Fri. Mar 24, 2023

K303

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

[K303-3am] 01. Education and History of Chemistry

Chair: Akira Ikuo, Masashi Osa
9:00 AM - 10:30 AM K303 (K303, Lecture Hall Bldg. [3F])

[K303-3am-01] Microscale Experiments for Physically Challenged Students -The Practice of Experiments on Quantitative Relationships in Chemical Reactions-
○Kazuyuki Yamada[1], Kazuko Ogino[2] (1. Kirigaoka School for the Physically Challenged, University of Tsukuba, 2. Graduate School of Science, Tohoku University)
9:00 AM - 9:20 AM

[K303-3am-02] Development of Superabsorbent Polymers into Chemistry Educational Materials
○Masashi Osa[1] (1. Aichi University of Education)
9:20 AM - 9:40 AM

[K303-3am-03] Development and Evaluation of Thermochemical Teaching Material for Visualizing Catalysis Using Cobalt Chloride
○Masashi Yamada[1], Izumi Imai[1] (1. Toho University)
9:50 AM - 10:10 AM

[K303-3am-04] Development of Experimental Program for Pre-serviceTeacher Education: Toward a conceptual understanding of reaction rate
○Takashi Hosoe[1], Akira Ikuo[2], Hisao Kokusen[1], Haruo Ogawa[2] (1. The United Graduate School of Education, Tokyo Gakugei University, 2. Faculty of Education, Tokyo Gakugei University)
10:10 AM - 10:30 AM

K202

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

[K202-3am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Yoshiki Ishii, Yosuke Sumiya
9:00 AM - 11:40 AM K202 (K202, Lecture Hall Bldg. [2F])

[K202-3am-01] Spatially-Decomposed Analysis of Molecular Interactions and OH Stretching Vibrational Modes at Polymer-Water Interfaces
○Yoshiki Ishii[1], Hajime Torii[2], Yuka Ikemoto[3], Hitoshi Washizu[1] (1. University of Hyogo, 2. Shizuoka University, 3. JASRI)
9:00 AM - 9:20 AM

[K202-3am-02] Local thermal transport property of protein
Tingting Wang[1], ○Takahisa Yamato[1], Wataru Sugiura[1] (1. Nagoya University)
9:20 AM - 9:40 AM

[K202-3am-03] Theoretical Study on Thermostabilization Mechanism of Thermophilic Rhodopsin (TR)
○Michiya Nishina[1], Kazuhiro Fujimoto[1], Takeshi Yanai[1] (1. The Univ. of Nagoya)
9:40 AM - 10:00 AM

[K202-3am-04] A Quantum Chemical Study on Anti-SARS-CoV-2 Activity of TMPRSS2 Inhibitors
○Akihiro Kondo[1], Kazuhiro J Fujimoto[1], Takeshi Yanai[1] (1. Nagoya University)
10:10 AM - 10:30 AM

[K202-3am-05] Feature engineering of ceramic materials based on conventinal knowledge in material chemistry
○Noriaki Ozaki[1], Jun Ikeda[1] (1. Murata Mfg.)
10:30 AM - 10:50 AM

[K202-3am-06] Theoretical Analysis of Adhesion Interaction for Oxide Materials: Molecular Understanding of Tensile, Shear, and Peel Processes
○Yosuke Sumiya[1], Yuta Tsuji[2], Takahiro Uwabe[1], Kazunari Yoshizawa[1] (1. Institute for Materials Chemistry and Engineering, Kyushu Univ., 2. Faculty of Engineering Sciences, Kyushu Univ.)
10:50 AM - 11:10 AM

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

[K202-3pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Toyokazu ISHIDA, Yuta Hori
1:00 PM - 3:40 PM K202 (K202, Lecture Hall Bldg. [2F])

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[K202-3pm-01] Molecular dynamics simulation of electrode-liquid interface using a universal neural network potential
○Kaoru Hisama[1], Gerardo Valadez Huerta[1], Michihisa Koyama[1] (1. Shinshu Univ.)
1:10 PM - 1:30 PM

[K202-3pm-02] Theoretical Analysis for Anisotropy of Proton Conduction in Imidazolium Hydrogen Succinate by First-Principles Calculations
○Yuta Hori[1], Yasuteru Shigeta[1] (1. University of Tsukuba)
1:30 PM - 1:50 PM

[K202-3pm-03] Protonation free-energy of amine-cured epoxy resin under deformation in water by first-principles calculations
○Shuji Ogata[1], Masayuki Uranagase[1] (1. Nagoya Institute of Technology)
1:50 PM - 2:10 PM

[K202-3pm-04] Quantum computing of molecular orbitals of linear polyenes and its application to probing qubit performance
○Yoshinori Ato[1], Yutaka Tachikawa[1], Ryuhei Yoshida[2], Erik Lötstedt[2], Kaoru Yamanouchi[2] (1. DIC Corporation, 2. The University of Tokyo)
2:10 PM - 2:30 PM

[K202-3pm-05] Requirements of Orbital Phase Continuity Revisited: A FMO Approach
○Yuji Naruse[1] (1. Gifu University)
2:40 PM - 3:00 PM

[K202-3pm-06] Direct calculation of numerical energy gradient by using Bayesian phase difference estimation algorithm and application to geometry optimization
○Kenji Sugisaki[1,2,3], Hiroyuki Wakimoto[1], Kazuo Toyota[1], Kazunobu Sato[1], Daisuke Shiomi[1], Takeji Takui[1] (1. Osaka Metropolitan University, 2. JST PRESTO, 3. CQuERE, TCG CREST)
3:00 PM - 3:20 PM

[K202-3pm-07] Prediction of experimental properties of organic molecules by quantum circuit learning
○Kan Hatakeyama-Sato[1], Kenichi Oyaizu[1] (1. Waseda University)
3:20 PM - 3:40 PM

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

[K202-3vn] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Kenji Sugisaki, Mitutaka Okumura
4:10 PM - 6:50 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-3vn-01] Theoretical study of the solvent fluctuation affecting the linear optical process in solution
○Naoki Negishi[1], Daisuke Yokogawa[1] (1. Graduate school of Arts and Sciences, The University of Tokyo)
4:10 PM - 4:30 PM

[K202-3vn-02] Relativistic DFT Calculations for Concentration Changes in Heavy-Element Chemical Shifts
○Yoshimitsu Asakura[1], Daisuke Kuwahara[1], Naoya Nakagawa[1] (1. The University of Electro-Communications)
4:30 PM - 4:50 PM

[K202-3vn-03] Computational Exploration for High Density Thermal Storage Materials based on Thermal Management Materials Database (PropertiesDB Web)
○Toyokazu ISHIDA[1,2], Yukiko Suda[2], Kazuya Ishimura[3] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Thermal Management Materials and Technology Research Association (TherMAT), 3. X-Ability)
4:50 PM - 5:10 PM

K201

Academic Program [Oral B] | 03. Physical Chemistry -Structure- | Oral B

[K201-3am] 03. Physical Chemistry -Structure-

Chair: Jun Miyazaki, Kiichirou Koyasu
9:00 AM - 10:30 AM K201 (K201, Lecture Hall Bldg. [2F])

[K201-3am-01] Fundamental vibrational frequency of H_2 by Strong-field ultrahigh-resolution Fourier-transform spectroscopy
○Toshiaki Ando[1], Kana Yamada[1], Atsushi Iwasaki[1], Kaoru Yamanouchi[1] (1. The University of Tokyo)

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9:00 AM - 9:20 AM

[K201-3am-02] LIF spectroscopy of jet cooled SiNSi: vibrational hot bands of the C $^2\Lambda_u$ - X $^2\Pi_g$ electronic transition

○Masaru Fukushima[1], Ishiwata Takashi[1], Chihaya Motoyoshi[2], Yoshihiro Motoyoshi[2], Yasuki Endo[2] (1. Hiroshima City University, 2. The Univ. of Tokyo)

9:20 AM - 9:40 AM

[K201-3am-03] Bottom-up approach to the ion recognition of K^+ channels by cryogenic double ion trap infrared spectroscopy

○Keisuke Hirata[1], James Lisy[2], Shun-ichi Ishiuchi[1], Masaaki Fujii[1] (1. Tokyo Institute of Technology, 2. University of Illinois)

9:50 AM - 10:10 AM

[K201-3am-04] Characterization of electronic structures of ligand-protected superatoms and superatomic molecules by gas-phase photoelectron spectroscopy

○Shun Ito[1], Emi Ito[1], Shinjiro Takano[1], Kiichirou Koyasu[1], Tatsuya Tsukuda[1] (1. The Univ. of Tokyo)

10:10 AM - 10:30 AM

Academic Program [Oral B] | 03. Physical Chemistry -Structure- | Oral B

[K201-3pm] 03. Physical Chemistry -Structure-

Chair: Hiroko Miwa, Kozo Mukai

2:20 PM - 3:40 PM K201 (K201, Lecture Hall Bldg. [2F])

[K201-3pm-01] Title CHARACTERIZATION OF CNT-DISPERSION GELS USING ABSORPTION SPECTRA AND RAMAN SPECTRA

○Yusuke Matsumiya[1] (1. SHIBAURA INSTITUTE OF TECHNOLOGY)

2:20 PM - 2:40 PM

[K201-3pm-02] Hydrogenation of formate on the Pd/Cu(977) single-atom alloy model catalyst using surface analysis methods

○Wataru Osada[1], Shunsuke Tanaka[1], Kozo Mukai[1], Jun Yoshinobu[1] (1. The Institute for Solid State Physics, University of Tokyo)

2:40 PM - 3:00 PM

[K201-3pm-03] Excess potential of anion adsorption/desorption at ionic liquid electrolyte/electrode interfaces

○Takashi Iwahashi[1], Wei Zhou[2], Doseok Kim[3], Yukio Ouchi[1] (1. Tokyo Tech., 2. Shanghai Univ., 3. Sogang Univ.)

3:00 PM - 3:20 PM

[K201-3pm-04] Multimodal measurement of electrocatalyst for fuel cell

○Hiroko Miwa, Takefumi Yoshida[1], Takuma Kaneko[3], Takehiko Sasaki[2], Tomoya Uruga[1,3], Yasuhiro Iwasawa[1] (1. The Univ. of Electro-Comm., 2. The Univ. of Tokyo, 3. JASRI)

3:20 PM - 3:40 PM

K203

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

[K203-3pm] 04. Physical Chemistry -Properties-

Chair: Masaki Matsuda, Ryo Tsunashima

1:10 PM - 3:40 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-3pm-01] Rhodium-Containing Ionic Liquid for the Solvent-Free Formation of Coordination Polymers

○Ryo Sumitani[1], Tomoyuki Mochida[1,2] (1. Graduate School of Science, Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University)

1:10 PM - 1:30 PM

[K203-3pm-02] Theory of the Superheating Induced by Microwave Heating

○Makoto Koike[1,2] (1. Micro Patent Office, 2. Makoto Koike Microwave Research Institute)

1:30 PM - 1:50 PM

[K203-3pm-03] Bottom-up measurement of entropy of fusion through single-unit-cell kinetic study

○Dongxin Liu[1], Takayuki Nakamuro[1], Koji Harano[1], Eiichi Nakamura[1] (1. The Univ. of Tokyo)

1:50 PM - 2:10 PM

[K203-3pm-04] Synthesis and Physicochemical Properties of Aromatic Amine-based Ionic Liquids That Exhibited Hydrophobicity

○Kenta Matsumoto[1], Yuki Murata[1], Daiki Mizobe[1], Takeru Sunada[1], Yuki Morita[2], Hiroaki Okamoto[1] (1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Advanced Technology Institute, Yamaguchi University)

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2:10 PM - 2:30 PM

[K203-3pm-05] Optical properties and magnetism derived from chirality exhibited by gyroidal MOFs with strongly isotropic structure

○Kazuya Nakashima[1], Rie Suizu[1,2], Masahisa Tsuchiizu[3], Hyuma Masu[4], Shuhei Morishita[5], Noriaki Tsurumachi[5], Masahiro Funahashi[5], Kunio Awaga[1] (1. Nagoya Univ., 2. JST-PRESTO, 3. Nara Women's Univ., 4. Chiba Univ., 5. Kagawa Univ.)

2:40 PM - 3:00 PM

[K203-3pm-06] Development of capture and release of ions and molecules in $Ni(dmit)_2$ crystals responding to the solution environment

○Jun Manabe[1], Mizuki Ito[1], Katsuya Ichihashi[1], Daisuke Konno[1], Masaru Fujibayashi[1], Goulven Cosquer[1,2], Katsuya Inoue[1,2,3,4], Tomoyuki Akutagawa[5], Kiyonori Takahashi[6], Takayoshi Nakamura[6], Sadafumi Nishihara[1,2,3,7] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. Chirality Research Center (CResCent), Hiroshima University, 3. Institute for Advanced Materials Research, Hiroshima University, 4. International Institute for Sustainability with Knotted Chiral Meta Matter (SKCM2), Hiroshima University, 5. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 6. Research Institute for Electronic Science(RIES), Hokkaido University, 7. Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency)

3:00 PM - 3:20 PM

[K203-3pm-07] Physical properties of a quantum spin liquid candidate κ-$(ET)_2Cu[Au(CN)_2]Cl$ with disorder-free anion layer at low temperature

○Yuki Tanaka[1], Mitsuhiko Maesato[1], Shinya Tomeno[1], Yukihiro Yoshida[1], Yasuhiro Shimizu[2], Hiroshi Kitagawa (1. Kyoto university, 2. Nagoya University)

3:20 PM - 3:40 PM

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

[K203-3vn] 04. Physical Chemistry -Properties-

Chair: Hiroyuki Nishikawa, Ryo Tsunashima

4:10 PM - 5:50 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-3vn-01] On-surface chemistry of crown ether molecules on Cu(111)

○Toyo Kazu Yamada[1], Masaki Horie[2] (1. Chiba University, 2. Taiwan Tsing Hua Univ.)

4:10 PM - 4:30 PM

[K203-3vn-02] Single amino acid molecule discrimination by molecular modification of nano-gap and machine learning analysis

○JIHO RYU[1], Yuki Komoto[1], Takahito Ohshiro[1], Masateru Taniguchi[1] (1. Osaka University)

4:30 PM - 4:50 PM

[K203-3vn-03] Effects of solid surfaces on diradical characters of adsorbed molecules

○Kohei Tada[1], Koji Fujimaru[1,2], Hiroyuki Ozaki[1], Yasutaka Kitagawa[2], Takashi Kawakami[2], Mitsutaka Okumura[2], Shingo Tanaka[1] (1. AIST, 2. Osaka Univ.)

4:50 PM - 5:10 PM

[K203-3vn-04] “Floating Island”, a Metastable Intermediate in Crystal Growth Revealed by Millisecond TEM Imaging

○Masaya Sakakibara[1], Takayuki Nakamuro[1], Hiroki Nada[2], Eiichi Nakamura[1] (1. The University of Tokyo, 2. Tottori University)

5:10 PM - 5:30 PM

[K203-3vn-05] Tip-enhanced second-order nonlinear optical processes in a nanomolecular system adsorbed on metal surface

○Shota Takahashi[1,2], Atsunori Sakurai[1,3], Tatsuto Mochizuki[1,3], Toshiki Sugimoto[1,3,4] (1. Institute for molecular science, 2. JSPS Research Fellow PD, 3. The Graduate University for Advanced Studies, 4. JST PRESTO)

5:30 PM - 5:50 PM

K205

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

[K205-3pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Shinichi Fukahori, Takuya Horio

1:20 PM - 3:40 PM K205 (K205, Lecture Hall Bldg. [2F])

[K205-3pm-01] Photodissociation and detachment processes of size-selected silver cluster

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anions, Ag_N^- (N = 3–11): Photon-energy dependent lifetime of excited states

○Shun Kawamura[1], Satoshi Kono[1], Masato Yamaguchi[1], Masashi Arakawa[1], Takuya Horio[1], Akira Terasaki[1] (1. Kyushu University)

1:20 PM - 1:40 PM

[K205-3pm-02] Photoelectron imaging of 3d-transition-metal-doped silver cluster anions with 18 valence electrons

○Tasuku Nishizato[1], Haruki Hashimoto[1], Kazuaki Matsumoto[1], Yuta Suzuki[1], Masashi Arakawa[1], Takuya Horio[1], Akira Terasaki[1] (1. Department of Chemistry, Kyushu University)

1:40 PM - 2:00 PM

[K205-3pm-03] Ultrafast pump-probe measurement of CO_2 by few-cycle NIR pulses and the high-order harmonics

○Takuya Matsubara[1], Hiroki Mashiko[1], Tomoya Yamauchi[1], Kana Yamada[1], Toshiaki Ando[1], Atsushi Iwasaki[1], Kaoru Yamanouchi[1] (1. Sch. Sci., The Univ. of Tokyo)

2:10 PM - 2:30 PM

[K205-3pm-04] Formation of molecular hydrogen ions during metal ablation by femtosecond laser pulses

Tatsuro Shirota[1], Yasufumi Kobayashi[2], ○Kennosuke Hoshina[1], Kaoru Yamanouchi[3] (1. Niigata Univ. of Pharmacy, 2. Niigata University Medical &Dental Hospital, 3. The Univ. of Tokyo)

2:30 PM - 2:50 PM

[K205-3pm-05] Observation of electrochemical Peltier effects by a simple method

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

3:00 PM - 3:20 PM

[K205-3pm-06] Electrochemical reduction of N_2 to NH_3 by boron and nitrogen doped carbon nanosphere in electrolytes with different pH values

○Mingyuan WANG[1], Akihiko Fukunaga[1] (1. Waseda university)

3:20 PM - 3:40 PM

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

[K205-3vn] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Koichi NOZAKI, Takashi Nagata

4:10 PM - 6:00 PM K205 (K205, Lecture Hall Bldg. [2F])

[K205-3vn-01] Unique characteristics in chromophore photoisomerization of the novel rhodopsin bestrhodopsin

○Takashi Nagata[1], Yuma Kawasaki[1], Masae Konno[1,2], Yujiro Nagasaka[1], Mako Aoyama[3], Kota Katayama[2,3], Andrey Rozenberg[4], Igor Kaczmarczyk[5], Donna Matzov[5], Moran Shalev-Benami[5], Oded Béjà[4], Hideki Kandori[3], Keiichi Inoue[1] (1. The Univ. of Tokyo, 2. PRESTO, JST, 3. Nagoya Inst. Tech., 4. Technion–Israel Inst. Tech., 5. Weizmann Inst. Sci.)

4:10 PM - 4:30 PM

[K205-3vn-02] Near-Infrared Two-Photon Absorption and Subsequent Excited State Dynamics of Fluorescent Diarylethene Derivatives

○Hikaru SOTOME[1], Tatsuhiro Nagasaka[1], Tatsuki Konishi[2], Kenji Kamada[2], Masakazu Morimoto[3], Masahiro Irie[3], Hiroshi Miyasaka[1] (1. Osaka Univ., 2. National Institute of Advanced Industrial Science and Technology, 3. Rikkyo Univ.)

4:30 PM - 4:50 PM

[K205-3vn-03] Exciton diffusion and excimer formation dynamics of perylene in polymer films

○Koichi NOZAKI[1], Koki IMAMURA[1], Munetaka IWAMURA[1] (1. Grad. Sch. Sci. Eng., Univ. of Toyama)

5:00 PM - 5:20 PM

[K205-3vn-04] Enhancing photocatalytic water splitting activity of TiO_2 by controlling the thickness of adsorbed water layer at the molecular level

○Zhongqiu Lin[1,2], Hikaru Saito[1], Hiromasa Sato[1,2], Toshiki Sugimoto[1,2,3,4] (1. Institute for Molecular Science, 2. The Graduate University for Advanced Studies, SOKENDAI, 3. Innovative Optics and Photonics, PRESTO-JST, Japan, 4. RIKEN SPring-8 Center, Japan)

5:20 PM - 5:40 PM

[K205-3vn-05] Control of the motion of benzoic acid disks by amphiphilic molecule and self-propulsive molecule interactions at the air-water interface.

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○Risa Fujita[1], Muneyuki Matsuo[1], Satoshi Nakata[1] （1. Hiroshima university）
5:40 PM - 6:00 PM

K701

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

[K701-3pm] 06. Analytical Chemistry

Chair: Kazuhiko Tsukagoshi, Tsuyoshi Minami
1:50 PM - 3:40 PM K701 (K701, Lecture Hall Bldg. [7F])

[K701-3pm-01] Evaluation of Banana Ripening Conditions using Metal Oxide Nanofilm Gas Sensor Array
○Haruka Honda[1], Xi Wang[1], Tsunaki Takahashi[1,3], Wataru Tanaka[1], Takuro Hosomi[1,3], Kazuki Nagashima[1,3], Takeshi Yanagida[1,2] （1. The Univ. of Tokyo, 2. Kyushu Univ., 3. JST PRESTO）
1:50 PM - 2:10 PM

[K701-3pm-02] Fluorescence recognition of D-glucose with excellent chiral selectivity exploiting cyclodextrin cavity as a reaction field
○Yota Suzuki[1], Takeshi Hashimoto[1], Takashi Hayashita[1] （1. Sophia Univ.）
2:10 PM - 2:30 PM

[K701-3pm-03] Chiral Pattern Recognition Utilizing Multi-Equilibria in Molecular Self-Assemblies
○Yui Sasaki[1], Tsuyoshi Minami[1] （1. IIS, The Uni. of Tokyo）
2:40 PM - 3:00 PM

[K701-3pm-04] Direct detection of amoxicillin and ciprofloxacin using flexible surface-enhanced Raman scattering (SERS) substrate
○Kullavadee Karn-orachai[1] （1. National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA)）
3:00 PM - 3:20 PM

[K701-3pm-05] A Raman spectroscopic investigation of intracellular water
○Ashok Samuel[1], Haruko Takeyama[2] （1. Research organization for nano and life innovation, waseda university, Tokyo, 2. waseda university, Tokyo）
3:20 PM - 3:40 PM

K501

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

[K501-3am] 07. Inorganic Chemistry

Chair: Kazuya Kobiro, Masato Goto
9:00 AM - 11:30 AM K501 (K501, Lecture Hall Bldg. [5F])

[K501-3am-01] Raman spectroscopy and electronic state calculation for high near-infrared (NIR) reflective black pigments based on Ca_2MnO_4
○Ryohei Oka[1], Tomokatsu Hayakawa[1] （1. Nagoya Institute of Technology）
9:00 AM - 9:20 AM

[K501-3am-02] Crystal structure and topochemical fluorination of $Bi_{12}O_{17}Cl_2$ photocatalyst
○Daichi Kato[1], Osamu Tomita[1], Hajime Suzuki, Chengchao Zhong[1], Cédric Tassel[1], Kohdai Ishida, Yosuke Matsuzaki[1], Koji Fujita[1], Ryu Abe[1], Hiroshi Kageyama[1], Ryky Nelson[2], Richard Dronskowski [2], Maria Kirsanova[3], Abakumov Artem[3], Craig Brown[4], Kotaro Fujii[5], Masatomo Yashima[5], Akinori Saeki[7], Itaru Oikawa[8], Hitoshi Takamura[8], Yoji Kobayashi[6], Tatiana Gorelik [9] （1. Kyoto Univ., 2. RWTH Aachen Univ., 3. Skolkovo Institute of Science and Technology, 4. NIST, 5. Tokyo Institute of Technology, 6. KAUST, 7. Osaka Univ., 8. Tohoku Univ., 9. Ulm Univ.）
9:20 AM - 9:40 AM

[K501-3am-03] Water-assisted solid-state reaction
○Kenji Toda[1] （1. Niigata University）
9:40 AM - 10:00 AM

[K501-3am-04] Solvothermal Synthesis of Porous SnO_2
○Ayano Taniguchi[1], Masataka Ohtani[1], Kazuya Kobiro[1] （1. Kochi Univ. of Tech.）
10:00 AM - 10:20 AM

[K501-3am-05] Structure and physical properties of *A*-site layer-ordered/disordered perovskites $NdBaFe_2O_6$ with unusually high valence $Fe^{3.5+}$
○Makoto Iihoshi[1], Masato Goto[1], Yuuichi Shimakawa[1] （1. Kyoto University）
10:30 AM - 10:50 AM

[K501-3am-06] Oxygen Release and Crystal Structural Changes of $BaFeO_3$ Polymorphs
○Rei Watanabe[1], Masato Goto[1], Yuichi

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Shimakawa[1] (1. Kyoto University)
10:50 AM - 11:10 AM

[K501-3am-07] Structure-property relationships in *B*-site ordered double perovskites Ln_2LiFeO_6
○Masato Goto[1], Yuichi Shimakawa[1] (1. Kyoto University)
11:10 AM - 11:30 AM

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

[K501-3pm] 07. Inorganic Chemistry

Chair: Takafumi Yamamoto, Takayuki Nakamuro
1:10 PM - 3:40 PM K501 (K501, Lecture Hall Bldg. [5F])

[K501-3pm-01] The Effects on Substitution of Thiocyanate Anion for $FAPbI_3$
○Takuya Ohmi[1], Masaki Azuma[1,2], Takafumi Yamamoto[1] (1. Tokyo Institute of Technology, 2. KISTEC)
1:10 PM - 1:30 PM

[K501-3pm-02] High-pressure phases of lanthanide oxyhydrides and anion ordering
○Ryo Terada[1], Yumi Tsuchiya[1], Hiroki Ubukata[1], Zefeng Wei[1], Hiroshi Kageyama[1] (1. Kyoto University)
1:30 PM - 1:50 PM

[K501-3pm-03] Reduction-induced Cs^+ ion capture with polyoxometalate encapsulated metal–organic frameworks
○Naoki Ogiwara[1], Cocoro Andrew Ngasaka[1], Sayaka Uchida[1] (1. School of Arts and Sciences, The University of Tokyo)
1:50 PM - 2:10 PM

[K501-3pm-04] High Proton conduction in Crystalline composites based on Eu Ion Bonded Polyoxometalates and Polymers
○Tsukasa Iwano[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)
2:10 PM - 2:30 PM

[K501-3pm-05] Synthesis of size-controlled small silver clusters utilizing porous ionic crystals as scaffolds
○Naoya Haraguchi[1], Naoki Ogiwara[1], Sayaka Uchida[1] (1. Grad. Sch. of Arts and Sci., The Univ. of Tokyo)
2:40 PM - 3:00 PM

[K501-3pm-06] Investigation of synthesis of thiol-protected Au clusters using dendrimers
○Hisanori Muramatsu[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2,3], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Tokyo Tech., Lab. Chem. Life Sci., 2. JST-ERATO, 3. JST-PRESTO)
3:00 PM - 3:20 PM

[K501-3pm-07] Between molecules and nanocrystals: synthesis and properties of perovskite nanoclusters
○Olivier Jan Chevalier[1], Takayuki Nakamuro[1], Naotaka Yoshikawa[1], Ryo Shimano[1], Rui Shang[1], Eiichi Nakamura[1] (1. The University of Tokyo)
3:20 PM - 3:40 PM

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

[K501-3vn] 07. Inorganic Chemistry

Chair: Kosuke Suzuki, Yuji Kikukawa
4:10 PM - 6:40 PM K501 (K501, Lecture Hall Bldg. [5F])

[K501-3vn-01] Precise synthesis of 3d metal clusters and evaluation of their properties
○Tatsuya Moriai[1], Takamasa Tsukamoto[1,2,3], Tetsuya Kambe[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. JST-ERATO, 3. JST-PRESTO)
4:10 PM - 4:30 PM

[K501-3vn-02] Development of metal nanoparticle catalysts modified using multidentate polyoxometalates
○Kang Xia[1], Takafumi Yatabe[1], Kentaro Yonesato[1], Tomohiro Yabe[1], Soichi Kikkawa[2], Seiji Yamazoe[2], Ayako Nakata[3], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The University of Tokyo, 2. Tokyo Metropolitan University, 3. National Institute for Materials Science)
4:30 PM - 4:50 PM

[K501-3vn-03] Synthesis of copper nanoclusters using inner cavity of a ring-shaped polyoxometalate
○Yoshihiro Koizumi[1], Kentaro Yonesato[1], Soichi Kikkawa[2], Seiji Yamazoe[2], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo, 2. Tokyo Metropolitan Univ.)
4:50 PM - 5:10 PM

[K501-3vn-04] Synthesis and Characterization of Phosphovanadates with Fruoride

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○Yuji Kikukawa[1], Ryu Hasegawa[1], Yoshihito Hayashi[1] (1. Kanazawa Univ.)
5:20 PM - 5:40 PM

[K501-3vn-05] Synthesis and Characterization of Novel Iron-Group Metal Nanoclusters Protected by Bulky Ligands
○Tatsuya Higaki[1], Kanata Tanaka[1], Shunya Oishi[2], Koki Kawamoto[2], Mizuki Tada[2], Yasuhiro Ohki[1] (1. ICR, Kyoto U., 2. Graduate School of Science and RCMS, Nagoya University)
5:40 PM - 6:00 PM

[K501-3vn-06] Evaporation-induced self-assembly process with centrifugal evaporator for obtaining mesoporous alumina powders
○Ryutaro Wakabayashi[1], Tatsuo Kimura[1] (1. National Institute of Advanced Industrial Science and Technology (AIST))
6:00 PM - 6:20 PM

[K501-3vn-07] Preparation of laminar composite membranes consisting of large niobate and graphene oxide nanosheets and electrochemical analysis of ion diffusion behaviors
○Fumitaka Hayashi[1], Ogiso Hisaki[1], Tanaka Atsushi[1], Nishina Yuta[2], Yamada Tetsuya[1], Teshima Katsuya[1] (1. Shinshu University, 2. Okayama University)
6:20 PM - 6:40 PM

K506

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

[K506-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Manabu Nakaya, Ryo Inoue
9:00 AM - 10:20 AM K506 (K506, Lecture Hall Bldg. [5F])

[K506-3am-01] Synthesis of two-dimensional layer-structured coordination polymer ELM-12/3 and gate-opening adsorption properties
○Hiroki Miura[1], Atsushi Kondo[2], Hirofumi Kanoh[3], Hiroshi Kajiro[1] (1. Nippon Steel Corporation, 2. Oita University, 3. Chiba University)
9:00 AM - 9:20 AM

[K506-3am-02] Helical Induction, Chiroptical Properties, and Quantitative Prediction of Dissymmetry Factor on the Circularly Polarized Phosphorescence of Iminopyrrolyl Platinum(II) Complexes
○Ryo Inoue[1], Riki Kondo[1], Yasuhiro Morisaki[1] (1. Kwansei Gakuin University)
9:20 AM - 9:40 AM

[K506-3am-03] pH effect on hydrothermal synthesis of the copper organodiphosphonate polymers: Investigation of luminescence and magnetic properties
○BURAK AY[1,2], TAKAYUKI ISHIDA[1] (1. The University of Electro-Communications, 2. Çukurova University)
9:40 AM - 10:00 AM

[K506-3am-04] External-stimuli responsiveness in luminescence properties of salophene-type platinum(II) complexes with carboxy substituents
○Shun Fujii[1], Manabu Nakaya[1] (1. Josai University)
10:00 AM - 10:20 AM

K504

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

[K504-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kentaro Kadota, Shinya Takaishi
1:10 PM - 3:40 PM K504 (K504, Lecture Hall Bldg. [5F])

[K504-3pm-01] Investigation of thermodynamics in melting Cu^{2+}-based 1D coordination polymers
○Yuki Ohara[1], Taichi Nishiguchi[1], Shin-ichiro Noro[3], Daniel Packwood[2], Satoshi Horike[1,2] (1. Graduate School of Engineering, Kyoto University, 2. Institute for Advanced Study, Kyoto University, 3. Faculty of Environmental Earth Science, Hokkaido University)
1:10 PM - 1:30 PM

[K504-3pm-02] Spatially Controlled Hybridization of Porous Metal-Organic Crystals
○Kunyi Leng[1,2], Takuzo Aida[1,2], Hiroshi Sato[2,3] (1. The University of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. JST-PRESTO)
1:30 PM - 1:50 PM

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[K504-3pm-03] Three-dimensional van der Waals frameworks assembled from octahedral metal-organic polyhedra
○Shun Tokuda[1], Shuhei Furukawa[1] (1. iCeMS, Kyoto University)
1:50 PM - 2:10 PM

[K504-3pm-04] Recognition of Copolymer Sequence via Gated Inclusion in Flexible Metal-Organic Frameworks
○Nobuhiko Hosono[1], Biplab Manna[2], Mizuki Asami[2], Takashi Uemura[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Frontier Sci., The Univ. of Tokyo)
2:10 PM - 2:30 PM

[K504-3pm-05] Structural and property evaluation of cyano-bridged coordination polymers exhibiting anisotropic thermal expansion
○Ryota Kosuge[1], Takashi KOSONE[1,2], Naoya ADACHI[1,2] (1. Graduate School of Tokyo Denki University, 2. Tokyo Denki University)
2:40 PM - 3:00 PM

[K504-3pm-06] Consideration on Gated CO_2 Adsorption Behavior in One-Dimensional Porous Coordination Polymers of Phenazine-Linked Paddlewheel diruthenium complex
○Wataru Kosaka[1], Jun Zhang[2], Hitoshi Miyasaka[1] (1. IMR, Tohoku Univ., 2. FRIS, Tohoku Univ.)
3:00 PM - 3:20 PM

[K504-3pm-07] Quinoid-Based Three-Dimensional Metal-Organic Framework, $Fe_2(dhbq)_3$: Porosity, Electrical Conductivity and Solid-State Redox Properties
○Shraddha Gupta[1], Haruki Tanaka[1], Shinya Takaishi[1] (1. Tohoku University)
3:20 PM - 3:40 PM

K505

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

[K505-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kazuhiro Uemura, Masaki Yoshida
1:10 PM - 3:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-3pm-01] Synthesis and Properties of Mixed-Valence Mn-oxo Clusters Ligated with Rigid Triptycene-Based Ligands
○Mikiya Kato[1,2], Tomoya Fukui[1,2], Ryosuke Takehara[1,2], Yoshiaki Shoji[1,2], Fukushima Takanori[1,2] (1. CLS, Tokyo Tech., 2. Sch. Mater. Chem. Tech., Tokyo Tech.)
1:10 PM - 1:30 PM

[K505-3pm-02] Near-infrared emission in Ag_{29} nanoclusters induced by the modification with metal complexes
○Wataru Ishii[1], Yoshinori Okayasu[2], Yoichi Kobayashi[2], Kawai Tsuyoshi[3], Takuya Nakashima[1] (1. Osaka Metropolitan University, 2. Ritsumeikan University, 3. Nara Institute of Science and Technology)
1:30 PM - 1:50 PM

[K505-3pm-03] Magnetic properties of paramagnetic one-dimensional chains where first transition metals are infinitely aligned with metal–metal bonds
○Atsushi Takamori[1], Kazuhiro Uemura[2] (1. Graduate School of Engineering, Gifu University, 2. Faculty of Engineering, Gifu University)
1:50 PM - 2:10 PM

[K505-3pm-04] Vapor, mechanical, and piezochromic multicolor switching of a carbon-centered hexagold(I) cluster with flexible N-heterocyclic carbene ligands
○Leonardo Hayato Takeshige[1], Xiao-Li Pei[1], Hitoshi Ube[1], Zhen Lei[1], Hiroki Kobayashi[2], Kazuki Komatsu[2], Hiroyuki Kagi[2], Mitsuhiko Shionoya[1] (1. Department of Chemistry, Grad. Sch. Sci, The Univ. of Tokyo, 2. Geochemical Research Center, Grad. Sch. Sci, The Univ. of Tokyo)
2:10 PM - 2:30 PM

[K505-3pm-05] Regioselective deprotonation of twisted trinuclear macrocycles to control the rate of helicity inversion
○Tomoki NAKAJIMA[1], Shohei TASHIRO[1], Masahiro EHARA[2], Mitsuhiko SHIONOYA[1] (1. Grad. Sch. of Sci.; The Univ. of Tokyo, 2. IMS)
2:40 PM - 3:00 PM

[K505-3pm-06] Stability Control and Luminescence of Porous Crystals of Self-assembled Platinum(II) Complexes Based on the

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Electronic Tuning of Ligands

○Masaki Yoshida[1], Takanari Mochizuki[2], Atsushi Kobayashi[2], Masako Kato[1] (1. Kwansei Gakuin Univ., 2. Hokkaido Univ.)

3:00 PM - 3:20 PM

[K505-3pm-07] Multi-step conversion of protonation state based on the coupling of proton, spin and molecular orientation

○Takumi Nakanishi[1], Osamu Sato[1] (1. Kyushu University)

3:20 PM - 3:40 PM

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

[K505-3vn] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Hironobu Ozawa, Yoshimasa Wada
4:10 PM - 6:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-3vn-01] Mechanistic Study on Chromium-catalyzed Ring-opening Arylation of 7-Oxabenzonorbornadiene Derivatives with Aryl Grignard Reagents

○Kohei Nishi[1], Hayato Tsurugi[1], Kazushi Mashima[2] (1. Graduate School of Engineering Science, Osaka University, 2. Graduate School of Pharmaceutical Sciences, Osaka University)

4:10 PM - 4:30 PM

[K505-3vn-02] [2+2+1]-Cycloaddition Reaction of Azobenzenes and Diarylacetylenes Catalyzed by Early Transition Metal Imido Complexes

○Takuya Akiyama[1], Yuya Kakiuchi[1], Ian A. Tonks[2], Hayato Tsurugi[1], Kazushi Mashima[3] (1. Graduate School of Engineering Science, Osaka University, 2. University of Minnesota, 3. Graduate School of Pharmaceutical Science, Osaka University)

4:30 PM - 4:50 PM

[K505-3vn-03] Mechanistic study of photocatalytic CO_2 reduction by a Ru(II)-Re(I) supramolecular photocatalyst

○Kei Kamogawa[1], Yuki Kato[2], Yuushi Shimoda[3], Kiyoshi Miyata[3], Ken Onda[3], Takumi Noguchi[2], Yusuke Tamaki[1], Osamu Ishitani[1,4] (1. Tokyo Institute of Technology, 2. Nagoya University, 3. Kyushu University, 4. Hiroshima University)

4:50 PM - 5:10 PM

[K505-3vn-04] Improvement of formation quantum yields of one-electron reduced species of Re(I)-complex photosensitizers and its utilization

○Naoki Hosokawa[1], Yusuke Tamaki[1], Osamu Ishitani[1,2] (1. Tokyo institute of technology, 2. Hiroshima University)

5:10 PM - 5:30 PM

[K505-3vn-05] Supramolecular Framework Catalyst Constructed by Iron Porphyrin Complexes for Photochemical CO_2 Reudction

○Kento Kosugi[1], Chiharu Akatsuka[1], Mio Kondo[1,2], Shigeyuki Masaoka[1] (1. Osaka University, 2. JST PRESTO)

5:40 PM - 6:00 PM

[K505-3vn-06] Iron-catalyzed ring-opening metathesis polymerization of olefins

○Satoshi Takebayashi[1], David Milstein[2] (1. Okinawa Institute of Science and Technology Graduate University, 2. Weizmann Institute of Science)

6:00 PM - 6:20 PM

K506

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

[K506-3vn] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Atsushi KOBAYASHI, Yohei Ogiwara
4:10 PM - 6:40 PM K506 (K506, Lecture Hall Bldg. [5F])

[K506-3vn-01] Effect of a Sulfur Atom in the Benzylidene Ligand of Hoveyda-Grubbs-type Complexes on Their Catalytic Activities

○Tsubasa Kinugawa[1], Shun Hirota[1], Takashi Matsuo[1] (1. Division of Materials Science, Nara Institute of Science and Technology)

4:10 PM - 4:30 PM

[K506-3vn-02] Multi-potential-step chronocoulospectrometry for electrocatalytic proton reduction by mononuclear ruthenium complexes

○Yuta Tsubonouchi[1], Norihisa Hoshino[1], Debraj Chandra[1], Zaki Zahran[1], Masayuki Yagi[1] (1. Grad. School of Sci. and Tech., Niigata univ.)

4:30 PM - 4:50 PM

[K506-3vn-03] A Highly Stable Molecular-based TiO_2

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Photoanode for Photoelectrochemical Water Splitting Achieved by Pyridyl Anchoring Technique

○Xin Yan[1], Ken Sakai[1], Hironobu Ozawa[1] (1. Dept. Chem. Kyushu Univ.)

4:50 PM - 5:10 PM

[K506-3vn-04] Photochemical Reduction of Carbon Dioxde Catalyzed by Ru-Pd Bimetallic Complexes

○Siteng Yang[1], Nobuharu Iwasawa[1], Jun Takaya[1] (1. Titech)

5:20 PM - 5:40 PM

[K506-3vn-05] Photo-induced pentafluoroethylation mediated by cobalt(III) complexes supported by naphthyridine-based ligands

○Hoan Minh Dinh[1], Julia R. Khusnutdinova[1] (1. Okinawa Institute of Science and Technology)

5:40 PM - 6:00 PM

[K506-3vn-06] Molecular Catalysis of Co-NHC Complexes in Hydrogen Evolution from Water

○Kosei Yamauchi[1], Yasunobu Wakafuji[1], Kaori Kawamura[1], Masanori Kan[1], Ken Sakai[1] (1. Kyushu University)

6:00 PM - 6:20 PM

[K506-3vn-07] Mechanistic Investigation of Electrochemical Hydrogen Evolution from Water Catalyzed by a Co-NHC Complex

○Masanori Kan[1], Kosei Yamauchi[1], Ken Sakai[1] (1. Dept. Chem. Kyushu Univ.)

6:20 PM - 6:40 PM

K404

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

[K404-3am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kenichi Michigami, Taiga Yurino
9:00 AM - 11:20 AM K404 (K404, Lecture Hall Bldg. [4F])

[K404-3am-01] Asymmetric Hydrogenation of α-Amino Esters through Dynamic Kinetic Resolution Catalyzed by Ruthenabicyclic Complexes (RUCY)

○Hiroki Ishikawa[1], Taiga Yurino[2,3], Ryo Komatsu[2], Ming-Yuan Gao[2], Noriyoshi Arai[2], Taichiro Touge[1], Kazuhiko Matsumura[1], Takeshi Ohkuma[2,3] (1. Takasago International corporation, 2. Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center, Hokkaido University)

9:00 AM - 9:20 AM

[K404-3am-02] Synthesis of Fused Cyclopentadienes and Cycloheptatrienes via Direct Carbon–Carbon Double Bond Cleavage of Cyclopropene Enabled by Ruthenium Catalysis

○Tomohiro Kikuchi[1], Takeshi Yasui[1], Yoshihiko Yamamoto[1] (1. Grad. Sch. Pharm. Sci., Nagoya Univ.)

9:20 AM - 9:40 AM

[K404-3am-03] 7-*Exo-dig* Hydrocarboxylation of Alkyne-Tethered Carboxylic Acids with Gold-Zinc Cooperative Catalysis

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

9:40 AM - 10:00 AM

[K404-3am-04] Chiral phosphoric acid-Au(I) hybrid complex catalyzed asymmetric synthesis of indole fused seven-membered ring compounds

○Naoya Taniguchi[1], Mitsuhiro Ueda[1,2], Kenichi Michigami[1,2], Masato Ohashi[1,2] (1. Osaka Prefecture Univ., 2. Osaka Metropolitan Univ.)

