllithium derivative **3** (formed by the lithiation of the bromide precursor **4**[5]). Oxidative dechlorination of **5** with $Na[B(C_6F_5)_4]$ produced the target $\mathbf{1}^+\cdot[B(C_6F_5)_4]^-$,[6] in which phosphenium center is stabilized by the intramolecular coordination of the PR_2 ligand. Particular structure and reactivity of phosphenium complexes $\mathbf{1}^+\cdot[B(C_6F_5)_4]^-$ are discussed on the basis of their spectral and computational data.



1) P. P. Power, *Nature*, **2010**, *463*, 171–177. 2) S. Weller, S. H. Schlindwein, C. M. Feil, *Organometallics*, **2019**, *38*, 4717–4725. 3) M. Olaru, S. Mebs, J. Beckmann, *Angew. Chem. Int. Ed.*, **2021**, *60*, 19133–19138. 4) T. Sasamori, T. Suzuki, N. Tokitoh, *Organometallics*, **2014**, *33*, 6696–6699. 5) a) W. Chen, F. Spindler, B. Pugin, *Angew. Chem. Int. Ed.*, **2013**, *52*, 8652–8656. b) I. R. Butler, R. L. Davies, *Synthesis*, **1996**, *11*, 1350–1354. 6) T. Zhang, V. Y. Lee, S. Morisako, S.Aoyagi, T.Sasamori, *Eur. J. Inorg. Chem.*, **2021**, 3988–3991.

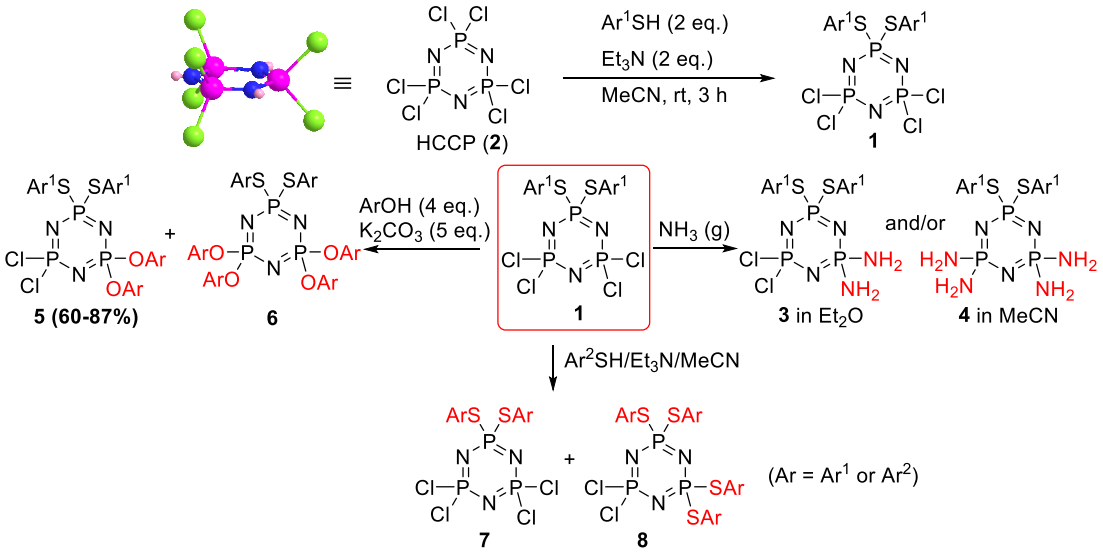
Nucleophilic Substitution of 2,2-Bis(arylthio)-4,4,6,6-tetrachlorocyclotriphosphazene with Ammonia, Phenoxide, and Thiophenoxide

(*Graduate School of Natural Science and Technology, Okayama University*)
○Manabu KUROBOSHI, Hideo TANAKA, Ayako UENO, Ayane KAWANO

Keywords：cyclotriphosphazene, nucleophilic substitution, arylthio, ammonia, phenol

Cyclotriphosphazene $N_3P_3R_6$ has a N_3P_3 ring in which N and P atoms are connected alternately and two substituents are placed on the each phosphorus atom upper and lower sides of the ring. If the substituents can be introduced regio- and stereoselectively, multi-functionalyzed materials can be developed easily. For this purpose, we investigated synthesis of cyclotriphosphazene having two kinds of nucleophiles starting from 2,2-bis(arylthio)-4,4,6,6-tetrachlorocyclotriphosphazene $N_3P_3Cl_4$-*gem*-$(Ar^1S)_2$ (**1**).

Nucleophilic substitution of hexachlorocyclotriphosphazene (HCCP, **2**) with Ar^1SH/Et_3N (2/2 eq.) in MeCN gave **1**. Aminolysis of **1** with gaseous ammonia gave *gem*-disubstituted $N_3P_3Cl_2$-*gem*-$(NH_2)_2$-*gem*-$(Ar^1S)_2$ (**3**) in Et_2O and tetrasubstituted $N_3P_3(NH_2)_4$-*gem*-$(Ar^1S)_2$ (**4**) in MeCN, respectively. The reaction of **1** with $ArOH/K_2CO_3$ (4/5 eq.) gave a mixture of *gem*-disubstituted $N_3P_3Cl_2$-*gem*-$(ArO)_2$-*gem*-$(ArS)_2$ (**5**) (60 – 87%) and tetrasubstituted $N_3P_3(ArO)_4$-*gem*-$(Ar^1S)_2$ (**6**) which ratio depended on the reaction solvent. On the other hand, in a reaction of **1** with another arylthiol Ar^2SH, ArS-groups were scrambled, and a mixture of disubstituted $N_3P_3Cl_4$-*gem*-$(ArS)_2$ (**7**) and tetrasubstituted N_3P_3-*gem*-$Cl_2(ArS)_4$ (Ar = Ar^1 and/or Ar^2) (**8**) was obtained. In all cases, no isomers having odd number of Cl and/or non-*gem*-substituted products were obtained.



[K307-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Yoshitaka Aramaki, Yasuhiro Yamashita, Takeshi Nanjo
Fri. Mar 25, 2022 1:00 PM - 3:40 PM K307 (Online Meeting)

[K307-3pm-01] Asymmetric Preparation of β-Amino-α-ketoacids by the Highly Stereoselective Mannich-type Addition for the Peptide Synthesis

○Yusuke Tokuhiro[1], Kosuke Yoshikawa[1], Sei Murayama[1], Takeshi Nanjo[1], Yoshiji Takemoto[1] （1. Grad. Sch. Pharm. Sci., Kyoto Univ.）

1:00 PM - 1:20 PM

[K307-3pm-02] Elucidation of the Stereocontrol Mechanism in Chiral Borate Catalysis toward Data-Driven Catalyst Design

○Fumito Ueoka[1], Shigeru Yamaguchi[2], Daisuke Uraguchi[3], Takashi Ooi[1] （1. Nagoya University, 2. RIKEN, 3. Hokkaido University）

1:20 PM - 1:40 PM

[K307-3pm-03] Development of Addition Reactions of Ketones with Alkenes through Photo-Induced Activation of Their Enolates

○Tsubasa Hirata[1], Yoshihiro Ogasawara[1], Yasuhiro Yamashita[1], Shu Kobayashi[1] （1. The University of Tokyo）

1:40 PM - 2:00 PM

[K307-3pm-04] Development of Catalytic Enantioselective Mannich Reactions of Esters and Effective Transformations of the Mannich Adducts toward Asymmetric Synthesis of β-Lactams

○Seiya Fushimi[1], Tomoya Kimura[1], Yasuhiro Yamashita[1], Shū Kobayashi[1] （1. The Univ. of Tokyo）

2:00 PM - 2:20 PM

[K307-3pm-05] Development of Bifunctional Cyclooctene Catalysts

○Tagui NAGANO[1], Keisuke ASANO[1], Seijiro MATSUBARA[1] （1. Kyoto Univ.）

2:20 PM - 2:40 PM

[K307-3pm-06] Tandem Enantioselective [3+2] and [4+2] Cycloaddition Reactions of *in situ*-generated *N*-allenoylpyrazoles induced by Chiral π–Cu(II) Catalyst

○Weiwei Guo[1], Masahiro Hori[1], Yoshihiro Ogura[1], Kazuki Nishimura[1] （1. Nagoya Univ.）

2:40 PM - 3:00 PM

[K307-3pm-07] Parallel kinetic resolution via bromocyclization reaction enabled by Lewis/Brø nsted base concerted catalysis of chiral bisphosphine oxide

○Ryo Hirokawa[1], Mamoru Ichikawa[1], Tatsunari Hisanaga[1], Yuji Kawato[1], Ryo Takita[2], Kohei Watanabe[2], Kenji Yamashita[1], Yoshitaka Hamashima[1] （1. School of Pharmaceutical Sciences, The Univ. of Shizuoka, 2. Graduate School of Pharmaceutical Sciences, The Univ. of Tokyo）

3:00 PM - 3:20 PM

[K307-3pm-08] 9-Fluorenol-Catalyzed Denitrative Radical Generation from Nitroalkanes

○Myuto Kashihara[1], Kohei Kosaka[1], Naoki Matsushita[1], Shunta Notsu[1], Ayumi Osawa[1], Yoshiaki Nakao[1] （1. Kyoto University）

3:20 PM - 3:40 PM

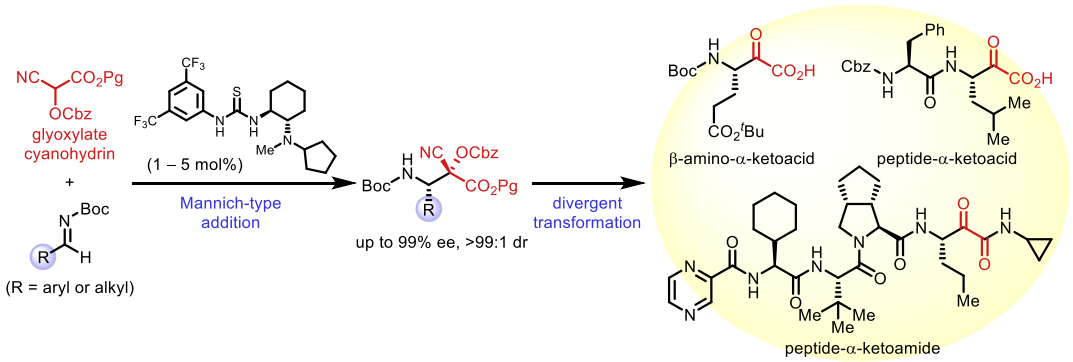
Asymmetric Preparation of β-Amino-α-ketoacids by the Highly Stereoselective Mannich-type Addition for the Peptide Synthesis

(*Graduate School of Pharmaceutical Sciences, Kyoto University*) ○Yusuke Tokuhiro, Kosuke Yoshikawa, Sei Murayama, Takeshi Nanjo, Yoshiji Takemoto

Keywords: β-Amino-α-ketoacid; Mannich Reaction; Organocatalysis; Asymmetric Synthesis; Peptide

β-Amino-α-ketoacids are important unnatural amino acids featured by an unique bioactivity and reactivity derived from a highly electrophilic carbonyl group at α-position. Despite of the broad utility of the motif, a reliable synthetic method of β-amino-α-ketoacids has been limited to oxidative homologation of α-amino acids based on chiral pool approach.[1] In addition, elongation of peptide chains for the synthesis of bioactive compounds requires an appropriate protection or late-stage installation of α-carbonyl group to avoid undesired reactivity.

In order to establish a novel approach providing a wide variety of β-amino-α-ketoacids and their peptide derivatives, we envisaged that asymmetric Mannich-type addition of glyoxylate cyanohydrin to imines would afford the equivalent of β-amino-α-ketoacids. As a result of catalyst screening, we found that sterically-tuned aminothiourea catalyst provided the desired adducts bearing variable residue including non-proteinogenic one with excellent enantio- and diastereoselectivity.[2,3] The asymmetric adducts are readily converted to β-amino-α-ketoacids by simple two-step operations. We also achieved the divergent transformation from the Mannich adducts to peptide-α-ketoacids and peptide-α-ketoamides by utilizing the cyanohydrin motif at α-position as an easily removable protecting group, and demonstrated the synthetic utility in decarboxylative peptide fragment coupling and preparation of α-ketoamide-containing pharmaceutical.



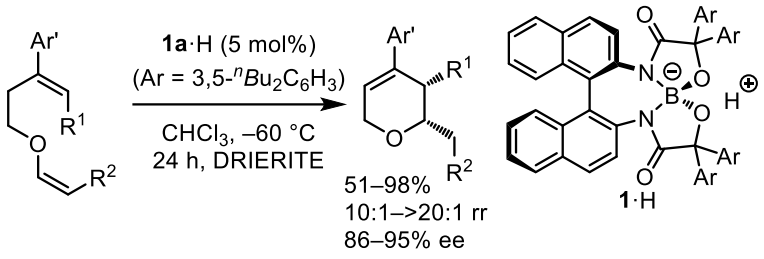
1) Ju, L.; Lippert, A. R.; Bode, J. W. *J. Am. Chem. Soc.* **2008**, *130*, 4253.
2) Nanjo, T.; Zhang, X.; Tokuhiro, Y.; Takemoto, Y. *ACS Catal.* **2019**, *9*, 10087.
3) Tokuhiro, Y.; Yoshikawa, K.; Murayama, S.; Nanjo, T.; Takemoto, Y. Manuscript in preparation.

Elucidation of the Stereocontrol Mechanism in Chiral Borate Catalysis toward Data-Driven Catalyst Design

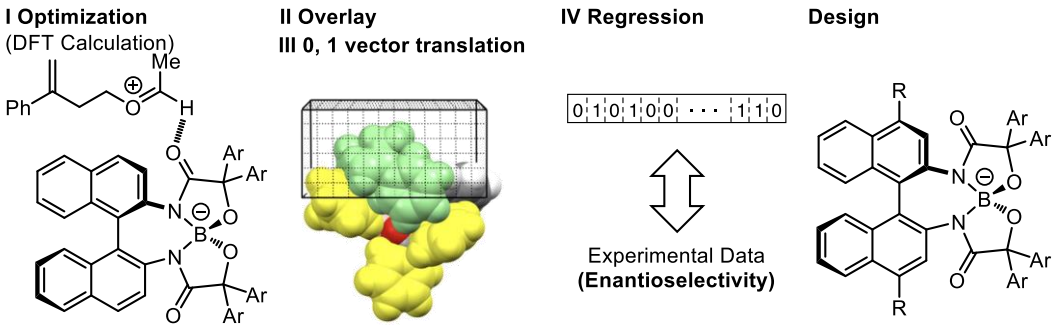
([1]*Graduate School of Engineering, Nagoya University*, [2]*WPI-ITbM, Nagoya University*, [3]*Riken*, [4]*Institute for Catalysis, Hokkaido University*) ○Fumito Ueoka,[1] Shigeru Yamaguchi,[3] Daisuke Uraguchi,[4] Takashi Ooi[1,2]

Keywords: Organocatalysis; Chemoinformatics; Chiral Anion Catalysis; Data-Driven

Prochiral cations are fundamental reactive species in organic synthesis and, upon reacting with nucleophiles, their enantiotopic faces should be precisely discriminated for obtaining stereochemically defined products. While ion-pairing with a chiral anion represents a direct and powerful approach for implementing this general mode of absolute stereocontrol, it is still underdeveloped because most of the existing chiral anions have innate nucleophilicity and could itself react with reactive cations. To address this intrinsic problem, we designed chiral borate **1** as a weakly nucleophilic anion and found that the corresponding hydrogen borate **1**·H acted as an effective catalyst for the Prins-type cyclization of vinyl ethers. The catalyst structure, specifically, structure of the aromatic substituents, was relevant to control the enantioselectivity, and exhaustive screening was necessary to identify the optimal catalyst.[1]



We reasoned that this is largely due to the fact that the borate ion does not have an apparent interaction with the intermediary generated prochiral oxonium ion, making it difficult to estimate the transition state structure. Therefore, we have visualized the important structural information by regression analysis using molecular fields derived from key intermediate structures, which has provided a new opportunity of catalyst design and structural optimization.



1) Uraguchi, D.; Ueoka, F.; Tanaka, N.; Kizu, T.; Takahashi, W.; Ooi, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 11456.

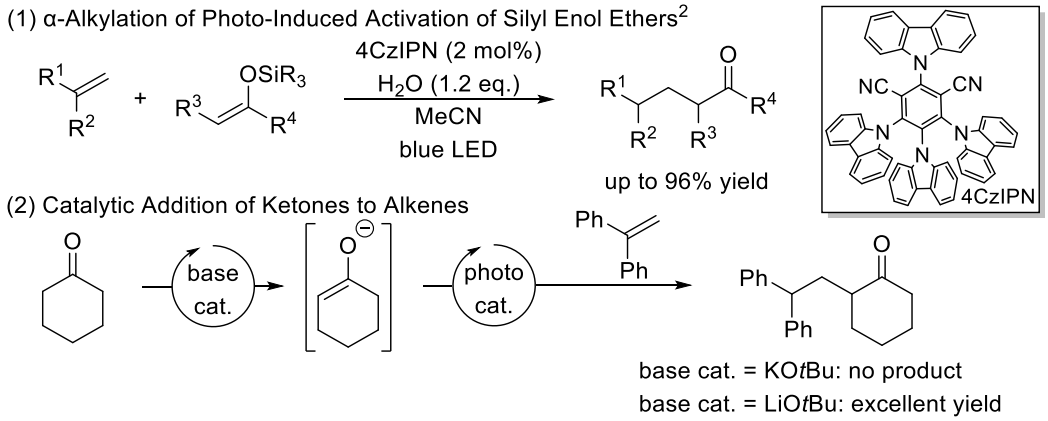
Development of Addition Reactions of Ketones with Alkenes through Photo-Induced Activation of Their Enolates

(School of Science, The Univ. of Tokyo) ○Tsubasa HIRATA, Yoshihiro OGASAWARA, Yasuhiro YAMASHITA, Shū KOBAYASHI

Keywords: Base Catalyst; Photoredox Catalyst; Ketone; Alkene; Visible Light

α-Alkylation of ketones is one of the most important and fundamental reactions in synthetic organic chemistry. Conventionally, alkyl halides have been employed as alkylating reagents such as Stork enamine alkylation. On the other hand, addition reactions are more efficient than substitution reactions because they proceed without any leaving groups. While enolates of ketones and their equivalents have been utilized to α-functionalization of ketones, their addition reactions with alkenes that afford alkylated ketones are quite slow due to low electrophilicity of alkenes. To overcome this problem, we focused on α-carbonyl radicals that can be prepared through single electron oxidation of enolates.

Initially, silyl enol ethers, which are precursors of α-carbonyl radicals, were employed.[1] In the presence of a photocatalyst, they reacted with alkenes under blue light irradiation to afford the alkylated ketones (eq. 1).[2] Furthermore, we figured out that approximate 1 equivalent of water to trap silyl cation *in situ* formed was effective to promote the reactions. To the best of our knowledge, this is the first example of intermolecular addition of silyl enol ethers to alkenes. For ideal atom economy, we challenged catalytic formation of enolates (eq. 2). Previously, our group reported Brønsted base-photo hybrid catalyst systems for alkylation of malonates with alkenes.[3] Based on this report, KO*t*Bu was employed as a base catalyst; however, the desired product was not obtained at all. This result was presumably caused by decomposition of the employed photocatalyst under strongly basic conditions. On the other hand, the desired reaction proceeded smoothly in the presence of LiO*t*Bu. Herein, we report our effort to develop photo-induced addition of ketones to alkenes in detail.



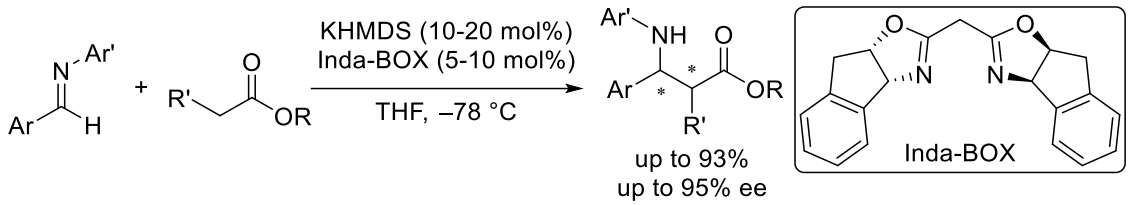
(1) Gassman, P. G. *et al. J. Org. Chem.* **1988**, *53*, 1097. (2) Kobayashi, S. *et al. Org. Lett.* **2021**, *23*, 5693. (3) Kobayashi, S. *et al. ACS Catal.* **2020**, *10*, 10546.

Development of Catalytic Enantioselective Mannich Reactions of Esters and Effective Transformations of the Mannich Adducts toward Asymmetric Synthesis of β-Lactams

(School of Science, The Univ. of Tokyo) ○ Seiya FUSHIMI, Tomoya KIMURA, Yasuhiro YAMASHITA, Shū KOBAYASHI

Keywords: Strong Base Catalysis; Asymmetric Mannich Reaction; Simple Ester; Oxidative *N*-aryl Bond Cleavage Reaction; *β*-Lactam Synthesis

Asymmetric Mannich reactions of esters are one of the important methods to synthesize optically active *β*-amino esters. These types of reactions have been conducted in the presence of chiral Lewis acid catalysts using ketene silyl acetals prepared from esters beforehand, or they have been conducted with stoichiometric amounts of strong Brønsted bases. However, catalytic asymmetric direct Mannich reactions using simple esters such as acetates, propionates, *etc.* without any electron-withdrawing groups at their *α*-positions have been difficult because *α*-hydrogen atoms of such esters are generally too weakly acidic to be promoted by typical chiral Lewis acid/Brønsted base catalysts. On the other hand, our group has developed catalytic direct addition reactions of simple esters by using a strong base catalyst, where strongly basic intermediates of the reactions were designed.[1,2] However, asymmetric addition reactions of simple esters have been still difficult and limited.[3] Recently we found that chiral potassium salts, formed by the deprotonation of chiral bisoxazoline (BOX) ligands and potassium hexamethyldisilazide (KHMDS), significantly accelerated Mannich reactions of weakly acidic simple amides.[4] Interestingly, this acceleration also occurred when simple esters were employed, and undesired side-reactions of acetates were suppressed. Here, we report the development of catalytic asymmetric direct Mannich reactions of simple esters with *N*-arylimines. The desired adducts were obtained in good yields with high enantioselectivities. Further transformations of the Mannich adducts were successfully performed.



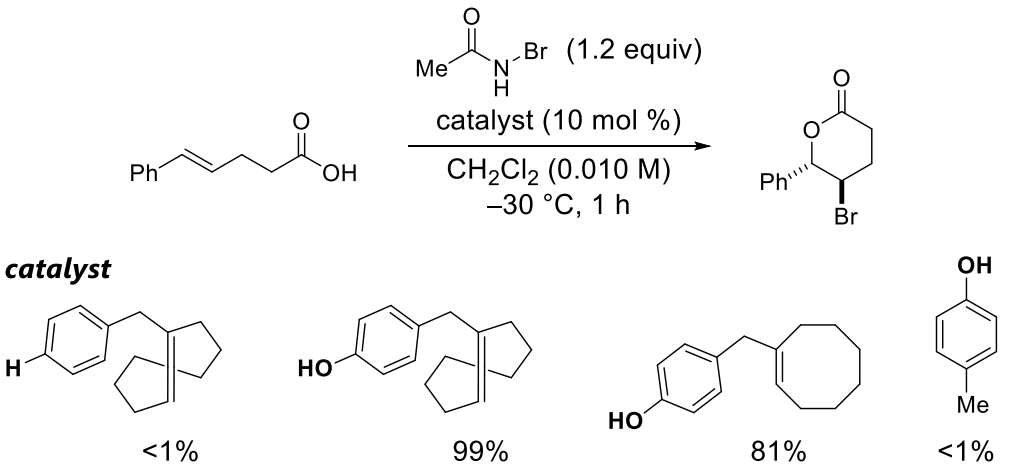
1) S. Kobayashi *et al. Org. Biomol. Chem.* **2012**, *10*, 5750. 2) S. Kobayashi. *et al. Synlett* **2021**, *32*, 14. 3) S. Kobayashi *et al. Org. Chem. Front*. **2016**, *3*, 124. 4) S. Kobayashi *et al. J. Am. Chem. Soc.* **2021**, *143*, 5598.

Development of Bifunctional Cyclooctene Catalysts

(*Graduate School of Engineering, Kyoto University*) ○Tagui Nagano, Keisuke Asano, Seijiro Matsubara

Keywords: Cyclooctene; Bifunctional Catalyst; Lewis Base Catalyst; Halogenation

Cyclooctenes have strained olefins, which serve as Lewis base catalysts.[1,2] We previously reported the *trans*-cyclooctene bearing a benzyl group has high catalytic activity in halolactonization reactions.[1] Currently, we are further trying to improve the catalytic performance of cyclooctene derivatives. In this study, we revealed remarkable substituent effects on the catalytic activity of benzyl group-substituted cyclooctenes, and bifunctional cyclooctene catalysts were developed. In particular, cyclooctenes bearing a phenol moiety exhibited high catalytic activity. It is also notable that the bifunctionality made not only *trans*-olefins but also *cis*-olefins catalytically active.



1) S. Einaru, K. Shitamichi, T. Nagano, A. Matsumoto, K. Asano, S. Matsubara, *Angew. Chem., Int. Ed.* **2018**, *57*, 13863.

2) T. Nagano, S. Einaru, K. Shitamichi, K. Asano, S. Matsubara, *Eur. J. Org. Chem.* **2020**, 7131.

キラルπ-銅(Ⅱ)触媒を用いる *in situ* で調製される *N*-アレノイルピラゾールのタンデム型エナンチオ選択的[3+2]及び[4+2]環化付加反応

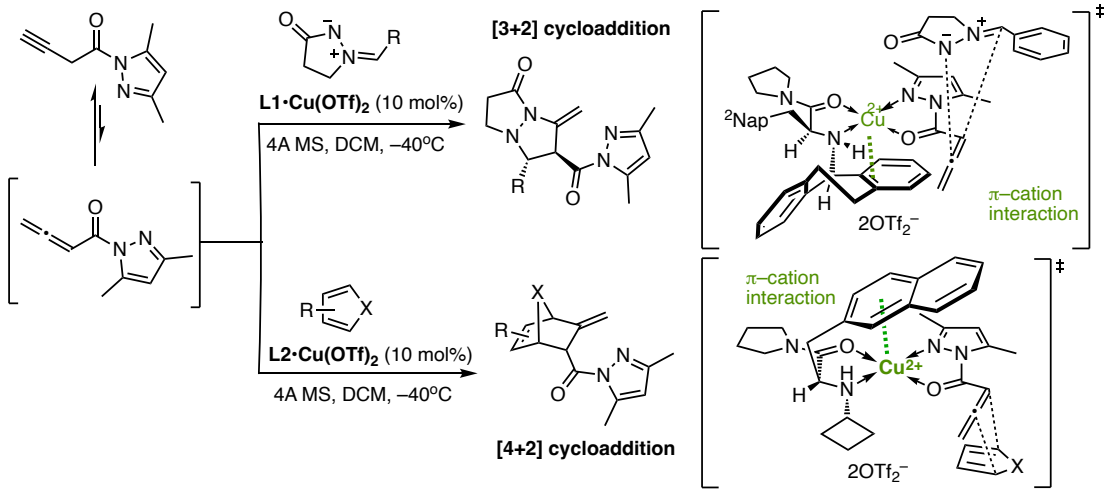
（名大院工）○郭 威威・堀 将寛・小倉 義浩・西村 和揮・石原 一彰

Tandem Enantioselective [3+2] and [4+2] Cycloaddition Reactions of *In Situ*-generated *N*-Allenoylpyrazoles Induced by Chiral π–Cu(II) Catalyst (*School of Engineering*, *Nagoya University*) ○Weiwei Guo, Masahiro Hori, Yoshihiro Ogura, Kazuki Nishimura, Kazuaki Ishihara

Allenes are important building blocks, and drivatation 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-catalyzed isomerization of *N*-(but-3-ynoyl)-3,5-dimethyl-1*H*-pyrazoles to *in situ* generate *N*-allenoylpyrazoles and successive enantioselective [3+2] and [4+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 allenoylpyrazoles.

Keywords: Isomerization; *N*-Allenoylpyrazole; Cycloaddition; Chiral π–Copper(II) Complex; Enantioselectivity

アレンは重要なビルディングブロックであり、その環化付加体の誘導はカルボン酸やヘテロ環構築の有力な方法となる。しかし、アレンの合成とそのエナンチオ選択的環化反応は未だ開発途上にある。今回、我々はキラル π–銅(II)錯体を触媒に用いる *N*-(3-ブチノイル)-3,5-ジメチル-1*H*-ピラゾールの異性化反応による *N*-アレノイルピラゾールの *in situ* 生成と、それに続くエナンチオ選択的[3+2]及び[4+2]環化付加反応を報告する。π–銅(II)相互作用によって構築される不斉環境は相当する生成物を高収率、高エナンチオ選択的に与えた。我々が知る限り、この成果はアレノイルピラゾールのLewis 酸触媒ワンポットエナンチオ選択的環化付加反応の最初の成功例である。



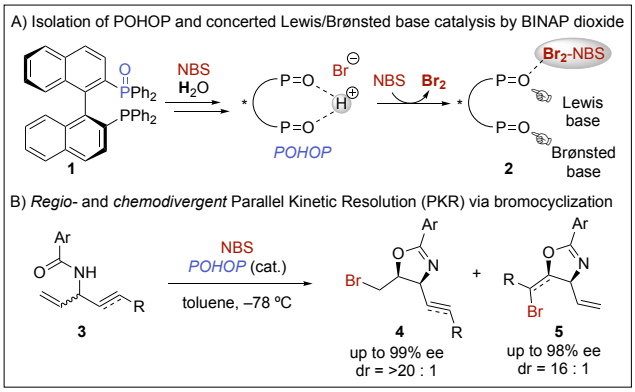
Parallel kinetic resolution via bromocyclization reaction enabled by Lewis/Brønsted base concerted catalysis of chiral bisphosphine oxide

([1]*School of Pharmaceutical Sciences, Univ. of Shizuoka*, [2]*Graduate School of Pharmaceutical Sciences, The Univ. of Tokyo*) ○Ryo Hirokawa[1], Mamoru Ichikawa[1], Tatsunari Hisanaga[1], Yuji Kawato[1], Ryo Takita[2], Kohei Watanabe[2], Kenji Yamashita[1], Yoshitaka Hamashima[1]

Keywords: Asymmetric synthesis; Organocatalyst; Halogenation; Parallel kinetic resolution; Phosphine oxide

We recently reported the desymmetrization of bisallylic amides through an enantioselective bromocyclization using (*S*)-BINAP monoxide (**1**).[1)] However, the catalytic role of **1** has remained unclear. Then, the catalytic mechanism of the above reactions was examined in detail by control experiments, X-ray analysis, NMR studies and CryoSpray MS analysis. **1** was transformed to a key catalyst precursor, proton-bridged bisphosphine oxide complex (POHOP). The thus-formed the POHOP further reacts with NBS to afford BINAP dioxide (**2**) and molecular bromine (Br_2) simultaneously. While the resulting Br_2 is activated by NBS to form a more reactive brominating reagent (Br_2-NBS), **2** serves as a bifunctional catalyst, acting as both a Lewis base that reacts with Br_2-NBS to form a chiral brominating agent, and also as a Brønsted base for activation of the substrate (Fig. A.).

By taking advantage of this novel concerted Lewis/Brønsted base catalysis, we have successfully developed *regiodivergent* parallel kinetic resolution (PKR) of racemic allylic amides (**3**) via bromocyclization (Fig. B.). When **3** having two different alkenes was employed as a substrate, both enantiomers of **3** were transformed into two distinct cyclization products (**4** and **5**) in a highly stereoselective manner via concurrent resolution processes. Moreover, the catalyst also promoted *chemodivergent* PKR of racemic ene-yne **3** to provide the corresponding products (**4** and **5**), regardless of the electronic difference between alkene and alkyne. To our knowledge, these are the first examples of *regio-* and *chemodivergent* PKRs via halocyclization.[2)]



1) Nagao, Y.; Hisanaga, T.; Egami, H.; Kawato, Y.; Hamashima, Y. *Chem. Eur. J.* **2017**, *23*, 16758.
2) Hirokawa, R.; Yamashita, K. and Hamashima, Y. *et al*., *Manuscript submitted*.

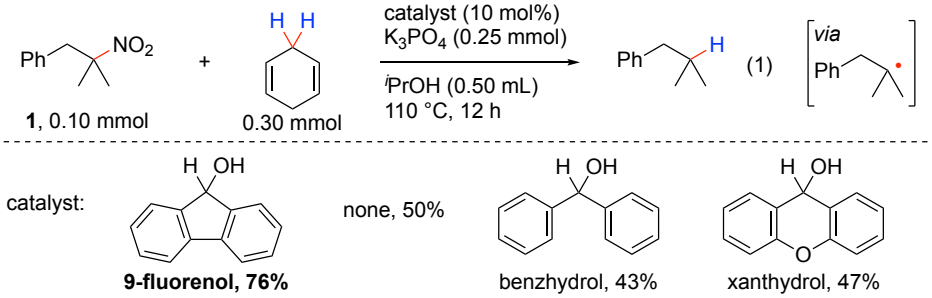
9-Fluorenol-Catalyzed Denitrative Radical Generation from Nitroalkanes

(*Graduate School of Engineering, Kyoto University*) ○Myuto Kashihara, Kohei Kosaka, Naoki Matsushita, Shunta Notsu, Ayumi Osawa, Yoshiaki Nakao

Keywords: Nitroalkane; Alkyl Radical; Single-Electron Transfer (SET); Denitration; the Giese Addition

Nitroalkanes are useful synthetic intermediates to construct complex molecules. Their highly acidic α-proton enables α-functionalization of them through deprotonation followed by the reaction with electrophiles under mild conditions.[1] Despite obvious benefits of denitrative transformations, however, reductive removal of a NO_2 group from nitroalkanes is still difficult because of competitive reduction of the NO_2 group itself to give nitroso compounds, hydroxylamines, and amines. Conventional denitration relied exclusively on the use of tin hydride (Bu_3SnH in most cases),[2] which is accompanied by some drawbacks such as toxicity of organotin compounds, trouble in separation, and functional group tolerance. In this context, a less toxic, inexpensive, easy-to-handle, and ideally catalytic substitute for tin hydride is of high demand to make the most of synthetic utility of nitroalkanes. We hypothesized that the C–NO_2 bond cleavage is induced by single-electron transfer (SET) from a non-oxophilic reductant, which is reluctant to abstract oxygen atom from radical anions of nitroalkanes.[3]

It turned out that the reductive denitration of nitroalkane **1** was efficiently catalyzed by 9-fluorenol in the presence of 1,4-cyclohexadiene as a hydrogen atom donor, K_3PO_4 as a base, and solvent ^{i}PrOH as a terminal reductant (eq. 1). Although the reaction gradually proceeded in the absence of 9-fluorenol, other alcohols such as benzhydrol and xanthydrol did not improve the efficiency, indicating the importance of a planar fluorene skeleton. The use of Michael acceptors instead of 1,4-cyclohexadiene afforded the corresponding alkylated products as well. The present system outperforms the conventional method using tin hydride in terms of cost, safety, and experimental manipulation.



1) a) Ballini, R.; Palmieri, A.; Righi, P. *Tetrahedron* **2007**, *63*, 12099. 2) Ono, N.; Miyake, H.; Kaji, A. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 121. 3) Guthrie, R. D.; Wesley, D. P.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5870.

[B104-3am] 16. Natural Products Chemistry, Chemical Biology

Chair: Taiki Kuribara, Takefumi Kuranaga

Fri. Mar 25, 2022 9:00 AM - 11:20 AM B104 (Online Meeting)

[B104-3am-01] Synthetic Study on Ellagitannins Using Stereocontrol of Sugar Conformations

○Shintaro Matsumoto[1], Kei Murakami[1], Shinnosuke Wakamori[2] （1. Kwansei Gakuin Univ., 2. Tokyo Univ. of Agriculture）

9:00 AM - 9:20 AM

[B104-3am-02] Synthetic Study of High-mannose-type Glycan Library Using Dendritic Glycosylation Strategy

○Ruchio Usui[1], Megumi Kabasawa[1], Tatsuya Hirukawa[1], Taiki Kuribara[1], Kiichiro Totani[1] （1. Seikei University）

9:20 AM - 9:40 AM

[B104-3am-03] Development of fluorescent-labeled glycan probe towards CRT

○Taiki Kuribara[1], Taiga Kojima[1], Keita Shibayama[1], Yoichi Takeda[2], Kiichiro Totani[1] （1. Seikei University, 2. Ritsumeikan University）

9:40 AM - 10:00 AM

[B104-3am-04] Design and evaluation of derivatives of a measles virus inhibitor peptide that inhibits conformational change of measles virus fusion protein

○Ziwei Gao[1], Jumpei Morimoto[1], Jiei Sasaki[2], Tateki Suzuki[2], Takao Hashiguchi[2], Shinsuke Sando[1] （1. Graduate School of Engineering, The University of Tokyo, 2. Institute for Frontier Life and Medical Sciences, Kyoto University）

10:00 AM - 10:20 AM

[B104-3am-05] Development of Macrocyclic Peptide Heterodimer as PPI Inhibitor against Immune Checkpoint CD47- SIRP α

○Jinxuan ZHAO[1], Yoji Murata[2], Naohiro Terasaka[1], Takashi Matozaki[2], Suga Hiroaki[1] （1. the University of Tokyo, 2. Kobe University）

10:20 AM - 10:40 AM

[B104-3am-06] *In vitro* selection of antibiotic peptides that inhibit the bacterial ribosome

○Rei Takahashi[1], Takayuki Katoh[1], Axel Innis[2], Hiroaki Suga[1] （1. The University of Tokyo Graduate School of Science Department of Chemistry, 2. Institut Européen de Chimie et Biologie (IECB)）

10:40 AM - 11:00 AM

[B104-3am-07] Total synthesis of acremoxanthone A, a naturally occurring heptacyclic aromatic polyketide

○Hiroshi Nakakohara[1], Yoichi Hirano, Hiroshi Takikawa[2], Keisuke Suzuki[3], Ken Ohmori[1] （1. Department of Chemistry, Tokyo Institute of Technology, 2. Graduate School of Pharmaceutical Sciences, Kyoto University, 3. Institute of Innovative Research, Tokyo Institute of Technology）

11:00 AM - 11:20 AM

糖の立体配座制御を利用したエラジタンニンの合成研究

（関西学院大理[1]・東農大生命[2]）○松本 慎太郎[1]・若森 晋之介[2]・村上 慧[1]
Synthetic Study on Ellagitannins Using Stereocontrol of Sugar Conformations ([1]*School of Science, Kwansei Gakuin University*, [2]*Faculty of Life Sciences, Tokyo University of Agriculture*) ○Shintaro Matsumoto,[1] Shinnosuke Wakamori,[2] Kei Murakami[1]

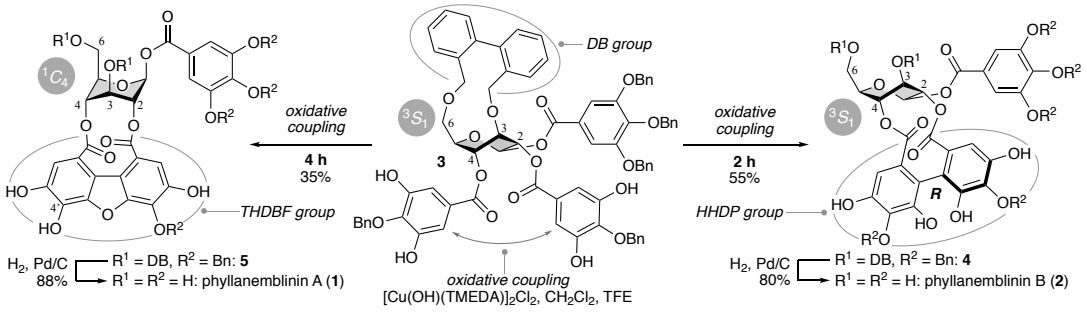
Phyllanemblinin A (**1**), a natural ellagitannin, contains a tetrahydroxydibenzofuranoyl (THDBF) group bridging between O-2 and O-4 of the D-glucose.[1] Phyllanemblinin B (**2**) is reported as the analogue also possesses an (*R*)-hexahydroxydiphenoyl (HHDP) group instead of the THDBF group.[1] For a unique feature of **1** and **2**, the functional groups differently deform their glucopyranose rings as $^1C_4$ and $^3S_1$ conformations, respectively.

In this study, we applied the stereocontrol method of the sugar conformations, resulting in the total syntheses of **1** and **2**. The introduction of the dibenzyl (DB) group bridging between O-3 and O-6 of **3** led the glucopyranose ring to $^3S_1$ conformation. The oxidative coupling[2] of **3** for 2 hours constructed the (*R*)-HHDP group to afford **4**. In contrast, extending the reaction time of the oxidative coupling provided **5** with the THDBF group formed unexpectedly. Hydrogenolysis of the DB and Bn groups of **4** and **5** synthesized **2** and **1**, respectively.

Keywords : natural product synthesis; polyphenols; ellagitannins; sugars; conformation

エラジタンニンである phyllanemblinin A（**1**）は，グルコースの 2,4 位酸素間にテトラヒドロキシジベンゾフラノイル（THDBF）基を有している [1]。その類縁体である phyllanemblinin B（**2**）は，THDBF 基の代わりに軸不斉が *R* のヘキサヒドロキシジフェノイル（HHDP）基を持つ [1]。官能基の種類によって，糖の立体配座が異なることが **1** と **2** の特徴であり，それぞれ $^1C_4$ と $^3S_1$ 配座である。

本研究では，架橋基を用いて糖の立体配座を制御し **1** と **2** の全合成を達成した。グルコースの 3,6 位酸素への架橋基（ジベンジル（DB）基）の導入によって，**3** の糖の立体配座を $^3S_1$ 配座に制御した。続いて，酸化的カップリング [2] を検討した。2 時間反応させると，(*R*)-HHDP 基が形成され **4** が得られた。その一方で，反応時間を 4 時間に延長すると，予想に反して THDBF 基を有する **5** を与えた。得られた **4** と **5** の架橋基と Bn 基を加水素分解によって除去し，**2** と **1** の全合成を達成した。



1) I. Kouno, Y. J. Zhang, T. Abe, T. Tanaka, C. R. Yang, *J. Nat. Prod.* **2001**, *64*, 1527.
2) S. Matsumoto, S. Wakamori, K. Nishii, T. Tanaka, H. Yamada, *Synlett* **2020**, *31*, 1389.

樹状型グリコシル化法を利用した高マンノース型糖鎖ライブラリーの合成研究

（成蹊大理工）○碓井 瑠智雄・樺澤 恵・比留川 達也・栗原 大輝・戸谷 希一郎

Synthetic Study of High-mannose-type Glycan Library Using Dendritic Glycosylation Strategy

(*Department of Materials and Life Science, Seikei University*) ○Ruchio Usui, Megumi Kabasawa, Tatsuya Hirukawa, Taiki Kabasawa, Kiichiro Totani

Various oligomannose plays important role in glycoprotein quality control. For rapid access to the biological work, we developed the facile methodology called dendritic glycosylation to assist the branched synthesis of various high-mannose-type glycans. Our Previous study achieved the model synthesis of various oligomannose branches by suspension of the regioselective branch expansion called dendritic glycosylation.

In this study, we evaluated the application of the dendritic glycosylation aimed to obtain the full set of natural oligomannose libraries. In the first steps, we obtained $Man_3GlcNAc_2$ (M3)-type tri-OH accepter by bottom-up chemical synthesis (Figure 1). Next, we synthesized $Man_6GlcNAc_2$ (M6) structure by the first dendritic glycosylation elongating triple branches. In the second dendritic glycosylation starting from the deprotected M6-type tri-OH acceptor, we estimated the intentional interruption of the glycosylation to yield eight types of oligomannose branches at the same units.

Keywords : Dendritic Glycosylation; High-mannose-type Glycans; Glycan Library Synthesis

多様な高マンノース型糖鎖は、小胞体糖タンパク質品質管理などの生体内機構に幅広く関与する。我々は研究試料である高マンノース型糖鎖の効率的供給のため、多様な高マンノース型糖鎖の分岐鎖骨格の効率的な合成を志向した樹状型グリコシル化法を開発した。先行研究において、我々は標的糖鎖の部分構造の合成を検討し、樹状型グリコシル化法の最適条件を決定した。

本研究では、天然の高マンノース型糖鎖ライブラリーの構築において、樹状型グリコシル化法を応用した例を紹介する（図 1）。我々は、化学合成で得られた $Man_3GlcNAc_2$（M3）型の tri-OH アクセプターに対して樹状型グリコシル化を適用し、3 本の分岐鎖が伸長した $Man_6GlcNAc_2$（M6）を合成した。さらに、脱保護された M6 型 tri-OH アクセプターに対する樹枝状グリコシル化法を意図的に反応中断し、同一系内で 8 種類の高マンノース型糖鎖の合成を検討した。

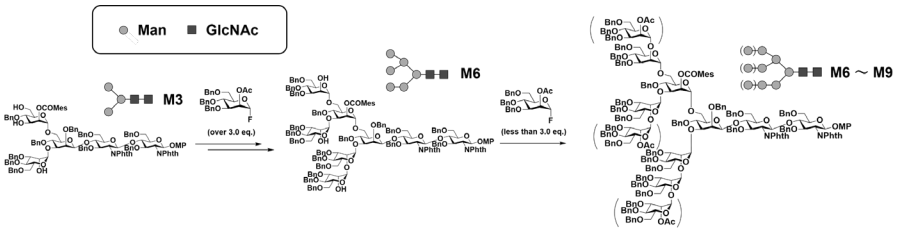


Figure 1. Synthesis of high-mannose glycan library by dendritic glycosylation

CRT 選択的蛍光糖鎖プローブの開発研究

(成蹊大理工[1]・立命館大生命科学[2]) ○栗原 大輝[1]・児島 大河[1]・柴山 佳大[1]・武田 陽一[2]・戸谷 希一郎[1]
Development of Fluorescent-labeled Glycan Probes towards CRT ([1]*Department of Materials and Life Science, Seikei University*, [2]*College of Life Science, Ritsumeikan University*)
○Taiki Kuribara,[1] Taiga Kojima,[1] Keita Shibayama,[1] Yoichi Takeda,[2] Kiichiro Totani[1]

Calreticulin (CRT) is a lectin chaperone which is assisting glycoprotein folding. It have been reported that the CRT levels in cancer cells are correlated with cancer proliferation[1)]. In addition, recent studies revealed cell surface exposed CRT acts as an eat me signal, inducing immunogenic cell death[2)]. Considering to the different functions in intra- and/or extracellular CRT, CRT-binding probe contributes to elucidating CRT functions in cancer cells.