10:20 AM - 10:40 AM

[K404-3am-05] Synthesis of SGLT2 Inhibitors by Means of Copper-Mediated Coupling Reactions with Grignard Reagents

○Sandeep Rameshrao Tapkir[1], N. Maheshwara Reddy[1], Shaheen Kasim Mulani[1], Masahiko Seki[1,2], Kazushi Mashima[1] (1. Graduate School of Pharmaceutical Science, Osaka University, Suita, Osaka 565-0871, Japan, 2. Marketting Group, Tokuyama Corporation, Tsukuba, Ibaraki 300-4247, Japan)

10:40 AM - 11:00 AM

[K404-3am-06] A Novel General Method for Preparation of Thioesters: In Quest of Direct Conversion of Esters to Aldehydes and Ketones

○Shaheen Kasim Mulani[1], Akinari Uchibayashi[1],

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Sandeep Ramesharao Tapkir[1], N. Maheshwara Reddy[1], Masahiko Seki[1,2], Kazushi Mashima[1] （1. Graduate School and School of pharmaceutical Sciences, Osaka University, 2. Tokuyama Corporation, Tsukuba）
11:00 AM - 11:20 AM

K603

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

[K603-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Makoto Yamashita, Yoshiaki Shoji
9:00 AM - 10:50 AM K603 (K603, Lecture Hall Bldg. [6F])

[K603-3am-01] Substituents on Boron of Organoboron Complexes Modulates Luminescent Properties via Excited Triplet States
○Shunichiro Ito[1], Keisuke Suwa[1], Kazuo Tanaka[1], Yoshiki Chujo[1] （1. Kyoto University）
9:00 AM - 9:20 AM

[K603-3am-02] Reactivity of diborylcarbenoid and properties as an equivalent to diborylcarbene
○Yuki Shibutani[1], Shuhei Kusumoto[1], Kyoko Nozaki[1] （1. The University of Tokyo）
9:20 AM - 9:40 AM

[K603-3am-03] Near-infrared Emissive Properties and Their Stimuli-responsiveness of π-Conjugated Polymers Based on Flexible Boron Complexes
○Masashi Nakamura[1], Masayuki Gon[1], Kazuo Tanaka[1] （1. Graduate School of Engineering, Kyoto University）
9:40 AM - 10:00 AM

[K603-3am-04] Evaluation of Stimulus Responsiveness by Hypervalent Bismuth Compounds with π-Conjugated Scaffolds
○Kazuya Tanimura[1], Masayuki Gon[1], Kazuo Tanaka[1] （1. Grad. Sch. of Eng., Kyoto Univ.）
10:10 AM - 10:30 AM

[K603-3am-05] Novel Template Synthesis for Disilacycloalkanes Utilizing Reactivity of a Siloxane Bond
○Tu Yuyang[1], Inagaki Yusuke[1], Setaka Wataru[1] （1. Tokyo Metropolitan University）
10:30 AM - 10:50 AM

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

[K603-3pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Manabu Abe, Yutaka Ie
1:10 PM - 3:40 PM K603 (K603, Lecture Hall Bldg. [6F])

[K603-3pm-01] Charge transporting properties of cationic diazulenomethenes
○Satoshi Takahashi[1], Masahito Murai[1], Yusuke Hattori[2], Shu Seki[2], Takeshi Yanai[1,3], Shigehiro Yamaguchi[1,3] （1. Nagoya University, Graduate School of Science, 2. Kyoto University, Graduate School of Engineering, 3. Nagoya University, ITbM）
1:10 PM - 1:30 PM

[K603-3pm-02] Development of Electroswitchable Organic π-Systems with Near-Infrared (NIR) Absorptions: Control of HOMO/LUMO Levels Based on Unique Structures
○Takashi Harimoto[1], Takanori Suzuki[2], Yusuke Ishigaki[2] （1. Graduate School of Chemical and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University）
1:30 PM - 1:50 PM

[K603-3pm-03] $S = 1$ Antiferromagnetic 1-D Heisenberg Chain of Verdazyl-Nitroxide Diradical with Long-Range Ordering and Haldane Gap
○Hodaka HAMAMOTO[1], Daiki SHIMIZU[1], Kenji MATSUDA[1] （1. Kyoto University）
1:50 PM - 2:10 PM

[K603-3pm-04] Quantum chemical evaluation of the effect of radical substituents on molecular open-shell characters and associated physical properties
○Tomohito Shinozuka[1], Daiki Shimizu[1], Kenji Matsuda[1] （1. Kyoto University）
2:10 PM - 2:30 PM

[K603-3pm-05] Synthesis and properties of Blatter radical oligomers showing spin-dependent photoexcitation behavior
○Daiki SHIMIZU[1], Takero AOKI[1], Kenji MATSUDA[1] （1. Graduate School of Engineering, Kyoto University）
2:40 PM - 3:00 PM

[K603-3pm-06] Stabilization by Cation-capped

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Orthogonal Approach: Isolation and Properties of a Series of Hydrocarbonic Dications with Multiple 14π-Aromatic Units

Yuki Hayashi[1], Shuichi Suzuki[2], Takanori Suzuki[1], ○Yusuke Ishigaki[1] (1. Faculty of Science, Hokkaido Univ., 2. Graduate School of Engineering Science, Osaka Univ.)

3:00 PM - 3:20 PM

[K603-3pm-07] 3D-shapted N-type organic semiconductors based on naphthothiophene diimide: synthesis and applications

○Masanori Sawamoto[1], Rukiya Matsidik[1], Takimiya Kazuo[1,2] (1. RIKEN, 2. Tohoku University)

3:20 PM - 3:40 PM

K606

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

[K606-3am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Hiroshi Katagiri, Shotaro Hayashi

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

[K606-3am-01] Photo-Induced Crawling Motion of Azobenzene Crystals on a Liquid-Like Surface and its Application for Object Transportation

○Makoto Saikawa[1,2], Mio Ohnuma[2], Yoshihiro Kikkawa[2], Kengo Manabe[2], Koichiro Saito[2], Yasuo Norikane[2,1] (1. Univ. of Tsukuba, 2. AIST)

9:00 AM - 9:20 AM

[K606-3am-02] Polymorphism Driven Photosalient Effect in Tetra-*ortho*-Bromo Azobenzene

○Keegan McGehee[1,2], Dennis Kwaria[1,2], Koichiro Saito[2], Rie Haruki[3], Shunsuke Nozawa[3], Ryo Fukaya[3], Yasuo Norikane[2,1] (1. Graduate School of Pure and Applied Science, University of Tsukuba, 2. Research Institute for Advanced Electronics and Photonics, National Institute of Advanced Industrial Science and Technology, 3. High Energy Accelerator Research Organization)

9:20 AM - 9:40 AM

[K606-3am-03] Reversible crystal stretching behavior of azobenzene with long alkoxy chains by thermal phase transition

○MINGHAO GAO[1,2], Dennis Kwaria[1,2], Hiroyuki Minamikawa[2], Yasuo Norikane[2,1] (1. University of Tsukuba, 2. AIST)

9:40 AM - 10:00 AM

[K606-3am-04] Machine-learning-based material design and condition optimization of generating higher force of photomechanical crystals

○Kazuki Ishizaki[1], Toru ASAHI[1], Takuya TANIGUCHI[1] (1. Waseda University)

10:00 AM - 10:20 AM

[K606-3am-05] Mechanochromic fluorescence properties and supramolecular structural changes exhibited by amphiphilic molecules with anthracene moieties

○QIMING LIU[1], yoshimitsu sagara[1] (1. Tokyo Institute of Technology)

10:20 AM - 10:40 AM

[K606-3am-06] Supramolecular polymer/supramolecular polymer transformation based on kinetic control and an external stimulus~Extended to Stacked forms

○Sukyeong Kim[1], Yusuke Kuramochi[1], Akiharu Satake[1] (1. Grad. Sch. of Sci., Tokyo Univ. of Sci.)

10:40 AM - 11:00 AM

[K606-3am-07] Organogel Actuators Consisting of Redox-Responsive Foldamers

○Taichi Ikeda[1] (1. National Institute for Materials Science)

11:00 AM - 11:20 AM

[K606-3am-08] High-Speed Actuation of Solvent Green 3 Crystals by Photothermally Induced Natural Vibration

○Shodai Hasebe[1], Yuki Hagiwara[1], Taiki Goto[1], Toru Asahi[1], Hideko Koshima[1] (1. Waseda Univ)

11:20 AM - 11:40 AM

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

[K606-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kiichi Amimoto, Yoshimitsu Sagara

1:40 PM - 3:40 PM K606 (K606, Lecture Hall Bldg. [6F])

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[K606-3pm-01] Synthetic design of nitrogen-containing Lewis basic π-conjugated molecules toward fluorescent molecular cocrystals
○Mahiro Nakabayashi[1], Takumi Matsuo[1], Shotaro Hayashi[1] (1. Kochi University of Technology)
1:40 PM - 2:00 PM

[K606-3pm-02] Creating Flexible Molecular Inclusion Crystals and Their Thermo-Triggered Crystal-to-Crystal Phase Transition
○Yuto Hino[1], Shotaro Hayashi[1] (1. Kochi University of Technology)
2:00 PM - 2:20 PM

[K606-3pm-03] Naphtyl-appended fluoranthene crystals with two 2D topologies and their anisotropic fluorescence waveguide
○Takumi Matsuo[1], Yuto Hino[1], Shoaro Hayashi[1] (1. Kochi Univ. of Tech.)
2:20 PM - 2:40 PM

[K606-3pm-04] Synthesis and Fluorescent Properties of Sulfonylaniline Positional Isomers
○Hiroki Sato[1], Kohei Tsujimura[1], Nanami Hoshino[2], Aki Sato[2], Shota Takizawa[1], Hiroshi Katagiri[1,2] (1. Grad. Sch. of Org. Mater. Sci., Yamagata Univ., 2. Grad. Sch. of Sci. and Eng., Yamagata Univ.)
2:40 PM - 3:00 PM

[K606-3pm-05] Crystal Structures and FET Characteristics of Diiodo-substituted Asymmetric Thienoacene Isomers
○Amane Matsunaga[1], Mai Hasada[2], Kakeru Hasumi[1], Daisuke Kumaki[2], Shizuo Tokito[2], Hiroshi Katagiri[1,2] (1. Grad. Sch. of Sci. and Eng., Yamagata Univ., 2. Grad. Sch. of Org. Mater. Sci., Yamagata Univ.)
3:00 PM - 3:20 PM

K602

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

[K602-3pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Shinsuke Inagi, Yousuke Ooyama
1:30 PM - 3:40 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-3pm-01] Electrocatalytic CO_2 insertion into unreactive organic molecules
○Yutaka Saga[1], Nozomi Yamaguchi[1], Toshimichi Kobayashi[1], Mio Kondo[1,2], Shigeyuki Masaoka[1] (1. Osaka Univ., 2. JST PRESTO)
1:30 PM - 1:50 PM

[K602-3pm-02] Electro-Conversion Utilizing Oxygen Reduction Reaction
○Takashi Yamamoto[1], Tsuyoshi Saitoh[2], Yasuaki Einaga[1] (1. Faculty of Science and Technology, Keio Univ., 2. International Institute for Integrative Sleep Medicine, Univ. of Tsukuba)
1:50 PM - 2:10 PM

[K602-3pm-03] Electrochemical Dearomative Carboxylation of Electron-deficient Aromatic Compounds
○Vishal Kumar Rawat[1], Hiroki Hayashi[1,2], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)
2:10 PM - 2:30 PM

[K602-3pm-04] Evaluation of reactivities of aryls under electrochemical conditions by using oxidation potential gap (ΔE_{ox})
○Kazuhiro Okamoto[1], Naoki Shida[1], Haruka Morizumi[2], Yoshikazu Kitano[2], Kazuhiro Chiba[2] (1. Yokohama National Univ., 2. Tokyo Univ. of Agric. and Technol.)
2:40 PM - 3:00 PM

[K602-3pm-05] Development of π-extended iodoarene mediator for electrochemical C-N coupling and its kinetics
○Naoki Shida[1], Shohei Yoshinaga[1], Mahito Atobe[1] (1. Yokohama National University)
3:00 PM - 3:20 PM

[K602-3pm-06] Electrochemical Synthesis of Hetero[7]helicenes, Dehydro-hetero[7]helicenes and Hetero[8]circulenes with Intriguing Optical Features
○Mohamed S. H. Salem[1], Md Imrul Khalid[1], Ahmed Sabri[1], Hiroaki Sasai[1], Shinobu Takizawa[1] (1. SANKEN, Osaka University, Ibaraki-shi, Osaka 567-0047, Japan)
3:20 PM - 3:40 PM

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

[K602-3vn] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Kazuhide Nakata, Satoshi Usui
4:10 PM - 6:00 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-3vn-01] Heterocyclic Effect on Quinoidal Character of Tetraradicals
○Takuma Miyamura[1], Jin Ayatsuka[1], Manabu Abe[1] (1. Hiroshima University)
4:10 PM - 4:30 PM

[K602-3vn-02] Substituent effects on gas-phase stabilities of phenylcyclopentyl cations
○Kazuhide Nakata[1] (1. Hosei Univ.)
4:30 PM - 4:50 PM

[K602-3vn-03] Automated Reaction Path Search for Stereospecific Pericyclic Reaction Using the AFIR Method
○Tsuyoshi Mita[1,2], Hideaki Takano[1,2], Hiroki Hayashi[1,2], Kanna Wataru[3], Yu Harabuchi[1,2,3], K N Houk[4], Satoshi Maeda[1,2,3] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ., 4. Univ. of California Los Angeles)
4:50 PM - 5:10 PM

[K602-3vn-04] Computational study of noncovalent interactions in Rh-catalyzed [2+2+2] cycloadditions
○Yuki Nagashima[1], Ryota Abe[1], Jin Tanaka[1], Ken Tanaka[1] (1. Tokyo Institute of Technology)
5:20 PM - 5:40 PM

[K602-3vn-05] Catalytic Olefin Aminocarboxylation with Aminium Radical Cation and CO_2: Synthesis of β-Amino Acids Based on Quantum Chemical Calculations
○Wataru Kanna[1], Yu Harabuchi[2,3,4], Hitomi Katsuyama[2,3], Hideaki Takano[2,3], Hiroki Hayashi[2,3], Tsuyoshi Mita[2,3], Satoshi Maeda[2,3,4] (1. Grad. School of Chem. Sci. and Eng, Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. JST-ERATO, 4. Fac. of Sci, Hokkaido Univ.)
5:40 PM - 6:00 PM

K705

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

[K705-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Kazunobu Igawa, Keisuke Asano
1:10 PM - 3:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-3pm-01] Photocatalytic transfer hydrogenation from water to carbon– carbon multiple bonds of unsaturated carboxylic acids
○Farzaneh SOLEYMANIMOVAHED[1], Shogo Mori[1], Daling Lu[2], Takashi Hisatomi[2], Kazunari Domen[2], Susumu Saito[1] (1. Nagoya University, 2. Shinshu University)
1:10 PM - 1:30 PM

[K705-3pm-02] Development of Photoinduced α-Alkylation Reactions of Carbonyl Compounds with Alkenes
○Yasuhiro Yamashita[1], Shu Kobayashi[1] (1. The University of Tokyo)
1:30 PM - 1:50 PM

[K705-3pm-03] Modular Synthesis of 1,4-Dicarbonyl Compounds via Sequential Photocatalysis Using Ambiphilic Radical Linchpin
○Akira Matsumoto[1], Keiji Maruoka[1,2] (1. Kyoto University, 2. Guangdong University of Technology)
1:50 PM - 2:10 PM

[K705-3pm-04] Development of Visible Light-Gated Bifunctional Cyclooctene Catalysts
○Tagui NAGANO[1], Keisuke ASANO[2], Daisuke URAGUCHI[2] (1. Kyoto Univ., 2. Hokkaido Univ.)
2:10 PM - 2:30 PM

[K705-3pm-05] Reduction of Nitriles, Aldehydes, and Ketones with Tetrahydroxydiborn Catalyzed by an Amphiphilic Resin-Supported Nanopalladium Catalyst
○Kaili Zhang[1,2], Aya Tazawa[1], Shintaro Okumura[1,2], Yasuhiro Uozumi[1,2] (1. Institute for Molecular Science , 2. The Graduate University for Advanced Studies)
2:40 PM - 3:00 PM

[K705-3pm-06] Electrochemical Allylation Reactions Catalyzed by Nitrogen-Doped Carbon Supported Zinc Electrodes
○Ryusuke Masuda[1], Tomohiro Yasukawa[1],

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Yasuhiro Yamashita[1], Shu Kobayashi[1] (1. The Univ. of Tokyo)
3:00 PM - 3:20 PM

[K705-3pm-07] Continuous-flow enantioselective hydroacylations with chiral heterogeneous Rh catalysts and sequential-flow transformations
○Yuki Saito[1], Shū Kobayashi[1] (1. The University of Tokyo)
3:20 PM - 3:40 PM

D1443

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

[D1443-3am] 16. Natural Products Chemistry, Chemical Biology

Chair: Atsushi Shimoyama, Daisuke Takahashi
9:00 AM - 10:00 AM D1443 (1443, Bldg. 14 [4F])

[D1443-3am-01] Posttranslational glycan modification in *Thermococcus kodakarensis*: discovery and synthesis of *myo*-inositol containing *N*-glycan
○Kohtaro Hirao[1], Yoshiyuki Manabe[1,2], Koichi Fukase[1,2] (1. Graduate School of Science, Osaka University, 2. Forefront Research Center, Osaka University)
9:00 AM - 9:20 AM

[D1443-3am-02] Synthesis of acetic acid bacteria *Acetobacter pasteurianus* lipid A
○Haruki Yamaura[1], Atsushi Shimoyama[1], Koichi Fukase[1] (1. Osaka university)
9:20 AM - 9:40 AM

[D1443-3am-03] Synthetic Study in Dendritic Glycosylation Contributing to Assembly of Diverse High-mannose-type Glycan Library
○Ruchio Usui[1], Megumi Kabasawa[1], Taiki Kuribara[1], Kiichiro Totani[1] (1. Seikei University)
9:40 AM - 10:00 AM

E1661

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

[E1661-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Shinya Ariyasu, Shun Hirota
9:00 AM - 11:30 AM E1661 (1611, Bldg. 16 [1F])

[E1661-3am-01] **Accumulation of Protein Cage into in-cell Protein Crystal**
○THUC TOAN PHAM[1], Koki Date[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology/ School of Life Science and Technology)
9:00 AM - 9:20 AM

[E1661-3am-02] Construction of Antifreeze protein like semi-clathrate hydrate in the ferritin cage
○Jiaxin Tian[1], Maity Basudev[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)
9:20 AM - 9:40 AM

[E1661-3am-03] Structure analysis of pH-responsive piston dynamics of R-body
○Koki DATE[1], Thuc Toan PHAM[1], Hyeonho LEE[1], Takayuki UCHIHASHI[2], Hironari KAMIKUBO[3], Chihong SONG[4], Kazuyoshi MURATA[4], Takafumi UENO[1] (1. School of Life Science and Technology, Tokyo Institute of Technology, 2. Graduate School of Science, Nagoya University, 3. School of Science and Technology, NAIST, MS, 4. ExCELLS/NIPS)
9:40 AM - 10:00 AM

[E1661-3am-04] Developing protein-cellulose nanocrystal hybrid films for structural coloration
○Kosuke Kikuchi[1], Bruno Frka-Petesic[2], Silvia Vignolini[2], Takafumi Ueno[1] (1. Tokyo Institute of Technology, 2. University of Cambridge)
10:00 AM - 10:20 AM

[E1661-3am-05] Construction of a stimuli-responsive cytochrome *c*-based hydrogel driven by its folding and unfolding behavior
○Kazuki Kageyama[1], Takahiro Urayama[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka university)
10:30 AM - 10:50 AM

[E1661-3am-06] Development of Myoglobin-based Artificial Metalloenzymes: Nitrile Synthesis via Dehydration of Aldoximes
○Miteki Abe[1], Shunsuke Kato[1], Takashi

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Hayashi[1] (1. Osaka University)
10:50 AM - 11:10 AM

[E1661-3am-07] ATP Responsive Two-Dimensional Biomaterial from Biomolecular machine GroEL
○TONMOY RAY[1,2], TAKUZO AIDA[1,2] (1. The University of Tokyo, 2. RIKEN CEMS)
11:10 AM - 11:30 AM

E1662

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

[E1662-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Hiroshi Nonaka, Yusuke Nasu
9:00 AM - 11:30 AM E1662 (1612, Bldg. 16 [1F])

[E1662-3am-01] Screening of catalytic antibodies against PD-1 and PD-L1 and the features of clones obtained
Emi Hifumi[2], Tamami Nonaka[2], Hiroaki Taguchi[3], ○Taizo Uda[1,2] (1. ISIT, 2. OIta Univ., 3. Suzuka Univ. Med. Sci.)
9:00 AM - 9:20 AM

[E1662-3am-02] Generation of stable microtubule superstructures induced by Tau-derived peptide-fused tetrameric proteins
○Hiroshi Inaba[1], Yurina Sueki[1], Muneyoshi Ichikawa[2], Arif Md. Rashedul Kabir[3], Takashi Iwasaki[4], Akira Kakugo[3], Kazuki Sada[3], Kazunori Matsuura[1] (1. Graduate School of Engineering, Tottori University, 2. Graduate School of Science and Technology, Nara Institute of Science and Technology, 3. Graduate School of Science, Hokkaido University, 4. Graduate School of Agricultural Sciences, Tottori University)
9:20 AM - 9:40 AM

[E1662-3am-03] Artificial control of protein secretion using thermogenetic dissociation module
○Mizuki Endo[1], Takeaki Ozawa[1] (1. The University of Tokyo)
9:40 AM - 10:00 AM

[E1662-3am-04] Genetically encoded fluorescent biosensors for L-lactate
○Yusuke Nasu[1], Yuki Kamijo[1], Giang Le[1], Saaya Hario[1], Robert E Campbell[1] (1. The University of Tokyo)
10:00 AM - 10:20 AM

[E1662-3am-05] Development of new labeling reagents for endogenous receptors in the live mouse brain and their application to multiplex imaging
○Hiroshi Nonaka[1,2], Mengchu Wang[3], Takuma Takeshi[1], Kazuki Shiraiwa[1], Seiji Sakamoto[1,2], Itaru Hamachi[1,2] (1. Graduate School of Engineering, Kyoto Univ., 2. JST, ERATO, 3. Faculty of Engineering, Kyoto Univ.)
10:30 AM - 10:50 AM

[E1662-3am-06] Photooxidation-driven proximity labeling for mapping neurotransmitter receptor interactome in live mouse brain
○Tomonori Tamura[1], Mikiko Takato[1], Seiji Sakamoto[1,2], Hiroshi Nonaka[1,2], Itaru Hamachi[1,2] (1. Kyoto University, 2. JST ERATO)
10:50 AM - 11:10 AM

[E1662-3am-07] Identification of a gene involved in lanthanide switch by analysis of the mutants isolated during the cultivation of *Methylosinus trichosporium* OB3b with glycerol
○Wataru Shiina[1], Hidehiro Ito[1], Toshiaki Kamachi[1] (1. Tokyo Institute of Technology)
11:10 AM - 11:30 AM

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

[E1662-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Hideaki Yoshimura, Kenji Monde
1:10 PM - 3:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-3pm-01] Signal transduction mechanism of membrane receptors on ligand binding and cluster formation: Analysis through single-molecule imaging.
○Hideaki Yoshimura[1], Takeaki Ozawa[1] (1. The University of Tokyo)
1:10 PM - 1:30 PM

[E1662-3pm-02] Quantitative analysis of Akt isoform-specific temporal activation dynamics and downstream signaling regulation

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with mathematical model-aided optogenetics

○Yuka Sekine[1], Genki Kawamura[1], Takeaki Ozawa[1] (1. The University of Tokyo)

1:30 PM - 1:50 PM

[E1662-3pm-03] Dissecting the role of Akt2 in cellular metabolism by optogenetics-aided trans-omics analysis

○Genki Kawamura[1], Takeaki Ozawa[1] (1. The University of Tokyo)

1:50 PM - 2:10 PM

[E1662-3pm-04] Development of photoreactive sphingomyelin synthase 2 inhibitors and evaluation of its binding domain analysis

○Mirano Abe[1], Yuta Murai[1], Takeo Sato[1], Miho Sanagi[1], Susumu Mitsutake[2], Makoto Taniguchi[3], Kenji Monde[1] (1. Hokkaido University, 2. Saga University, 3. Kanazawa Medical University)

2:10 PM - 2:30 PM

[E1662-3pm-05] Contribution of moleculae weight of ligand functionalized poly-L-glutamates to the inhibition of cancer cell proliferation

○Masahiko Nakamoto[1], Yuki Koba[1], Michiya Matsusaki[1] (1. Osaka University)

2:40 PM - 3:00 PM

[E1662-3pm-06] Point-of-care electrochemical biosensors for measuring anti-SARS-CoV-2 neutralising IgG/sIgA antibodies and antioxidant activity in saliva

○Eiichi Tamiya[1,2], Shuto Osaki[1], Tomoko Tsuchihashi[3], Hiromi Ushijima[3], Keiichi Tsukinoki[4] (1. AIST, 2. Osaka Univ., 3. Biodevicetechnology Ltd., 4. Kanagawa Dental Univ.)

3:00 PM - 3:20 PM

[E1662-3pm-07] Determination of Permeation Kinetics of Coumarin at Lipid Bilayer of Liposomes by Using Capillary Electrophoresis with Moment Analysis Theory

○Kanji Miyabe[1], Shunta Inaba[1], Momoko Umeda[1] (1. Rikkyo University)

3:20 PM - 3:40 PM

E1661

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

[E1661-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Hisae Tateishi-Karimata, Yousuke Katsuda
1:30 PM - 3:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-3pm-01] Exploring new methods in regulating circular RNA production using cellular model

○Lu Ni[1], Takeshi Yamada[1], Kazuhiko Nakatani[1] (1. Osaka University)

1:30 PM - 1:50 PM

[E1661-3pm-02] Synthesis of Hoechst-modified DNA that accumulated in the cell nucleus and its application.

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

1:50 PM - 2:10 PM

[E1661-3pm-03] A nucleic acid medicine that suppresses target gene expression based on RNA structure hacking

○Takuto Kamura[1], Yousuke Katsuda[1], Taishi Nakamura[2,3], Kenichi Tsujita[3], Yusuke Kitamura[1], Masaki Hagihara[4], Shin-ichi Sato[5], Toshihiro Ihara[1] (1. Faculty of Advanced Science and Technology, Kumamoto University, 2. Department of Medical Information Sciences and Administration Planning, Kumamoto University Hospital, 3. Department of Cardiovascular Medicine, Faculty of Life Sciences, Kumamoto University, 4. Faculty of Science and Technology, Hirosaki University, 5. Institute for Chemical Research, Kyoto University)

2:10 PM - 2:30 PM

[E1661-3pm-04] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (88): Mechanism of C-quadruplexes formations in response to environmental changes in cancer cells

○Hisae Tateishi-Karimata[1], Keiko Kawauchi[2], Naoki Sugimoto[1,2] (1. Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, 2. Graduate School of Frontiers of Innovative Research in Science

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and Technology (FIRST), Konan University)
2:40 PM - 3:00 PM

[E1661-3pm-05] Epigenetic methylations suppress droplet formation of DNA G-quadruplex and Arg-rich peptide
○Mitsuki Tsuruta[1], Keiko Kawauchi[1], Naoki Sugimoto[1,2], Daisuke Miyoshi[1] (1. Konan university, FIRST, 2. Konan university, FIBER)
3:00 PM - 3:20 PM

[E1661-3pm-06] Effect of structural selective G4 ligand on telomere length and TERRA expression level
○Yoshiki Hashimoto[1], Takeru Torii[1], Natsuki kinoshita[1], Keiko Kawauchi[1], Hisae Tateishi-Karimata[2], Naoki Sugimotgo[1,2], Daisuke Miyoshi[1] (1. FIRST, Konan University, 2. FIBER, Konan University)
3:20 PM - 3:40 PM

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

[E1661-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Hidetaka Torigoe, Yuichiro Aiba
4:10 PM - 6:30 PM E1661 (1611, Bldg. 16 [1F])

[E1661-3vn-01] The first detection of the formation of DNA triplex structure in living human cells and an analysis of base pair dynamics under molecular crowding environment
○Tomoki Sakamoto[1,2], Yudai Yamaoki[1,2], Takashi Nagata[1,2], Masato Katahira[1,2] (1. Institute of Advanced Energy, 2. Graduate School of Energy Science, Kyoto University)
4:10 PM - 4:30 PM

[E1661-3vn-02] Investigation of parallel-stranded PNAs for the formation of an invasion complex with double-stranded DNA
○Masanari Shibata[1], Yuichiro Aiba[1], Masaki Hibino[1], Osami Shoji[1] (1. Nagoya University)
4:30 PM - 4:50 PM

[E1661-3vn-03] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (81) : Stability prediction of RNA duplexes under various molecular crowding in vitro and in cell
○Saptarshi Ghosh[1], Shuntaro Takahashi[1], Dipanwita Banerjee[1], Tatsuya Ohyama[1], Tamaki Endoh[1], Hisae Tateishi-Karimata[1], Naoki Sugimoto[1,2] (1. FIBER, Konan University, 2. FIRST, Konan University)
4:50 PM - 5:10 PM

[E1661-3vn-04] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (82) : Applications of nearest-neighbor parameters for RNA/DNA hybrid duplexes in the advancement of therapeutics
○Dipanwita Banerjee[1], Hisae Tateishi-Karimata[1], Saptarshi Ghosh[1], Shuntaro Takahashi[1], Tatsuya Ohyama[1], Tamaki Endoh[1], Maria Toplishek[2], Marko Trajkovski [2], Janez Plavec[2,3,4], Naoki Sugimoto[1,5] (1. FIBER, Konan University, 2. Slovenian NMR Centre, National Institute of Chemistry, 3. EN→FIST Centre of Excellence, 4. Faculty of Chemistry and Chemical Technology, University of Ljubljana, 5. FIRST, Konan University)
5:10 PM - 5:30 PM

[E1661-3vn-05] Development of single nucleotide polymorphism detection method based on the specific formation of T-Hg-T and C-Ag-C metal-mediated base pair
Kohsei Sekiya[1], Akira Ono[2], ○Hidetaka Torigoe[1] (1. Tokyo University of Science, 2. Kanagawa University)
5:30 PM - 5:50 PM

[E1661-3vn-06] Photosensitized oxidation of NADH analogue by hydrophobic phosphorus(V) porphyrins
○Hiroko Hasegawa[1], Kazutaka Hirakawa[1,2] (1. Department of Optoelectronics and Nanostructure Science, Graduate School of Science and Technology, Shizuoka University, 2. Applied Chemistry and Biochemical Engineering Course, Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University)
5:50 PM - 6:10 PM

[E1661-3vn-07] Pore-wall modification of platinum porphyrin co-condensed mesoporous silica nanoparticles and their application to intracellular oxygen concentration imaging

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○Shunsuke Odai[1], Junpei Noguchi[1], Arisa Yamauchi[1], Hidehiro Ito[1], Masaki Okamoto[2], Toshiaki Kamachi[1] （1. Tokyo institute of technology, 2. Keio University）
6:10 PM - 6:30 PM

K304

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

[K304-3am] 18. Polymer

Chair: Takashi Miyata, Toshikazu Ono
9:00 AM - 11:20 AM K304 (K304, Lecture Hall Bldg. [3F])

[K304-3am-01] Mechanochromic elastomer showing optical property modulation by planarization and aggregation of bent boron complexes
○Toshikazu Ono Ono[1,2], Momoka Maeda[1], Luxia Cui[1], Shimakoshi Hisashi[1], Hoshino Yu[1] （1. Graduate School of Engineering, Kyushu University, 2. Center for Molecular Systems (CMS), Kyushu University）
9:00 AM - 9:20 AM

[K304-3am-02] Thermoelectric conversion and electrochemical refrigeration using a coil–globule phase transition
○Hongyao Zhou[1], Fumitoshi Matoba[1], Ryohei Matsuno[1], Yusuke Wakayama[1], Teppei Yamada[1] （1. The University of Tokyo）
9:20 AM - 9:40 AM

[K304-3am-03] Supramolecular Miktoarm Star Copolymer with a Zinc Phthalocyanine Core for Organic Transistor Memory
○XINHAO ZHONG[1,2], JUNKO AIMI[2], MASAYUKI TAKEUCHI[1,2] （1. University of Tsukuba, 2. National Institute for Materials Science）
9:40 AM - 10:00 AM

[K304-3am-04] Interplay Between π-Conjugated Polymer Donors and Acceptors Determines Crystalline Order of Their Blends and Photovoltaic Performance
○Kodai Yamanaka[1], Masahiko Saito[1], Itaru Osaka[1] （1. The Univ. of Hiroshima）
10:00 AM - 10:20 AM

[K304-3am-05] Development of the new high metallic waterborn paint which cellulose nano fiber is used for as a viscosity agent
○Takao Tsukimori[1] （1. Toyota Motor Corporation）
10:20 AM - 10:40 AM

[K304-3am-06] Design of aromatic polyesters having sulfobetaine structure and their surface properties
○Akifumi Kawamura[1,2], Rika Itomitsu[1], Takashi Miyata[1,2] （1. Fac. Chem. Materials, Bioeng., Kansai Univ., 2. ORDIST, Kansai Univ.）
10:40 AM - 11:00 AM

[K304-3am-07] Design of Stimuli-responsive Polymers with Cyclodextrins and Detection of Denatured Proteins
○Takashi Miyata[1], Kanoko Murayama[1], Akifumi Kawamura[1] （1. Kansai Univ.）
11:00 AM - 11:20 AM

K301

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

[K301-3pm] 18. Polymer

Chair: Kohsuke Kawabata, Tsuyoshi Nishikawa
1:20 PM - 3:40 PM K301 (K301, Lecture Hall Bldg. [3F])

[K301-3pm-01] Polymer Degradation Unlocked by Synergistic Dual Stimuli: Base Interaction and Photocatalysis on Boryl Pendants Leading to Main-Chain Scission
○Hiroshi Makino Makino[1], Tsuyoshi Nishikawa[1], Makoto Ouchi[1] （1. Grad. Sch. of Eng., Kyoto Univ.）
1:20 PM - 1:40 PM

[K301-3pm-02] Synthesis of Self-Healing Elastomers by Scandium-Catalyzed Terpolymerization of Ethylene, Styrene and Dimethylaminophenyl-Substituted Propylene
○Haoran Zhang[1,2], Xia Wu[2], Lin Huang[2], Masayoshi Nishiura[2], Tetsuro Murahashi[1], Zhaomin Hou[2] （1. Tokyo Tech, 2. RIKEN）
1:40 PM - 2:00 PM

[K301-3pm-03] Polymers containing ester and ketone groups in chains: synthesis and their biodegradability
○Haobo Yuan[1], Kohei Takahashi[1], Shinya Hayashi[1], Chifeng Li[2], Kazuya Yamaguchi[2], Miwa Suzuki[3], Kenichi Kasuya[3,4], Kyoko Nozaki[1]

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（1. Grad. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Applied Chem., The Univ. of Tokyo, 3. GUCFW, 4. Grad. Sch. of Sci. Tech., Gunma Univ.）

2:00 PM - 2:20 PM

[K301-3pm-04] Synthesis of self-healing elastomers by scandium-catalyzed copolymerization of ethylene with thioether substituted propylenes

○Mingjun Chi[1,2], Hao Wang[2], Lin Huang[2], Haoran Zhang[2], Xiaobin Lin[2], Masayoshi Nishiura[2], Zhaomin Hou[2] （1. Saitama University, 2. RIKEN）

2:20 PM - 2:40 PM

[K301-3pm-05] Designing Thermally Stable Organocatalysts for Poly(ethylene terephthalate) Synthesis: Toward a One-Pot, Closed-Loop Chemical Recycling System for PET

○Shu Kaiho[1,2], Ali Al Rida Hmayed[2], Kayla R. Delle Chiaie[2], Joshua C. Worch[2], Andrew P. Dove[2] （1. Toray Industries, Inc., 2. University of Birmingham）

2:40 PM - 3:00 PM

[K301-3pm-06] Self-assembled Structure of Amphiphilic Polythiophenes with Asymmetric Electronic Structures and its Photovoltaic Properties

○Kohsuke Kawabata[1,2], Kazuo Takimiya[1,2] （1. Tohoku Univ., 2. RIKEN）

3:00 PM - 3:20 PM

[K301-3pm-07] Pathway complexity in the self-assembly process of platinum complexes possessing TEG chains

○Takehiro Hirao[1], Masaya Yoshida[1], Takeharu Haino[1,2] （1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM2, Hiroshima University）

3:20 PM - 3:40 PM

B444

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

[B444-3pm] 19. Colloid and Interface Chemistry

Chair: Taisuke Banno, Yusuke Yonamine

1:30 PM - 3:40 PM B444 (444, Bldg. 4 [4F])

[B444-3pm-01] Challenges and recent progresses in experimental quantification of materials optical properties

○Dongmao Zhang[1] （1. Mississippi State University）

1:30 PM - 1:50 PM

[B444-3pm-02] Glycolipid-Type Amphiphiles with An Anilinochloromaleimide-Based Luminogen Exhibiting Aggregation-Induced Emission

Naoki Tsutsumi[1], Akitaka Ito[2], Yosuke Niko[1], Yui Bando[1], Kiyonori Takahashi[3], Masato Ikeda[4], Takayoshi Nakamura[3], Masayuki Izumi[1], ○Rika Ochi[1] （1. Kochi Univ., 2. Kochi Univ. of Tech., 3. Hokkaido Univ., 4. Gifu Univ.）

1:50 PM - 2:10 PM

[B444-3pm-03] Aggregation behavior and thickening ability of nonionic low molecular amphiphiles having CO_2-philic trimethylsilyl and CO_2-phobic hydrocarbon groups in supercritical CO_2

○Kosuke Sato[1], Atsushi Yshizawa[1], Shirin Alexander[2], Julian Eastoe[3], Masanobu Sagisaka[1] （1. Graduate School of Science and Technology, Hirosaki University, 2. Energy Safety Research Institute (ESRI), Swansea University, 3. School of Chemistry, University of Bristol）

2:10 PM - 2:30 PM

[B444-3pm-05] Formation of organic-inorganic hybrid cubic phase by the self-assembly of a synthetic lipid with alkoxysilyl groups.

○Miki Kariya[1], Kenichiro Omoto[1], Gwénaël Rapenne[1], Kazuma Yasuhara[1] （1. Nara Institute of Science and Technology）

3:00 PM - 3:20 PM

[B444-3pm-06] Clarification of the relationship between the lipid membrane properties and membrane deformation

○Yukihiro Okamoto[1,2], Zach Nicolella[1], Yoichiro Hasunuma[1], Nobuyuki Yoshioka[1], Nozomi Watanabe[1], Hiroshi Umakoshi[1] （1. Graduated School of Engineering Science, Osaka University, 2. Graduated School of Engineering Science, the Multidisciplinary Research Laboratory System at Osaka

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University)

3:20 PM - 3:40 PM

K206

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

[K206-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Kazu Okumura, Tsukasa Torimoto
1:30 PM - 3:40 PM K206 (K206, Lecture Hall Bldg. [2F])

[K206-3pm-01] Evaluation of Photostability and Photodegradation Reaction in Lanthanide Complex

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

1:30 PM - 1:50 PM

[K206-3pm-02] Mechano-Bactericidal Effect in Water Synthesis and Functional Evaluation of TiO_2 Nanopillars

○Tomoya Shirasaka[1,2], Kaoru Igarashi[1], Yukari Miyazaki[2], Nobuaki Negishi[2] (1. ChibaTech., 2. AIST)

1:50 PM - 2:10 PM

[K206-3pm-03] In Operando XAFS on Local Structure and Electronic State of Tungsten Oxide Nanoparticles with Different Crystal Structure under Electrochromism

○Mari Takahashi[1], Yuki Kitazaki[1], Masafumi Harada[2], Shinya Maenosono[1] (1. Japan Advanced Institute of Science and Technology, 2. Nara Women's University)

2:10 PM - 2:30 PM

[K206-3pm-04] *ortho*-Substituent Structure Effects of Aryldiazonium Salts on Defect Photoluminescence Generation in Locally Functionalized Single-walled Carbon Nanotubes

○Tomohiro Shiraki[1,2], Sadahito Naka[1], Boda Yu[1], Tsuyohiko Fujigaya[1,2,3] (1. Grad. School of Eng., Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)

2:40 PM - 3:00 PM

[K206-3pm-05] Photoinduced electron doping of single-walled carbon nanotubes

○Naoki Tanaka[1,2], Taiki Ishii[1], Tsuyohiko Fujigaya[1,2,3] (1. Department of Applied Chemistry, Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)

3:00 PM - 3:20 PM

[K206-3pm-06] Flash Lamp Annealing Synthesis of Platinum Group High-Entropy Alloy Nanoparticles

○Yuji Shinkai[1], Tetsu Yonezawa[1] (1. Hokkaido University)

3:20 PM - 3:40 PM

K303

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

[K303-3pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Ryoichi Tatara, Takane Imaoka
1:30 PM - 3:40 PM K303 (K303, Lecture Hall Bldg. [3F])

[K303-3pm-01] Gas-fed liquid-covered cathode electrodes used for direct electrochemical reduction of dilute CO_2 in a flue gas

○Yasuhiko Takeda[1], Shintaro Mizuno[1], Ryuichi Iwata[1], Takeshi Morikawa[1], Naohiko Kato[1] (1. Toyota Central Research and Development Laboratories, Inc.)

1:30 PM - 1:50 PM

[K303-3pm-02] Composition dependence of sub-nanoparticle catalysts in electrocatalytic reactions

○Tadatoshi Iitsuka[1], Kana Shimizu, Takane Imaoka[1], Kimihisa Ymamoto[1] (1. Lab. Chem. Life Sci., Tokyo Tech.)

1:50 PM - 2:10 PM

[K303-3pm-03] Reduced Graphene Oxide Supported Transition Metal Oxide Electrocatalysts for Zinc-Air and Zinc-Air Flow Batteries

○Wei Jian Sim[1], Mai Thanh Nguyen[1], Tetsu Yonezawa[1] (1. Hokkaido University)

2:10 PM - 2:30 PM

[K303-3pm-04] Application of Sulfolane-based Concentrated Electrolytes to Potassium-ion Battery

○Ryoichi Tatara[1], Daisuke Igarashi[1], Tomooki Hosaka[1], Shinichi Komaba[1] (1. Tokyo University of Science)

2:40 PM - 3:00 PM

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[K303-3pm-05] Li and Na organic batteries with porphyrinoid electrodes
○Ji-Young Shin[1], Jikwang Hwang[2] (1. Nagoya Univerity, 2. Kyoto University)
3:00 PM - 3:20 PM

[K303-3pm-06] Study of Cathodic Reaction for Lithium-O_2 Battery by Opelando XRD Measurements
○Makoto Aoki[1], Dilinigeer Dilixiati[1], Minako Ushijima[1], Suzumi Yamada[1], Toshihiro Kondo[1] (1. Ochanomizu university)
3:20 PM - 3:40 PM

K207

Academic Program [Oral B] | 22. Resources Utilization Chemistry, Environmental and Green Chemistry | Oral B

[K207-3pm] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Chair: Kenji Kitayama, Seiji Yamazoe
1:10 PM - 3:40 PM K207 (K207, Lecture Hall Bldg. [2F])

[K207-3pm-01] Catalytic terpolymerization of CO_2, epoxides and heteroallenes (2)
○Koichi Nakaoka[1], Satoshi Muranaka[1], Io Yamamoto[1], Chihiro Maeda[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Technol., Okayama Univ.)
1:10 PM - 1:30 PM

[K207-3pm-02] Formic acid formation from supercritical CO_2 catalyzed by Ir complexes
○Seo Ono[1,2], Ryoichi Kanega[2], Hajime Kawanami[2] (1. University of Tsukuba, 2. AIST)
1:30 PM - 1:50 PM

[K207-3pm-03] Synthesis of Glyoxal by Oxidation of Glycolaldehyde Using Ruthenium Complex Catalysts
○Takuya Sagawa[1], Atsushi Kondo[1], Mineo Hashizume[1] (1. Tokyo University of Science)
1:50 PM - 2:10 PM

[K207-3pm-04] Black coloration of wool fibers using inositol oxides
○Takeru Ohe[1], Yurika Yoshimura[1] (1. Osaka Research Institute of Industrial Science and Technology)
2:10 PM - 2:30 PM

[K207-3pm-05] Fabrication of amine immobilized silica with high amine density for capturing low-concentration CO_2
○Soichi Kikkawa[1], Miori Kataoka[1], Seiji Yamazoe[1,2] (1. Tokyo Metropolitan Univ., 2. PREST, JST)
2:40 PM - 3:00 PM

[K207-3pm-06] Development of Direct Air Capture system using liquid-Solid Phase Separation
○Seiji Yamazoe[1,2,3], Soichi Kikkawa[1,3], Kazushi Amamoto[1], Yu Fujiki[1], Jun Hirayama[1,3], Gen Kato[1], Hiroki Miura[1,3], Tetsuya Shishido[1,3] (1. Tokyo Metropolitan University, 2. PRESTO, 3. ESICB, Kyoto University)
3:00 PM - 3:20 PM

[K207-3pm-07] Solubilization of lignocelluloses in organic acid and structural characterization of biomass film
○Naoko Kobayashi[1,2], Tomohiro Hashizume[1,3], Keiko Kondo[1,4], Masato Katahira[1,4], Kenji Kitayama[1,3], Takashi Watanabe[1,2] (1. Biomass Product Tree Industry-Academia Collaborative Research Laboratory, 2. Research Institute for Sustainable Humanosphere, 3. Daicel Corporation, 4. Institute of Advanced Energy)
3:20 PM - 3:40 PM

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

[K303-3am] 01. Education and History of Chemistry

Chair: Akira Ikuo, Masashi Osa

Fri. Mar 24, 2023 9:00 AM - 10:30 AM K303 (K303, Lecture Hall Bldg. [3F])

[K303-3am-01] Microscale Experiments for Physically Challenged Students -The Practice of Experiments on Quantitative Relationships in Chemical Reactions-

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

9:00 AM - 9:20 AM

[K303-3am-02] Development of Superabsorbent Polymers into Chemistry Educational Materials

○Masashi Osa[1] （1. Aichi University of Education）

9:20 AM - 9:40 AM

[K303-3am-03] Development and Evaluation of Thermochemical Teaching Material for Visualizing Catalysis Using Cobalt Chloride

○Masashi Yamada[1], Izumi Imai[1] （1. Toho University）

9:50 AM - 10:10 AM

[K303-3am-04] Development of Experimental Program for Pre-serviceTeacher Education: Toward a conceptual understanding of reaction rate

○Takashi Hosoe[1], Akira Ikuo[2], Hisao Kokusen[1], Haruo Ogawa[2] （1. The United Graduate School of Education, Tokyo Gakugei University, 2. Faculty of Education, Tokyo Gakugei University）

10:10 AM - 10:30 AM

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肢体不自由生徒のためのマイクロスケール実験
～「化学反応の量的関係」を実験する上での工夫～

（筑波大附属桐が丘特支[1]・東北大院理[2]）○山田　一幸[1]・荻野　和子[2]

Microscale Experiments for Physically Challenged Students
-The Practice of Experiments on Quantitative Relationships in Chemical Reactions-

([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.

In this paper, we report the practice of experiment on the quantitative relationships in chemical reactions carried out by physically challenged students.

Keywords : Microscope Experiment, Physically Challenged Students, Quantitative Relationships in Chemical Reactions

肢体不自由のある児童生徒には、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が肢体不自由児に学習上の困難を生じさせ、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)]。

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 の開発と実践例として、「化学反応の量的関係」の工夫と実践について報告する。

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

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高吸水性ポリマーの化学実験教材化の検討

（愛知教育大）長　昌史

Development of Superabsorbent Polymers into Chemistry Educational Materials

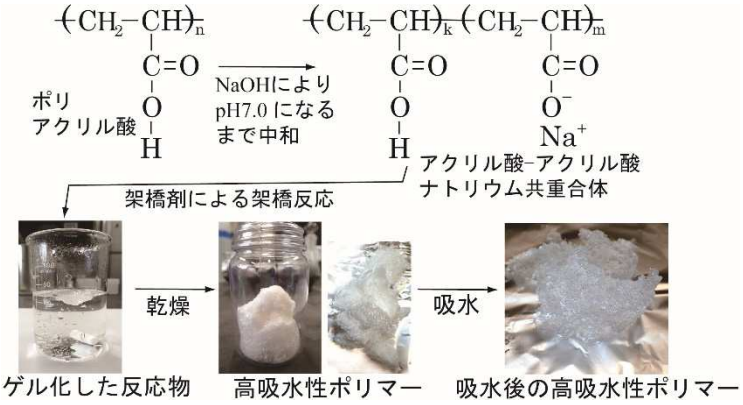
(*Department of Chemistry, Aichi University of Education*) Masashi Osa

We have developed a method for synthesizing superabsorbent polymers that can be practiced in the field of education. The water absorption of the synthesized superabsorbent polymers against pure water or aqueous solutions of some kinds of salts was measured. It was shown that the water absorption of the superabsorbent polymers varies widely depending on the salt concentration of the aqueous solutions, the kind of salt, and the kind and molecular weight of the polymer used as the material for the superabsorbent polymer.

Keywords : Superabsorbent Polymers; Chemistry Educational Materials; Water Absorption; Poly(acrylic acid); Polymer gel

教育現場においても実践可能な方法で、高吸水性ポリマーの合成方法および吸水率の測定方法を開発した。合成により得られた高吸水性ポリマーの、純水や塩水溶液に対する吸水率を測定した。高吸水性ポリマーの吸水率は、吸水させた水溶液の塩濃度、塩の種類、および高吸水性ポリマーの材料として用いた高分子の種類や分子量に依存して、多様に変化することを示した。

高吸水性ポリマーの合成方法および吸水率の測定方法を解説した実験動画を作成し、You Tube で限定公開し、URL にアクセスすることで視聴できるようにした。右下に、演者が作成した実験動画を視聴するための QR コードを示す。ご興味のある方は、ご視聴いただければ幸いです。



塩化コバルトを用いた触媒作用を可視化する熱化学教材の開発とその評価

（東邦大院理 [1]，東邦大 [2]）○山田 将司 [1]，今井 泉 [2]

Development and Evaluation of Thermochemical Teaching Material for Visualizing Catalysis Using Cobalt Chloride

([1]*Graduate School of Science, Toho University*, [2]*Toho University*) ○Masashi Yamada,[1] Izumi Imai[2]

This research aims to develop and evaluate a thermochemistry teaching material that visualizes catalytic action designed from the Green and sustainable chemistry (GSC) concept. Specifically, first, we develop and evaluate a reaction without adding a catalytic cobalt chloride solution. Second, we will develop and evaluate a reaction by adding a catalytic cobalt chloride solution.

In the first step, we quantitatively tracked the oxidation reaction rate of tartaric acid solution and potassium dichromate solution using an absorptiometer under acidic conditions of sulfuric acid (Fig. 1). In addition, compared with previous research, we evaluated how good the teaching materials are in terms of environmental load and safety using four evaluation axes constructed from the concept of GSC (Fig. 2). As a result, compared to previous studies, the amount of energy used in the experiment greatly exceeded the quantitative follow-up. However, using it as teaching material can reduce it because we use a simple absorbance meter.

Keywords: Thermochemical Teaching Material, Catalysis, Green and Sustainable Chemistry

本研究では，グリーン・サステイナブル ケミストリー（GSC）の概念から設計した触媒作用を可視化する熱化学教材の開発とその評価を目的とする。具体的には，第一段階として触媒作用をもつ塩化コバルト溶液を添加しない反応を，第二段階として触媒作用をもつ塩化コバルト溶液を添加する反応を開発・評価する。

第一段階では，硫酸酸性条件下で酒石酸溶液と二クロム酸カリウム溶液の酸化反応速度を，吸光光度計（HITACHI U-5100 形）を用いて定量的に追跡した（Fig. 1）。また，先行研究 [1)]と比較し，どれだけ環境負荷と安全性に優れた教材であるのか，GSC の概念から構築された 4 つの評価軸を用いて評価した（Fig. 2）。その結果，先行研究と比較して定量的に追跡するため，実験で使用するエネルギー量（「地球からもらうエネルギー量」）が大きく上回った。しかし，実際に教材とする際は，簡易吸光度計（ヤマト科学株式会社 PICOEXPLORER PAS-110-YU）を用いるため，削減可能である。

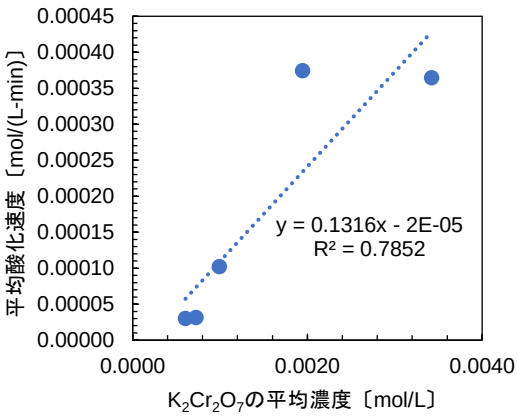


Fig.1　吸光光度計を用いた酸化反応速度の追跡

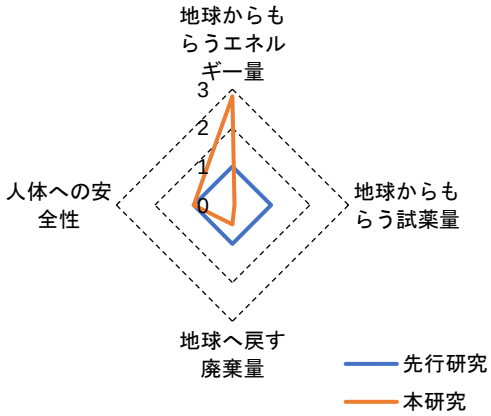


Fig.2　GSC の概念を取り入れた評価

1) 実験による化学への招待，日本化学会編，丸善，**1987**，101-102.

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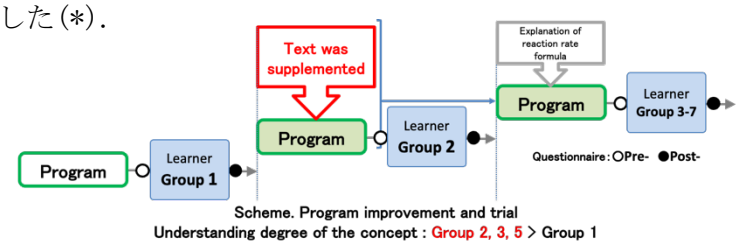
教員養成用実験学習プログラムの開発：反応速度に関する概念の理解に向けて

(学芸大院教育[1]・学芸大教育[2]) ○細江 剛史[1]・生尾 光[2]・國仙 久雄[1]・小川 治雄[2]
Development of Experimental Program for Pre-service Teacher Education: Toward a conceptual understanding of reaction rate ([1]*The United Graduate School of Education, Tokyo Gakugei University,* [2]*Faculty of Education, Tokyo Gakugei University.*) ○Takashi Hosoe,[1] Akira Ikuo,[2] Hisao Kokusen,[1] Haruo Ogawa[2]

An experimental learning program for pre-service teacher training has been developed[1)]. Herein, we are trying to develop an experimental learning program for training pre-services teachers on hydrogen peroxide decomposition reaction[2)]. The program will have following components: (1) formulating a plan for an appropriate experimental procedure to obtain the reaction rate; (2) obtaining the time course of hydrogen peroxide concentration by titration and calculating its reaction rate; and (3) calculating the apparent activation energy by experimenting with varying temperatures. The program was tested, and a survey was conducted on the degree of comprehension regarding the concept of ”apparent activation energy”. Based on the results, when trying to improve the text using the image diagram, the degree of comprehension of the concept became high for Group 2, 3 and 5(Scheme). The concept of reaction rate acquired by learners by taking the program was organized. Some of them are listed below (*).
Keywords: pre-service teacher training; experimental learning program; reaction rate; hydrogen peroxide

教師の理科の素養の向上をめざした教師教育用実験学習プログラムの開発が行われてきた[1)]．本研究では，主に初等教育教員養成課程・理科選修，中等教育教員養成課程・理科専攻の学生を対象とした，過酸化水素分解反応[2)]の温度依存性に関する実験学習プログラムの開発を行った．学習者は(1)反応速度を求めるための適切な実験方法の計画，(2)滴定による過酸化水素濃度の経時変化の測定および反応速度の算出，(3)温度を変えた実験による見かけの活性化エネルギーの算出を行う．プログラムの試行の前後において，反応速度に関する概念「見かけの活性化エネルギー」に対する理解度の自己評価を調査した．群 1 の結果をもとに，イメージ図を用いてテキストの改善を試みた群 2,3,5 において当該概念に対する理解度が高くなった(Scheme)．プログラムの履修によって学習者が獲得する反応速度に関する概念について整理し，一部を以下に示した(*)．



The concept acquired by learners by taking the program：
Measurement and expression of reaction rate in liquid phase, Verification of reaction rate formula (*)

1） 生尾 光，吉永裕介，小川治雄：教師教育用学習プログラムの開発：食塩を題材とする実験プログラムを例として，科学教育研究，**32** (1)，pp.39-55，2008；2）寺谷 敞介：化学実験の設計：I「反応速度」実験の指導，東京学芸大学紀要第 4 部門 数学・自然科学，**42**，35-59，1990.

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

[K202-3am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Yoshiki Ishii, Yosuke Sumiya

Fri. Mar 24, 2023 9:00 AM - 11:40 AM K202 (K202, Lecture Hall Bldg. [2F])

[K202-3am-01] Spatially-Decomposed Analysis of Molecular Interactions and OH Stretching Vibrational Modes at Polymer-Water Interfaces

○Yoshiki Ishii[1], Hajime Torii[2], Yuka Ikemoto[3], Hitoshi Washizu[1] （1. University of Hyogo, 2. Shizuoka University, 3. JASRI）

9:00 AM - 9:20 AM

[K202-3am-02] Local thermal transport property of protein

Tingting Wang[1], ○Takahisa Yamato[1], Wataru Sugiura[1] （1. Nagoya University）

9:20 AM - 9:40 AM

[K202-3am-03] Theoretical Study on Thermostabilization Mechanism of Thermophilic Rhodopsin (TR)

○Michiya Nishina[1], Kazuhiro Fujimoto[1], Takeshi Yanai[1] （1. The Univ. of Nagoya）

9:40 AM - 10:00 AM

[K202-3am-04] A Quantum Chemical Study on Anti-SARS-CoV-2 Activity of TMPRSS2 Inhibitors

○Akihiro Kondo[1], Kazuhiro J Fujimoto[1], Takeshi Yanai[1] （1. Nagoya University）

10:10 AM - 10:30 AM

[K202-3am-05] Feature engineering of ceramic materials based on conventinal knowledge in material chemistry

○Noriaki Ozaki[1], Jun Ikeda[1] （1. Murata Mfg.）

10:30 AM - 10:50 AM

[K202-3am-06] Theoretical Analysis of Adhesion Interaction for Oxide Materials: Molecular Understanding of Tensile, Shear, and Peel Processes

○Yosuke Sumiya[1], Yuta Tsuji[2], Takahiro Uwabe[1], Kazunari Yoshizawa[1] （1. Institute for Materials Chemistry and Engineering, Kyushu Univ., 2. Faculty of Engineering Sciences, Kyushu Univ.）

10:50 AM - 11:10 AM

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高分子と水のナノ界面における水分子の相互作用と OH 伸縮振動モードの空間分割解析

（兵庫県大院情報 [1]・静岡大工 [2]・JASRI[3]）
〇石井 良樹 [1]・鳥居　肇 [2]・池本 夕佳 [3]・鷲津　仁志 [1]

Spatially-Decomposed Analysis of Molecular Interactions and OH Stretching Vibrational Modes at Polymer-Water Interfaces

([1]*Graduate School of Information Science, University of Hyogo*, [2]*Faculty of Engineering, Shizuoka University*, [3]*Spectroscopy Division, JASRI*)
〇Yoshiki Ishii,[1] Hajime Torii,[2] Yuka Ikemoto,[3] Hitoshi Washizu[1]

Hydrogen-bonding properties of water molecules onto polymer interfaces play an important rule to design the molecular structure of biocompatible materials. In this study, by using the prediction method of OH stretching vibrational mode derived by first-principles calculation with density functional theory (DFT), we developed the computational approach of a spatially-decomposed infrared (IR) band analyses by using a molecular dynamics (MD) calculation for water molecules adsorbed in the polymer environment of poly(2-methoxyethyl acrylate) (PMEA). With the spatially-decomposed analysis of IR spectrum for OH stretching vibrational mode, physicochemical relationships of polymer-water interaction and its change in response to local environments of adsorbed water molecules can be clarified. For example, we find that the peak-frequency transition from 3561 cm^{-1} to 3404 cm^{-1} is related to the dissociation of hydrogen bond between water and carbonyl oxygen in the PMEA.

Keywords：Molecular Dynamics, IR Spectroscopy, Density Functional Theory, Polymer, Water

高分子界面における水分子の水素結合特性は，生体適合性材料の分子設計において重要な指針に位置付けられており [1)]，IR スペクトルを用いた高分子と水の間の水素結合様態の解析が進められてきた [2-4)]。そこで本研究では，密度汎関数法を用いて構築された静電相互作用に基づく OH 伸縮振動モードの予測法 [5)] を応用することで，PMEA 界面に吸収された水分子の MD 計算から IR スペクトルを解析した。ここで本手法の IR 解析は，水分子の OH 伸縮振動モードに由来する IR バンドのみに限定されるが，PMEA 界面における IR シフトを定量的に再現することができた。そこで本研究では，IR 振動数と高分子と水の相互作用の 2 つを変数とした空間分割 IR バンド解析を新たに考案した。これにより，高分子と水の相互作用の変化が OH 伸縮振動モードの IR シフトに及ぼす影響や，局所的な高分子環境に応じた物性・スペクトル変化について考察することが可能となり，例えば 3561-3404 cm^{-1} の IR シフトがカルボニル酸素と水の水素結合の破断に由来することが明らかになった。

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Local thermal transport property protein

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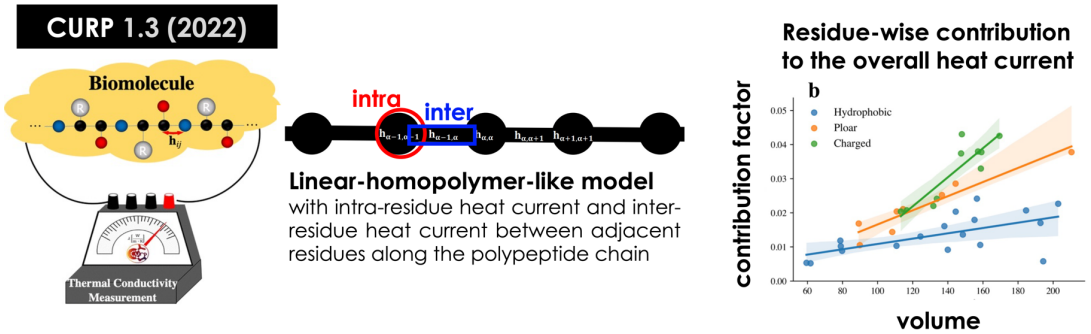
Keywords: residue-wise thermal conductivity; linear response theory; hp36, residue-type dependence; equilibrium MD simulation

Although thermal transport is among essential biophysical properties of proteins, its relationship with protein structures, dynamics, and functions, such as allosteric signal transduction, is still elusive. Previously[1], we developed our CURP[2] program and applied it to study the thermal transport properties of protein materials using an α-helical protein (HP36) as a model. We are particularly interested in the thermal transport network in proteins because the interatomic heat current carries important information regarding, structure, dynamics and interactions. The value of its thermal conductivity was in good agreement with both theoretical/computational and experimental studies.

The protein functions rely on the interactions between amino acids, the building units of protein materials. The structures of folded proteins are highly inhomogeneous, giving rise to anisotropic and non-uniform energy/heat transport network. The heterogeneity of thermal transport from site to site might play the key role in species-specific protein functions. Based on the linear response theory using equilibrium molecular dynamics simulation, we considered the HP36 as a linear-homopolymer-like model and calculated the thermal conductivity within each amino acid residue, in such a way that the cross-correlations of heat currents between different parts are accounted for as a boundary effect on each residue. Interestingly, the residue-wise thermal conductivity exhibits distinct residue-type dependence, and its magnitude dominated over the inter-residue thermal conductivity, as expected. In addition, local density dependence of the residue-wise thermal transport property was analyzed. We also evaluated non-uniform thermal diffusivity based on the calculated values of local thermal conductivities.



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サーモフィリックロドプシン(TR)の熱安定性機構に関する理論的研究

（名大院理[1]・名大 ITbM[2]）○仁科 道也[1]・藤本 和宏[1,2]・柳井 毅[1,2]

Theoretical Study on Thermostabilization Mechanism of Thermophilic Rhodopsin (TR)

([1]*Graduate School of Science, Nagoya University,* [2]*ITbM, Nagoya University*)
○Michiya Nishina,[1] Kazuhiro J. Fujimoto,[1,2] Takeshi Yanai,[1,2]

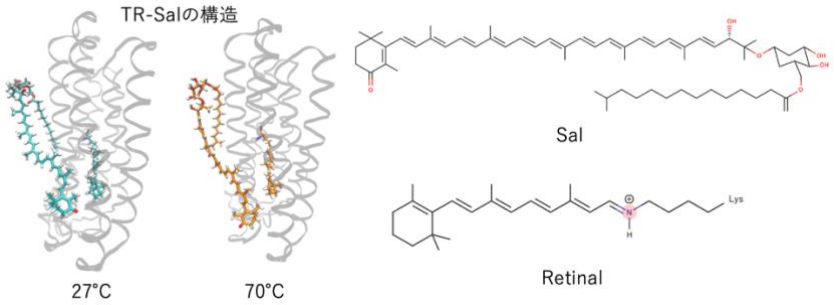
Thermophilic rhodopsin (TR) is one of the retinal proteins and is known to be stable under high temperature conditions above 70°C. The thermostability of TR is thought to be due to its higher activation energy for the transition to the denatured state than those of other retinal proteins. However, the molecular mechanism for the thermostability of TR remains elusive, mainly due to the difficulty in searching for the protein structure in the transition state.

In this study, we explored the physicochemical factors contributing to the thermostability of TR by calculating the binding energy of TR to salinixanthin (Sal) and their CD spectra. The calculations confirmed that TR can retain its protein structure more stably than xanthorhodopsin (XR) at 70°C. Further analysis revealed that TR can bind Sal more strongly than XR at 70°C.

Keywords :Molecular Dynamics Simulation; Thermophilic Rhodopsin; Free Energy; Quantum Chemical Calculation; CD Spectra

レチナールタンパク質の一種、サーモフィリックロドプシン（TR）は 70℃以上の高温条件においても安定な光受容タンパク質である。TR の熱安定性は、変性状態への遷移に必要となる活性化エネルギーが他のレチナールタンパク質と比べて高いことに起因すると考えられている [1)]。しかしながら、遷移状態におけるタンパク質構造の探索の困難さなどにより、TR の熱安定性に関する分子機構は不明のままである。

本研究では、カロテノイドの一種であるサリニキサンチン（Sal）を用いて TR と Sal の結合エネルギーや CD スペクトルを計算することで、TR の熱安定性に寄与する要因を探った。計算の結果、TR は他のレチナールタンパク質である XR と比べ、70℃の高温条件下でもタンパク質構造が高く保持されることが確認できた。さらなる解析から、70℃において TR は XR よりも Sal と強く結合できることが明らかとなった。本発表では結合自由エネルギーや構造の特徴について詳細に議論する。



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TMPRSS2 阻害剤の抗 SARS-CoV-2 活性に関する量子化学的研究

（名大院理 [1]・名大 ITbM [2]）○近藤朗大 [1]・藤本 和宏 [1,2]・柳井 毅 [1,2]

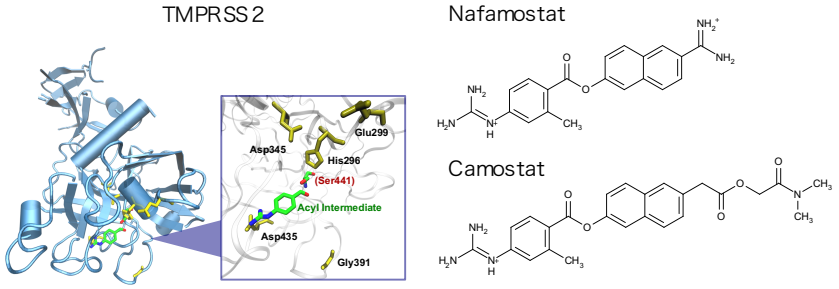
A Quantum Chemical Study on the Anti-SARS-CoV-2 Activity of TMPRSS2 Inhibitors

([1]Graduate School of Science, Nagoya University, [2]ITbM, Nagoya University)
○Akihiro Kondo[1], Kazuhiro J. Fujimoto[1,2], Takeshi Yanai[1,2]

Nafamostat and camostat exhibit anti-SARS-CoV-2 activity by forming a covalent bond with human transmembrane serine protease 2 (TMPRSS2). Nafamostat is known to have higher inhibitory activity than camostat, but their molecular mechanisms remain elusive[1)]. In this study, quantum chemical calculations for the acylation reactions of three compounds (nafamostat, camostat, and a nafamostat derivative) were used to explore the physicochemical factors contributing to TMPRSS2 inhibitory activity. Energy profile calculations revealed higher TMPRSS2 inhibitory activity of nafamostat in terms of thermodynamics and kinetics. Further analysis successfully identified the origin of the differences in TMPRSS2 inhibitory activity between nafamostat, camostat, and the nafamostat derivative.
Keywords : Quantum chemical calculations, COVID-19, Computational drug discovery, TMPRSS2, Nafamostat

ナファモスタットおよびカモスタットは、ヒト由来のセリンプロテアーゼである TMPRSS2 と共有結合を形成することで（TMPRSS2 阻害）、抗 SARS-CoV-2 活性を発揮する。ナファモスタットの方がカモスタットよりも高い阻害能を示すことが知られているが、これらの分子機構は不明のままである [1)]。

本研究では、３種の化合物（ナファモスタット、カモスタット、およびナファモスタット誘導体）のアシル化反応に対する量子化学計算を実施することで、TMPRSS2 阻害活性に寄与する物理化学的要因を探った。エネルギープロファイルの計算により、ナファモスタットの高い TMPRSS2 阻害能が熱力学的・速度論的な観点から明らかにされた。さらなる解析から、ナファモスタット、カモスタット、およびナファモスタット誘導体における TMPRSS2 阻害活性の違いを生み出す原因を特定することに成功した。



1) In Silico Analysis and Synthesis of Nafamostat Derivatives and Evaluation of Their Anti-SARS-CoV-2 Activity. K. J. Fujimoto *et al., Viruses* **2022**, 14, 389.

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従来の材料化学の知識に立脚したセラミックス材料の特徴量エンジニアリング

（村田製作所 [1]）○尾崎 仁亮 [1]・池田 潤 [1]

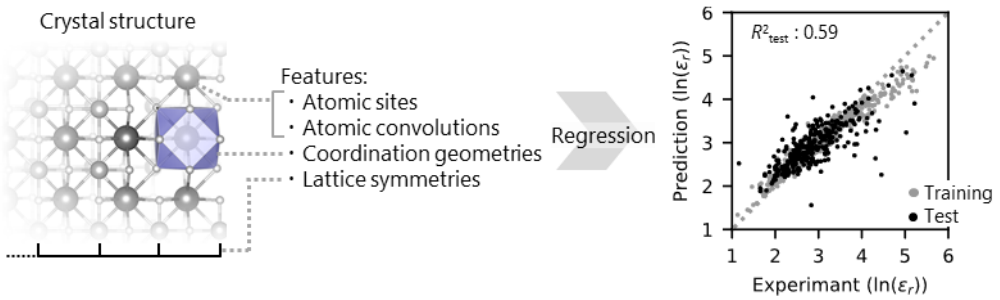
Feature Engineering of Ceramic Materials Based on Conventional Knowledge in Material Chemistry

([1]*Murata Manufacturing Co. Ltd.*) ○Noriaki Ozaki,[1] Jun Ikeda[1]

Material research based on mathematics and statistics, in short, materials informatics (MI), has been acquired a reputation as a useful approach for improving efficiency of material research. In implementing MI, generation of accurate machine learning (ML) models is often a technical problem. One important solution is to develop features (input data for ML) which can encode materials. However, with respect to ceramics, currently proposed features are not always apprehensible for experimental chemists, making it difficult to understand results of ML and to introduce MI to day-to-day work. In this work, we developed ML features that are highly usable for material chemists by interpreting knowledges acquired in material chemistry in history, i.e., information about atomic sites (valence states, ionic radii, et al.) and their convolutions, coordination geometries around metals, and lattice symmetries. Then, dielectric constants of paraelectric materials are predicted for the demonstration, resulting in sufficient accuracy.

Keywords : Feature Engineering; Machine Learning; Materials Informatics; Dielectric Property; Ceramics

数理・統計的な知識や技術を積極的に活用した材料研究、すなわち、マテリアルズ・インフォマティクス（MI）が、研究開発の促進に効果が高いことが、広く認知されるようになっている。MI 実装に際しては、精度の高い機械学習（ML）モデルの作成が技術的課題となることが多く、これを解決するための方策の 1 つとして、材料の情報を十分に抽出できるような特徴量（ML への入力データ）の開発が行われている。しかし、現在提案されている特徴量のうち、ことセラミックスに関するものの多くは、実験化学者にとって理解・解釈しやすいとは言い難く、これが ML の結果の解釈や、研究現場への MI の導入を困難にしている。本研究では、材料化学において長らく用いられてきた考え方を、特徴量の設計に反映することで、実験化学者にとって、使いやすい特徴量の開発を目指した。具体的には、各原子サイトの情報（価数やイオン半径など）および、その畳み込み、配位構造の幾何的情報、格子の対称性の情報を、特徴量に変換した。また、作成した特徴量により特性が予測可能であることを示す目的で、常誘電体の比誘電率に対する予測を行い、良好な予測結果を得ることに成功した。



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酸化物材料に対する接着相互作用の理論解析：引張・せん断・はく離過程における分子論的理解

（九大先導研 [1]・九大総理工 [2]）○住谷 陽輔 [1]・辻 雄太 [2]・上部 岳洋 [1]・吉澤 一成 [1]

Theoretical Analysis of Adhesion Interaction for Oxide Materials: Molecular Understanding of Tensile, Shear, and Peel Processes

([1]*Institute for Materials Chemistry and Engineering, Kyushu University*, [2] *Faculty of Engineering Sciences, Kyushu University*) ○Yosuke Sumiya,[1] Yuta Tsuji,[2] Takahiro Uwabe,[1] Kazunari Yoshizawa[1]

Recently, adhesion technology using adhesives has been attracting attention from the viewpoint of energy conservation and global environmental protection. The strength of interaction at an adhesive interface is evaluated based on adhesive strength. Adhesive strength is measured by adhesion tests defined in the Japanese Industrial Standards (JIS) and other standards. Typical adhesion tests are (a) tensile, (b) peel, and (c) shear as shown in Figure 1, and their strengths vary greatly depending on the direction of the force applied to the interface.

We have developed a method to estimate tensile adhesive force corresponding to (a) based on density functional theory (DFT) calculations[1)] and applied it to various systems. However, a method for estimating the peel and shear adhesion forces corresponding to (b) and (c) has not been established, and theoretical analysis of these forces and the understanding of their molecular mechanisms are required. In this study, we developed methods to estimate these adhesive forces, and obtained the adhesive forces of epoxy resins to various oxide materials.[2,3)]

Keywords：Adhesion, Density Functional Theory, Interfacial Interaction, Oxide Material

近年、省エネルギー化や地球環境保護の観点から、接着剤を用いた接着技術が注目されている。接着界面における相互作用の強さは接着強度に基づいて評価される。接着強度は日本産業規格(JIS)などに規定された接着試験で測定される。代表的な接着試験は図 1 に示す(a)引張、(b)剥離、および(c)せん断試験であり、接着面にかかる力の方向によってその強度は大きく変化する。

我々は、(a)に対応する引張接着力を密度汎関数理論(DFT)計算に基づいて求める方法を開発し[1)]、様々な系に適用してきた。しかしながら、(b)および(c)に対応する剥離・せん断接着力を見積もる方法は確立しておらず、理論解析と分子論的理解が求められる。そこで本研究では、各接着力を求める理論手法を開発し、様々な酸化物材料に対するエポキシ樹脂の接着力を求めた[2,3)]。最近では接着歯学分野にも展開し、歯の補綴物に利用されるジルコニアとの接着機構の解析に応用している。以上の結果を当日報告する。

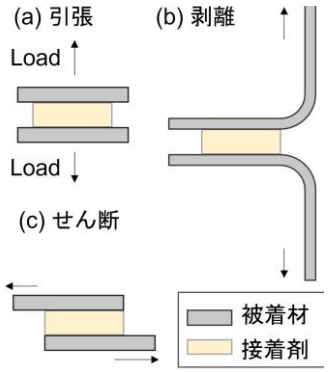

Fig. 1. Typical adhesion tests.

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2) **Y. Sumiya**, Y. Tsuji, K. Yoshizawa, *Phys. Chem. Chem. Phys*. **2022**, *24*, 27289.
3) **Y. Sumiya**, Y. Tsuji, K. Yoshizawa, *ACS Omega* **2022**, *7*, 17393.

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

[K202-3pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Toyokazu ISHIDA, Yuta Hori

Fri. Mar 24, 2023 1:00 PM - 3:40 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-3pm-01] Molecular dynamics simulation of electrode-liquid interface using a universal neural network potential

○Kaoru Hisama[1], Gerardo Valadez Huerta[1], Michihisa Koyama[1] (1. Shinshu Univ.)

1:10 PM - 1:30 PM

[K202-3pm-02] Theoretical Analysis for Anisotropy of Proton Conduction in Imidazolium Hydrogen Succinate by First-Principles Calculations

○Yuta Hori[1], Yasuteru Shigeta[1] (1. University of Tsukuba)

1:30 PM - 1:50 PM

[K202-3pm-03] Protonation free-energy of amine-cured epoxy resin under deformation in water by first-principles calculations

○Shuji Ogata[1], Masayuki Uranagase[1] (1. Nagoya Institute of Technology)

1:50 PM - 2:10 PM

[K202-3pm-04] Quantum computing of molecular orbitals of linear polyenes and its application to probing qubit performance

○Yoshinori Ato[1], Yutaka Tachikawa[1], Ryuhei Yoshida[2], Erik Lötstedt[2], Kaoru Yamanouchi[2] (1. DIC Corporation, 2. The University of Tokyo)

2:10 PM - 2:30 PM

[K202-3pm-05] Requirements of Orbital Phase Continuity Revisited: A FMO Approach

○Yuji Naruse[1] (1. Gifu University)

2:40 PM - 3:00 PM

[K202-3pm-06] Direct calculation of numerical energy gradient by using Bayesian phase difference estimation algorithm and application to geometry optimization

○Kenji Sugisaki[1,2,3], Hiroyuki Wakimoto[1], Kazuo Toyota[1], Kazunobu Sato[1], Daisuke Shiomi[1], Takeji Takui[1] (1. Osaka Metropolitan University, 2. JST PRESTO, 3. CQuERE, TCG CREST)

3:00 PM - 3:20 PM

[K202-3pm-07] Prediction of experimental properties of organic molecules by quantum circuit learning

○Kan Hatakeyama-Sato[1], Kenichi Oyaizu[1] (1. Waseda University)

3:20 PM - 3:40 PM

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汎用ニューラルネットワークポテンシャルを用いた電極-液体界面系の分子動力学シミュレーション

(信州大学) ○久間 馨・Gerardo Valadez Huerta・古山 通久

Molecular dynamics simulation of electrode-liquid interface using a universal neural network potential

(*Center for Research Initiative for Supra-Materials, Shinshu-University*) Kaoru Hisama, Gerardo Valadez Huerta, Michihisa Koyama

The behavior of a liquid on a charged electrode is important for applications in devices such as electric double layer capacitors. The challenge in using neural network potentials (NNPs) to realize such charge-applied simulations is that most NNP models do not explicitly differentiate Coulomb potentials from the other interactions. Therefore, in this study, we propose a method to analyze liquid-electrode interfaces by integrating a pre-trained universal neural network potential, Preferred potential (PFP) and Coulomb potentials using the ONIOM method and extend the use of machine learning force fields to electrode-liquid interface systems. Molecular dynamics (MD) simulations between graphite electrodes are performed as a model system. As shown in Figure 1 (a), MD simulations are performed at 300 K for 1.0 ns by introducing charges -*q* and +*q* (*q*=0.0*e* and 0.001*e* /atom) into the electrodes. The result of number density distribution of H atoms for *q*=0.001*e* shows a change in structure by the charges, compared to the case with *q*=0.0*e* [Fig. 1 (b)].

Keywords : Molecular dynamics, Neural network potential, Electrical double layer

電荷が注入された電極上での液体の振る舞いは，電気二重層コンデンサなどのデバイス応用上重要である．このような電荷注入シミュレーションについて，ニューラルネットワークポテンシャル(NNP)を使って表現しようとする場合，NNP の多くはクーロンポテンシャルがあらわに記述されていないモデルであることが課題となる．本研究では，汎用的な学習済み NNP である Preferred potential (PFP)とクーロンポテンシャルを ONIOM 法で統合し，機械学習力場の活用を電極-液体界面系に拡張する手法を提案する．モデル系としてグラファイト電極間の分子動力学(MD)シミュレーションを扱う．Figure 1 (a) のように，グラファイトの内側の層に電荷-*q*, +*q* (*q*=0.0*e*, 0.001*e* /atom)をそれぞれ導入し，300 K で 1.0 ns の MD シミュレーションを行った．*q*=0.001*e* の場合は，電荷を印加しない *q*=0.0*e* の場合と比べて H 原子の数密度分布が変化しており，構造変化が電荷によって誘起されたことを示している [Fig. 1 (b)].

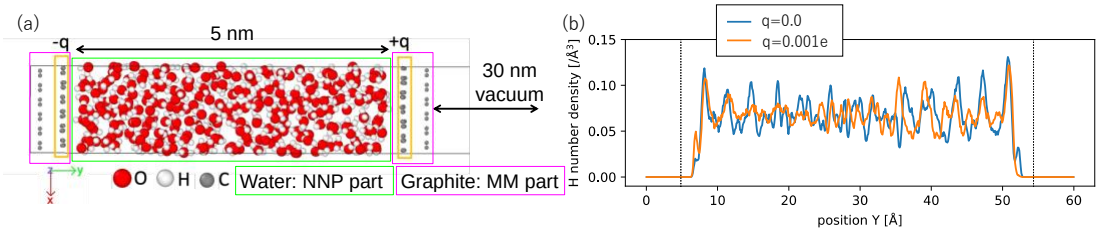

Figure 1 (a) MD simulation setup and (b) Number density of H atoms along Y axis in this study.

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第一原理計算によるコハク酸イミダゾリウム結晶中のプロトン伝導異方性の解析

（筑波大計算セ [1]）○堀 優太 [1]・重田 育照 [1]

Theoretical Analysis for Anisotropy of Proton Conduction in Imidazolium Hydrogen Succinate by First-Principles Calculations

([1]*Center for Computational Sciences, University of Tsukuba*)
○Yuta Hori,[1] Yasuteru Shigeta[1]

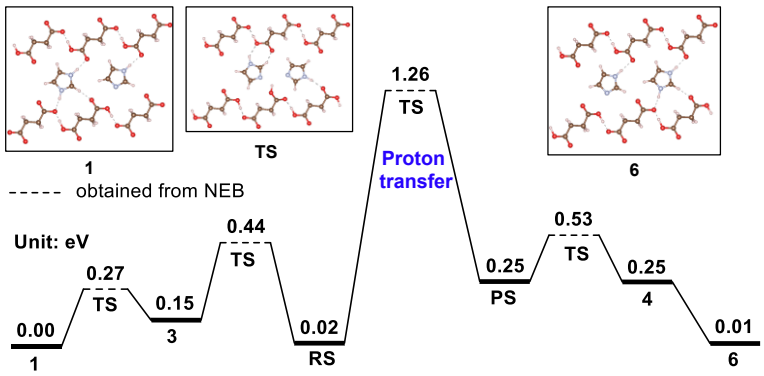
Anhydrous imidazolium hydrogen succinate (Im-Suc) has two-dimensional hydrogen-bond structure and exhibits high proton conduction through two proton conduction pathways despite its crystalline nature. Notably, the proton conductivities through the two pathways are anisotropic. Therefore, the proton conduction mechanisms are attractive. Herein, first-principle calculations are utilized for proton conduction mechanisms through the two proton conduction pathways and for the discussion of the difference between them.

The calculated potential energy surface involving proton transfer (PT) and rotational motion of imidazole showed that proton conductions along both pathways proceeded via the successive coupling of PT and rotational motion of imidazole. In addition, we observed the differences in the stability of the proton defect structures on the two pathways, suggesting that the formation of proton defects affects the difference of proton conductivities between the two pathways.

Keywords : Proton Conduction; First-Principles Calculation; Imidazole; Succinic Acid

コハク酸イミダゾリウム(Im-Suc)結晶は、二次元の水素結合構造を有している。Im-Suc は結晶でありながら比較的高いプロトン伝導性を示しており、そのプロトン伝導機構に興味が持たれている。特に Im-Suc は水素結合を介した 2 つのプロトン伝導経路を持っており、異なるプロトン伝導性を示すことが報告されている。本研究では、プロトン伝導経路上のプロトン伝導機構の解明および 2 つのプロトン伝導経路に対する伝導性の違いについて考察するために、第一原理計算による解析を行った。

計算によって得られたポテンシャルエネルギーダイアグラム（下図）から、Im-Suc 中のプロトン伝導は、Im の回転運動と Im と Suc 間の分子間のプロトン移動のカップリングにより生じることがわかった。また、2 つのプロトン伝導経路上ではプロトン欠陥構造の安定性の違いが見られ、プロトン欠陥の形成がプロトン伝導性の違いに影響を与えていることが示唆される。



1) Proton Conduction Mechanism for Anhydrous Imidazolium Hydrogen Succinate Based on Local Structures and Molecular Dynamics. Y. Hori, S. Dekura, Y. Sunairi, T. Ida, M. Mizuno, H. Mori, and Y. Shigeta, *J. Chem. Phys. Lett.*, **2021**, *12*, 5390.

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歪んだアミン系硬化エポキシ樹脂の湿潤環境でのプロトン化自由エネルギーに関する第一原理計算

（名工大院工 [1]）〇尾形 修司 [1]・浦長瀬 正幸 [1]

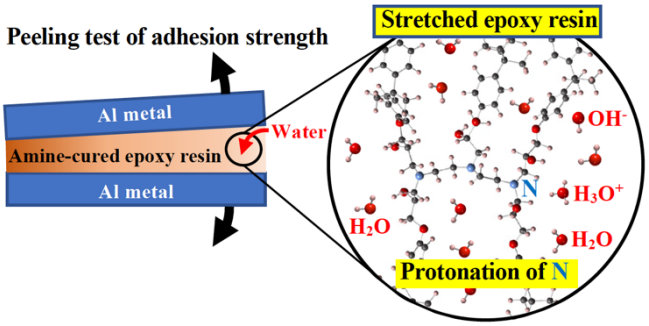
Protonation free-energy of amine-cured epoxy resin under deformation in water by first principles calculations

([1]*Graduate School of Engineering, Nagoya Institute of Technology*)
〇Shuji Ogata,[1] Masayuki Uranagase[1]

A significant challenge in adhesive bonding is accelerated breaking of stretched adhesive under wet conditions, known as the cohesive failure. Amine-cured epoxy resin is a particularly common adhesive. Possible failure mechanism where breaking originates in protonated amine base of the amine-cured epoxy resin in neutral or acidic condition has been proposed recently based on deprotonation free-energy calculations of unstrained resin in water [1]. In this study, we made a comprehensive investigation of protonation degree of the amine base in both stretched and compressed conditions by devising a robust first-principles protonation calculation method applicable to strained materials. It is thereby found that the amine base is partially protonated in neutral water at 298 K and that the amine group is stronger protonated when the epoxy resin is more stretched in water, and vice versa. The findings support the physicochemical cause of the cohesive failure due to protonation of amine group in stretched amine-cured epoxy resin.

Keywords：Amine-cured epoxy resin, Protonation free-energy, DFT, Molecular dynamics

湿潤環境で引っ張られた接着剤が破壊することは，凝集破壊として広く知られている．アミン硬化エポキシ樹脂は接着剤として一般的であり，多くの産業分野で利用されている．アミン硬化エポキシ樹脂が中性あるいは酸性環境でプロトン化を経て破壊が促進される凝集破壊の機構が，歪みがないアミン硬化エポキシ樹脂についてプロトン化の自由エネルギー計算結果から最近提案された[1]．本研究では，実際の実験状況を踏まえて，歪んだ状況でのアミン硬化エポキシ樹脂についてのプロトン化の度合いを，歪みがある対象系にも適用できる新しいプロトン化の自由エネルギー計算法を考案し実際に適用することで，第一原理的に明らかにした．本計算の結果，298 K で中性環境においては，アミン硬化エポキシ樹脂のアミン基は，応力ゼロの状況では部分的にプロトン化すること，また引っ張られた状況ではプロトン化がより進むこと等がわかった．これらの結果は，湿潤環境で引っ張られたアミン硬化エポキシ樹脂がアミン基のプロトン化を起点として凝集破壊を起こす機構をサポートする．



[1] Ogata et al.: J. Phys. Chem. B (2021) 125, 8989.