In this study, we synthesized CRT-binding compound which has glycan moiety and a hydrophobic compound (Fmoc). The compound showed 1000-fold higher affinity than glycan alone toward CRT by hybrid binding concept. We also report synthesis of fluorescent-labeled CRT-binding compound and preliminary data of interaction analysis.

Keywords : Calreticulin; hybrid binding concept; Fluorescent-labeled CRT glycan probe

カルレティキュリン (CRT) は糖鎖認識部位およびシャペロン部位を併せもち、小胞体にて糖タンパク質フォールディングの促進に関与するレクチン様分子シャペロンである。興味深いことに、ある種のがん細胞では、小胞体内 CRT 発現量と細胞増殖の間に相関が示されている[1)]。また、がん細胞の抗がん剤処理によって細胞内 CRT が細胞表面に露出され、これをシグナルとした免疫原性細胞死が報告されている[2)]。これらに鑑みると、CRT 選択的な標識化合物の開発はがん細胞における相反する CRT 機能の解明に寄与すると期待される。

そこで本研究では、 CRT 認識糖鎖および疎水性アグリコンとして Fmoc を適切なリンカーで連結した化合物を合成した。本化合物は、CRT に対して認識糖鎖をリガンドとした際と比較して 1000 倍の親和性を示し、我々はハイブリッド結合型 CRT 糖鎖プローブの開発に成功した。本発表では、環境応答性色素であるダンシル基を連結した蛍光型 CRT 選択的糖鎖プローブ (図 1) の合成と本プローブを用いた CRT との相互作用解析の初期的な知見を併せて報告する予定である。

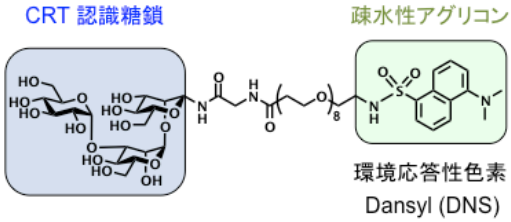


図 1. ハイブリッド結合型 CRT 選択的蛍光糖鎖プローブ

1) Y.C. Lu *et al. BioMed Res. Int.* **2015**, 526524. 2) M. Obeid *et al. Nat. Med.* **2007**, *13*, 54-61.

麻疹ウイルス膜融合タンパク質の変形阻害ペプチドの構造展開と阻害能評価

(東大院工[1]・京大ウイルス再生研[2]) ○高 紫維[1]・森本 淳平[1]・佐々木 慈英[2]・鈴木 干城[2]・橋口 隆生[2]・山東 信介[1]

Design and Evaluation of Derivatives of a Measles Virus Inhibitor Peptide that Inhibits Conformational Change of Measles Virus Fusion Protein ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute for Frontier Life and Medical Sciences, Kyoto University*) ○Ziwei Gao,[1] Jumpei Morimoto,[1] Jiei Sasaki,[2] Tateki Suzuki,[2] Takao Hashiguchi,[2] Shinsuke Sando[1]

MeV-F is a fusion protein located on measles virus (MeV) envelope. MeV-F undergoes a conformational change to fuse host cell membrane and virus envelope, which leads to virus infection. FIP (fusion inhibitor peptide)[1] binds to a hydrophobic pocket located at the region connecting the head and the stalk of MeV-F's pre-fusion state and stabilizes the pre-fusion state, which inhibits membrane fusion. FIP is potentially useful as an orally available drug candidate with small side effects because it binds to a protein unique to MeV and the molecular weight is small. However, the inhibitory activity of FIP is relatively weak and needs to be improved.

In this study, we optimized the chemical structure of FIP based on the co-crystal structure of MeV-F complexed with FIP[2] to design a membrane fusion inhibitor that has an improved inhibitory activity. In this presentation, the results of evaluation of the inhibitory activity and physical properties of designed FIP derivatives are shown.

Keywords : Peptide; Structure optimization; Measles virus; Membrane fusion inhibitor

MeV-Fは麻疹ウイルス (MeV) のエンベロープ上に存在する膜融合タンパク質である。MeV-Fは構造変化することにより、宿主細胞膜とウイルスエンベロープを融合し、感染を引き起こす。FIP[1]と呼ばれるペプチドは、MeV-Fの融合前状態の頭部と軸部分の間に存在する疎水ポケットに結合し、この構造変化を阻害することによりMeVの感染を阻害できる。FIPは、MeV特有のタンパク質を標的とすることと、分子量が小さいために、副作用の少ない経口投与薬候補として期待できる。しかしながら、FIPの膜融合阻害能は比較的弱く、改善する必要がある。

本研究では、より強力な膜融合阻害剤の創出を目標とし、MeV-FのFIPとの共結晶構造[2]に基づき、FIPの構造展開を行った。本発表では、設計したFIP誘導体の阻害活性評価の結果と物性評価の結果について示す。

1) Specific inhibition of paramyxovirus and myxovirus replication by oligopeptides with amino acid sequences similar to those at the N-Termini of the F_1 or HA_2 viral polypeptides. C. D. Richardson, A. Scheid, P. W. Choppin, *Virology* **1980**, *105*, 205.

2) Structures of the prefusion form of measles virus fusion protein in complex with inhibitors. T. Hashiguchi, Y. Fukuda, R. Matsuoka, D. Kuroda, M. Kubota, Y. Shirogane, S. Watanabe, K. Tsumoto, D. Kohda, R. K. Plemper, Y. Yanagi, *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 2496.

Development of Macrocyclic Peptide Heterodimer as PPI Inhibitor against Immune Checkpoint CD47- SIRPα

([1]*Graduate School of Science, The University of Tokyo,* [2]*Kobe University, Graduate School of Medicine*) ○Jinxuan ZHAO[1], Yoji Murata[2], Naohiro Terasaka[1], Takashi Matozaki[2], Suga Hiroaki[1]

Keywords: Immune Checkpoint Inhibitor, Protein-protein Interaction, SIRP-alpha-CD47, mRNA display

Tumor cell can disguise itself as a normal cell and thus escapes from the phagocytosis by macrophage through the protein-protein interaction (PPI) between immune checkpoint CD47-SIRPα. We recently developed a macrocyclic peptide D4-2 as a specific target binder to SIRPα by Random nonstandard Peptides Integrated Discovery (RaPID). The following *in vitro* and *in vivo* assays confirmed that D4-2 allosterically inhibited the CD47 from binding to SIRPα, raised the phagocytosis ratio and control the tumor size[1]. It has been shown that dimerization of macrocyclic peptides could be effective in strengthening macrocyclic peptides' binding affinity[2] and thus promote the curative effect. Here, we report the improvement of CD47-SIRPα PPI inhibitor D4-2 by hetero-dimerizing D4-2 with another binder. To get another SIRPα binding peptide, as the dimerization partner of D4-2, the RaPID selection against D4-2-SIRPα complex was performed. The discovered D4-2-SIRPα complex binders were then 50% mutated and adapted into SIRPα binders by additional RaPID selection. The new candidates' binding affinity was measured by surface plasma resonance (SPR), which revealed a new SIRPα binder mD2r3. Then mD2r3 was linked with D4-2 by a polyethylene glycol (PEG) linker (Fig. 1c). Compared with the D4-2 monomer, the SPR result of PEG_2, PEG_5, and PEG_{11} linker showed a considerable improvement in off-rate (k_{off}) and overall dissociation constant (K_D). The following *in vitro* CD47 inhibiting assay and phagocytosis assay confirmed the heterodimer linked with PEG_{11} had better activity inhibiting the PPI between CD47 and SIRPα and inducing macrophages' attack toward tumor cells than monomeric D4-2 peptide (Fig. 1d). In the presentation, due to the potential patent filing, the sequence identities will not be shown.

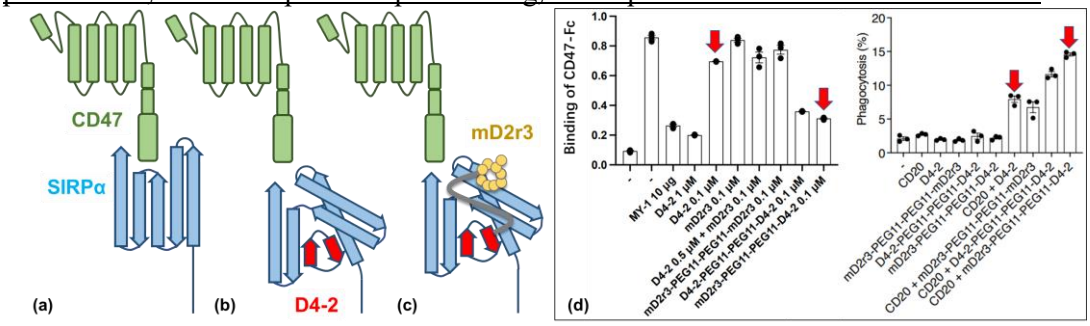


Figure 1 a) CD47-SIRPα complex. b) D4-2 as an allosteric inhibitor. c) D4-2-mD2r3 heterodimer. d) Dimerization with mD2r3 improved the function of D4-2 monomer.

1) Hazama, D., et al., *Cell Chemical Biology*, **2020**, 27, 1181–1191. 2) Bashiruddin, N., et al., *Bioconjugate Chemistry*, **2018**, 29(6), pp.1847-1851.

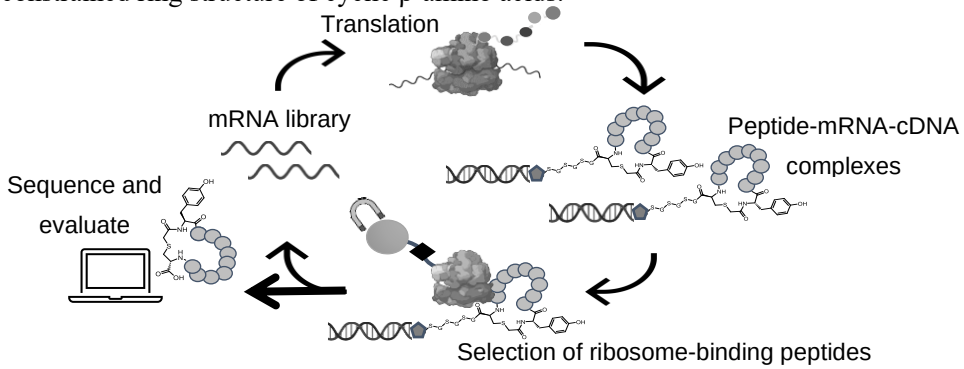
In vitro selection of antibiotic peptides that inhibit the bacterial ribosome

(*[1]The University of Tokyo Graduate School of Science Department of Chemistry, [2]Institut Européen de Chimie et Biologie (IECB)*) ○Rei Takahashi,[1] Takayuki Katoh,[1] Axel Innis,[2] Hiroaki Suga[1]

Keywords: Molecular biology; Drug discovery; Antibiotics; Peptides; Bacterial ribosome

The ribosome is a complex molecule found in living organisms responsible for translating genetic information encoded in mRNA into proteins. Although ribosomes exist in both prokaryotes and eukaryotes, there are structural differences that can be ideal target locations for an effective antibiotic – thus, the bacterial ribosome is a target for more than half of the antibiotics available today.[1] Traditional discovery platforms heavily screened soil-derived antibiotics which led to the discovery of numerous antibiotics used in clinical settings today; however, this once successful platform is now unreliable as the speed of resistance is much faster than the discovery of new antibiotics classes.[1] This research explores *de novo* discovery of macrocyclic peptides as a new platform for antibiotic discovery and development by utilizing an mRNA display-based method called the Random nonstandard Peptide Integrated Discovery (RaPID) that can achieve up to a 10^{13} chemical diversity.

To conduct RaPID screening, a peptide library with ClAc-L/D-Tyr at the N-terminus, a repeat of six to fifteen random α-amino acid region, and a free cysteine at the C-terminus were constructed. Macrocyclization was achieved through nucleophilic substitution of the thiol of a free cysteine residue with the initiator chloroacetyl moiety. Several rounds of RaPID screening were conducted to enrich the diverse libraries to identify the high-affinity ribosome-peptide binders. Through the biochemical evaluation of candidate antibiotic peptides, five peptides were found that exhibited successful binding and inhibitory activity. To explore more potent antibiotic peptides, we are currently attempting to incorporate cyclic β-amino acids as previous work from our lab has shown increased binding affinity to the target of interest due to the constrained ring structure of cyclic β-amino acids.[2]



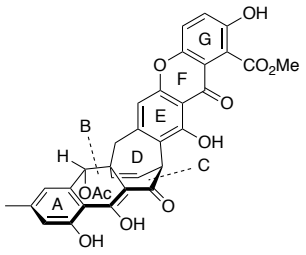
[1] Lin, J.; Zhou, D.; Steitz, T. A.; Polikanov, Y. S.; Gagnon, M. G. *Annu. Rev. Biochem.* **2018**, *87* (1), 451–478. [2] Katoh, T., Sengoku, T., Hirata, K. *et al. Nat. Chem.* **2020,** *12,* 1081–1088.

Total synthesis of acremoxanthone A, a naturally occurring heptacyclic aromatic polyketide

([1]*Department of Chemistry, Tokyo Institute of Technology*, [2]*Graduate School of Pharmaceutical Sciences, Kyoto University,* [3]*Institute of Innovative Research, Tokyo Institute of Technology*) ○Hiroshi Nakakohara[1], Yoichi Hirano, Hiroshi Takikawa[2], Keisuke Suzuki[3], Ken Ohmori[1]

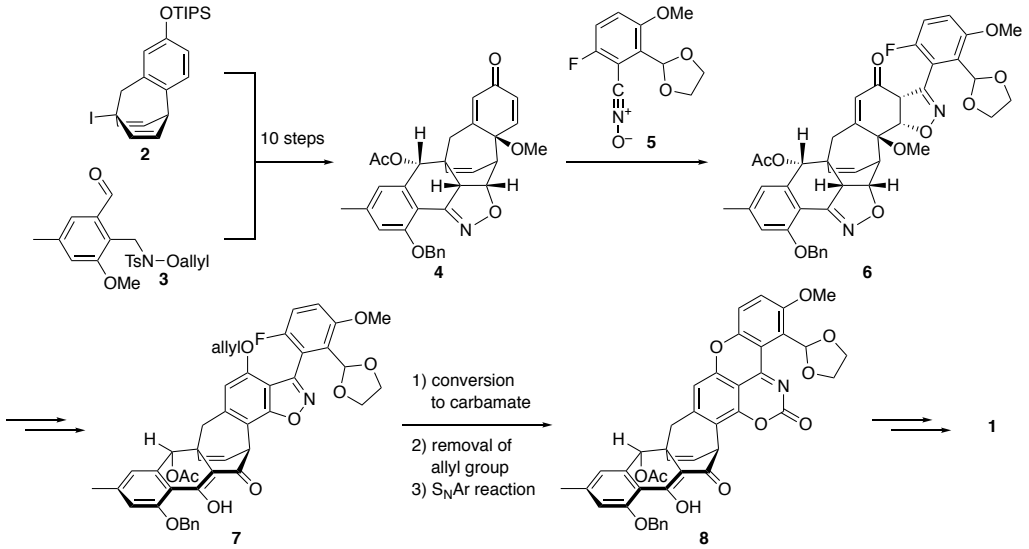
Keywords: aromatic polyketide, total synthesis, nitrile oxide, cycloaddition, S_NAr reaction

Acremoxanthone A (**1**) is a naturally occurring aromatic polyketide isolated from a fungus and has a characteristic heptacyclic structure containing a bicyclo[3.2.2]nonane skeleton. We have previously reported the construction of A–E and E–G ring system, respectively.[1] Pursuing this study, we herein report the total synthesis of **1**.



acremoxanthone A (**1**)

The synthesis was begun by the ten-step conversion with iodide **2** and aldehyde **3** to dienone **4**. In next, the 1,3-dipolar cycloaddition of **4** with nitrile oxide **5** gave bisisoxazoline **6**. The site-selective conversion of the isoxazoline moiety in **6** followed by aromatization of the enone moiety led to diketone **7**. After conversion to the corresponding cyclic carbamate, the removal of the allyl group and intramolecular S_NAr reaction gave the xanthone derivative **8**, having all-carbon skeleton of **1**. Subsequent several manipulations accomplished the total synthesis of acremoxanthone A (**1**).



1) (a) Y. Hirano, K. Tokudome, H. Takikawa, K. Suzuki, *Synlett* **2017**, *28*, 214. (b) H. Nakakohara, Y. Hirano, K. Ohmori, H. Takikawa, K. Suzuki, *Synlett* **2021**, *32*, 423.

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

[G301-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Takayuki Miki, Takashi Hayashi

Fri. Mar 25, 2022 1:00 PM - 3:40 PM G301 (Online Meeting)

[G301-3pm-01] Development of peptide tags self-assembling in cells 1: Protein-protein interaction analysis accompanied by cluster formation

○Masahiro Hashimoto[1], Takayuki Miki[1], Taichi Nakai[1], Tatsuya Niwa[1,2], Hisakazu Mihara[1] （1. Tokyo Institute of Technology, School of Life Science and Technology, 2. Tokyo Institute of Technology, Institute of Innovative Research）

1:00 PM - 1:20 PM

[G301-3pm-02] Development of peptide tags self-assembling in cells 2: Design and construction of highly-ordered protein assemblies

○Takayuki Miki[1], Hiroki Takahashi[1], Masahiro Hashimoto[1], Keigo Kajiwara[1], Sae Nakayama[1], Hisakazu Mihara[1] （1. Tokyo Institute of Technology）

1:20 PM - 1:40 PM

[G301-3pm-03] Energy Transfer in a Disulfide Bond-Mediated Heterodimer Consisting of a Fluorescent Protein and a Hemoprotein

○Julian Wong Soon[1], Koji Oohora[1], Takashi Hayashi[1] （1. Osaka University）

1:40 PM - 2:00 PM

[G301-3pm-04] Directed Evolution of Myoglobin Reconstituted with an Iron Corrole Complex Using a New High-throughput Screening Platform Based on an Affinity Purification System

○Koki Takeuchi[1], Shunsuke Kato[1], Takashi Hayashi[1] （1. Graduate School of Engineering, Osaka University）

2:00 PM - 2:20 PM

[G301-3pm-05] Development of a Protein Purification System using MBP-tagged Streptavidin and its Application for the Construction of Reconstituted Heme Protein Library

○Motonao Iwaki[1], Shunsuke Kato[1], Takashi Hayashi[1] （1. Osaka University）

2:20 PM - 2:40 PM

[G301-3pm-06] Millisecond absorption change and its molecular origin of blue light sensor BLUF protein

○Shunrou Tokonami[1], Morihiko Onose[1], Yusuke Nakasone[1], Masahide Terazima[1] （1. Kyoto University）

2:40 PM - 3:00 PM

[G301-3pm-07] Enhancing the signal response of the auto-fluorescent protein-based NO biosensor

○Shunsuke Tajima[1], Eiji Nakata[1], Reiko Sakaguchi[2], Masayuki Saimura[1], Yasuo Mori[3], Takashi Morii[1] （1. Institute of Advanced Energy, Kyoto University, 2. School of Medicine, University of Occupational and Environmental Health, 3. Graduate School of Engineering, Kyoto University）

3:00 PM - 3:20 PM

[G301-3pm-08] Genetically encoded biosensors for L-lactate

○Yusuke Nasu[1], Saaya Hario[1], Robert E Campbell[1] （1. The University of Tokyo）

3:20 PM - 3:40 PM

細胞内で自己集合するペプチドタグ開発１：クラスター形成を伴う蛋白質間相互作用解析

（東工大生命理工[1]・東工大科学技術創成研究院[2]）○橋本 匡浩[1]・三木 卓幸[1]・中井 太一[1]・丹羽 達也[1,2]・三原 久和[1]

Development of peptide tags self-assembling in cells 1: Protein-protein interaction analysis accompanied by cluster formation

([1]*School of Life Science and Technology, Tokyo Institute of Technology,* [2]*Institute of Innovative Research, Tokyo Institute of Technology)* ○Masahiro Hashimoto[1], Takayuki Miki[1], Taichi Nakai[1], Tatsuya Niwa[1,2], Hisakazu Mihara[1]

In a living system, protein-protein interactions triggered by protein clustering are frequently observed. For in situ analysis of these interactions, we need a technology that can artificially integrate bait proteins into clusters and analyze the interaction with prey proteins. Recently, we have developed a Y15 peptide tag that can assemble proteins in cells, and have found AzamiGreen fused with Y15 peptide tag (Y15-AG) forms granules in cells. Furthermore, the Y15-AG granules provided a scaffold to enrich various proteins by fusion of Y15 peptide tag.

In this study, based on the Y15 peptide tag-based technology, we enriched the bait protein into the Y15-AG scaffold and analyzed the subsequent interaction with the prey protein. Consequently, we artificially controlled the partition coefficient of bait proteins. Also, we labeled and identified the endogenous prey proteins enriched in the clusters by proximity labeling.

Keywords: Self-assembling peptide; Cluster formation; Protein-protein interaction analysis; Partition coefficient; Proteomics

細胞内の様々な生理イベントにおいて、蛋白質のクラスター化を契機として生じる蛋白質間相互作用がよく見られる。このような相互作用を細胞内で解析するためには、bait 蛋白質を人工的にクラスター化し、そこに濃縮される prey 蛋白質との相互作用を解析できる技術が必要である。当研究室では、細胞内で蛋白質をクラスター化できる Y15 ペプチドタグを開発し、Y15 ペプチドタグを融合した AzamiGreen (Y15-AG) が細胞内で顆粒状の集合体を形成することを見出している[1)]。さらに、Y15-AG の集合体をスキャホールドとし、そこへ様々な機能性蛋白質を Y15 ペプチドタグの融合によって濃縮することができた。

そこで我々は、bait 蛋白質を Y15-AG スキャホールドに濃縮し、その後に生じる prey 蛋白質との相互作用を解析する技術の開発を目指した。具体的には、bait 蛋白質の濃縮率を人為的に制御し、prey 蛋白質の集積化過程を分析する技術[2)]と、集積化した細胞内在性の prey 蛋白質を近接ラベル化法を用いたプロテオーム解析により同定する技術を、Y15 ペプチドタグを基軸として開発した。

1) T. Miki, T. Nakai, M. Hashimoto, K. Kajiwara, H. Tsutsumi and H. Mihara, *Nat. Commun.*, **2021**, 12, 3412.
2) T. Miki, M. Hashimoto, T. Nakai and H. Mihara, *Chem. Commun.*, **2021**, 57, 11338.

細胞内で自己集合するペプチドタグ開発２：蛋白質高次構造体の設計と構築

（東工大生命理工[1]）○三木　卓幸[1]・高橋　広樹[1]・橋本　匡浩[1]・梶原　圭悟[1]・中山　彩恵[1]・三原　久和[1]

Development of peptide tags self-assembling in cells 2: Design and construction of highly-ordered protein assemblies ([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Takayuki Miki[1], Hiroki Takahashi[1], Masahiro Hashimoto[1], Keiko Kajiwara[1], Sae Nakayama[1], Hisakazu Mihara[1]

More than 25% of the proteins encoded in the human genome express their functions by forming assemblies. Therefore, a technology to artificially design and construct protein assemblies in the cell will not only provide an approach to elucidate the molecular mechanisms in the cell, but also have potential engineering applications. In recent years, we have developed a Y15 self-assembling peptide tag that can integrate arbitrary proteins.[1] Y15 tag is consisting of alternative repeats of hydrophobic Tyr and hydrophilic Glu and Lys, and its amphiphilic nature promotes the self-assembly of Y15 into fibers. However, it is difficult to rationally design the subcellular localization and rigidity of the assemblies due to the lack of insight into peptide sequences suitable for protein assembly. In this study, we systematically modified the hydrophobic and hydrophilic residues of Y15 tag to investigate the effect on self-assembly. For this purpose, peptides were genetically fused to sfGFP (superfolder GFP), which was then expressed in COS-7 cells. We investigated the intracellular assembly of the peptide-fused GFPs by fluorescence imaging and fluorescence anisotropy.

Keywords : Self-assembling peptide; Liquid-liquid phase separation; Living cells

ヒトゲノムにコードされた 25%以上もの蛋白質は集合体を形成して機能を発現する。そのため、人工的に蛋白質集合体を設計し細胞内で構築する手法は、複雑な細胞内の分子メカニズムを解明する契機になるだけでなく、工学的な応用も期待できる。そこで近年、我々は任意の蛋白質を集積化できる自己集合性 Y15 ペプチドタグを開発した[1]。Y15 は、疎水性の Tyr と親水性の Glu と Lys を交互に繰り返したペプチドであり、その両親媒性の特徴から水溶液でファイバー状に集積する。Y15 タグを融合した蛋白質もファイバー状に集積化し、細胞内でも同様な集合体が観察された。

しかし、細胞内での蛋白質集積化に適したペプチドタグ配列に関する知見に乏しく、集合体の細胞内局在や剛直性等の合理的設計が困難であった。そこで、本研究では Y15 タグを基本配列として疎水性および親水性残基を体系的に変更することで、細胞内での自己集合への影響を調べた。遺伝子工学的にペプチドを sfGFP (superfolder GFP) に融合し、COS-7 細胞に発現した。sfGFP の細胞内での集合体形成を蛍光イメージングや蛍光異方性などから評価した。本講演で、これらの結果について報告する。

1) T. Miki, T. Nakai, M. Hashimoto, K. Kajiwara, H. Tsutsumi & H. Mihara, *Nat. Commun.* **12**, 3412 (2021)

Energy Transfer in a Disulfide Bond-Mediated Heterodimer Consisting of a Fluorescent Protein and a Hemoprotein

(*Graduate School of Engineering, Osaka University*) ○Julian Wong Soon, Koji Oohora, Takashi Hayashi

Keywords: Green Fluorescent Protein; Cytochrome b_{562}; Disulfide Bond; Protein Heterodimer

Inter-protein resonance energy transfer between the green fluorescent protein and its color variants has been widely reported toward practical applications such as biomarkers and biosensors.[1] Genetic fusion of multiple proteins has been a common approach in these applications, because this method allows the donor component to be in close proximity towards its acceptor to enable energy transfer.[2] In this work, the green fluorescent protein (GFP) is used as a donor protein, and cytochrome b_{562} (Cyt b_{562}), a simple electron transfer hemoprotein, as an acceptor protein.

A disulfide bond is employed for the covalent linkage of the donor and acceptor proteins. In general, selective heterodimerization via disulfide bond is difficult. However, the rapid thiol–pyridyl disulfide exchange reaction[3] allows the selective heterodimerization. First, site direct mutagenesis was carried out for the insertion of cysteine residues on GFP and Cyt b_{562} at K26 and N80 positions, respectively, as illustrated in Fig. 1, resulting in GFP^{K26C} and Cyt b_{562}^{N80C} mutants. Next, the 2,2'-dipyridyl disulfide was reacted with Cyt b_{562}^{N80C} providing an attached pyridyl disulfide moiety, and then the obtained protein selectively conjugated with GFP^{K26C}. The heterodimer was purified and characterized by SDS-PAGE, size exclusion chromatography, and UV-vis spectroscopy. The fluorescence quenching efficiency in the heterodimer was determined to be 87%. Furthermore, a much shorter fluorescence lifetime of the heterodimer was observed relative to the GFP^{K26C} monomeric protein, suggesting rapid energy transfer.

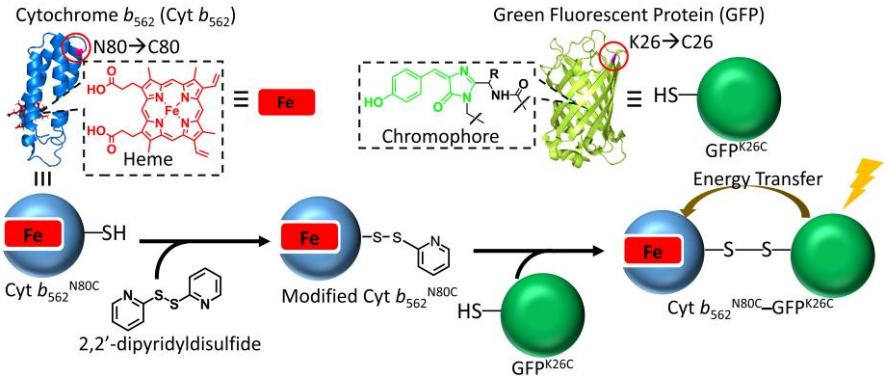


Figure 1. Schematic representation for heterodimerization of Cyt b_{562}^{N80C} and GFP^{K26C}.

1) E.C. Greenwald, S. Mehta, J. Zhang, *Chem. Rev.* **2018**, *118*, 11707–11794. 2) E. Hirata, E. Kiyokawa, *Biophys. J.* **2016**, *111*, 1103–1111. 3) I. Antinbasak, M. Arslan, R. Sanyal, A. Sanyal, *Polym. Chem.* **2020**, *11*, 7603–7624.

Directed Evolution of Myoglobin Reconstituted with an Iron Corrole Complex Using a New High-throughput Screening Platform Based on an Affinity Purification System

(*Graduate School of Engineering, Osaka University*) ○Koki Takeuchi, Shunsuke Kato, Takashi Hayashi

Keywords: Myoglobin, Iron corrole complex, High-throughput screening, Directed evolution

Artificial metalloenzymes (ArMs), where a synthetic metal cofactor is incorporated into a protein scaffold, have emerged as a new class of biocatalysts. ArMs hold a great potential to combine attractive features of natural enzymes and artificial transition metal catalysts. For example, the non-natural catalytic activities of ArMs can be tuned by a series of genetic engineering techniques, such as directed evolution technology. Our group has previously constructed an ArM, termed rMb-**1**, in which myoglobin (Mb) is reconstituted with an iron corrole complex **1** (Fig 1).[1] Notably, rMb-**1** was found to show higher H_2O_2-dependent peroxidase activity compared to the native Mb. Based on this promising result, we here set out to perform the directed evolution of rMb-**1** to further improve its peroxidase activity.

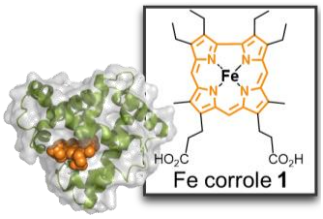


Fig 1. ArM (rMb-**1**)

To realize the directed evolution campaign of rMb-**1**, we first developed a new high-throughput screening (HTS) platform based on an affinity purification system using maltose binding protein (MBP) tag (Fig 2).[2] This HTS platform enabled us to quickly purify the recombinant protein scaffolds in a 96-well format and allowed to assemble the target ArMs without any influence of the host cellular contaminants. Furthermore, we have screened a site-saturation mutagenesis (SSM) library of rMb-**1** using the HTS platform to accomplish the directed evolution campaign. In this presentation, we will present the details of the HTS platform and the results of the screening for the directed evolution of rMb-**1**.

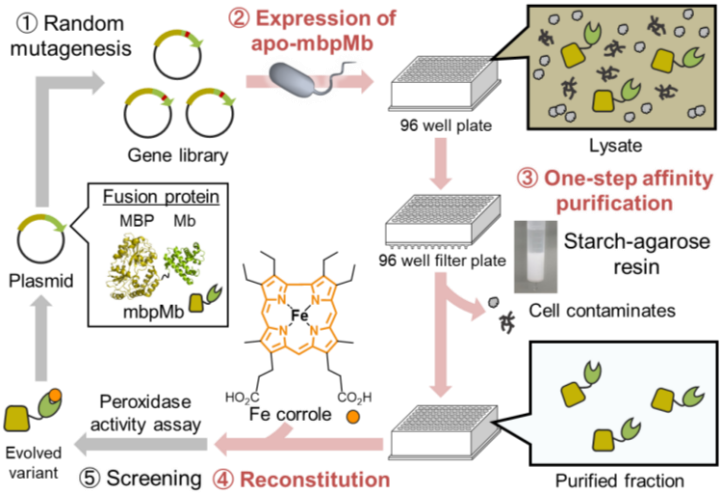


Fig 2. HTS platform that involves an affinity purification step

1) T. Matsuo, A. Hayashi, M. Abe, T. Matsuda, Y. Hisaeda, T. Hayashi, *J. Am. Chem. Soc.* **2009**, *131*, 15124. 2) S. Kato, A. Onoda, N. Taniguchi, U. Schwaneberg, T. Hayashi, *ChemBioChem*, **2021**, *22*, 679.

MBP タグ融合ストレプトアビジンを利用したタンパク質精製手法の開発：再構成ヘムタンパク質のライブラリ構築を目指した精製戦略

（阪大院工）○岩木 元直・加藤 俊介・林 高史

Development of a Protein Purification System using MBP-tagged Streptavidin and its Application for the Construction of Reconstituted Heme Protein Library

(*Graduate School of Engineering, Osaka University*) ○Motonao Iwaki, Shunsuke Kato and Takashi Hayashi

Simple and cost-effective protein purification systems provide a powerful platform to screen recombinant proteins in a chemically defined cell-free medium. Our group previously developed an affinity chromatography matrix, named starch-agarose (SA) resin for the purification of recombinant proteins.[1] Since SA resin shows a specific binding ability to MBP-tag, recombinant proteins with MBP-tag sequence were able to be purified with high efficiency.

In this study, to further extend the utility of the SA resin, we developed a new affinity purification system for recombinant proteins with strep-tag II sequence. We constructed a co-expression plasmid pMaS which carries the gene of MBP-fused streptavidin (mbpSAm1). This construct was designed to work as a mediator between SA resin and strep-tag II (Figure 1). Since the co-expressed mbpSAm1 forms a supramolecular assembly with the strep-tag II, the target proteins were able to be purified by the SA resin-based affinity chromatography. Furthermore, we have applied this purification system for the construction of purified heme protein library reconstituted with an artificial metal cofactor as a demonstration.

Keywords: Directed evolution, Affinity chromatography, Protein purification, Heme protein

タンパク質工学の分野において、簡便かつ費用対効果の高いタンパク質精製手法は、有用タンパク質の効率的な探索を実現する有効な手段となる。先行研究において我々は、スターチ・アガロース（SA）レジンという独自のクロマトグラフィー担体を開発した[1]。SA レジンは、MBP-tag に対して特異的な結合能力を発揮し、MBP-tag 融合タンパク質の精製用担体として機能する。本研究では、この SA レジンの新たな研究展開として、strep-tag II 融合タンパク質を対象とする精製手法を確立したので報告する。まず我々は、MBP 融合ストレプトアビジン mbpSAm1 の遺伝子をコードする共発現用プラスミド pMaS を作製した。mbpSAm1 は、SA レジンと strep-tag II 配列の両者への特異的な結合能力を有し、大腸菌発現系において mbpSAm1 を共発現させることで、strep-tag II 融合タンパク質を SA レジンにより高効率で精製することが可能となった（Figure 1）。更に我々は、この新規精製手法を、人工金属補因子を有する再構成ヘムタンパク質のライブラリスクリーニングへと応用したので発表する。

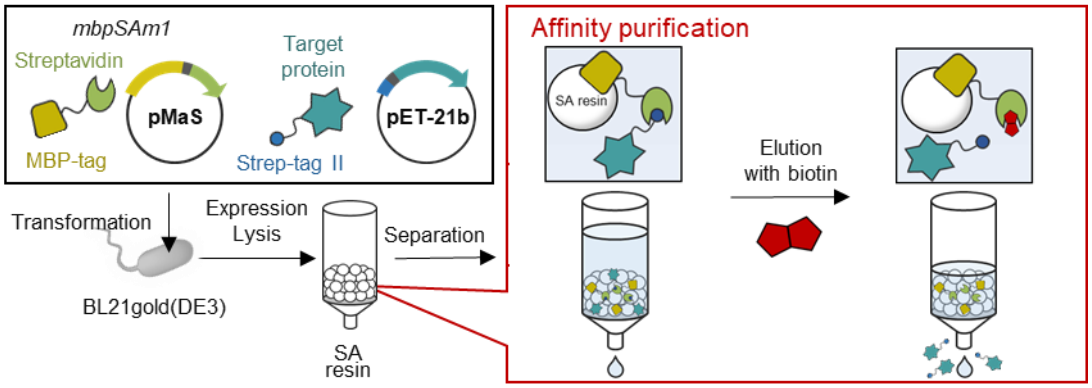


Figure 1. An affinity purification system using co-expression plasmid pMas.

1) S. Kato, A. Onoda, N. Taniguchi, U. Schwaneberg, T. Hayashi, *ChemBioChem* **2021**, *22*, 679.

青色光センサーBLUF タンパク質のミリ秒の吸収変化とシグナル伝達機構

（京大院理 [1]）○床次 俊郎 [1]・小野瀬 森彦 [1]・中曽根 祐介 [1]・寺嶋正秀 [1]

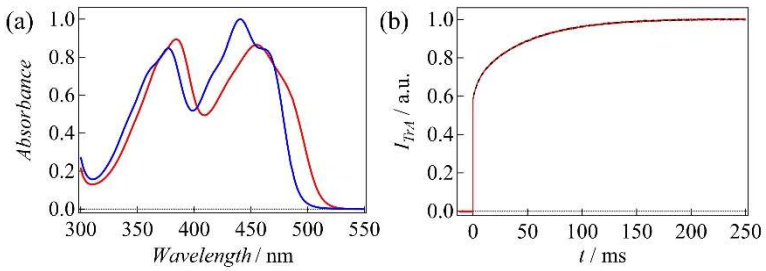
Millisecond absorption change and its molecular origin of blue light sensor BLUF proteins

([1]*Graduate School of Science, Kyoto University*) ○Shunrou Tokonami,[1] Morihiko Onose,[1] Yusuke Nakasone,[1] Masahide Terazima[1]

Blue light sensor BLUF proteins, which contain a flavin molecule as a chromophore, undergo spectral red shift changes upon photoexcitation due to changes in hydrogen-bonding network around the flavin. Although previous works have suggested that this red-shifted state is formed within a nanosecond upon photoexcitation, we newly found that there are additional steps in milliseconds time scale for all BLUF proteins studied here. Interestingly, the amplitude of the slowest phase is strongly dependent on the properties of the C-terminus of the BLUF domain, which may indicate that the change is related to the signal transduction to the C-terminal domain. Furthermore, we found that a Trp residue in the BLUF domain which locates near the C-terminus is vital for the slowest phase. Based on these findings, we discuss the intramolecular signal transduction mechanism of BLUF proteins.

Keywords : BLUF protein; Blue light sensor; Millisecond; Absorption change; Signal transduction

青色光センサーBLUF タンパク質は, N 末端側に発色団フラビンを結合する BLUF ドメイン, C 末端には走光性や光合成系タンパク質の発現といった生理機能を制御するドメインを持つ. 青色光励起でフラビンとタンパク質部分の水素結合環境が変化することで, 可視域の吸収スペクトルがレッドシフトする特徴をもつ（下図 a）. このスペクトル変化は従来ナノ秒以内に完了すると考えられてきた.[1] しかし我々は AppA, OaPAC, BlrP1, PapB, SyPixD などの多種多様な BLUF タンパク質を網羅的に調べ, BLUF ドメインに保存されたミリ秒の時間領域に遅い反応があることを見出した（下図 b, 492 nm における SyPixD の過渡吸収変化例）. また, C 末端を除去・交換した変異体の結果から, この反応が機能発現に重要な C 末端のタンパク質構造変化と関連することを発見した. さらに部位特異的変異体の結果から, C 末端近傍の Trp 残基がフラビンと C 末端の構造変化を媒介する重要な役割があることが分かった. 発表では以上の知見を基に, BLUF タンパク質の分子内シグナル伝達機構について議論する.



1) M. Gauden *et al.*, *Biochemistry* **2005**, 44, 3653

Enhancing the signal response of auto-fluorescent protein-based NO biosensor

([1]*Institute of Advanced Energy, Kyoto University*, [2]*School of Medicine, University of Occupational and Environmental Health,* [3]*Graduate School of Engineering, Kyoto University*)
○ Shunsuke Tajima,[1] Eiji Nakata,[1] Reiko Sakaguchi,[2] Masayuki Saimura,[1] Yasuo Mori,[3] Takashi Morii[1]

Keywords: Auto-Fluorescent Protein; Nitric Oxide; Structural Change; Fluorescent Biosensor; Transient Receptor Potential Canonical 5 (TRPC5) Channel

Nitric oxide (NO) act as the second messenger in cellular signal transduction processes such as cardio vascular, nervous and immne systems.[1] Developing a simple method for sensitive and selective detection of NO is one of the key requirements for studying the functions of NO. Genetically encoded biosensors based on the auto-fluorescent protein (AFP) are useful to explore cellular dynamics because of their easiness for localization and suitability for the long-time imaging. Structural changes of the recognition module induced by the recognition/reaction event with the target are transduced to a conjugated AFP to induce fluorescence signal changes of AFP.[2,3] However, the optimization process for enhancing the signal response of AFP-based biosensor remains to be explored.[2,3]

An EGFP fused putative NO sensing segment of TRPC5 (EGFP-TRPC5) successfully detected a structural change upon disulfide bond formation in the segment as a small change of fluorescence signal.[4] To construct an NO biosensor based on EGFP-TRPC5, a two-step screening method with deletion of amino acid residues in the NO-sensing module from N- and/or C-terminal was applied to enhance the signal response (Fig 1). The deletion of amino acid residues would bring the disulfide bond more proximal to the EGFP chromophore, which is expected to promote an effective transduction of structural changes upon the disulfide bond formation (Fig 1). In the first screening, the structural changes upon disulfide bond formation of 47 mutants were evaluated by RMSD of the backbone of sensing module with *in silico* simulation. Candidates were selected for *in vitro* measurement as the second screening. Further investigations of the mutants *in vitro* and *in vivo* will be discussed.

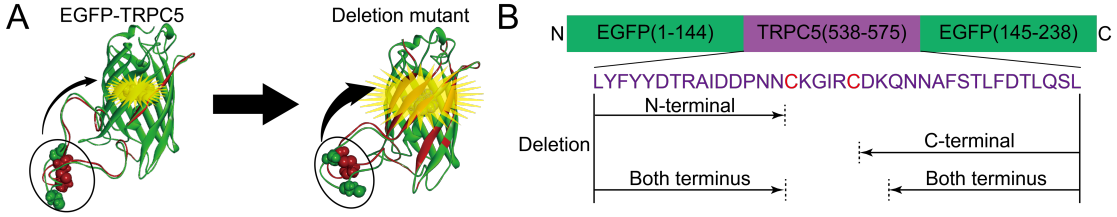


Fig. 1. (A) Deletion of amino acid residues in the NO-sensing module of EGFP-TRPC5 would enhance the signal response upon disulfide bond formation. (B) Illustration of EGFP-TRPC5.

1) DG. Hirst *et al. Methods Mol. Biol.* **2011**, *704*, 1. 2) J. Nakai *et al. Nat. Biotechnol.* **2001**, *19*, 137.
3) M. Jing *et al. Nat. Biotechnol.* **2018**, *36*, 726. 4) S. Tajima *et al. Bioorg. Med. Chem.* **2020**, *28*, 115430.