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Quantum computing of molecular orbitals of linear polyenes and its application to probing qubit performance

([1] *DIC Corporation*, [2] *Department of Chemistry, School of Science, The University of Tokyo*)
〇Yoshinori Ato,[1] Yutaka Tachikawa,[1] Ryuhei Yoshida,[2] Erik Lötstedt,[2] Kaoru Yamanouchi[2]
Keywords: Quantum computing; Quantum error mitigation; Hückel molecular orbitals; Linear polyenes

Recent advances in quantum computers have enabled researchers to explore a possibility of computing complex systems having many degrees of freedom, which has been practically impossible using classical computers. However, as long as we use currently available quantum computers, categorized into NISQ (noisy intermediate-scale quantum) devices, the results of the calculations suffer from the noise and consequently, we need to develop methods with which the effect of the noise can be mitigated. In a series of our recent studies, we have demonstrated that quantum computing can be applied efficiently to vibration of small-sized polyatomic molecules [1,2] and electronic structures of small-sized π-bonding molecular systems [3]. It would be meaningful to increase the size of molecular systems to be investigated and examine to what extent the quantum computing using currently available NISQ devices can contribute to solving molecular problems. In the present study, based on the quantum circuits we developed for Hückel molecular orbital (HMO) calculations [3], we calculate the orbital energies of linear conjugated polyenes C_NH_{N+2} (N = 2–20) by a superconducting-qubit type quantum computer (*ibm_kawasaki*) and examine how the error mitigation methods work for larger-sized linear conjugated polyenes, using the direct mapping for the 2p atomic orbitals. Their electronic energies are given by applying the excitation operator $\varepsilon(\boldsymbol{\theta})$ and the unitary transformations $U_r^{m,n}$ as

$$E_k = \frac{\beta}{2} \sum_{(m,n)\in\{\text{bonds}\}} \langle \phi_k | \varepsilon^\dagger(\boldsymbol{\theta}) U_r^{\dagger m,n} (\sigma_z^n - \sigma_z^m) U_r^{m,n} \varepsilon(\boldsymbol{\theta}) | \phi_k \rangle, \tag{1}$$

The results of the quantum computation have shown that the probability of the appearance of spurious states, which need to be discarded in the error mitigation process, increases as the polyene chain becomes longer and that the spurious-state appearance probability can be less than 20 % as long as the number of qubits is less than or equal to five. For N = 2, 3, 4, and 5, the spurious-state appearance probabilities are 4 %, 13 %, 18 %, and 20 %, respectively. We have revealed that the elimination of such spurious states improves largely the HMO energies. For example, when N = 5, the raw data of the energy of the lowest-lying MO, $-1.32|\beta|$, is improved to be $-1.64|\beta|$, which is very close to the exact value of $-1.73|\beta|$, after discarding spurious states.

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Requirements of Orbital Phase Continuity Revisited: A FMO Approach

([1]*Departnment of Chemistry and Biomolecular Science, and* [2]*Department of Materials Chemistry and Processing, Gifu University*) ○Yuji Naruse[1,2]

Keywords: Cyclic Orbital Interaction; Requirements of Orbital Phase Continuity; Delocalization; FMO Theory

Cyclic orbital interaction, in which a series of orbitals interact with each other so as to make a monocyclic system, affords stabilization if the requirements of orbital phase continuity are satisfied.[1] We have demonstrated that the phase-continuous cyclic orbital interaction determines the selectivity, especially the diastereoselectivity in the electrophilic addition of α-substituted ethylenes[2] and Felkin-Anh model for the nucleophilic addition.[3]

Requirements of orbital phase continuity consist of five terms: (i) donating orbitals are out-of-phase; (ii) a donating orbital and an accepting orbital are in-phase; and (iii) accepting orbitals are in-phase (Figure). When the number of corresponding orbitals in the interaction is more than three, two additional requirements should also be satisfied: (iv) interaction among the orbitals is monocyclic, and (v) the series of orbital interactions should be divided into two, a donor part and an acceptor part, and not into four, six or more. Note that the overlap between the orbitals is less than 1; $|S| < 1$, cyclic orbital interaction with fewer orbitals is often preferred.

These requirements are initially derived from consideration of three-body system. The perturbation term of the third order in the orbital interaction results in stabilization when all the requirements are satisfied.

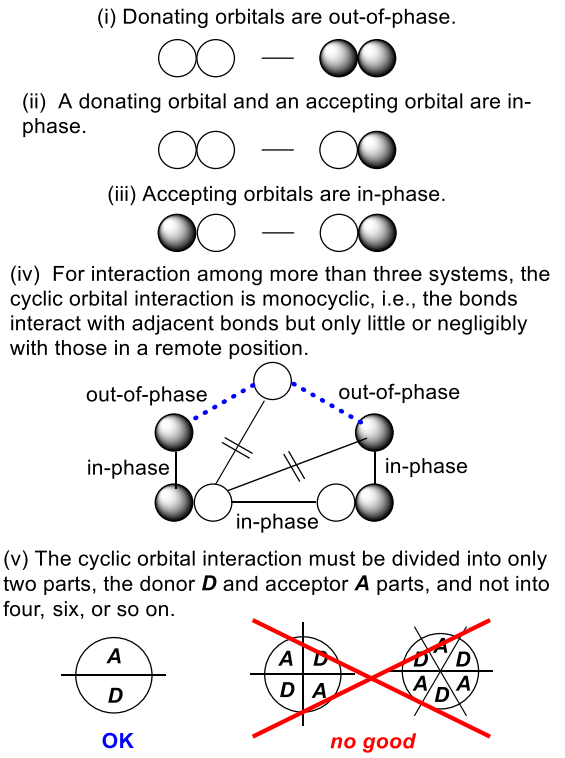

Figure. Requirements of orbital phase continuity

Here I present that these conditions are readily obtained from the FMO theory, and show some further applications.

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量子位相差推定によるエネルギー数値微分の直接計算手法開発と分子構造最適化への応用

（大阪公大院理[1]・JST さきがけ[2]・CQuERE, TCG-CREST[3]）○杉﨑 研司[1,2,3]・脇本 浩幸[1]・豊田 和男[1]・佐藤 和信[1]・塩見 大輔[1]・工位 武治[1]

Direct calculation of numerical energy gradient by using Bayesian phase difference estimation algorithm and application to geometry optimization ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*JST PRESTO,* [3]*CQuERE, TCG-CREST*) ○ Kenji Sugisaki,[1,2,3] Hiroyuki Wakimoto,[1] Kazuo Toyota,[1] Kazunobu Saho,[1] Daisuke Shiomi,[1] Takeji Takui[1]

In quantum chemical calculations, geometry optimization requires computation of the energy derivatives with respect to nuclear coordinates. In the quantum phase estimation-based quantum chemical calculations on a quantum computer, the energy derivatives are calculated numerically by using the finite difference method. In this work, we have extended the Bayesian phase difference estimation algorithm, a general quantum algorithm for the direct calculation of an energy gap, to the direct calculation of numerical energy derivatives based on the finite difference method. Applications of the proposed approach to geometry optimization will be discussed. *Keywords : Quantum computer, Quantum chemical calculation, Quantum algorithm, Geometry optimization, Finite difference method*

量子化学計算は量子コンピュータの近い将来の応用先として非常に注目を集めており、国内外で様々な研究が展開されている。我々は、化学で最終的に議論されるのは全エネルギーではなくエネルギー差であること、および量子コンピュータは量子重ね合わせ状態を計算資源として活用できることに注目し、全エネルギーを求めることなくエネルギー差を直接計算できる量子位相差推定アルゴリズムを提案した[1)]。量子位相差推定はこれまで、励起エネルギーやイオン化エネルギーなど、与えられたハミルトニアンのもとでの異なる電子状態間のエネルギー差直接計算へと適用されてきた[1–3)]。今回我々は、異なる分子構造でのエネルギー差の直接計算が可能となるように量子位相差推定アルゴリズムの理論拡張を行った[4)]。これにより、有限差分法に基づくエネルギー数値微分を 1 回の計算から直接求められるようになった。

本研究では量子位相差推定によるエネルギー数値微分計算法を H_2, LiH, BeH_2, N_2 分子のエネルギー核座標微分に適用した。さらに、以前に報告されている微分値のみを用いる最適化アルゴリズム[5)]と本手法を組み合わせることで、全エネルギーを一度も求めることなく、分子構造最適化を実行できることを示した。量子アルゴリズムの詳細および数値シミュレーション結果については当日発表する。

1) K. Sugisaki et al, *Phys. Chem. Chem. Phys.* **2021**, *23*, 20152–20162.
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量子回路学習を用いた有機分子の実測物性の予測検討

（早大理工）○畠山 歓・小柳津 研一
Prediction of experimental properties of organic molecules by quantum circuit learning
(*Department of Applied Chemistry, Waseda University*)
○Kan Hatakeyama-Sato, Kenichi Oyaizu

Quantum circuit learning is a new algorithm for quantum computers. The regression model was employed to predict regular 1-dimensional functions and experimental molecular properties from their structures. We analyzed the basic characteristics of QCL by comparing it with regular regression models. Its extrapolating prediction performances could exceed conventional models under some conditions with small databases.
Keywords ： Quantum circuit learning, Cheminformatics, Materials informatics

ゲート型量子コンピュータは次世代の計算マシンとして知られ、化学分野でも量子化学計算への適用を主眼に基礎研究が進んでいる。マシンを機械学習タスクに活用する試みも広がり、量子回路学習(Quantum circuit learning, QCL)などの古典・量子マシンを併用するアルゴリズムなどが知られる。

本報では有機分子の構造から実測物性を推定する回帰タスクを QCL で実装するとともに、一般的な回帰モデルと比較することでその性質を分析した [1]。QCL は線形変換で記述される量子ゲート操作と非線形の観測操作で構成される(**Figure**)。回路パラメータ $\boldsymbol{\theta}$をうまく調節することで入力値$\boldsymbol{x}$に対して出力yが定まる回帰モデル$y = f(\boldsymbol{x})$が得られる。その回帰性能を標準的な 1 次関数や融点などの分子物性の予測タスクで評価した。適切な回路構成を設計することで、非線形性を持ちながらも、小規模なデータセットと適合性に優れたモデルが得られる場合があることが分かった。当日は QCL の詳しい原理や特徴について説明する。

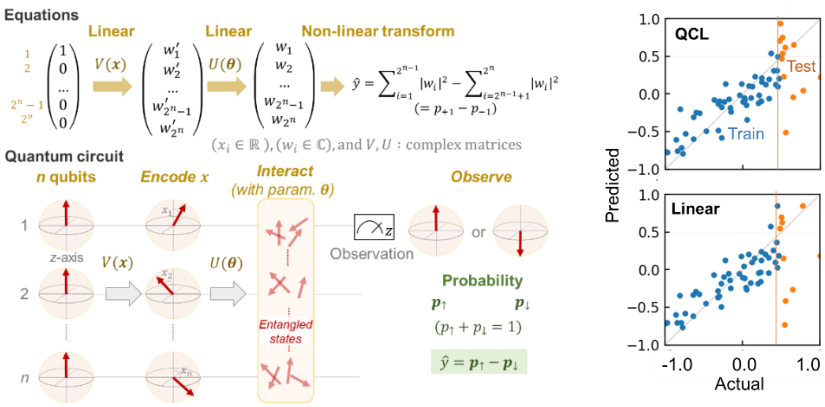

Figure Left: scheme of QCL. Right: typical prediction results of molecular properties. Reprinted from ref[1] under a CC license.

(1) Hatakeyama-Sato, K.; Igarashi, Y.; Kashikawa, T.; Kimura, K.; Oyaizu, K. Quantum circuit learning as a potential algorithm to predict experimental chemical properties. *Digital Discovery* **2023**. DOI: 10.1039/d2dd00090c.

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

[K202-3vn] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Kenji Sugisaki, Mitutaka Okumura

Fri. Mar 24, 2023 4:10 PM - 6:50 PM K202 (K202, Lecture Hall Bldg. [2F])

[K202-3vn-01] Theoretical study of the solvent fluctuation affecting the linear optical process in solution

○Naoki Negishi[1], Daisuke Yokogawa[1] （1. Graduate school of Arts and Sciences, The University of Tokyo）

4:10 PM - 4:30 PM

[K202-3vn-02] Relativistic DFT Calculations for Concentration Changes in Heavy-Element Chemical Shifts

○Yoshimitsu Asakura[1], Daisuke Kuwahara[1], Naoya Nakagawa[1] （1. The University of Electro-Communications）

4:30 PM - 4:50 PM

[K202-3vn-03] Computational Exploration for High Density Thermal Storage Materials based on Thermal Management Materials Database (PropertiesDB Web)

○Toyokazu ISHIDA[1,2], Yukiko Suda[2], Kazuya Ishimura[3] （1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Thermal Management Materials and Technology Research Association (TherMAT), 3. X-Ability）

4:50 PM - 5:10 PM

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分子性液体論に基づいた溶液系における線形光学応答の溶媒揺らぎの効果に関する理論的検討

（東大院総合文化 [1]）○根岸直輝 [1]，横川大輔 [1]
Naoki Negishi[1], Daisuke Yokogawa[1]
([1]*Graduate School of Arts and Sciences, The University of Tokyo, Japan*)

A theoretical study of a linear optical process in solution based on the liquid state theory of molecular solvents.

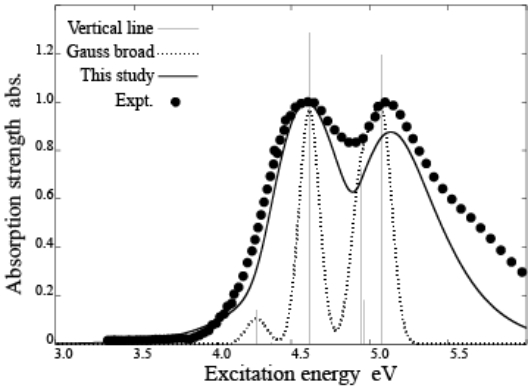
E-Mail to Negishi: negsihi-naoki@g.ecc.u-tokyo.ac.jp

The "shape" of the electron spectral lines in solution contains information on fluctuations of solutes and solvents. However, theoretical calculations to evaluate these fluctuations are still in the developmental stage. To overcome this problem, we concentrate on a bottom-up approach evaluating the quantal vibrational states of a solute and thermal fluctuations of solvents.

Keywords: Solvent fluctuation, linear optical process, RISM-SCF, path integral

光による分子制御を溶液系においても実現するためには，溶液系全体における電子励起状態についての理解が必要不可欠である．各電子励起状態におけるポテンシャル曲面を求めればよい孤立分子系と異なり，モルオーダーで存在している溶媒の自由度を効果的に取り扱うことが要求される．溶媒の静電相互作用をモデル化し，電子状態の補正に伴うエネルギーや振動子強度の変化に注目した数値解法は確立されているものの，吸収バンドがブロードすることによる吸光断面積の著しい変化までを予測出来てはいない.[1] 吸収バンド幅を算出するには溶質分子の振動状態や，溶媒の熱揺らぎ効果を評価する必要があるが，その一方で溶質の電子状態と溶媒構造が互いに無矛盾になるように取り扱える枠組みが確立されてこなかったためである．

そこで本研究では，分子液体論と量子化学計算のハイブリッド法である RISM-SCF-cSED 法[2]と，調和振動モデルの経路積分法の融合によって見積もる新たな手法を提案し，この無矛盾性の問題を解消した．核酸の類似体であり，極性溶媒によく溶ける 2-Thiocytosine ケト体の水中での電子スペクトル線を算出した結果， 図に示すように，垂直励起エネルギー点を中心とした半値幅 0.15 eV の Gauss 型吸収バンドを重ね合わせた破線から，著しく吸収バンドがブロードしている様子を記述することが出来， 溶媒依存性を効果的に取り込むことを可能にした．



2-Thiocytosine ケト体水溶液の電子スペクトル線

【参考文献】

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重元素の NMR 化学シフト濃度変化に関する相対論的 DFT 計算

（電通大院情報理工 [1]）○朝倉 由光 [1]・桑原 大介 [1]・中川 直哉 [1]

Relativistic DFT Calculations for Concentration Changes in Heavy-Element Chemical Shifts

([1]*Graduate School of Informatics and Engineering, The University of Electro-Communications*) ○Yoshimitsu Asakura,[1] Daisuke Kuwahara,[1] Naoya Nakagawa[1]

When metal nitrate salts are dissolved in water and the nuclear magnetic resonance (NMR) lines of the metal nuclei are observed, the resonance frequency changes depending on the concentration of the solution. We attempted to explain this phenomenon through a relativistic density functional theory (DFT) calculation. We prepared models of hydrated ions in which only water molecules were bound around the single atomic cations of the observed metal (dilution model) and hydrated ions in which one nitrate ion was bound to a single atomic cation (concentration model). We then calculated the NMR shielding constants of both models by DFT using the Spin-Orbit Zeroth order regular approximation Hamiltonian. As a result, it was found that the shielding constant σ, especially for cations with a $6s^2$ outer shell electron configuration in the 6th period P-block, changes due to the relativistic shielding constant term $\sigma_{\mathrm{SO/FC}}$ caused by orbital-Zeeman, spin-orbit, and Fermi contact interactions. Additionally, it was revealed through visualization of the electron spin density that as the $\sigma_{\mathrm{SO/FC}}$ increases from the dilution to the concentration model in the case of lead nitrate $Pb(NO_3)_2$, the electron spin density around the lead nucleus also increases. The dissociation constant and thermodynamic equilibrium constant of $Pb(NO_3)_2$ in aqueous solution will also be discussed in the presentation..

Keywords : Lead; NMR chemical Shift; Heavy Element; Density Functional Theory; Relativistic Effect

重金属硝酸塩を水に溶かし、重金属核の NMR 共鳴線を観測すると、溶液の濃度に応じて共鳴周波数が変化する。我々はこの現象を相対論的な密度汎関数法計算によって解明しようと試みた。観測核である重金属の単原子カチオンの周りに水分子のみが結合している水和イオン（希釈モデル）と、単原子カチオンに対し硝酸イオンが１つ結合した水和イオン(濃縮モデル)を用意し、それぞれの NMR 遮蔽定数を Spin-Orbit Zeroth order regular approximation ハミルトニアンを用いて DFT 計算した。その結果、特に第 6 周期 P ブロックで最外殻電子配置が $6s^2$ のカチオンの遮蔽定数σが軌道ゼーマン、スピン軌道、フェルミ接触相互作用に由来する相対論的な遮蔽定数の項$\sigma_{\mathrm{SO/FC}}$により、変化することが分かった [1)]。また$\sigma_{\mathrm{SO/FC}}$が希釈モデルから濃縮モデルにかけて増加する硝酸鉛 $Pb(NO_3)_2$ の場合、鉛原子核近傍の電子スピン密度もまた増加していることがスピン密度の可視化によって明らかになった [1)]。発表では水溶液中の $Pb(NO_3)_2$ の解離定数、熱力学的平衡定数に関して検討した内容も報告する。

1)Y. Asakura, D. Kuwahara, N. Nakagawa, *Journal of Computer Chemistry, Japan -International Edition* **2022**, *8*, 2021.

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計算化学と熱関連材料データベース（PropertiesDB Web）を活用した高密度蓄熱材の探求

（産総研[1]・未利用熱技術組合[2]・クロスアビリティ[3]）○石田 豊和[1,2]・須田 幸子[2]・石村 和也[3]

Computational Exploration for High Density Thermal Storage Materials based on Thermal Management Materials Database (PropertiesDB Web)

([1]*National Institute of Advanced Industrial Science and Technology*, [2]*Thermal Management Materials and Technology Research Association,* [3]*X-Ability*) ○Toyokazu Ishida,[1,2] Yukiko Suda,[2] Kazuya Ishimura[3]

Effective handling of reusable heat is one of the important technologies for reducing energy consumption as well as promoting energy conservation. Especially, heat storage is the practical way to solve the mismatch of energy utilization across the space and time interval. In the TherMAT project, we are investigating the basic mechanism of thermal storage materials based on the computation and thermochemical data. As for computational study of thermo chemical materials, we are focusing on the hydration process of periclase (MgO) based on the QM calculations. Besides, we are developing "PropertiesDB Web" system that contains thermal characteristics and chemical compositions of thermal storage materials.

Keywords : Thermal Management; Unused Heat Energy; Thermal Energy Storage; Thermochemical Energy Storage; Thermal Management Materials Database

環境中に排出される未利用熱エネルギーの再利用は省エネの視点から重要であり、特に蓄熱技術の高度化は未利用熱の有効活用に不可欠である。NEDO プロジェクトの実施母体である未利用熱エネルギー革新的活用技術研究組合（TherMAT）では未利用熱活用のための多様な研究を実施しており[1)]、基盤データとして熱関連材料データベース（PropertiesDB Web）の整備／公開を進めつつ、同時に計算化学と熱物性データを活用した高密度蓄熱材料の探索を実施している。様々な蓄熱材の中でも、蓄熱密度が 1MJ/kg を超える高密度蓄熱を想定する場合、現状では化学蓄熱が唯一の候補材料となる。そこで今回、化学蓄熱反応の具体例として酸化マグネシウムの水和反応を取り上げて、気相中で安定とされる (001) 面を対象とし、固－液界面で水／水酸化物イオンと金属イオンが反応して水酸化物を形成する反応過程のエネルギー変化を第一原理計算から直接計算した。(001) 面から金属イオンが移動して下層まで水分子が侵入、内壁が水和されることにより、この結晶面に水酸化マグネシウムの水和結晶核が形成されうること、またこの時の化学変化が発熱反応であること等が確認できた。

また PropertiesDB Web は下記３つの文献から熱的特性情報に該当するデータを整理したもので、TherMAT の HP 上から公開している[1)]： 1) Landolt Börnstein, 2) NBS tables of chemical thermodynamic properties, 3) 電子技術総合研究所調査報告書 196 号。

1) Thermal Management Materials and Technology Research Association: http://www.thermat.jp

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Academic Program [Oral B] | 03. Physical Chemistry -Structure- | Oral B

[K201-3am] 03. Physical Chemistry -Structure-

Chair: Jun Miyazaki, Kiichirou Koyasu

Fri. Mar 24, 2023 9:00 AM - 10:30 AM K201 (K201, Lecture Hall Bldg. [2F])

[K201-3am-01] Fundamental vibrational frequency of H_2 by Strong-field ultrahigh-resolution Fourier-transform spectroscopy

○Toshiaki Ando[1], Kana Yamada[1], Atsushi Iwasaki[1], Kaoru Yamanouchi[1] （1. The University of Tokyo）

9:00 AM - 9:20 AM

[K201-3am-02] LIF spectroscopy of jet cooled SiNSi: vibrational hot bands of the C $^2\Lambda_u$ - X $^2\Pi_g$ electronic transition

○Masaru Fukushima[1], Ishiwata Takashi[1], Chihaya Motoyoshi[2], Yoshihiro Motoyoshi[2], Yasuki Endo[2] （1. Hiroshima City University, 2. The Univ. of Tokyo）

9:20 AM - 9:40 AM

[K201-3am-03] Bottom-up approach to the ion recognition of K^+ channels by cryogenic double ion trap infrared spectroscopy

○Keisuke Hirata[1], James Lisy[2], Shun-ichi Ishiuchi[1], Masaaki Fujii[1] （1. Tokyo Institute of Technology, 2. University of Illinois）

9:50 AM - 10:10 AM

[K201-3am-04] Characterization of electronic structures of ligand-protected superatoms and superatomic molecules by gas-phase photoelectron spectroscopy

○Shun Ito[1], Emi Ito[1], Shinjiro Takano[1], Kiichirou Koyasu[1], Tatsuya Tsukuda[1] （1. The Univ. of Tokyo）

10:10 AM - 10:30 AM

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Fundamental vibrational frequency of H_2 by Strong-field ultrahigh-resolution Fourier-transform spectroscopy

(*School of Sciense, The University of Tokyo*) ○Toshiaki Ando, Kana Yamada, Atsushi Iwasaki, Kaoru Yamanouchi

Keywords: Intense laser science; Intense few-cycle laser pulses; High-resolution spectroscopy; Fourier transform spectroscopy

By pump probe measurements using few-cycle intense near-infrared (NIR) laser pulses, we can probe the motion of electrons and nuclei in a molecule in real-time. Recently, we showed that the energy level intervals of molecular cations and atomic cations can be determined by the Fourier-transform of the ion yields obtained by pump-probe measurements using NIR laser pulses.[1,2] The spectral resolution achieved by this method called strong-field ultrahigh-resolution Fourier-transform (SURF) spectroscopy is proportional to the inverse of the scanned range of the pump-probe time delay. In the previous SURF measurements for D_2^+ and Ar^+,[1,2] we achieved spectral resolution of 0.06 cm^{-1} and determined the level energies with precision of ~10^{-4} cm^{-1} by scanning the pump-probe time delay up to 500 ps. In the present study, we have extended the time delay range up to 6.4 ns and performed SURF measurements of H_2 using intense few-cycle laser pulses (1.4×10^{14} W/cm^2, 5.9 fs) to determine the fundamental vibrational frequency of H_2 with 10 ppb level precision. Because H_2 is composed only of two electrons and two protons, the rovibrational energy levels of H_2 have been calculated theoretically with very high accuracy and the comparison with experimental values will give us an opportunity to examine the accuracy of the QED corrections.

Figure 1 shows the SURF spectrum near 4120 cm^{-1}. The strong peaks assigned to the rovibrational level energy differences of H_2. By the least-squares fit, we have determined the fundamental vibrational frequency of H_2 to be 4161.166098(66) cm^{-1}. The uncertainty in the present measurement is about three times as small as that in that of the previous measurement,[3] 4161.16636(15) cm^{-1} and the resultant fundamental vibrational frequency deviates only by –0.000024(71) cm^{-1} from the most reliable theoretical value of 4161.166122(26) cm^{-1},[4] obtained with the relativistic corrections and the radiative corrections up to the order of $\alpha^7 m$.

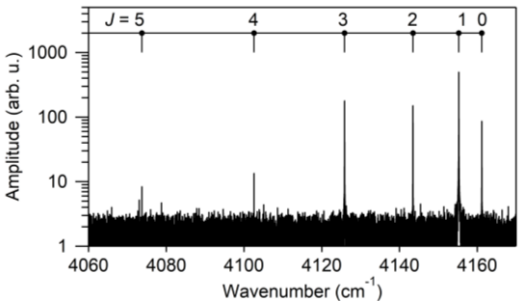

Figure 1. SURF spectrum (4060 – 4170 cm^{-1}) of H_2 obtained by the Fourier transform of the ion yield difference of H^+ and H_2^+ in the time-delay range from 20 ps to 6.4 ns. The spectral resolution is 5×10^{-3} cm^{-1}.

1) T. Ando, A. Iwasaki, K. Yamanouchi, *Phys. Rev. Lett.* **120**, 263002 (2018). 2) T. Ando, A. Liu, N. Negishi, A. Iwasaki, K. Yamanouchi, *Phys. Rev. A* **118**, 2 (2021). 3) M. L. Niu E. J. Salumbides, G. D. Dickenson, K. S. E. Eikema, W. Ubachs, *J. Mol. Phys.* **300**, 44-55 (2014). 4) J. Komasa, M. Puchalski, P. Czachorowski, G. Łach, K. Pachucki, *Phys. Rev. A* **100**, 032519 (2019).

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ジェット冷却した SiNSi の LIF 分光: $\tilde{C}\ ^2\Delta_u - \tilde{X}\ ^2\Pi_g$ 電子遷移のホットバンド

（広島市大情報 [1]・東大教養 [2]）○福島 勝 [1]・石渡 孝 [1]・本良千隼 [2]・住吉吉英 [2]・遠藤泰樹 [2]

LIF Spectroscopy of Jet Cooled SiNSi: Vibrationally Hot Bands of the $\tilde{C}\ ^2\Delta_u - \tilde{X}\ ^2\Pi_g$ Electronic Transition

([1]*Graduate School of Information Science, Hiroshima City University*, [2]*Department of Basic Science, The University of Tokyo*) ○Masaru Fukushima[1], Takashi Ishiwata[1], Chihaya Motoyoshi[2], Yoshihide Sumiyoshi[2], and Yasuki Endo[2]

We have observed the laser induced fluorescence (LIF) of the $\tilde{C}\ ^2\Delta_u - \tilde{X}\ ^2\Pi_g$ transition of SiNSi generated under supersonic free jet expansion, and measured the LIF excitation spectrum. In the spectrum, some vibrationally hot hands, $\tilde{C}\ (01^10)\ ^2\Pi_g - \tilde{X}\ (01^10)\ \mu\ ^2\Sigma_u^{(+)}$ and $\tilde{C}\ (01^10)\ ^2\Phi_g - \tilde{X}\ (01^10)\ ^2\Delta_u$, are identified. The hot bands provide information on the vibronic levels with the *g*/*u* parity different from that can be obtainable from the cold bands, i.e. the *u* and *g* parity levels for the $\tilde{X}\ ^2\Pi_g$ and $\tilde{C}\ ^2\Delta_u$ electronic states, respectively. The molecular constants obtained from the rotational analyses of the hot bands are consistent with those resulted from the rotational analyses of the cold bands. With the help of the vibrational structures of the dispersed fluorescence spectra and computational works on the structures, the vibrational structures affected by Renner-Teller (R-T) interaction have been able to be studied.

Keywords : Supersonic Free Jet Expansion; Laser Induced Fluorescence; Laser Ablation; Metal Containing Free Radical; Renner-Teller Interaction

SiNSi は、数少ない $D_{\infty h}$ フリーラジカルの１つであり、分子分光学において歴史的に重要な CNC [1)] と等原子価な分子である。今回、我々は SiNSi を超音速自由噴流中に生成させ、そのレーザー誘起ケイ光（LIF）を観測し、極低温化（回転温度 ～ 30 K）における LIF 励起スペクトルを測定した。観測された振電バンドに対し、回転分離したスペクトルを測定し、回転解析を行ったところ、このスペクトル中に、電子基底状態 $\tilde{X}\ ^2\Pi_g$ の振動基底準位からの振電遷移（ 通称 コールドバンド ）に加え、変角振動モードの励起準位 $v_2'' = 1$ からの遷移（ ホットバンド ）が観測された。直線分子の変角構造は、Renner−Teller 効果により、遷移の始状態 $v_2'' = 1$ は $\mu\ ^2\Sigma_u^{(+)}$、$\kappa\ ^2\Sigma_u^{(-)}$、および、$^2\Delta_u$ の準位に分裂する。今回、$\tilde{C}\ (01^10)\ ^2\Pi_g - \tilde{X}\ (01^10)\ \mu\ ^2\Sigma_u^{(+)}$ と $\tilde{C}\ (01^10)\ ^2\Phi_g - \tilde{X}\ (01^10)\ ^2\Delta_u$ のホットバンドが帰属できた。SiNSi は $D_{\infty h}$ 対称性のため、g/u パリティをもつが、これらのホットバンドは v_2'' モードの奇数量子数準位のため、振動角運動量量子数 l が奇数となり、基底、励起の両状態とも電子状態とは異なる g/u 準位をもつ。これらのホットバンドの回転解析により得られた振動準位の分子定数は、コールドバンドにより観測された振電準位と矛盾のないものであった。

1) A. J. Merer and D. N. Travis, Can. J. Phys. *44*, 353 (1966).

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冷却二重イオントラップ赤外分光による K^+チャネルのイオン選択性へのボトムアップアプローチ

（東工大理[1]・イリノイ大[2]）○平田 圭祐[1]・James Lisy[2]・石内 俊一[1]・藤井 正明[1]

Bottom-up approach to the ion recognition of K^+ channels by cryogenic double ion trap infrared spectroscopy

([1]*Graduate School of Science, Tokyo Institute of Technology*, [2] *Illinois University*)
○Keisuke Hirata,[1] James Lisy,[2] Shun-ichi Ishiuchi,[1] Masaaki Fujii[1]

K^+ channels are membrane proteins that selectively transport K^+ but not Na^+. X-ray crystallographic studies revealed that K^+ is recognized by a partial peptide called the selectivity filter (SF). However, it has been difficult to elucidate at the molecular level why SF does not trap Na^+. We succeeded in clarifying the molecular structure of complexes of SF's partial peptide (Ac-Tyr-NHMe) and a metal ion by gas-phase infrared spectroscopy and found a correlation between the ion permeability and the distributions of conformers. In the presentation, we will show the temperature dependence of the conformer distribution and discuss the origin of the K^+ selectivity.

Keywords : Infrared Spectroscopy; Ion Recognition; Gas-phase Spectroscopy; Cryogenic Ion Trap Infrared Spectroscopy; Potassium Channel

K^+チャネルは K^+を選択的に透過させ、K^+よりもイオン半径の小さい Na^+を透過させない膜タンパク質である。X 線結晶構造解析の結果から選択フィルター（SF）と呼ばれるペプチド部位が K^+を選択的に捕捉することが分かった[1]。しかし、なぜ Na^+の透過性が低いのかという点は、Na^+を捕捉した状態での結晶化が困難であるためよくわかっていなかった。我々は SF と金属イオンの局所構造に着目し、SF 部分ペプチド Ac-Tyr-NHMe とアルカリ金属イオンの錯体に対して気相中で赤外分光測定を行った。その結果、K^+錯体ではチャネルに類似した二配位型構造(O/O, O/O')が観測されたが、チャネルを透過しない Na^+との錯体では結晶構造とは異なる三配位型の構造(O/O/R)をとることがわかり(Figure 1)、イオン選択性とコンフォメーションの相関が示唆された[2]。講演では、コンフォマー分布の温度依存性をもとにイオン選択性の起源を議論する。

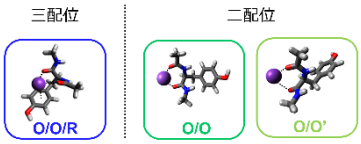

Figure 1 Molecular structures of M^+-Ac-Tyr-NHMe.

1) D. A. Doyle, *et al*., *Science* **1998**, *280*, 69. 2) S. Ishiuchi, *et al*., *Phys. Chem. Chem. Phys*. **2019**, *21*, 561.; R. Otsuka *et al*., *ChemPhysChem* **2010**, *21*, 712.; Y. Suzuki *et al*., *J. Phys. Chem. A* **2021**, *125*, 9609.

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Characterization of electronic structures of ligand-protected superatoms and superatomic molecules by gas-phase photoelectron spectroscopy

([1]*Graduate School of Science, The University of Tokyo*) ○Shun Ito[1], Emi Ito[1], Shinjiro Takano[1], Kiichirou Koyasu[1], Tatsuya Tsukuda[1]

Keywords: Gold cluster, Thiolate-protected, Gas-phase spectroscopy, Supervalence bond

Gold/silver clusters protected by organic ligands have been gathering much interest as next-generation functional nanomaterials.[1] Extraordinary stabilities of $[Au_{25}(PET)_{18}]^-$ (PET = 2-PhC_2H_4S) with an icosahedral Au_{13} core and its derivatives have been well explained by the electronic shell closure of superatomic orbitals.[2] Superatom concept was extended to supervalence bond (SVB) model to rationalize an anisotropic bi-icosahedral Au_{23} core of $Au_{38}(PET)_{24}$.[3] To probe the superatomic orbitals directly, we have developed and conducted gas-phase photoelectron spectroscopy (PES) on mass-selected beam of $[Au_{25}(PET)_{18}]^-$, $[MAg_{24}(DMBT)_{18}]^-$ (M = Ag, Au, Pd^-, Pt^-, DMBT = 2,4-$Me_2C_6H_3S$),[4] and $[MAu_{37}(PET)_{24}]^-$ (M = Pd, Pt)[5] by using a home-built apparatus (Figure 1a) equipped with an electrospray ionization (ESI) source, a quadrupole linear ion trap, a time-of-flight mass spectrometer, and a magnetic-bottle type photoelectron spectrometer. PES on $[Au_{25}(PET)_{18}]^-$ and $[MAg_{24}(DMBT)_{18}]^-$ (M = Ag, Au, Pd^-, Pt^-) revealed that doping of Pd/Pt upshifted the energy levels of 1P superatomic orbitals while the effect of Au/Ag exchange was small (Figure 1b).[4] PES on $[MAu_{37}(PET)_{24}]^-$ (M = Pd, Pt) exhibited two distinct peaks, which is in accordance with the SVB model theoretically predicted (Figure 1c).[5]

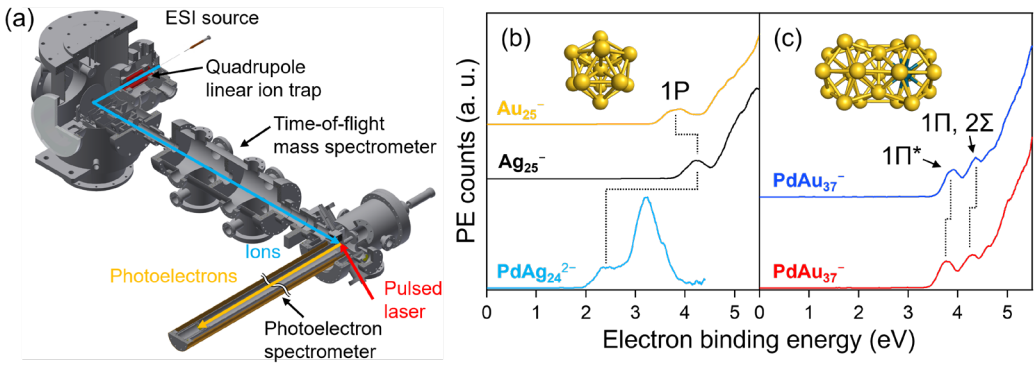

Figure 1. (a) Schematic view of an apparatus. PE spectra of (b) $[Au_{25}(PET)_{18}]^-$, $[PdAg_{24}(DMBT)_{18}]^-$, and $[PtAg_{24}(DMBT)_{18}]^-$ and (c) $[MAu_{37}(PET)_{24}]^-$ (M = Pd, Pt).

1) S. Takano et al. *J. Am. Chem. Soc.* **2021**, *143*, 1683. 2) M. Walter et al. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 9157. 3) Cheng, L. et al. *Nanoscale* **2013**, *5*, 1475. 4) S. Ito et al. *J. Phys. Chem. Lett.* **2022**, *13*, 5049. 5) E. Ito et al. *JACS Au*, **2022**, *2*, 2627.

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Academic Program [Oral B] | 03. Physical Chemistry -Structure- | Oral B

[K201-3pm] 03. Physical Chemistry -Structure-

Chair: Hiroko Miwa, Kozo Mukai

Fri. Mar 24, 2023 2:20 PM - 3:40 PM K201 (K201, Lecture Hall Bldg. [2F])

[K201-3pm-01] Title CHARACTERIZATION OF CNT- DISPERSION GELS USING ABSORPTION SPECTRA AND RAMAN SPECTRA

○Yusuke Matsumiya[1] （1. SHIBAURA INSTITUTE OF TECHNOLOGY）

2:20 PM - 2:40 PM

[K201-3pm-02] Hydrogenation of formate on the Pd/Cu(977) single-atom alloy model catalyst using surface analysis methods

○Wataru Osada[1], Shunsuke Tanaka[1], Kozo Mukai[1], Jun Yoshinobu[1] （1. The Institute for Solid State Physics, University of Tokyo）

2:40 PM - 3:00 PM

[K201-3pm-03] Excess potential of anion adsorption/desorption at ionic liquid electrolyte/electrode interfaces

○Takashi Iwahashi[1], Wei Zhou[2], Doseok Kim[3], Yukio Ouchi[1] （1. Tokyo Tech., 2. Shanghai Univ., 3. Sogang Univ.）

3:00 PM - 3:20 PM

[K201-3pm-04] Multimodal measurement of electrocatalyst for fuel cell

○Hiroko Miwa, Takefumi Yoshida[1], Takuma Kaneko[3], Takehiko Sasaki[2], Tomoya Uruga[1,3], Yasuhiro Iwasawa[1] （1. The Univ. of Electro-Comm., 2. The Univ. of Tokyo, 3. JASRI）

3:20 PM - 3:40 PM

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吸収スペクトルおよびラマン散乱スペクトルを用いたカーボンナノチューブ分散ゲルの特性評価

（芝浦工業大学　理工学研究科　応用化学専攻 [1]）○松宮 侑亮 [1]・小西 利史 [1]

CHARACTERIZATION OF CNT- DISPERSION GELS USING ABSORPTION SPECTRA AND RAMAN SPECTRA

([1] *Graduate School of Science and Technology, Shibaura Institute of Technology*) ○Yusuke Matsumiya,[1] Toshifumi Konishi,[1]

Carbon nanotubes (CNTs) are expected to be the next generation of carbon materials and nanomaterials, and various applications are being developed. One of the problems with CNTs is their tendency to aggregate due to intermolecular interactions between CNTs. In the aggregated state, CNTs are unable to exhibit their original useful characteristics. In our laboratory, we have succeeded in producing nanodispersion gels of agglomerated CNTs by adding an aromatic compound to the agglomerated CNTs and applying agitation and ultrasonic irradiation. In this study, CNT-dispersed gels were evaluated using an absorption spectrophotometer and a Raman spectrophotometer. These analytical instruments allow us to consider CNTs, aromatic compounds and their complexes from a photochemical point of view[1)]. The results suggest that aniline may be the dispersant that can maximize the characteristics of CNTs.

Keywords：*Carbon nanotube ;Charge transfer complex ;Absorption spectrum ;Raman spectrum*

カーボンナノチューブ(CNT)は次世代の炭素素材、ナノマテリアルと期待され、様々な用途開発が行われている。CNT が抱える問題点として、CNT 同士が分子間相互作用によって凝集する性質があげられる。凝集した状態では CNT 本来の有用な特徴を発揮することが不能となる。当研究室では凝集した CNT に芳香族化合物を加え、撹拌と超音波照射を行うことで CNT のナノ分散ゲルの作製に成功している。本研究では吸光光度計とラマン分光光度計を用いて CNT 分散ゲルの評価を行った。これらの分析機器は CNT と芳香族化合物及びその複合体を光化学の観点から考察できる [1)]。結果的にアニリンが CNT の特徴を最大に活かせる分散媒である可能性が示唆された。

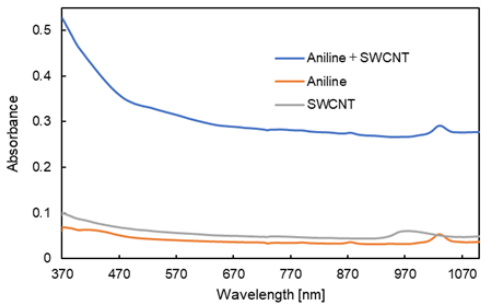

Fig. 1. Absorption spectra of Aniline and SWCNTs, and composite gels

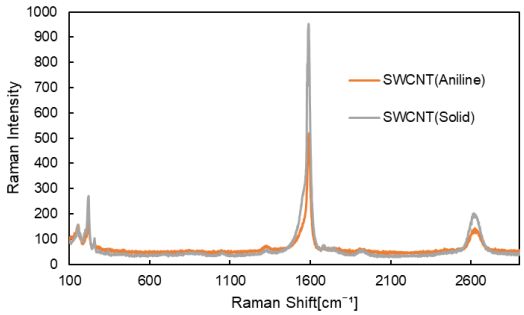

Fig. 2. Raman spectra of SWCNTs and SWCNTs after composite with aniline

1) Entrapment into charge transfer complexes for resonant Raman scattering enhancement.
A. Sidorov , O. Vashkinskaya , A. Grigorieva , T. Shekhovtsova , I. Veselova and E. Goodilin,
Chem. Commun. **2014**, 50, 6468-6470.

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Hydrogenation of formate on the Pd/Cu(977) single-atom alloy model catalyst using surface analysis methods

(*The Institute for Solid State Physics, The University of Tokyo*) ○Wataru Osada, Shunsuke Tanaka, Kozo Mukai, Jun Yoshinobu

Keywords: Formate, Surface chemistry, Stepped surface, Infrared reflection absorption spectroscopy, Temperature programmed desorption

Mitigation of industrial emissions of carbon dioxide (CO_2) is one of the most significant issues to lower the risk of serious climate change. The conversion of CO_2 to valuable chemical feedstocks, such as formaldehyde, methanol, etc., has been investigated for the past several decades because of its potential for a sustainable chemical industry. Cu-based catalysts show high activity for methanol synthesis from CO_2 and H_2, but the detailed reaction mechanism is still under debate.[1)] Understanding the mechanism would provide guiding principles for lowering the reaction temperature which is favorable for the exothermic methanol synthesis reaction. Formate species have been recognized as a critical and stable intermediate leading to the formation of methoxy species. However, the hydrogenation process of formate species has little observed, because the complex reaction mechanism makes it difficult to detect intermediate species. Recently, a few studies have claimed that dioxymethylene species were detected as hydrogenated species of formate.[2, 3)] In these studies, the evidence of dioxymethylene is only one vibrational peak, i.e. 1389 cm^{-1} for $\omega(CH_2)$[2)] or 1365 cm^{-1} for $\delta(CH_2)$.[3)] Their claims remain somewhat questionable because they have not mentioned other vibrational modes such as ν_s(OCO). Here, we conducted experiments using temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) to investigate the hydrogenation process of formate. As a model catalyst, we use a Pd-deposited Cu(977) surface, where formate species and adsorbed hydrogen atoms (H_{ad}) are easily prepared. Therefore, we are allowed to focus on only the surface chemistry of formate and H_{ad}.

The formate pre-adsorbed Pd/Cu(977) surface was prepared via the adsorption of formic acid and subsequent heating to 320 K. Thus prepared surface was exposed to the 1500 L of H_2 at 83 K, and TPD measurement was performed. A desorption peak of m/e=30 species was observed at ~190 K, assigned to the desorption of formaldehyde formed via the hydrogenation of formate species. In IRAS, vibrational peaks at 1366, 1359, and 1346 cm^{-1} developed upon the H_2 exposure and subsequent heating. In the controlled experiment using deuterium, these peaks were again observed, indicating that these peaks do not originate from hydrogenated species of formate species. We assigned the peaks at 1366, 1359, and 1346 cm^{-1} to the ν_s(OCO) mode for the bidentate formate species chemically interacting with adsorbed hydrogen atoms.

1) J. Zhong *et al.*, *Chem. Soc. Rev.*, 2020, **49**, 1385. 2) Y. Kim *et al.*, *ACS Catal.* 2016, **6**, 1037. 3) K. Takeyasu et al., *J. Am. Chem. Soc.* 2022, **144**, 12158.

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イオン液体/電極界面におけるアニオン吸脱着の過電圧要因の研究

（東工大物質理工 [1]・上海大化学系 [2]・Sogang 大 [3]）○岩橋 崇 [1]・周 尉 [2]・Kim Doseok[3]・大内 幸雄 [1]

Excess Potential of Anion Adsorption/desorption at Ionic Liquid Electrolyte/electrode Interfaces

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Room temperature ionic liquids (RTILs) provide electrolyte/electrode interfaces without neutral solvent, causing characteristic electrochemical properties and reactions. It has been reported that the RTIL/electrode interfaces exhibit hysteresis behavior in the ion adsorption/desorption; the applied potential response of ion adsorption/desorption differs with respect to the previous history of the potential application. It indicates that the ion adsorption/desorption requires an excess potential, which is needed to overcome the activation energy for ion desorption. In this study, we examined the anion adsorption/desorption processes at the RTIL/Pt electrode interfaces by combining infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy and electric double layer (EDL) model analysis to elucidate the factors determining the excess potential for anion desorption/adsorption.

Keywords : Ionic Liquid; Hysteresis; Electric Double Layer; Electrode Interface

イオン液体は常温で液相を呈する塩である。このイオンのみで構成されるイオン液体/電極界面において、電気二重層（EDL）構造の電位応答ヒステリシス、すなわち電位の変更履歴に依存してイオン吸脱着挙動が異なる現象が見出された [1]。これは、イオン液体/電極界面において、イオン吸脱着がゼロ電荷電位では生じず、過剰な電圧（過電圧）を要することを示唆する [2]。我々はイオン液体/電極界面のイオン吸脱着に要する過電圧要因の理解を目的として、界面敏感な振動分光法の赤外-可視和周波発生振動分光（infrared-visible sum-frequency generation vibrational spectroscopy; IV-SFG）にてイオン液体/電極界面のアニオン吸脱着挙動の電位応答を追跡した。

図 1 にイオン液体 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide と多結晶 Pt 電極との界面における、アニオン由来の SF シグナルの電位応答ヒステリシスを示す。過電圧を考慮しない EDL モデルから予測した SF シグナルの電位応答（モデル曲線）も示した。アニオン脱離過程はモデル曲線より負電位シフトするが、アニオン吸着過程はモデル曲線と一致する。これは、電位応答ヒステリシスがアニオン脱離過電圧に由来することを示唆する。当日は、他のイオン液体/Pt 界面の電位応答も検討し、顕著なアニオン脱離過電圧の由来を詳しく議論する。

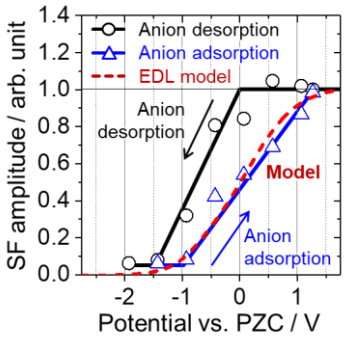

Fig. 1. Hysteretic potential response of SF signal from the anion along with that deduced from EDL model.

1) Hysteretic potential response of anion ads./des. has been reported. W. Zhou et al., *Electrochem. Commun.* **2010,** *12,* 672.

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Operando multimodal measurements of electrocatalysts in polymer electrolyte fuel cells

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Keywords: Polymer electrolyte fuel cell; Pt nanoparticle; HERFD-XANES/RIXS/XAFS/XRD; DFT calculations

Polymer Electrolyte Fuel cell (PEFC) is one of the most promising power sources, which has potential to realize low or even zero emissions. Cost reduction, performance increase and durability improvement of electrocatalysts (Pt or Pt-based alloy nanoparticles) on cathode are critical issues to be solved for a wide range of commercialization of PEFC vehicles. The PEFC performance and durability suffers severely from poisoning by sulfur-containing compounds in air, but the actual states of sulfur poisoning and recovering on the electrodes in PEFC are not clear particularly under operating conditions. Thus, obtaining atomistic insights of platinum nanoparticle electrocatalysts under sulfur contaminating conditions during PEFC operations requires urgent attentions and active efforts toward practical applications.

We have applied multimodal measurements, involving High Energy Resolution Fluorescence Detected X-ray Absorption Near-Edge Structure (HERFD-XANES), X-ray Absorption Fine Structure (XAFS), Resonant Inelastic X-ray Scattering (RIXS) and X-ray Diffraction (XRD) for MEA Pt/C cathode catalysts in PEFCs under operating conditions at BL36XU beamline in SPring-8. Appling potential from 0.4 to 0.8 V (Figure 1), Pt L_{III}-edge HERFD-XANES difference spectra showed three types of sulfur adsorbates, which inhibit oxygen adsorption. The performance of PEFC decreased with the sulfur adsorption. In addition, the sulfur adsorbates drastically decreased hydrogen adsorption at low potentials. A part of sulfur adsorbates was removed by a recovery process. Spectra simulations by FDMNES for DFT optimized structure models were also performed. The variation of HERFD-XANES spectra with sulfur poisoning at different potentials, assignments of the spectra, and recovery from the poisoning will be discussed.

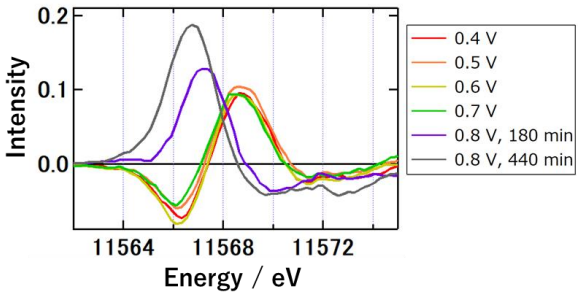

Figure 1. Pt L_{III}-edge HERFD-XANES difference spectra (vs 0.4 V) at various potentials in 25 ppm SO_2/N_2.

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

[K203-3pm] 04. Physical Chemistry -Properties-

Chair: Masaki Matsuda, Ryo Tsunashima

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-3pm-01] Rhodium-Containing Ionic Liquid for the Solvent-Free Formation of Coordination Polymers

○Ryo Sumitani[1], Tomoyuki Mochida[1,2] （1. Graduate School of Science, Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University）

1:10 PM - 1:30 PM

[K203-3pm-02] Theory of the Superheating Induced by Microwave Heating

○Makoto Koike[1,2] （1. Micro Patent Office, 2. Makoto Koike Microwave Research Institute）

1:30 PM - 1:50 PM

[K203-3pm-03] Bottom-up measurement of entropy of fusion through single-unit-cell kinetic study

○Dongxin Liu[1], Takayuki Nakamuro[1], Koji Harano[1], Eiichi Nakamura[1] （1. The Univ. of Tokyo）

1:50 PM - 2:10 PM

[K203-3pm-04] Synthesis and Physicochemical Properties of Aromatic Amine-based Ionic Liquids That Exhibited Hydrophobicity

○Kenta Matsumoto[1], Yuki Murata[1], Daiki Mizobe[1], Takeru Sunada[1], Yuki Morita[2], Hiroaki Okamoto[1] （1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Advanced Technology Institute, Yamaguchi University）

2:10 PM - 2:30 PM

[K203-3pm-05] Optical properties and magnetism derived from chirality exhibited by gyroidal MOFs with strongly isotropic structure

○Kazuya Nakashima[1], Rie Suizu[1,2], Masahisa Tsuchiizu[3], Hyuma Masu[4], Shuhei Morishita[5], Noriaki Tsurumachi[5], Masahiro Funahashi[5], Kunio Awaga[1] （1. Nagoya Univ., 2. JST-PRESTO, 3. Nara Women's Univ., 4. Chiba Univ., 5. Kagawa Univ.）

2:40 PM - 3:00 PM

[K203-3pm-06] Development of capture and release of ions and molecules in $Ni(dmit)_2$ crystals responding to the solution environment

○Jun Manabe[1], Mizuki Ito[1], Katsuya Ichihashi[1], Daisuke Konno[1], Masaru Fujibayashi[1], Goulven Cosquer[1,2], Katsuya Inoue[1,2,3,4], Tomoyuki Akutagawa[5], Kiyonori Takahashi[6], Takayoshi Nakamura[6], Sadafumi Nishihara[1,2,3,7] （1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. Chirality Research Center (CResCent), Hiroshima University, 3. Institute for Advanced Materials Research, Hiroshima University, 4. International Institute for Sustainability with Knotted Chiral Meta Matter (SKCM2), Hiroshima University, 5. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 6. Research Institute for Electronic Science(RIES), Hokkaido University, 7. Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency）

3:00 PM - 3:20 PM

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[K203-3pm-07] Physical properties of a quantum spin liquid candidate κ-$(ET)_2Cu[Au(CN)_2]Cl$ with disorder-free anion layer at low temperature

○Yuki Tanaka[1], Mitsuhiko Maesato[1], Shinya Tomeno[1], Yukihiro Yoshida[1], Yasuhiro Shimizu[2], Hiroshi Kitagawa （1. Kyoto university, 2. Nagoya University）

3:20 PM - 3:40 PM

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Rhodium-Containing Ionic Liquid for the Solvent-Free Formation of Coordination Polymers

([1]*Graduate School of Science, Kobe University,* [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Ryo Sumitani,[1] Tomoyuki Mochida[1,2]

Keywords: Ionic liquids, Rhodium complexes, Coordination polymers, Solvent-free reactions, Thermal properties

We synthesized various ionic liquids containing metal complexes that change structurally in response to external stimuli.[1] In this study, we synthesized a chemically reactive ionic liquid containing a cationic rhodium complex with 1,5-cyclooctadiene (cod) to develop liquids that can readily form coordination polymers (**Fig. 1a**). Cationic Rh-cod complexes undergo facile ligand exchange reactions.[2]

The desired ionic liquid was obtained as a yellow solid (T_m = 40 °C, **Fig. 1a**), and it remains in a liquid state at room temperature once melted. When the ionic liquid was mixed with a bidentate bridging ligand in the liquid state, the hexylbenzene dissociated from the cation, and the mixture transformed into a one-dimensional coordination polymer, bridged by the Rh-cod units (**Fig. 1b**). The polycrystalline solid coordination polymer had a melting point of 145°C. However, when the ionic liquid was mixed with a tridentate bridging ligand, an amorphous coordination polymer solid was formed. We also investigated the effects of bridging ligands and anions on the structure and properties of the products.

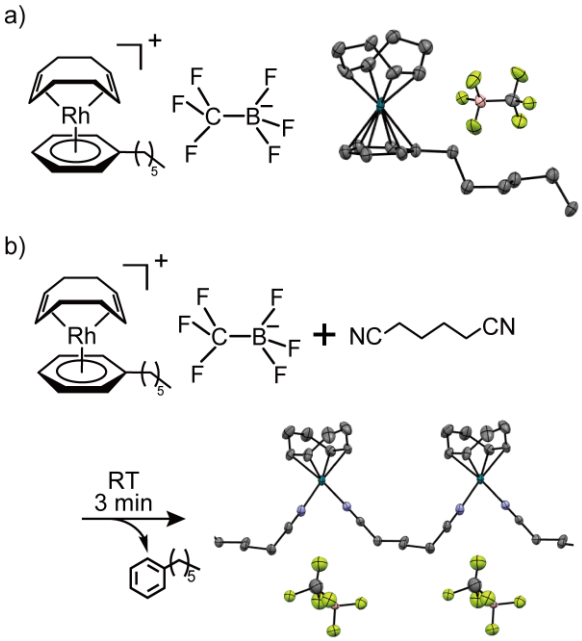

Fig. 1. (a) Structural formula and X-ray structure of the cationic Rh-cod complex (ionic liquid) prepared in this study. (b) Reaction scheme of the ionic liquid and a bidentate bridging ligand. The product's crystal structure is also presented.

1) R. Sumitani, T. Mochida, *Soft Matter*, **16**, 9946–9954 (2020).
2) R. Sumitani, D. Kuwahara, T. Mochida, *Inorg. Chem.*, *in press*.

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Theory of the Superheating Induced by Microwave Heating

([1]*Micro Patent Office*, [2]*Makoto Koike Microwave Research Institute*) ○Makoto Koike[1, 2]

Keywords: Microwave Heating; Microwave Chemistry; Superheating; Boiling points

Microwave heating of a polar liquid induces superheating and increases the boiling point in reflux,[1] and this presentation pursues a theory of this phenomena. The microwave heating is compared with the conventional heating by thermal conduction, which would induce the thermal equilibrium at the boiling point in gas-liquid interfaces.

In the conventional thermal conduction, as shown in the left figure, molecules in the gas phase (G) have the same energy level as molecules in the liquid phase (L), and the molecules in rotation in the liquid phase (L, rot) have the same energy level as the molecules in translation in the liquid phase (L, trans). These energy levels follow the Boltzmann distribution.

On the other hand, in the microwave heating, as shown in the right figure, photons induce a rotational transition from a lower energy level (E1) to a higher energy level (E3) for molecules in rotation in the liquid phase (L, rot). Regardless of the energy levels, the molecules in rotation in the liquid phase (L, rot) exchange kinetic energy with molecules in translation in the liquid phase (L, trans) through collisions. Molecules in the gas phase (G) are presumed to have the same energy level (E2) as molecules in translation in the liquid phase (L, trans) since gravity allows molecules in translation in the liquid phase, especially, those in the upward direction to the phase transition from liquid to gas in the interface. Please note that the following inequalities stand; E1<E2<E3.

In the microwave heating, the numbers of molecules at the energy level E3 and at the energy level E1 do not follow the Boltzmann distribution, and the kinetic energy in the form of rotation of the molecules, which corresponds to energy level E3, allows to store the internal energy in the liquid phase, thereby inducing the superheating and increased boiling point.

Thermal Conduction
Thermal Equilibrium

Eeq — ⇄ — ⇄ —
(L, rot) (L, trans) (G)

Microwave heating
Non-thermal Equilibrium

E3 — ↘
E2 ↑ — ⇄ —
E1 — ↙
(L, Rot) (L, trans) (G)

1) A. Ferrari; J. Hunt; A. Stiegman; G. B. Dudley, *Molecules* **2015**, *20(12)*, 21672-21680.

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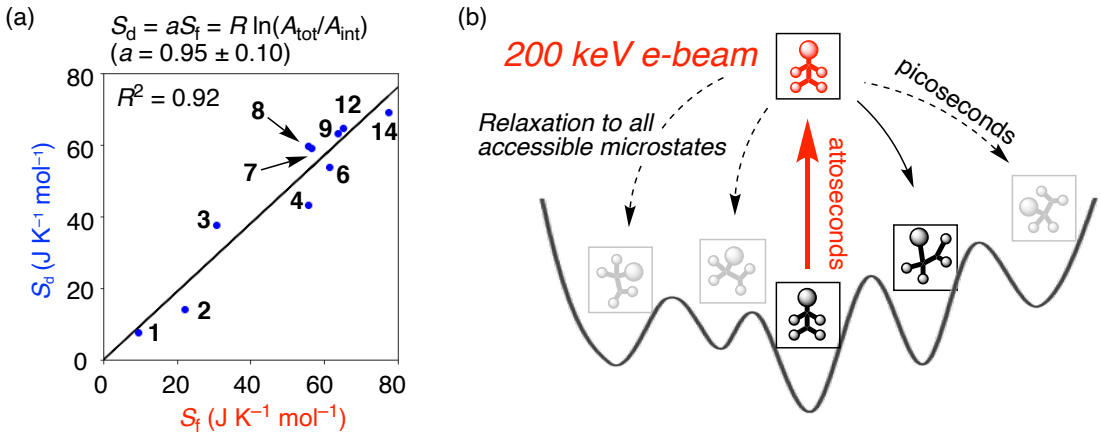
Bottom-up Measurement of Entropy of Fusion through Single-Unit-Cell Kinetic Study

(*Department of Chemistry, The University of Tokyo*)
○Dongxin Liu, Takayuki Nakamuro, Koji Harano, Eiichi Nakamura

Keywords: Entropy of Fusion; Molecular Crystal; Electron Beam; Kinetics; Electron Diffraction

Entropy is a fundamental observable that describes the order of a system. While enthalpy reflects thermodynamics of a system, entropy expresses the kinetics, for example, through steric features. However, entropy is difficult to access directly, and research has been accumulated through enthalpies measured thermodynamically.

Diffraction contains information about molecular order in systems such as crystals. We observed disordering of molecules induced by electron beams (e-beams) by following the decay of the electron diffraction (ED) intensity..[1,2] From kinetic studies with Arrhenius plots, we found that the entropy term (S_d), which can be defined in the ED analysis, correlates well with the melting entropy (S_f) of the bulk crystal, and the frequency factors (A_{tot} and A_{int}) reflect the number of accessible microstates of molecules (Figure a). Molecules receive energy from e-beams within attoseconds of interaction time that relaxes into accessible microstates (Figure b). The ED experiments only require sub-attogram amount of samples to realize an ultimate form of microanalysis of thermodynamic parameters that unachievable through thermal measurements.



1) J. R. Fryer *Ultramicroscopy* **1992**, *40*, 163. 2) J. Hattne *Structure* **2018**, *26*, 759.

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Synthesis and Physicochemical Properties of Aromatic Amine-based Ionic Liquids That Exhibited Hydrophobicity

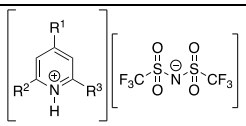
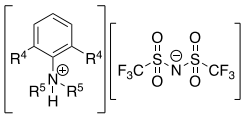
([1]*Graduate School of Sciences and Technology for Innovation, Yamaguchi University*, [2]*Advanced Technology Institute, Yamaguchi University*) ○Kenta Matsumoto,[1] Yuki Murata,[1] Daiki Mizobe,[1] Takeru Sunada,[1] Yuki Morita,[2] Hiroaki Okamoto[1]

Keywords: Pyridine; Aniline; Protic Ionic Liquid; Bis(trifluoromethanesulfonyl)amide; Hydrophobicity

"Ionic liquids" is a general term for salts with melting points below 100°C. In particular, the substances that become liquid at room temperature and pressure are being considered for applications in electrochemical devices and CO_2 sorption materials. In previous studies, protic ionic liquids (PILs) obtained by neutralization of Brønsted acid and Brønsted base have been found.[1, 2]

In this study, the novel PILs were synthesized by neutralization of aromatic amines such as pyridine and aniline derivatives with Tf_2NH to be co-exist hydrophobicity and proton conductivity (Table 1).

Table 1. Chemical structures of PILs and their 1-octanol – water coefficient (log P_{ow}).

Basic structure	Name	R^1	R^2	R^3	log P_{ow}
	[2,4-Lut][TFSA]	Me	Me	H	0.96±0.20
	[2,6-Lut][TFSA]	H	Me	Me	0.74±0.29
	[2,4,6-Col][TFSA]	Me	Me	Me	0.29
Basic structure	**Name**	**R^4**		**R^5**	**log P_{ow}**
	[2,6-^{i}Pr$_2$AN][TFSA]	*i*-Pr		H	0.65±0.33
	[*N*,*N*-Me$_2$AN][TFSA]	H		Me	1.1±0.29
	[*N*,*N*-Et$_2$AN][TFSA]	H		Et	1.1±0.64
	[*N*,*N*,2,6-Et$_2$AN][TFSA]	Et		Et	0.97±0.55

[2,6-^{i}Pr$_2$AN][TFSA] was solid in room temperature (m.p. = 76 – 77 ºC) due to little steric hindrance in H^+ sources. Other PILs were liquid state in room temperature and exhibited hydrophobicity confirmed by visual and 1-octanol – water coefficient (Table 1, log P_{ow}) examined by HPLC. Arrhenius plots of ionic conductivities in [2,6-Lut][TFSA] and [*N*,*N*-Me$_2$AN][TFSA] were shown in Figure 2. The former followed Arrhenius's equation, whereas the latter followed Vogel-Fulcher-Tammann's equation. It was considered that the mechanisms of ionic conduction were difference between them.

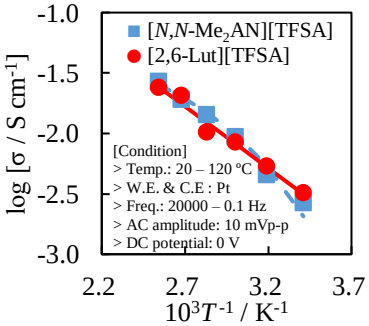


Figure 2. Arrhenius plots of ionic conductivity.

[1] H. Nakano *et al*, *Chem. Commun*. **2007**, *24*, 2539. [2] C. Mao *et al*, *J. Org. Chem.* **2015**, *80*, 8384.

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Optical properties and magnetism derived from chirality exhibited by gyroidal MOFs with strongly isotropic structures

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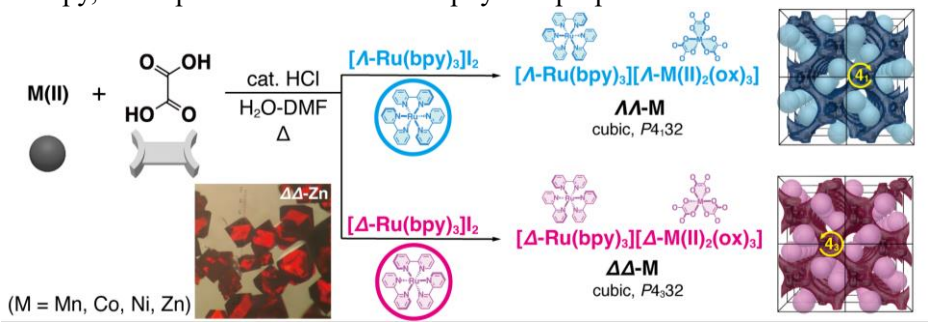
Keywords: Chiral MOFs, Strong Isotropy, Gyroidal lattice, Antiferromagnetic, Circularly Polarized Luminescence

Chiral materials have attracted a great deal of attention in a wide range of fields because of their chirality-based physical properties such as circular dichroism and chiral magnetism. In particular, the single gyroid lattice is a chiral structure belonging to the space group of cubic $I4_132$, in which steric 10-membered rings create a huge internal vacancy. This lattice also has been mathematically proven to have a property called "strong isotropy," and make unique band dispersion from its high symmetry. [1] Materials with gyroid lattice, which has both chirality and strong isotropy, are expected to exhibit novel physical properties.



Scheme 1. Synthetic scheme of single gyroidal MOFs with chiral resolution

Recently, we found that the homochiral metal-organic-frameworks (MOFs) $[Ru(bpy)_3][M_2(ox)_3]$ (M=Zn (**2**), Mn (**3**))[2] with gyroidal structures exhibit the circularly polarized luminescence (CPL) with large dissymmetry factors ($g_e > 10^{-2}$). Although their absorption and luminescence spectra showed similar shapes for each of the parent complex $[Ru(bpy)_3]I_2$ (**1**), **2** and **3**, the intensities were very different: those of **1** and **2** were almost same, while that of **3** was significantly lower. We measured the luminescence lifetimes and quantum yields to understand this difference. Solid-state time-resolved photoluminescence spectra are shown in **Fig. 1**, which indicates the luminescence lifetimes of **3** is much shorter than those of **1** and **2** due to the host-guest interaction between luminescent molecule **1** and the gyroidal MOF. Based on these data, we will discuss the CPL in **1**~**3**, especially the enhanced CPL in **3**, mentioning to their magnetic properties.

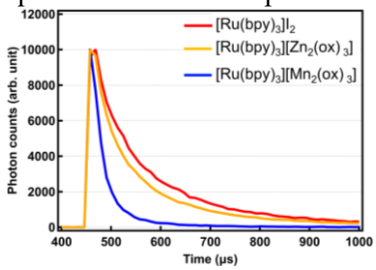


Fig. 1. Solid-state time-resolved PL

1) M. Tsuchiizu, *Phys. Rev. B* **94**, 195426 (2016).
2) a) F. Pointillart, et al., *Tetrahedron: Asymmetry* **17,** 1937 (2006). b) C. A. Kent, et al., *J. Mater. Chem. A*, **1**, 14982 (2013).

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Development of capture and release of ions and molecules in $Ni(dmit)_2$ crystals responding to the solution environment

([1]*Grad. Sch. Adv. Sci. Eng.;* [2]*CResCent;* [3]*IAMR;* [4]*International Institute for SKCM*[2]*; Hiroshima University,* [5]*IMRAM, Tohoku University,* [6]*RIES, Hokkaido University,* [7]*PRESTO, JST*) ○ Jun Manabe,[1] Mizuki Ito,[1] Katsuya Ichihashi,[1] Daisuke Konno,[1] Masaru Fujibayashi,[1] Goulven Cosquer,[1,2] Katsuya Inoue, [1,2,3,4] Tomoyuki Akutagawa,[5] Kiyonori Takahashi,[6] Takayoshi Nakamura,[6] Sadafumi Nishihara[1,2,3,7]

Keywords: *supramolecular cation, solid-state ion exchange, crystal structure, Ni(dmit)$_2$, magnetic property*

The concentration of metal ions such as calcium *in vivo* is closely related to muscle contraction. Hence, the control systems for the capture and release of metal ions have recently attracted attention to mimic the physical function of biological proteins. From that point of view, we focused on $Li_2([18]crown\text{-}6)_3[Ni(dmit)_2]_2(H_2O)_4$ (**Li salt**), which is combining a Li^+ and [18]crown-6 supramolecular cation and a $[Ni(dmit)_2]^-$ complex.[1)] In the crystal, ion channel structure along *b*-axis was formed by two Li^+ ions and three [18]crown-6 molecules per unit, through which Li^+ ions can be conducted. Furthermore, solid-state ion exchange occurs by immersing **Li salt** in a KCl aqueous solution, where Li^+ ions were exchanged by K^+ ions.[2)] In the case of Ca^{2+} ion exchanged crystal (**Li→Ca salt**), SC-XRD analysis has clarified the exchange process. The replacement of Li^+ ions is accompanied by a partial release of [18]crown-6 molecules from the crystal (Fig. 1a).

In this work, we aimed to control the capture and release of ions and molecules functions of **Li salt** in response to the environment. To control the Ca^{2+} ion exchange (capture), as [18]crown-6 molecules were released from the crystal during the process, we added [18]crown-6 to the solution to suppress the exchange by equilibrium. Soaking **Li salt** in an aqueous solution containing Ca^{2+} ion and [18]crown-6 preserved the crystal structure of **Li salt** (Fig. 1b). The release control of Ca^{2+} ions was achieved by soaking **Li→Ca salt** in an aqueous solution containing only Li^+ ion (Fig. 1c), or Li^+ ion and [18]crown-6 (Fig. 1d). The results showed that **Li→Ca salt** can return to its original structure only in the presence of both solutes.

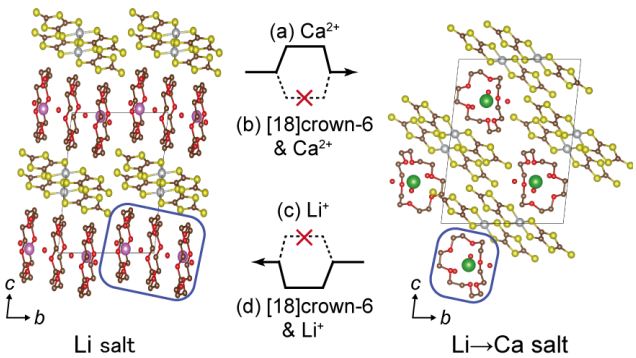

Fig. 1 Schematic diagram of the relation of capture and release of ions and molecules. Blue circles show the supramolecular cation unit.

1) K. Ichihashi, *et al., Chem. Mater.* **2018**, *30*, 7130.
2) K. Ichihashi, *et al., Angew. Chem. Int. Ed.*, **2019**, *58*, 4169.

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Physical properties of a quantum spin liquid candidate κ-(ET)$_2$Cu[Au(CN)$_2$]Cl with disorder-free anion layer at low temperature

([1]*Graduate School of Science, Kyoto University*, [2]*Graduate School of Science, Nagoya University*) ○Yuki Tanaka,[1] Mitsuhiko Maesato,[1] Shinya Tomeno,[1] Yukihiro Yoshida,[1] Yasuhiro Shimizu,[2] Hiroshi Kitagawa[1]

Keywords: ET; Quantum spin liquid; Transport properties; Magnetic properties; Spin frustration

Quantum spin liquids (QSLs) have attracted much attention because they are exotic quantum phases of matter where a long-range magnetic ordering is suppressed by strong spin frustration even at low temperature. Several QSL candidates with triangular lattice have been reported in organic conductors so far.[1,2] However, all the reported organic QSL candidates have some disorders in their crystal structures. Such structural disorders have been discussed as one of the key factors for realizing QSL. To evaluate the intrinsic role of spin frustration in QSL, disorder-free QSL candidates are highly desired.

Here we report our recent investigation on physical properties of the QSL candidate κ-(ET)$_2$Cu[Au(CN)$_2$]Cl. This is the first organic QSL candidate with disorder-free polyanion layers (Fig.).[3] This salt has nearly regular triangular lattice and shows no magnetic order down to 0.45 K, which is more than two orders of magnitude lower than the exchange interaction J/k_B = 210 K. This new QSL candidate can provide an ideal research platform to investigate a genuine QSL state. We have investigated the ground states of κ-(ET)$_2$Cu[Au(CN)$_2$]Cl by ESR measurements and high-pressure transport measurements up to 7 kbar.

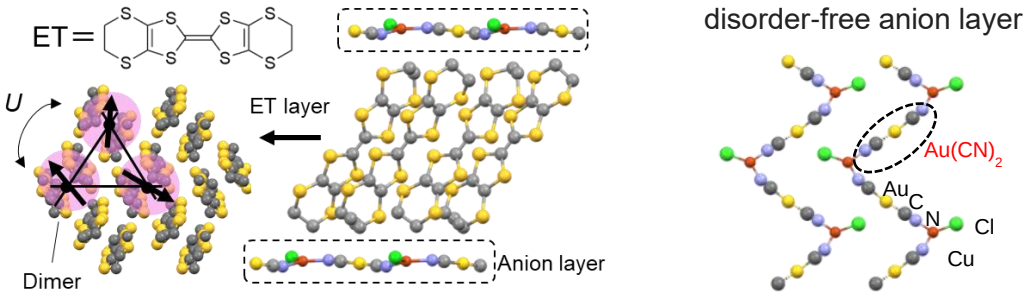

Fig. Crystal structure of κ-(ET)$_2$Cu[Au(CN)$_2$]Cl

1) Y. Zhou, K. Kanoda, T. Ng, *Rev. Mod. Phys.*, **2017**, *89*, 025003.
2) M. Maesato, Recent Topics on Organic Spin Liquid Candidates. In: Nishimura K., Murase M., Yoshimura K. (eds) *Creative Complex Systems. Creative Economy*, **2019**, Springer, Singapore.
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Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B

[K203-3vn] 04. Physical Chemistry -Properties-

Chair: Hiroyuki Nishikawa, Ryo Tsunashima

Fri. Mar 24, 2023 4:10 PM - 5:50 PM K203 (K203, Lecture Hall Bldg. [2F])

[K203-3vn-01] On-surface chemistry of crown ether molecules on Cu(111)

○Toyo Kazu Yamada[1], Masaki Horie[2] （1. Chiba University, 2. Taiwan Tsing Hua Univ.）

4:10 PM - 4:30 PM

[K203-3vn-02] Single amino acid molecule discrimination by molecular modification of nano-gap and machine learning analysis

○JIHO RYU[1], Yuki Komoto[1], Takahito Ohshiro[1], Masateru Taniguchi[1] （1. Osaka University）

4:30 PM - 4:50 PM

[K203-3vn-03] Effects of solid surfaces on diradical characters of adsorbed molecules

○Kohei Tada[1], Koji Fujimaru[1,2], Hiroyuki Ozaki[1], Yasutaka Kitagawa[2], Takashi Kawakami[2], Mitsutaka Okumura[2], Shingo Tanaka[1] （1. AIST, 2. Osaka Univ.）

4:50 PM - 5:10 PM

[K203-3vn-04] “Floating Island”, a Metastable Intermediate in Crystal Growth Revealed by Millisecond TEM Imaging

○Masaya Sakakibara[1], Takayuki Nakamuro[1], Hiroki Nada[2], Eiichi Nakamura[1] （1. The University of Tokyo, 2. Tottori University）

5:10 PM - 5:30 PM

[K203-3vn-05] Tip-enhanced second-order nonlinear optical processes in a nanomolecular system adsorbed on metal surface

○Shota Takahashi[1,2], Atsunori Sakurai[1,3], Tatsuto Mochizuki[1,3], Toshiki Sugimoto[1,3,4] （1. Institute for molecular science, 2. JSPS Research Fellow PD, 3. The Graduate University for Advanced Studies, 4. JST PRESTO）

5:30 PM - 5:50 PM

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表面場でのクラウンエーテル分子の多様性：電圧構造制御・一次元ポリマー化・磁性微粒子

（千葉大院工 [1]・千葉大キラ研 [2]・台湾清華大 [3]）○山田 豊和 [1,2], 堀江 正樹 [3]
On-surface chemistry of crown ether molecules on Cu(111) ([1]*Graduate School of Engineering, Chiba Univ.*, [2]*Chiral Research Center, Chiba Univ.*, [3]*Taiwan Tsing Hua Univ.*) ○Toyo Kazu Yamada[1,2] and Masaki Horie[3]

An ordered array of crown ether ring molecules (4,4',5,5'-tetrabromodibenzo[18]crown-6 ether (Br-CR)) prepared on Cu(111) at room temperature in ultrahigh vacuum (UHV) was used [1,2]. Because of the flexible ring, the Br-CR could have an ability of trapping guest atoms, molecules and ions, providing a functional supramolecule.

In this study, we show three research topics: (1) guest Ferrocene-Amine molecules on the Br-CR array, (2) one-dimensional (1D) polymer formation via Ullmann reaction using the Br-CR array, and (3) 2-nm-size metal-organic nanocluster formation fabricated by cobalt atom adsorption on the Br-CR array.

All experiments were performed using a home-built ultrahigh vacuum low-temperature scanning tunneling microscopy (STM) setup.

Keywords： Crown Ether; Ferrocene; Polymer, Cobalt, Scanning Tunneling Microscopy

臭素終端クラウンエーテル(Br-CR)分子は、炭素原子と酸素原子からなる環を中心に持ち、その両脇にベンゼン環二個を持つ。この Br-CR 分子を超高真空内で Cu(111)表面に吸着すると、自己組織的に二次元規則配列膜ができる [1,2]。Br-CR は中心の柔軟な環を持つため、ゲスト原子・分子・イオンをトラップできる機能を持ち、表面場にて新たな超分子構造体を作製できるホストとなる。

この Cu(111)上の Br-CR 規則配列を使って以下の三つの研究を行ったので報告する。(1)Ferrocene-Amine ゲスト分子を吸着すると Br-CR ホスト分子がトラップ機能により補足し、新たな規則配列を形成した。電圧依存による構造変化を計測した。その原因を解明する。(2) Br-CR 配列を前駆体として、表面場でウルマン反応させる一次元ポリマー化した。(3)Br-CR 配列にコバルト原子を吸着すると、2 nm サイズの均一なナノ粒子化が作製できた。

本研究は全て自作の超高真空・低温・走査トンネル顕微鏡(STM)装置を用いて実施した。詳細を報告する。

1) Well-Ordered Monolayer Growth of Crown-Ether Ring Molecules on Cu(111) in Ultra-High Vacuum: A STM, UPS, and DFT Study. R. Nemoto, P. Krueger, A. N. P. Hartini, T. Hosokai, M. Horie, S. Kera, T K. Yamada, *J. Phys. Chem. C* **2019**, *123*, 18939.
2) クラウンエーテル環状分子(7×4)配列へのコバルト単原子層の室温吸着：超高真空 STM・UPS 研究. R. Nemoto, P. Krueger, T. Hosokai, M. Horie, S. Kera and T. K. Yamada, *表面と真空* **2020**, *63*, 465. https://doi.org/10.1380/vss.63.465

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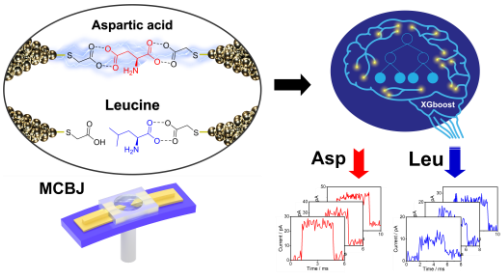
Single amino acid molecule discrimination by molecular modification of nano-gap and machine learning analysis

(SANKEN (The Institute of Scientific and Industrial Research), Osaka University)
○ Jiho Ryu, Yuki Komoto, Takahito Ohshiro, Masateru Taniguchi
Keywords: Neurotransmitters; Nano-gap; Machine learning; Single-molecule study

The development of detection/identification methods for amino acids is an important issue for understanding of biological systems. Until now, there have been few analytical methods for amino acids because of limited selectivity and low detection limit. Single-molecule measurement is one of the promising candidates for identification of amino acids. However, molecules with similar structures are difficult to identify because their electronic structures are also similar. In this study, we focused on the development of an amino acid discrimination method by hydrogen-bond facilitated quantum tunneling enhancement.

We selected L-aspartic acid (Asp) and L-leucine (Leu) as target molecules for the diagnosis of several diseases such as epilepsy and schizophrenia. Mechanically controllable break junction (MCBJ) was applied as a platform to measure single-molecule conductance. The MCBJ devices have gold nanowire formed on the flexible silicon substrates. The pushing rod controlled by the piezo bends the substrate and the nanowire is mechanically broken, eventually the nano-gap is formed. Target molecules were measured in mercaptoacetic acid (MAA) aqueous solution and Milli-Q water. The measured current was investigated by machine learning based time series analysis for accurate discrimination.

Compared to measurements using bare nano-gap, it is found that MAA modification improves the difference in the conductance-time profiles between Asp and Leu through the hydrogen bond facilitated tunneling phenomena for Asp, and not for Leu. We found that the accuracy of discrimination with MAA is 0.99 using over thirteen conductance signals. It is also found that this method enables determination of concentration even in the mixture of Asp and Leu. This method demonstrates the improvement of selective analysis of amino acids so that this will be potentially applicable for medical application, diagnosis and single-molecule peptide sequencer.



1) J. Ryu, Y. Komoto, T. Ohshiro, M. Taniguchi, *Chem. Asian J.*, **2022**, e202200179. 2) Y. Komoto, T. Ohshiro, T. Yoshida, E. Tarusawa, T. Yagi, T. Washio, M. Taniguchi, *Sci. Rep.*, **2020**, *10*(1), 1-7. 3) T. Ohshiro, M. Tsutsui, K. Yokota, M. Furuhashi, M, Taniguchi, T. Kawai, *Nat. Nanotech.*, **2014**, *9*(10), 835-840.

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ジラジカル分子に対する表面吸着効果の検討

（産総研 [1]・阪大院理 [2]・阪大院基礎工 [3]）○多田 幸平 [1]・藤丸 航志 [1,2]、尾崎 弘幸 [1]、北河 康隆 [3]、川上 貴資 [2]、奥村 光隆 [2]、田中 真悟 [1]
Effects of solid surfaces on diradical characters of adsorbed molecules ([1]AIST, [2]*Graduate School of Science, Osaka University*, [3]*Graduate School of Engineering Science, Osaka University*) ○Kohei Tada,[1] Koji Fujimaru[1,2], Hiroyuki Ozaki[1], Yasutaka Kitagawa[3], Takashi Kawakami[2], Mitsutaka Okumura[2], Shingo Tanaka[1]

To realise novel molecular devices, immobilising functional open-shell molecules (e.g., diradical molecules) on solid surfaces have been attempted. However, the effects of surface interactions on molecular functions are still unclear. DFT/plane-wave is a first-principles calculation scheme for solid surfaces and can calculate electronic states and energies with relatively low cost and high accuracy. We have developed a scheme to estimate spin contamination error (computational errors in DFT calculations of diradical molecules) and diradical character (features of diradical molecules) in a few seconds using the standard output of DFT/plane-wave calculations. Using the developed technique, the Au_2/MgO(001) system is analysed (Fig. 1). The spin contamination error and diradical character depend on the distance between the Au_2 and MgO; this is caused by orbital polarisation due to the surface.
Keywords : Molecule/surface interaction; Diradical character; Density functional theory

ジラジカル分子などの機能性開殻分子を固体表面で固定化することで新規な分子デバイスの創生を目指す試みがある。一方で、表面相互作用の分子機能への影響については不明瞭な点が多い。DFT/plane-wave 計算は固体表面の一般的な第一原理計算手法であり、比較的低コストかつ高精度に電子状態・エネルギーを計算できる。我々は DFT/plane-wave 計算の標準出力を用いて数秒でスピン混入誤差（ジラジカル分子の DFT 計算で生じる計算誤差）とジラジカル性（ジラジカル分子の特徴量）を算出する技術を開発した。開発技術を用い、Au_2/MgO(001)を解析した結果が Fig. 1 である。表面との距離に依存してスピン混入誤差とジラジカル性が変化しており、これは表面による軌道分極によって引き起こされていることが明らかとなった。

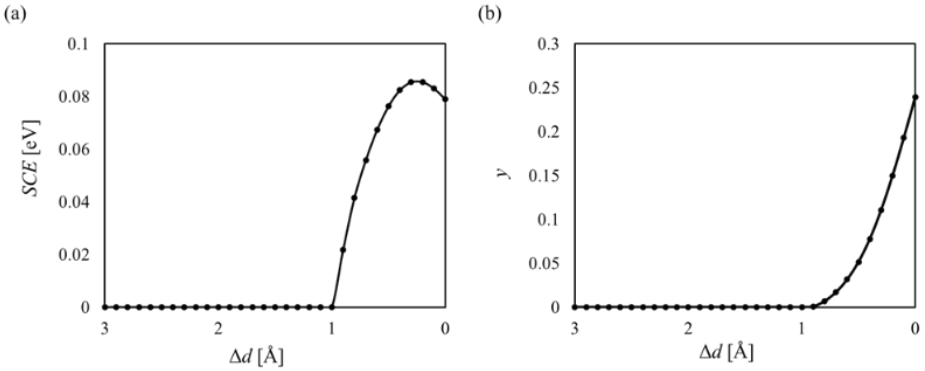

Fig. 1. (a) Spin contamination error (*SCE*) and (b) diradical character (*y*) of the Au_2/MgO(001). Δd is a difference from the equilibrium adsorption distance.

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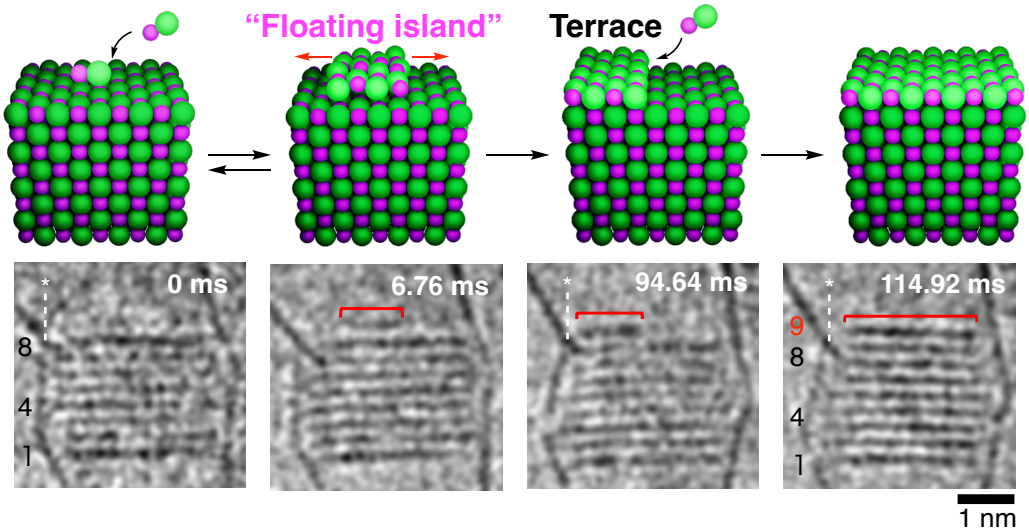
“Floating Island”, a Metastable Intermediate in Crystal Growth Revealed by Millisecond TEM Imaging

([1]*Department of Chemistry, The University of Tokyo*, [2]*Division of Mechanical and Physical Engineering, Tottori University*)
○Masaya Sakakibara,[1] Hiroki Nada,[2] Takayuki Nakamuro,[1] Eiichi Nakamura[1]
Keywords: Crystallization; 2-D Nucleation; Transmission Electron Microscopy; Atomic Resolution; Cluster

Crystal growth consists of 2-D nucleation and 2-D growth. The former is a process in which atoms, ions, and molecules adsorbed on the crystal surface assemble to form a 2-D nucleus.[1] Since this process determines the direction and rate of crystal growth, its mechanism has been studied to precisely control the shape and quality of crystals. However, the atomistic mechanism of crystal growth has not been clarified in detail because of limitations in spatial and temporal resolutions of analytical methods. In this context, we have demonstrated the direct observation of sodium chloride (NaCl) nanocrystal growth by single-molecule atomic-resolution time-resolved electron microscopy (SMART-EM).[2,3]

SMART-EM observations allowed us to record the entire process of NaCl nanocrystal growth at 300 frames per second, as shown in the following images. Before the formation of a 2-D nucleus (e.g., 94.64 ms), we found a metastable surface cluster or "floating island (FIs)" dynamically migrating on the surface. It was also revealed that the reaction vessel wall contributed to the formation of the FIs. Since conventional crystal growth theory did not assume such intermediates or surface catalysis mechanisms, the atomic-level insights obtained here will contribute to future advances in the theory.