乳酸バイオセンサーの開発

（東大院理 [1]）○那須 雄介 [1]・針尾 紗彩 [1]・Robert E. Campbell[1]

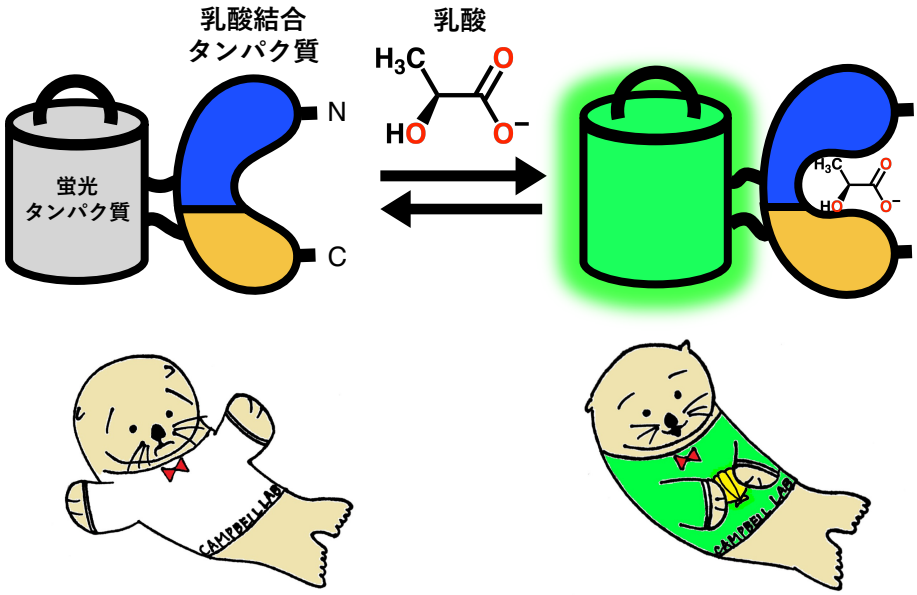
Genetically encoded biosensors for L-lactate

([1]*School of Science, The University of Tokyo*) ○Yusuke Nasu,[1] Saaya Hario,[1] Robert E. Campbell[1]

L-Lactate, traditionally considered a metabolic waste product, is increasingly recognized as an important intercellular energy currency. We have worked on the engineering of genetically encoded fluorescent biosensors using protein engineering[1) 2)]. To enable investigations of the emerging roles of intercellular shuttling of L-lactate, we apply our protein engineering technology to develop genetically encoded L-lactate biosensors, designated LACCO series.

Keywords : Fluorescent protein; Biosensor; L-Lactate

これまで長い間、グルコースが主要な細胞間伝達エネルギー物質であり、乳酸はグルコースの単なる代謝副産物と考えられてきた。しかし近年、この乳酸が細胞間でやりとりされてエネルギー物質として再利用されているのではないかという説が提唱され、乳酸の役割が見直されつつある。我々はこれまで、タンパク質工学を用いて非侵襲的に標的を観察することが可能な蛍光バイオセンサーの開発を行ってきた [1) 2)]。ここでは、細胞間でやりとりされる乳酸の新たな役割の検証を可能とする蛍光乳酸バイオセンサー（LACCO シリーズ, 図）を報告する。



1) **Nasu Y.**, Shen Y., Kramer L., Campbell R. E., “Structure- and mechanism-guided design of single fluorescent protein-based biosensors”, *Nature Chemical Biology*, **17**, 509−518 (2021).
2) **Nasu Y.**, et al. “A genetically encoded fluorescent biosensor for extracellular L-lactate”, *Nature Communications*, accepted (2021).

[G201-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Tatsuya Nishihara, Tomonori Tamura

Fri. Mar 25, 2022 1:00 PM - 3:40 PM G201 (Online Meeting)

[G201-3pm-01] Prototype Screening and Optimization of HaloTag-based Chemigenetic Fluorescent Indicators

○Dazhou CHENG[1], Wenchao ZHU[1], Takuya TERAI[1], Yusuke NASU[1], Robert Earl CAMPBELL[1,2] (1. Department of Chemistry, Graduate School of Science, The University of Tokyo, 2. Department of Chemistry, University of Alberta)

1:00 PM - 1:20 PM

[G201-3pm-02] Orthogonal activation of GPCR-type glutamate receptor via coordination-based chemogenetics

○Akinobu Senoo[1], Yamada Yutaro[1], Ojima Kento[1,2], Doura Tomohiro[1], Kiyonaka Shigeki[1] (1. Nagoya Univ., 2. Kyoto Univ.)

1:20 PM - 1:40 PM

[G201-3pm-03] Comprehensive imaging of hypoxic cells by fluorescent probes with azide group

○Hiroki Makanai[1], Miei Kanda, Tatsuya Nishihara[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

1:40 PM - 2:00 PM

[G201-3pm-04] *FixEL*: a new method for visualizing ligand dynamics in the brain by reframing the PFA fixation chemistry.

○Takeharu Mino[1], Hiroshi Nonaka[1,2], Seiji Sakamoto[1], Jae Hoon Oh[2], Yu Watanabe[1], Mamoru Ishikawa[2], Akihiro Tsushima[1], Kazuma Amaike[1], Shigeki Kiyonaka[2,3], Tomonori Tamura[1,2], Radu Aricescu[4,5], Wataru Kakegawa[2,6], Eriko Miura[6], Michisuke Yuzaki[6], Itaru Hamachi[1,2] (1. Graduate School of Engineering, Kyoto University, 2. JST ERATO, 3. Graduate School of Engineering, Nagoya University, 4. Division of Structural Biology, University of Oxford, 5. Neurobiology Division, MRC Laboratory of Molecular Biology, 6. Keio University School of Medicine)

2:00 PM - 2:20 PM

[G201-3pm-05] Mapping a glutamate receptor interactome in living mice by photoactivated proximity labeling

○Mikiko Takato[1], Hayata Utsunomiya[1], Tomonori Tamura[1], Itaru Hamachi[1,2] (1. Kyoto University, 2. JST ERATO)

2:20 PM - 2:40 PM

[G201-3pm-06] Fluorogenic labeling of lipid droplets via intralipid click reaction

○Hiro Shiotani[1], Junwei Wang[1], Masayasu Taki[1], Shigehiro Yamaguchi[1] (1. Nagoya university)

2:40 PM - 3:00 PM

[G201-3pm-07] Fluorescence Imaging of Fatty Acid Beta Oxidation Pathway in Tissue Samples Using An Activity-Based Probe

○Shohei Uchinomiya[1], Tomoki Nagaura[1], Naoya Matsunaga[1], Akito Tsuruta[1], Kazuya Inoue[1], Shigehiro Ohdo[1], Akio Ojida[1] (1. pharmaceutical science, Kyushu University)

3:00 PM - 3:20 PM

[G201-3pm-08] Substituted *meso*-Vinyl-BODIPY as Thiol-Selective Fluorogenic Probes for Sensing Unfolded Proteins in Living Cells

○HUIYING MU[1], Koji Miki[1], Kouichi Ohe[1] （1. Kyoto University）

3:20 PM - 3:40 PM

Prototype Screening and Optimization of HaloTag-based Chemigenetic Fluorescent Indicators

([1]*Department of Chemistry, Graduate School of Science, The University of Tokyo*, [2]*Department of Chemistry, University of Alberta*) ○Dazhou CHENG,[1] Wenchao ZHU,[1] Takuya TERAI,[1] Yusuke NASU,[1] Robert E. CAMPBELL[1,2]

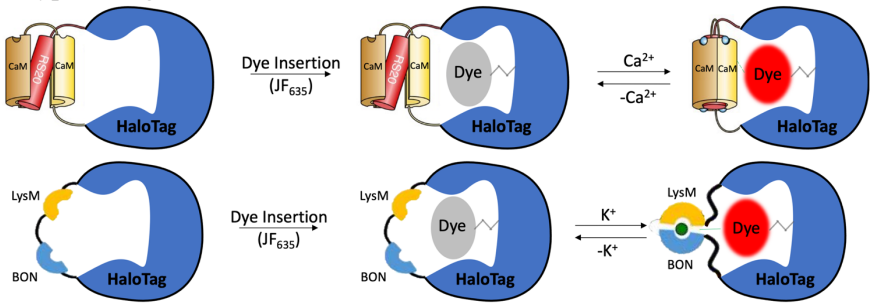
Keywords: Chemigenetic Fluorescent Indicator; HaloTag Protein; Synthetic Fluorogenic Dye; Calcium Ion Indicator; Potassium Ion Indicator

Bioimaging using fluorescent indicators has revolutionized modern biology. Recently, a new class of self-labeling chemigenetic indicators has been developed. In these chemigenetic indicators, a synthetic fluorophore is introduced onto a protein framework consisting of a self-labeling protein and a target-binding domain. The fluorescence intensity is altered due to a conformational change resulting from binding of the target analyte. To date there're only a few representative examples of chemigenetic indicators, the HaloCaMP1 and rHCaMP Ca^{2+} indicators[1,2] and the HASAP1 Voltage indicator[2]. As of yet, this approach hasn't been shown to be broadly applicable to many analytes. Furthermore, optimization and improvement of first-generation indicators are largely unexplored[3].

Here, we explore the chemigenetic indicator's versatility based on the self-labeling HaloTag protein, a fluorogenic rhodamine derivative dye[3], and a protein-based molecular recognition moiety. In principle, this design strategy should enable the versatile design of different indicators by simply changing the sensing domain of the protein framework. So far, we have designed two kinds of chemigenetic indicators based on this framework: a Ca^{2+} indicator and a K^+ indicator.

In this work, we inserted the sensing domain (calmodulin-RS20 for the Ca^{2+} indicator, and kbp for the K^+ indicator) into different sites on the loop of the HaloTag protein from position 143 to 178. We then treated each protein with a synthetic fluorophore (JF_{635}-HTL, which has a chloroalkane linker[3]) and tested the fluorescence change in response to Ca^{2+} and K^+, respectively (**Figure**). In total, 32 different insertion sites for each indicator design were tested. We found that inserting the sensing domain onto the loop around position 165-166 of HaloTag gave the highest fluorescence response for the Ca^{2+} indicator (HaloCI), and the position 145-146 gave highest fluorescence response for the K^+ indicator (HaloPI). Both showed similar λ_{ex} (~658 nm) when labeled with JF_{635}-HTL. Both HaloCI and HaloPI showed robust fluorescence intensity change in response to Ca^{2+} and K^+ respectively (-94% for 39 μM of Ca^{2+}, +88% for 100 mM of K^+).

In summary, our results demonstrate the versatility of this chemigenetic indicator design. In future work, we will pursue indicators for additional target molecules, and further optimize the indictor prototypes using directed evolution.



1) Wang, L. *et al*, *Angew. Chem. Int. Ed.*, **2020**, *59*, 21880-21884. 2) Deo, C., *et al*, *Nature Chemical Biology*, **2021**, *17*, 718–723. 3) Grimm, J. *et al*, *Nat Methods*, **2017,** *14*, 987–994.

配位ケモジェネティクス法による GPCR 型グルタミン酸受容体の直交的活性制御

（名大院工[1]・京大院工[2]）○妹尾　暁暢[1]・山田　裕太郎[1]・小島　憲人[1,2]・堂浦　智裕[1]・清中　茂樹[1]

Orthogonal activation of GPCR-type glutamate receptor via coordination-based chemogenetics
([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Engineering, Kyoto University*) ○Akinobu Senoo,[1] Yutaro Yamada,[1] Kento Ojima,[1,2] Tomohiro Doura[1], Shigeki Kiyonaka[1]

Cell-surface receptors play a pivotal role as transducers of extracellular input. Although different cell types express the same receptor, the physiological roles of the receptor are highly dependent on cell type. To understand each role, tactics for cell-specific activation of the target receptor are in high demand. In this study, we report an orthogonal activation method targeting metabotropic glutamate receptor 1 (mGlu1) as a model protein. In this method, activation via coordination-based chemogenetics (A-CBC)[1-3] was adopted, where activation of mGlu1 was artificially induced by a protein conformational change in response to the coordination of a metal ion or metal-ion complex. Our structure-based protein design and screening approach identified mGlu1 mutants that were directly activated by the coordination of Cu^{2+} or Zn^{2+}, in addition to our previous Pd-complex-sensitive mGlu1 mutant. Notably, the activation of the mutants was mutually orthogonal, allowing for the cell-type selective activation in a model system using HEK293 cells[4].

Keywords：Chemogenetics, Coordination chemistry, GPCR, Metabotropic glutamate receptor, Orthogonality

細胞膜受容体は細胞外の刺激を細胞内へ伝達する役割を担うタンパク質である。同一種の受容体が様々な細胞種に発現しているが、その生理学的機能は発現する細胞種によって異なる。細胞種それぞれにおける受容体機能を解明するためには、細胞種特異的に受容体を活性化する手法が求められる。本発表では代謝型グルタミン酸受容体 1(mGlu 1)をモデルタンパク質として複数の直交的な mGlu1 活性制御法を報告する。mGlu1 の活性制御法として筆者らのグループが報告している配位ケモジェネティクス法[1-3]を利用した。配位ケモジェネティクス法では mGlu1 の活性化に必要なタンパク質の構造変化を金属錯体の配位によって人工的に惹起する。本研究では結晶構造に基づく変異体デザインとスクリーニングにより、Cu^{2+}や Zn^{2+}によって活性化される mGlu1 変異体を同定した。さらに、これらの変異体が既に報告されている Pd 錯体活性型の mGlu1 変異体と共に、互いに直交的に活性化できる変異体であることを見出した。これらの変異体を用いて、HEK293 細胞におけるモデル実験により細胞種選択的な活性制御を実証した[4]。

1) Kiyonaka *et al.*, *Nat. Chem*. **2016**, 8, 958. 2) Ojima *et al.*, *bioRxiv*, **2021**. 3) Kubota *et al.*, *Methods Enzymol.*, **2019**, 622, 411. 4) Senoo *et al.*, *Front. Chem*., **2022**, 9, 825669.

アジド基を備えた蛍光プローブによる低酸素細胞の包括的イメージング

（青学大院理工）○蒔苗 宏紀・神田 美瑛・西原 達哉・田邉 一仁

Comprehensive imaging of hypoxic cells by fluorescent probes with azide group

(*Graduate School of Engineering, Aoyama Gakuin University*) ○Hiroki Makanai, Miei Kanda, Tatsuya Nishihara, Kazuhito Tanabe

Tracking hypoxic environments and the accompanying biological changes contribute to elucidation of pathological mechanism. Previously, several fluorescent probes have been reported to visualize hypoxia environment by us and other research groups. However, it is difficult to accurately track the various environmental changes that occur in the cytoplasm at the same time, since all conventional probes fluoresce in the cytoplasm. In this study, we attempted to design molecular probes that can visualize the nucleus and cytoplasm of hypoxic cells, respectively. Focusing on the evidence that azide groups are activated and converted to amino groups in hypoxic cells, we designed and synthesized a Hoechst molecule (Hoechst-N3) and a cyanine molecule (Cy-N3) equipped with azide groups. These probes accumulated and emitted their fluorescence in the nucleus and cytoplasm in hypoxic cells. Thus, we achieved comprehensive imaging of hypoxic cells.

Keywords : Hypoxia; Azide compounds; Fluorescence probe; Bioreduction; Comprehensive imaging

生体組織に発生する低酸素環境とそれに付随する生体環境の変化の追跡することは、病理メカニズムの解明へとつながる。我々の研究グループを始めとして、国内外の研究グループからこれまでに低酸素環境を可視化する蛍光プローブが多数報告されてきた。しかし、それらは全て、細胞質内で蛍光を発することから、細胞質で起こる多様な環境の複数の変化を同時に捉えることは困難であった。そこで本研究では、低酸素細胞の細胞核と細胞質をそれぞれ可視化可能な分子プローブを開発することを目指した。細胞内小器官をそれぞれ可視化することで、より汎用性が高い低酸素イメージングを実現できると考えた。

アジド基が低酸素細胞内で活性化され、アミノ基に変換される事実に着目し、アジド基を備えた Hoechst 分子(Hoechst-N_3)およびシアニン系分子(Cy-N_3)を設計・合成した。実際に合成した蛍光プローブは肝ミクロソームで処理すると、それぞれ低酸素環境下で発光した。また、低酸素細胞に投与すると、細胞核、細胞質でそれぞれ蛍光強度の増加が観察された。

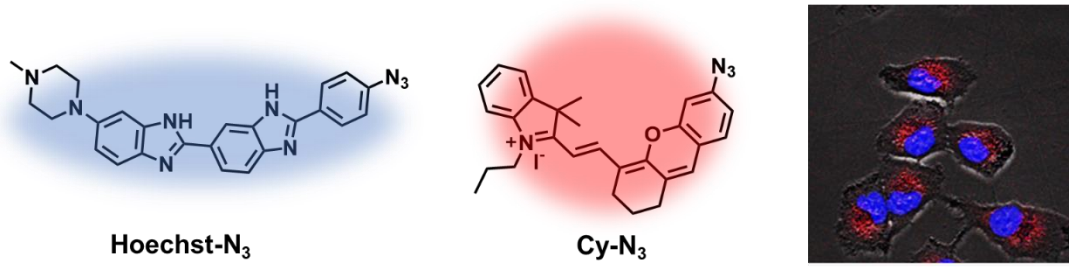


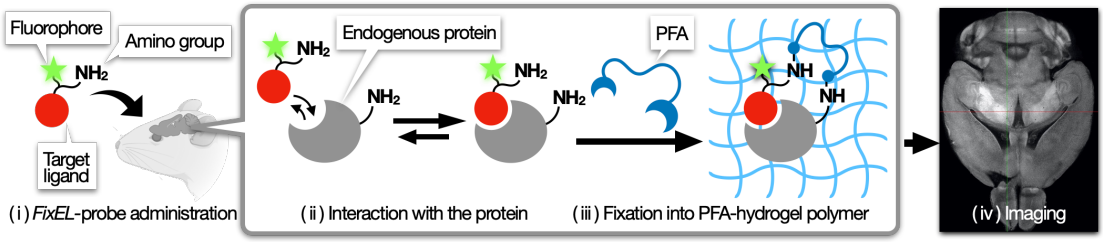
Figure 1. Chemical structures of Hoechst-N3 and Cy-N3, and Hypoxic cell imaging by these probes.

FixEL: a new method for visualizing ligand dynamics in the brain by reframing the PFA fixation chemistry.

([1]*Graduate School of Engineering, Kyoto University,* [2]*JST ERATO,* [3]*Graduate School of Engineering, Nagoya University,* [4]*Division of Structural Biology, University of Oxford,* [5]*Neurobiology Division, MRC Laboratory of Molecular Biology,* [6]*Keio University School of Medicine*) ○Takeharu Mino[1], Hiroshi Nonaka[1,2], Seiji Sakamoto[1], Jae Hoon Oh[2], Yu Watanabe[1], Mamoru Ishikawa[2], Akihiro Tsushima[1], Kazuma Amaike[1], Shigeki Kiyonaka[2,3], Tomonori Tamura[1,2], Radu Aricescu[4,5], Wataru Kakegawa[2,6], Eriko Miura[6], Michisuke Yuzaki[6], Itaru Hamachi[1,2]

Keywords: *Protein-ligand interaction, Endogenous glutamate receptor, Endogenous dopamine receptor, Nanobody, 3D imaging.*

Various small molecules have been used as functional probes for pharmaceuticals and medical diagnostics. However, there are still limited methods to accurately evaluate the spatial distribution and diffusion/excretion dynamics of small molecules in tissues for elucidating their functions. In this study, we developed a novel chemical biology method termed "***Fix*ation-driven chemical crosslinking of *e*xogenous *l*igands** (***FixEL***)", which enables the visualization of the small molecule distributions in complex tissues[1]. In the *FixEL* method, we employ a designer *FixEL* probe, which is a small molecule ligand modified with a nucleophilic functional group that can react with PFA polymer. After the probe is administered to the animal, a hydrogel-like three-dimensional structure consisting of protein and PFA is formed in the tissue by PFA-fixation treatment. Simultaneously, the nucleophilic functional groups on the probe rapidly form covalent bonds with the PFA polymer, and the 3D distribution of the probe based on the protein-ligand interaction is immobilized on the hydrogel-tissue complex. This chemistry allows us to capture and analyze a snapshot of the small molecule dynamics based on the protein-ligand interactions in tissues. Indeed, we succeeded by *FixEL* in evaluation of the diffusion/excretion kinetics of small molecule ligands for the mGlu1 receptor in mouse brain. Moreover, we further applied the *FixEL* method to other glutamate receptors (AMPARs) and dopamine receptors (DRD2s). In addition to small molecules, clear 3D imaging of nanobodies distributed throughout the brain was also achieved by *FixEL* method with high spatial resolution.



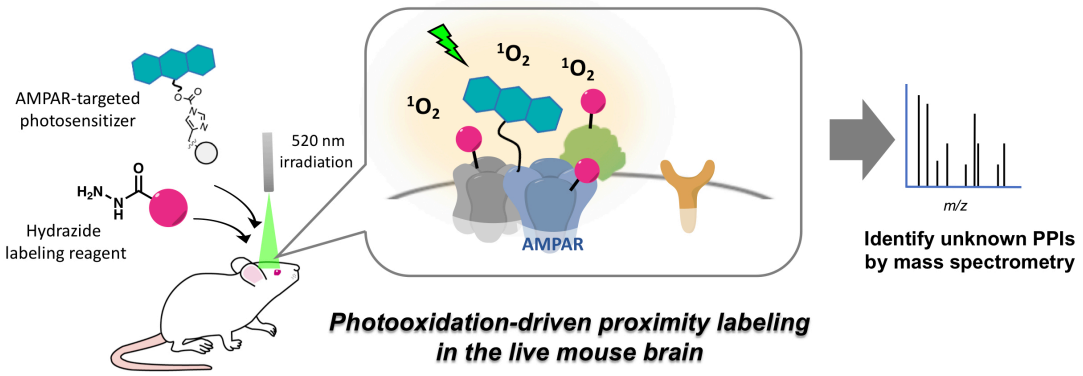
1) bioRxiv 2021.12.21.473647

Mapping a glutamate receptor interactome in living mice by photoactivated proximity labeling

([1]*Graduate School of Engineering, Kyoto University*, [2]*JST ERATO*)
○Mikiko Takato[1], Hayata Utsunomiya[1], Tomonori Tamura[1], Itaru Hamachi[1,2]
Keywords: Proximity labeling; Interactome; Proteomics; Photosensitizers; Brain

Nearly all aspects of cellular activity are regulated by an intricate network of protein-protein interactions (PPIs), and the discovery of unknown PPIs is essential to deciphering biological processes at the molecular level. In the past decade, enzymatic proximity labeling has emerged as a powerful tool for detecting potential PPIs in the native environment of the cell, and has been particularly effective for identifying transient and low-affinity associations.[1] However, when applied to live animal studies, existing methods suffer either from toxicity or a low temporal resolution on the order of hours to days, as well as the need for a potentially disruptive genetic modification of the organism under study.[2]

To address this challenge, we have developed **PhoxID** (photooxidation-driven proximity labeling for protein identification),[3] an optochemical proximity labeling method for profiling protein interactions that can be applied to live, genetically intact animals. In this strategy, an organic small-molecule photosensitizer is tethered to a protein of interest and irradiated with visible light to locally generate singlet oxygen ($^1O_2$). The diffusion radius of $^1O_2$ in biological environments is estimated to be several tens of nanometers[4] – thus, only proteins that are physically proximal to the protein of interest are oxidized by $^1O_2$ and tagged by a nucleophilic labeling reagent for identification by mass spectrometry. We demonstrated the tissue and *in vivo* compatibility of PhoxID by identifying multiple members of the α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid-type glutamate receptor (AMPAR)-interactome in the brains of live mice with just minutes of photoirradiation.



1) W. Qin et al., *Nat. Methods* **2021**, *18*, 133. 2) a) A. Uezu et al., *Science* **2016**, *353*, 1123. b) T. C. Branon et al., *Nat. Biotechnol.* **2018**, *36*, 880. 3) T. Tamura et al., *Chem. Lett.* **2020**, *49*, 145. 4) A. Baker, J.R. Kanofsky, *Photochem. Photobiol.* **1992**, *55*, 523.

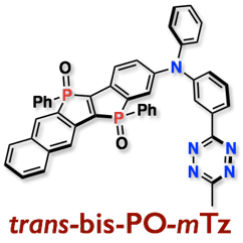
脂質内クリック反応による細胞内脂肪滴の蛍光ラベル化

（名大院理[1]・名大 ITbM[2]）○塩谷 大[1]・Junwei Wang[2]・多喜 正泰[2]・山口 茂弘[1,2]
Fluorogenic labeling of lipid droplets via intralipid click reaction ([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules(WPI-ITbM)*) ○Hiro Shiotani,[1] Junwei Wang,[2] Masayasu Taki,[2] Shigehiro Yamaguchi[1,2]

Fluorescent markers for lipid droplets (LDs) are a promising chemical tool for monitoring LD dynamics in cells. To tune the excitation wavelength in a suitable visible range and improve the retention time of the markers in LDs, in this study, we developed *trans*-bis-PO-*m*Tz, a tetrazine-conjugated bis-phosphoryl-bridged fluorophore. We hypothesized that if the inverse electron-demand Diels–Alder (IEDDA) reaction occurs between *trans*-bis-PO-*m*Tz and an artificial lipid containing an alkene in LDs, the release of the dye from the cell would be significantly suppressed. In toluene, *trans*-bis-PO-*m*Tz was efficiently quenched by tetrazine (Φ_F = 0.01), while a 38-fold increase in the fluorescence intensity was observed when treated with methyl 10-undecenoate. HuH-7 cells were incubated in the presence of 14-pentadecenoic acid, followed by the addition of *trans*-bis-PO-*m*Tz, resulting in the emergence of intense fluorescence from LDs. This result suggests that 14-pentadecenoic acid is metabolically incorporated into the LDs as triglycerides followed by the IEDDA reaction in the LDs. The fluorescence intensity of cells retained 95% of the original value even after 24 h of incubation in a culture medium containing serum.
Keywords : Fluorogenic Probe; Lipid Droplets; Click Chemistry; Tetrazine; Live-cell Imaging

細胞内脂肪滴の動態追跡には，脂肪滴蛍光染色剤が有用である．しかし，既存の脂肪滴染色剤は脂肪滴特異性や耐光性に乏しいため，微小な脂肪滴動態を長時間追跡することができなかった．これに対して当研究室では，超耐光性脂肪滴染色剤として LAQ1 を開発し，脂肪滴イメージングにおける有用性を示してきた[1)]．しかし，生理的条件における脂肪滴動態を理解するためには，血清を含む完全培地中で長時間にわたり観察可能な新たな染色剤開発が必要である．そこで本研究では，励起波長の長波長化と色素の脂肪滴内保持時間の向上を目指し，2 つのホスホリル基を有する蛍光色素に対してテトラジンを導入した *trans*-bis-PO-*m*Tz を開発した．テトラジンとアルケンとの逆電子要請型 Diels-Alder (IEDDA) 反応はクリックケミストリーの一種として知られている．脂肪滴内で *trans*-bis-PO-*m*Tz とアルケンを含む人工脂質との間で IEDDA 反応が進行した場合，色素の細胞外への流失が抑制されるものと考えた．

trans-bis-PO-*m*Tz の蛍光は，トルエン中，テトラジンにより効率的に消光されているが(Φ_F = 0.01), 10-ウンデセン酸メチルを作用させると蛍光強度が 38 倍に増大した．次に，HuH-7 細胞を 14-ペンタデセン酸存在下で培養後，*trans*-bis-PO-*m*Tz を加えたところ，脂肪滴からの強い蛍光が観察された．これは，14-ペンタデセン酸が中性脂肪として脂肪滴内に代謝的に取り込まれ，脂肪滴内でクリック反応が進行したためと考えられる．実際，本手法で染色した場合は，血清存在下で細胞を 24 時間培養しても蛍光強度は当初の 95%を保持することがわかり，長時間観察の可能性が示唆された．



trans-bis-PO-*m*Tz

1) M. Taki, K. Kajiwara, E. Yamaguchi, Y. Sato, S. Yamaguchi, *ACS Materials Lett.*, **3**, 42-49 (2021).

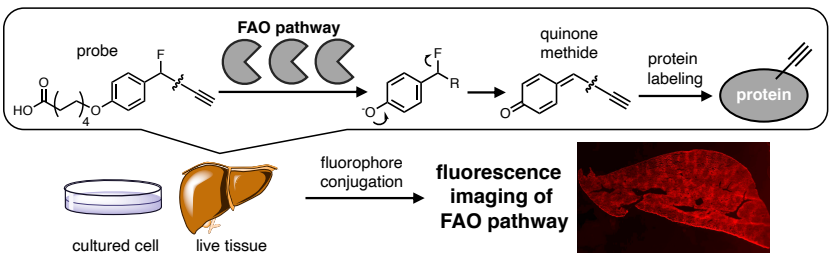
Fluorescence Imaging of Fatty Acid Beta Oxidation Pathway in Tissue Sample Using Activity-Based Probe

(*Graduate School of Pharmaceutical Sciences, University of Kyushu*) ○ Shohei Uchinomiya, Tomoki Nagaura, Naoya Matsunaga, Akito Tsuruta, Kazuya Inoue, Shigehiro Odo, Akio Ojida

Keywords: Fluorescence Imaging; Fatty Acid Beta Oxidation; Tissue Sample; Activity-Based Probe

Metabolic pathways, chemical reactions that consist of multiple enzyme reactions, play pivotal role for maintaining cellular functions and elucidation of the activity of metabolic pathways is indispensable for understanding of disease mechanism and drug discovery. Fluorescence imaging would be a powerful tool for elucidating heterogeneity of metabolic activity in individual cells. However, targets of current fluorescent probes are generally limited in single enzyme reactions. Because metabolic pathways consist of multiple enzyme reactions, it has been challenging to elucidate activity of whole flux of a certain metabolic pathway using a single fluorescent probe. We here report an activity-based probe for fluorescence imaging of fatty acid beta oxidation (FAO) pathway. FAO is an important metabolic pathway that degrades fatty acids to generate acetyl CoA for ATP production. For fluorescence imaging of FAO, we designed a chemical probe possessing fatty acid moiety that is metabolically degraded by FAO and releases a reactive quinone methide (QM) possessing an alkyne moiety. The QM is covalently trapped by intracellular proteins and the introduction of fluorophore into the labeled proteins enables fluorescence detection of FAO.

Hepatocellular carcinoma HepG2 cells were treated with the probe, fixed and conjugated with TAMRA possessing azide group by CuAAC reaction. Confocal microscopy analysis observed bright fluorescence inside the cells. In contrast, negligible fluorescence was observed in the cells pre-treated with etomoxir, an inhibitor of FAO. We next applied our probe to fluorescence imaging of FAO in mouse liver tissue. Mouse were intraperitoneally administrated with our probe and the liver of the mouse was isolated. The liver slice was treated with TAMRA-azide and subjected to confocal microscopy. Bright fluorescence of TAMRA was observed in the liver slice. In contrast, the fluorescence was effectively suppressed in the liver slice of the mousse pre-treated with etomoxir. These data indicated that our probe enabled detection of FAO not only in cultured cells but also mouse liver tissue.



Substituted *meso*-Vinyl-BODIPY as Thiol-Selective Fluorogenic Probes for Sensing Unfolded Proteins in Living Cells

(*Graduate School of Engineering, Kyoto University*) ○Huiying Mu, Koji Miki, Kouichi Ohe

Keywords: thiol-reactive probe, BODIPY, unfolded protein, fluorescence

Cytotoxic aggregation of unfolded proteins causes a loss of protein function and endoplasmic reticulum (ER) stress which associated with cell apoptosis and neurodegenerative disorders. Thiol-reactive fluorogenic probes have recently found their use to sense protein unfolding process. Here we wish to report a new type of selective thiol-activatable fluorogenic probes (VBs) based on *meso*-vinyl-BODIPY dye, including **VB**, **VB1Cl** and **VB2Cl** (Figure 1a).[1] The electron-deficient BODIPY core confers thiol reactivity to the vinyl group, which was then further improved by introduction of electron-withdrawing groups at the BODIPY core. The monochloro-substituted derivative **VB1Cl** exhibiting high selectivity to thiols (Figure 1b), is applicable for sensing unfolded proteins with high sensitivity and large fluorescence enhancement (Figure 1c). In living cell imaging, we demonstrate the utility of **VB1Cl** for sensitively reporting the protein unfolding process under ER stress induced by antibiotic active tunicamycin and proteasome inhibitor MG132 in living cells (Figure 1d).

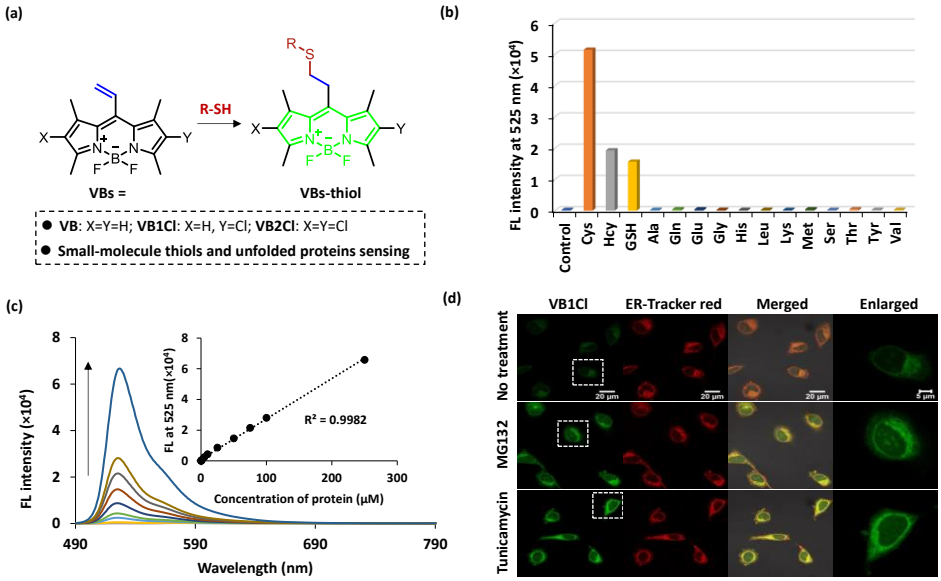


Figure 1. (a) Reaction scheme of **VBs** with thiol-containing compounds. (b) Selectivity of **VB1Cl** (5 μM) towards a variety of amino acids (1 mM). (c)Fluorescence spectra of **VB1Cl** upon the addition of unfolded protein *β*-lactoglobulin (LGB, 0–250 μM). (e) Confocal images of controlled and stressed HeLa cells stained with **VB1Cl** (5 μM) for 1 h and ER-Tracker red (1 μM) for 15 min, followed by methanol fixation.

[1] H. Mu, K. Miki, T. Kubo, K. Otsuka, K. Ohe. *Chem. Commun.* **2021**, *57*, 1818-1821.

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

[G101-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Yuichiro Aiba, Yasuaki Kimura

Fri. Mar 25, 2022 1:00 PM - 3:40 PM G101 (Online Meeting)

[G101-3pm-01] Color-changing fluorescent barcode based on strand displacement reaction for multiplexed imaging of biomolecules

○Koki Makino[1], Hiroyuki Asanuma[1], Hiromu Kashida[1] (1. Graduate School of Engineering, Nagoya University)

1:00 PM - 1:20 PM

[G101-3pm-02] Nucleic Binding Selectivity of RGG Domain in TLS/FUS Regulated by Arginine Methylation

○Tatsuki Masuzawa[1], Ryota Yagi[2], Shinnosuke Kawai[2], Takanori Oyoshi[2] (1. Graduate school of Science and Technology, Shizuoka University, 2. Graduate school of Integrated Science and Technology, Shizuoka University)

1:20 PM - 1:40 PM

[G101-3pm-03] NMR study on the binding of naphthyridine dimer to d(CGG) triad

○Shuhei Sakurabayashi[1,2], Kyoko Furuita[1], Takeshi Yamada[2], Toshimichi Fujiwara[1], Kazuhiko Nakatani[2], Chojiro Kojima[1,3] (1. SANKEN, Osaka University, 2. Institute for Protein Research, Osaka University, 3. Yokohama National University)

1:40 PM - 2:00 PM

[G101-3pm-04] Recognition of double-stranded DNA by using parallel-stranded PNAs

○Masanari Shibata[1], Yuichiro Aiba[1], Masaki Hibino[1], Hiroshi Sugimoto[2], Osami Shoji[1] (1. Nagoya University, 2. Riken/SPring-8)

2:00 PM - 2:20 PM

[G101-3pm-05] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (78) : Analysis of structural dynamics of *c-Myc* G-quadruplex DNA using high pressure

○Shuntaro Takahashi[1], Tatsuya Ohyama[1], Shuo-Bin Chen[2], Jia-Heng Tan[2], Naoki Sugimoto[1,3] (1. Konan Univ. FIBER, 2. Sun Yat-sen Univ., 3. Konan Univ. FIRST)

2:20 PM - 2:40 PM

[G101-3pm-06] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (75): Development of RNA-ligand pairs for multicolor RNA imaging in cells

○Tamaki Endoh[1], Jia-Heng Tan[2], Shuo-Bin Chen[2], Naoki Sugimoto[1,3] (1. FIBER, Konan University, 2. Sun Yat-sen Universsity, 3. FIRST, Konan University)

2:40 PM - 3:00 PM

[G101-3pm-07] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (73):Effect of G-quadruplex stability change on transcriptional repression in cancer cells

○Hisae Tateishi-Karimata[1], Keiko Kawauchi[2], Tatsuya Ohyama[1], Hirano Masaki[3], Atsushi Natsume[4], Naoki Sugimoto[1,2] (1. Frontier Institute for Biomolecular Engineering Research (FIBER) Konan University, 2. Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Ko-nan University, 3. Division of

Molecular Oncology, Aichi Cancer Center Research Institute, 4. Nagoya University, The Institute of Innovation for Future Society)

3:00 PM - 3:20 PM

[G101-3pm-08] Membrane permeable oligonucleotide (MPON) modified with disulfide units induces efficient exon skipping through enhanced membrane permeability and nucleus internalization

○Haruka Hiraoka[1], Zhaoma Shu[1], Bao Tri Le[2], Keiko Masuda[3], Kosuke Nakamoto[1], Kotaro Hayashi[4], Naoko Abe[1], Yasuaki Kimura[1], Rakesh N. Veedu[2], Yoshihiro Shimizu[3], Satoshi Uchida[5], Hiroshi Abe[1,3,6] (1. Nagoya Univ., 2. Murduch Univ., 3. RIKEN, 4. iCONM, 5. Kyoto Pref. Univ. of Med., 6. iGCORE)

3:20 PM - 3:40 PM

Color-changing fluorescent barcode based on strand displacement reaction for multiplexed imaging of biomolecules

([1]*Graduate School of Engineering, Nagoya University*) ○Koki Makino[1], Hiroyuki Asanuma[1], Hiromu Kashida[1]

Keywords: Strand displacement reaction; Fluorescent probes; Nucleic acids nanotechnology; Artificial nucleic acid

Fluorescence imaging has been used in a wide field of biotechnological applications. However, the number of detectable biomolecules is strictly limited, typically to five, due to spectral overlaps of excitation and emission spectra. This limitation prevents the understanding of complex biological functions involving many biomolecules.

In this study, we developed a novel fluorescence labeling method, color-changing fluorescent barcode (CCFB), where fluorescence colors are changed via toehold-mediated strand displacement reaction of nucleic acids (Fig. 1). The CCFB enables the detection of multiple molecules with fluorescence color sequences. The targets are labeled with barcode complex of F strands tethering a fluorophore or a quencher at each terminus. In the initial state, only the terminal fluorophore can emit fluorescence whereas the other fluorophores are quenched by neighboring quenchers. The fluorescence color sequence of barcode can be decoded by the sequential addition of Q strands (Q1, Q2, and Q3) that are fully complementary to F strands. The sequential removal of F strands changes emissive fluorophores in the pre-determined order, allowing simultaneous detection of a large number of targets. When four types of fluorophores are used and fluorescence color is changed three times, $4^{3+1} = 256$ types of molecules can be discriminated. Therefore, this method will allow us to detect an enormous variety of biomolecules simultaneously.

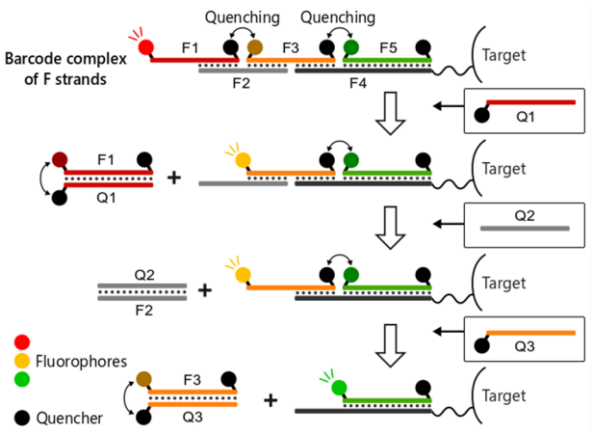


Fig. 1 Schematic illustration of color-changing fluorescent barcode method based on strand displacement reaction.

We synthesized oligonucleotides with three fluorophores Cy5, Cy3, and FAM, as components of fluorescent barcode. When Q strands are added to barcode complex, the intended fluorescence color changes were confirmed by fluorescence measurements. Furthermore, the applicability of our method to immunofluorescence was investigated. Fluorescent barcode was conjugated to antibody through the heterobifunctional crosslinker. Immunostaining with fluorescent barcode-antibody conjugates successfully visualized three proteins in fixed HeLa cells.[1]

1) K. Makino, E. Susaki, M. Endo, H. Asanuma, H. Kashida, *J. Am. Chem. Soc.*, **2022**, *accepted*.

TLS/FUS の RGG 領域の核酸結合性のアルギニンメチル化による制御

（静大院創造[1]・静大院理[2]）○増澤樹[1]・八木涼太[2]・河合信之輔[2]・大吉崇文[1,2]

Nucleic Binding Selectivity of RGG Domain in TLS/FUS Regulated by Arginine Methylation

(*[1]Graduate School of Science and Technology, Shizuoka University, [2] Graduate School of Integrated Science and Technology, Shizuoka University*)○Tatsuki Masuzawa,[1] Ryota Yagi,[2] Shinnosuke Kawai,[2] Takanori Oyoshi[1,2]

TLS (Translocated in liposarcoma)/FUS (Fused in sarcoma) is a one of the G-quadruplex (G4) binding protein. Previously we reported secondary structure of Arg-Gly-Gly repeat (RGG) domain in TLS/FUS is important for its G4 binding activity. Furthermore, Arg in RGG domain is methylated by Protein Arginine Methyltransferase 1 (PRMT1). However, not knowing about the effect of Arg methylation for nucleic binding activity of RGG domain, we purposed to elucidate it.

In result, Arg methylation altered nucleic binding selectivity of RGG domain from G4 DNA/RNA to single stranded DNA/RNA. Moreover, Arg methylation disrupted the secondary structure of RGG domain. Taken together, it is suggested that Arg methylation regulates nucleic binding selectivity of TLS/FUS by changing secondary structure of RGG domain.(Fig.1)

Keywords : G-quadruplex; TLS/FUS; methylation; G4 binding protein; β-turn structure

TLS (Translocated in liposarcoma)/FUS (Fused in sarcoma)はグアニン四重鎖(G4)結合性タンパク質の 1 つで、当研究室はこれまでに TLS/FUS が Arg-Gly-Gly 繰り返し(RGG)領域の二次構造依存的に G4 に結合していることを明らかにしている。過去の研究から G4 結合に重要な RGG 領域中の Arg は細胞内でメチル化修飾を受けることが知られているが、Arg のメチル化が核酸結合性にどのように影響しているかは不明である。そこで本研究は RGG 領域中の Arg のメチル化が TLS/FUS の G4 結合性をどのように制御しているかを明らかにすることを目的とした。

その結果、メチル化修飾を受けた RGG 領域は G4 結合性を失い、一本鎖核酸結合性へと変化した。また、メチル化により G4 結合性に重要な RGG 領域の二次構造の形成率が低下した。以上の結果から、RGG 領域中の Arg のメチル化が二次構造を変化させることにより核酸結合性を制御していることが明らかになった(Fig.1)。

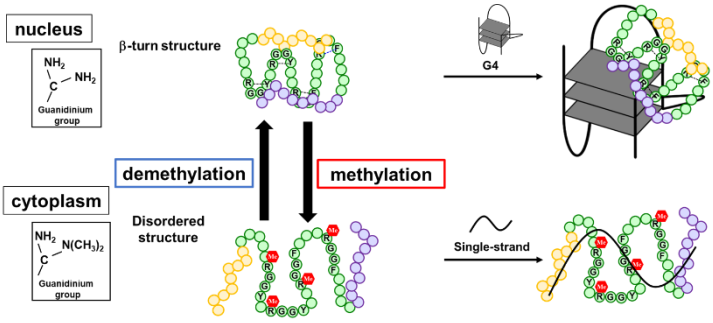


Fig. 1 Model of nucleic binding selectivity regulation mechanism by Arg methylation in RGG domain

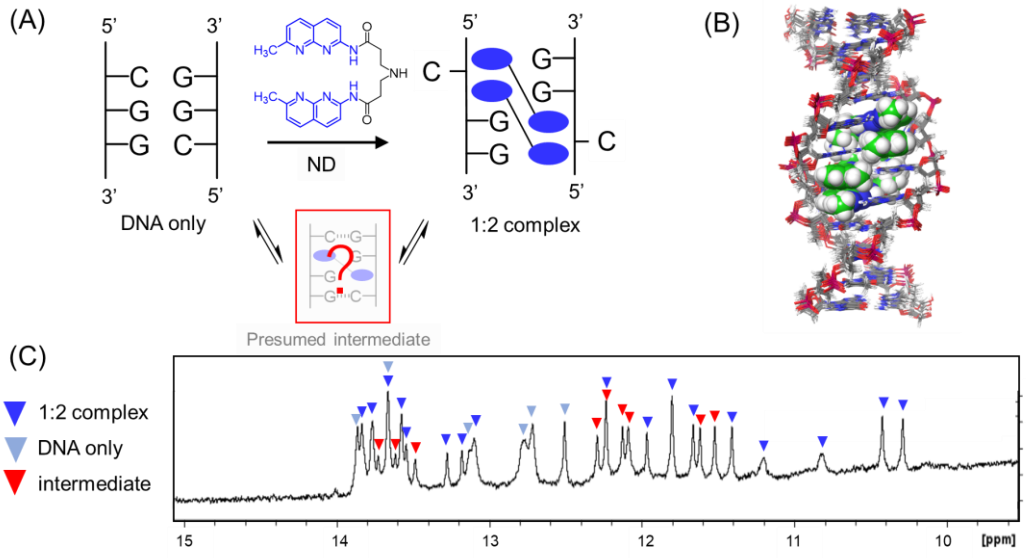
NMR study on the binding of naphthyridine dimer to d(CGG) triad

([1]*SANKEN, Osaka University,* [2]*Institute for Protein Research, Osaka University,* [3]*Yokohama National University)* ○Shuhei Sakurabayashi,[1,2] Kyoko Furuita,[2] Takeshi Yamada,[1] Toshimichi Fujiwara,[2] Kazuhiko Nakatani,[1] Chojiro Kojima[2,3]

Keywords: NMR, structural analysis, naphthyridine, triplet repeat, mismatch

More than 40 neurodegenerative disorders are caused by expansions of simple sequence repeats in the human genome. Fragile X syndrome is a repeat expansion disease caused by the aberrant CGG repeat expansions in an *FMR1* gene. Naphthyridine dimer (**ND**, Fig. 1B) is a synthetic small molecule, which binds to d(CGG) triad, a structural motif found in the hairpin structure found in CGG repeat.[1] Our previous studies have shown that two molecules of **ND** bind to the CGG sequence, but we did not obtain presice structural information of the complex of **ND** and d(CGG) triad.