1) A. E. S. Van Driessche *et al.*, *Cryst. Growth Des.* **2007**, *7*, 1980. 2) T. Nakamuro *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 1763. 3) M. Sakakibara *et al.*, *ACS Cent. Sci.* **2022**, *8*, 1704.

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Tip-enhanced second-order nonlinear optical processes in a nanomolecular system adsorbed on metal surface

([1]*Institute for molecular science*, [2]*JSPS Research Fellow PD,* [3]*The Graduate University for Advanced Studies,* [4]*JST PRESTO*) ○Shota Takahashi,[1,2] Atsunori Sakurai,[1,3] Tatsuto Mochizuki,[1,3] Toshiki Sugimoto[1,3,4]

Keywords: Plasmons, Tip enhancement, Second-order nonlinear optics, Surface nanomolecular system

The light confined by tip-substrate plasmonic nanocavities carries information on physical properties in molecular/atomic scale. Their outstanding ability to shrink light beyond the diffraction limit renders them highly attractive to nanoscale photonics. While linear optical responses are a central issue in this field, recent years have seen several meaningful attempts for nanoscale detection of a variety of nonlinear optical processes.[1,2] In this context, we have confirmed recently that tip-enhancement of nonlinear optics is applicable to a broad range of near- or mid-infrared light as well as visible light.[3] This suggests the possiblility of the nanoscale spectroscopic detection of molecular vibrational modes via nonlinear optical processes. In particular, if vibrational sum frequency generation (VSFG) is combined with scanning probe microscope, it could become a powerful tool for studying molecular orientation at the nanoscale. In this study, as a proof-of-principle experiment, we introduce the first demonstration of tip-enhanced VSFG spectroscopy for the model nanomolecular system adsorbed on a metal surface (Fig. 1).

We chose a self-assembled monolayer (SAM) of 4-Methylbenzenethiol (MBT) on Au(111) substrate as the SFG-active model analyte. The idler output from an optical parametric oscillator pumped by an Yb-fiber laser (1035 nm, 300 fs, 50 MHz) is used to resonantly excite the vibrational mode of methyl moiety of MBT. The idler beam and the attenuated fundamental wave of the Yb-fiber laser are collinearly combined at a dichroic mirror and irradiated to stimulate VSFG. We successfully capture the characteristics of vibrational resonance band of MBT molecules. The detail of the light emission property and critical advantage of tip-enhanced VSFG will be discussed in the presentation.

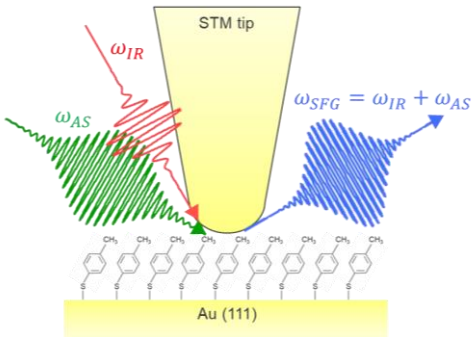

Fig. 1 Schematic diagram of tip-enhanced VSFG of SAM on Au(111) surface.

1) C. F. Wang and P. Z. El-Khoury, *J. Phys. Chem. Lett.* **2022**, *13*, 7350. 2) V. Kravtsov, R. Ulbricht, J. M. Atkin, and M. B. Raschke, *Nat. Nanotechnol.* **2016**, 11, 459. 3) S. Takahashi, A. Sakurai, T. Mochizuki, and T. Sugimoto, *to be submitted*.

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

[K205-3pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Shinichi Fukahori, Takuya Horio

Fri. Mar 24, 2023 1:20 PM - 3:40 PM K205 (K205, Lecture Hall Bldg. [2F])

[K205-3pm-01] Photodissociation and detachment processes of size-selected silver cluster anions, Ag_N^- (N = 3–11): Photon-energy dependent lifetime of excited states

○Shun Kawamura[1], Satoshi Kono[1], Masato Yamaguchi[1], Masashi Arakawa[1], Takuya Horio[1], Akira Terasaki[1] （1. Kyushu University）

1:20 PM - 1:40 PM

[K205-3pm-02] Photoelectron imaging of 3d-transition-metal-doped silver cluster anions with 18 valence electrons

○Tasuku Nishizato[1], Haruki Hashimoto[1], Kazuaki Matsumoto[1], Yuta Suzuki[1], Masashi Arakawa[1], Takuya Horio[1], Akira Terasaki[1] （1. Department of Chemistry, Kyushu University）

1:40 PM - 2:00 PM

[K205-3pm-03] Ultrafast pump-probe measurement of CO_2 by few-cycle NIR pulses and the high-order harmonics

○Takuya Matsubara[1], Hiroki Mashiko[1], Tomoya Yamauchi[1], Kana Yamada[1], Toshiaki Ando[1], Atsushi Iwasaki[1], Kaoru Yamanouchi[1] （1. Sch. Sci., The Univ. of Tokyo）

2:10 PM - 2:30 PM

[K205-3pm-04] Formation of molecular hydrogen ions during metal ablation by femtosecond laser pulses

Tatsuro Shirota[1], Yasufumi Kobayashi[2], ○Kennosuke Hoshina[1], Kaoru Yamanouchi[3] （1. Niigata Univ. of Pharmacy, 2. Niigata University Medical &Dental Hospital, 3. The Univ. of Tokyo ）

2:30 PM - 2:50 PM

[K205-3pm-05] Observation of electrochemical Peltier effects by a simple method

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

3:00 PM - 3:20 PM

[K205-3pm-06] Electrochemical reduction of N_2 to NH_3 by boron and nitrogen doped carbon nanosphere in electrolytes with different pH values

○Mingyuan WANG[1], Akihiko Fukunaga[1] （1. Waseda university）

3:20 PM - 3:40 PM

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サイズ選別銀クラスター負イオン 3–11 量体の光解離・脱離過程：光子エネルギーに依存する励起状態寿命

（九大院理）〇河村駿・河野聖・山口雅人・荒川雅・堀尾琢哉・寺嵜亨

Photodissociation and detachment processes of size-selected silver cluster anions, Ag_N^- (N = 3–11): Photon-energy dependent lifetime of excited states

(Department of Chemistry, Kyushu University) 〇Shun Kawamura, Satoshi Kono, Masato Yamaguchi, Masashi Arakawa, Takuya Horio, Akira Terasaki

Typical values of electron detachment thresholds of metal cluster anions are a few electron volts. Consequently, the excess electrons are detached by visible (VIS) and ultraviolet (UV) light, which also induces electronic transitions into bound excited states. Such bound states embedded in the continuum have not been fully explored for metal cluster anions. Here, we present photodestruction action spectra of Ag_N^- (N = 3–19) using a temperature-controlled ion trap to reveal their bound excited states in the energy range of 2–5 eV.

Keywords : silver cluster; electron detachment; photodissociation; lifetime broadening; hot band

金属クラスター負イオン M_N^-の電子脱離エネルギーの閾値は、一般的に数 eV であるため、可視・紫外光により余剰電子の脱離（連続状態 $M_N + e^-$ への遷移）が起こる。一方、同波長域の光は、M_N^-の束縛励起状態 M_N^{-*}への遷移も誘起するため、閾値以上のエネルギーでは 2 つの状態への遷移が競合する。このような連続状態に“埋もれた”束縛状態の探究は極めて限定的であった[1]。本研究では、温度制御可能なイオントラップを用い、約 0.015 eV の測定間隔で、Ag_N^-(N = 3–19)の光解離・脱離の作用スペクトル（光吸収スペクトル）を測定し、束縛励起状態の全容解明を目指した。

例として、10 量体の作用スペクトルを図 1 に示す。図中の破線は垂直電子脱離エネルギー（VDE）の実測値（2.13 eV [2]）であり、その高エネルギー側に明確な構造が現れている。300 K での測定（●）では、2.8 eV に鋭いピーク(i)、3.6 eV に幅広な吸収帯(ii)が現れた。このピークの分裂は幾何構造が扁長型であることに起因する。さらに、100 K で再測定したところ（青線）、ピーク(i)のみが先鋭化した。これは、(i)のピーク幅がホットバンドの影響を強く受けているのに対し、(ii)のバンド幅は主に寿命幅に起因することを示唆している。さらに、ピーク(i)では光吸収後に電子脱離と解離が競合することも実験的に確認できた。解離は内部転換、分子内振動エネルギー再分配（IVR）の後に発生するため、一般的に脱離よりも長寿命である。以上より、VDE の近傍では励起状態寿命が長く、逆に高エネルギー側では短寿命であることが示唆された。講演では他のサイズの結果についても議論する。

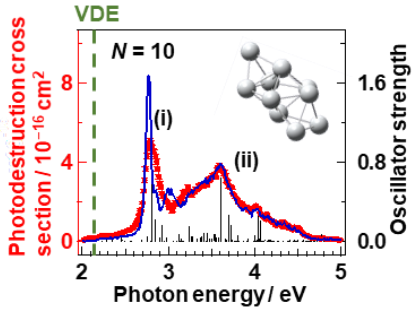

Figure 1. Action spectrum of Ag_{10}^-. ●: experiment at 300 K, blue line: experiment at 100 K, bar: VEEs obtained by TDDFT, green dashed line: VDE obtained by experiment [2], inset: geometric structure.

[1] J. Tiggesbäumker et al., *Chem. Phys. Lett.* **260**, 428 (1996). [2] G. Ganteför *et al.*, *J. Chem. Phys.* **102**, 6406 (1995).

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3d 遷移金属添加銀クラスター負イオン 18 電子系の光電子画像観測

（九大院理）○西里将・橋本治暉・松本一陽・鈴木悠太・荒川雅・堀尾琢哉・寺嵜亨

Photoelectron imaging of 3d-transition-metal-doped silver cluster anions with 18 valence electrons

(Department of Chemistry, Kyushu University) ○Tasuku Nishizato, Haruki Hashimoto, Kazuaki Matsumoto, Yuta Suzuki, Masashi Arakawa, Takuya Horio, Akira Terasaki

The spherical jellium model predicts that valence electrons of metal clusters occupy so-called superatomic orbitals (1S, 1P, 1D, …). In this study, we investigated 3d-transition metal (M = Sc–Ni) doped silver cluster anions, Ag_NM^-, with 18 valence electrons by photoelectron imaging. For instance, the vertical electron detachment energy of Ag_NSc^- showed a local maximum at the size with 18 valence electrons. This is due to the delocalization of 3d electrons, which contributes to the formation of superatomic orbitals and 18-electron closed-shell structures ($1S^21P^61D^{10}$). In this talk we present the electronic and geometric structures of a series of 3d-transition metal doped silver cluster anions with 18 valence electrons with the aid of density functional theory.

Keywords : Silver Cluster; 3d transition-metal-doped Silver Cluster; Photoelectron Imaging; Superatomic Orbitals; 18 Valence Electrons

貨幣金属クラスター中の価電子はジェリウムモデルのもとで超原子軌道(1S,1P,1D,…)を形成することが報告されている[1]。その中でも 3d 遷移金属添加銀クラスター正イオン Ag_NM^+（M = Sc–Ni）の研究が Lievens らにより行われ[2]、前期遷移金属(M = Sc–V)では総価電子数が 18 個となるサイズにおいて特異的な安定性を示すことが光解離後の質量スペクトルに見出された。そこで我々は酸素分子との反応性を利用し、正負両イオン種 $Ag_NM^{+/-}$の安定性を調べたところ、18 電子則は電荷を問わず成立することを見出した[3]。このことは前期遷移金属の価電子が非局在化することで超原子軌道の形成に寄与し、$1S^21P^61D^{10}$ のような電子閉殻構造を形成するためと推察される。しかし、いずれの実験においても直接的な電子構造の観測には至っていない。本研究では総価電子数が 18 個となる 3d 遷移金属添加銀クラスター負イオン Ag_NM^-（M = Sc–Ni）に対する光電子イメージングを行い、電子閉殻構造の形成について探究した。

例として、Ag_{17}^-, $Ag_{14}Sc^-$の光電子画像を図 1 に示す。光電子脱離には波長 404 nm（3.07 eV）の CW レーザーを使用した。クラスターのサイズを変えながら測定を行った結果、VDE の値がこれらで極大となることが分かった。銀クラスター負イオンでは 18 電子系で VDE が極大を示すことが知られており、今回得られた結果と矛盾しない。以上から電子構造の観測により 3d 遷移金属添加種 18 電子系においても VDE が極大を示すことを見出した。密度汎関数理論による結果も踏まえ、一連の 3d 遷移金属添加種の電子・幾何構造を議論する。

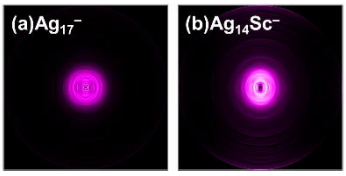

Figure 1
2D slices of photoelectron distributions for (a) Ag_{17}^- and (b) $Ag_{14}Sc^-$.

[1] de Heer, *Rev. Mod. Phys.,* **65**, 611 (1993). [2] Janssens *et al*., *Phys. Rev. Lett.* **94**, 113401 (2005). [3] Minamikawa *et al*., *Phys. Chem. Chem. Phys.* **24**, 1447 (2022).

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Ultrafast pump-probe measurement of CO_2 by few-cycle NIR pulses and the high-order harmonics

([1]*School of Science, The University of Tokyo*) ○Takuya Matsubara,[1] Hiroki Mashiko,[1] Tomoya Yamauchi,[1] Kana Yamada,[1] Toshiaki Ando,[1] Atsushi Iwasaki,[1] Kaoru Yamanouchi[1]
Keywords: Carbon dioxide; High-order harmonics; Pump-probe measurement; Ultrafast phenomena

When polyatomic molecules are irradiated with extreme ultraviolet (XUV) light, their cations are produced by photoionization not only in the ground electronic states but also in the electronically excited states, and the evolution of electronic, nuclear, and rotational wave packets starts. Thanks to recent advances in the ultrashort XUV light pulse generation technology, it has become possible to probe in time domain the dynamics of molecules induced by an ultrashort XUV light pulse. In the present study, we have performed pump-probe measurements of CO_2 by ionizing CO_2 by XUV light pulses generated as the high-order harmonics of few-cycle near-IR (NIR) laser pulses whose pulse duration is ~6 fs and probing subsequent ultrafast nuclear wave packet dynamics of CO_2^+ by the few-cycle NIR laser pulses. We have revealed the ultrafast dissociation dynamics of CO_2^+ occurring within 20 fs associated with the inner-valence photoionization and the vibrational dynamics proceeding with the period of ~30 fs associated with the outer-valence photoionization.

The yields of CO^+ and O^+ fragment ions whose kinetic energy release (KER) E_{KER} is in the range of $4.5 \leq E_{KER} \leq 6.5$ eV recorded as a function of the pump-probe delay time, Δt, exhibit an immediate increase at $\Delta t \sim 0$ fs followed by the decay fitted by a double exponential form with the fast time constant of 14 fs and the time constant much slower than 100 fs. We find that electronically excited singly charged ions $(CO_2^+)^*$ are produced by the inner-valence ionization by the XUV pump pulses[1] and are further ionized to CO_2^{2+} by the NIR probe pulses, resulting in the increase in the yields of the fragment ions with high E_{KER}. The subsequent decay reflects the ultrafast dissociation processes of $(CO_2^+)^*$. On the other hand, the yield of C^+ fragment ions in the range of $0.5 \leq E_{KER} \leq 2.5$ eV, originating from the dissociation of $(CO_2^+)^*$, exhibits an increase with the time constant of 17 fs.

The yield of CO^+ in the range of $0 \leq E_{KER} \leq 0.3$ eV and that of O^+ in the range of $0.4 \leq E_{KER} \leq 0.6$ eV oscillate with the period of 27 fs. This oscillation appearing in the yields of CO^+ and O^+ with the low KER, both which are created via the predissociation of CO_2^+ in the $\tilde{C}\,^2\Sigma_g^+$ state,[2] can be assigned to that of the symmetric stretching vibration of CO_2^+ in the electronic ground $\tilde{X}\,^2\Pi_g$ state. The vibrational wave packet is probed by the four-photon excitation to the vibrationally excited states of the $\tilde{C}\,^2\Sigma_g^+$ state, decomposing into $CO^+ + O$ and $O^+ + CO$. On the other hand, the yield of O^+ in the range of $0 \leq E_{KER} \leq 0.3$ eV exhibits an oscillation with the period of 30 fs. This oscillation can be assigned to the symmetric stretching vibration of CO_2^+ in the first electronically excited $\tilde{A}\,^2\Pi_u$ state, whose wave packet evolution is probed by the one-photon excitation to the vibrational ground state of the $\tilde{C}\,^2\Sigma_g^+$ state, decomposing only into $O^+ + CO$.

1) Q. Tian *et al.*, *J. Chem. Phys.* **136**, 094306 (2012). 2) J. Liu *et al.*, *J. Chem. Phys.* **118**, 149 (2003).

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フェムト秒レーザーによる金属アブレーションに伴う水素分子イオンの生成

（新潟薬大薬 [1]・新潟大学病院薬剤部 [2]・東大院理 [3]）城田 起郎 [1]・小林 将文 [2]・○星名賢之助 [1]・山内 薫 [3]

Formation of hydrogen molecular ions during the metal ablation by femtosecond laser pulses

([1]*Faculty of Pharmaceutial Sciences, Niigata University of Pharacy and Applied Life Sciecnes,* [2]*Division of Pharmacy,Niigata University Medical & Dental Hospital,* [3]*The University of Tokyo*) Tasuro Shirota,[1] Yasufumi Kobayashi,[2] ○Kennosuke Hoshina,[1] Kaoru Yamanouchi[3]

It is known that hydrogen atoms dissolve and permeate in stainless steel. From the viewpoint of hydrogen energy utilization, it has been awaited to clarify the mechanism of the process of the hydrogen atom dissolution and permeation. In the present study, we aim to detect hydrogen atoms dissolved below and exudating from the surface of stainless steel, we irradiate the surface of stainless stee (SUS304) with femtosecond (fs) laser pulses and detect ion species created by the laser irradiation by TOF mass spectrometry. In the mass spectrum, hydrogen atom ions, H^+, and molecular hydrogen ions, H_2^+ and H_3^+, are identified and their yields exhibit almost the same laser intensity dependence as those of Cr^+ and Fe^+ of which SUS304 is composed. When the target is heated up to 250°C to remove surface adsorbed molecules, only H^+, H_2^+, and H_3^+ appear in the mass spectrum in addition to the metal ions. When the SUS sample is in advance immersed into heavy water so that D_2O is adsorbed on the surface of the SUS sample, no D-atom containing ion species are observed, indicating that hydrogen atom ions or hydrogen molecular ions are not produced from surface adsorbed H_2O. These results show that the recombination reaction of dissolved H atoms proceeds during the heating and evaporation process in the vicinity of the SUS surface by the fs laser irradiation, resulting in the formation of molecular hydrogen ions, H_2^+ and H_3^+, in addition to H^+. *Keywords : Femtosecond laser irradiation; Stainless steel; Metal dissolved hydrogen; TOF mass spectra*

水素原子がステンレス鋼に溶解し，透過することが知られている．近年の水素エネルギー利用の観点から、この水素の溶存過程の機構を明らかにすることが待ち望まれている．本研究では，ステンレス鋼の表面近傍に溶存している水素原子や表面近傍から浸み出しつつある水素原子を検出することを目標とし、ステンレス鋼（SUS304）にフェムト秒 (fs) レーザーパルスを照射し、生成したイオン種を質量分析の後検出した。質量スペクトルには，水素原子イオン H^+，および，水素分子イオン H_2^+, H_3^+が，SUS の成分である Cr^+, Fe^+とほぼ同じレーザー強度依存性で観測された．表面吸着分子を 250℃で加熱除去したターゲットでは，金属イオン以外は H^+, H_2^+, H_3^+のみが明確に観測された．また，重水に液浸して D_2O を表面吸着させたターゲットでは，重水素原子が含まれたイオン種は観測されなかったため，表面吸着水分子からは H^+, H_2^+, H_3^+が生成されないことが示された．以上の結果は，fs レーザー照射により SUS304 表面近傍が加熱されるとともに蒸散する過程において，溶存水素の再結合反応が進行し，H^+に加えて，水素分子イオン H_2^+, H_3^+が生成したことを示している．

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Observation of electrochemical Peltier effects by a simple method

(1 *The University of Tokyo*) ○Yusuke Wakayama,[1] Hongyao Zhou,[1] Teppei Yamada[1]

Keywords: electrochemistry, electrochemical Peltier effect

The growing demand for air conditioning requires an alternative cooling system. We focused on the electrochemical Peltier (ECP) effect. It consists of the solution of redox-active species in a redox equilibrium (Figure 1). When an external current is applied to the solution, oxidation and reduction occurs at the anode and cathode, resulting in the transport of the latent heat. Since thermos-electrochemical cells show one order higher Seebeck coefficient (*Se*) than semiconductors,[1] the ECP device should show a high Peltier coefficient by Kelvin's law, while few studies have been done.[2,3] Here I propose a simple method for the observation of ECP effect.

Two representative systems, aqueous 0.40 M $K_3[Fe(CN)_6]$|0.4 M $K_4[Fe(CN)_6]$ (*Se*: −1.4 mV K^{-1}) and 2.0 M I_2|0.4 M KI (*Se*: +0.35 mV K^{-1}), were investigated. The current was applied to the assembled cell, and the current direction was switched to reduce the contribution of Joule heating. The temperature of one electrode was monitored (Figure 2) and cooling and heating switched by current direction were observed. The observed temperature differences are highly dependent on the *Se* of the solutions (Figure 3), indicating observed effects must be by ECP effect not by Joule heating or Seebeck effect of Pt electrode. These results will pave the way for applications of thermogalvanic electrolytes as temperature control.

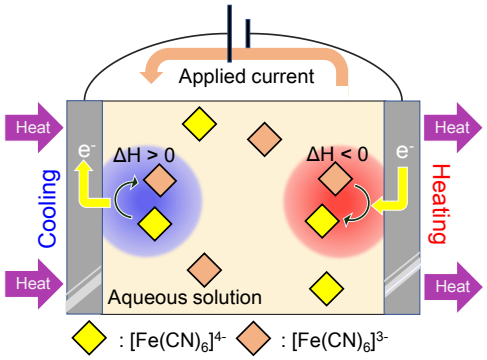

Figure 1. Schematic image of ECP effect.

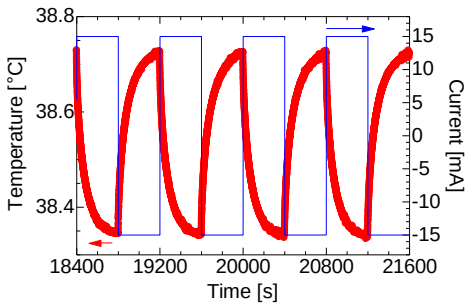

Figure 2. The temperature changes of aqueous $[Fe(CN)_6]^{4-/3-}$ solution by applying current (15 mA). Every 400 s, current was switched.

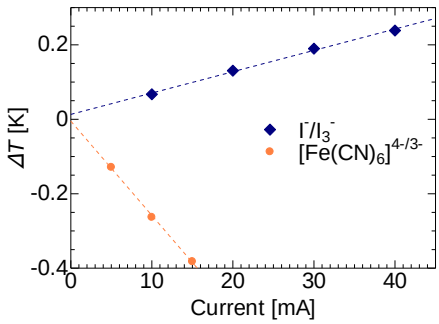

Figure 3. The current dependence of the average temperature differences of a couple of electrolytes within a cycle.

1) I. Burmistov *et al*, Sustainability **14** 9483 (2022). 2) I. S. McKay, L. Y. Kunz and Arun Majumdar, Sci. Rep. **9** 13945 (2019). 3) A. Rajan, I. S. McKay and S. K. Yee, Nat. Energy **7** 320 (2022).

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Boron and nitrogen co-doped carbon catalyst with acid-washing treatment for enhanced nitrogen electroreduction to ammonia

([1]*Graduate School of Advanced Science and Engineering, Waseda University*) ○Mingyuan Wang,[1] Akihiko Fukunaga[1]

Keywords: NRR, BNC, Acid-washing

Electrocatalytic synthesis of NH_3 under ambient condition is a promising process. And heteroatom doped carbon material is an effective catalyst[1]. In previous study, we prepared boron and nitrogen co-doped carbon (BNC) precursor catalyst by supramolecular pyrolysis process[2]. However, according to the characterization results, the surface of the prepared precursor catalyst had a high content of B_2O_3, and the performance of the catalyst was not ideal. We believed that surface B_2O_3 hindered the active site of the catalyst. In order to improve the catalytic performance of BNC material, B_2O_3 should be removed.

Therefore, in this work, the previously reported BNC precursor catalyst was acid-washed with H_2SO_4 to remove the surface B_2O_3 to prepare the BNC nanosphere catalyst. And the catalytic performance of BNC in different pH (pH=1, 8.3, 9.3, 13) electrolytes were investigated. It was found that the prepared BNC catalyst achieved a Faraday efficiency of up to 20% at -0.05 V vs. RHE in the mild alkaline electrolyte (0.5 M $KHCO_3$) with pH of 8.3, which was much higher than that in the acidic condition. We proposed the possible reaction model as shown in Fig. 1, where the interaction between OH^- and boron sites could effectively inhibit the adsorption and dissociation of H_2O, thus promoting the selectivity of NRR.

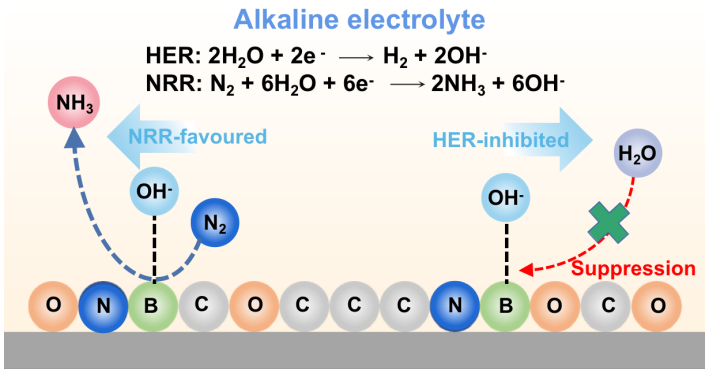

Fig.1 Reaction model of BNC catalyst in alkaline electrolyte

1) Wan, Y., Xu, J., & Lv, R. *Materials Today*, **2019**, 27, 69-90.
2) Wang, M. Fukunaga, A. **2022**. *The 102nd CSJ Annual Meeting, 25 March*, Tokyo.

Acknowledgments: This study was partly supported by the "FY2021 Waseda University - ENEOS FS Research Grant".

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

[K205-3vn] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Koichi NOZAKI, Takashi Nagata

Fri. Mar 24, 2023 4:10 PM - 6:00 PM K205 (K205, Lecture Hall Bldg. [2F])

[K205-3vn-01] Unique characteristics in chromophore photoisomerization of the novel rhodopsin bestrhodopsin

○Takashi Nagata[1], Yuma Kawasaki[1], Masae Konno[1,2], Yujiro Nagasaka[1], Mako Aoyama[3], Kota Katayama[2,3], Andrey Rozenberg[4], Igor Kaczmarczyk[5], Donna Matzov[5], Moran Shalev-Benami[5], Oded Béjà[4], Hideki Kandori[3], Keiichi Inoue[1] （1. The Univ. of Tokyo, 2. PRESTO, JST, 3. Nagoya Inst. Tech., 4. Technion–Israel Inst. Tech., 5. Weizmann Inst. Sci.）

4:10 PM - 4:30 PM

[K205-3vn-02] Near-Infrared Two-Photon Absorption and Subsequent Excited State Dynamics of Fluorescent Diarylethene Derivatives

○Hikaru SOTOME[1], Tatsuhiro Nagasaka[1], Tatsuki Konishi[2], Kenji Kamada[2], Masakazu Morimoto[3], Masahiro Irie[3], Hiroshi Miyasaka[1] （1. Osaka Univ., 2. National Institute of Advanced Industrial Science and Technology, 3. Rikkyo Univ.）

4:30 PM - 4:50 PM

[K205-3vn-03] Exciton diffusion and excimer formation dynamics of perylene in polymer films

○Koichi NOZAKI[1], Koki IMAMURA[1], Munetaka IWAMURA[1] （1. Grad. Sch. Sci. Eng., Univ. of Toyama）

5:00 PM - 5:20 PM

[K205-3vn-04] Enhancing photocatalytic water splitting activity of TiO_2 by controlling the thickness of adsorbed water layer at the molecular level

○Zhongqiu Lin[1,2], Hikaru Saito[1], Hiromasa Sato[1,2], Toshiki Sugimoto[1,2,3,4] （1. Institute for Molecular Science, 2. The Graduate University for Advanced Studies, SOKENDAI, 3. Innovative Optics and Photonics, PRESTO-JST, Japan, 4. RIKEN SPring-8 Center, Japan）

5:20 PM - 5:40 PM

[K205-3vn-05] Control of the motion of benzoic acid disks by amphiphilic molecule and self-propulsive molecule interactions at the air-water interface.

○Risa Fujita[1], Muneyuki Matsuo[1], Satoshi Nakata[1] （1. Hiroshima university）

5:40 PM - 6:00 PM

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新奇光受容タンパク質ベストロドプシンの特異な発色団光異性化反応

(東大[1]・JST さきがけ[2]・名工大[3]・Technion-Israel Inst. Tech.[4]・Weizmann Inst. Sci.[5])
○永田 崇[1]・川﨑 佑真[1]・今野 雅恵[1,2]・長坂 勇次郎[1]・青山 真子[3]・片山 耕大[2,3]・Andrey Rozenberg[4]・Igor Kaczmarczyk[5]・Donna Matzov[5]・Moran Shalev-Benami[5]・Oded Béjà[4]・神取 秀樹[3]・井上 圭一[1]

Unique characteristics in chromophore photoisomerization of the novel rhodopsin, bestrhodopsin

([1]*The University of Tokyo,* [2]*PRESTO, JST,* [3]*Nagoya Institute of Technology,* [4]*Technion - Israel Institute of Technology,* [5]*Weizmann Institute of Science*) ○Takashi Nagata,[1] Yuma Kawasaki,[1] Masae Konno,[1,2] Yujiro Nagasaka,[1] Mako Aoyama,[3] Kota Katayama,[2,3] Andrey Rozenberg,[4] Igor Kaczmarczyk,[5] Donna Matzov,[5] Moran Shalev-Benami,[5] Oded Béjà,[4] Hideki Kandori,[3] Keiichi Inoue[1]

Bestrhodopsins, a novel microbial rhodopsin subfamily, were recently discovered in marine unicellular algae[1)]. Bestrhodopsins are composed of 1–2 rhodopsin domains and a C-terminally fused bestrophin ion channel domain. The retinal-binding pockets in the rhodopsin domains differ significantly from those in other rhodopsins, implying that bestrhodopsins might have characteristic photochemical properties. Here, the chromophore isomerization in a bestrhodopsin was investigated using high-performance liquid chromatography, and novel isomerization properties were found. Moreover, we will describe amino acid residues specific in bestrhodopsins that confer bestrhodopsin-like photochemical properties to another canonical microbial rhodopsin.

Keywords : Photoisomerization; Photo-sensitive protein; Rhodopsin; Retinal; Bestrophin

最近、新奇微生物ロドプシンサブファミリーとして、ロドプシンとイオンチャネルタンパク質ベストロフィンの融合タンパク質であるベストロドプシンが発見された[1)]。ベストロドプシン中の発色団レチナールの結合ポケットは、他の微生物ロドプシンとは大きく異なる特徴を示す。本発表では、ベストロドプシンの示す微生物ロドプシンとして新奇な発色団光異性化反応について報告し、その特性をもたらす構造的要因について議論する。

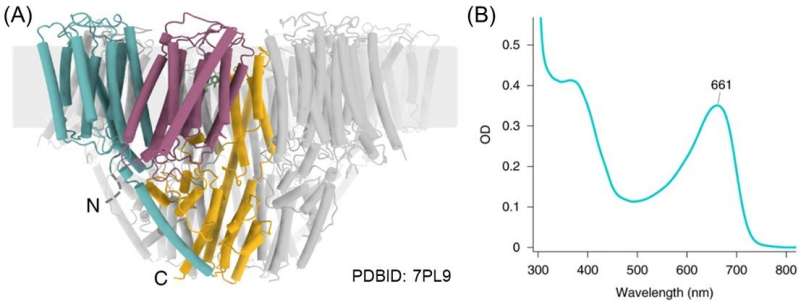

Fig. 1. The pentameric megacomplex consisting of five pseudodimers of rhodopsin domains (green and purple) and five bestrophin domains of bestrhodopsin *Tara*-RRB (A) and its UV–visible absorption spectrum with the red-shifted absorption maximum (B) [1)].

1) Rhodopsin-bestrophin fusion proteins from unicellular algae form gigantic pentameric ion channels. Rozenberg, A., Kaczmarczyk, I., Matzov, D., Vierock, J., Nagata, T. *et al.*, *Nat. Struct. Mol. Biol.* **2022**, 29(6), 592.

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蛍光性ジアリールエテン誘導体の近赤外２光子吸収特性と励起状態ダイナミクス

(阪大院基礎工[1]・産業技術総合研究所[2]・立教大[3]) ○五月女 光[1]・長坂 龍洋[1]・小西 龍生[2]・鎌田 賢司[2]・森本 正和[3]・入江 正浩[3]・宮坂 博[1]

Near-Infrared Two-Photon Absorption and Subsequent Excited State Dynamics of Fluorescent Diarylethene Derivatives

([1]*Graduate School of Engineering Science, Osaka University*, [2]*National Institute of Advanced Industrial Science and Technology*, [3]*Rikkyo University*)
○Hikaru Sotome,[1] Tatsuhiro Nagasaka,[1] Tatsuki Konishi,[2] Kenji Kamada,[2] Masakazu Morimoto,[3] Masahiro Irie,[3] Hiroshi Miyasaka[1]

Fluorescent diarylethene derivatives show a reversible photoisomerization between the open- (OFF state) and closed-ring (ON state) isomers, and can be applied to fluorescent dyes for super-resolution microscopies such as PALM and RESOLFT. In the present work, to extend the ON-OFF switching capability of fluorescent diarylethene derivatives toward the near-infrared region, we investigated the two-photon absorption property and excite-state dynamics.
Keywords : Photochromism; Two-Photon Absorption; Fluorescence Switching; Diarylethene; Transient Absorption Spectroscopy

開環体と閉環体の間で蛍光 ON-OFF スイッチングが可能な蛍光性ジアリールエテン（蛍光性 DAE）は、PALM や RESOLFT などの超解像蛍光イメージングの色素として利用可能である。我々はこれまでに、開環体の長波長域の微弱な吸収帯を励起することにより、可視単一波長における光照射で、蛍光 ON-OFF スイッチングと蛍光誘起が可能であることを実証した[1]。本研究では、蛍光性 DAE のスイッチング特性を、生体透過性が高く光毒性の少ない近赤外域に拡張することを目的として、蛍光性 DAE の近赤外２光子吸収特性と励起状態ダイナミクスを調べた。Z スキャン法による測定から、Fig. 1a に示す閉環体が 750 nm において 1400 GM をこえる大きな断面積をもつことが確認された。さらに、過渡吸収測定（Fig. 1b）から近赤外２光子励起では、１光子励起条件より高い約 5%の ON→OFF 収率を示すことが明らかになった。

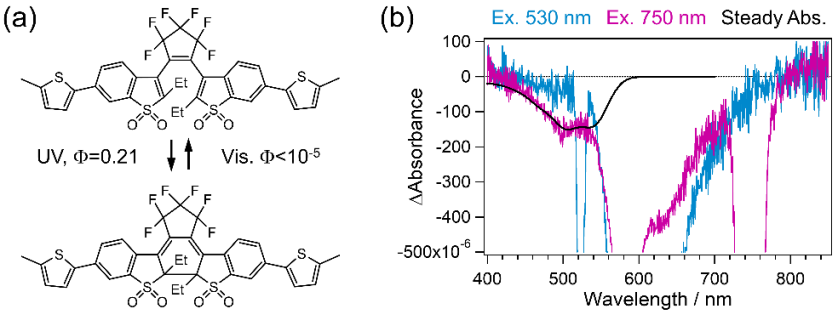

Figure 1. (a) Chemical structure of a fluorescent diarylethene derivative. (b) Transient absorption spectra at 20 ns under one-photon and two-photon excitation conditions.

[1] Y. Arai et al., *Chem. Commun.* **2017**, *53*, 4066-4069.

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Exciton diffusion and excimer formation dynamics of perylene in polymer films

(*Grad. Sch. Sci. Eng., Univ. of Toyama*) IMAMURA, Koki; IWAMURA, Munetaka; ○NOZAKI, Koichi

Keywords: Excimer; Exciton diffusion; Perylene; Polymer film

Pyrene or perylene-dispersed films have been paid attention recently as color-tunable emissive materials[1]. In this work, the photo-relaxation processes in perylene-dispersed PMMA films were studied by fluorescence up-conversion(UPC) and time-correlated single photon counting (TCSPC) spectroscopy. Film samples were prepared by spin-casting of $CHCl_3$ solutions containing different weight ratios(<0.01 wt% to 10 wt%) of perylene and PMMA.

While a 5 wt% dispersed film exhibited only broad excimer emission at around 550nm (Fig. 1), intense emission from S_1 of perylene monomer was observed at around 450 nm in time-resolved emission spectra. The monomer emission was then decayed within 200ps, followed by the rise of excimer emission. The decay rate of the monomer emission increased with increasing dispersion density. Time-resolved fluorescence anisotropy at 450nm for a 3 wt% film (Fig. 2) showed biexponential decay with 46 ps and ~3 ns time constants. The former time constant, decreasing with the dispersion density, corresponds to energy migration of free monomer exciton while the latter, almost independent of the concentration, would be due to self-trapped exciton.

Assuming that free excitons are quenched by small amount of perylene dimer sites, the temporal profiles of the monomer emission decay were analyzed using the Smoluchowski's diffusion-controlled reaction model [2]. With consideration of the presence of small amount of self-trapped excitons, the observed temporal profiles were well reproduced by the diffusion-controlled reaction model using the diffusion constants determined from the anisotropy (red line in Fig. 3).

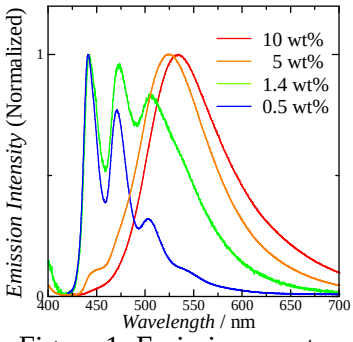

Figure 1. Emission spectra for perylene/PMMA films with various perylene density (λ_{ex}=405 nm)

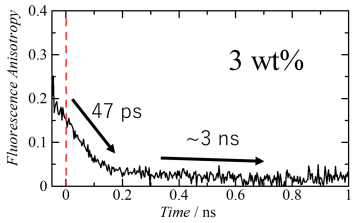

Figure 2. Temporal profiles of fluorescence anisotropy for monomer excitons for 3 wt%

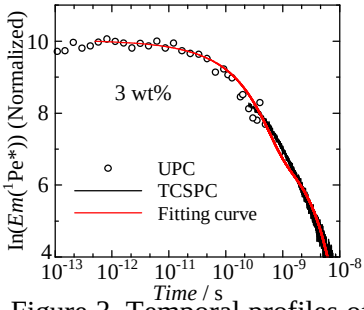

Figure 3. Temporal profiles of emission intensity of perylene monomer in a 3 wt% film and fitting curve using the Smoluchowski's model.

[1] Pujari, S. R. *et al.*, *Mater. Res. Bull.*, **2002**, 37, 1641; Ito, F. *et al.*, *J. Phys. Chem.* B, **2013**, 117, 3675. [2] Naqvi, K. R. *et al.*, *J. Phys. Chem. B*, **2000**, 104, 12035.

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吸着水分子層数の制御による TiO_2 光触媒水分解の高活性化

(分子研[1]・総研大[2]・JST さきがけ[3]・理研播磨[4]) ○林 仲秋[1,2]・斎藤 晃[1]・佐藤 宏祐[1,2]・杉本 敏樹[1,2,3,4]

Enhancing photocatalytic water splitting activity of TiO_2 by controlling the thickness of adsorbed water layer at the molecular level

([1]*Institute for Molecular Science*, [2]*The Graduate University for Advanced Studies, SOKENDAI*, [3]*Innovative Optics and Photonics, PRESTO-JST, Japan*, [4]*RIKEN SPring-8 Center, Japan*) ○Zhongqiu Lin,[1,2] Hikaru Saito,[1] Hiromasa Sato,[1,2] Toshiki Sugimoto[1,2,3,4]

Photocatalytic water splitting is an environmentally friendly and sustainable hydrogen production process. However, molecular-level understanding of water splitting remains a challenge because the bulk water hinders observation of the interfacial water. We performed mass spectrometry and infrared absorption spectroscopy to observe hydrogen bonding networks of adsorbed water on TiO_2 surfaces at the level of single molecular layer under water vapor atmosphere. We found an optimum amount of the adsorbed water molecules (2400 Pa) for the hydrogen evolution reaction. Moreover, the results of infrared absorption spectroscopy indicate the hydrogen bonding networks markedly impact on the photocatalytic activities.

Keywords : Photocatalytic Water Splitting; Adsorbed Water; Surface Reaction; Infrared Absorption Spectroscopy; Hydrogen Bonding Network

光触媒を用いた水分解反応を利用すれば、水から持続可能に水素を生成することができる。しかし、大量のバルク水の存在により、反応場となる界面水を選択的に測定することが困難であった。そのため、表面反応メカニズムの詳細は明らかでない。そこで本研究では、水蒸気雰囲気下で TiO_2 光触媒の表面に一分子層レベルで吸着水の極薄膜を形成させ、ここに励起光を照射することで活性評価を行った。その結果、水素生成速度は水蒸気圧力約 2400 Pa の領域までは水蒸気圧力に対して単調増加し、それ以上の圧力では減少に転じた。水蒸気圧力の増加は表面吸着した水分子量の増加に対するので[1]、光触媒水分解反応に最適な吸着水分子の量が存在することがわかった。更にこの界面水を赤外分光によって観測すると、界面の水素結合ネットワーク環境によって反応活性が大きく変化することもわかった。これらの結果は従来の水中より水蒸気雰囲気の条件のほうが高い反応活性が得られることを示唆している。

1) K. Shirai *et al.*, *Nano Lett.*, **16**, 1323 (2016)

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気水界面での両親媒性分子ー駆動体分子の相互作用による安息香酸円板の運動様相制御

（広島大学大学院統合生命 [1]）○藤田　理沙 [1]・松尾　宗征 [1]・中田　聡 [1]

Control of the Motion of Benzoic Acid Disks by Amphiphilic Molecule and Self-propulsive Molecule Interactions at the Air-water Interface

([1]*Graduate School of Integrated Sciences for life, Hiroshima University*) ○Risa Fujita,[1] Muneyuki Matsuo,[1] Satoshi Nakata,[1]

Benzoic acid (BA) tablets molded as disks were driven by surface tension differences. In this study, by deploying a 4-stearoyl amidobenzoic acid (SABA) monolayer, a molecule that interacts with BA molecules, at the air-water interface, we constructed an experimental system in which the motion of the BA disk and the properties of the SABA monolayer feedback each other. As a result, due to the interaction between SABA and BA molecules (Figure 1), the BA disk exhibited a highly autonomous movement phase that memorized the trajectory once passed.
Keywords : Amphiphilic monolayer, Remembering the trajectory, Molecular interactions

円板状に成型した安息香酸(BA)タブレットを気水界面に浮かべると、BA 分子の不均一な展開によって生じる表面張力差を駆動力として駆動する。本研究では、気水界面に BA 分子と分子間相互作用する両親媒性分子 4-stearoyl amidobenzoic acid (SABA) の単分子膜を展開し、単分子膜上に BA 円板を浮かべた。これは、BA 円板からの BA 分子の展開が SABA 単分子膜と相互作用して膜の状態を変化させ、SABA 単分子膜の状態変化を BA 円板の運動様相にフィードバックする実験系の構築を目的としている。さらに、BA 円板の他に、分子間相互作用しない樟脳駆動体を対照実験として使用した。その結果、SABA-BA 分子間相互作用によって BA 円板が一度通過した軌跡を記憶する自律性の高い運動様相が見られた。さらに対照実験では、軌跡の記憶は起こらなかった。これらの結果から、BA 円板から展開した BA 分子が SABA 単分子膜間に配向して凝集膜を形成し（Figure 1）、円板周辺の膜圧を不可逆的に高めることで軌跡の記憶が生じると考察した。

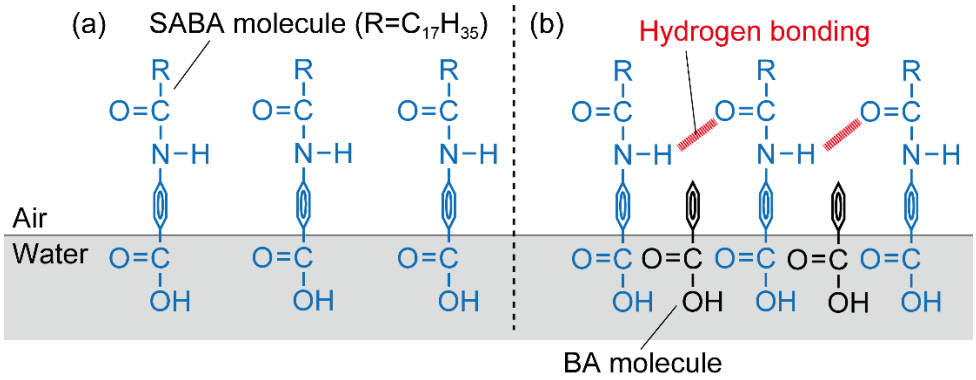

Figure 1. Schematic illustration of the difference in intermolecular interactions between (a) SABA monolayer and (b) BA-SABA mixed monolayer at the air-water interface.

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

[K701-3pm] 06. Analytical Chemistry

Chair: Kazuhiko Tsukagoshi, Tsuyoshi Minami

Fri. Mar 24, 2023 1:50 PM - 3:40 PM K701 (K701, Lecture Hall Bldg. [7F])

[K701-3pm-01] Evaluation of Banana Ripening Conditions using Metal Oxide Nanofilm Gas Sensor Array

○Haruka Honda[1], Xi Wang[1], Tsunaki Takahashi[1,3], Wataru Tanaka[1], Takuro Hosomi[1,3], Kazuki Nagashima[1,3], Takeshi Yanagida[1,2] （1. The Univ. of Tokyo, 2. Kyushu Univ., 3. JST PRESTO）

1:50 PM - 2:10 PM

[K701-3pm-02] Fluorescence recognition of D-glucose with excellent chiral selectivity exploiting cyclodextrin cavity as a reaction field

○Yota Suzuki[1], Takeshi Hashimoto[1], Takashi Hayashita[1] （1. Sophia Univ.）

2:10 PM - 2:30 PM

[K701-3pm-03] Chiral Pattern Recognition Utilizing Multi-Equilibria in Molecular Self-Assemblies

○Yui Sasaki[1], Tsuyoshi Minami[1] （1. IIS, The Uni. of Tokyo）

2:40 PM - 3:00 PM

[K701-3pm-04] Direct detection of amoxicillin and ciprofloxacin using flexible surface-enhanced Raman scattering (SERS) substrate

○Kullavadee Karn-orachai[1] （1. National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA)）

3:00 PM - 3:20 PM

[K701-3pm-05] A Raman spectroscopic investigation of intracellular water

○Ashok Samuel[1], Haruko Takeyama[2] （1. Research organization for nano and life innovation, waseda university, Tokyo, 2. waseda university, Tokyo）

3:20 PM - 3:40 PM

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金属酸化物ナノ薄膜ガスセンサアレイによるバナナの追熟度の判定

（東大院工 [1]・九大総理工 [2]・JST さきがけ）○本田 陽翔 [1]・Xi Wang [1]・高橋 綱己 [1,3]・田中 航 [1]・細見 拓郎 [1,3]・長島 一樹 [1,3]・柳田 剛 [1,2]

Evaluation of Banana Ripening Conditions using Metal Oxide Nanofilm Gas Sensor Array([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering Sciences, Kyushu University*, [3]JST PRESTO) ○ Haruka Honda[1], Xi Wang[1], Tsunaki Takahashi[1,3], Wataru Tanaka[1], Takuro Hosomi[1,3], Kazuki Nagashima[1,3], Takeshi Yanagida[1,2]

Monitoring and controlling food conditions is crucial for reduction of food loss[1)]. At present, there are several methods to monitor food conditions, such as optical sensor and confirmations by skilled workers. However, the cost of these methods is a major issue because they require human resource development and inspection of the total number of food products. In this study, we developed a low-cost and simple method to monitor the condition of food products using gas molecules volatilized from food products.

As a specific example, ripening conditions (sugar-acidity ratio) of bananas were evaluated via analyzing gas molecules generated during ripening. To analyze the compositional changes of the gas molecules in real-time and easily, we fabricated a gas sensor array based on Tin Oxide (IV) nanofilms. A regression model was successfully developed to predict the sugar-acidity ratio from the gas sensor array response (Fig. 1).

Keywords : Gas Sensor; Metal Oxide; Volatile Organic Compounds; Food

食品ロスを削減するためには物流過程での食品の状態をモニタリングすることが重要である[1)]．現状の食品モニタリング手法としては，熟練者による確認や光センサによるものがある．しかし，人材育成や全数検査が必要になることから，コスト面での課題が大きい．そこで，本研究では食品から揮発するガス分子群を介した低コストかつ簡便な食品の状態把握を試みた．

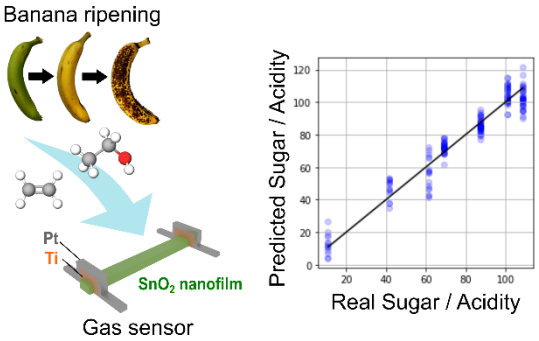

Fig. 1 Prediction of sugar-acidity ratio of banana thorough gas molecules.

具体例として，バナナの追熟中に発生するガス分子群が持つ情報からバナナの追熟度(糖酸比)の判定を行った．ガス分子群の組成変化をリアルタイムかつ簡便に分析するための手法として，酸化スズ(IV)ナノ薄膜をベースとしたガスセンサアレイを作製した．このガスセンサアレイのセンサ応答から糖酸比を予測する回帰モデルを作成することに成功した(Fig. 1).

1) *Compr Rev Food Sci Food Saf.* **21**, 4189 (2022)

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シクロデキストリン空孔を反応場として活用したD-グルコースの高選択なキラル蛍光認識

（上智大理工）〇鈴木 陽太・橋本 剛・早下 隆士

Fluorescence recognition of D-glucose with excellent chiral selectivity exploiting cyclodextrin cavity as a reaction field (Faculty of Science and Technology, Sophia University) 〇Yota Suzuki, Takeshi Hashimoto, Takashi Hayashita

Various biologically important molecules, including glucose, have chirality and therefore exist as D- and L- isomers, i.e., enantiomers. The physiological properties of enantiomer pairs are completely different; however, the physical properties are almost the same. Therefore, chiral discrimination of such molecules is important but typically difficult.[1)]

We present inclusion complexes composed of γ-cyclodextrin and fluorescent mono-boronic acid-based probes; two molecules of a probe are encapsulated in the hydrophobic cavity of γ-cyclodextrin. These inclusion complexes recognize D-glucose in water with excellent selectivity, exhibiting significant turn-on responses. Interestingly, **2N/CyD** shows 6-folds stronger fluorescence intensity in the presence of D-glucose compared with that of L-glucose (Fig. 1). To the best of our knowledge, this chiral selectivity in fluorescence response is the highest among the boronic acid-based chemosensors reported so far.[2)]

Keywords : Molecular Recognition; Chiral Recognition; Supramolecular Chemistry; Boronic Acid; Fluorescence

グルコースを含む多くの生体分子はキラリティを有し，鏡像異性体の関係にあるD体とL体が存在する。これらの生理学的性質は大きく異なる一方で，物理学的性質はほとんど一致するため，その識別は重要であるが非常に困難である[1)]。

本研究では，γ-シクロデキストリンが持つキラルな疎水的空孔に，単純な構造のボロン酸型プローブを二分子同時に内包させた超分子複合体によって，水中での高選択的なD-グルコースのキラル認識を達成した。この超分子複合体はD-グルコースを高い選択性で認識して，顕著な蛍光強度の増大を示した。興味深いことに，**2N/CyD** はL-グルコース添加時と比較してD-グルコース添加時に6倍大きな蛍光強度を示した（Fig. 1）。我々が知る限り，この値は既報のボロン酸型分析試薬の中で最も大きい[2)]。

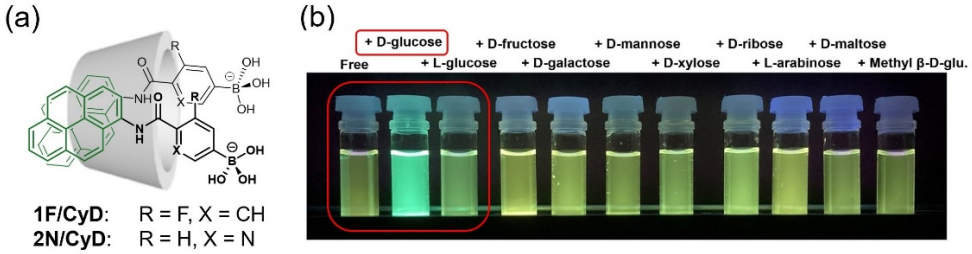

Fig. 1. (a) The structure of the inclusion complexes. (b) Photograph of **2N/CyD** solutions in the absence and presences of various saccharides in DMSO/water (2/98 in *v/v*) at pH 7.4.

1) X. Zhang *et al.*, *Chem. Rev.* **2014**, *114*, 4918-4959.
2) Y. Suzuki *et al.*, *ACS Sens.* in press.

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Chiral Pattern Recognition Utilizing Multi-Equilibria in Molecular Self-Assemblies

([1]*Institute of Industrial Science, The University of Tokyo*) ○Yui Sasaki, Tsuyoshi Minami
Keywords: Supramolecular Sensor; Pattern Recognition; Self-Assembly; Multi-Equilibria; Chirality

A chemosensor array enabling simultaneous discrimination of the types of species and their concentrations is a potent analytical method for invisible molecular information.[1)] Among them, we have mainly focused on the molecular self-assembled chemosensor arrays comprising a small number of building blocks to maximize the optical properties of each chemosensor.[2),3)] In this study, the concept of self-assembled chemosensors has been applied to chiral pattern recognition, which is one of the challenging topics in molecular recognition chemistry. BINAMINE (**1**) and 2-formylphenylboronic acid (**2**) were employed as the building blocks for the chemosensor, which spontaneously formed the chiral iminobornates with hydroxy acid (*e.g.*, (*R*)- or (*S*)-mandelic acid (**3**)) at room temperature (Fig. 1(a)). Upon the formation of the iminoboronates, the chiral ensembles showed fluorescence properties depending on differences in the chirality of the guest (Fig. 1(b)). Namely, the different optical responses based on multi-equilibria indicated the potential of the chiral iminoboronates for pattern recognition, *albeit in a non-array system*. The details of the strategy for chiral pattern recognition based on the fluorescent iminoboronate formation will be presented.

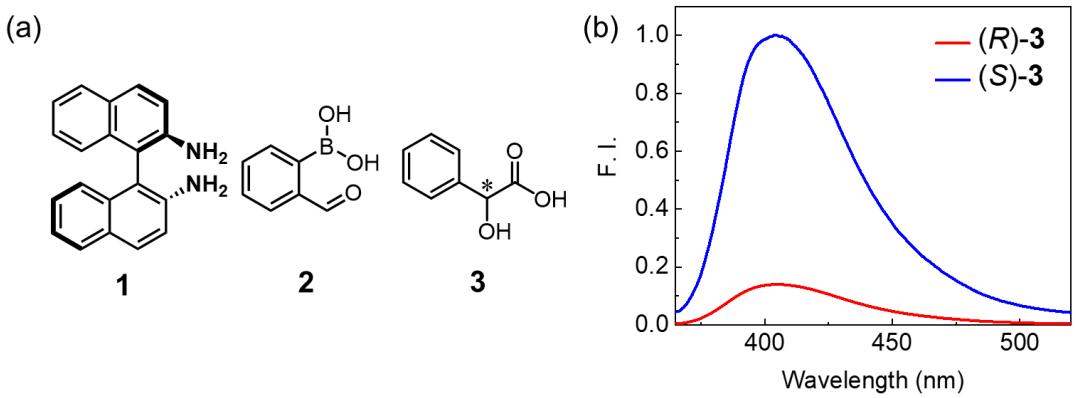

Figure 1. (a) Chemical structures of the building blocks (**1** and **2**) and the guest (**3**) for chiral pattern recognition. (b) Fluorescent spectra of the chiral iminoboronates made of **1** (10 μM), **2** (50 μM), and **3** (20 μM) in MeCN at 25 °C. λ_{ex} = 350 nm. The mixtures of **1**, **2**, and **3** were incubated in MeCN at 400 rpm at 25 °C for 10 h.

1) E. Anslyn et al., *Chem. Soc. Rev.,* **2006**, *35*, 14.
2) Y. Sasaki et al., *Coord. Chem. Rev*. **2021**, *429*, 213607.
3) Y. Sasaki et al., *Chem. Sci.* **2020**, *11*, 3790 (**Cover and HOT Article**).

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Direct detection of amoxicillin and ciprofloxacin using flexible surface-enhanced Raman scattering (SERS) substrate

([1]*National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand*) ○ Kullavadee Karn-orachai[1]

Keywords: Surface-enhanced Raman spectroscopy; Amoxicillin; Ciprofloxacin; Cotton; Gold-silver alloy nanoparticles

Recently, the flexible SERS substrates have been widely developed as a promising SERS substrate instead of rigid one because of their benefits including affordable price, and flexibility. Regarding the complex structure and good solvent absorption, cotton textile is selected as a supporter for fabrication of flexible SERS substrate. Gold-silver alloy nanoparticles (Au-Ag NPs) are decorated on cotton fiber through in-situ growth process to produce strong electric field on fabric substrate.[1] The flexible SERS substrate performance including stability, uniformity, and enhancement factor is evaluated by monitoring the signal of 5,5′ -dithiobis (succinimidyl-2-nitrobenzoate); DSNB. Moreover, the active hotspot profile on the substrate is constructed using two-dimensional (2D) Raman mapping measurement by investigating the 1345 cm^{-1} signal of DSNB molecule on the textile. The SERS hotspot can be discovered along and between the woven fiber. The SERS fabric can homogeneously absorb solution without coffee ring effect; therefore, this substrate provides less spot-to-spot signal variation with low relative standard deviation (%RSD) less than 10%. The label-free amoxicillin and ciprofloxacin detections are demonstrated using our developed Au-Ag NPs coated cotton textile coupled with handheld Raman spectrometer. The fingerprint of amoxicillin and ciprofloxacin can be identified by observing the dominant characteristic band of COO^- of β-lactam ring moiety at 1115 cm^{-1} and C-N symmetric stretching at 1389 cm^{-1}, respectively.[2-3] The detection limit of amoxicillin and ciprofloxacin was calculated to be 2.9, and 0.3 μM, respectively. This proposed study shows the alternative low-cost SERS substrate for further application of rapid screening and on-site monitoring of antibiotic contamination in water.

1) S. R. Ahmed, J. Kim, V. T. Tran, T. Suzuki, S. Neethirajan, J. Lee, E. Y. Park, *Sci. Rep*., **2017**, 7, 44495. 2) L. Wang, G. Zhou, X.-L. Guan, L. Zhao, *Spectrochim. Acta A Mol*., **2020**, 235, 118262. 3) V. T. Thu, N. M. Coung, D. T. Cao, L.T. Hung, L. T.-Q. Ngan, *Optik*, **2022**, 260, 169043.

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A Raman spectroscopic investigation of intracellular water

([1]*Research organization for nano and life innovation, waseda university, Tokyo*, [2]*Waseda university, Tokyo*) ○Ashok Zachariah Samuel,[1] Haruko Takeyama[2]
Keywords: *Raman spectroscopy, Bound water, single cell imaging*

Water molecules form complex networks around biomolecules in aqueous solutions, which play crucial roles in their structure and functions.[1] For instance, bound-water has been shown to impart specific properties to ice binding proteins (IBPs), which are believed to enable the survival of living organisms in cold environments.[2] The chemical structure of solute molecules, in general, affects the structure of associated water cluster. Such changes in water structure have also been observed in aqueous solutions of linear alcohols, surfactant micelles, solutions of ionic salts, thermo-responsive polymers, etc.[3] Even in human cells/tissues different hydration structures are thought to exist, which are believed to change depending on the phenotypic/genotypic changes.[4] Investigation of biomolecule specific bound water inside cells with Raman spectroscopy is the aim of the present work.

Water vibrational band in Raman spectrum changes depending on the structure of water cluster "network".[5] Here, we explore the possibility of examining biomolecule specific water structure directly inside cells. Intracellular distribution of biomolecules is spatially heterogeneous,[6] and hence we believe that biomolecule associated water "network" structure can also change in a spatially correlated way. This can be probed with Raman spectroscopy by mathematically isolating the perturbed water spectrum and the bulk water spectrum from the recorded single cell water-spectral data. Due to the intracellular molecular crowding, it can be assumed that relative composition of bulk-like and bound-water inside cells are comparable. Therefore, the changes in water band associated with the hydration shell of biomolecules should be detectable with linear Raman spectroscopy. Here, we provide evidence to suggest that multiple biomolecule-specific bound-water structures exists inside cells.[7]

1) P. Ball, *Proc. Natl. Acad. Sci. U. S. A.*, **2017**,*114*, 13327 2) M. Kuramochi, C. Takanashi, A. Yamauchi, M. Doi, K. Mio, S. Tsuda, Y.C. Sasaki, *Sci. Rep.,* **2019**, *9*, 1. 3) J.A. Long, B.M. Rankin, D. Ben-Amotz, *J. Am. Chem. Soc*., **2015***, 137*, 10809. 4) G.I. McIntyre, *Med. Hypotheses.*, **2006***, 66*, 518. 5) S. Tiwari, M. Ando, H.-o. Hamaguchi, *J. Raman Spectrosc*., **2013**, *44*, 167. 6) A. Z. Samuel, K. Sugiyama, M. Ando, H. Takeyama, *Commun. Biol.* **2022**, *5*, 1383. 7) A. Z. Samuel, K. Sugiyama, H. Takeyama, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.,* **2014**, *129*, 609-623,

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

[K501-3am] 07. Inorganic Chemistry

Chair: Kazuya Kobiro, Masato Goto

Fri. Mar 24, 2023 9:00 AM - 11:30 AM K501 (K501, Lecture Hall Bldg. [5F])

[K501-3am-01] Raman spectroscopy and electronic state calculation for high near-infrared (NIR) reflective black pigments based on Ca_2MnO_4

○Ryohei Oka[1], Tomokatsu Hayakawa[1] (1. Nagoya Institute of Technology)

9:00 AM - 9:20 AM

[K501-3am-02] Crystal structure and topochemical fluorination of $Bi_{12}O_{17}Cl_2$ photocatalyst

○Daichi Kato[1], Osamu Tomita[1], Hajime Suzuki, Chengchao Zhong[1], Cédric Tassel[1], Kohdai Ishida, Yosuke Matsuzaki[1], Koji Fujita[1], Ryu Abe[1], Hiroshi Kageyama[1], Ryky Nelson[2], Richard Dronskowski [2], Maria Kirsanova[3], Abakumov Artem[3], Craig Brown[4], Kotaro Fujii[5], Masatomo Yashima[5], Akinori Saeki[7], Itaru Oikawa[8], Hitoshi Takamura[8], Yoji Kobayashi[6], Tatiana Gorelik [9] (1. Kyoto Univ., 2. RWTH Aachen Univ., 3. Skolkovo Institute of Science and Technology, 4. NIST, 5. Tokyo Institute of Technology, 6. KAUST, 7. Osaka Univ., 8. Tohoku Univ., 9. Ulm Univ.)

9:20 AM - 9:40 AM

[K501-3am-03] Water-assisted solid-state reaction

○Kenji Toda[1] (1. Niigata University)

9:40 AM - 10:00 AM

[K501-3am-04] Solvothermal Synthesis of Porous SnO_2

○Ayano Taniguchi[1], Masataka Ohtani[1], Kazuya Kobiro[1] (1. Kochi Univ. of Tech.)

10:00 AM - 10:20 AM

[K501-3am-05] Structure and physical properties of *A*-site layer-ordered/disordered perovskites $NdBaFe_2O_6$ with unusually high valence $Fe^{3.5+}$

○Makoto Iihoshi[1], Masato Goto[1], Yuuichi Shimakawa[1] (1. Kyoto University)

10:30 AM - 10:50 AM

[K501-3am-06] Oxygen Release and Crystal Structural Changes of $BaFeO_3$ Polymorphs

○Rei Watanabe[1], Masato Goto[1], Yuichi Shimakawa[1] (1. Kyoto University)

10:50 AM - 11:10 AM

[K501-3am-07] Structure-property relationships in *B*-site ordered double perovskites Ln_2LiFeO_6

○Masato Goto[1], Yuichi Shimakawa[1] (1. Kyoto University)

11:10 AM - 11:30 AM

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近赤外反射能を有する Ca_2MnO_4 系黒色顔料のラマンスペクトル解析及び電子状態計算

（名工大院工）○岡 亮平・早川 知克

Raman spectroscopy and electronic state calculation for high near-infrared (NIR) reflective black pigments based on Ca_2MnO_4 (*Graduate School of Engineering, Nagoya Institute of Technology*) ○Ryohei Oka, Tomokatsu Hayakawa

Black pigments based on Ca_2MnO_4 were studied by Raman spectroscopy and electronic state calculation to elucidate the enhancement of NIR-reflectivity by doping Ti^{4+}. Raman peaks at around 178, 290, 330, 463, 500, and 562 cm^{-1} were observed for all samples, while an additional peak was observed at around 780 cm^{-1} for the Ti^{4+}-doped samples, indicating that a silent A_{2g} mode was activated by doping Ti^{4+}, which mode was similar to a A_{1g} (breathing) mode found in B-site substituted simple perovskite structure. This result was attributed to the presence of the Ti-Ti correlation with a certain distance. The DFT calculations also revealed that one of the factors for the enhancement of NIR reflectivity is the reduced DOS near the Fermi level.

Keywords : Inorganic pigments, NIR reflective properties, Raman spectroscopy, Layered perovskite, DFT calculation

近年，省エネルギーの必要性が高まるにつれ，熱を吸収しない（遮熱）顔料の要求が高まっている。一般にカーボンブラックを代表とする黒色顔料は熱吸収が大きいため、黒色遮熱顔料の開発が求められている。このような背景下、これまでに黒色遮熱顔料として Ca_2MnO_4 が有望であり、その Mn^{4+}サイトに Ti^{4+}を固溶させることで近赤外線反射能が向上することが明らかとなっている[1]。そこで本研究では Ca_2MnO_4:Ti 顔料について、ラマンスペクトル測定により構造を、密度汎関数理論（DFT）に基づく量子化学計算により電子状態を解析した[2]。

合成した試料と原料に用いた MnO_2 及び TiO_2 のラマンスペクトル、Ca_2MnO_4 ($I4_1/acd$) と同じ空間群をもつ Sr_2IrO_4 のデータを Fig. 1 に示す。Ti^{4+}固溶量 $x \geq 0.05$ の試料では、ピーク①～⑥に加えて、新たに 780 cm^{-1} 付近にピーク⑦が観測された。DFT フォノン計算の結果より、Ca_2MnO_4 は同波数域にラマン活性な振動モードをもたないが、739 cm^{-1} 付近にラマン不活性かつ breathing モードに酷似した A_{2g} モードを有することがわかった。ABO_3 で表わされる単純ペロブスカイト構造においては、B サイト置換でホスト格子本来の秩序性が失われ、かつ新たに短距離秩序が生まれた場合は同波数域に新たに A_{1g} 振動ピーク（breathing モード）が観測されると報告されている[4]。このことから、上記の結果は、ラマン不活性な A_{2g} モードが、Ti^{4+}の固溶によりラマン活性な A_{1g} モードに変化し、新たなピークとして観測されたものと考えられる。また上記に加え、状態密度（DOS）計算により、Ti^{4+}イオンの固溶による近赤外線反射能の向上の原因の一つとして、伝導帯底部の DOS の減少であることがわかった。

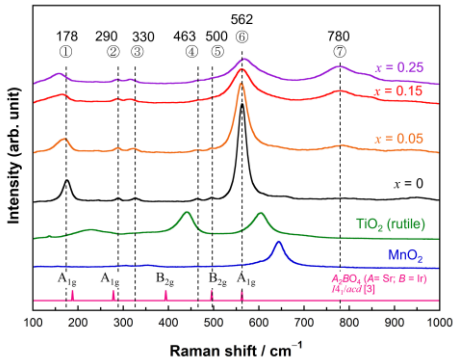

Fig. 1 Raman spectra of $Ca_2Mn_{1-x}Ti_xO_4$ (x = 0, 0.05, 0.15, 0.25) and raw reagents (MnO_2 and TiO_2). The bottom solid line is the assignment data of A_2BO_4 (A = Sr; B = Ir; $I4_1/acd$) [3].

[1] R.Oka et al., *RSC Adv.* **6** (2016) 90952–90957; *ibid.* **9** (2019) 38822–38827. [2] R.Oka, T.Hayakawa, *Inorg. Chem.* **61** (2022) 6500–6507. [3] K.Samanta et al., *Phys. Rev. B*, **98** (2018) 094101. [4] H.Zheng et al., *J. Eur. Ceram. Soc.*, **23** (2003) 2653–2659.

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光触媒 $Bi_{12}O_{17}Cl_2$ の結晶構造とトポケミカルフッ素化による構造変化

（京都大学[1]・アーヘン工科大学[2]・スコルコボ科学技術大学[3]・アメリカ国立標準技術研究所[4]・東京工業大学[5]・キング・アブドゥッラー科学技術大学[6]・大阪大学[7]・東北大学[8]・ウルム大学[9]） ○加藤 大地[1]・富田 修[1]・鈴木 肇[1]・鐘 承超[1]・タッセル セドリック[1]・石田 耕大[1]・松崎 洋介[1]・藤田 晃司[1]・阿部 竜[1]・陰山 洋[1]・ネルソン リキー[2]・ドロンスコウスキー リチャード[2]・キルサノヴァ マリア[3]・アバクモフ アーテム[3]・ブラウン クレイグ[4]・藤井 孝太郎[5]・八島 正知[5]・佐伯 昭紀[7]・及川 格[8]・高村 仁[8]・小林 洋治[6]・ゴレリク タチアナ[9]

Crystal structure and topochemical fluorination of $Bi_{12}O_{17}Cl_2$ photocatalyst

([1]*Kyoto University,* [2]*RWTH Aachen University*, [3]*Skolkovo Institute of Science and Technology,* [4] *National Institute of Standards and Technology,* [5]*Tokyo Institute of Technology*, [6]*King Abdullah University of Science and Technology*, [7]*Osaka University*, [8]*Tohoku University*, [9]*Ulm University*) ○Daichi Kato[1]・Osamu Tomita[1]・Hajime Suzuki[1]・Chengchao Zhong[1]・Cédric Tassel[1]・Kodai Ishida[1]・Yosuke Matsuzaki[1]・Koji Fujita[1]・Ryu Abe[1]・Hiroshi Kageyama[1]・Ryky Nelson[2]・Richard Dronskowski[2]・Maria A. Kirsanova[3]・Artem M. Abakumov[3]・Craig M. Brown[4]・Kotaro Fujii[5]・Masatomo Yashima[5]・Akinori Saeki[7]・Itaru Oikawa[8]・Hitoshi Takamura[8]・Yoji Kobayashi[6]・Tatiana E. Gorelik[9]

Oxyhalides with M_2O_2 fluorite layer have recently emerged as promising visible-light responsive photocatalyst due to their excellent stability and narrow band gap, which is attributed to their unique valence band structure mainly composed of unusually high O 2p orbitals. Here, we will present the crystal structure of $Bi_{12}O_{17}Cl_2$ with sextuple Bi–O layer and its topochemical fluorination.

Keywords : Oxyhalide photocatalyst, topochemical fluorination, fluorite layer, rock

ここ 5 年間ほどの間に、M_2O_2 (M = Bi, Pb 等)で表されるダブル蛍石層（$n = 2$）を骨格とする層状酸ビスマス酸ハロゲン化物が、安定かつ高効率な光触媒として注目を集めている[1]。最近我々は、トリプル蛍石層 Bi_2MO_4 ($n = 3$)において、ダブル蛍石層（$n = 2$）では困難であった大幅な伝導体制御が可能となることを見出した[2]。これは、蛍石層の厚み n に着目した物質開発の有効性を示しているが、蛍石層の厚みとしては $n = 3$ が最大であり、蛍石層のバリエーションは限られていた。

本研究では、構造が未解明であった酸塩化物光触媒 $Bi_{12}O_{17}Cl_2$ に着目し、本物質の結晶構造を明らかにした。本物質は、図に示したような $n = 6$ の Bi–O ブロックを有する層状構造を有しており、波のような変調構造を有していることが明らかとなった。さらに、この構造の知見を元に、トポケミカルフッ化反応に成功し、有機物分解に対する光触媒活性の向上を達成した。

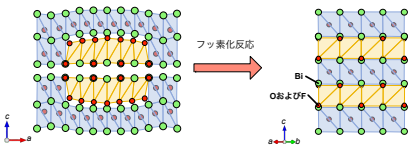

図. $Bi_{12}O_{17}Cl_2$のビスマス酸素層とフッ化による構造変化

1. H. Fujito, *et al., J. Am. Chem. Soc.* **2016**, 138, 2082-2085.
2. A. Nakada, *et al., J. Am. Chem. Soc.* **2021**, 143, 2491.

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水により加速する無機固相反応

（新潟大院自然）○戸田 健司
Water-assisted solid-state reaction (Graduate School of Science and Technology, Niigata University) ○Kenji Toda
Keywords : Soft chemistry; Water; Solid-state reaction; Nano particle; Crystallite

Nano-sized inorganic materials were synthesized using a novel water-assisted solid-state reaction (WASSR) method. This novel soft chemical synthesis method is very simple and can synthesize nanoparticle materials just by storing or mixing raw materials added a small amount (typically 10wt%) of water in a reactor at low temperature below 500 K. Typical particle sizes (under 100 nm) of the samples prepared by the WASSR method were smaller than that (2 - 10 micrometer size) of the sample prepared by the conventional solid-state reaction method. We can synthesize nano-sized practical materials such as $LiCoO_2$, $SrMoO_4$, $BiVO_4$, YVO_4, Ba_2SiO_4:Eu, $CsPbCl_3$ and $BaTiO_3$ by the WASSR method below 500 K. Most probable mechanism is a new type water accelerated solid acid-base reaction on the surface.

溶媒に難溶である原料粒子に微量の水を加え、室温で混合または密閉容器の中で200℃以下の低温で保持するだけで、ナノスケールの粒子サイズを持つセラミックス材料を合成することに成功した。これらの合成法を、微量の水により固相反応が加速することから Water-assisted solid-state reaction 法（WASSR 法）と名付けた。現在までに $LiCoO_2$、$SrMoO_4$、$BiVO_4$、YVO_4、Ba_2SiO_4:Eu、$CsPbCl_3$ および $BaTiO_3$ のナノ粒子の低温合成に成功している。重要な因子は原料粒子の固体酸性と固体塩基性の差が大きいことであり、水により酸ー塩基反応が促進されていると考えられる。

低温での加熱、安価な原料そして少量の水の添加という特徴から WASSR 法は従来のナノ粒子合成法と比較して極めて簡便であり、量産性から見ても低コストである有望な合成法と言える。

謝辞

本研究の一部は、科研費基盤研究(B)（一般）「水により加速する固相反応のメカニズム解明にむけた水の役割の解明」として実施された。

1) Synthesis of YVO_4 Nano Particles by Novel Room Temperature Synthesis Method, T. Kaneko, S. W. Kim, A. Toda, K. Uematsu, T. Ishigaki, K. Toda, M. Sato, J. Koide, M. Toda, Y. Kudo, T. Masaki, and D. H. Yoon, *Sci. Adv. Mater.*, **2015,** 7, 1502.

2) Nanophosphors synthesized by the water assisted solid state reaction (WASSR) method: Luminescence properties and reaction mechanism of the WASSR method, S-W. Kim, T. Hasegawa, M. Watanabe, M. Muto, T. Terashima, Y. Abe, T. Kaneko, A. Toda, T. Ishigaki, K. Uematsu, K. Toda, M. Sato, E. Kawakami, J. Koide, M. Toda, Y. Kudo, T. Masaki and D. H. Yoon, *Appl. Spect. Rev.*, **2017**, 52, 1.

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Solvothermal Synthesis of Porous SnO_2

([1]*Graduate School of Engineering, Kochi University of Technology*) ○Ayano Taniguchi,[1] Masataka Ohtani,[1] Kazuya Kobiro[1]

Keywords: Solvothermal Synthesis; Tin Oxide; Nanoparticles

Tin(IV) oxide (SnO_2) is an attractive material for various applications. Especially, porous structure, high specific surface area and high electrical conductivity of SnO_2 and SnO_2-based composites are highly desirable for applications to electrodes.[1] Various SnO_2-based composites have been produced, while no simple and versatile reaction affording SnO_2-based materials modified with hetero-element by single-step procedure was reported to our best knowledge. The specific surface area of SnO_2 reported so far is not so high, and few of them exceed 100 m^2/g.[2] In this study, we aimed to develop a versatile single-step synthetic method for yielding SnO_2-based composites by solvothermal reactions.

Reaction conditions of the solvothermal method such as solvents, additives, and heating were exhaustively investigated to obtain porous SnO_2 with high specific surface area. Different products, SnO_2, SnO and $Sn_6O_4(OH)_4$ or their mixture, were afforded depending on the solvents and reaction temperatures. As a result, porous SnO_2 without byproducts was obtained by using methanol as a solvent and triethylene glycol as an additive.[3] Obtained porous SnO_2 has a spherical higher-order structure composed of numerous SnO_2 single-crystal nanoparticles (Fig. 1a,b) and has a high specific surface area exceeding 200 m^2/g. The electrical conductivity of porous SnO_2 was equivalent to or greater that of commercially available SnO_2. Moreover, 8-type SnO_2-based composites were readily obtained (Fig. 1c) by simply adding hetero-element sources to the optimized precursor solution. Thus, these results open up a facile, versatile and useful technique for the synthesis of porous SnO_2-based composites.

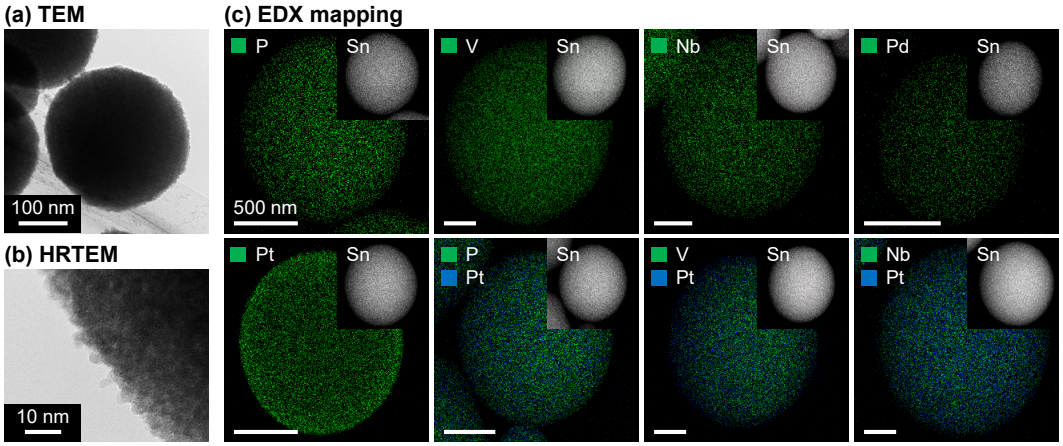

Figure 1. TEM (a) and high-resolution TEM (b) images of porous SnO_2 and EDX mapping images (c) of 8 type SnO_2-based composites.

1) Y. Inoue et al., *ECS Trans.* **2020**, *98*, 565. 2) L. Zhang et al., *J. Alloy. Compd.* **2020**, *814*, 152266. 3) A. Taniguchi et al., *RSC Adv.* **2022**, *12*, 22902.

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Structure and Physical Properties of *A*-site Layer-ordered/disordered Perovskites $NdBaFe_2O_6$ with Unusually High Valence $Fe^{3.5+}$

([1]*ICR*, *Kyoto University*) ○Makoto Iihoshi,[1] Masato Goto,[1] Yuichi Shimakawa[1]
Keywords: Perovskite; Phase transition; Unusually high valence

A-site layer-ordered perovskites $RBaFe_2O_6$ (R = rare-earth metals) were recently found to have successive phase transitions. In the previous presentation, it was reported that the transitions were related to not only relieving of charge instability of unusually high valence $Fe^{3.5+}$ but also ionic radius of rare-earth metals. However, it has not been revealed the effect of *A*-site layer-ordering on the successive phase transitions of $RBaFe_2O_6$ although the behavior of phase transition depends on *A*-site order/disorder in similar perovskite compounds.[1] Then we tried to synthesize *A*-site disordered sample $Nd_{0.5}Ba_{0.5}FeO_3$ and compared its physical properties with those of *A*-site layer-ordered $NdBaFe_2O_6$.

A-site disordered sample was successfully synthesized by high-temperature solid state reaction with flowing O_2 gas while *A*-site layer-ordered sample was synthesized by ozone oxidation. Their crystal structures were determined by Rietveld refinement of Synchrotron X-ray Powder Diffraction data (Figure 1). Physical properties such as magnetic susceptibility of both samples were measured and the results suggested that *A*-site layer-ordering had an important role in the phase transitions of $NdBaFe_2O_6$ (Figure 2). We will discuss the effect of *A*-site layer-ordering on physical properties of $NdBaFe_2O_6$ and the possibility of causing phase transitions by cation-orderings in perovskite metal oxides.

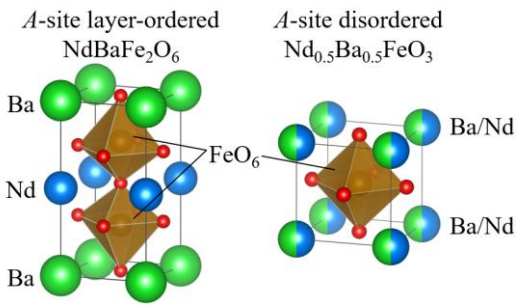

Figure 1 : Crystal structures of *A*-site layer-ordered/disordered $NdBaFe_2O_6$

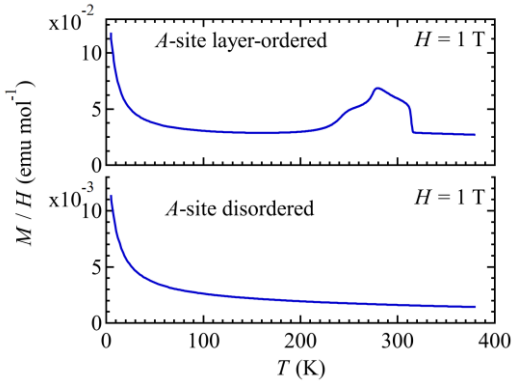

Figure 2 : Temperature-dependent magnetic susceptibility upon cooling

1) F. Denis Romero *et al.*, *Chem. Commun.*, **2019**, *55 (26)*,3690-3696

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結晶多形 $BaFeO_3$ の酸素放出と結晶構造変化

（京大化研 [1]）〇渡邊 澪 [1]・後藤 真人 [1]・島川 祐一 [1]
Oxygen Release and Crystal Structural Changes of $BaFeO_3$ Polymorphs ([1]*Institute for Chemical Research, Kyoto University*) 〇Rei Watanabe,[1] Masato Goto,[1] Yuichi Shimakawa[1]

Oxides containing unusually high valence transition-metal cations can easily release their oxygen ions to relieve the electronic instability of the unusual valence states. In this work, we focus on Fe^{4+} containing $BaFeO_3$, which shows three distinct 3C-, 6H-, and 12R-type polymorphic structures. When the samples are heated in ambient air, oxygen ions are released but the temperature at which the oxygen release starts was found to strongly depend on the polymorphic structures. Detailed results on the oxygen release behaviors and corresponding structural changes will be discussed.
Keywords : Unusually High Valence Ion; Oxygen Release; Perovskite-Type Oxide

遷移金属酸化物では、その遷移金属イオンの価数に応じて酸素量が変化し、酸素イオンの放出、吸収が生じる。中でも、異常高原子価イオンを含む酸化物は、典型的な価数のイオンを含む酸化物と比べて非常に低い温度で酸素イオンの放出、吸収が起こることが期待される。そのため、この放出、吸収挙動を理解することは基礎・応用の観点から重要である。

本研究では異常高原子価 Fe^{4+} イオンを含む $BaFeO_3$ に着目した。$BaFeO_3$ には、FeO_6 八面体が全て頂点共有で接続される 3C 型構造と、頂点共有と面共有を併せもつ 6H 型構造、12R 型構造の 3 種の結晶多形がある (Fig. 1)。これらの試料を大気中で加熱すると 3C 型構造では酸素放出が 130 ℃程度と非常に低い温度から生じる一方で、6H 型構造では 320 ℃、12R 型構造では 460 ℃程度から生じることが明らかになった。高温での放射光 X 線回折データによる詳細な結晶構造解析では、3C 型構造では頂点共有サイトの酸素がランダムに抜け始めることが明らかになった。一方で、6H 型、および 12R 型構造では、八面体が面共有したサイトから酸素が優先的に抜けていくことが示唆された。講演では、結晶構造変化の詳細を含め積層構造の違いが酸素脱離挙動に与える影響についても議論する予定である。

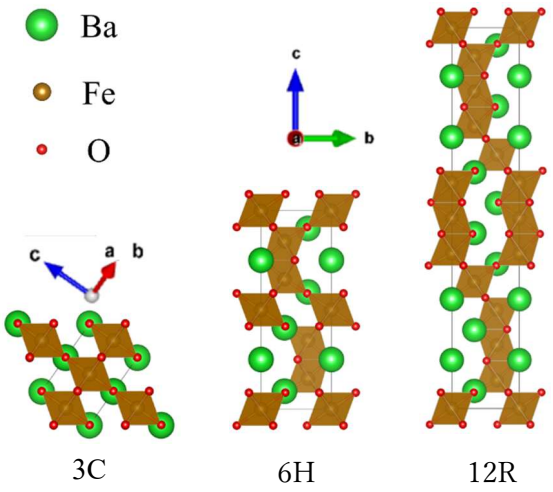

Fig. 1. Crystal structures of $BaFeO_3$

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B サイト秩序型ダブルペロブスカイト Ln_2LiFeO_6 の構造物性相関

（京大化研 [1]）○後藤　真人 [1]・島川 祐一 [1]

Structure-property relationships in *B*-site ordered double perovskites Ln_2LiFeO_6

([1] *ICR, Kyoto university*) ○Masato Goto,[1] Yuichi Shimakawa,[1]

Geometrically frustrated magnets have attracted attention owing to their magnetic physical properties. Previously, we elucidated structure-property relationships in *B*-site-ordered double perovskites Ln_2LiFeO_6 (*Ln* = La, Nd, Sm, Eu) with a frustrated f.c.c. lattice of unusually high valence Fe^{5+} ions[2,3]. Despite large antiferromagnetic interactions between Fe^{5+} spins, the magnetic ordering is strongly suppressed. In this work, we succeeded in synthesizing two new compounds Ln_2LiFeO_6 (*Ln* = Gd, Dy). We will report their structural and physical properties.