In this study, the binding of **ND** to a dsDNA oligonucleotide containing a d(CGG) triad was investigated by NMR spectroscopy. The complex structure of the 1:2 (= dsDNA : **ND**) complex was determined using ^{1}H-^{1}H NOESY spectra. Also, to obtain the information on binding dynamics of **ND** toward DNA, we optimized the NMR measurement conditions such as temperature, the concentration of **ND**, and magnetic field to observe the intermediate. As a result, we revealed that approximately 30% of the intermediate corresponding to 1:1 (= dsDNA : **ND**) could be observed under the optimized conditions, and constructed the binding model of the intermediate. These obtained structural insights allow to improve the molecular properties of **ND**, and understand dynamic binding profiles.



(A) The binding mode of **ND** to d(CGG) triad. (B) the 1:2 complex structure of d(CGG) triad and **ND** determined by NMR. (C) 1D ^{1}H-NMR spectrum of the binding intermediate of imino proton region.

Recognition of double-stranded DNA by using parallel-stranded PNAs

([1]*Graduate School of Science, Nagoya University*, [2]*RIKEN, SPring-8*) ○Masanari Shibata,[1] Yuichiro Aiba,[1] Masaki Hibino,[1] Hiroshi Sugimoto,[2] Osami Shoji[1]

Keywords: Peptide Nucleic Acids; Recognition of dsDNA; Double-duplex invasion

Small molecules to recognize target sequences in double-stranded DNA (dsDNA) have been extensively studied because of their applicability. Peptide nucleic acid (PNA), a type of DNA analog (Fig. 1a),[1] has been utilized for the direct recognition of dsDNA via the formation of a unique invasion complex (Fig. 1b).[2] However, nucleobase modifications of PNAs are necessary to inhibit undesired PNA/PNA duplex formation and have been an obstacle to a wide range of applications of dsDNA recognition by PNAs. Recently, only using PNAs without any modifications of their nucleobases and backbones, we succeeded in efficient recognition of target dsDNA sequences.[3]

Herein, we have designed a pair of PNAs in not antiparallel but parallel to inhibit the binding between PNAs (Fig. 1c) and developed a new strategy for PNA invasion. The efficiency of invasion complex formation can be evaluated by electrophoretic mobility shift assay (EMSA), since the complex shows a lower mobility than corresponding dsDNA. The EMSA showed the formation of the invasion complex (lanes 3 & 4 in Fig. 1d) as well as high sequence selectivity, enabling discrimination of 1 base mismatch (lanes 5 & 6 in Fig. 1d). The melting temperature of the duplex with the parallel PNA/PNA was much lower than the antiparallel PNA/PNA duplex, suggesting destabilization of PNA/PNA duplex formation and improvement on the efficient formation of the invasion complex. Moreover, we succeeded in the X-ray crystal structure analysis of the parallel PNA/PNA duplex. Details of the structure and comparison with antiparallel one will be discussed in the presentation.

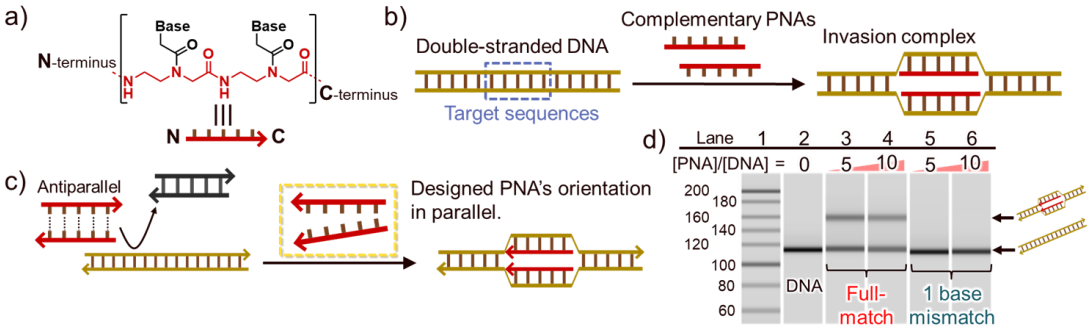


Fig. 1 (a) Structure and orientation of PNA. (b) Double-stranded DNA recognition of PNA via invasion complex formation. (c) Newly developed PNA invasion using parallel-stranded PNAs. (d) EMSA for evaluation of the sequence selectivity.

1) P. E. Nielsen *et al., Science.* **1991**, 254, 1497-1500. 2) J. Lohse *et al., Proc. Natl. Acad. Sci. U.S.A.* **1999**, 96, 11804-11808. 3) M. Shibata *et al., manuscript in preparation.*

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (78) : Analysis of structural dynamics of *c-Myc* G-quadruplex DNA using high pressure

(*[1]FIBER, Konan Univ., [2]Sun Yat-sen Univ., [3]FIRST, Konan Univ.*) ○Shuntaro Takahashi[1], Tatsuya Ohyama[1], Shuo-Bin Chen[2], Jia-Heng Tan[2], Naoki Sugimoto[1,3]

Keywords: Nucleic acids; Thermodynamics; High pressure; Guanine quadruplex; Mg^{2+} ion

Nucleic acids (DNA and RNA) form not only duplexes but also non-duplexes such as the guanine quadruplex (G4). These structural changes between these structures regulate the function of proteins that interact with nucleic acids. Thus, the formation of G4 regulates reactions such as gene replication and transcription.[1,2] The interaction of cations is also highly important in such changes in nucleic acid structure. In cells, the concentration of cations (Na^+, K^+, Mg^{2+}, etc.) changes dynamically, which may affect physical properties of G4 and regulate gene expression. We studied previously the dynamics of hydration during the G4 formation using high pressure.[3] In this study, we investigated the effect of Mg^{2+} on G4 formation using high pressure.

The results of CD melting curves of G4 from the *cMyc* gene under ambient pressure showed that there was little change in stability for both Mg^{2+} concentrations of 0 and 8 mM. Under high pressure, a tendency for the structural stability of *cMyc* G4 to decrease with increasing pressure was observed under both conditions (Fig. 1). This indicates that the volume of the G4 structure including hydration is larger than the single-stranded state. On the other hand, the decrease in stability was greater in the 8 mM condition than in the absence of Mg^{2+}. The CD spectral analysis showed no conformational change of *cMyc* G4 with Mg^{2+} concentration. Therefore, the Mg^{2+}-dependent of the volume change of *cMyc* G4 was not due to a change in the overall G4 structure, but rather to dehydration associated with the specific binding of Mg^{2+} to *cMyc* G4. The replication inhibition by *cMyc* G4 in the presence of 8 mM Mg^{2+} was strongly observed. These results suggest that *cMyc* G4 may regulate the gene expression by altering the mechanism of its formation and melting without changing the stability of G4 depending on the Mg^{2+} concentration.

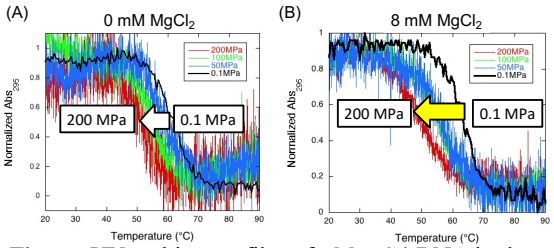


Figure. UV melting profiles of *cMyc* G4 DNA in the absence (A) or presence (B) of 8 mM $MgCl_2$. The measurements were carried out in 10 mM Tris-HCl pH 7.5, 2 mM KCl, and 0 or 8 mM $MgCl_2$. The solution contained 10 uM DNA.

1) S. Takahashi, N. Sugimoto, *Chem. Soc. Rev.* **2020**, *49*, 8439. 2) S. Takahashi, A. Kotar, H. Tateishi-Karimata, S. Bhowmik, Z.-F. Wang, T.-C., Chang, S. Sato, S. Takenaka, J. Plavec, N. Sugimoto, *J. Am. Chem. Soc.* **2021**, *143*, 16458. 3) S. Takahashi, N. Sugimoto, *Angew. Chem. Int. Ed.,* **2013**, *52*, 13774.

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (75): Development of RNA-ligand pairs for multicolor RNA imaging in cells

(*[1]FIBER, Konan University, [2] Sun Yat-sen Universsity, [3]FIRST, Konan University*) ○Tamaki Endoh[1], Jia-Heng Tan,[2] Shuo-Bin Chen[2], Naoki Sugimoto[1,3]

Keywords: RNA; Aptamer; Selection; Imaging; Broccoli

Recent successes in RNA selection toward chemicals that mimic chromophore of fluorescent protein has intensified development of light-up RNA aptamers, which drastically enhance fluorescence of small chemicals. For examples, Spinach, Broccoli, and their derivatives, which interact with a 3,5-difluoro-4-hydroxybenzylidene imidazolinone (DFHBI), enabled real-time imaging of RNA in living cells.[1]

Based on a structural analysis, the binding pocket of DFHBI in Spinach was revealed to consist of U-A-U triad and G-quartet. DFHBI is sandwiched by the triad and quartet interacting with a nucleobase connecting the triad and the quartet.[2] Here, we envisioned that the basic structure core of the binding pocket would be suitable scaffold for accommodating various chemicals as well as DFHBI. Especially, G-quadruplex ligands, some of which show unique light-up properties, likely be accommodated with relatively high affinity because the core contains G-quartet unit. We have recently demonstrated a simple optimization technology of the light-up aptamer by using RNA-capturing microsphere particles (R-CAMPs), which immobilize DNA and RNA clones of identical sequence on the surface of the same particle.[3] In this study, we tried simultaneous selection of light-up aptamers, which emit fluorescence in different colors, by using a mutated Broccoli and a mixture of G-quadruplex ligands and DFHBI as an initial RNA library and target ligands, respectively (Figure). Two of three light-up aptamers selected successfully functioned in cells. In addition, by combinational use with another RNA aptamer targeting malachite green, we have succeeded triple color imaging of different RNAs in cells.

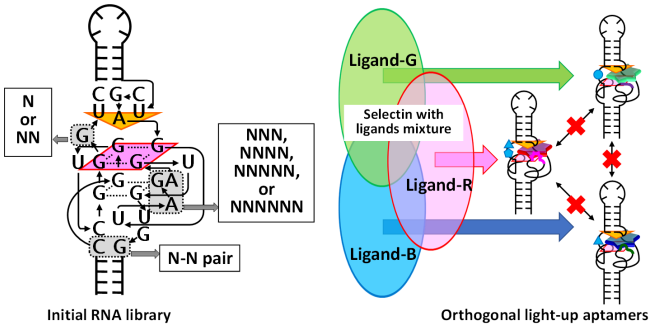


Figure. Schematic illustration of RNA derivatization and selection of orthogonal light-up aptamers.

1) a) S. R. Jaffrey *et al.*, *Science*, **2011**, *333*, 642. b) S. R. Jaffrey *et al.*, *J. Am. Chem. Soc.*, **2014**, *136*, 16299. 2) A. R. Ferré-D'Amaré *et al.*, *Nat. Struct. Mol. Biol.*, **2014**, *21*, 658. 3) a) N. Sugimoto *et al.*, Small, **2019**, *15*, 1805062. b) T. Endoh and N. Sugimoto, *Anal. Chem.*, **2020**, *92*, 7955.

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (73): Effect of G-quadruplex stability change on transcriptional repression in cancer cells

([1]*Frontier Institute for Biomolecular Engineering Research (FIBER) Konan University,* [2] *Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University,* [3]*Division of Molecular Oncology, Aichi Cancer Center Research Institute,* [4]*Nagoya University, The Institute of Innovation for Future Society*) ○ Hisae Tateishi-Karimata,[1] Keiko Kawauchi,[2] Tatsuya Ohyama,[1] Hirano Masaki,[3] Atsushi Natsume,[4] Naoki Sugimoto[1,2]

Keywords: transcript mutation; cancer cell; malignant alteration; G-quadruplex; potassium ion concentration

Transcription is the first step in gene expression; it is highly regulated during both initiation and elongation.[1] DNA structures are known to affect cellular processes. We have shown that G-quadruplex formations are highly responsive to surrounding conditions including cation concentration and the G-quadruplexes in the template DNA induce transcription mutation.[2] Malignant cancer cells have a much lower K^+ concentration than normal cells, thus, G-quadruplexes may be unstable in the cells. However, relationships between G-quadruplex formation and tumor progression are still unclear.

Here, we designed and studied template DNAs (Figure 1): a linear sequence that does not have significant higher-order structure and several G-rich sequences from proto-oncogene. Transcription reaction *in vitro*, G-rich templates induced the production of arrested and slipped transcripts in a solution containing 150 mM KCl (normal conditions), although the linear sequence produced only a full-length transcript. The production efficiency of full-length and slipped transcripts from templates that formed the stable G-quadruplex was lower than that from the linear sequence. With decreasing K^+ concentration, which decreases G-quadruplex stability, transcription efficiencies increased. The trend in transcription efficiency versus G-quadruplex stability in normal cells was similar to that *in vitro* experiments. Interestingly, higher transcription levels from G-rich templates were observed in Ras-transformed and highly metastatic breast cancer cells than in non-transformed and control cells. These results suggest that in normal cell, K^+ ions attenuate the transcription of certain oncogenes by stabilizing G-quadruplex structures.[3] In our presentation, we will discuss how the stability of G-quadruplexes in cell is changed during tumor progression.

1) H. Tateishi-Karimata, N. Sugimoto *Nucleic Acids Res,* **2021**, *49,* 7839. 2) H. Tateishi-Karimata, N. Isono, N. Sugimoto, *PLoS ONE.* **2014**, *9,* e90580. 3) H. Tateishi-Karimata, K. Kawauchi, N. Sugimoto, *J. Am. Chem. Soc.* **2018**, *140*, 642.

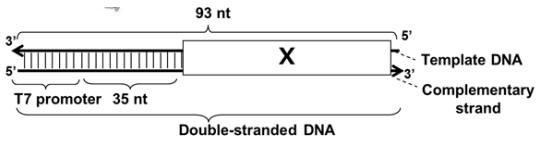


Figure 1. Illustration of the template DNA. The region denoted by the box marked with X contains the sequence designed to form a random coil or a G-quadruplex.

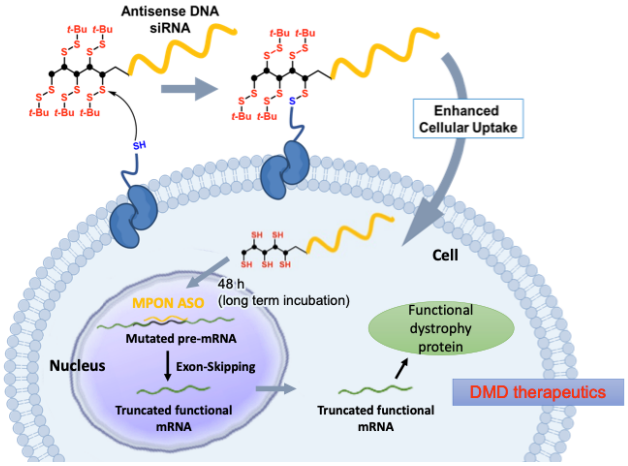
膜透過性核酸 MPON は効率的に核移行しエキソンスキッピングを促進する

(名大院理[1]・マードック大学[2]・理研[3]・ナノ医療イノベーションセンター[4]・京都府立医科大医[5]・糖鎖生命コア研究所[6]) ○平岡 陽花[1]・Zhaoma Shu[1]・Bao Tri Le[2]・益田 恵子[3]・中本 航介[1]・林 光太朗[4]・阿部 奈保子[1]・木村 康明[1]・Rakesh N. Veedu[2]・清水 義宏[3]・内田 智士[5]・阿部 洋[1,2,6]

Membrane permeable oligonucleotide (MPON) modified with disulfide units induces efficient exon skipping through enhanced membrane permeability and nucleus internalization ([1]*Grad. Sch. of Sci., Nagoya Univ.*, [2]*CMMIT, Murdoch Univ.*, [3]*RIKEN*, [4]*iCONM*, [5]*Grad. Sch. of Med., Kyoto Pref. Univ. of Med.*, [6]*iGCORE*) ○Haruka Hiraoka[1], Zhaoma Shu[1], Bao Tri Le[2], Keiko Masuda[3], Kosuke Nakamoto[1], Kotaro Hayashi[4], Naoko Abe[1], Yasuaki Kimura[1], Rakesh N. Veedu[2], Yoshihiro Shimizu[3], Satoshi Uchida[5], Hiroshi Abe[1,2,6]

In order to improve the cell permeability of nucleic acid drugs, we developed membrane permeable oligonucleotide (MPON) modified with disulfide units. Microscopic observation and inhibitory assay suggested that MPON achieved ultrafast and spontaneous uptake by direct transfer into cytosol via the binding with membrane proteins. We also found that MPON existed in nucleus 48-72 hours after addition, implicating the potential of MPON to target nuclear DNA. So then, MPON targeting the mutated *dmd* gene, a responsible factor of muscle dystrophy, was administrated to disease-modeled mice cells. As a result, it induced the removal of mutated sequence due to the inhibition of splicing by MPON binding. This research indicated the possibility to achieve the efficient delivery of nucleic acid drugs using MPON.
Keywords ***: Nucleic acid drug, antisense DNA, disulfide modification, exon skipping***

核酸医薬の課題である膜透過性の低さを解決する手段として、我々の研究室では、**ジスルフィドユニットを修飾したオリゴ核酸**を開発し、膜透過性核酸 MPON と名付けた。顕微鏡観察および阻害実験の結果から、MPON は、エンドサイトーシスを介さず膜タンパク質との結合によって直接かつ超高速に細胞質へ導入されると示唆された。さらに MPON の添加後 48-72 時間で核移行が観察され、核内 DNA を標的とできる可能性が示された。そこで、筋ジストロフィーの原因となる変異 *dmd* 遺伝子のスプライシング部位を標的とするアンチセンス核酸を MPON 化して疾患モデルマウスの細胞に導入したところ、やはり 48-72 時間後に、核内でのスプライシング阻害を介した変異配列の除去が確認された。これは **MPON を利用した有用な医薬品送達の実現可能性**を示すものである。



Graphical abstract：Hiraoka and Shu et al., *ChemBioChem*, **22(24)**, 3437, 2021

[G202-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Ryo Okamoto, Shinya Hanashima
Fri. Mar 25, 2022 1:00 PM - 3:40 PM G202 (Online Meeting)

[G202-3pm-01] Elucidation of dynamic behavior of exosome membranes involved in intracellular uptake efficiency

○Tomokazu Yasuda[1], Koichiro M Hirosawa[2], Kenichi G.N. Suzuki[2], Kazuya Kabayama[1], Michio Murata[1], Shinya Hanashima [1] （1. The University of Osaka, 2. Institute for Glyco-core Research (iGCORE), Gifu University）

1:00 PM - 1:20 PM

[G202-3pm-02] Membrane Deformations by Designed Molecules: Endocytosis-like Vesicle Fission Induced by a Photoreactive Amphiphilic Molecule

Noriyuki Uchida[1], ○Takahiro Muraoka[1] （1. Tokyo Univ. of Agriculture and Technology）

1:20 PM - 1:40 PM

[G202-3pm-03] Control of molecular localization in artificial cells using chemical inputs

○Keita Tsutsui[1], Masaru Yoshikawa[1], Tomoaki Matsuura[2], Shinya Tsukiji[1] （1. Grad. Sch. of Eng. Nagoya Inst. of Tech., 2. Tokyo Inst. of Tech. ELSI）

1:40 PM - 2:00 PM

[G202-3pm-04] Asymmetric lipid-protein vesicles facilitate function of membrane proteins and construction of cell fission model

○Masato Suzuki[1], Koki Kamiya[1] （1. Gunma Univ）

2:00 PM - 2:20 PM

[G202-3pm-05] Preparation and functional analysis of single chain antibodies bound to sialyl Tn antigen sugar chains

○Mitsuki Hashiguchi[1], Komi Yoshimatsu[1], Yumi Matsubayashi[1], Kaito Hashiguchi[1], Nana Masunaga[1], Hiroyuki Shinchi[1], Masahiro Wakao[1], Yuji Ito[1], Yasuo Suda[1] （1. The Univ. of Kagoshima）

2:20 PM - 2:40 PM

[G202-3pm-06] One Pot-Chemical Synthesis of Glycoproteins and Their Specific Glycan-Hydration Effect

○Hiroyuki Shibata[1], Yuya Tanaka[1], Donglin Zhao[1], Yuta Maki[1,2], Yasuhiro Kajihara[1,2], Ryo Okamoto[1,2] （1. Dept. Chem., Grad. Sch. Sci., Osaka Univ., 2. PRC,Grad. Sch. Sci., Osaka Univ.）

2:40 PM - 3:00 PM

[G202-3pm-07] Synthesis of *N*-glycolylneuraminic acid derivatives (IV) ~Investigation of the glycosylation reaction~

○Jianhong Zhang[1], Tetsuo Koyama[1], Takahiro Matsushita[1,2], Ken Hatano[1,2], Koji Matsuoka[1,2] （1. graduate school of science and engineering, saitama university, 2. advanced institute of innovative technology, saitama university）

3:00 PM - 3:20 PM

[G202-3pm-08] Orientation of the Ganglioside GM3 Glycan in Lipid Bilayers as Elucidated by Solid-State NMR

○Katsuaki Sasaki[1], Yuichi Umegawa[1], Michio Murata[1], Shinya Hanashima[1] （1. Grad. Sch. Sci., Osaka Univ.）

3:20 PM - 3:40 PM

Elucidation of dynamic behavior of exosome membranes involved in intracellular uptake efficiency

([1]*Graduate School of Science, Osaka University*, [2]*Institute for Glyco-core Research (iGCORE), Gifu University*) ○ Tomokazu Yasuda,[1] Koichiro M. Hirosawa,[2] Kenichi G.N. Suzuki,[2] Kabayama Kazuya, [1] Michio Murata,[1] Shinya Hanashima[1]

Keywords: exosome, fluorescence spectroscopy, membrane fluidity, intracellular uptake, fluorescent microscopy

Exosomes, a type of extracellular vesicles (EVs), are small vesicles with a diameter of 40-150 nm. The exosomes regulate biological processes by transporting proteins and nucleic acids as an intracellular communication tool. Through the recent lipidomics studies [1], exosome membranes are found to be often enriched with sphingomyelin and cholesterol (Cho), which are typical lipids for the microdomains (lipid rafts) in the plasma membrane. However, the membrane dynamics of exosomes involved in regulating the activity of functional biomolecules have hardly been elucidated.

We evaluated the membrane dynamics of exosomes by fluorescent spectroscopy (anisotropy and lifetime) and compared them with the artificial model membranes. The results suggested the presence of raft-like ordered domains, and the different dynamics between outer and inner leaflets in a similar manner to those of plasma membranes. In addition, these lateral and interleaflet heterogeneities of exosome membranes were variable depending on the exosome-derived donor cell lines.

Moreover, we artificially prepared Cho-poor exosomes using methyl-β-cyclodextrin, and observed the uptake of the exosomes into the cells with fluorescence microscopy. By comparing with the uptake of the intact exosomes, we were able to clarify the importance of the exosomal Cho in the cellular uptakes of exosomes.

[1] Skotland, T.; Sandvig, K.; Llorente, A. *Prog. Lipid Res.* **2017**, *66*, 30-41.

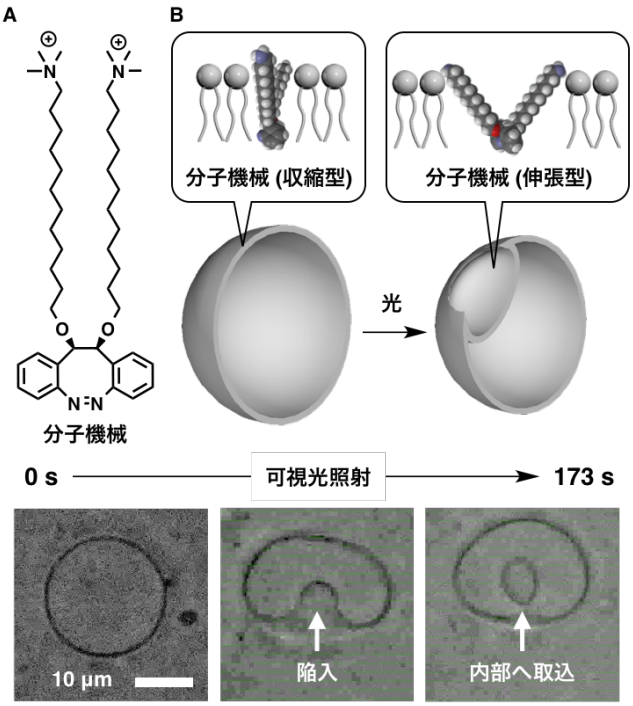
リン脂質膜変形分子素子の開発(1)：光応答性両親媒性分子を用いたエンドサイトーシス様ベシクル分裂

（東農工大院工[1]、KISTEC[2]）○内田紀之[1]・村岡貴博[1,2]
Membrane Deformations by Designed Molecules: Endocytosis-like Vesicle Fission Induced by a Photoreactive Amphiphilic Molecule ([1]*Tokyo University of Agriculture and Technology*, [2]*KISTEC*) ○Noriyuki Uchida[1], Muraoka Takahiro[1,2]

Endocytosis is an important membrane deformation event associated with virus invasions. Here, we designed an amphiphilic molecular machine whose structure changes by light. Upon light irradiation of the vesicle containing the molecular machine, endocytosis-like outside-in fission was induced with extension of the membrane. Furthermore, we successfully incorporated micro-meter scale objects into the vesicle by the endocytosis.

Keywords: Phospholipid Bilayers; Photoresponsiveness; Molecular Machine; Vesicle Fission; Membrane Deformation

エンドサイトーシスはウイルスの侵入などの生体現象に関わる重要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分子機械（図A）の合成に成功した。さらに、分子機械を導入した DOPC ベシクルに対して可視光を照射したところ、分子機械による膜の伸張と共に、エンドサイトーシスのような外部から内部への膜分裂が引き起こされることを見出した（図 B）。このユニークな膜変形現象を利用することで、溶液中のマイクロスケールの粒子をベシクル内部へと高効率で取り込むことができる。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、および応用に関して報告する。



化学インプットを用いた人工細胞内分子局在制御

(名工大院工[1]・東工大地球生命研[2]) ○筒井 啓太[1]・吉川 優[1]・松浦 友亮[2]・築地 真也[1]
Control of molecular localization in artificial cells using chemical inputs ([1]*Graduate School of Engineering, Nagoya Institute of Technology*, [2]*Earth-Life Science Institute, Tokyo Institute of Technology*) ○Keita Tsutsui,[1] Masaru Yoshikawa,[1] Tomoaki Matsuura,[2] Shinya Tsukiji[1]

The bottom-up creation of “artificial cells” is an approach to understanding the origin of life and the function of live cells constitutively. Most of the previously reported artificial cells have a simple structure consisting of the liposome membrane and inner solution, and the molecules encapsulated in the liposome are diffused homogeneously in the inner solution. However, natural cells have a variety of organelles and control various biochemical reactions in space and time by dynamically localizing proteins to organelles in response to external stimuli. Therefore, controlling the molecular localization in liposomes by external stimuli is an important challenge in creating highly functionalized artificial cells. In this presentation, we report an approach to control molecular localization in artificial cells by using designed synthetic molecules as chemical inputs. We established a method for rapidly inducing translocation of proteins from the solution phase to the liposome membrane or nucleus-like artificial organelles by the addition of synthetic molecules. The chemically triggered protein translocation enabled to control biochemical reactions in a spatiotemporal manner in liposomes.
Keywords*: liposome; artificial cell; artificial organelle; signal transduction; small-molecule ligand*

生命の起源や細胞の機能を構成的に理解するためのアプローチとして、細胞と類似の機能を発現する“人工細胞”をボトムアップに創る研究が注目されている。例えばこれまでに、細胞分裂を模倣した人工細胞や、遺伝子の転写と翻訳を同時に行う人工細胞などが報告されている[1-3]。これらの人工細胞のほとんどはリポソーム膜と内水相で構成されたシンプルな構造体であり、リポソーム内に封入した分子は内水相を均一に拡散させて用いている。一方、実際の細胞を見てみると、細胞膜で囲まれた細胞質には様々なオルガネラが存在する。細胞は、外部刺激に応答してオルガネラや膜などの区画にタンパク質を動的に局在させることで様々な生化学反応を時空間的に制御している。従って、人工細胞内の特定の区画への分子局在を外部刺激によってコントロールすることは、さまざまな分子プロセスの時空間制御が可能な高次人工細胞を創生する上で重要な課題の一つである。

本発表では、デザインした合成化合物を化学インプットとして用いることで、人工細胞内の分子局在を制御するアプローチについて報告する。我々は、合成化合物の添加によってリポソーム内のタンパク質を脂質膜や核様人工オルガネラへ迅速に局在移行させる手法を確立した。さらに、その局在移行をトリガーとしてリポソーム内での生化学反応を時空間制御できることを実証した。

1) Y. Dreher et al., *Angew. Chem. Int. Ed.* **2021**, *60*, 10661–10669. 2) K. Kurihara et al., *Nature Chem.* **2011**, *3*, 775–781. 3) S. M. Nomura et al., *ChemBioChem* **2003**, *4*, 1172–1175.

脂質-タンパク質非対称小胞を用いた膜タンパク質の機能と細胞分裂モデルの構築

（群大院理工）○鈴木 允人・神谷 厚輝
Asymmetric lipid-protein vesicles facilitate function of membrane proteins and construction of cell fission model (*Graduate School of Science and Technology, Gunma University*) ○Masato Suzuki, Koki Kamiya

Lipid vesicles, or liposomes, possess a phospholipid bilayer and have been used as artificial cell models. Recently, vesicles formed by amphiphilic proteins have been reported[1]. However, a formation of micro-sized amphiphilic protein vesicles and an observation of membrane protein function on the amphiphilic protein vesicles are different. In this study, we generate the cell-sized asymmetric lipid-protein vesicles that allow the growth and fission of vesicles. First, we formed the lipid-protein vesicles by a droplet transfer method. Next, we observed the membrane protein function by the transportation of the fluorescent molecules on the asymmetric lipid-protein vesicles. Finally, we demonstrated the growth and fission of the asymmetric lipid-protein vesicles by an external stimulation (Figure 1).
Keywords : Lipid vesicles; Amphiphilic protein; Membrane protein; Artificial cell model

リポソームは細胞膜と同様、リン脂質二重膜から構成され、人工細胞の構築、細胞の成長・分裂等の研究分野に用いられている。近年、両親媒性のタンパク質から構成された小胞が報告されている[1]。しかし、タンパク質小胞はマイクロサイズにおける形成例が少ない。また、タンパク質小胞の膜は細胞膜よりも厚いため、膜タンパク質の機能観察が困難である。今回、私たちは膜タンパク質の機能観察と小胞の成長・分裂が可能な細胞サイズのリン脂質-両親媒性タンパク質非対称小胞を形成した。まず、界面通過法によって外膜をリン脂質、内膜を両親媒性タンパク質で構成した小胞を作製した。次に、脂質-タンパク質非対称小胞上において、膜タンパク質による蛍光分子の輸送を観察した。最後に、外部刺激に応答して脂質-タンパク質小胞の成長・分裂が生じる系を構築した(Figure 1)。

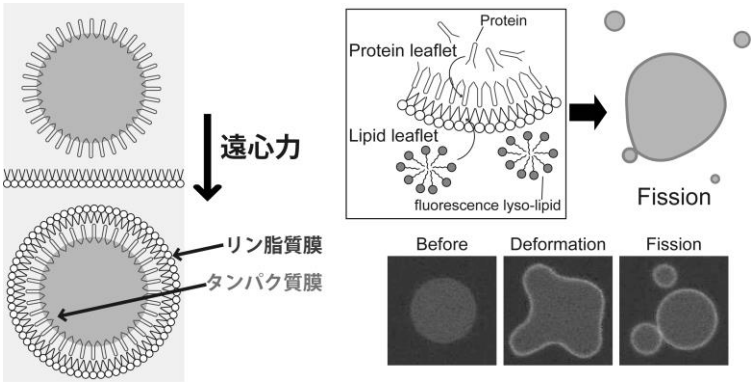


Figure 1. 脂質-タンパク質非対称小胞の作製概略図と変形・分裂の様子

[1] K. B. Vargo, R. Parthasarathy, D. A. Hammer, *Proc. Natl. Acad. Sci.* **2012**, *109*, 11657.

シアリル Tn 抗原糖鎖に結合する一本鎖抗体の調製と機能解析

（鹿児島大・院理工）○橋口 允紀・吉松 幸美・松林 由眞・橋口 海斗・増永 成菜・新地 浩之・若尾 雅広・伊東 祐二・隅田 泰生

Preparation and functional analysis of single chain antibodies bound to sialyl Tn antigen sugar chains (*Grad. School. Sci. and Eng.*, *Kagoshima Univ.*) ○ Mitsuki Hashiguch, Komi Yoshimatsu, Yumi Matsubayashi, Kaito Hashiguchi, Nana Masunaga, Hiroyuki Shinchi, Masahiro Wakao, Yuji Ito, Yasuo Suda

Cancer cells express aberrant levels and/or types of sugar chains named as tumor-associated carbohydrate antigens (TACAs) on their cell surface. *N*-Glycolylneuraminic acid-containing Tn (Neu5Gc-Tn) antigen is one of the TACAs and is an ideal target for developing novel anticancer agents. In the previous study, we established a sugar chain binding single chain variable fragment antibody (scFv) as a novel molecularly targeted agent for adult T-cell leukemia using fiber type Sugar Chip (fiSC) and a phage display method. In this study, we applied the technology to prepare scFvs binding to Neu5Gc-Tn sugar chain and analysed their binding potency to various cancer cell membrane proteins.

Keywords : Tumor-associated carbohydrate antigens; Phage display method;

細胞のがん化に伴い、がん関連糖鎖抗原と呼ばれる異常型糖鎖が発現する。*N*-グリコリルノイラミン酸（Neu5Gc）を有するシアリル Tn 抗原は、腫瘍特異性の高い糖鎖抗原であり、新たな腫瘍マーカーとして期待されている。我々はこれまでに、独自のファイバー型シュガーチップ（fiSC）[1]とファージディスプレイ法を用いて、がん細胞表層の糖鎖に結合する一本鎖抗体（scFv）を得る手法を確立している[2]。本研究では、有機化学的手法で合成した Neu5Gc-Tn 抗原糖鎖を固定化した fiSC（Neu5Gc-Tn-chip）を用いて、Neu5Gc-Tn 抗原糖鎖に優先的に結合する一本鎖抗体（scFv）を調製し、得られた scFv のがん細胞由来膜タンパク質への結合性を解析した。

Neu5Gc-Tn-chip を用いて、scFv 提示ファージをスクリーニングし、計 23 個のファージクローンを得た。これらのファージミドの scFv 発現遺伝子を pET-26b(+) vector に組換え、大腸菌 Lemo21(DE3)株を用いて可溶性の scFv の発現を誘導した。アミノ酸配列の異なる 17 個の可溶性の scFv が得られた。これらの scFv の糖鎖結合性を、種々のシアル酸糖鎖を固定化した fiSC を用いて評価したところ、3 個の scFv がシアリル Tn 抗原糖鎖に結合性を示した。次いで、HepG2 細胞や CaSki 細胞から調製した細胞膜タンパク質画分をプラスチックプレートに固定化し、上記 3 個の scFv の結合性を ELISA 法によって評価した。その結果、いずれの scFv も細胞に依存しかつ scFv の濃度依存的な結合活性が観測され、さらに膜タンパク質画分を種々のグリコシダーゼで処理すると、scFv の結合活性は減少した。以上から、得られた 3 つの scFv は細胞膜タンパク質のシアル酸糖鎖に結合することが示唆された。

1) Wakao, M., *et al*., Anal. Chem. **2017**, *17*, 1086-1091.
2) Muchima, K., *et al*., J. Biochem. **2018**, *163*(*4*), 281–291.

One-Pot Chemical Synthesis of Glycoproteins and Their Specific Glycan-Hydration Effect

([1]*Graduate School of Science and* [2]*Project Research Center for Fundamental Science, Osaka University*) ○Hiroyuki Shibata[1], Yuya Tanaka[1], Donglin Zhao[1], Yuta Maki[1, 2], Yasuhiro Kajihara[1, 2], Ryo Okamoto[1, 2]

Keywords: Glycoprotein, Hydration, HDX, One-Pot

The glycosylation of proteins is the ubiquitous posttranslational modification of proteins. The functional study of structurally-defined glycoproteins prepared by chemical synthesis is a powerful approach to elucidate the function of oligosaccharides on glycoproteins at a molecular level. Recently, we proposed that the hydration of oligosaccharides potentially influences the function of glycoproteins[1)]. However, the character of hydration shell of oligosaccharides on glycoproteins was still unclear. To address this issue, we carried out the chemical synthesis of the glycoforms of chemokine CCL1 and evaluated the hydration volume of various oligosaccharides on glycoproteins.

For the efficient synthesis of CCL1 glycoforms, we developed one-pot peptide coupling reaction using peptidyl-2-aminothiazoline[2)]. After extensive optimization, this synthetic method allowed us to efficiently couple two peptides and one glycopeptide followed by folding in one-pot manner. To evaluate the hydration property of CCL1 glycoforms, we carried out the hydrogen deuterium exchange mass spectrometry (HDX-MS). This revealed the unique correlation of the structures of oligosaccharides and their hydration regions that influences the hydration of protein moiety. In this presentation, we would like to present the detail of the results of HDX-MS and discuss the hydration of glycoproteins.

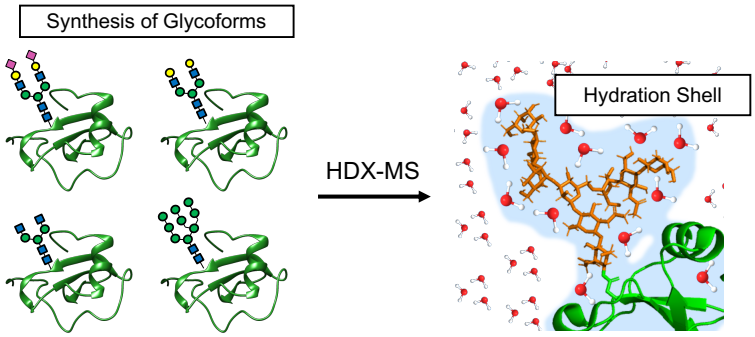


Fig. 1 Scheme of the experiment

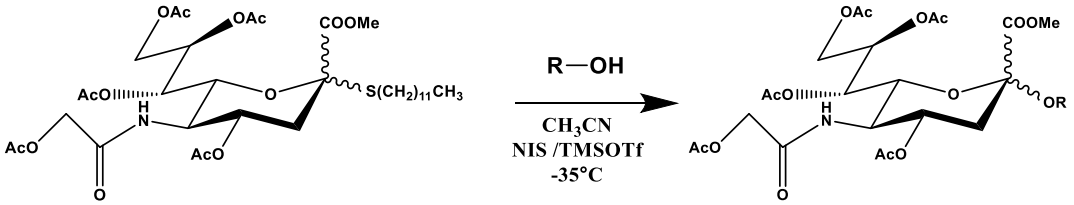
1) Y. Maki, et. al, *J. Am. Chem. Soc.* **2020**, 142, 49, 20671
2) H. Shibata, et. al, The *101st CSJ Annual Meeting*, **2021**, A22-4am

N-グリコリルノイラミン酸誘導体の合成研究（IV）： ～グリコシル化反応の検討～

（埼大院理工[1]、・埼大先端ラボ[2]）○張堅洪[1]・小山 哲夫[1]、松下 隆彦[1,2]、幡野 健[1,2]、松岡 浩司[1,2]
Synthetic Studies of *N*-Glycolylneuraminic Acid Derivatives (IV): - Investigation of Glycosylation Reactions ([1]*Graduate School of Science and Engineering, Saitama University*, [2]*Advanced Institute of Innovative Technology*) ○Jianhong Zhang[1], Tetsuo Koyama[1], Takahiro Matsushita[1,2], Ken Hatano[1,2], Koji Matsuoka[1,2]

An efficient synthesis of lauryl thioglycoside of *N*-glycolylneuraminic acid (Neu5Gc) was accomplished from lauryl thioglycoside of Neu5Ac as a key starting material. The reactivities of the lauryl glycosides of Neu5Gc as a glycosyl donor for glycosidation reaction were evaluated by means of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and *N*-iodosuccinimide (NIS) as a combined-mediator system.[1)] The glycosidation reactions proceeded smoothly and the lauryl thioglycoside showed good yields when aliphatic alcohols were used as acceptors. In addition to the simple alcohols, glycosyl acceptors derived from glucose and lactose were used as the candidates, and the glycosidation reactions yielded the corresponding glycosides with desired anomeric configurations.[2)]
Keywords: Sialic acids; Thioglycosides; Glycosidation; Oligosaccharides; Carbohydrates

Neu5Ac のラウリルチオグリコシドを出発物質として、*N*-グリコリルノイラミン酸（Neu5Gc）のラウリルチオグリコシドを効率的に合成することに成功した。トリフルオロメタンスルホン酸トリメチルシリル(TMSOTf) と *N*-ヨードスクシンイミド（NIS）を複合メディエーター[1)]として用いて、Neu5Gc のラウリルグリコシドの *O*-グリコシル化に対する反応性を評価した。簡単なアルコールをアクセプターとして用いた場合、グリコシル化反応はスムーズに進行し、ラウリルチオグリコシドは良好な収率により生成物を与えた。単純なアルコールの他に、グルコースやラクトース由来のグリコシルアクセプターを用いたグリコシル化反応についても検討し、α 選択的にグリコシドを得ることができた。[2)]



1) K. Matsuoka, *et al.*, *Tetrahedron Lett.*, **2004**, *45*, 9383-9386.
2) J. Zhang, *et al.*, *Tetrahedron Lett.*, **2021**, *83*, 153403.

Orientation of the Ganglioside GM3 Glycan in Lipid Bilayers as Elucidated by Solid-State NMR

([1]*Graduate School of Science, Osaka University*) ○Katsuaki Sasaki,[1] Yuichi Umegawa,[1] Michio Murata,[1] Shinya Hanashima,[1]

Keywords: Ganglioside; Lipid Raft; Model Membrane; Solid-State NMR; Conformational Analysis

Gangliosides are one of the important components in the bio-functional membrane domains, so called lipid rafts. Gangliosides generally consist of hydrophobic ceramide and hydrophilic sialo-glycan moieties. This amphiphilic feature is involved in various biological functions; one of which is binding activity for exogeneous proteins like viral spike-proteins and bacterial toxins.

Cholesterol-ganglioside interaction occurring at the lipid rafts has been considered to regulate the ganglioside interplay with proteins by altering the orientation of the ganglioside headgroup [1]. We previously elucidate the conformational change of the sphingomyelin headgroup induced by cholesterol [2]. For gangliosides, however, there are few lines of experimental evidence supporting glycan conformational difference [3].

We here examined the conformational difference in the glycan moiety of ganglioside GM3 by solid-state NMR experiments using isotope-labeled GM3 probes (Fig.1). A series of probes labeled on each sugar residue was synthesized, and incorporated in the model membrane mimicking the rafts or the non-rafts. The parameters obtained by solid-state NMR were compared with the theoretical predictions, in which all conformations were comprehensively considered. As a result, the orientation of the sialic acid moiety was remarkably altered depending on the presence or absence of cholesterol, while that of the glucose moiety was not significantly changed. In this presentation, we will also discuss about the whole structure of GM3 glycan moiety on the membrane surface.

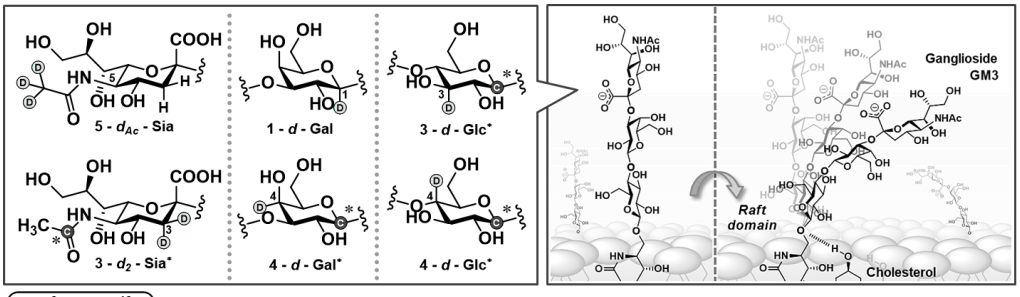


Fig.1 Schematic illustration of conformational analysis using isotope-labeled GM3 probes

[1] Lingwood, D.; Binnington, B.; Rog, T.; Vattulainen, I.; Grzybek, M.; Coskun, U.; Lingwood, C.; Simons, K. *Nat. Chem. Biol.* **2011**, *7*, 260-262. [2] Hanashima, S.; Murakami, K.; Yura, M.; Yano, Y.; Umegawa, Y.; Tsuchikawa, H.; Matsumori, N.; Seo, S.; Shinoda, W.; Murata, M. *Biophys. J.* **2019**, *117*, 307-318. [3] Takahashi, M.; Shirasaki, J.; Komura, N.; Sasaki, K.; Tanaka, H.; Imamura, A.; Ishida, H.; Hanashima, S.; Murata, M.; Ando, H. *Org. Biomol. Chem.* **2020**, *18*, 2902–2913.

[G202-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Takafumi Ueno, Osami Shoji

Fri. Mar 25, 2022 4:10 PM - 6:50 PM G202 (Online Meeting)

[G202-3vn-01] Analysis of activation mechanisms of P450BM3 by decoy molecules

○Kai Yonemura[1], Shinya Ariyasu[1], Hiroshi Sugimoto[2], Shigeru Matsuoka[3], Osami Shoji[1]
（1. Nagoya University, 2. RIKEN/SPring-8, 3. Oita University）

4:10 PM - 4:30 PM

[G202-3vn-02] Structural investigations of a semi-clathrate hydrate formation using porous ferritin crystal

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

4:30 PM - 4:50 PM

[G202-3vn-03] Structural analysis by engineering cell-free protein crystals

○Junko Tanaka[1], Satoshi Abe[1], Shuji Kanamaru[1], Takafumi Ueno[1] （1. The Univ. of Tokyo Institute of Technology）

4:50 PM - 5:10 PM

[G202-3vn-04] In-cell crystal engineering for the development of solid biomaterials

○Satoshi Abe[1], Mariko Kojima[1], Junko Tanaka[1], Yuto Nakasuji[1], Takafumi Ueno[1] （1. Tokyo Tech）

5:10 PM - 5:30 PM

[G202-3vn-05] Dynamics structural analysis of miniprotein by in-cell crystal engineering

○Mariko Kojima[1], Yuki Hishikawa[1], Satoshi Abe[1], Tadaomi Furuta[1], Duy Phuoc Tran[1], Akio Kitao[1], Takafumi Ueno[1] （1. Tokyo Institute of Technology）

5:30 PM - 5:50 PM

[G202-3vn-06] Experimental and theoretical study on converting myoglobin into a stable domain-swapped dimer by utilizing a tight hydrogen bond network at the hinge region

○Cheng Xie[1], Hiromitsu Shimoyama[2], Masaru Yamanaka[1], Satoshi Nagao[1], Hirofumi Komori[4], Naoki Shibata[3], Yoshiki Higuchi[3], Yasuteru Shigeta[2], Shun Hirota[1] （1. Nara Inst. Sci. Tech. (NAIST), 2. Univ. of Tsukuba, 3. Univ. of Hyogo, 4. Kagawa Univ.）

5:50 PM - 6:10 PM

[G202-3vn-07] Re-design of an artificial protein nanocage TIP60: structural analysis of a mutant assembled by responding to metal ions

○Naoya Ohara[1], Norifumi Kawakami[1], Ryoichi Arai[2], Naruhiko Adachi[3], Toshio Moriya[3], Masato Kawasaki[3], Toshiya Senda[3], Kenji Miyamoto[1] （1. Keio University, 2. Shinshu University, 3. High Energy Accelerator Research Organization）

6:10 PM - 6:30 PM

[G202-3vn-08] Construction of hydrogel containing an engineered hexameric hemoprotein and evaluation of its redox-responsive mechanical properties

○Kazuki Kageyama[1], Koji Oohora[1], Hayashi Takashi[1] （1. Osaka univ.）

6:30 PM - 6:50 PM

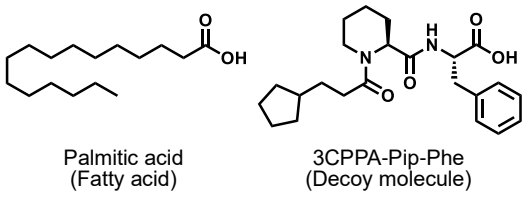
Analysis of Activation Mechanisms of Cytochrome P450BM3 by Decoy Molecules

([1]*Graduate School of Science, Nagoya University*, [2]*RIKEN/SPring-8,* [3]*Graduate School of Medicine, Oita University*) ○Kai Yonemura,[1] Shinya Ariyasu,[1] Hiroshi Sugimoto,[2] Shigeru Matsuoka,[3] Osami Shoji[1]

Keywords: Enzyme; Hydroxylation; Cytochrome P450BM3; Decoy molecule; Isothermal titration calorimetry

Cytochrome P450BM3 (P450BM3) is a heme enzyme which exhibits the highest monooxygenase activity toward long chain fatty acids among reported P450s while the enzyme does not hydroxylate non-native substrates such as benzene. However, we achieved benzene hydroxylation catalyzed by wild-type P450BM3 by adding amino acid derivatives.[1] We named such functional molecules “decoy molecules.” Decoy molecules activate P450BM3 by binding to P450BM3 in a similar manner to native substrates. However, decoy molecules themselves are not hydroxylated because of shortage of chain length. The small reaction space for non-native substrate hydroxylation is therefore formed at the catalytic site. The structure of decoy molecules has been improved to enhance catalytic activity of P450BM3. Recently, we demonstrated that the systematic screening of dipeptide derivatives is effective way to discover more effective decoy molecules in benzene hydroxylation.[2] However, activation mechanism in the reaction system is still unclear.

Herein, we performed isothermal titration calorimetry (ITC) analysis of the binding of ligands such as fatty acids and decoy molecules to P450BM3 to discuss the difference of the binding between fatty acids and the decoy molecules developed by the screening. We utilized liposome-bound ligands for the analysis because the ligands are insoluble to buffer due to their hydrohpobicity.[3] The thermodynamic parameters indicates that the binding of both fatty acids and decoy molecules (Figure 1) is entropy driven (Figure 2). From the results of the ITC analysis and other data, we discuss the activation mechanisms of P450BM3 by decoy molecules.



Palmitic acid (Fatty acid)　　3CPPA-Pip-Phe (Decoy molecule)

Figure 1. Structures of the typical fatty acid and decoy molecule

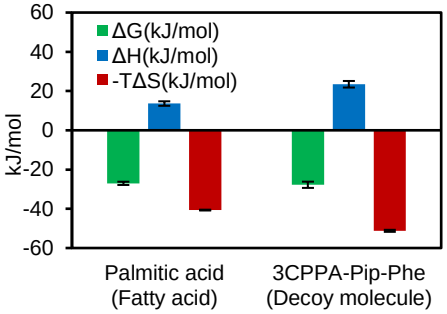


Figure 2. Thermodynamic parameters in the binding of ligands to P450BM3

1) O. Shoji *et al., Angew. Chem. Int. Ed.* **2017**, *56*, 10324–10329. 2) K. Yonemura *et al., ACS Catal.* **2020**, *10*, 9136-9144. 3) S. Matsuoka *et al., Angew. Chem. Int. Ed.*, **2015**, *54*, 1508-1511.

Structural investigation of a semi-clathrate hydrate formation using porous ferritin crystals

(*[1]Tokyo Institute of Technology*) ○ Jiaxin Tian[1], Basudev Maity[1], Satoshi Abe[1], Takafumi Ueno[1]

Keywords: ferritin, crystal engineering, antifreeze protein, semi-clathrate hydrate

Water molecules play essential roles in maintaining the structure and functions in proteins through either hydrogen bonding networks or coordinating to metal centers. Besides such roles, the water molecules can form polynuclear clathrates in antifreeze proteins, such as “maxi,” commonly known as semi-clathrate hydrate[1]. Such unique clathrates in antifreeze protein prevent ice formation in organisms in sub-zero temperature[2]. Artificial development of such semi-clathrate hydrates is an emerging area of research considering potential applications in cryotechnology, including food preservation, organ storage, cryo-medicine, etc. However, limited information about their design, construction, structure, and dynamics in variable temperatures is known.

This presentation will describe the X-ray crystal structures of a single semi-clathrate hydrate structure formation on the surface of the ferritin cage (Figure 1). The semi-clathrate hydrate formation is useful for fundamental understanding and applications. We determined the structures at variable temperatures ranging from -180℃ to 0℃ to explore the formation mechanism of the semi-clathrate hydrate and its stability. In addition, we performed mutational analysis to find out the key residues responsible for the formation and stability of the water cluster networks. Overall, the work is significant not only for fundamental understanding but also for the design and construction of artificial semi-clathrate hydrates on a protein.

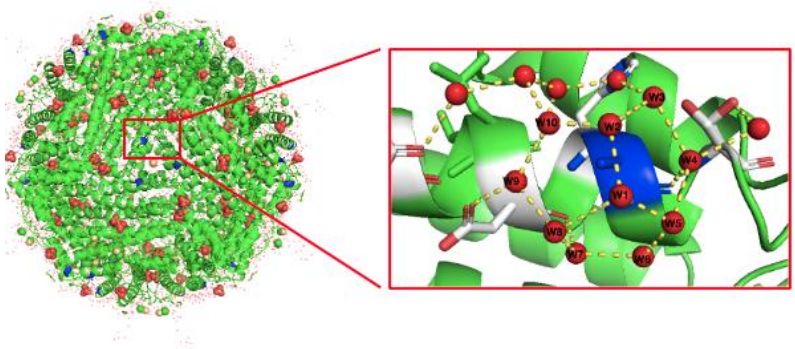


Figure 1. A semi-clathrate water network on the ferritin cage.

Reference:

[1] T. Sun, et al., *Science*. 343, 795-798 (2014)

[2] P. L. Davies, *Trends Biochem. Sci*, 39, 548-555 (2014)

無細胞タンパク質結晶エンジニアリングによる構造解析

（東工大生命理工学院[1]）○田中 潤子[1]・安部 聡[1]・金丸 周司[1]・上野 隆史[1]
Structural analysis by engineering cell-free protein crystals ([1]*Graduate School of Life-Science and Technology, Tokyo Institute of Technology*) ○ Junko Tanaka[1], Satoshi Abe[1], Shuji Kanamaru[1], Takafumi Ueno

In recent years, “In-cell protein crystals,” spontaneously formed in a living cell, have attracted attention as new templates of solid materials. The development of X-ray structural analysis has made it possible to analyze the structure of micro- and sub-micro sized crystals.[1] However, the protein crystallization in living cells is dependent on the culture conditions, and it is difficult to control the crystallization. Therefore, the establishment of a new crystallization method is desired. In conventional crystallization in vitro, crystallization with additives is a general method to obtain crystals having a high diffraction quality. We focused on a cell-free protein synthesis system that is a cell-mimicking environment and enables the introduction of additives directly into the systems. In this study, we crystallized Crystalline inclusion protein A (CipA), which forms crystals in *P. luminescens,* using cell-free protein synthesis (Cell-Free Protein Crystallization, CFPC) and controlled the crystal packing by adding organic compounds or macromolecules (Figure 1). As a result, the structure of CipA was successfully determined by introducing additives.
Keywords : Protein Crystal, X-ray crystal structure analysis, Cell-free protein synthesis

近年、細胞内で自発的に形成するタンパク質結晶が新しい固体材料の鋳型として注目されている。さらに、X 線構造解析法の発展によりマイクロやサブマイクロサイズの微小タンパク質結晶の構造解析が可能になっている[1]。しかし、培養細胞を用いたタンパク質の結晶化は、細胞の培養条件に大きく依存し、結晶化制御が困難であるため、新しい結晶化手法の開発が望まれている。従来の In vitro での結晶化では、回折品質の高い結晶を得るために、結晶化条件に添加剤を導入する手法が一般的に用いられている。そこで我々は、細胞模倣環境であり、合成反応溶液に直接添加剤の導入が可能な無細胞タンパク質合成系に着目した。本研究では、昆虫病原性細菌で結晶化する Crystalline inclusion protein A(CipA)の無細胞タンパク質合成系を利用した結晶化(Cell-Free Protein Crystallization, CFPC)と有機化合物や高分子化合物を添加することによる結晶制御と構造解析を試みた（図 1）。その結果、添加剤を加えることにより、構造未知であった CipA の構造決定に成功した。

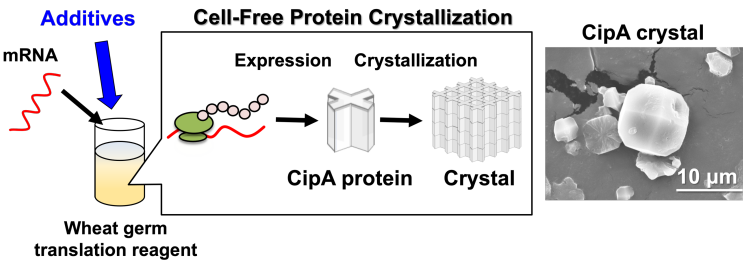


図 1.無細胞タンパク質合成による CipA の結晶化

1. Schönherr, R., Rudolph, J. M. & Redecke, L. Protein crystallization in living cells. *Biol. Chem.* **399**, 751–772 (2018).

In-cell crystal engineering for the development of solid biomaterials

(*School of Life Science and Technology, Tokyo Institute of Technology*) ○Satoshi Abe, Mariko Kojima, Junko Tanaka, Yuto Nakasuji, and Takafumi Ueno

Keywords: Protein crystals, In-cell crystals, Crystal structural analysis

Protein crystals, which have a highly ordered arrangement of protein molecules, have a great potential for applications in molecular storage, separations, and catalysis.[1] Protein crystals formed in living cells are known to have various natural functions such as virus and toxin storage, immune activation, and solid catalysts. However, the crystallization process in living cells, which is the key to the functions, is still unclear. We have previously reported in-cell crystal engineering to construct solid catalyst-containing enzymes and prepare the protein assemblies using protein crystals formed in insect cells.[2] In addition, we have found that polyhedra crystal (PhC), which is thought to crystallize only in insect cells, is also formed in E.coli. In this study, we attempt to elucidate the mechanism of in-cell protein crystallization using crystallization systems in E.coli for the design of solid materials (Figure 1).

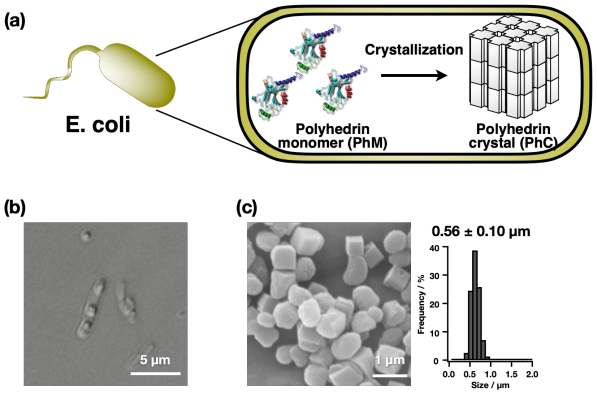


Figure 1. Crystallization of PhMs in E. coli. (a) Schematic representation of crystallization of PhM, (b) Phase-contrast image and (c) SEM image and a size histogram of recombinant PhCs purified from E. coli.

We elucidated the temperature- and time-dependent crystallization of polyhedrin monomers. The crystal formation was confirmed by scanning electron microscopy (SEM), small angle X-ray scattering (SAXS), and X-ray diffraction. SEM image of isolated PhC revealed the cubic crystals with an average size of 0.56 μm which is similar morphology to PhC formed in insect cells (Figure 1).. Time-dependent crystallization indicates that the cubic crystals were formed within 1h after IPTG induction, and crystal size was increased up to 6h. X-ray diffraction experiments showed that PhC grown for 4 and 6 h were analyzed, although PhC grown for 1 and 2 h could not be analyzed because of the small number of indexed images. Now, we are investigating the crystallinity of the PhC, especially, the initial stage of crystallization using SAXS.

1) M. Kojima et al, *Biomaterials Sci.* **2022**, *in press*.

2) T. Nguyen *et al. ACS Appl. Nano Mater*. **2021**, 4, 1672. S. Abe *et al. Angew. Chem. Int. Ed.* **2021**, 60, 12341.

Dynamics structural analysis of miniprotein by in-cell crystal engineering

([1]*Graduate School of Life Science and Technology, Tokyo Institute of Technology*)
○Mariko Kojima,[1] Yuki Hishikawa,[1] Satoshi Abe,[1] Tadaomi Furuta,[1] Duy Phuoc Tran,[1] Akio Kitao,[1] Takafumi Ueno,[1]
Keywords: Protein crystal; Biomaterial; X-ray crystallography; Unstable state

Protein crystals are attracted attention in the field of biomaterial science[1]. The porosity of protein crystals leads to preparing the scaffold to capture the foreign molecules with various sizes, such as organic molecules, peptides, and proteins. One of the unique functions of scaffold protein crystal is to stabilize the unstable structure of target molecules by noncovalent interactions at the target-scaffold interface of crystal packing. Then, we focused on the peptide conformation controlled by the surrounding environment. In this study, we analyzed the structure of CLN025, a miniprotein consisting of 10 amino acid residues exhibiting an unstable state in a crystalline scaffold by X-ray crystallography (Fig. 1a). Polyhedra crystal (PhC) was employed as a scaffold because of the high-resolution structure. The dynamic mechanism of conformational change assisted by protein-protein interaction (PPI) was elucidated by molecular dynamics simulation.

CLN025 was inserted in the loop region of PhC, which interacts with the adjacent monomer. As a result of X-ray crystal structure analysis, the electron density of the full length of CLN025 was determined as a helix structure that had never been observed experimentally (Fig. 1b). To elucidate the pathway to fix the helix structure, targeted molecular dynamics simulation (TMD) was performed by modeling the obtained dimeric structure of PhC as the target structure. TMD indicated that salt bridge formation between CLN025 and PhC drove helix formation followed by the hydrogen bonds and aromatic interaction at both ends of CLN025. Therefore, peptide structure can be controlled by designing scaffold protein crystals. This result suggests the novel use of protein crystal as a template to observe the PPI of intrinsically disordered protein and create functional peptides.

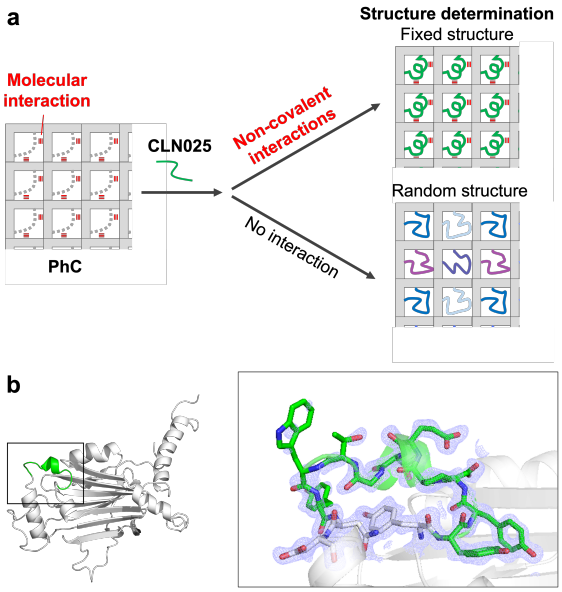


Fig. 1 a) Scheme of structure determination of unstable state CLN025 in PhC. b) The helix structure of CLN025 observed in PhC. CLN025 is colored in green.

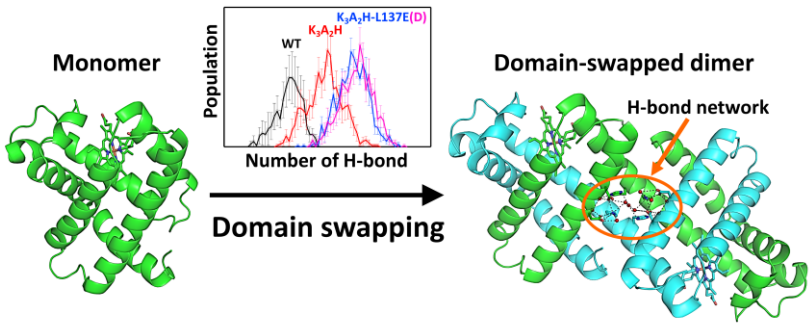
1) M. Kojima, *et al., Biomater. Sci.,* **2022**.

Experimental and theoretical study on converting myoglobin into a stable domain-swapped dimer by utilizing a tight hydrogen bond network at the hinge region

([1]*Division of Materials Science, Nara Institute of Science and Technology*, [2]*Division of Life Science, Center for Computational Sciences, University of Tsukuba,* [3]*Faculty of Education, Kagawa University,* [4]*Graduate School of Science, University of Hyogo*) ○Cheng Xie,[1] Hiromitsu Shimoyama,[2] Masaru Yamanaka,[1] Satoshi Nagao,[1] Hirofumi Komori,[3] Naoki Shibata,[4] Yoshiki Higuchi,[4] Yasuteru Shigeta,[2] and Shun Hirota[1]

Keywords: Domain swapping; Protein structure; Hydrogen bond network; Protein design; Molecular dynamics simulation

Various factors, such as helical propensity and hydrogen bonds, control protein structures. We have previously shown that a frequently used model protein, myoglobin (Mb), can form a domain-swapped dimer, and we succeeded in obtaining monomer–dimer equilibrium in the native state by introducing a high α-helical propensity residue, Ala, to the hinge region.[1] In this study, we focused on another factor that governs the protein structure, hydrogen bonding. X–ray crystal structures and thermodynamic studies showed that the Mb dimer is stabilized over the monomer when the H-bond network at the hinge region of the dimer is enhanced by keeping His82 to interact with Lys79 and Asp141 and mutating Leu137, which is located close to the H-bond network, to a hydrophilic amino acid, namely, Glu or Asp.[2] Molecular dynamics simulation studies confirmed that the number of H-bonds increased for mutants with a tighter H-bond network. The simulation also showed that the distance between the helices at the hinge region becomes shorter as the H-bond network is enhanced, supporting the hypothesis that the helices at the hinge region become tighter and the Mb dimer is stabilized when the H-bond network at the hinge region is enhanced. This reveals the importance and utility of hydrogen bonds for designing a protein dimer from its monomer.



1) a) S. Nagao, *Dalton Trans*. **2012**, *41*, 11378; b) S. Nagao, *Chem. Asian. J.* **2020**, *15*, 1743. 2) C. Xie, *RSC Adv.* **2021**, *11*, 37604.

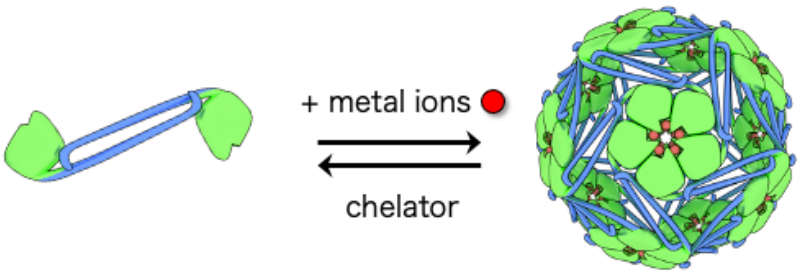
Re-design of an artificial protein nanocage TIP60: structural analysis of a mutant assembled by responding to metal ions

([1]*Faculty of Sci. and Tech., Keio University*, [2]*Faculty of Textile Sci. and Tech., Shinshu University,* [3]*Structural Biology Research Center, High Energy Accelerator Research Organization*) ○Naoya Ohara[1], Norifumi Kawakami[1], Ryoichi Arai[2], Naruhiko Adachi[3], Toshio Moriya[3], Masato Kawasaki[3], Toshiya Senda[3], Kenji Miyamoto[1]

Keywords: *Protein supramolecule, Protein-protein interactions, Metal ions, Cryo-EM*

Protein cages composed of multiple protein molecules hold promise of nanomaterials for cargo delivery. The most widely accepted approach to introduce cargo molecules in the inner space is the dissociation and association of protein cage in the presence of the cargo. However, dissociation process of protein cages requires harsh treatment such as acidification that reduces the yield of the cargo encapsulated cages. Thus, developing a protein cage that can reversibly associate/dissociate under mild conditions is beneficial for applications.

We have previously produced an artificial protein nanocage TIP60 composed of 60-mer designed fusion proteins[1,2]. However, TIP60 could not dissociate without harsh treatments. In this study, TIP60 was re-designed for conferring reversibly associate/dissociate mechanisms. For this purpose, we initially introduced mutations at the interface of subunits and found a mutant, K67E, that does not spontaneously assemble into 60-mer. We assumed that the typical metal ions that favored to interact with the side chain of glutamate would recover subunit interactions. As a result, the mutant was reassembled to 60-mer in response to typical metal ions, such as Ba ions. Removal of metal ions by EDTA dissociated the 60-mer again. Cryo-EM structure of the metal-induced 60-mer (mTIP60) showed the potential map corresponding to the Ba ions at the interface region of the subunit near the mutation position, indicating that the metal ions bridge the subunits. We believe that this mild association/dissociation system of mTIP60 would be broadly used for cargo encapsulations.



1) N. Kawakami *et al., Angew. Chem. Int. Ed.*, **57**, 12400–12404 (2018).
2) J. Obata *et al., Chem. Commun.*, **57**, 10226–10229 (2021).

Construction of Hydrogel Containing an Engineered Hexameric Hemoprotein and Evaluation of its Redox-responsive Mechanical Properties

(*Graduate School of Engineering, Osaka University*) ○Kazuki Kageyama, Koji Oohora, Takashi Hayashi

Keywords: Polyacrylamide gel; Heme; Reconstitution

Stimuli-responsive hydrogels exhibit changes in physicochemical properties and/or shapes triggered by external stimuli such as photo irradiation, redox and pH changes. These hydrogels have been receiving widespread attention as new smart biomaterials. Especially, hydrogels having mechanical properties controlled by external stimuli are expected as potent extracellular matrices (ECM) because the importance in cellular behavior has been reported.[1] In this work, we have constructed a metalloprotein-based hydrogel changing the mechanical properties by redox states of the metal center. Toward the redox responsive behavior, heme-heme pocket interaction in hemoprotein was employed as a crosslinker in the hydrogel. Heme *b*, an iron porphyrin complex, is strongly bound into a protein matrix in hemoprotein and the heme-heme pocket interaction depends on the redox of the iron center. Here, hexameric tyrosine-coordinated heme protein (HTHP)[2] was chosen as a cross-linkage unit of a polyacrylamide gel (Fig. 1) due to the expected high affinity of heme and its multimeric structure.

First, the redox-dependent heme-heme pocket interaction of HTHP was investigated though chemical denaturant titration. In the Fe^{3+} state, HTHP shows the highly stable heme-heme pocket interaction, whereas this interaction in the Fe^{2+} state dramatically weakens. Next, a heme derivative tethering an acryloyl group was synthesized to introduce the reaction sites on the HTHP (Fig. 1). The modified heme was inserted into the apo-form of HTHP to obtain the reconstituted protein (rHTHP). Polymerization of acrylamide and rHTHP provided hydrogel. Soaking the hydrogel into a reductant solution promoted reduction of the iron center. The mechanical properties of the hydrogel were evaluated by the compression test, showing decrease of the modulus upon the addition of reductant.

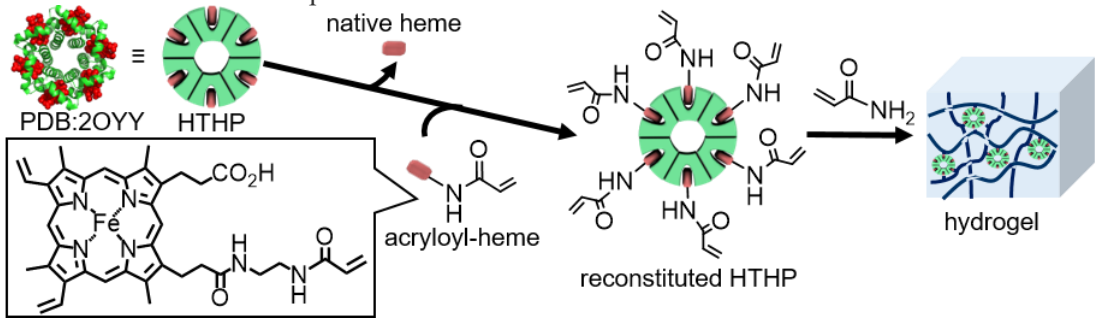


Fig 1. Schematic representation for preparation of hydrogel containing rHTHP as a cross-linkage.

1) L. Wang *et al., Science*, **2005**, *310*, 1139. 2) H. Dobbek *et al*., *J. Mol. Biol*., **2011**, *368*, 1122.

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

[G201-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Takahiro Muraoka, Kazuma Amaike

Fri. Mar 25, 2022 4:10 PM - 5:50 PM G201 (Online Meeting)

[G201-3vn-01] Design, synthesis, and chiroptical properties of macrocyclic oligomers composed of bispyrrolidinoindoline scaffold

○Tasuku honda[1], Daiji Ogata[2], Junpei Yuasa[2], Takahiro Muraoka[3], Hiroki Oguri[1] (1. The University of Tokyo, 2. Tokyo University of Science, 3. Tokyo University of Agriculture and Technology)

4:10 PM - 4:30 PM

[G201-3vn-02] Development of functional oligonucleotide for target metabolite analysis

○Tatsuya Nishihara[1], Shuhei Moritani[1], Yuto Motohashi[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

4:30 PM - 4:50 PM

[G201-3vn-03] Identification and molecular control of diapause-inducing signal in silkworm

○Hayato Yamada[1], Kazuma Amaike[1], Kenichiro Itami[1] (1. Nagoya University)

4:50 PM - 5:10 PM

[G201-3vn-04] Development of Nanocarbon Molecules Accelerating Nucleic Acid Transport

○Erika Kato[1], Zetschok Dominik[1], Kazuma Amaike[1], Kenichiro Itami[1,2] (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University)

5:10 PM - 5:30 PM

[G201-3vn-05] Development of a novel stomatal opening inhibitor and its mechanistic study

○Ayaka Ueda[1], Yusuke Aihara[1], Hiroyuki Kitano[1], Shigeo Toh[3], Kazuma Amaike[1], Hideto Ito[1], Shinya Hagihara[4], Toshinori Kinoshita[1,2], Kenichiro Itami[1,2] (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University, 3. Faculty of Agriculture, Meijo University, 4. CSRS)

5:30 PM - 5:50 PM

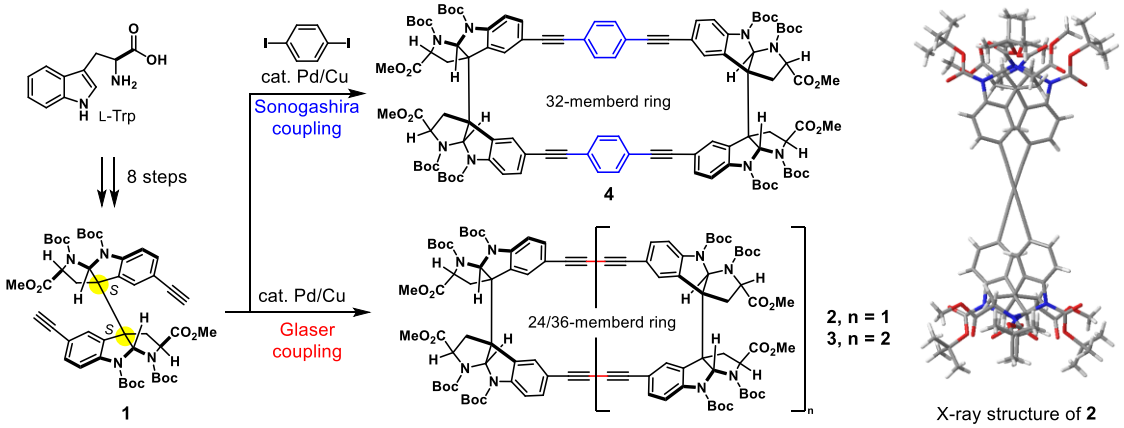
Design, synthesis, and chiroptical properties of macrocyclic oligomers composed of bispyrrolidinoindoline scaffold

([1]*Graduate School of Science, The University of Tokyo*, [2]*Graduate School of Science, Tokyo University of Science,* [3]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○ Tasuku Honda,[1] Daiji Ogata,[2] Takahiro Muraoka,[3] Junpei Yuasa,[2] Hiroki Oguri[1]

Keywords: Indole alkaloids; Bispyrrolidinoindoline; Macrocyclic oligomer; Chiroptical property; Chirality

The figure of eight macrocyclic structure bearing D_2-symmetry has been regarded as the privileged scaffold for displaying strong circular polarized luminescence (CPL). Most of the reported studies employ rigid non-planar aromatic scaffolds, such as helicene,[1] binaphthyl,[2] para-cyclophane,[3] to induce chirality of the π-conjugated macrocycles. In contrast to the reported synthetic studies that require optical resolutions to provide enantiopure macrocycles, we are exploring an alternative approach employing bispyrrolidinoindoline (BPI) scaffold as a key chiral C_2-symmetric segment for the modular and rapid asymmetric synthesis of the shape-persistent macrocycles bearing π-extended aromatic components.

In this study, we designed and synthesized macrocyclic oligomers composed of chiral C_2-symmetric BPI unit **1** readily synthesized from L-tryptophane on gram scale.[4] Glaser coupling of **1** furnished D_2-symmetric 24-membered figure-eight macrocycle **2** as the major product along with 36-membered macrocycle **3**. Sonogashira coupling reaction of **1** with 1,4-diiodobenzene proceeded smoothly to afford 32-membered macrocycle **4** bearing benzene units as linkers. Further investigations for synthesizing the π-extended macrocycles and for elucidating their optical and chiroptical properties will be reported.



1) Kubo, H.; Shimizu, D.; Hirose, T.; Matsuda, K. *Org. Lett.* **2020**, *22*, 9276.
2) Nojima, Y.; Hasegawa, M.; Hara, N.; Imai, Y.; Mazaki, Y. *Chem. Eur. J.* **2021**, *27*, 5923.
3) Morisaki, Y.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **2019**, *92*, 265.
4) Tsuchiya, N.; Ryu, Y.; Muraoka, T.; Oguri, H. *Org. Biomol. Chem*. **2018**, *16*, 9305.

標的代謝物の多検体解析を指向した機能性人工核酸の開発

（青山学院大理工）○西原 達哉・本橋 優人・盛谷 周平・田邉 一仁

Development of functional oligonucleotide for target metabolite analysis (*Graduate School of Science and Engineering, Aoyama Gakuin University*) ○Tatsuya Nishihara, Yuto Motohashi, Shuhei Moritani, Kazuhito Tanabe.

Analysis of metabolites provides valuable information to understand the living system. In this study, we have constructed a novel molecular system to encode target metabolite in each sample into the DNA sequence and quantify each DNA sequences at once.

We prepared the DNA binding magnetic beads with disulfide-tethered oligonucleotide to encode the glutathione (GSH) information. We found that the magnetic beads can release the DNA upon the reaction with the GSH in dose dependent manner. Therefore, the amount of GSH was indirectly quantified using the released DNA. In fact, we succeeded in the quantification of GSH in the cellular extract and liver extract. To demonstrate the feasibility to analyze multi-sample simultaneously, the quantification using next generation sequencer is in progress.

Keywords : Metabolite; Functional oligonucleotide

生体内で産生される代謝物は、生命機能を理解する上で非常に重要な生体分子に位置づけられる。我々は、これまでに検体中に含まれる代謝物情報を DNA 配列に置き換え可能とする分子システムの開発を進めてきた。実際に、標的代謝物としてグルタチオン (GSH) を選択し、GSH 存在下で DNA が遊離される分子システムを構築した。具体的には、ジスルフィド結合を介してビオチン修飾した DNA を合成し、ストレプトアビジン修飾磁性ビーズに担持した。磁性ビーズに対して、検体を検体中に含まれる GSH と反応し DNA が遊離するため、一定時間経過後サンプルを回収し、検体内に含まれる DNA を定量することで間接的に GSH を定量する。

本研究では、細胞抽出液、組織破砕液など様々な生体サンプルを作成し、それぞれの検体中に含まれる GSH 濃度を正確に定量可能か検証した。実際に、HCT116 細胞の抽出液を用いて、細胞内 GSH の定量に成功した。また、肝臓破砕液を用いて、単位重量あたりの肝臓内 GSH 量を定量可能であることを明らかにした。市販の GSH 検出キットを用いた際に、いずれも同程度の値を示すことを確かめている。以上より、本定量手法は、様々な生体サンプルへ適用可能であることが示唆された。

現在、GSH との反応に伴い遊離した DNA 配列に対して、検体情報をコードした配列を付与し、次世代シーケンサーによる標的代謝物の多検体定量解析が可能か検証を進めている。

Identification and molecular control of diapause-inducing signal in silkworm

([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*) ○Hayato Yamada,[1] Kazuma Amaike,[1] Kenichiro Itami[1,2]
Keywords: Silkworm; Diapause

Diapause is a programmed developmental arrest in insects to survive unfavorable environmental conditions. Diapause research is most advanced in the domestic silkworm *Bombyx mori*, and they induce embryonic diapause beyond generations as a maternal effect. Offspring diapause is determined by the environmental temperature and photoperiod during the embryonic development of the mother moths. Female moths destined to produce diapause eggs release diapause hormone (DH) into hemolymph during the pupal-adult stages. DH acts on a DH receptor in the ovaries to induce offspring diapause. Recently, *pnd* (*pigmented and non-diapausing*) and *pnd-2* have been identified as the downstream factors of DH signaling.[1] However, the molecular mechanism of diapause regulation through the PND and PND-2 signals is still unclear.

We began by bioinformatic analysis which led us to discover that PND and PND-2 are structural homologs of mammalian interleukin-17 (IL-17) and its receptor (IL-17R), respectively. Transient expression analysis in *B. mori*-derived cells demonstrated that PND-2 localized on the cell membrane and PND co-localized with PND-2. Protein-protein interaction between PND and PND-2 was shown with a NanoBiT split luciferase complementation assay. These results indicated PND and PND-2 may act as a ligand-receptor pair to induce diapause in silkworm. We have further shown that cyanidin, an IL-17 signaling inhibitor, can inhibit PND/PND-2 interaction, meaning the cyanidin may work as a diapause inhibitor.[2] Our SAR study revealed the critical structure of cyanidin to inhibit PND/PND-2 interaction and identified a cyanidin derivative with at least ten times more active than cyanidin. These findings lead to the complete control of silkworm diapause and the development of diapause-disrupting pesticides.

1) T. Yaginuma, *Sanshi-Kontyu Biotec* **2015**, *84*, 99. 2) C. Liu, L. Zhu, K, Fukuda, S. Ouyang, X. Chen, C. Wang, C. J. Zhang, B. Martin, C. Gu, L. Qin, S. Rachakonda, M. Aronica, J. Qin, X. Li, *Sci. Signal* **2017**, *10*, 467.

核酸輸送を加速するナノカーボン分子の開発

（名大院理[1]・名大 WPI-ITbM[2]）○加藤江莉佳[1]・Zetschok Dominik[1]・天池一真[1]・伊丹健一郎[1,2]

Development of Nanocarbon Molecules Accelerating Nucleic Acid Transport ([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*) ○Erika Kato,[1] Zetschok Dominik,[1] Kazuma Amaike,[1] Kenichiro Itami[1,2]

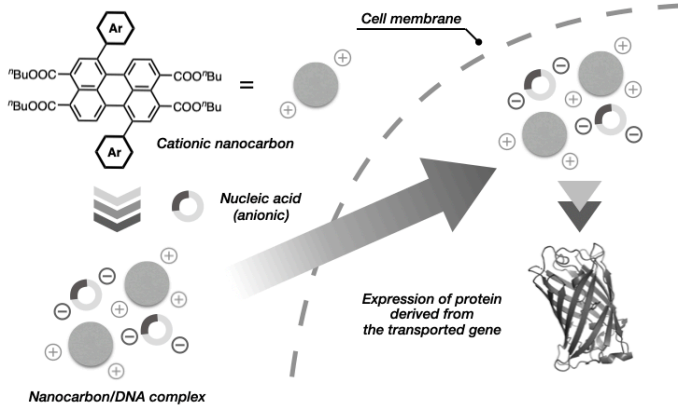
Nucleic acid delivery, an introduction of DNA or RNA into host cells from the outside, is an essential technology for life science research such as drug discovery, breeding, and basic biology. Thus, the development and improvement of nucleic acid delivery systems are of great importance. Recently nanocarbons such as cationic carbon nanotubes are expected to be the next generation carriers for nucleic acid delivery.[1] However, the nanocarbons reported so far are structurally impure, and the structure-function relationships are mostly unknown. In addition, there is no practical molecular framework providing various functions.

In this study, we have developed a new molecular nanocarbon accelerating nucleic acid delivery in mammalian cells. The structure-function relationship studies of the obtained molecular nanocarbons indicated that the number and type of charges strongly affect the nucleic acid delivery activity. These nanocarbon molecules are expected to create not only a new trend in the field of nucleic acid delivery, but also a completely new molecular platform for the foundation of nanocarbon biology.

Keywords: Transfection, Cationic nanocarbon, Structure-function relationship

核酸輸送は DNA や RNA を外部から宿主細胞に導入することであり、創薬や育種の現場から基礎生物学に至るまで生命科学研究に必要不可欠な技術である。そのため現在においても核酸輸送法の開発、改良が進められている。近年、カチオン性カーボンナノチューブをはじめとするナノカーボンが、新たな核酸輸送のための次世代キャリアとして期待が高まっている[1]。しかし、これまでに報告された核酸輸送可能なナノカーボンは分子構造が単一に決まっていない複雑な混合物であり、核酸輸送効率と構造の相関関係も不明であるばかりでなく、種々の機能の付与・調整が可能な実用的な分子骨格の開発には至っていない。

今回、哺乳細胞に対して核酸輸送を加速させる全く新しい分子性ナノカーボンを見出した。また得られた分子性ナノカーボンの構造機能相関研究を行い、電荷の数や種類が核酸輸送活性に強く影響することが示唆された。今回見出した分子は核酸輸送分野の新潮流を生み出すだけでなく、ナノカーボンバイオロジーの礎となる全く新しい分子プラットホームとなることが期待される。



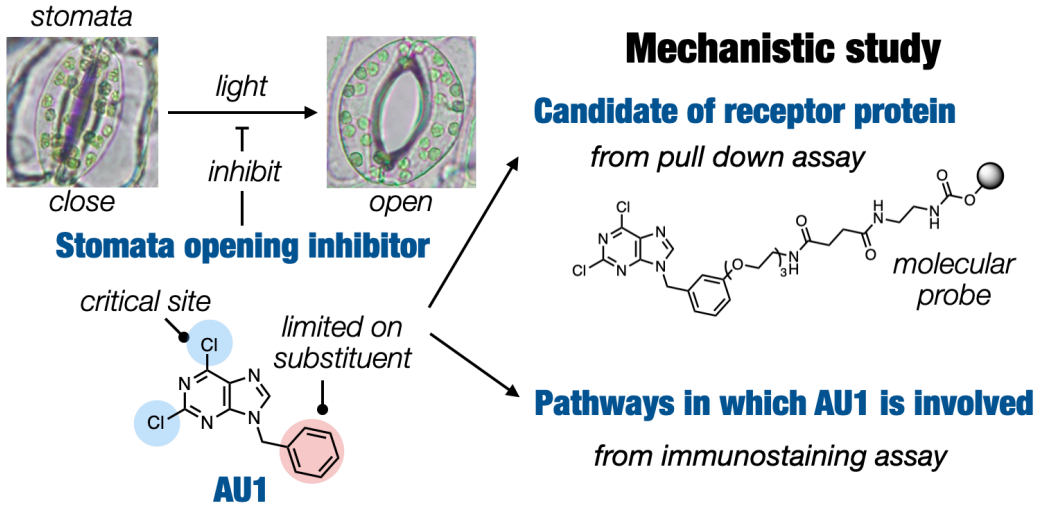
[1] Gao, L.; Nie, L.; Wang, T.; Qin, Y.; Guo, Z.; Yang, D.; Yan, X. *ChemBioChem* **2006**, *7*, 239.

Development of a novel stomatal opening inhibitor and its mechanistic study

([1]*Graduate School of Science, Nagoya University*, [2]*Faculty of Agriculture, Meijo University,* [3]*RIKEN, CSRS,* [4]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*)
○Ayaka Ueda,[1] Yusuke Aihara,[1] Hiroyuki Kitano,[1] Shigeo Toh,[2] Kazuma Amaike,[1] Hideto Ito,[1] Shinya Hagihara,[3] Toshinori Kinoshita,[1,4] and Kenichiro Itami[1,4]
Keywords: Bioactive compound; Plants; Inhibition of stomata opening; SAR study

Stomata are pores in the epidermis of plants which open under light and close in dark or under dry condition. These stomatal movements relate to exchange of water and gas for respiration, photosynthesis, and stress tolerance. In the mechanism of these movements, a plasma membrane proton pump (H^+-ATPase) acts as an engine, but its detail molecular mechanism has been unclear yet. To understand the mechanism, a method controlling these movements at will have attracted much attention. In recent years, molecules that can control the stomatal movement, especially stomatal opening inhibitors, have been developed.[1] However, their receptors have been not identified due to a lack of enough investigation.

In this study, we newly discovered a synthetic small molecule AU1 that inhibit stomatal opening. The structure-activity relationship studies of AU1 were conducted to reveal that two chloride atoms on the purine structure were essential and to find the derivatization position causing low effect for the bioactivity. Based on this result, we synthesized a molecular probe for the pull-down assay, obtaining several candidates of target protein. In addition, the immunostaining assay revealed the pathways involved in the AU1.



1) Toh, T.; Inoue, S.; Toda, Y.; Yuki, T.; Suzuki, K.; Hamamoto, S.; Fukatsu, K.; Aoki, S.; Uchida, M.; Asai, E.; Uozumi, N.; Sato, A.; Kinoshita, T. *Plant Cell Physiol.* **2018**, *59*, 1568.

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

[C203-3pm] 18. Polymer

Chair: Akifumi Kawamura, Rintaro Takahashi

Fri. Mar 25, 2022 1:40 PM - 3:40 PM C203 (Online Meeting)

[C203-3pm-01] Development of Poly(Ester– Carbonate)s Comprising Aromatic Mesogens and Aliphatic Oligocarbonates with Hydrophilic Side-Chains

○Yuya Watanabe[1], Riki Kato[1], Kazuki Fukushima[1], Takashi Kato[1] （1. Sch. of Eng., The Univ. of Tokyo）

1:40 PM - 2:00 PM

[C203-3pm-02] Relationship between viscoelastic properties and molecular behavior of physical gels with ideal network cross-linked by duplex DNA

○Masashi Ohira[1], Katashima Takuya[1], Naito Mitsuru[1], Aoki Daisuke[2], Sakai Takamasa[1], Shibayama Mitsuhiro[3], Xiang Li[4] （1. The Univ. of Tokyo, 2. Tokyo Tech., 3. CROSS, 4. Hokkaido Univ.）

2:00 PM - 2:20 PM

[C203-3pm-03] Design and Synthesis of Amphiphilic Alternating Peptides with LCST Behaviors

Namiki Komuro[1], Noriyuki Nakajima[1], Masahiro Hamada[1], ○Yasuhito Koyama[1] （1. Toyama Pref. Univ.）

2:20 PM - 2:40 PM

[C203-3pm-04] Synthesis of Zwitterionic Polymers with 4-Armed Structures and Their Photo-gelation

○Takashi Miyata[1], Kurumi Fukao[1], Akifumi Kawamura[1] （1. Kansai Univ.）

2:40 PM - 3:00 PM

[C203-3pm-05] Nanostructure formation on fiber surfaces of filter paper via hydrolysis and self-assembly of cellulose

○Yuuki Hata[1], Sumiyo Hiruma[1], Hiromi Miyazaki[1], Shingo Nakamura[1] （1. Nat'l Def. Med. Coll.）

3:00 PM - 3:20 PM

[C203-3pm-06] Construction of a Novel System for Cancer Cell-specific Delivery Utilizing MMP-9 Activity IV: Effect of Polymer Structure upon MMP Responsibility and Cellular Uptake Efficiency

Nagisa Kanazawa[1], Ryota Azuma[1], Yuka Matsuhashi[1], Ikuhiko Nakase[2], Tsuyoshi Yamamoto[3], Masaki Nishijima[1], Yasuyuki Araki[1], Asako Yamayoshi[3], ○Takehiko WADA[1] （1. Tohoku Univ., 2. Osaka Prefecture Univ., 3. Nagasaki Univ.）

3:20 PM - 3:40 PM

Development of Poly(Ester–Carbonate)s Comprising Aromatic Mesogens and Aliphatic Oligocarbonates with Hydrophilic Side-Chains

(*School of Engineering, The University of Tokyo*) ○Yuya Watanabe, Riki Kato, Kazuki Fukushima, Takashi Kato

Keywords: Condensation polymers; Biodegradable polymers; Liquid-crystalline polymers

Condensation polymers containing rigid-rod aromatic structures can exhibit high thermal and high mechanical properties. Main-chain liquid-crystalline polyesters and polyamides are also included in this family of polymers.[1] They are known to show high melting points and high mechanical strength resulting from molecular orientation.[1] However, their high chemical stability may not be compatible with degradation in the natural environment.

Aliphatic polyesters and polycarbonates such as polylactides (PLAs) and poly(trimethylene carbonate) (PTMC) have drawn increasing attention as biodegradable polymers that can be applied to both biomedical devices and sustainable materials.[2] In addition, much effort has been made to develop PLA and PTMC analogs with functional side groups in the last few decades. Nevertheless, few aliphatic condensation polymers with high thermal and mechanical stabilities have been studied.

Herein, we designed poly(ester–carbonate)s **1** comprising aromatic three-ring mesogens and aliphatic oligocarbonates with ether side-chains to combine the thermal and mechanical stabilities and bio-functionality. The aromatic/aliphatic poly(ester–carbonate)s **1** were obtained by two-step polymerizations. The aliphatic oligocarbonates were first synthesized by ring-opening polymerization of a corresponding cyclic carbonate initiated by a bis(hydroxy)-functionalized mesogen. The oligocarbonate diols were then reacted with adipoyl chloride for chain extension by polycondensation. Polymers with more than 1×10^5 in the weight-average molecular weights were obtained. The composition of the aromatic mesogens was controlled, ranging 6–17 wt%, by the length of the aliphatic oligocarbonates. We found that polymer **1** showed a considerable increase in Young's moduli from the aliphatic polycarbonate with ether side-chains.

1) T. Kato *et al.*, *Polym. J.* **2018**, *50*, 149-166. 2) K. Fukushima, *Biomater. Sci.*, **2016**, *4*, 9-24.

Relationship between viscoelastic properties and molecular behavior of physical gels with ideal network cross-linked by duplex DNA

○Masashi Ohira[1], Katashima Takuya[1], Naito Mitsuru[1], Aoki Daisuke[2], Sakai Takamasa[1], Shibayama Mitsuhiro[3], Xiang Li[4] ([1]*Graduate School of Engineering, The University of Tokyo*, [2] *Department of Chemical Science and Engineering, Tokyo Institute of Technology,*[3] *Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS),*[4] *Faculty of Advanced Life Science, Hokkaido University*).

Keywords: Physical gel, DNA, Thermodynamics, Kinetics

Dynamically crosslinked gels exhibit a time-dependent mechanical responses, which is solid for a short time but fluid for a long time. These unique properties are attributed to the repeated breaking and reforming of the crosslinkers that bridge the polymer chains in the gels. DNA duplexes are promising dynamic crosslinkers because its thermodynamic and kinetics properties of DNA duplexes can be continuously adjusted by changing the sequences and the length. Ideally, dynamic crosslinked gels with arbitrary viscoelastic properties can be fabricated by designing the DNA sequence. Here, we demonstrated a homogeneous DNA gel with highly predictable mechanical behaviors.

We used a star polymer strategy to improve the homogeneity of the gel network[1,2] and designed a pair of DNA sequences showing a two-state transition as the dynamic crosslinkers. The UV spectroscopy analysis of the DNA gels revealed the good correspondence between the thermodynamic free energy of the DNA crosslinkers in the gel and the simulated values via software package of DNA. Viscoelastic properties tests and dissociation kinetics measurements showed that the macroscopic stress relaxation time of the DNA gels is approximately equal to the lifetime of the duplexes over four orders of magnitude from 0.1-2,000 sec. Furthermore, a series of durability tests found that the DNA gels has self-healing ability for temperature and mechanical stimuli. These results exhibit the great potential of star-polymer-DNA precursors for building gels with tunable and predictable viscoelastic properties, suitable for various applications.

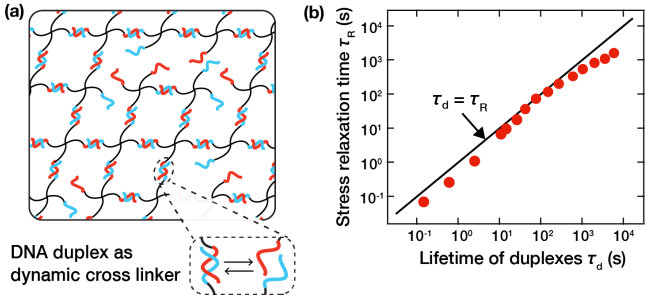


Figure 1(a) An illustration of star-polymer-DNA network. (b) Correlation plot of lifetime of duplexes and stress relaxation time.

[1] T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, R. Yoshida, S. Suzuki, N. Sasaki, M. Shibayama, U. Chung, *Macromolecules* 2008, *41*, 5379.[2] X. Li, S. Nakagawa, Y. Tsuji, N. Watanabe, M. Shibayama, *Sci Adv* 2019, *5*, eaax8647.

LCST 型挙動を示すペプチド交互共重合体の設計と合成

（富県大工[1]・富県大生医工研セ[2]）小室波輝[1]・中島範行[1,2]・濱田昌弘[1,2]・
○小山靖人[1,2]

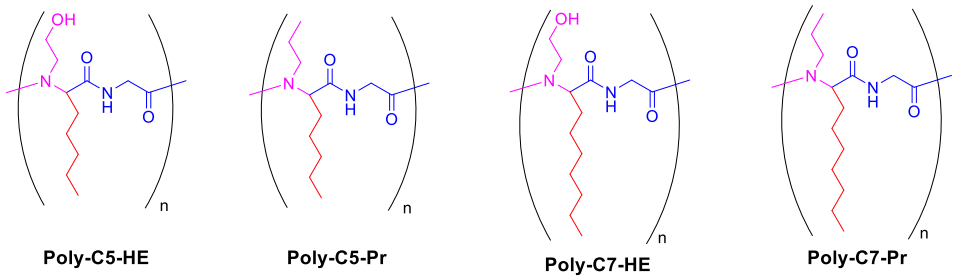
Design and Synthesis of Amphiphilic Alternating Peptides with LCST Behaviors ([1]*Department of Pharmaceutical Engineering, Faculty of Engineering, Toyama Prefectural University*, [2]*Biotechnology Research Center, Toyama Prefectural University*) Namiki Komuro,[1] Noriyuki Nakajima,[1,2] Masahiro Hamada,[1,2] ○Yasuhito Koyama[1,2]

We have recently reported one-pot synthetic technique for alternating peptide via three-component polymerization. Through the technique, we have evaluated the themo-responsiveness of copolypeptides comprising a stoichiometric amount of valine and glycine. It turned out that diblock polymer exhibits LCST behaviors while alternating polymer shows the opposite behavior, UCST behaviors. In this work, we synthesized the new series of alternating peptides with LCST behaviors. We will discuss the effect of polymer structure on the thermo-responsiveness.

Keywords : Alternating Peptide; Thermo-Responsiveness; Amphiphilic Peptide; LCST; Multi-Component Polymerization

1. 当研究室では 3 成分重合によるペプチド交互共重合体のワンポット合成法について報告している[1]。また、これまでにバリンとグリシンを当モル量含むポリペプチドにおいて、交互共重合体は UCST 型、ブロック共重合体は LCST 型の温度応答性を示すことを明らかとしている[2]。今回、重合コンポーネントを種々変更した結果、LCST 型挙動を示すペプチド交互共重合体を得たので、分子構造と温度応答性の関連性について詳細を述べる。

2. 親水性のグリシンと、疎水性のアルキレン鎖含有人工アミノ酸骨格を交互に含むペプチド交互共重合体を合成した。水溶液中において、**Poly-C5-HE** は UCST 型、**Poly-C5-Pr** は LCST 型の温度応答性を示すことが分かった。一方、**Poly-C7-HE** は低温域に UCST を高温域に LCST を示すことが分かった。**Poly-C7-Pr** は水に不溶であった。発表では、温度応答性を示すペプチド交互共重合体のライブラリー合成と、ペプチド交互共重合体を架橋点に含むヒドロゲルの合成と性質についても述べる。



1) **Koyama, Y.**; Gudeangadi, P. G. *Chem. Commun.* **2017**, *53*, 3846-3849.
2) Ihsan, A. B.; **Koyama, Y.** *Polymer*, **2019**, *161*, 197-204.

四分岐構造を有する双性イオンポリマーの合成とその光ゲル化挙動

（関西大化学生命工[1]・関西大 ORDIST[2]）○宮田 隆志[1,2]・深尾 胡桃[1]・河村 暁文[1,2]

Synthesis of Zwitterionic Polymers with 4-Armed Structures and Their Photo-gelation

([1]*Faculty of Chemistry, Materials and Bioengineering and* [2]*ORDIST, Kansai University*)
○Takashi Miyata[1,2], Kurumi Fukao[1], Akifumi Kawamura[1,2]

Poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) which mimics phospholipid molecules provides biocompatible polymer materials with cell membrane-like surfaces. PMPC gels have many potential applications such as contact lenses and artificial joints because of their high hydrophilicity and excellent biocompatibility. However, gels synthesized by free radical polymerization (FRP) have inhomogeneous network structure, which causes low mechanical strength and low controllability of drug release. Recently, Poly(ethylene glycol) (PEG) gels with homogeneous networks developed using Tetra-PEGs were reported[1)]. We also synthesized poly(*N*-isopropylacrylamide) gels with homogeneous networks by controlled radical polymerization[2)]. In this study, we synthesized 4-armed zwitterionic polymers by controlled radical polymerization to prepare biocompatible gels with homogeneous networks. Tetra-PMPC was synthesized by single-electron transfer living radical polymerization (SET-LRP) using a tetra-branched initiator. The resulting polymers were gelatinized by thiol-ene reaction using dithiol cross-linker and photoinitiator after 5 min of visible light irradiation.
Keywords: Hydrogel; 4-Armed Polymer; Zwitterionic Polymer; Homogeneous Network; Photo-gelation

リン脂質分子を模倣した poly(2-methacryloyloxyethyl phosphorylcholine)（PMPC）は高い親水性や優れた生体適合性を示す。PMPC を用いたゲルはコンタクトレンズや人工関節など医療材料として応用されている。しかし，一般的なゲルは網目構造が不均一であるため，力学強度の不足や薬物拡散制御の困難などの課題がある。近年，四分岐構造の poly(ethylene glycol)（Tetra-PEG）から形成された均一な網目構造を有する Tetra-PEG ゲルが報告されている[1)]。一方，われわれは精密重合により網目構造の不均一性が低い温度応答性ゲルや高分子鎖の絡み合いを利用したタフゲルの調製に成功している[2, 3)]。本研究では，四分岐構造をもつ PMPC（Tetra-PMPC）を合成し，網目構造の均一な Tetra-PMPC ゲルの調製を試みた。四分岐状の開始剤を用いた単電子移動リビングラジカル重合（SET-LRP）により，Tetra-PMPC を合成した。得られた Tetra-PMPC は，ジチオール架橋剤と光開始剤を用いたチオールエン反応により，5 分間の可視光照射によりゲル化した。

1) Sakai, T. *et. al. Macromolecules* **2008**, *41*, 5379.
2) Norioka, C.; Kawamura, A.; Miyata, T. *Polym. Chem.* **2017**, *8*, 6050.
3) Norioka, C.; Inamoto, Y.; Hajime, C.; Kawamura, A.; Miyata, T. *NPG Asia Mater.* **2021**, *13*, 34.

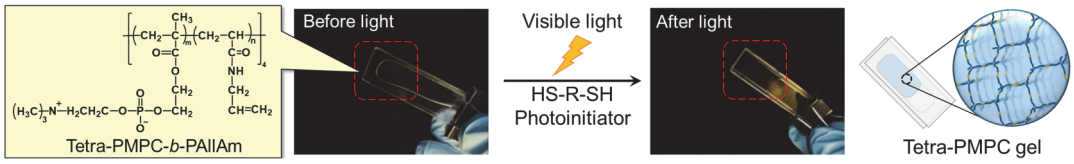


Fig. 1. Images of an aqueous solution of Tetra-PMPC-*b*-PAllAm before and after visible light irradiation.

セルロースの加水分解と自己集合化によるろ紙繊維表面でのナノ構造形成

（防衛医大研セ）○秦 裕樹・比留間 寿美代・宮﨑 裕美・中村 伸吾

Nanostructure Formation on Fiber Surfaces of Filter Paper via Hydrolysis and Self-Assembly of Cellulose (*National Defense Medical College Research Institute*) ○Yuuki Hata, Sumiyo Hiruma, Hiromi Miyazaki, Shingo Nakamura

Cellulose represents a sustainable raw material and has been used for a long time as versatile polymer materials for cloth, paper, and healthcare and hygiene products. Furthermore, recent studies have developed nanostructured cellulose, such as cellulose nanofibers and nanocrystals, which is opening up new applications of cellulose. Nevertheless, it is still challenging to add nanostructure to conventional cellulosic materials, even though such technology will enhance versatility and usability of the sustainable polymer materials. In this study, we have developed a simple method based on hydrolysis and subsequent self-assembly of cellulose that induces nanostructure formation on fiber surfaces of conventional cellulosic materials. Furthermore, we explored potential applications of the produced nanostructured cellulose as biomedical materials.

Keywords: Cellulose; Self-Assembly; Nanostructure; Paper; Biomedical Material

セルロースは代表的なサステイナブル高分子素材であり、古くから紙や布、衛生材料などに利用されてきた。さらに、近年では、セルロースナノファイバーやナノ結晶をはじめとするナノ構造化セルロースが開発され、セルロースの新たな応用可能性が開拓されている。しかしながら、既存のセルロース材料にナノ構造を付加することは依然として困難となっている。そのような技術が確立すれば、セルロースの多目的性や有用性がさらに拡張すると期待される。

本研究では、既存のセルロース材料の繊維表面にナノ構造を付与できる、セルロース分子の加水分解と自己集合化に基づく簡便な手法を見出した。さらに、生成されるナノ構造化セルロース（Figure 1）の医用材料としての応用可能性を探索した。セルロース分子の自己集合化[1]に基づく本手法は、分子集合化挙動を変調することで、応用目的に応じてテーラーメイドにナノ構造を制御できることが期待される。

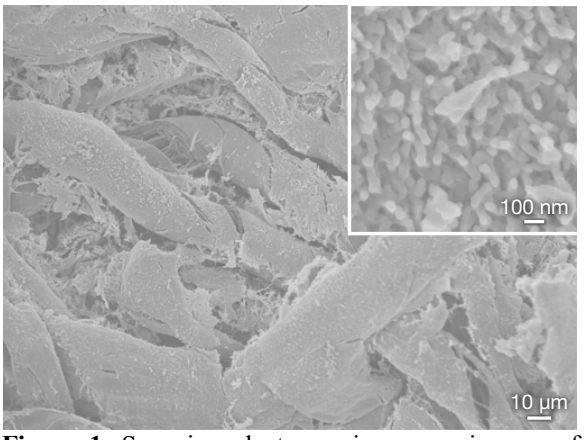


Figure 1. Scanning electron microscopy images of nanostructured surfaces of filter paper. The inset is a magnified image of fiber surfaces.

1) Hata, Y.; Serizawa, T. Self-assembly of cellulose for creating green materials with tailor-made nanostructures. *J. Mater. Chem. B* **2021**, *9*, 3944–3966.

MMP-9 活性を利用した新規がん細胞選択的細胞内導入システムの構築Ⅳ : ポリマー構造の酵素分解速度ならびに細胞内導入に対する影響

(東北大多元研[1]・阪府大ナノ科学材料セ[2]・長崎大院医歯薬[3]・) ○金澤 なぎさ[1]・東 亮太[1]・松橋 由佳[1]・中瀬 生彦[2]・山本 剛史[4]・西嶋 政樹[1]・荒木 保幸[1]・山吉 麻子[4]・和田 健彦[1]

Construction of a Novel Carrier System for Cancer Cell-specific Delivery Utilizing MMP-9 Activity IV: Effect of Polymer Structure upon Enzymatic Cleavage and Cellular Uptake Ability

([1]*IMRAM, Tohoku University,* [2]*Nanoscience and Nanotechnology Research Center, Osaka Prefecture University,* [3]*School of Pharmaceutical Sciences, Nagasaki University*) ○Nagisa Kanazawa,[1] Ryota Azuma,[1] Yuka Matsuhashi,[1] Ikuhiko Nakase,[2] Tsuyoshi Yamamoto,[3] Masaki Nishijima,[1] Yasuyuki Araki,[1] Asako Yamayoshi,[3] Takehiko Wada[1]

Cancer is one of the leading causes of death in the world. Cancer treatments have been a major challenging issue. So far a huge number of anti-cancer chemotherapy compounds have been developed. However, these conventional pharmaceuticals reported that often attack to not only target cancer cells but also non-target normal cells, inducing serious side-effects and cytotoxicities. Therefore, as one of the promising improvements of these serious issues, the development of a drug delivery system (DDS) that can be selectively delivered a pharmaceutical to target cells has been actively discussed.

Based on the background, we have proposed the creation of a cancer-cell-selective delivery system. We focused on and employ matrix metalloproteinase-9 (MMP-9) substrate peptide as cancer cell specific ligand with polyethylene glycol (PEG)-decorated oligoarginine. MMPs are well known as one of the cancer cell-specific over-expressed protease. From the cellular uptake experiment, it was successfully demonstrated that cell membrane permeability of PEG-decorated oligoarginine was remarkably enhanced by endogenous MMPs. In this presentation, we will report the polymer structural effects for cleavage activities and cellular uptake of the system.

Keywords : Cell Penetrating Peptide; Matrix Metalloproteinase; Cancer Targeting; Drug Delivery System

がんは世界の主要な死因の 1 つであり、世界中で治療薬の開発が精力的に推進されている。しかし、標的細胞のみならず正常細胞にも薬物が送達されてしまい、深刻な副作用や毒性を生じてしまうなどの解決すべき課題が指摘されている。本課題解決法の 1 つとして、標的細胞へ選択的に送達可能なドラッグデリバリーシステム (DDS) の開発が提案され、精力的に研究されている。

このような背景を踏まえ本研究では、がん細胞選択的薬剤送達システムの開発を指向し、がん細胞で特異的に過剰発現されることが報告され、膜放出型分解酵素の一つとして知られているマトリックスメタロプロテアーゼ-9 (MMP-9) に注目し、標的がん細胞近傍で選択的に膜透過性が活性化され得る、ポリエチレングリコール (PEG) 複合化オリゴアルギニンの設計・合成および機能評価に取り組んだ。

当研究室では既に細胞取り込み実験の結果から、MMP-9 認識ペプチドをリンカーに組み込んだ PEG 複合化オリゴアルギニンが、エンドジニアス MMP-9 により切断･活性化され、細胞への取り込み量が劇的に増大することを実証している。今回はポリマー構造の切断活性ならびに細胞取り込みに及ぼす影響について、詳細に検討した結果を報告する。

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

[A202-3pm] 19. Colloid and Interface Chemistry

Chair: Tsuyoshi Akiyama, Toshiki Sawada

Fri. Mar 25, 2022 1:40 PM - 3:40 PM A202 (Online Meeting)

[A202-3pm-01] Formation of Spherical Colloidal Clusters with Icosahedral Structure: Dependence on Colloidal Particle Size

○Ryosuke Ohnuki[1], Yukikazu Takeoka[2], Yoshioka Shinya[1] （1. Tokyo University of Science, 2. Nagoya University）

1:40 PM - 2:00 PM

[A202-3pm-02] Synthesis and Solution Properties of Amino Acid-Sugar Hybrid Surfactants Using Glycine and Maltose

○Yumi Nagahama[1], Ayami Kobayashi[1], Yohsuke Hada[2], Shigetoyo Sawaki[2], Shiho Yada[1], Tomokazu Yoshimura[1] （1. Grad. Sch. Human. Sci., Nara Women's Univ., 2. Technoble Co., Ltd.）

2:00 PM - 2:20 PM

[A202-3pm-03] Guest-responsive supramolecular hydrogels expressing selective sol– gel transition for sulfated glycosaminoglycans

○Shun-ichi Tamaru[1], Naofumi Kuroda[1] （1. Sojo University）

2:20 PM - 2:40 PM

[A202-3pm-04] Correlation between Liquid Crystalline and Gelation Properties with Ionic Liquid Gels Formed by Fluorine-Containing Phenyl Benzoate Derivatives That Exhibits Liquid Crystallinity

Tatsuya Tomarino[1], ○Kenta Matsumoto[1], Yuta Kawamoto[1], Junya Yamaguchi[1], Kotaro Kanetada[1], Masashi Akiyama[2], Yuki Morita[3], Hiroaki Okamoto[1] （1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University, 3. Advanced Technology Institute, Yamaguchi University）

2:40 PM - 3:00 PM

[A202-3pm-05] Construction of covalent cluster framework by using the reactivities of surface ligands

Yuki Saito[1], Yukatsu Shichibu[1,2], ○Katsuaki KONISHI[1,2] （1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University）

3:00 PM - 3:20 PM

[A202-3pm-06] Coherent Motion of Billions of Nanosheets for Generating Propagating Wave

○Koki Sano[1,2,3], Ebina Yasuo[4], Takayoshi Sasaki[4], Yasuhiro Ishida[3] （1. Shinshu Univ., 2. JST PRESTO, 3. RIKEN, 4. NIMS）

3:20 PM - 3:40 PM

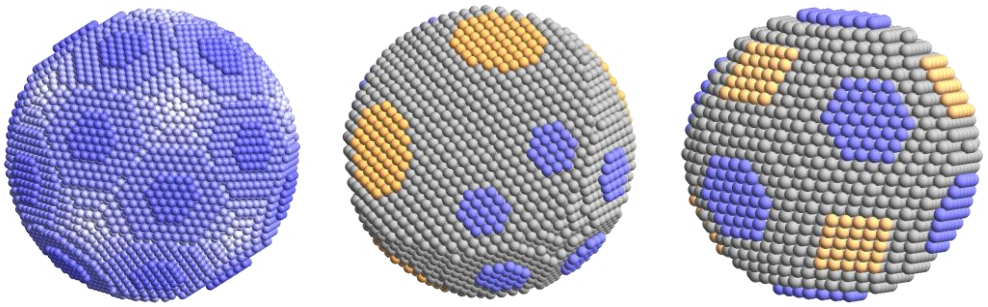
正二十面体構造の球状コロイドクラスターの作製：コロイド粒子サイズ依存性

（東理大理工[1]・名大工[2]）○大貫 良輔[1]・竹岡敬和[2]・吉岡 伸也[1]
Formation of Spherical Colloidal Clusters with Icosahedral Structure: Dependence on Colloidal Particle Size ([1]*Graduate School of Science and Technology, Tokyo University of Science*, [2]*Graduate School of Engineering, Nagoya University*)
○Ryosuke Ohnuki[1], Yukikazu Takeoka[2], Shinya Yoshioka[1]

Spherical colloidal clusters are formed by evaporating water from a droplet with dispersed colloidal particles in oil. Its structure depends on the preparation conditions and varies from icosahedral structure, decahedral structure, single FCC structure, etc. The number of constituent particles and the evaporation speed of the droplet are considered to be particularly important factors. In this study, we fabricated spherical colloidal clusters with various colloidal particle sizes and investigated the fraction of the structure. As a result, it was found that the fraction of colloidal clusters with icosahedral structure increased as colloidal particle size increased, suggesting that colloidal particle size is another parameter that affects the structure of spherical colloidal clusters.
Keywords：Colloidal cluster; Icosahedral structure; Colloidal crystals; Structural color; Self-assembly

球状コロイドクラスターは、油中にコロイド粒子が分散した液滴を作り、水分を蒸発させることで作製される。その構造は作製条件に依存して正二十面体構造や十面体構造、FCC の単結晶型構造などに変化し、特に構成粒子数と液滴の蒸発速度が重要であると考えられている[1-4]。本研究では、様々なコロイド粒子サイズで球状コロイドクラスターを作製し、いくつかの構造の出現割合を調べた。その結果、コロイド粒子サイズが大きくなるほど正二十面体構造のコロイドクラスターの割合が多くなることが分かり、コロイド粒子サイズは球状コロイドクラスターの構造に影響を与えるもう一つのパラメータであることを示している。

正二十面体構造　　**十面体構造**　　**FCC構造**



[1] J. Wang *et al.*, *Nat. Commun.*, **9**, 5259, (2018). [2] C. Kim *et al.*, *Chem. Mater.*, **32**, 9704, (2020).
[3] B. de Nijs *et al.*, *Nat. Mater.*, **14**, 56, (2015). [4] S. Park *et al.*, *Nanoscale*, **12**, 18576, (2020).

グリシンとマルトースを用いたアミノ酸ー糖ハイブリッド界面活性剤の合成と水溶液物性

（奈良女大院人間文化総合科学[1]・（株）テクノーブル[2]）○長濱 佑美[1]・小林 礼実[1]・羽田 容介[2]・澤木 茂豊[2]・矢田 詩歩[1]・吉村 倫一[1]

Synthesis and Solution Properties of Amino Acid-Sugar Hybrid Surfactants Using Glycine and Maltose ([1]*Graduate School of Humanities and Sciences, Nara Women's University*, [2]*Technoble Co., Ltd.*) ○Yumi Nagahama,[1] Ayami Kobayashi,[1] Yohsuke Hada,[2] Shigetoyo Sawaki,[2] Shiho Yada,[1] Tomokazu Yoshimura[1]

Amino acid-sugar hybrid surfactants (alkyl chain length = 10–16) were synthesized by using glycine as amino acid and maltose as sugar, and their solution properties were investigated by measuring Krafft temperature, surface tension, small-angle X-ray scattering and rheology, etc. The effects of sugar structure, presence or absence of amino acid skeleton and alkyl chain length on the solution properties of the hybrid surfactants were investigated by comparing with those of amino acid-sugar hybrid surfactants using lactose and sugar-based surfactants using maltose.

Keywords : Amino Acid-type Surfactant; Sugar-based Surfactant; Surface Tension; Rheology; Small-Angle X-ray Scattering

1. 緒言 アミノ酸系界面活性剤は優れた水溶性や低刺激性を有することから、シャンプーや洗顔料などに用いられている。糖型界面活性剤は、良好な起泡力を示し、硬水中でも適度な洗浄力から、食器用洗剤などに用いられている。本研究では、アミノ酸としてグリシン、糖として麦芽糖由来のマルトースに着目し、アミノ酸–糖ハイブリッド界面活性剤（C_nGlyMal、n はアルキル鎖長で 10～16、Fig. 1）を新規に分子設計・合成し、水溶液物性をクラフト温度、表面張力、X 線小角散乱、レオロジーなどの測定により調べた。これらの物性を糖にラクトースを用いたハイブリッド界面活性剤（C_nGlyLac）や糖型界面活性剤（C_nMal、Fig. 1）の水溶液物性と比較することにより、物性に及ぼす糖構造やアミノ酸骨格の有無、アルキル鎖長の影響について検討した。

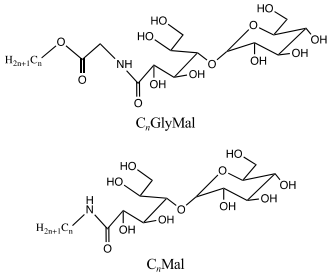


Fig. 1 Structures of amino acid–sugar type hybrid surfactant (C_nGlyMal) and sugar–based surfactant (C_nMal).

2. 結果と考察 アミノ酸–糖ハイブリッド界面活性剤 C_{12}GlyMal および糖型界面活性剤 C_{12}Mal の 1.0 wt%の水溶液におけるクラフト温度は、それぞれ< 5、34.5 ºC であり、C_{12}GlyMal は高い水溶性を示した。C_{12}GlyMal の水溶液における粘度のずり速度依存性と粘弾性の角周波数依存性（Fig. 2）から、低濃度ではミセルを形成し、濃度が増加すると紐状ミセル、さらにゲルに転移することがわかった。これらの結果は SAXS によっても支持された。一方、糖型の C_{12}Mal は水溶性が低く、40 ºC において溶解した濃度範囲でミセル形成が確認された。このように、アルキル鎖と糖の間にアミノ酸を導入することにより、水溶性が劇的に向上し、ミセルー紐状ミセルーゲル転移を示すことが明らかになった。

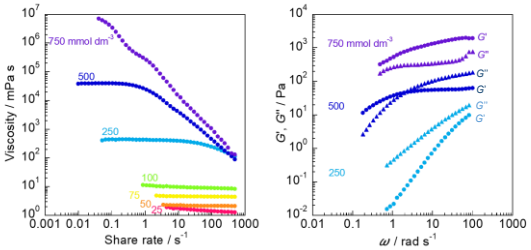


Fig. 2 Share rate dependence of viscosity (left) and frequency dependence of storage and loss moduli (G', G'') (right) for C_{12}GlyMal at 25ºC. From the bottom: 25, 50, 75, 100, 250, 500, 750 mmol dm^{-3}.

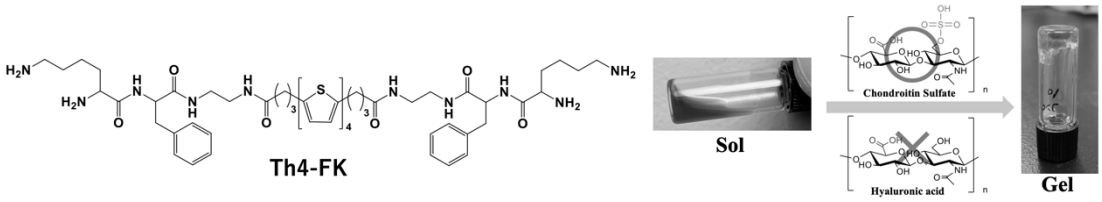
ゲスト応答型超分子ヒドロゲルを用いたグリコサミノグリカン類の識別

（崇城大院工）○田丸 俊一・黒田 尚史
Guest-responsive supramolecular hydrogels expressing selective sol–gel transition for sulfated glycosaminoglycans (*Graduate School of Engineering,Sojo University*)○Shun-ichi Tamaru, Naofumi Kuroda

This paper describes the stimuli-responsive hydrogels constructed from bola-type amphiphiles composed of two dipeptides containing phenylalanine attached to the ends of a hydrophobic tetrathiophene. The hydrogel formation ability of the amphiphiles was affected by the N-terminal amino acid residue, which is an amphiphile-possessing phenylalanine-lysine sequence that formed a hydrogel under limited pH conditions. Gel formation occurred because of the phase transition of the gelator assembly from a granular aggregate to a fibrous architecture, in a process controlled by pH. This stimuli-responsive sol–gel transition was also accomplished by the addition of an anionic polymer, and sulfated glycosaminoglycans was successfully discriminated using the hydrogel system.
Keywords : Supramolecular Chemistry; hydrogel; Glycosaminoglycans; stimuli-responsiveness; Molecular Recognition

Th4-FK は pH 変化による分子上の荷電状態の変化に起因して、顆粒状から繊維状の構造体へと相転移し、この繊維状構造体が三次元的なネットワークを構築することでヒドロゲルが形成することが明らかとなった。同様の相転移はアニオン性高分子の添加によっても誘起することが可能であり、硫酸化アニオン性多糖類であるヘパリン**(Hep)**やコンドロイチン硫酸 C**(CS-C)**の添加によるゲスト選択的なヒドロゲル形成を誘導することに成功した。一方、ヒアルロン酸**(HA)**などの硫酸アニオンを持たない高分子を添加しても **Th4-FK** はヒドロゲルを形成しなかった。

以上の結果から、**Th4-FK** のヒドロゲル形成能を利用することで、硫酸化アニオン性多糖を選択的に識別するヒドロゲル系の構築に成功した [1]。この系は pH とアニオン性多糖類の種類という 2 つの条件が両方満たされた場合のみ駆動する and ゲート型の識別系であることから、高い選択性を発現する検出系構築のための有用な知見となると考えられる。



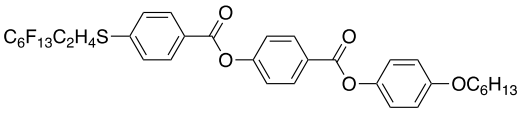
1) Naofumi Kuroda, Yukie Tounoue, Kouichiro Noguchi, Yutaro Shimasaki, Hitoshi Inokawa, Masayoshi Takano, Seiji Shinkai, Shun-ichi Tamaru, *Polym J*. **2020**, *52*, 939–946.

Correlation between Liquid Crystalline and Gelation Properties with Ionic Liquid Gels Formed by Fluorine-Containing Phenyl Benzoate Derivatives That Exhibits Liquid Crystallinity

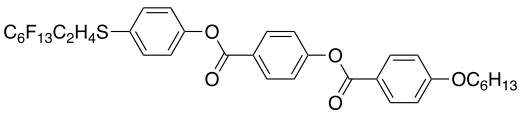
([1]*Graduate School of Sciences and Technology for Innovation, Yamaguchi University*, [2]*Faculty of Engineering, Yamaguchi University*, [3]*Advanced Technology Institute, Yamaguchi University*)
Tatsuya Tomarino,[1] ○ Kenta Matsumoto,[1] Yuta Kawamoto,[1] Junya Yamaguchi,[1] Kotaro Kanetada,[1] Masashi Akiyama,[2] Yuki Morita[3], Hiroaki Okamoto[1]
Keywords: Phenyl Benzoate Derivatives; Low-Molecular Gel; Ionic Liquid Gel; Thermotropic Liquid Crystal; Lyotropic Liquid Crystal.

In our previous work, it was found that some low molecular weight compounds containing perfluoroalkyl group at terminal position showed smectic A (SmA) phase in bulk state and gelated several organic and/or ionic liquid.[1)] While correlation between liquid crystallinity and gelation mechanism were not elucidated.

In this study, a famous ionic liquid; [BMIM][TFSA] was gelated by phenyl benzoate derivatives containing perfluoroalkyl group (Figure 1) and evaluated liquid crystallinity of gels by polarized microscope (POM) observation and differential scanning calorimetry (DSC).



Compound **1**



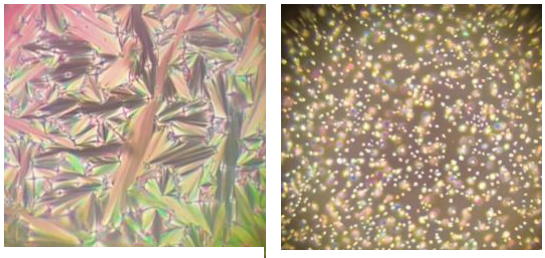
Compound **2**

Figure 1. Chemical structures of compounds **1** and **2**.

Compound **1** showed SmA phase, however the gels showed fibrous aggregates formed by self-assembly phenomena observed by POM and scanning electron microscope. On the other hands, compound **2** showed SmA phase in bulk state and 5wt% [BMIM][TFSA] gel also showed optically anisotropic textures at room temperature (Figure 2).

In addition, it was confirmed that 5wt% [BMIM][TFSA] gel formed by compound **2** was highly dispersion stability.

In this presentation, the correlation between liquid crystalline and gelation properties will be considered by spectroscopic analysis and molecular dynamics (MD) simulation.



170℃ in cooling　　*r.t.*

Figure 2. POM images of compound **2** in bulk state (left) and 5wt% [BMIM][TFSA] gel formed by compound **2** (right).

1) Yuki Morita *et al*., *Mol. Cryst. Liq. Cryst*. **2005**, 435, 813.

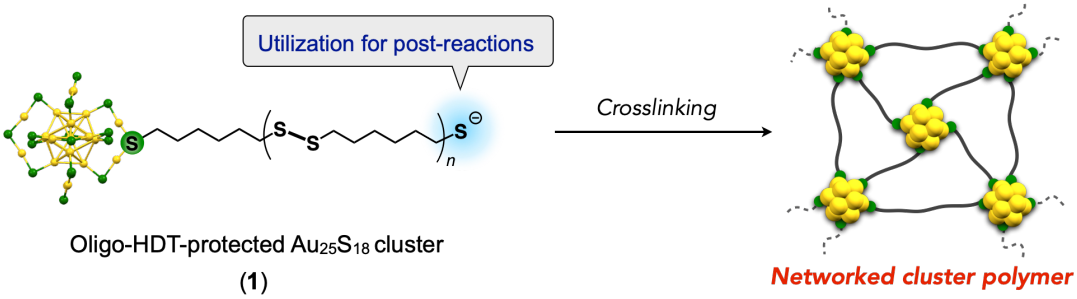
配位子の反応性を活用した共有結合架橋型クラスター集積体の設計

（北大院環境[1]・北大院地球環境[2]）齋藤 結大[1]・七分 勇勝[1,2]・○小西 克明[1,2]
Construction of covalent cluster framework by using the reactivities of surface ligands ([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) Yuki Saito,[1] Yukatsu Shichibu,[1,2] Katsuaki Konishi[1,2]

Self-assemblies of molecular gold clusters held by intermolecular interactions are expected to exhibit unique properties that are not found in single clusters, but are stable only under specific conditions. In this study, we attempted the covalent networking of gold clusters by using the ligand reactivity.[1] The Au_{25} cluster (**1**) prepared from 1,6-hexanedithiol (HDT) possesses uncoordinated thiolates at the outermost surface of the ligand layer. These surface free thiolates are usable for the inter-cluster covalent bond formation, and finally, two types of networked cluster polymer were obtained by different crosslinking methods.
Keywords : Gold cluster; Network polymer; Ligand

有機配位子で保護された金属クラスターは、金属コアの幾何構造に依存したユニークな光学・触媒特性を示すことが知られている。これまで、「単一の分子」としてのクラスターの物性解析を目指した研究が展開されてきたが、近年はクラスターを凝集・組織化させることで初めて生み出される機能の創出に注目が集まっている。そのようなクラスター凝集体を作り出す駆動力として、疎水性相互作用等の分子間力を利用した報告は多いが、特定の溶媒条件でしか維持できないという課題もあった。そこで本研究では、金クラスターの配位子層の反応性に着目し、クラスター同士を三次元的に共有結合架橋することでネットワークポリマーへと変換する方法を考案した。[1]

1,6-hexanedithiol (HDT)を配位子に用いて、構造既知の $Au_{25}(SR)_{18}$ クラスターを合成すると、HDT オリゴマーにより保護された Au_{25} クラスター(**1**)が得られた。この HDT オリゴマーの一端はクラスターに配位し、他端は未配位のチオラートアニオンとして存在していた。この表面の未反応チオラートを反応点として活用することで、Au_{25} クラスターのネットワーク化を検討した。その結果、**1** を固体状態で酸素と反応させると、末端チオラートの酸化によるクラスター間ジスルフィド形成によってアモルファスの Au_{25} ポリマーが得られることがわかった。一方、**1** を溶液中で静置すると、末端チオラートを起点としたクラスター間での配位子交換が起こり、結晶性を持つ Au_{25} ポリマーが得られた。本発表では、これら 2 種の合成法とポリマー構造の詳細について説明する。



1) Y. Saito, Y. Shichibu, K. Konishi *Nanoscale* **2021**, *13*, 9971.

数十億枚のナノシートが協働する繊毛運動のような波

（信州大繊維[1]・JST さきがけ[2]・理研 CEMS[3]・物材機構 MANA[4]）
○佐野 航季[1,2,3]・海老名 保男[4]・佐々木 高義[4]・石田 康博[3]

Coherent Motion of Billions of Nanosheets for Generating Propagating Wave

([1]*Faculty of Textile Science and Technology, Shinshu University,* [2]*JST PRESTO,* [3]*RIKEN CEMS,* [4]*NIMS MANA*) ○Koki Sano,[1,2,3] Yasuo Ebina,[4] Takayoshi Sasaki,[4] Yasuhiro Ishida[3]

Coherent operation under a non-equilibrium state is essential in living organisms for amplifying tiny molecular-scale motions of their movable components into a macroscopic mechanical force. Here we report that around ten billion pieces of colloidal nanosheets in water can be made to operate coherently to generate a propagating macroscopic wave.

Keywords : Nanosheet; Liquid Crystal; Biomimetic System; Spatiotemporal Pattern

生体内では、タンパク質などの動的ナノユニットが三次元秩序構造へと集積化・協働することで、個々の小さく単純な動きが巨視的で精緻な動きへとつながっている。今日まで、分子機械や自己駆動コロイド粒子といった動的ナノユニットが人工的に合成されてきたが、これらの協働による巨視的な機能発現は依然困難を極める。

今回我々は、酸化チタンナノシート[1–5]を水中に精密に配列させて化学的刺激を与えると、数十億枚ものナノシートが協働的に動き、空間的かつ時間的に秩序を持つ巨視的な波運動が発生することを見いだした（図 1）[6]。この波運動は、水中にてナノシート間に働くファンデルワールス引力と静電斥力のバランス[2,5]が、化学的刺激（イオンの拡散）によって徐々に変化することで駆動される。この波は繊毛運動のように一方向に伝播し、均一な速度で微粒子を輸送できることも明らかになった。

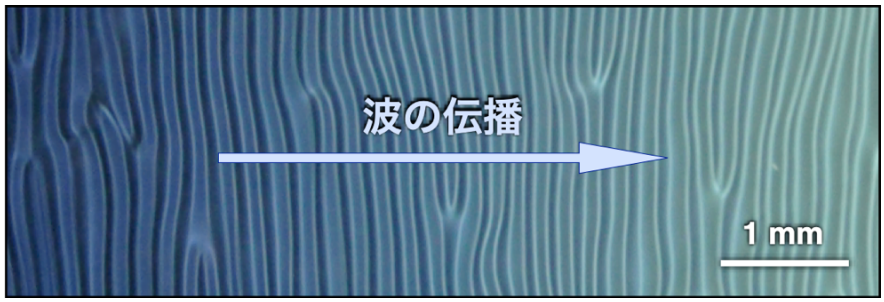


図 1. 数十億枚の無機ナノシートが水中にて協働することで生じる波運動

(1) T. Sasaki *et al. J. Am. Chem. Soc.* **118**, 8329–8335 (1996).
(2) K. Sano *et al. Nat. Commun.* **7**, 12559 (2016).
(3) K. Sano *et al. Angew. Chem. Int. Ed.* **57**, 2532–2543 (2018).
(4) K. Sano *et al. Angew. Chem. Int. Ed.* **57**, 12508–12513 (2018).
(5) K. Sano *et al. Nat. Commun.* **11**, 6026 (2020).
(6) K. Sano *et al. Nat. Commun.* **12**, 6771 (2021).

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

[C204-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Mihoko Yamada, Naoki Tanaka

Fri. Mar 25, 2022 1:00 PM - 3:40 PM C204 (Online Meeting)

[C204-3pm-01] Electron doping of single-walled carbon nanotubes starting from diborane compounds

○Naoki Tanaka[1,2], Aoi Hamasuna[1], Koichiro Kato[1,2,3], Tsuyohiko Fujigaya[1,2,3] (1. Department of Applied Chemistry, Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)

1:00 PM - 1:20 PM

[C204-3pm-02] Near Infrared Photoluminescence Modulation of Biotin-functionalized Single-walled Carbon Nanotubes Based on Avidin Binding

○Yoshiaki Niidome[1], Rie Wakabayashi[1], Masahiro Goto[1,2], Tsuyohiko Fujigaya[1,3,4], Tomohiro Shiraki[1,3] (1. Graduate School of Engineering, Kyushu Univ., 2. CFC, Kyushu Univ., 3. WPI-I2CNER, Kyushu Univ., 4. CMS, Kyushu Univ.)

1:20 PM - 1:40 PM

[C204-3pm-03] Near Infrared Emission Property Variation of Chemically Functionalized Single-walled Carbon Nanotubes Based on Structures of Chemical Modifiers

○Tomohiro Shiraki[1,2], Haruka Aoki[1], Keita Hayashi[1], Tsuyohiko Fujigaya[1,2,3] (1. Department of Applied Chemistry, Kyushu University, 2. I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)

1:40 PM - 2:00 PM

[C204-3pm-04] Preparation and characterization of carbon nanotube dispersions exhibiting liquid crystal phase

○Keiko Kojima[1,2], Miho Aizawa[2,3], Takahiro Yamamoto[2], Kazufumi Kobashi[2], Toshiya Okazaki[2,1] (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST), 3. JST PRESTO)

2:00 PM - 2:20 PM

[C204-3pm-05] Control of near-infrared photoluminescence of single-walled carbon nanotube by chemical functionalization with dendron and its end group conversion

○Yui Konno[1], Michio Yamada[1], Yutaka Maeda[1] (1. Tokyo Gakugei University)

2:20 PM - 2:40 PM

[C204-3pm-06] Precise synthesis of graphene nanoribbon in metal-organic framework

○Takashi Kitao[1,2], Kazuki Nakata[1], Takashi Uemura[1] (1. The Univ. of Tokyo, 2. JST-PRESTO)

2:40 PM - 3:00 PM

[C204-3pm-07] Carbon-doped Graphitic Carbon Nitride Based Films as New Functional Materials

○Niannian Wu[1,2], Nobuhiko Mitoma[2], Takuzo Aida[1,2] (1. University of Tokyo, 2. Riken)

3:00 PM - 3:20 PM

[C204-3pm-08] Syntheses of new photochromic tetrathienylcorannulenes with a curved aromatic skeleton and their optical properties

○Mihoko Yamada[1], Tomoya Sawazaki[1], Mae Fujita[1], Tomoki Fujitani[1], Tsuyoshi Kawai[1]
（1. NAIST）

3:20 PM - 3:40 PM

ジボランを起点とした単層カーボンナノチューブの n 型化

（九大院工[1]・九大 WPI-I2CNER[2]・九大 CMS[3]）○田中 直樹[1,2]・浜砂 碧[1]・加藤 幸一郎[1,2,3]・藤ヶ谷 剛彦[1,2,3]

Electron doping of single-walled carbon nanotubes starting from diborane compounds

(*[1]Department of Applied Chemistry, Kyushu Univ., [2]WPI-I2CNER, Kyushu Univ., [3]CMS, Kyushu Univ.*) ○Naoki Tanaka,[1,2] Aoi Hamasuna,[1] Koichiro Kato,[1,2,3] Tsuyohiko Fujigaya[1,2,3]

The chemical doping of SWCNTs using electron donor and acceptor molecules is a crucial step for controlling the frontier orbital energy gap of SWCNTs. The application of SWCNTs to thermoelectric devices requires p-type and n-type SWCNTs, but the development of n-type SWCNTs has lagged that of p-type SWCNTs because of the instability in air. Recently, we developed long-term stable n-doped SWCNTs using tetrahydroxydiboron ($B_2(OH)_4$) and 4-phenylpyridine (4-Phpy). In this presentation, we will report the air-stable mechanism of the n-doped SWCNTs based on the results of experiments and theoretical analysis.

Keywords: Thermoelectric generation, Single-walled carbon nanotube, Boron, Diborane, Electron transfer

単層カーボンナノチューブ (SWCNTs) は、高い電気伝導率、加工性や軽量性に加え、p 型、n 型特性の両方を付与できる点から、熱電発電分野において注目を集めている。しかし n 型 SWCNT は、水や大気酸化による p 型化が進行するため、大気安定な n 型 SWCNT の開発は未だ重要課題である。これまで当研究室では、ビスピナコラートジボランと 4-シアノピリジンを混合することで発生するピリジンホウ素ラジカルを用いて、SWCNT の n 型化を達成している[1]。しかし得られた SWCNT シートは、24 時間後には p 型特性を示したことから、大気安定性には乏しかった。一方で、テトラヒドロキシジボラン ($B_2(OH)_4$) と 4-フェニルピリジン (4-Phpy) を混合して作成した SWCNT シートは、50 日以上の n 型特性を示したことから、大気安定性の向上が明らかになった。本研究では、この大気安定性メカニズムを SWCNT 表面解析および理論計算から考察した。

光電子分光測定および赤外分光測定の結果から、ドープ後の SWCNT 表面には、ドーパントカチオンと $B_2(OH)_4$ の存在が明らかになり、$B_2(OH)_4$ の被覆が大気安定性の向上につながっていることが示唆された。また理論計算から、$B_2(OH)_4$ と 4-Phpy の混合により発生すると考えられるピリジンホウ素ラジカルが、ジボランの置換基サイズの減少およびピリジン上のフェニル基と SWCNT との π-スタッキングにより、SWCNT と強く相互作用していることが予想された。発表では、本ドープメカニズムも併せて発表する。

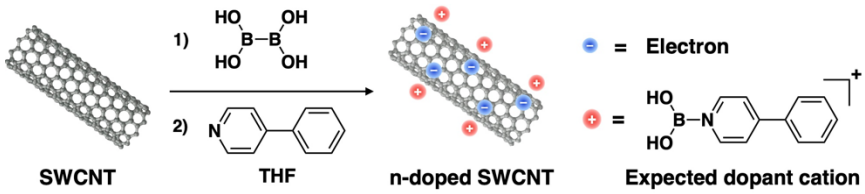


Figure 1. Schematic image of electron doping of SWCNT using tetrahydroxydiborane ($B_2(OH)_4$) and 4-phenylpyridine (4-Phpy).

参考文献: [1] N. Tanaka, T. Fujigaya et al., *Chem. Commun.*, **2021**, *57*, 6019.

Near Infrared Photoluminescence Modulation of Biotin-functionalized Single-walled Carbon Nanotubes Based on Avidin Binding

([1]*Graduate School of Engineering, Kyushu University*, [2]*CFC, Kyushu University*, [3]*WPI-I[2]CNER, Kyushu University,* [4]*CMS, Kyushu University*) ○ Yoshiaki Niidome,[1] Rie Wakabayashi[1], Masahiro Goto[1,2], Tsuyohiko Fujigaya,[1,3,4] Tomohiro Shiraki[1,3]

Keywords: Carbon Nanotube; Near Infrared Photoluminescence; Chemical Functionalization; Molecular Recognition; Avidin-biotin Interaction

Photoluminescence (PL) in near infrared (NIR) regions from single-walled carbon nanotubes (SWCNTs) is useful for biomedical applications such as imaging and sensing due to the advantages of NIR light that show low-autofluorescence and high transparency to biological tissues.[1] The PL properties of SWCNTs can be enhanced by local chemical functionalization that allows sp^3 carbon doping to their sp^2 carbon networks.[2] The resultant locally functionalized SWCNTs (lf-SWCNTs) emit red-shifted and bright E_{11}* PL over 1000 nm regions. Recently we have reported that E_{11}* PL of lf-SWCNTs showed larger spectral shifts than E_{11} PL of non-factionalized tubes by differences in polarities of surrounding environments.[3] The enhanced wavelength shifts of E_{11}* PL are expected to develop new sensing systems based on adsorption of analyte molecules on the lf-SWCNT surfaces.

Here, we investigate E_{11}* PL wavelength shifts of lf-SWCNTs by the adsorption of proteins using a selective biomolecular binding system that is based on avidin-biotin interactions (dissociation constant is ~10^{-15} M). The lf-SWCNTs tethering biotin groups (lf-SWCNTs-b) were synthesized through the chemical functionalization using an aryldiazonium salts, followed by its post-modification (Fig. 1). When neutravidin was mixed with a lf-SWCNTs-b solution, E_{11}* PL peak was red-shifted, indicating the higher polarity environment formation by neutravidin adsorption on the lf-SWCNTs-b. When avidin or streptavidin was used for lf-SWCNTs-b binding experiments, wavelength shifting behaviors of E_{11}* PL from lf-SWCNTs-b were clearly changed depending on the used avidin derivatives. The results would be due to different polar environment formation deriving from structural differences of each avidin derivative. Therefore, lf-SWCNTs are expected for development of advanced protein detection devices using NIR PL.

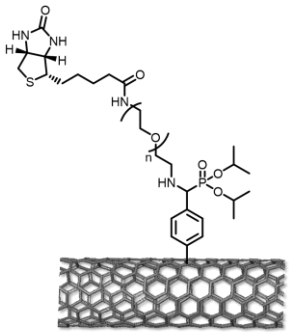


Fig. 1. Structural images of lf-SWCNTs-b

1) J. H. Choi *et al*., *J. Mater. Chem. B* **2017**, *5*, 6511. 2) a) Y. Wang *et al*., *Nat. Rev. Chem.* **2019**, *3*, 375. b) S. Tretiak *et al*., *Acc. Chem. Res.* **2020**, *53*, 1791.c) T. Shiraki *et al*., *Acc. Chem. Res.* **2020**, *53*, 1846. d) T. Shiraki, *Chem. Lett.* **2021***, 50,* 397. 3) a) T. Shiraki *et al*., *Chem. Commun.* **2019**, *55*, 3662.b) T. Shiraki *et al*., *J. Phys. Chem. C* **2021**, *125*, 12758.

Near Infrared Emission Property Variation of Chemically Functionalized Single-walled Carbon Nanotubes Based on Structures of Chemical Modifiers

([1]*Department of Applied Chemistry, Kyushu University,* [2]*International Institute for Carbon-Neutral Energy Research (I2CNER), Kyushu University,* [3]*Center for Molecular Systems (CMS), Kyushu University*) ○ Tomohiro Shiraki[1,2], Haruka Aoki[1], Keita Hayashi[1], Tsuyohiko Fujigaya[1,2,3]

Keywords: Carbon Nanotube, Photoluminescence, Near Infrared Light, Chemical Modification, Defect

Local chemical functionalization of single-walled carbon nanotubes (SWCNTs) has been developed to enhance their photoluminescence (PL) properties in the near infrared (NIR) region.[1-4] In this functionalization, local defects such as sp^3 carbon are doped to the semiconducting crystalline sp^2 carbon networks of SWCNTs based on chemical bond formation between modifier molecules and the tube walls. As a result, emissive doped sites that have narrower bandgaps and exciton trapping features are created in the locally functionalized SWCNTs (lf-SWCNTs). Accordingly, new E_{11}* PL appears with red-shifted wavelengths and increased PL quantum yields compared with original E_{11} PL of pristine SWCNTs. To date, chemical modifiers such as aryldiazonium salts and halogenated compounds have been used and the molecular functionalization has allowed to modulate E_{11}* PL emission properties of lf-SWCNTs.

Here, organic azide compounds are used for a [2+1] cycloaddition reaction with SWCNTs, which aims for the synthesis of lf-SWCNTs (lf-SWCNTs>N). The local chemical functionalization was conducted by mixing solubilized SWCNTs in an aqueous micelle solution and an azide compound under light irradiation. Fig. 1 shows PL spectra of SWCNTs before and after the functionalization. For the lf-SWCNTs>N, a new PL peak appeared at 1116 nm that was observed in the longer wavelength region than E_{11} PL at 977 nm. In the XPS measurements of the lf-SWCNTs>N, N1s peak was clearly observed around 400 eV. Therefore, azide compounds could offer new series of defect doping modifiers to produce E_{11}* PL characters for lf-SWCNTs.

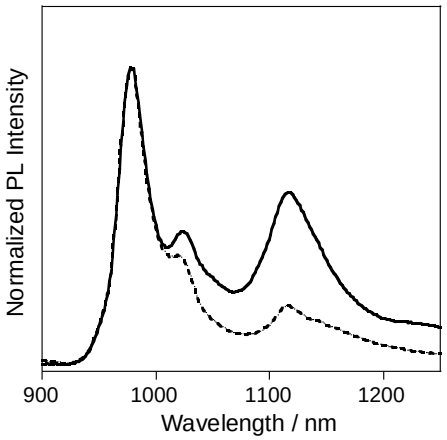


Fig. 1 Normalized PL spectra of lf-SWCNTs>N (solid line) and pristine SWCNTs (dashed line), λ_{ex} = 570 nm.

1) T. Shiraki, *Chem. Lett*., **2021**, *50*, 397. 2) T. Shiraki *et al*., *Acc. Chem. Res.*, **2020**, *53*, 1846. 3) S. Tretiak *et al*., *Acc. Chem. Res.*, **2020**, *53*, 1791. 4) Y. Wang *et al*., *Nat. Rev. Chem.*, **2019**, *3*, 375.

Preparation and Characterization of Carbon Nanotube Dispersion Exhibiting Liquid Crystal Phase

([1]*University of Tsukuba*, [2]*National Institute of Advanced Industrial Science and Technology (AIST),* [3]*JST PRESTO*) ○ Keiko Kojima,[1,2] Miho Aizawa,[2,3] Takahiro Yamamoto,[2] Kazufumi Kobashi,[2] Toshiya Okazaki[2,1]

Keywords: Carbon nanotubes; Liquid crystal

Carbon nanotubes (CNTs) are tubular carbon allotrope showing high electrical conductivity (900,000 S/cm[1]) and tensile strength (43-80 GPa[2]). Because of their superior physical properties, CNTs have been expected as lightweight flexible fibers. One of the most promising methods for producing CNT fibers is wet spinning. In this process, CNT solution is injected into a coagulation liquid bath to form the fibers. To improve the fiber properties, CNTs need to be aligned in the fiber. Therefore, liquid crystalline CNT dispersions have been used for the wet spinning. However, systematic study on the liquid crystal (LC) phase behavior of CNT dispersions has so far been limited.

We here used single-walled CNTs purchased from Meijo Nanocarbon (e-Dips) and OCSiAl (Tuball). To disperse CNTs in water, we added sodium-cholate (SC) as dispersants. After sonication, the CNT solution was centrifuged to remove large CNT aggregates and concentrated by ultrafiltration. At the CNT concentration of 0.18 vol %, the dispersion shows isotropic phase (Fig. 1(a)). At the higher concentration (0.49 vol %), nematic LC phase was observed (Fig. 1(b)). The CNT dispersion show biphasic state at the intermediate concentration (0.38 vol %) (Fig. 1(c)). The characteristic spindle LC phases called “tactoid” can be seen in the biphasic phase. By changing the sonication time, we prepared the CNT dispersions which contain different aspect ratio of CNT bundles (L/D). As increasing the aspect ratio, the LC transition occurs at the lower concentration. This trend is consistent with the Onsager theory, but the observed cloud points were lower than the predicted values. This can be explained by van der Waals interaction between CNT bundles[3]. In this meeting, we will also discuss the relationship between the observed tactoid shapes and L/D.

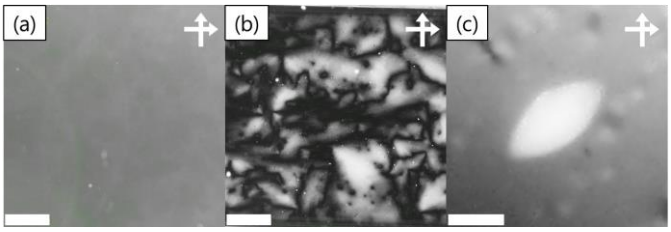


Figure 1. Polarized optical microscope image of CNT micelle solutions with different CNT concentrations ((a) 0.18 vol %, (b) 0.49 vol % and (c) 0.38 vol %). Scale bar: (a, b) 400 μm and (c) 10 μm.

1) J. Kong, *et al.*, *Appl. Phys. A*, 69 (3), 305-308 (1999). 2) Y. Bai, *et al.*, *Nat. Nanotechnol.*, 13, 589-595 (2018). 3) M. J. Green *et al.*, *J. Chem. Phys.* 131, 084901 (2009).

デンドロンを用いた単層カーボンナノチューブの化学修飾による近赤外発光制御とその末端官能基の変換

([1] 学芸大院連合教育, [2] 学芸大教) ○紺野優以 [1]・山田道夫 [2]・前田優 [1,2]

Control of near-infrared photoluminescence of single-walled carbon nanotube by chemical functionalization with dendron and its end group conversion ([1] *The United Graduate School of Education, Tokyo Gakugei University,* [2]*Dep. of Chemistry, Tokyo Gakugei University*)

○Yui Konno, Michio Yamada, Yutaka Maeda

The chemical functionalization of single-walled carbon nanotubes (SWNTs) is attracting attention as an effective method for controlling their optical properties and introducing functional molecules. Since the π-electron system decreases as the addition reaction of SWNTs proceeds, it is important to control their functionalization degree. Recently, it had been reported that new near-infrared photoluminescence (PL) appears in high quantum yields at low functionalization degree. Focusing on the bulkiness of dendrons depending on their generations, we had previously reported that both functionalization degree and PL properties of SWNTs can be tuned dependent on the generation of dendrons used as functionalization reagents.

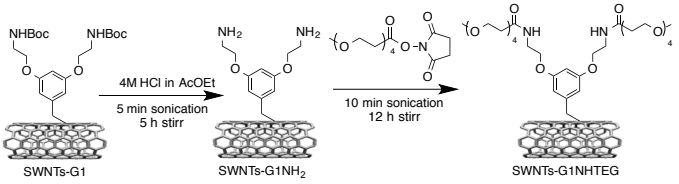
In this presentation, we conducted functionalization of SWNTs using dendrons and their functional group transformation including deprotection of Boc groups followed by amidation reaction. The deprotection and amidation reactions were monitored by the Kaiser test. Interestingly, the Raman spectra of the SWNTs adduct after the deprotection indicated that the functionalization degree of SWNTs decreased accompanied by the deprotection.

In addition to the characterization of the PL properties of the adducts before and after the end group conversion, we investigated the effect of ultrasonic irradiation of SWNTs in organic solvents, which is contained in the procedure of the deprotection process.

Keywords: Carbon nanotube; Photoluminescence; Functional group transformation; Ultrasonic

単層カーボンナノチューブ（SWNTs）の化学修飾は、発光特性制御[1]や機能性分子の導入[2]の方法として着目されている。付加反応に伴いπ電子系を消失することから[1]、SWNTs の機能化において化学修飾率制御は重要である。適切な化学修飾では、量子収率の高い近赤外発光の発現も観察されている。

樹状化合物として知られるデンドロンは、基点に対して世代を増やすことによって嵩高さや末端基数を増加することができる。これまでに化学修飾に用いるデンドロンの世代を変えることで、SWNTs の化学修飾率と発光特性を制御できることを報告している[3]。



反応式. SWNTs 付加体の分子変換反応

本発表では、デンドロンを用いた SWNTs の化学修飾による発光特性の制御と、SWNTs 付加体に導入したデンドロンの末端官能基の分子変換を検討した（反応式）。モデル分子を導入した SWNTs 付加体の Kaiser test では、脱保護反応と引き続き行ったアミド化反応の進行を支持する結果が得られた。一方、Raman スペクトルでは脱保護反応に伴う SWNTs の化学修飾率の低下が示唆された。これらの分子変換が SWNTs の近赤外発光に与える影響と、分子変換の反応方法に含まれる SWNTs 付加体への有機溶媒中での超音波照射が与える影響についても、発光スペクトルやラマンスペクトルによって評価した。

1) Piao, Y. *et al.* Brightening of carbon nanotube photoluminescence through the incorporation of sp^3 defects. *Nat. Chem.* **5**, 840–845 (2013).
2) Campidelli, S. *et al.* Dendrimer-functionalized single-wall carbon nanotubes: Synthesis, characterization, and photoinduced electron transfer. *J. Am. Chem. Soc.* **128**, 12544–12552 (2006).
3) Maeda, Y. *et al.* Control of near infrared photoluminescence properties of single-walled carbon nanotubes by functionalization with dendrons. *Nanoscale* **10**, 23012–23017 (2018).

MOF ナノ空間によるグラフェンナノリボンの精密合成

（東大院工[1]・JST さきがけ[2]）○北尾 岳史[1,2]・中田 和希[1]・植村 卓史[1]
Precise synthesis of graphene nanoribbon in metal-organic framework
([1]*The University of Tokyo*, [2]*JST-PRESTO*) ○ Takashi Kitao,[1,2] Kazuki Nakata,[1] Takashi Uemura[1]

Graphene nanoribbons (GNRs) have recently attracted increasing interest because of their tunable optical, electronic, and magnetic properties achieved through the tailoring of their edge structure and width. However, the widespread implementation of GNRs into the various optelectronic devices has yet to be realized, as methods for the synthesis of GNRs in precise and scalable fashion are currently lacking. Metal–organic frameworks (MOFs), porous materials formed through the self-assembly of metal ions and organic ligands, have been applied to a variety of applications, including gas storage, separation, and catalysis. MOFs have the advantages of the tunable and regulated nature of their nanospaces and have been shown to provide an ideal compartment for controlling the arrangement of guest species through the geometrical constraint of host pores[1]. Here, we report on the precise and scalable synthesis of GNRs utilizing the one-dimensional nanochannels of MOFs (**Fig. 1**)[2].
Keywords : Metal-Organic Framework; Graphene Nanoribbon; Optoelectronic properties

グラフェンナノリボン（GNR）は、高い電子移動度を有し、様々な光電子デバイスへの利用が期待される機能性ナノ炭素材料である。GNR はリボン幅やエッジ構造に応じて異なる電子物性を示すため、その構造制御は非常に重要である。一方、多孔性金属錯体(MOF)は、その構成要素を適切に選択することで、サイズ、形状、表面環境など、細孔構造を緻密にデザインすることが可能である[1]。本研究では、MOF が有する一次元ナノ細孔内で多環芳香族化合物を重合することで、原子レベルで構造が制御された GNR を高効率・高収率で合成することに成功した(**Fig. 1**)[2]。

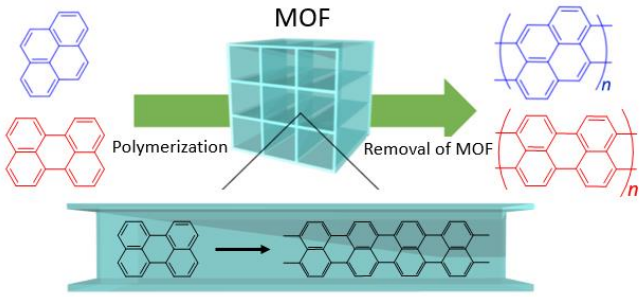


Fig. 1. Schematic image for synthesis of GNRs using a MOF as the host.

References

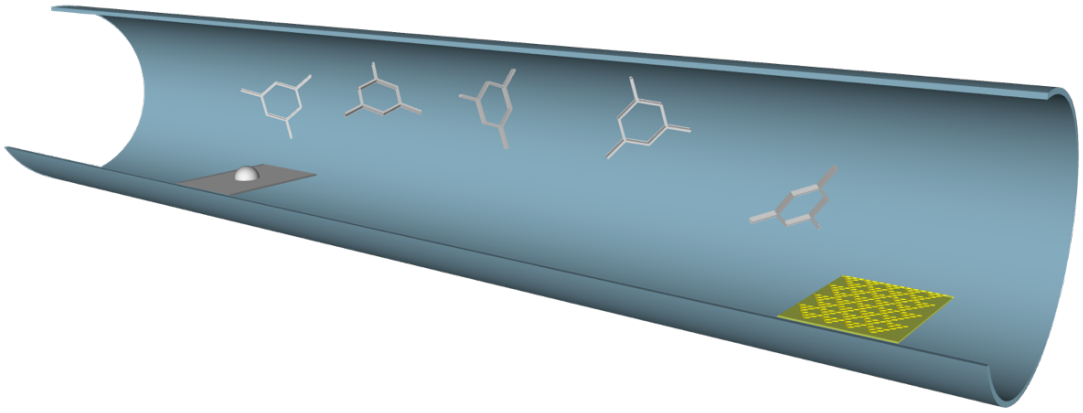
1. T. Kitao, Y. Zhang, S. Kitagawa, B. Wang, T. Uemura, *Chem. Soc. Rev*., **2017**, *46*, 3108-3133.
2. a) T. Kitao, M. W. A. MacLean, K. Nakata, M. Takayanagi, M. Nagaoka, T. Uemura, *J. Am. Chem. Soc.,* **2020**, *142*, 5509-5514. b) X. Zhang, T. Kitao, D. Piga, R. Hongu, S. Bracco, A. Comotti, P. Sozzamo, T. Uemura, *Chem. Sci.*, **2020**, *11*, 10844-10849.

Carbon-doped Graphitic Carbon Nitride Based Films as New Functional Materials

([1]*Sch. of Eng., The Univ. of Tokyo, 3-7-1 Hongo, Bunkyo-ku Tokyo 113-8654, Japan.*
[2]*RIKEN CEMS, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*)
○Niannian Wu,[1,2] Nobuhiko Mitoma,[2] Takuzo Aida[1,2]
Keywords: Graphitic Carbon Nitride; Carbon Doping; Chemical Vapor Deposition

Graphitic carbon nitride (GCN) has been of interest because it offers high performance as a photocatalyst, the absence of rare metals, non-toxicity and biocompatibility. However, GCN has traditionally been a powdery material that is difficult to process, making it unsuitable for a variety of applications. Recently, some works have developed methods to form GCN film, and properties as sensors, actuators, and optical materials have been reported.[1,2] However, the energy band gap of pure GCN film is ca. 2.7 eV, which is too large to be used as a semiconductor, and its optical and electrical properties have not reached the required level. The disadvantage of this large energy band gap is confirmed by the fact that the photocatalytic activity of GCN can only be performed in ultraviolet light. In order to explore the potential of GCN films for electronic and optical devices, it is essential to develop methods to narrow the band gap.

Here, we propose a way for narrowing the band gap of GCN films by carbon doping. We obtained homogeneous carbon-doped GCN films by chemical vapor deposition [2,3]. While maintaining the molecular and layered structure of carbon-doped GCN, the maximum carbon/nitride ratio of the carbon-doped GCN film reached 1.016, which was 26.6% higher than that of the pure GCN film, allowing the film to achieve more redshift, lower band gap, and higher electrical conductivity.



References

[1] Hiroki Arazoe, Takuzo Aida *et al.*, *Nat. Mater.* **2016**, *15*, 1084.

[2] Paolo Giusto, Takuzo Aida *et al.*, *Adv. Mater*. **2020**, *32*, 1908140.

[3] Paolo Giusto, Markus Antonietti *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 20883.

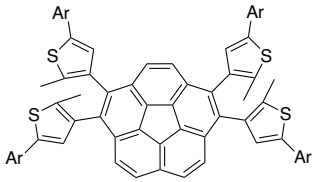
新規フォトクロミックテトラチエニルコラニュレンの合成とその光学特性

（奈良先端大物質）○山田 美穂子・澤崎 智哉・藤田 真江・藤谷 智樹・河合 壯
Syntheses of New Photochromic Tetrathienylcorannulenes with a Curved Aromatic Skeleton and their Optical Properties (*Division of Materials Science, Nara Institute of Science and Technology*) ○Mihoko Yamada, Tomoya Sawazaki, Mae Fujita, Tomoki Fujitani, Tsuyoshi Kawai

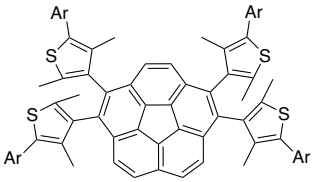
The terarylene derivatives show photochromism through photocyclization and cycloreversion depending on their conformation. A curved aromatic compound, corannulene, shows photophysical properties different from the typical planar aromatic compounds, which are derived from the geometrically and electronically non-equivalent concave and convex surfaces and their bowl-to-bowl inversion behavior. In this work, we synthesized new photochromic compounds $\mathbf{1}_{Ar}$ and $\mathbf{2}_{Ar}$ by fusing two units of terarylenes by introducing four thienyl groups to a corannulene skeleton and studied their photoreactivity and optical properties. In addition, we compared with the terarylene derivative $\mathbf{3}_{Ar}$ having a planar aromatic phenanthrene skeleton.
Keywords : Corannulene; Photochromism; Terarylene; Curved Aromatic Compound; Photochemistry

ターアリーレン誘導体は立体配座に依存した光閉環/開環反応によるフォトクロミズムを示す。一方、湾曲状芳香族コラニュレンは、構造・電子的に表裏非等価な曲面構造や特異な曲面反転運動などに由来して、典型的な平面芳香族化合物とは異なる性質を示す。本研究では、湾曲状コラニュレン骨格に四つのチエニル基を導入することで、二つのターアリーレン部位を連結した新規フォトクロミック化合物を合成し、その反応性及び光学特性を評価した。

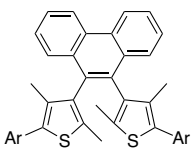
1,2,7,8-テトラブロモコラニュレンから鈴木カップリグ反応により新規テトラチエニルコラニュレン誘導体 $\mathbf{1}_{Ar}$ および $\mathbf{2}_{Ar}$ を合成し、それぞれ NMR および MS により同定した。誘導体 $\mathbf{1}_{Ar}$ および $\mathbf{2}_{Ar}$ に紫外光照射を行うと、可視光領域に新たな吸収帯が現れ、さらに可視光を照射すると元のスペクトルに戻ったことから、フォトクロミズムが示された。一方、フェナントレン骨格を導入した平面状ターアリーレン誘導体 $\mathbf{3}_{Ar}$ は、同様の条件でフォトクロミズムを示さなかった。当日は、これらの反応性の違いについて議論する。



$\mathbf{1}_{Ar}$



$\mathbf{2}_{Ar}$



$\mathbf{3}_{Ar}$

[C205-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Toshihiro Okamoto, Shinya Takaishi

Fri. Mar 25, 2022 1:20 PM - 3:40 PM C205 (Online Meeting)

[C205-3pm-01] Chromatography separation of hydrogen isotopes at room temperature using dihydrogen complexes

○Shinya Takaishi[1], Tamon Yamauchi[1], Kaiji Uchida[1], Shin-ichiro Noro[2], Naoki Kishimoto[1] （1. Tohoku University, 2. Hokkaido University）

1:20 PM - 1:40 PM

[C205-3pm-02] Semi-Rational Molecular Design for Achieving Ferroelastic Properties

○Chi Feng[1], Mingoo Jin[2], Tomohiro Seki[3], Satoshi Takamizawa[4], Hajime Ito[1,2] （1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. Faculty of Science, Shizuoka University, 4. Graduate School of Nanobioscience, Yokohama City University）

1:40 PM - 2:00 PM

[C205-3pm-03] Aggregated structures and single-crystal n-type transistor properties of N-doped perylene diimides with cyclohexyl-type substituents

○Shohei Kumagai[1], Yutaro Arai[1], Craig P. Yu[1], Naotaka Kasuya[1], Hiroyuki Ishii[2], Go Watanabe[3], Shun Watanabe[1], Jun Takeya[1], Toshihiro Okamoto[1,4,5] （1. The Univ. of Tokyo, 2. Univ. of Tsukuba, 3. Kitasato Univ., 4. PRESTO, JST, 5. CREST, JST）

2:00 PM - 2:20 PM

[C205-3pm-04] A fundamental look at the lab-to-fab transition of a new permanent magnet

○T. Thuy Trinh[1], Ryota Sato[1], Toshiharu Teranishi[1] （1. Kyoto University）

2:20 PM - 2:40 PM

[C205-3pm-05] Diradical character of near-infrared absorbing polymethine dyes consisting of oxocarbon residues

○Taishi Oka[1], Takeshi Maeda[1], Daisuke Sakamaki[2], Hideki Fujiwara[2], Shigeyuki Yagi[1], Tatsuki Konishi[4], Kenji Kamada[3] （1. Graduate School of Engineering, Osaka Prefecture University, 2. Graduate School of Science, Osaka Prefecture University, 3. National Institute of Advanced Industrial Science and Technology, 4. Graduate School of Science and Technology, Kwansei Gakuin University）

2:40 PM - 3:00 PM

[C205-3pm-06] Effect of heavier element on the ultra-low frequency phonons in Nd(III) based luminescent nanomagnets

○KUNAL KUMAR[1], Olaf Stefanczyk[1], Koji Nakabayashi[1], Yuuki Mineo[1], Shin-ichi Ohkoshi[1] （1. University of Tokyo）

3:00 PM - 3:20 PM

[C205-3pm-07] Nanoscale local structural analysis of organic crystal by micro electron diffraction

○Hikaru Sakamoto[1], Masataka Ohtani[1] （1. Kochi university of technology）

3:20 PM - 3:40 PM

二水素錯体を利用した水素同位体の常温クロマトグラフィー分離

（東北大院理[1]・北大院環境[2]）○高石 慎也[1]・山内 多聞[1]・内田 海路[1]・野呂 真一郎[2]・岸本 直樹[1]
Chromatography separation of hydrogen isotopes at ambient temperature using dihydrogen complexes ([1]*Graduate School of Science, Tohoku University*, [2]*Graduate School of Environmental Science, Hokkaido University*) ○Shinya Takaishi,[1] Tamon Yamauchi,[1] Kaiji Uchida,[1] Shin-ichiro Noro,[2] Naoki Kishimoto[1]

Hydrogen isotopes (D and T) have been widely used in our current society and the demands of them will be further increased in near future. At present, cryogenic distillation technique of dihydrogen molecules (H_2, HD or D_2) has been used for the separation. This technique requires much energy because dihydrogen need to be cooled down to 20 K. In order to reduce the energy costs, new separation techniques which works at ambient condition is required.

In recent years, we have studied hydrogen adsorption properties of the solid dihydrogen complexes, and clarified that reversible adsorption of H_2 is possible at ambient temperatures.[1] More recently, we found that adsorption energy of D_2 is higher than that of H_2. In this presentation, we report the H_2 and D_2 adsorption isotherms and resultant adsorption enthalpy (ΔH) and entropy (ΔS) in various dihydrogen complexes, and discuss the possible mechanism for the difference in the adsorption energy. In addition, we report the demonstration of the H_2-D_2 separation using gas chromatography at ambient conditions.

Keywords： Hydrogen; Isotope separation; Dihydrogen Complexes

水素の同位体(D および T)は社会の様々な分野で用いられており、それらの需要は今後さらに高まっていくことが予想される。現在、水素分子(H_2, HD, D_2)の同位体分離には深冷蒸留法が用いられているが、水素の液化(約 20 K)に多大なエネルギーを要する。そのため、よりエネルギーコストの低い常温での分離法が求められているが、未だ実現していない。我々は近年、固相の二水素錯体による水素吸着に関する研究を行っており、常温での可逆的な H_2 の吸着を報告した[1]。また最近、本錯体系に対して D_2 のほうが H_2 よりも大きい吸着エネルギーを示すことを見いだした。本発表では、各種二水素錯体の H_2 および D_2 吸着等温線から算出した熱力学的パラメータ(吸着エンタルピー(ΔH), 吸着エントロピー(ΔS))および、考えられる同位体分離機構について議論する。

また、本錯体を用いた常温ガスクロマトグラフィー法による水素同位体分離のデモンストレーションについても報告する。

1) Reversible hydrogen adsorption at room temperature using a molybdenum–dihydrogen complex in the solid state, K. Uchida, N. Kishimoto, S.-i. Noro, H. Iguchi, S. Takaishi, *Dalton Trans.,* **2021**, *50*, 12630-12634.

強弾性を示す金属錯体の半合理的な分子設計

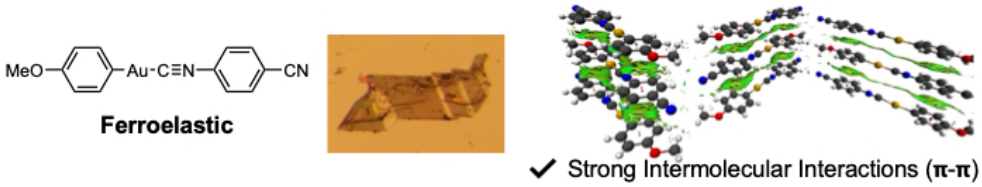
(北大院工[1]・北大 WPI-ICReDD[2]・静大院理[3]・横市大院生命ナノ[4]) ○馮 馳[1]・陳 旻究[2]・関 朋宏[3]・高見澤 聡[4]・伊藤 肇[1,2]
Semi-Rational Molecular Design for Achieving Ferroelastic Properties ([1]Graduate School of Engineering, Hokkaido University, [2]WPI-ICReDD, Hokkaido University, [3]Faculty of Science, Shizuoka University, [4]Graduate School of Nanobioscience, Yokohama City University) ○Chi Feng,[1] Mingoo Jin,[2] Tomohiro Seki,[3] Satoshi Takamizawa,[4] Hajime Ito[1,2]

Ferroelasticity is the phenomenon where crystal samples show plastic bending with a spontaneous strain upon application of mechanical stress. This phenomenon has been applied to switches, pressure sensors, etc. In the past, this phenomenon has been observed only in inorganic materials. There have been very few reports of organic ferroelasticity.[1)] Here, we have found the structural features of the crystals with ferroelasticity and succeeded in designing the organometallic complexes with ferroelasticity.

The mechanical properties of isocyanide gold(I) complex crystals were investigated. It was found that two gold(I) complexes exhibit ferroelasticity. The crystal structures of the crystals were also evaluated, and the structural features of the ferroelastic crystals were clarified. The gold(I) complexes of ferroelastic crystal adopt a flat molecular conformation and form stacked columns in a head-to-tail arrangement. The presence or absence of the ferroelastic behavior and the crystal structure change were evaluated, and the necessary conditions for the discovery of ferroelasticity were clarified.
Keywords: Ferroelasticity; Gold Complex

強弾性とは、ある材料が力学的に変形し自発的なひずみを示す現象である。この現象はスイッチ、圧力センサーなどに応用されている。従来は、無機・合金材料でのみ見られる特異な現象であり、有機分子材料においては、その報告例は極めて少なかった[1)]。本研究では、強弾性を示す結晶の構造特徴を見出し、強弾性を示す金属錯体の半合理的なデザインに成功した。

複数イソシアニド金(I)錯体からなる結晶の機械的特性を調査した結果、2 つの金(I)錯体が強弾性を示すことを見出した。また、強弾性金(I)錯体の結晶構造を評価し、強弾性結晶の構造的特徴を明らかにした。すべての強弾性金(I)錯体の結晶では、分子はフラットなコンホメーションをとり、head-to-tailed スタッキング構造が観察された。さらに、強弾性挙動の有無や結晶構造変化などの結果から、強弾性の発見に必要な条件を明らかにした。



1) Seki, T.; Feng, C.; Kashiyama, K.; Sakamoto, S.; Takasaki, Y.; Sasaki, T.; Takamizawa, S.; Ito, H. *Angew. Chem. Int. Ed.* **2020**, *59*, 8839.

シクロヘキシル類を側鎖に有する含窒素ペリレンジイミド誘導体の集合体構造と単結晶 n 型トランジスタ特性

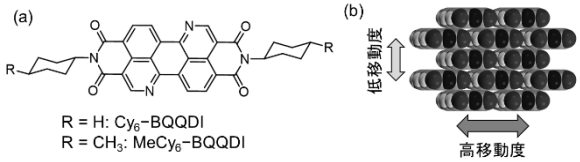
（東大院新領域 [1]・筑波大数物 [2]・北里大理 [3]・さきがけ(JST)[4]・CREST(JST)[5]）○熊谷翔平 [1]・荒井勇太郎 [1]・Craig P. Yu[1]・糟谷直孝 [1]・石井宏幸 [2]・渡辺豪 [3]・渡邉峻一郎 [1]・竹谷純一 [1]・岡本敏宏 [1,4,5]

Aggregated structures and single-crystal n-type transistor properties of N-doped perylene diimides with cyclohexyl-type substituents ([1]*Graduate School of Frontier Sciences, The University of Tokyo*, [2]*Faculty of Pure and Applied Sciences, University of Tsukuba*, [3]*School of Science, Kitasato University*, [4]*PRESTO, JST*, [5]*CREST, JST*) ○Shohei Kumagai,[1] Yutaro Arai,[1] Craig P. Yu,[1] Naotaka Kasuya,[1] Hiroyuki Ishii,[2] Go Watanabe,[3] Shun Watanabe,[1] Jun Takeya,[1] Toshihiro Okamoto[1,4,5]

Single-crystalline organic semiconductors have been studied from chemical, physics and engineering viewpoints due to their promising applications for high-mobility thin-film transistors (TFTs) owing to their long-range ordered structures and grain boundary-free features. Based on this concept, we have recently developed a new π-core of N-doped perylene diimide analogue, namely, BQQDI.[1,2] Here, BQQDI derivatives with cyclohexyl-type side chains[3] (Fig. a) were investigated by crystal structure and TFT analyses. Particularly, $MeCy_6$–BQQDI is suitable for solution processes and exhibits the band-like transport property. Despite the balanced brickwork structures (Fig. b) and isotropic effective masses, the TFTs showed anisotropic electron mobilities, which could be explained by the band theory.

Keywords: Organic Semiconductors; Single Crystals; Thin-Film Transistors; Electron Transport; Band-Like Transport

長距離秩序構造およびグレインバウンダリーフリーな性質を持つ有機半導体単結晶は高移動度薄膜トランジスタ (thin-film transistor: TFT) の有用な基盤材料として注目され，材料開発や物性研究から実デバイス応用まで幅広く研究がおこなわれている。最近我々は代表的な n 型有機半導体の一つであるペリレンジイミドに窒素元素をドープした BQQDI 骨格を開発し，様々なイミド側鎖を導入することで集合体構造や単結晶 n 型 TFT 特性を明らかにしてきた [1,2]。本研究では，シクロヘキシル類側鎖を有する BQQDI 誘導体 [3] (Fig. a) を合成し，結晶構造解析および単結晶 n 型 TFT 評価を実施した。特に，溶解性に優れる $MeCy_6$–BQQDI では mm 級の単結晶を成膜でき，ホール効果測定によりバンドライク伝導が確認された。また，均整なブリックワーク構造を形成し等方的な有効質量を持つことが推定されたが，移動度に明瞭な異方性が見られた (Fig. b)。発表では結晶構造と TFT 特性との相関について詳しく議論する。



1) Okamoto, T. *et al.*, *Sci. Adv.* **2020**, *6*, eaaz0632. 2) Kumagai, S. *et al.*, *Acc. Chem. Res.* accepted. 3) Yu, C. P. *et al.*, *Commun. Chem.* **2021**, *4*, 155.

A Fundamental Look at the Lab-to-Fab Transition of a New Permanent Magnet

([1]*Institute for Chemical Research, Kyoto University*) ○T. Thuy Trinh,[1] Ryota Sato,[1] Toshiharu Teranishi[1]

Keywords: Permanent Magnet Materials

$SmFe_{12}$ ($ThMn_{12}$, *I*4/*mmm*) compound has excellent intrinsic magnetic properties, superior to the current high-end-magnet $Nd_2Fe_{14}B$ compound.[1] Yet, the synthesis of $SmFe_{12}$-based bulk materials with sufficiently large coercivities (H_c) for fabricating permanent magnets has not been realized. The most obvious obstacle to improving H_c is critical issues of microstructure, especially the inevitable formation of magnetically-soft $SmFe_x$ surface.

Recently, we have already succeeded in preparing $Sm(Fe,Co,Ti)_{12}$ microparticles with ever-larger H_c and remanence (M_r) based on precise control over their microstructure by advanced chemical synthesis, opening a new era of $SmFe_{12}$-based permanent magnet materials.[2,3] In particular, synthesized $Sm(Fe,Co,Ti)_{12}$ microparticles possessed various surfaces from Sm-enriched and Ti-enriched surfaces to a depleted surface (Fig. 1A), and $\mu_0 H_c$ and $\mu_0 M_r$ values of their isotropic powders at 300 K were as large as 1.6 T and 1.2 T, respectively (Fig. 1B).

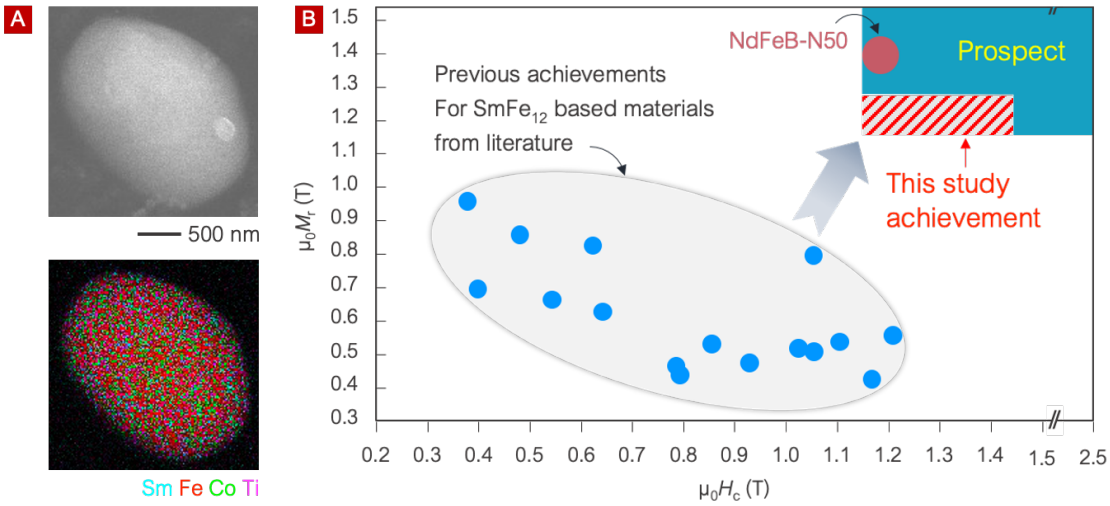


Fig. 1 A. SEM image and EDS elemental map of a $Sm(Fe_{0.8}Co_{0.2})_{11}Ti$ microparticle. B. Extrinsic magnetic properties of isotropic $Sm(Fe_{0.8}Co_{0.2})_{11}Ti$ micropowders at 300 K. NdFeB-N50 is a commercial $Nd_2Fe_{14}B$-based magnet.

1. T. T. Trinh *et al.*, *Sci. Technol. Adv. Mater.* 2021, 22, 37–54.
2. 特願 2021-079367
3. T. T. Trinh *et al.*, Manuscript in preparation.

オキソカーボン中心骨格を持つ近赤外吸収ポリメチン色素のジラジカル特性

(阪府大院工 [1]・阪府大院理 [2]・産業技術総合研究所 関西センター ナノ材料研究部門 [3]・関西学院大院理工 [4]) ○岡 大志 [1]・前田 壮志 [1]・酒巻 大輔 [2]・藤原 秀紀 [2]・八木 繁幸 [1]・小西 龍生 [3,4]・鎌田 賢司 [3,4]

Diradical character of near-infrared absorbing polymethine dyes consisting of oxocarbon residues ([1]Graduate School of Engineering, Osaka Prefecture University, [2]Graduate School of Science, Osaka Prefecture University, [3]National Institute of Advanced Industrial Science and Technology, [4]Graduate School of Science and Technology, Kwansei Gakuin University)

○Taishi Oka[1], Takeshi Maeda[1], Daisuke Sakamaki[2], Hideki Fujiwara[2], Shigeyuki Yagi[1], Tatsuki Konishi[3,4], Kenji Kamada[3,4]

Polymethine dyes exhibiting electronic absorption in the near-infrared (NIR) region are conventionally regarded as closed-shell compounds so far, although quantum chemical calculations predicted they would take an intermediate electronic state between the closed-shell singlet and the open-shell triplet state.[1] In this study, we experimentally evaluated the intermediate open-shell character of NIR absorbing polymethine dyes, croconaine (**CR1**) and squaraine dyes (**SQ1**) in order better to recognize their proper electronic states. These dyes showed significant temperature-dependent ^{1}H-NMR and EPR spectra. In SQUID measurements of **CR1** and **SQ1**, products of magnetic susceptibility and temperature were increased with increasing temperature. These results indicate their intermediate open-shell character appearing from the contribution of thermally excitable triplet states.

Keywords : Open Shell; Diradicaloid; Near-Infrared; Croconate; Squaraine

ポリメチン色素の電子遷移エネルギーが近赤外光 (NIR) 領域まで低下すると, 閉殻一重項状態と開殻三重項状態の中間的な状態を取ることが量子化学計算で予想されている[1]。しかし，それら色素はこれまで閉殻分子として取り扱われており, 開殻性は実験的に明らかにされていない。本研究では，NIR 領域に卓越した電子吸収を示すポリメチン色素であるクロコナイン色素（**CR1**）とスクアレン色素（**SQ1**）の中間的な開殻性を実験的に評価した (Fig. 1)。

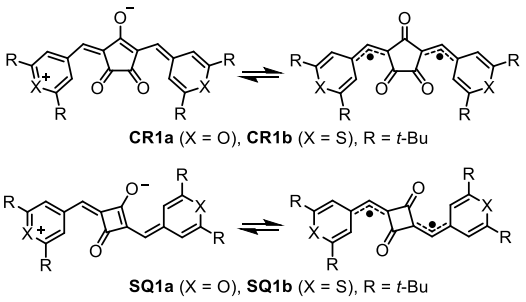


Fig. 1 Structures of **CR1** and **SQ1**.

それら色素溶液の ^{1}H NMR では，室温下で芳香族領域にシグナルは観測されず，より低温下でシグナルが出現した。また, EPR 測定では，昇温に伴うシグナルの増強が観測された。SQUID 磁気測定の結果から, **CR1** と **SQ1** は温度上昇とともに磁化率が上昇した。これら一連の結果より, **CR1** と **SQ1** は低温下では閉殻状態を取り，高温下では熱励起により開殻状態を取るという，中間的な開殻性を有していることが実験的に裏付けられた。さらに，一連の色素の一光子および二光子吸収特性からも中間開殻性を評価したので，併せて報告する。

1) Fabian *et al*., *Angew Chem Int. Ed.*, **1998**, *28*, 6772.

Effect of heavier element on the ultra-low frequency phonons in Nd(III) based luminescent nanomagnets

([1]*School of Science, Department of Chemistry, The University of Tokyo*) ○Kunal Kumar,[1] Olaf Stefanczyk,[1] Koji Nakabayashi,[1] Yuuki Mineo,[1] Shin-ichi Ohkoshi[1]

Keywords: Terahertz time–domain spectroscopy; sub−terahertz Raman; ratiometric thermometer; ab initio calculation; single–molecule magnetism

The ultralow-frequency (ULF) vibrations in the sub-terahertz (sub-THz) region are explored due to their potential applications in various fields such as - aerospace industry and information technology.[1,2] Combining such ability in the molecular complexes allows us to incorporate other physical properties like luminescence, magnetism etc. With the above aim, we prepared two supramolecular assemblies with the pseudohalides $[Nd^{III}(phen)_3(NCX)_3]\cdot 0.3EtOH$ (X = S, **1**–**S**; Se, **1**–**Se**), crystallizing in the centrosymmetric triclinic *P*-1 space group, and characterized them extensively through various spectroscopy, and quantum chemical calculations for both compounds (**Figure 1a**).

The powdered samples for both assemblies exhibit minimum THz-wave absorption of 0.59 THz (19.7 cm^{-1}) for **1**–**Se** and 0.65 (21.7 cm^{-1}) for **1**–**S** (**Figure 1b**). We found out that the THz–wave absorption is redshifted upon heavy element substitution. Further monocrystals of both compounds also have ULF Raman scattering in the sub–THz (below one terahertz) region (**Figure 1c**). As a result, we discovered that both complexes reveal exceptionally low−frequency Raman shifts, which also shifts towards the low–frequency region for selenium–containing assemblies. The quantum chemical calculations were performed on the optimized geometry to visualize the vibrations indicating the nature of these vibrations to be of pendulum type. Additionally, near-infrared (NIR) emission from the Nd(III) centre is also studied with varying temperatures revealing ratiometric thermometric behaviour. They also reveal field–induced single–molecule magnetic properties.

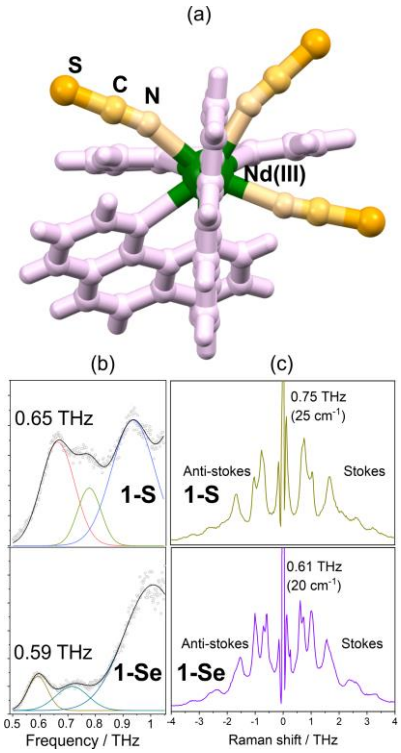


Figure 1. Crystal structure of **1-S** with assigned elements name (a), terahertz signal from **1-S** and **1-Se** (b), and Raman shift of **1-S** and **1-Se** in the specified region (c).

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nature Photonics*, **2014**, *8*, 65-71. 2) S. Ohkoshi, M. Yoshikiyo, A. Namai, K. Nakagawa, K. Chiba, R. Fujiwara, and H. Tokoro, *Scientific Reports,* **2017**, *7,* 8088.

マイクロ電子回折を用いた有機結晶の局所構造観察

（高知工大院工）○坂本 ひかる・大谷 政孝

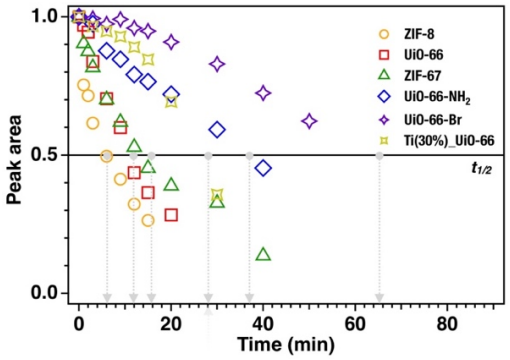
Nanoscale local structural analysis of organic crystal by micro electron diffraction

(*Kochi University of Technology*) ○Hikaru Sakamoto, Masataka Ohtani

Recently, micro electron diffraction (microED) has been in high demand in the field of material science, especially for the analysis of submicron-sized organic crystals. Meanwhile, the ED analysis for such organic crystals needs advanced techniques because organic crystals are very sensitive and damaged under electron-beam irradiation. However, the collapse mechanism of organic crystals due to electron irradiation has yet to be scrutinized. This study focused on the quantitative evaluation of electron damage in organic crystals to establish microED conditions. From the systematic analysis of time-course changes of diffraction intensities, we found that the density of organic crystals is a crucial factor for the stability of the material against the electron beam.

Keywords : Micro electron diffraction; Metal-organic framework; Quantitative evaluation; Electron beam damage; Crystal density

近年、マイクロ電子線回折法を利用した材料の構造解析が注目されており、特にサブミクロンオーダーの有機微結晶の分析において高い需要がある。一方で、有機結晶は電子線に対して脆弱であるため測定・解析に高度な技術を必要とする。そのため、これまでの研究では、電子線照射によって材料がいつ、どのように崩壊するのかといったメカニズムについて不明瞭な点が多い。本研究では、有機結晶のマイクロ電子回折条件を確立するために、電子線照射によって有機材料が受けた電子線ダメージの定量的評価を行った。電子線照射下で種々の有機結晶の電子線回折強度の時間変化を追跡した結果、電子線照射による材料の崩壊速度は大きく異なることがわかった（Fig. 1, left）。一連の結果より、結晶崩壊の半減期（$t_{1/2}$）は、材料の結晶密度に依存することがわかった（Fig. 1, right）。



sample	density (g/cm^3)	half-life ($t_{1/2}$)
ZIF-8	0.92	6 min
ZIF-67	0.95	16 min
UiO-66	1.20	11 min
Ti-doped UiO-66	--	28 min
UiO-66-NH_2	1.29	37 min
UiO-66-Br	1.48	65 min
L-histidine	1.55	> 120 min

Figure 1. Time course of total diffraction peak intensity (left) and summary of the estimated half-life for various crystals (electron dose rate: 0.05 $e^-/Å^2 \cdot s$).

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

[D103-3am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Takaya Kubo, Masayuki Yagi
Fri. Mar 25, 2022 9:00 AM - 11:40 AM D103 (Online Meeting)

[D103-3am-01] Substituents effects of spirobifluorene-based dopant-free hole-transporting materials for perovskite solar cells

○Daisuke Tsuchiya[1], Shinichi Inoue[1], Toshiya Ueno[1], Nobuko Onozawa-Komatsuzaki[2], Atsushi Kogo[2], Takashi Funaki[2], Masayuki Chikamatsu[2], Takurou N. Murakami[2] (1. Nippon Fine Chemical Co., Ltd., 2. National Institute of Advanced Industrial Science and Technology (AIST))

9:00 AM - 9:20 AM

[D103-3am-02] Dopant-free cyano-substituted spiro-type hole-transporting materials for perovskite solar cells

○Nobuko Onozawa-Komatsuzaki[1], Atsushi Kogo[1], Takashi Funaki[1], Masayuki Chikamatsu[1], Takurou Murakami[1], Daisuke Tsuchiya[2], Shinichi Inoue[2], Toshiya Ueno[2] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Nippon Fine Chemical Co., Ltd.)

9:20 AM - 9:40 AM

[D103-3am-03] The effect of ligand coverage on nanocrystals on the carrier collection efficiency of $AgBiS_2$ nanocrystal-based solar cells

○Yun Xiao[1], Haibin Wang[1], Fumiyasu Awai[1], Naoyoki Shibayama[2], Takaya Kubo[1], Hiroshi Segawa[1] (1. The University of Tokyo, 2. Toin University of Yokohama)

9:40 AM - 10:00 AM

[D103-3am-04] Solvent engineering of liquid-phase ligand exchanged PbS quantum dot inks for infrared photovoltaics

○Haibin Wang[1], Yun Xiao[2], Jotaro Nakazaki[2], Takaya Kubo[2], Hiroshi Segawa[1,2] (1. Grad. Sch. Arts and Sci. The Univ. of Tokyo, 2. RCAST, The Univ. of Tokyo)

10:00 AM - 10:20 AM

[D103-3am-05] Solution-phase synthesis of Ag-Bi-S quantum dots for the application to photovoltaics

○Kazutaka Akiyoshi[1], Wentao Zhang[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)

10:20 AM - 10:40 AM

[D103-3am-06] Efficient water oxidation on N-doped $CuWO_4$ photoanodes by immobilization of iron complexes.

○Tomohiro Katsuki[1], Yuta Tsubonouchi[1], Zaki Zahran[1], Masayuki Yagi[1] (1. Grad. School of Sci. Tech., Niigata Univ.)

10:40 AM - 11:00 AM

[D103-3am-07] Investigation of isotopic selectivity on plasmon-induced photoconversion system

○Daiki Sato[1], Hiro Minamimoto[2], Kei Murakoshi[2] (1. Hokkaido University Graduate School of Chemical Sciences and Engineering, 2. Hokkaido University Faculty of Science)

11:00 AM - 11:20 AM

[D103-3am-08] Formate production from CO_2 and water using a $1m^2$-sized artificial photosynthetic cell with a solar-to-chemical conversion efficiency of 10.5%

○Naohiko Kato[1], Yasuhiko Takeda[1], Yasuaki Kawai[1], Natsumi Nojiri[1], Masahito Shiozawa[1], Shintaro Mizuno[1], Ken-ichi Yamanaka,[1], Takeshi Morikawa,[1], Tsuyoshi Hamaguchi[1]
（1. Toyota Central R&D Labs., Inc.）

11:20 AM - 11:40 AM

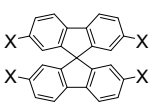
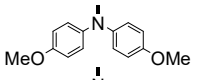
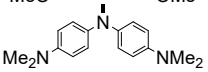
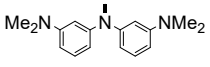
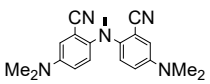
ペロブスカイト太陽電池用スピロ型ホール輸送材料のドーパントフリー化における置換基の影響

（日本精化株式会社[1]・産総研[2]）○土屋 大輔[1]・井上 真一[1]・上野 敏哉[1]・小野澤 伸子[2]・古郷 敦史[2]・舩木 敬[2]・近松 真之[2]・村上 拓郎[2]
Substituents effects of spirobifluorene-based dopant-free hole-transporting materials for perovskite solar cells ([1]*Nippon Fine Chemical Co., Ltd*., [2]*National Institute of Advanced Industrial Science and Technology (AIST)*) ○ Daisuke Tsuchiya,[1] Shinichi Inoue,[1] Toshiya Ueno,[1] Nobuko Onozawa-Komatsuzaki,[2] Atsushi Kogo,[2] Takashi Funaki,[2] Masayuki Chikamatsu,[2] Takurou N. Murakami[2]

Various spiro-type hole-transporting materials (HTMs) for perovskite solar cells (PSCs) were newly synthesized. The PSCs by using these HTMs with or without dopants were fabricated, and their solar cell performance were evaluated. As a result, for a new HTM obtained by replacing p-methoxy substituents in spiro-OMeTAD with dimethylamino groups, it was found that there is almost no significant difference in cell performance between with and without dopants. The effects of the substitution position of the dimethylamino groups and the introduction of additional substituents on the cell performance were also investigated.
Keywords： Perovskite solar cells; hole-transporting materials; dopant free

ペロブスカイト太陽電池は高効率で安価な次世代型太陽電池として注目を集めている。今回、我々は種々のホール輸送材料を新規に合成し、それらを用いたペロブスカイト太陽電池を作製して性能を評価した。その結果、Spiro-OMeTAD の OMe 基を NMe_2 基に置換した場合、ドーパントフリーでも性能にほとんど差異がないと判明した。さらに NMe_2 基の置換位置や追加の置換基等を検討した結果、CN 基と NMe_2 基を有するホール輸送材料を用いた太陽電池がドーパントフリーでも高い変換効率を示し、耐久性も向上することがわかった。

Table 1. HOMO energy levels (E_{HOMO}) of spiro-type HTMs and power-conversion efficiencies (PCEs) of PSCs using them with or without dopant. Device structure is FTO/c-TiO_2/meso-TiO_2/$MAPbI_3$/HTMs/Au.

Chemical structure of HTMs	E_{HOMO}(eV)[a]	PCE (%) (with dopant)	PCE (%) (without dopant)
 X = 	-4.81	17.6	13.1
X = 	-4.43	12.6	12.1
X = 	-4.82	16.9	8.6
X = 	-4.83	15.2	16.2

[a] E_{HOMO} was estimated by the differential pulse voltammetry (DPV) method.

新規シアノ置換スピロ型ドーパントフリーホール輸送材料を用いたペロブスカイト太陽電池

（産総研[1]・日本精化株式会社[2]）○小野澤 伸子[1]・古郷 敦史[1]・舩木 敬[1]・近松 真之[1]・村上 拓郎[1]・土屋 大輔[2]・井上 真一[2]・上野 敏哉[2]

Dopant-free cyano-substituted spiro-type hole-transporting materials for perovskite solar cells
([1]*National Institute of Advanced Industrial Science and Technology (AIST),* [2]*Nippon Fine Chemical Co., Ltd.*) ○Nobuko Onozawa-Komatsuzaki,[1] Atsushi Kogo,[1] Takashi Funaki,[1] Masayuki Chikamatsu,[1] Takurou N. Murakami,[1] Daisuke Tsuchiya, [2] Shinichi Inoue, [2] Toshiya Ueno[2]

Two new cyano-substituted spirobifluorene-based hole-transporting materials, **SF27** (*m*-CN) and **SF48** (*o*-CN) were synthesized. These compounds were derived from spiro-OMeTAD analogue obtained by replacing it p-methoxy substituent with *p-N,N*-dimethylamino groups. The influence of a cyano substituent on the optoelectronic properties, power-conversion efficiencies (PCEs) and charge-transport behavior in mesoporous type perovskite solar cells (PSCs) were studied. PSCs using these new HTMs without doping are fabricated and compared their cell performance with the devices using spiro-OMeTAD. PSCs with non-doped **SF48** exhibited a high PCE of 18.7%, comparable to the reference PSC device with doped spiro-OMeTAD (18.6%).
Keywords： Perovskite solar cell; hole-transporting material; dopant-free

ペロブスカイト太陽電池(PSC)は、軽量、フレキシブル低コスト製造等の特徴を持ち、次世代型太陽電池として注目を集めている。今回我々は PSC の構成要素の一つであるホール輸送材料としてビフルオレン骨格を有する **SF27** (*m*-CN) と **SF48** (*o*-CN) を新規に合成し、物性を評価した。これらを用いて PSC を作製し、その性能について調べたところ、**SF48** を用いたセルはドーパントを加えなくても高い効率を与えることがわかった(Figure 1)。更にそれを用いて作製した電池の耐久性について検討した結果、熱的安定性が大きく向上することがわかった。

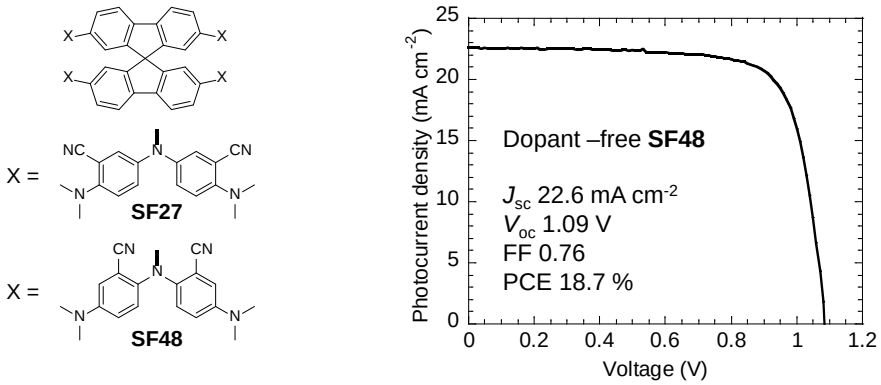


Figure1. Chemical structures of **SF27** and **SF48**. (a) *J-V* curve measured under AM 1.5G solar irradiance (100 mW/cm^2) for the highest efficiency solar cell based on non-doped **SF48**. (b)

The effect of ligand coverage on nanocrystal surface on the carrier collection efficiency of $AgBiS_2$ nanocrystal-based solar cells

([1]*RCAST, The University of Tokyo,* [2]*Graduate School of Arts and Sciences, The University of Tokyo,* [3]*Department of Biomedical Engineering, Toin University of Yokohama*) ○Yun Xiao, [1] Haibin Wang, [1] Fumiyasu Awai[2], Naoyuki Shibayama, [3] Takaya Kubo, [1] Hiroshi Segawa[1,2]
Keywords: Ligand exchange; Halide; $AgBiS_2$; Solar cell.

The semiconducting properties of colloidal nanocrystal assemblies make them attractive materials for developing emerging optoelectronic devices such as photovoltaics and LEDs. Recently, infrared absorbing $AgBiS_2$ colloidal nanocrystals (NCs) have been attracting much attention as photovoltaic materials for solution-processed solar cells.[1, 2] To achieve good carrier transport properties of $AgBiS_2$ NC films, the choice of ligands is crucially important. In this work, we focused on halide ligands (I^-, Br^-, Cl^- and F^-), with the aim of reducing the inter-nanocrystal distance as well as passivating the surface defects, thereby improving carrier transport property of the nanocrystal films. The coverage of the ligands on the $AgBiS_2$ NCs, and the influence on the resulted performance of the $AgBiS_2$ NC solar cells (ITO/$AgBiS_2$ NC dense layer/P3HT/Au)[2] were studied. The $AgBiS_2$ NC solar cells using I^-, Br^-, Cl^- and F^- ligands were denoted as I-SC, Cl-SC, Br-SC and F-SC, respectively.

The coverage of ligands was defined as the atomic ratio of the halides to the sum of Ag and Bi measured by X-ray photoelectron spectroscopy. The coverage values are 0.27, 0.17, 0.11 and 0.04 for I^-, Br^-, Cl^- and F^- treated $AgBiS_2$ films, respectively. This is chiefly due to the adsorption strength of halide anions on the NC surface, which is attributed to the kinetic energy required for desorption of halide anions under the attack of hydrogen protons in the methanal solvent. The weak adsorption of Cl^- and F^- may have resulted in insufficient passivation. Therefore, Cl-SCs and F-SCs are considered to have lower power conversion efficiency (PCE) compared to I- and Br-SCs. On the other hand, the strong adsorption of I^- might cause excess coverage of I^- on the surface of some $AgBiS_2$ NCs. The excess coverage of I^- has been reported to produce mid-gap states.[3] The recombination process via the mid-gap states is thought to degrade the photoelectric conversion properties of I-SCs. When Br^- was used for ligand exchange, the highest carrier collection efficiency was achieved among the solar cells using the four ligands, as confirmed by the EQE spectra shown in Figure 1. As a result, the Br-SCs exhibited the highest PCE of 3.12%. These results indicate that the selection of ligand species and the control of coverage are extremely important to achieve good passivation of $AgBiS_2$ NCs.

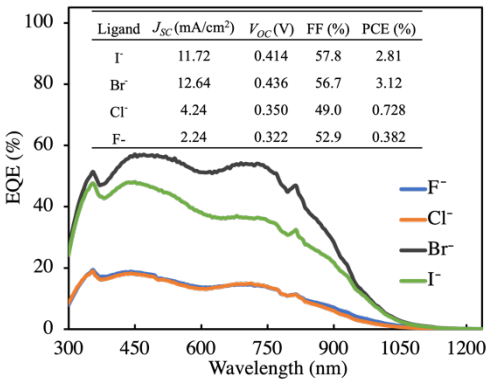


Figure 1. EQE spectra of the best performing I-SC, Br-SC, Cl-SC and F-SC. (Inset table: the corresponding solar cell performance).

[1] Bernechea, M.; Miller, N. C.; Xercavins, G.; Stavrinadis, D. So, A.; Konstantatos, G., *Nat. Photonics* 2016, 10, 521–525.
[2] Xiao, Y.; Wang, H.; Awai, F.; Shibayama, N.; Kubo, T.; Segawa, H., *ACS Appl. Mater. Interfaces* 2021, 13 (3), 3969-3978.
[3] Ju, M.-G.; Dai, J.; Ma, L.; Zhou, Y.; Zeng, X. C., *Nanoscale Advances* 2020, 2 (2), 770-776.

Solvent Engineering of Liquid-phase Ligand Exchanged PbS Quantum Dot Inks for Infrared Photovoltaics

([1]*Graduate School of Arts and Science, The University of Tokyo,* [2]*RCAST, The University of Tokyo,*) ○Haibin Wang,[1] Yun Xiao,[2] Jotaro Nakazaki,[2] Takaya Kubo,[2] Hiroshi Segawa[1,2]

Keywords: Solar cell, PbS quantum dots; Liquid-phase, Solvent

Colloidal PbS quantum dots (QDs) have received significant attention as promising candidate materials toward infrared photovoltaics due to their size-dependent-bandgap and solution-processability. PbS QDs bear long alkyl chains as ligands to maintain a uniform dispersion in solution. Therefore, to construct solar cells, alkyl chains must be replaced with small ligands such as halide ions. In doing so, a liquid-phase ligand exchange process has been widely used to prepare ligand-exchanged PbS QD solution (QD ink), which enables to avoid a disruptive solid-phase ligand exchange process. So far QD inks have been synthesized using near-infrared absorbing QDs (exciton peak: ~950 nm)[1]. However, there are few reports on infrared PbS QD. In the previous paper, a mixed solution of butylamine (BA, 78°C) and a high boiling point solvent such as DMF (153°C) or DMSO (189°C) was used to prepare infrared absorbing QD ink[2]. However, it is difficult to obtain QD layers with stable film quality by using mixed solvents because of the influence of the difference in boiling points. In this study, we synthesized infrared PbS inks exhibiting the first exciton peak near 1280 nm, and investigated how the dispersion solvent affected the performance of the infrared PbS QD/ZnO solar cells (the inset figure in Fig. 1).

With reference to previous studies[2], a solution of BA or hexylamine (HA, 123°C) mixed with DMF (9:1 v/v) was used to obtain a QD ink in which the I-PbS QDs were uniformly dissolved. However, the QD film formed by the spin coating method had a rough surface and non-uniform film thickness, indicating the difficulty in controlling a mixed solvent system with large difference in boiling points. Then we focused on a BA or HA single solvent to uniformly dissolve the I-PbS QDs. By adjusting the dissolution time, we have succeeded to prepare QD inks with uniformly dissolved I-PbS QDs. From these QD inks, it was possible to deposit homogeneous solid films of QDs. After depositing the QDs on the ZnO layer, the QD layer was annealed at 80°C for 20 min to fabricate the solar cells[3]. Although homogeneous QD films were deposited using HA, the film thickness was only about 200 nm. This is probably because the high boiling point of HA caused insufficient evaporation of the solvent during spin coating, resulting in less QD ink remaining on the ZnO layer. On the other hand, when BA was used, a QD layer of about 500 nm could be fabricated with a single spin-coat deposition. The corresponding solar cell exhibited a power conversion efficiency of 8% (Jsc=31.1mA/cm^2, Voc=0.45V, FF=0.568). In the case of QD inks prepared with a single amine solvent, homogeneous QD films could be formed with high reproducibility. The formation of high-quality QD films and further improvement of solar cell efficiency can be expected by exploring the preparation method and annealing conditions of QD inks.

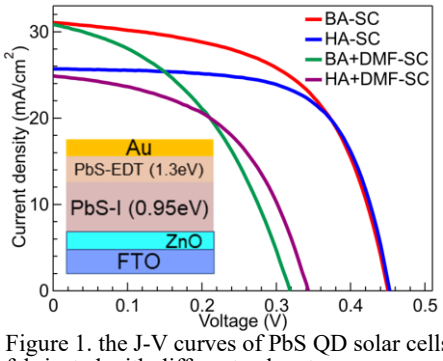


Figure 1. the J-V curves of PbS QD solar cells fabricated with different solvents.

(1) M. Liu, O. Voznyy, R. Sabatini, F. P. Garcia de Arquer, R. Munir et at. *Nat. Mater*. **2017**, *16*, 258.
(2) J. Z. Fan, M. Vafaie, K. Bertens, M. Sytnyk, J. M. Pina, L. K. Sagar et at. *Nano lett.* **2020,** *20,* 5284
(3) A. Takahashi, H. Wang, T. Fukuda, N. Kamata, T. Kubo and H. Segawa, *Energies* **2020**, *13*, 5037.

光電変換素子への応用に向けた Ag-Bi-S 量子ドットの液相化学合成

（名大院工）〇秋吉 一孝・張 文韜・亀山 達矢・鳥本 司
Solution-phase synthesis of Ag-Bi-S quantum dots for the application to photovoltaics (*Nagoya Univ,*) 〇Kazutaka Akiyoshi, Wentao Zhang, Tatsuya Kameyama, Tsukasa Torimoto

Quantum dot (QD) solar cells have been intensively investigated because of their controllable optical properties for improving energy conversion efficiency. However, conventional binary QDs such as PbS and CdSe contain highly toxic heavy metals and then have been severely limited in their use for practical applications. In this study, we report the colloidal preparation of less-toxic Ag-Bi-S QDs with the bandgap in the near-IR region. The obtained QDs had a tunable electronic energy structure and their photoelectrochemical properties were varied by modifying the particle size and composition.
Keywords : semiconductor photoelectrode; quantum size effect; $AgBiS_2$

【緒言】量子ドット(QD)太陽電池は、CdSe や PbS などの近赤外光応答する QD を用いることで高い変換効率が期待されるため、活発に研究されている。しかしこれらの二元 QD は高毒性な Cd や Pb を含有するため、広範囲な利用は制限されている。本研究では、近赤外域にバンドギャップ(Eg)を有する低毒性な Ag-Bi-S QD に注目した [1]。液相化学合成法を開発し、粒径・組成の変調によるエネルギー構造と光電気化学特性の制御を試みた。

【実験】酢酸銀と酢酸ビスマス、硫黄粉末を前駆体とし、1-ドデカンチオールとオレイルアミンの混合溶媒に分散させ、100～200℃で 30 分間加熱して $AgBiS_2$ QD を合成した。QD の粒径と組成は、加熱条件や前駆体の仕込み組成比で制御した。

【結果・考察】加熱温度を 100℃から 200℃へ増加させると Ag 割合が増大しつつ、QD の粒径は 3.2 nm から 8.1 nm へ増大した(Fig. 1)。XRD からは立方晶構造の $AgBiS_2$ の生成が確認できた(Fig. 2)。吸収端は粒径増大に応じて 1000 nm から 1200 nm へシフトし、Eg は 1.45 eV から 1.05 eV に減少した。大気中光電子収量分光法より電子エネルギー構造を求めたところ、伝導帯下端準位(CBM)はほぼ一定であったが、価電子帯上端準位(VBM)は Eg 減少とともに負電位側にシフトした。これら QD を ITO 電極に担持して光電気化学測定を行うと、カソード及びアノード光電流の両方が検出され、その割合は粒子組成によって変化した。光電流の立ち上がり電位は $AgBiS_2$ の CBM や VBM とは大きく異なったことから、禁制帯内にキャリア再結合を起こす欠陥サイトの存在が示唆された。

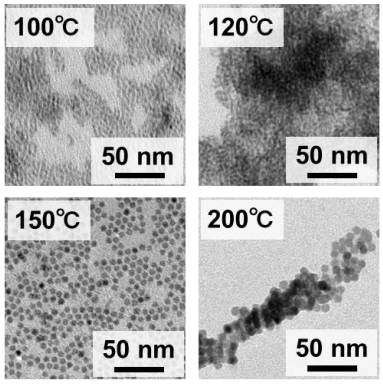


Fig. 1. TEM images of $AgBiS_2$.

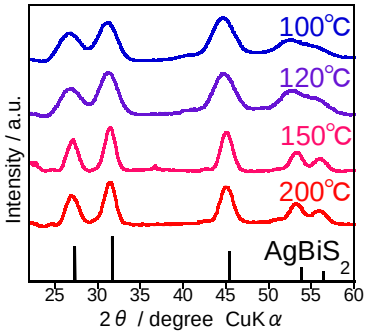


Fig. 2. XRD patterns of $AgBiS_2$.

1) M. Bernechea, *et al*., *Nat. Photonics*, **2016**, 10, 521.

窒素ドープ $CuWO_4$ 光アノードへの平面 N_4 配位型鉄錯体修飾による高効率酸素発生反応

（新潟大院自然）○勝木 友洋・坪ノ内 優太・ザキ ザハラン・八木 政行
Efficient water oxidation on N-doped $CuWO_4$ photoanodes by immobilization of iron complexes. (*Grad. School of Sci. and Tech., Niigata Univ.*) ○Tomohiro Katsuki, Yuta Tsubonouchi, Zaki N. Zahran, Masayuki Yagi

A photoanode capable of efficiently promoting water oxidation is a key component for realizing a photoelectrochemical water splitting cell for hydrogen production. $CuWO_4$ has attracted attention as a promising photoanode for water oxidation because of the narrow band gap (2.3 eV) compared with well-known WO_3 (2.8 eV). Herein, we synthesized a N-doped $CuWO_4$ (N-$CuWO_4$) photoanode using a facile preparation method, exhibiting the high photocatalytic current of 130 μA cm^{-2} for water oxidation at 1.23 V vs. RHE at pH 7. Moreover, immobilization of a Fe complex (Febpb) on the N-$CuWO_4$ electrode enhanced the photocatalytic performance for water oxidation.
Keywords : Artificial photosynthesis; Water oxidation; Photoanode; molecular catalysts; Fe-complexes

$CuWO_4$ は 2.3 eV のバンドギャップ（BG）を有する n 型半導体であり、WO_3（BG＝2.8 eV）よりも長波長の可視光を利用できることから有望な酸素発生光アノードとして近年注目されている。本研究では、前駆体懸濁液にブチルイミダゾール（BIm）を添加することで高耐久性かつ高活性の窒素ドープ $CuWO_4$ 電極（N-$CuWO_4$）の開発に成功した。さらに、N-$CuWO_4$ 光アノードに助触媒として N_4 型平面配位子を有する鉄単核錯体（Febpb）[1]を修飾することにより酸素発生触媒活性の更なる向上を達成した。

BIm を含む $CuWO_4$ 前駆体懸濁液を FTO 基板上に塗布して 550℃で焼成することで N-$CuWO_4$ 電極を作製した。N-$CuWO_4$ 電極に Febpb 溶液を滴下して乾燥させることで Febpb/N-$CuWO_4$ 電極を作製した。N-$CuWO_4$ 電極の電位-電流曲線の 1.23 V vs. RHE における光電流値（130 μA cm^{-2}）は、BIm を用いずに作製した $CuWO_4$ 電極に比べて 20 倍高い値を記録した（Fig. 1）。N-$CuWO_4$ 電極の 1.23 V における定電位電解実験では、15 時間にわたり安定した光電流が観測されたことから、優れた耐久性が示された。さらに、助触媒として Febpb を N-$CuWO_4$ 電極表面に修飾することにより、1.23 V における光電流値は 21%向上した（Fig. 1）。電気化学的インピーダンス測定から、Febpb の修飾により N-$CuWO_4$ の表面触媒反応が促進されることを明らかにした。

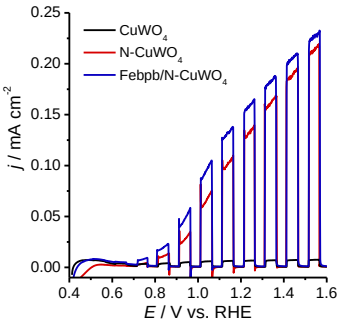


Fig. 1 *j-E* curves of Febpb/N-$CuWO_4$ (blue), N-$CuWO_4$ (red) and $CuWO_4$ (black) in KPi (pH 7) with chopped visible light irradiation (100 mW cm^{-2}).

1) Che, C. M.; Leung, W. H.; Li, C. K.; Hei-Ying, C.; Shie-Ming, P. *Inorganica Chim. Acta* **1992**, *196* (1), 43–48.

Investigation of Isotopic Selectivity on Plasmon-Induced Photoconversion System

([1]*Graduate School of Chemical Sciences and Engineering*, *and* [2]*Department of Chemistry, Faculty of Science, Hokkaido University*) ○Daiki Sato,[1] Hiro Minamimoto,[2] Kei Murakoshi[2]
Keywords: Plasmon; Photoconversion; Hydrogen Evolution Reaction; Isotopic Selectivity

Illumination of visible light onto metal nanoparticles with a several tens or hundreds nanometer scales can induce a collective oscillation of free electrons, which is called as the localized surface plasmon resonance. The combination of metal nanoparticles and wide gap semiconductor recognized as the plasmonic photoconversion system enables to convert the visible to near-infrared light energy into the chemical energy.[1] Up to date, the plasmonic cathode electrodes have been established by the introduction of plasmonic nanostructures on the p-type semiconductor electrodes.[2] In our previous study, we have observed the unique pH dependent on the plasmon-induced hydrogen evolution reaction (HER).[3] In the present study, we have investigated the isotopic selectivity on plasmon-induced HER process for the clarification of the unique molecular behavior at the plasmonic structure surface. Through the investigations, we have observed the characteristic isotopic selectivity at the plasmonic field.

The metal nanostructures prepared by the nanosphere lithography method were prepared on p-type GaP electrode. The extinction spectrum of nanostructures shows the resonance peak at around 800 nm. The photocurrent measurements using the plasmonic cathode electrode in both H_2O and D_2O solutions. In the general isotopic effect on HER, the photocurrent values decrease as increasing the content of D_2O in the electrolyte solution. By contrast, interestingly, we have observed the inverse isotope effect on the plasmon-induced HER system as shown in Fig. In addition, the photocurrent increments depending on the contents of D_2O were also observed. Numerical kinetic equation analyses were performed to discuss the molecular behavior. As the results, it was found that the surface adsorption process of D atoms was selectively accelerated in the plasmonic field as compared with the non-plasmonic HER system. Additionally, a wavelength dependence also clarified the contribution of the plasmon to the phenomena. From above results, the surface molecular process in the plasmon induced proton coupled electron transfer reaction has been proposed.

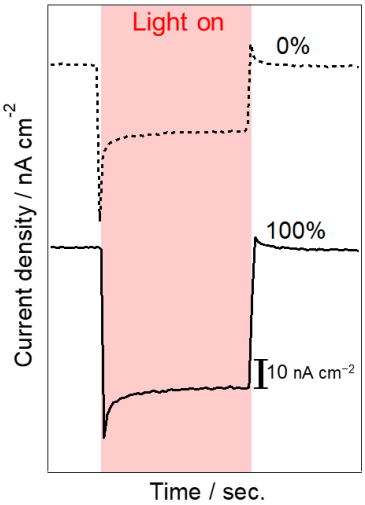


Fig. Photocurrents for GaP/Au electrode obtained under visible light illumination (1000 nm > λ > 640 nm). The electrolyte solutions were 0.5 M $NaClO_4$aq. Percentages indicate the content of D_2O in solution. The electrochemical potential of the electrode was −0.3 V vs. Ag/AgCl.

1) H. Minamimoto, *et al.*, *Electrochem.* **2021**, *89*, 525. 2) Harry A. Atwater, *et al.*, *Nano Lett.* **2018**, *18*, 2545. 3) D. Sato, *et al.*, *Chem. Lett.* **2020**, *49*, 806.

大型人工光合成セル(1㎡)による CO_2 と水からのギ酸合成－太陽光変換効率 10.5%の実証－

(豊田中研[1]) ○加藤直彦[1]・竹田康彦[1]・河合泰明[1]・野尻菜摘[1]・塩澤真人[1]・水野真太郎[1]・山中健一[1]・森川健志[1]・濱口豪[1]
Formate production from CO_2 and water using a 1m^2-sized artificial photosynthetic cell with a solar-to-chemical conversion efficiency of 10.5% ([1]Toyota Central R&D Labs., Inc.)
○Naohiko Kato, Yasuhiko Takeda, Yasuaki Kawai, Natsumi Nojiri, Masahito Shiozawa, Shintaro Mizuno, Ken-ichi Yamanaka, Takeshi Morikawa, and Tsuyoshi Hamaguchi.

Artificial photosynthetic cells have been extensively studied for carbon neutrality, yet in lab-scale. We constructed large-sized cells consisting of electrochemical (EC) reactors and c-Si photovoltaic (PV) modules. Our reactors use a Ru complex polymer catalyst realizing a low overpotential for CO_2 reduction, and an IrO_x catalyst with a high catalytic activity for water oxidation.[1] The 1000 cm^2-sized cell achieved a solar-to-chemical energy conversion efficiency (η_{STC}) of 7.2%,[2] and a further scaled-up 1 m^2-cell demonstrated a higher η_{STC} of 10.5%, yielding a large formate production rate of 1.2 mol/h.[3] The advantageous features are a low operating voltage of 1.65 V (overpotential of 0.22 V) at a large current of 65 A, and low cost owing to the use of single-compartment reactors without expensive ion-exchange membranes and no use of high-cost PV modules consisting of III–V group semiconductors (GaAs etc.). We overcame the tasks unique to scale-up of the cell: lowering electric resistance of the electrode catalysts, homogenous supply of CO_2, and suppressing crossover reaction.

Keywords : Solar fuels; Artificial photosynthesis; Electrochemical reactors; Solar-driven CO_2 reduction; Formate

カーボンニュートラルを実現するため人工光合成の研究が精力的に行われている。我々は、低過電圧である Ru 錯体ポリマー還元触媒と高活性な IrO_x 酸化触媒[1)]を用いて、電気化学リアクターと結晶 Si 太陽電池を組み合わせた大型の人工光合成セルを構築した。面積 1000 cm^2 のセルでは太陽光変換効率 η_{STC} 7.2%を[2)]、更に大型の 1 m^2 セルでは η_{STC} 10.5 %とギ酸生成速度 1.2 mol/h を達成した[3)]。このセルの特長は、1.65 V の低電圧（過電圧 0.22 V）で 65 A の大電流動作が可能である点と、高価なイオン交換膜を使わない 1 室型リアクターの採用と、やはり高価なⅢ−Ⅴ族化合物(GaAs 等)太陽電池を使用しないことから低コスト化が可能となる点である。大型化に特有の課題である、①電極触媒の低抵抗化、②電解液の流れ制御による均一な CO_2 供給、③クロスオーバー反応の抑制、を克服したことにより、大型化と高効率化が両立した。

1) T. Arai, S. Sato, T. Morikawa, *Energy Environ. Sci.*, **2015**, 8, 1998.
2) N. Kato, S. Mizuno, M. Shiozawa, N. Nojiri, Y. Kawai, K. Fukumoto, T. Morikawa, Y. Takeda, *Joule*, **2021**, 5, 687.
3) N. Kato, Y. Takeda, Y. Kawai, N. Nojiri, M. Shiozawa, S. Mizuno, K. Yamanaka, T. Morikawa, T. Hamaguchi, *ACS Sustain. Chem. Eng.*, **2021**, https://doi.org/10.1021/acssuschemeng.1c06390.