Keywords : B-Site-Ordered Double Perovskite; Geometrically Frustrated Magnet; Unusually High Valence Ion; High Pressure Synthesis

幾何学的フラストレート磁性体は反強磁性秩序の抑制に起因した新奇物性の発現の舞台として注目を集めている。磁性イオンが面心立方格子を形成する *B* サイト岩塩秩序型ダブルペロブスカイト $A_2BB'O_6$ は、その代表的な物質系の一つであり、bond valence glass などの興味深い磁性が多く報告されている[1]。我々は、異常高原子価の Fe^{5+} を含む Ln_2LiFeO_6（*Ln*：ランタノイド）に着目して研究に取り組んでいる[2,3]。 これまでの研究から、*Ln* = La は菱面体晶の結晶構造をもつ一方で、*Ln* = Nd, Sm, Eu はいずれも単斜晶構造をもつ（図 1）こと、また *Ln* = La, Nd, Sm, Eu はいずれもワイス温度の絶対値よりも非常に低い温度で反強磁性的な磁気相転移を示すことが判明している。一方で、*Ln* = Sm, Eu では磁気転移温度以下で自発磁化が生じることから、磁気的基底状態がランタノイドに強く依存することも示唆されている。最近、新たに *Ln* = Gd, Dy の物質の合成に成功し、これらの構造と物性を調べたのでそれらの結果を報告する。

Ln = Gd, Dy の物質は *Ln* = Nd, Sm, Eu と同様に単斜晶構造をもつこと、また鉄の価数については、^{57}Fe メスバウアー分光測定から+5 価であることが確かめられた（図 2）。一方で、これらの物質ではいずれも強磁性的な相互作用が支配的であることが明らかになった。さらに、*Ln* = Dy では磁気相転移温度以下で強磁性秩序を形成することが判明した。講演では、結果の詳細を示すとともに、それらのランタノイド依存性について議論する予定である。

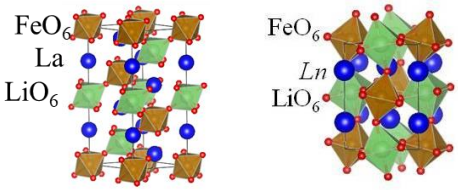

図 1. Ln_2LiFeO_6 (*Ln* = La, Nd, Sm, Eu）の結晶構造。

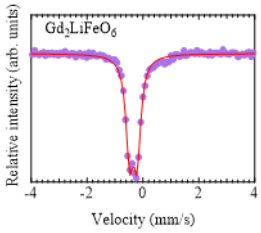

図 2. Gd_2LiFeO_6 の室温での ^{57}Fe メスバウアースペクトル。

[1] M.A. de Vries *et al*., Phys. Rev. Lett. **104**, 177202 (2010). [2] P. Xiong *et al.*, Inorg. Chem. **55**, 6218, (2016). [3]M. Goto *et al*.: J. Am. Chem. Soc., **143**, 19207 (2021).

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

[K501-3pm] 07. Inorganic Chemistry

Chair: Takafumi Yamamoto, Takayuki Nakamuro

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K501 (K501, Lecture Hall Bldg. [5F])

[K501-3pm-01] The Effects on Substitution of Thiocyanate Anion for $FAPbI_3$

○Takuya Ohmi[1], Masaki Azuma[1,2], Takafumi Yamamoto[1] （1. Tokyo Institute of Technology, 2. KISTEC）

1:10 PM - 1:30 PM

[K501-3pm-02] High-pressure phases of lanthanide oxyhydrides and anion ordering

○Ryo Terada[1], Yumi Tsuchiya[1], Hiroki Ubukata[1], Zefeng Wei[1], Hiroshi Kageyama[1] （1. Kyoto University）

1:30 PM - 1:50 PM

[K501-3pm-03] Reduction-induced Cs^+ ion capture with polyoxometalate encapsulated metal– organic frameworks

○Naoki Ogiwara[1], Cocoro Andrew Ngasaka[1], Sayaka Uchida[1] （1. School of Arts and Sciences, The University of Tokyo ）

1:50 PM - 2:10 PM

[K501-3pm-04] High Proton conduction in Crystalline composites based on Eu Ion Bonded Polyoxometalates and Polymers

○Tsukasa Iwano[1], Sayaka Uchida[1] （1. Grad. Sch. Arts and Sci., The Univ. of Tokyo）

2:10 PM - 2:30 PM

[K501-3pm-05] Synthesis of size-controlled small silver clusters utilizing porous ionic crystals as scaffolds

○Naoya Haraguchi[1], Naoki Ogiwara[1], Sayaka Uchida[1] （1. Grad. Sch. of Arts and Sci., The Univ. of Tokyo）

2:40 PM - 3:00 PM

[K501-3pm-06] Investigation of synthesis of thiol-protected Au clusters using dendrimers

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

3:00 PM - 3:20 PM

[K501-3pm-07] Between molecules and nanocrystals: synthesis and properties of perovskite nanoclusters

○Olivier Jan Chevalier[1], Takayuki Nakamuro[1], Naotaka Yoshikawa[1], Ryo Shimano[1], Rui Shang[1], Eiichi Nakamura[1] （1. The University of Tokyo）

3:20 PM - 3:40 PM

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The Effects on Substitution of Thiocyanate Anion for $FAPbI_3$

([1]*Laboratory for Materials and Structures, Tokyo Institute of Technology*, [2]*Kanagawa Institute of Industrial Science and Technology*) ○Takuya Ohmi,[1] Masaki Azuma,[1,2] Takafumi Yamamoto[1]

Keywords: Organic-inorganic hybrid perovskite, Lead halide perovskite, Perovskite solar cell, Crystal structure analysis, Structural phase transition

α-$FAPbI_3$ (FA = $CH(NH_2)_2$) with a pseudo-cubic perovskite structure has attracted attention for photovoltaic application. However, there is a problem in their low stability. α-$FAPbI_3$ is metastable at room temperature, and it transforms to δ-phase with hexagonal perovskite structure at a certain period of time. Since δ-phase has a large bandgap of 2.43 eV, stabilization of α-phase with narrow band gap (1.48 eV) is strongly desired for solar cell application. We have studied the hybrid perovskite compounds containing pseudo-halide anion such as SCN^-.[1] Recently, it was reported that the SCN^- surface treatment to $FAPbI_3$ improves their stability,[2] but no information about the precise structure of SCN-substituted crystal.

Herein, we successfully synthesized a powder and a single crystal of thiocyanate-substitution of $FAPbI_3$. SCN-substitution into $FAPbI_3$ was found to be effective in stabilizing the metastable α-phase. In this presentation, I will show the details of the crystal structure and properties of SCN^- substituted $FAPbI_3$ bulk revealed by synchrotron X-ray diffraction and diffuse-reflectance spectra measurement. I will also report the phase stability obtained by the analysis of the temperature-dependent XRD data and propose the mechanism of the stabilizing effect from the bulk point of view.

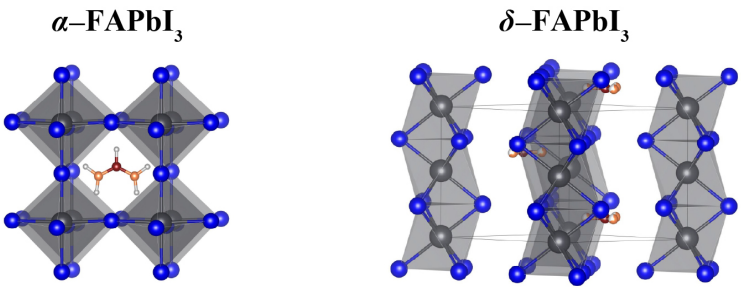

Figure. Crystal structure of α-$FAPbI_3$ and δ-$FAPbI_3$.

1) a) T. Yamamoto, T. Ohmi, et al. *Inorg. Chem.* **2020**, *59*, 17379-17384. b) T. Ohmi, et al. *Cryst.Eng.Comm.* **2022**, *24*, 5428-5434. 2) H. Lu, et al. *Science*, **2020**, *370*, 6512, eabb8985.

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ランタノイド酸水素化物の高圧相とアニオン秩序

(1. 京都大学)○寺田 凌[1]、土屋 優美[1]、生方 宏樹[1]、Zefeng Wei[1]、陰山 洋[1]

High-pressure phases of lanthanide oxyhydrides and anion ordering

(1. Kyoto University) ○Ryo Terada[1], Yumi Tsuchiya[1], Hiroki Ubukata[1], Zefeng Wei[1], Hiroshi Kageyama[1]

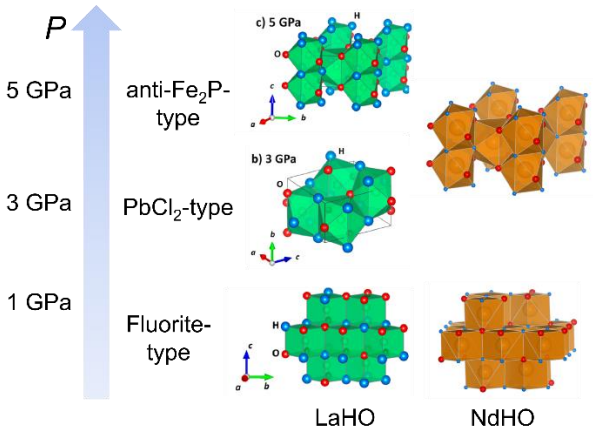
Unique hydride-derived phenomena have been reported in fluorite-type *Ln*HO by high-pressure synthesis. One is the phenomenon that the order-disorder arrangement of anions is controlled by the size of the cation. Another is the decrease in the coordination number of LaHO to hydride under high pressure. These effects are thought to be due to the size flexibility of the hydride.

In this study, we investigated the behavior of NdHO, which is anion ordered at ambient pressure like LaHO, and *Ln*HO (*Ln* = Gd, Er), which is anion disordered at ambient pressure, under high pressure. In these high-pressure phases, the $PbCl_2$-type structure observed in LaHO is no longer observed.

Keywords : Mixed anion, High pressure

これまでに、高圧合成法により蛍石型 *Ln*HO において、ヒドリドに由来するユニークな現象が報告されている。ひとつは，カチオンの大きさによってアニオンの秩序ー無秩序配列が制御されるという現象である。もうひとつは，LaHO の高圧下でのヒドリドに対する配位数の減少である。これらはヒドリドの大きさの柔軟性による効果だと考えられる。

本研究では，LaHO と同様に常圧でアニオン秩序配列した NdHO および，常圧でアニオンが無秩序配列した *Ln*HO(*Ln* = Gd, Er)の高圧下での振る舞いを調べた。これらの高圧相では，LaHO で見られた $PbCl_2$ 型構造が見られなくなった。



1) Broux, T. *et al.* High-Pressure Polymorphs of LaHO with Anion Coordination Reversal. *J. Am. Chem. Soc.* **141**, 8717–8720 (2019).
2) Yamashita, H. *et al.* Chemical Pressure-Induced Anion Order-Disorder Transition in LnHO Enabled by Hydride Size Flexibility. *J. Am. Chem. Soc.* **140**, 11170–11173 (2018).

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多孔性金属錯体に内包されたポリオキソ酸の還元を利用した Cs^+ イオン吸着

（東大院総合 [1]）○荻原 直希 [1]・永坂 心 [1]・内田 さやか [1]

Reduction-induced Cs^+ Ion Capture with Polyoxometalate Encapsulated Metal–Organic Frameworks

([1]*Graduate School of Arts and Sciences, The University of Tokyo*) Naoki Ogiwara[1], Cocoro Andrew Nagasaka[1], Sayaka Uchida[1]

Removal of Cs^+ ions continues to be an essential topic for the treatment of solutions. POM@MOFs are hybrid materials of polyoxometalates (POMs), which are nano-sized metal-oxygen clusters, and metal–organic frameworks (MOFs), which are three-dimensional frameworks consisting of metal cations and organic ligands. POM@MOFs are able to adsorb significantly more Cs^+ when compared to the MOF material alone. Furthermore, another increase in Cs^+ uptake capacity was recorded after introducing ascorbic acid as a reducing agent. XPS results suggest that the incorporation of Cs^+ into the POM@MOF is enhanced with the increased negative charge of POM due to the reduction process.

Keywords : Polyoxometalate; Metal–Organic Framework,; Ion Capture

溶液中からの Cs^+イオン除去は、水や有機溶媒の処理において重要な課題である。これまで活性炭やゼオライト等の多孔性材料を用いた Cs^+吸着が検討されてきたが、その吸着性能は頭打ちになりつつあり、新たな吸着材料の開発が求められている。

本研究では、Cs^+吸着材料としてポリオキソメタレート（POM）と多孔性金属錯体（MOF）を複合化させた POM–MOF 複合体（POM@MOF）に着目した(Fig.1)。POM@MOF を構成する MOF としては、高い構造安定性を有する Zn[2-methylimidazolate]$_2$ (ZIF-8) [1]、POM としては酸化還元活性を有する Keggin 型 POM [α-$PMo_{12}O_{40}]^{3-}$ (PMo_{12})を選定した。PMo_{12}@ZIF-8 複合体の合成は PMo_{12} の存在下で ZIF-8 の前駆体を液相中で反応させることで行った。メタノール溶液中における Cs^+吸着特性を評価したところ、PMo_{12}@ZIF-8 は ZIF-8 単体を凌駕する吸着特性を示した。さらに Cs^+吸着条件下で還元剤となるアスコルビン酸を添加すると、Cs^+吸着量の増加が観測された。吸着機構解明のために、還元的に Cs^+吸着させた PMo_{12}@ZIF-8 の XPS 測定を行ったところ、PMo_{12} の Mo^{VI} の一部が Mo^{V} に還元され、PMo_{12} の負電荷が増大することが観測された。これらの結果より、PMo_{12} の還元により増加した負電荷の電荷補償として、Cs^+が PMo_{12}@ZIF-8 の構造中に取り込まれることが、吸着機能の向上の鍵になることが示唆された。

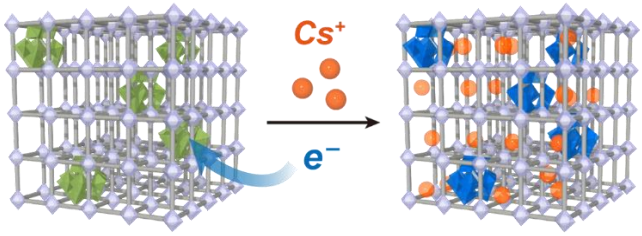

Figure 1. POM@MOF を用いた Cs^+イオンの吸着のイメージ。

1) K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103* (27), 10186–10191.

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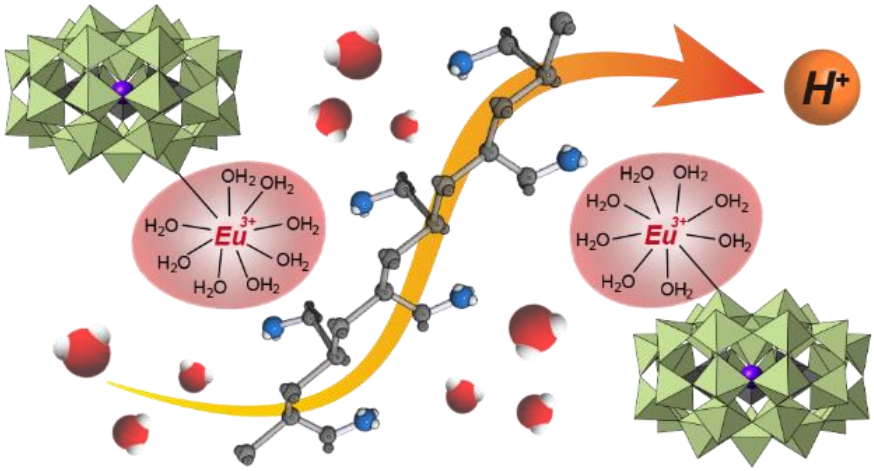
High Proton conduction in Crystalline composites based on Eu Ion Bonded Polyoxometalates and Polymers

([1]*Graduate School of Arts and Sciences, The University of Tokyo*)
○Tsukasa Iwano,[1] Sayaka Uchida [1]

Keywords: ionic crystal, solid electrolyte, lanthanide elements, polyoxometalate, polymer

Polyoxometalate (POM) based solids are promising candidates of proton-conducting solid electrolytes, while application has been limited because of the low structural stability. On the other hand, polymers such as Nafions and poly(ethylene glycol)s have achieved great success commercially as cation-conducting electrolytes. We have previously reported that crystalline composites of Preyssler-type POMs with K^+ and poly(allylamine) (PAA) can circumvent the hygroscopicity induced low durability by the electrostatic interaction between the POM and protonated amine moieties, and that these composites show high proton conductivity close to 10^{-2} S cm^{-1}.[1] Besides, appropriate selection of counter cation of POMs is also important, and it has been reported that lanthanide ions with high coordination numbers can attract water molecules and extend the hydrogen-bonding network, which would facilitate proton conduction.[2] In our previous work, K^+-encapsulated Preyssler-type phosphotungstate $K_{11}Eu[P_5W_{30}O_{110}K]$•$26H_2O$ (**EuK**). exhibited very high proton conductivity of ca. 10^{-2} S cm^{-1} at 368 K and 90% relative humidity (RH)[3]. Then, we synthesized crystalline composites based on **EuK** and PAA or poly(vinyl alcohol) (PVA), and $EuK_5H_6[KP_5W_{30}O_{110}]$ •0.032PAA3000•$30H_2O$ [**EuK-PAA**] and $K_{10.6}H_{0.4}Eu[KP_5W_{30}O_{110}]$·0.044PVA500·$39H_2O$ [**EuK-PVA**] were obtained. The Chemical formula of each compound were determined by elemental analyses. Both compounds exhibited very high proton conductivity of 10^{-2} S cm^{-1} at 358 K and 90% RH. In my presentation, proton conduction mechanism of these compounds with different kind of polymers will be shown.



[1] T. Iwano et al., *Commun. Chem.*, **2**, Article number: 9 (2019). [2] Q. Peng et al., *Dalton Trans.* **46**, 4157-4160 (2017). [3] T. Iwano *et al., ACS Appl. Mater. Interfaces,* **13**, 19138–19147 (2021).

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多孔性イオン結晶を鋳型としたサイズ制御された小核銀クラスターの合成

（[1]東大院総合）○原口直哉[1]・荻原直希[1]・内田さやか[1]
Synthesis of size-controlled small silver clusters utilizing porous ionic crystals as scaffolds
([1]*Grad. Sch. of Arts and Sci., The Univ. of Tokyo*) ○Naoya Haraguchi,[1] Naoki Ogiwara,[1] Sayaka Uchida[1]

Small silver clusters consisting of a few atoms have unique catalytic and optical properties, which are not observed in the corresponding bulk samples. While the properties of small silver clusters are highly dependent on their size, size-controlled synthesis is still challenging because small clusters tend to aggregate. Although we have previously reported synthesis of small silver clusters in pores of redox-active porous ionic crystal[1)], size-control has remained as our next challenge. In this work, we utilized pore of $A_3[Cr_3O(OOCH)_6(C_7H_9N)_3]_3[P_2M_{18}O_{62}]$ (**A-I$_M$**, A/M = K/Mo, NH_4/Mo, K/W) to form and stabilize small silver clusters and investigate correlation between the amount of transferred electrons to Ag ion and size of clusters formed in **A-I$_M$** to realize size-controlled synthesis of small silver clusters.
Keywords ： Metal Clusters; Porous Crystalline Materials; Polyoxometalates

数個から十数個程度の銀原子/イオンからなる小核銀クラスターはバルクの銀とは異なるユニークな発光特性・触媒活性などの性質を示すが、その性質は強くサイズに依存するため、サイズを制御した合成法の開発は重要な課題である。当研究室の先行研究では、レドックス活性な多孔性のイオン結晶（Porous Ionic Crystals, PICs）の内部空間に小核銀クラスターが形成される現象を報告した[1)]が、そのサイズ制御は達成できなかった。そこで本研究では、PICs の違いが銀クラスターのサイズに与える影響を調べるために、レドックス活性な 3 種類の PICs $A_3[Cr_3O(OOCH)_6(C_7H_9N)_3]_3[P_2M_{18}O_{62}]$ (**A-I$_M$**, A/M = K/Mo, NH_4/Mo, K/W)を利用して、結晶の内部空間に小核銀クラスターを形成し各種測定による特性評価を行った。その結果、得られる銀クラスターのサイズが結晶の構成イオンと反応条件の調整によって制御可能であることを明らかにした。

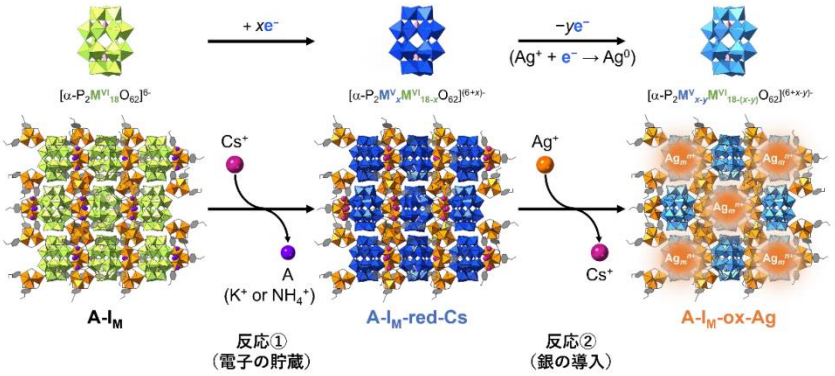

Figure 1 PICs 内部での小核銀クラスターの形成

1) S. Uchida et al., *Nanoscale*, **2019**, *11*, 5460.

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Investigation of synthesis of thiol-protected Au clusters using dendrimers

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

Keywords: *Cluster, Au, Dendrimer, Thiol protected cluster*

Metal clusters are generally smaller than nanoparticles and consist of a few to several dozen metal atoms. Since the liquid-phase synthesis of thiol-protected Au clusters was reported by Brust and Schiffrin,[1] various Au clusters have been reported. However, synthesizing these Au clusters and hetero-metal Au clusters requires a high-yield method at low-temperature,[2] synthesis method using an etching reaction,[3] and a synthesis method using metal exchange for different metals, all of which require time. On the other hand, there is a liquid-phase synthesis method for metal clusters that use dendrimers as templates. In this method, elements to be formed clusters can be collected in dendrimers in advance, allowing direct synthesis. The 4th-generation phenylazomethine dendrimer (TPM G4) developed in our laboratory has been reported to be used for 2-5 kinds of metal salts assembly and cluster synthesis.[4] The synthesis using the TPM G4 has also been reported. Cluster synthesis of Al_{13}^- in the liquid phase, which has been synthesized in the gas phase, has been discovered so far [5]. In this study, we discuss further extensions of the synthesis of thiol-protected Au clusters using dendrimers.

$AuCl_3$ was coordinated to the dendrimer (TPM G4). The $Au_{25}PET_{18}$ cluster was synthesized by addition of $NaBH_4$ and thiol ligands to the solution of dendrimer metal complexes at the same time, to conduct reduction and thiol coordination. The synthesis of the $Au_{25}PET_{18}$ cluster was confirmed by MADLI-TOF-MS (Figure 1a). We will report on the extended results of the new synthesis of thiol-protected Au clusters achieved with $Au_{25}PET_{18}$ (Figure 1b).

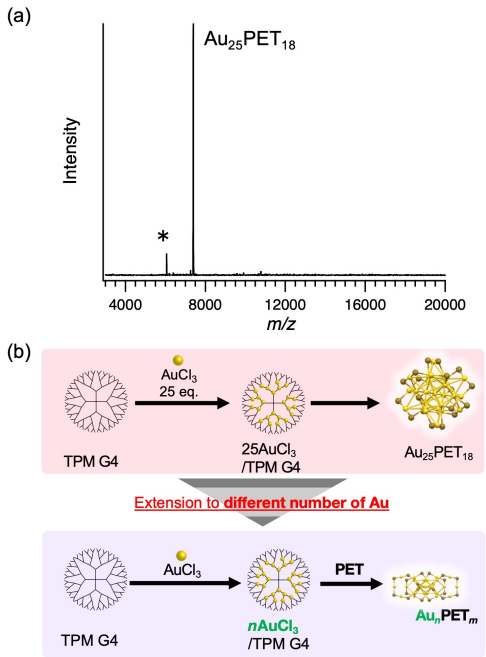

Figure 1. (a) MALDI-TOF-MS spectrum of the sample obtained after synthesis. * is $[Au_{21}PET_{14}]^+$ of the fragment of $Au_{25}SR_{18}$.[6] (b) Schematic illustration of the concept of this study.

1) Brust, M.; Schiffrin, D. J.; *et al.*, *J. Chem. Soc. Chem. Commun.*, **1994**, *0*, 801–802. 2) Zhu, M.; *et al.*, *J. Am. Chem. Soc.*, **2008**, *130*, 5883–5885. 3) Dharmaratne, A. C.; *et al.*, *J. Am. Chem. Soc.*, **2009**, *131*, 13604–13605. 4) Tsukamoto, T.; Yamamoto, K. *et al.*, *Nat. Commun.*, **2018**, *9*, 3873. 5) Kambe, T.; Yamamoto, K. *et al.*, *Nat. Commun.*, **2017**, *8*, 2046. 6) **Muramatsu, H.**; Kambe, T.; Yamamoto, K. *et al.*, *Molecules*, **2022**, *27*, 3398. (**Cover article**)

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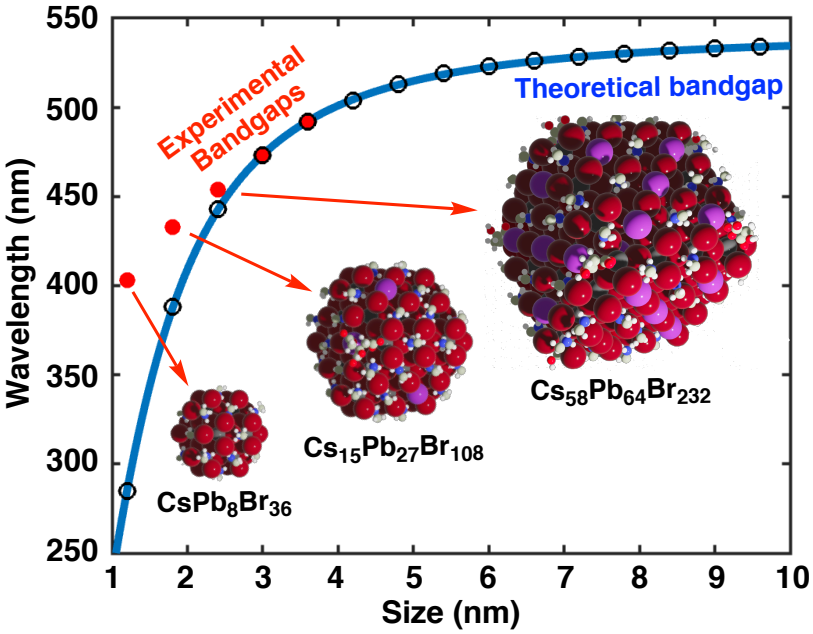
Between molecules and nanocrystals: synthesis and properties of perovskite nanoclusters

○Olivier Jan Chevalier[1], Takayuki Nakamuro[1], Naotaka Yoshikawa[2], Ryo Shimano[2], Rui Shang[1], Eiichi Nakamura[1]

([1]*Molecular Technology Innovation, Department of Chemistry, The University of Tokyo,* [2]*Department of Physics, The University of Tokyo*)

As a nanomaterial becomes smaller and smaller, bonds vibrate, quantum effects emerge and bulk effects become negligible: nanocrystals start to behave more like molecules and less like crystals. However, it is not yet clearly understood how molecular effects such as atomic vibrations and distortions affect ultrasmall clusters.

In this work, we investigate the transition between lead bromide complexes (i.e. $PbBr_6^{4-}$) and perovskite quantum dots. By using highly stable lead-ligand complexes as precursor, we were able to isolate monodisperse 1.2 nm, 1.8 nm, and 2.4 nm perovskite nanocubes. We investigate their optical and structural properties and demonstrate that the transition between multinuclear complexes and nanocrystals lies between cubes containing a total of 8 Pb atoms and cubes containing 27 Pb atoms. With temperature studies we determined that molecular distortions were the primary source of non-radiative recombination for smaller clusters and not surface defects. We expect our results to tremendously help understanding the fundamental properties of lead halide perovskite nanomaterials and their limitations as light-emitters.



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

[K501-3vn] 07. Inorganic Chemistry

Chair: Kosuke Suzuki, Yuji Kikukawa

Fri. Mar 24, 2023 4:10 PM - 6:40 PM K501 (K501, Lecture Hall Bldg. [5F])

[K501-3vn-01] Precise synthesis of 3d metal clusters and evaluation of their properties

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

4:10 PM - 4:30 PM

[K501-3vn-02] Development of metal nanoparticle catalysts modified using multidentate polyoxometalates

○Kang Xia[1], Takafumi Yatabe[1], Kentaro Yonesato[1], Tomohiro Yabe[1], Soichi Kikkawa[2], Seiji Yamazoe[2], Ayako Nakata[3], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The University of Tokyo, 2. Tokyo Metropolitan University, 3. National Institute for Materials Science)

4:30 PM - 4:50 PM

[K501-3vn-03] Synthesis of copper nanoclusters using inner cavity of a ring-shaped polyoxometalate

○Yoshihiro Koizumi[1], Kentaro Yonesato[1], Soichi Kikkawa[2], Seiji Yamazoe[2], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo, 2. Tokyo Metropolitan Univ.)

4:50 PM - 5:10 PM

[K501-3vn-04] Synthesis and Characterization of Phosphovanadates with Fruoride

○Yuji Kikukawa[1], Ryu Hasegawa[1], Yoshihito Hayashi[1] (1. Kanazawa Univ.)

5:20 PM - 5:40 PM

[K501-3vn-05] Synthesis and Characterization of Novel Iron-Group Metal Nanoclusters Protected by Bulky Ligands

○Tatsuya Higaki[1], Kanata Tanaka[1], Shunya Oishi[2], Koki Kawamoto[2], Mizuki Tada[2], Yasuhiro Ohki[1] (1. ICR, Kyoto U., 2. Graduate School of Science and RCMS, Nagoya University)

5:40 PM - 6:00 PM

[K501-3vn-06] Evaporation-induced self-assembly process with centrifugal evaporator for obtaining mesoporous alumina powders

○Ryutaro Wakabayashi[1], Tatsuo Kimura[1] (1. National Institute of Advanced Industrial Science and Technology (AIST))

6:00 PM - 6:20 PM

[K501-3vn-07] Preparation of laminar composite membranes consisting of large niobate and graphene oxide nanosheets and electrochemical analysis of ion diffusion behaviors

○Fumitaka Hayashi[1], Ogiso Hisaki[1], Tanaka Atsushi[1], Nishina Yuta[2], Yamada Tetsuya[1], Teshima Katsuya[1] (1. Shinshu University, 2. Okayama University)

6:20 PM - 6:40 PM

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Precise synthesis of 3d metal clusters and evaluation of their properties

([1]*Lab. Chem. Life Sci.*, *Tokyo Tech*, [2]*JST-ERATO*, [3]*JST-PRESTO*) ○ Tatsuya Moriai,[1] Takamasa Tsukamoto,[1,2,3] Tetsuya Kambe,[1,2] Takane Imaoka,[1,2] Kimihisa Yamamoto[1,2]
Keywords: cluster; 3d metal; dendrimer; catalyst; CO oxidation

The metal clusters have attracted worldwide attention due to the unique reactivity and property beyond the extension of the bulk and nanoparticles. However, it has been technically difficult to systematically evaluate the property of various clusters since the synthesis method and the stable atomicity of clusters have been different for each element. To overcome this obstacle, we focused on the template method using a phenylazomethine dendrimer as a template molecule. This molecule has many imine sites which coordinate to metal ions and possesses a potential gradient of electronic density. Consequently, this dendrimer accumulates the regulated number of the metal salts and realizes synthesis of metal clusters with the finely controlled atomicity and elemental composition by chemical reduction of complexes.[1,2]

In this work, we focused on 3d metals which are relatively low-cost and abundant from Ti to Zn, and systematically evaluated the property of 3d metal clusters by unification of the synthesis method. We built the new liquid-phase reaction system using the same solvent and the counter anion of metal salts on the template method, leading to unification of the complexation behavior and synthesis condition for each cluster. In actual, we applied this system to 9 kinds of 3d metals and succeeded in the stepwise accumulation of each element into a dendrimer (Fig. 1A). The precise synthesis of 3d metal clusters with an atomicity of 28 was subsequently achieved by chemical reduction of these complexes. It was demonstrated that their clusters had the specific oxidation state peculiar to a cluster-size scale by UV-vis, XPS, and XAFS measurements. The reduction behavior of their clusters oxidized in air was also investigated through CO-TPR. Moreover, their clusters showed the unique reactivity as catalysts not found in conventional bulk metals over CO oxidation (Fig. 1B).

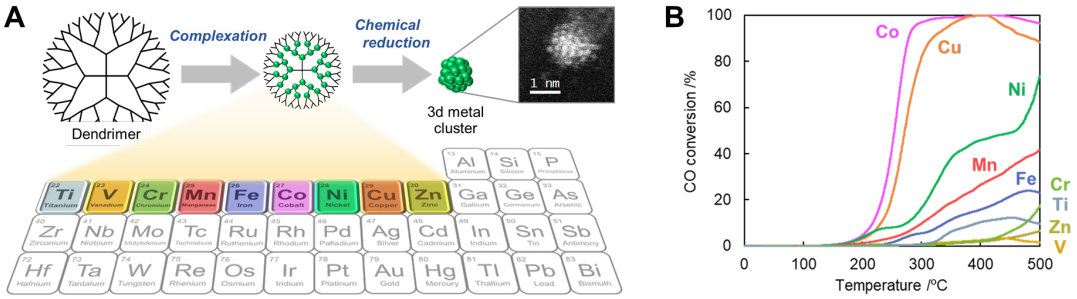

Fig. 1. (A) The schematic view of this work and a STEM image of Ni_{28} cluster. (B) Catalytic activity of 3d metal clusters with an atomicity of 28 over CO oxidation.

1) T. Tsukamoto *et al., Nat. Commun.* **2018**, *9*, 3873. 2) T. Moriai *et al., Angew. Chem. Int. Ed.* **2020**, *59*, 23051-23055.

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Development of metal nanoparticle catalysts modified using multidentate polyoxometalates

([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Science, Tokyo Metropolitan University*, [3]*National Institute for Materials Science*) ○Kang Xia,[1] Takafumi Yatabe,[1] Kentaro Yonesato,[1] Tomohiro Yabe,[1] Soichi Kikkawa,[2] Seiji Yamazoe,[2] Ayako Nakata,[3] Kosuke Suzuki,[1] Kazuya Yamaguchi[1]

Keywords: Polyoxometalates; Metal Nanoparticles; Au Nanoparticles; Hybrid Materials; Catalysis

Metal nanoparticles modified with polyoxometalates (POMs) have been extensively studied because these modifications can modulate their catalytic performance and achieve concerted catalysis.[1,2] Despite utilization of unique multielectron transfer and photoredox property of POMs in photo- and electro-catalysis, the inherent low stability of POM-modified metal nanoparticles still limits their catalytic applications.[2] In this regard, we designed two strategies towards robust Au nanoparticle catalysts utilizing an electronic interaction between Au nanoparticles and multivacant lacunary POMs as multidentate ligands. Firstly, we developed anionic Au nanoparticle catalysts on a carbon support with both increased activity and improved stability for oxidative dehydrogenation of piperidone derivatives to the corresponding enaminones.[3] Interestingly, by modulating these electronic interactions, their catalytic performance can be correspondingly altered. However, unless being immobilized on a carbon support, agglomeration of POM-modified Au nanoparticles inevitably occurs in an aqueous solvent. Hence, in a further study, we developed a rather feasible strategy to obtain ultrasmall stable Au nanoparticles (~3 nm) modified with multidentate POMs in a non-polar organic solvent. It is noted that they possess an extraordinarily high stability that is tolerant to high concentration, temperature, and long time, having them well-perform in the selective aerobic oxidation of benzyl alcohol to benzaldehyde without noticeable particle size changes even after the reaction. Such fascinating properties may be attributed to the enhanced electronic effect and steric effect of multidentate POM ligands.

1) Y. Wang, I. A. Weinstock, *Chem. Soc. Rev.* **2012**, *41*, 7479. 2) K. Xia, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214506. 3) K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205873.

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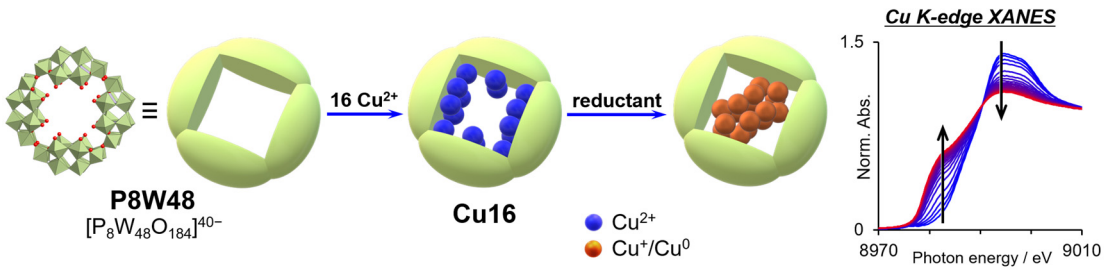
Synthesis of copper nanoclusters using inner cavity of a ring-shaped polyoxometalate

([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Science, Tokyo Metropolitan University*) ○Yoshihiro Koizumi,[1] Kentaro Yonesato,[1] Soichi Kikkawa,[2] Seiji Yamazoe,[2] Kosuke Suzuki,[1] Kazuya Yamaguchi[1]

Keywords: Polyoxometalates; Copper nanoclusters; Solid state reduction

Copper nanoclusters have attracted attention in various fields such as catalysis and materials science.[1] A ring-shaped polyoxometalate (POM) $[P_8W_{48}O_{184}]^{40-}$ (**P8W48**) possesses a large cavity of approximately 10 Å in diameter, into which polynuclear metal atoms can be incorporated. Until now, we succeeded in the selective synthesis of several multinuclear Cu^{2+}-containing ring-shaped POMs with different number and arrangement of copper ions in organic solvents.[2] More recently, we also succeeded in synthesizing silver nanoclusters within the cavity of **P8W48** by reduction of the introduced silver ions in organic solvents and showed that these nanoclusters exhibit specific synergistic catalysis between POM and silver nanoclusters. However, it is difficult to prepare copper nanoclusters in a similar way to silver nanoclusters owing to instability of the reduced copper species.

In this work, we developed a novel method to synthesize copper nanoclusters inside the cavity of **P8W48** by solid-state reduction of 16-Cu^{2+}-containing **P8W48** (**Cu16**). The color of **Cu16** changed gradually from green to dark brown during the reaction, suggesting the reduction of **Cu16**. *In-situ* Cu K-edge XANES spectra indicated that Cu^{2+} ions were reduced to Cu^{+} and Cu^{0} by the solid-state reduction. In addition, Cu K-edge EXAFS analysis revealed that Cu–Cu bonds having a low coordination number were formed upon the reduction of copper ions, demonstrating the formation of small copper nanoclusters. X-ray crystallographic analysis and elemental analysis of the reduced species suggested that nanoclusters with 16 nuclear copper cores were constructed within the cavity of **P8W48**. These results showed that the rigid and stable **P8W48** acted as an inorganic template for the formation of copper nanoclusters with exposed surfaces inside the cavity. Furthermore, we also revealed that reversible reduction-oxidation of copper nanoclusters proceeded in the solid-state reaction.



1) A. Baghdasaryan, T. Bürgi, *Nanoscale* **2021**, *13*, 6283. 2) Y. Koizumi, K. Yonesato, K. Yamaguchi, K. Suzuki, *Inorg. Chem.* **2022**, *61*, 9841.

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フッ化物イオン含有ホスホバナデートの合成とキャラクタリゼーション

（金沢大理工）〇菊川 雄司・長谷川 隆・林 宜仁
Synthesis and Characterization of Phosphovanadates with Fruoride (*Graduate School of Science and Engineering, Kanazawa University*) 〇Yuji Kikukawa, Ryu Hasegawa, Yoshihito Hayashi

Polyoxovanadates sometimes adopt non-metallic elements as addenda atoms. By the reaction of vanadium-phosphate and fruoride, phosphovanadate clusters with fruoride were synthesized and isolated as tetra-n-butylammonium salts. From the x-ray crystallographic analysis, the obtained products possessed vanadium and phosphorous atoms with 1:1 ratio and the fluoride was stabilized at the center of the clusters. The terminal oxygen atoms of phosphate acted as proton accepter sites and protonation and deprotonation was controlled by the reaction with acid and base, respectively.
Keywords : Polyoxometalates; Phosphovanadates; Acid and base; crystal structures

ポリオキソメタレートは外骨格を形成する元素を欠損させるあるいは他の元素に置換することで特性を制御することが可能であり、発展してきた。ポリオキソバナデートでは、外骨格を形成する元素がバナジウムであるが、同等の数の非金属元素を有する構造が報告されてきた。その多くはゲルマニウム、ヒ素、アンチモンなど p ブロック元素である。[1] リン酸バナジウムはブタンを無水マレイン酸に変換させる工業触媒であるが、ポリオキソバナデートの外骨格にリンを複合化させた化合物はこれまで 1 報のみである。[2] 本研究では、フッ化物イオンをテンプレートにリン酸バナジウムを反応させることで、バナジウムとリンが 1:1 で複合化したアニオン性クラスターが得られることが明らかとなった。得られた化合物は複数のプロトンを有し、酸や塩基と反応させることでプロトン化状態を制御することが可能であることが明らかとなった。

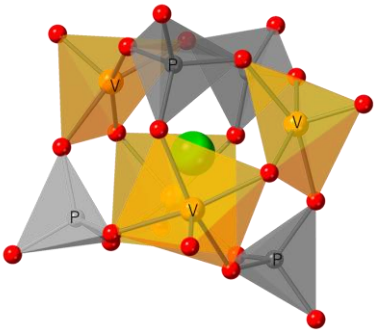

図 1. フッ化物イオン含有ホスホバナデートのアニオン構造

1) K. Y. Monakhov, W. Bensch, P. Kögerler, *Chem. Soc. Rev.*, **2015**, *44*, 8443.
2) D. L. Thorn, R. L. Harlow, N. Herron, *Inorg. Chem.* **1995**, *34*, 2629.

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Synthesis and Characterization of Novel Iron-Group Metal Nanoclusters Protected by Bulky Ligands

([1]*Institute for Chemical Research, Kyoto University*, [2]*Graduate School of Science and RCMS, Nagoya University*) ○Tatsuya Higaki,[1] Kanata Tanaka,[1] Shunya Oishi,[2] Koki Kawamoto,[2] Mizuki Tada,[2] Yasuhiro Ohki[1]

Keywords: Metal Cluster; Nanocluster; Crystal Structure; Iron-Group Elements

Iron-group metal nanoclusters have captured significant attention because of their unique structures and intriguing properties.[1,2] However, few examples have been reported for nanoclusters with >10 metal atoms, so the structure library still needs to be improved. In this study, two novel Fe or Ni nanoclusters, $[Fe_{55}H_x(P^tBu_3)_{12}]$ and $[Li_8Ni_{13}(Bpin)_{12}]$ ($[Fe_{55}]$ and $[Ni_{13}]$ in short, respectively), were synthesized and characterized.

$[Fe_{55}]$ was synthesized by reacting $[Fe\{N(SiMe_3)_2\}_2]$ and pinacolborane (HBpin) in the presence of P^tBu_3. Single-crystal X-ray diffraction analysis revealed that $[Fe_{55}]$ has an icosahedral core made up of an inner Fe_{13} icosahedron covered by an outer shell of Fe_{42} (Fig. 1). The $[Fe_{55}]$ core is protected by twelve P^tBu_3, which are located on twelve vertices of the icosahedron. The $[Fe_{55}]$ crystallizes with a $[Fe_6H_8\{N(SiMe_3)_2\}_6]$ ($[Fe_6]$ for short) and forms an ion pair (i.e., $[Fe_{55}][Fe_6]$). The charge state and molecular formulae of $[Fe_{55}]$ and $[Fe_6]$ were studied by ESI mass spectrometry.

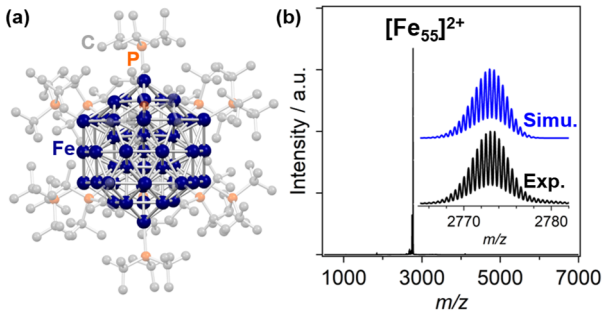

Fig. 1. (a) Crystal structure of $[Fe_{55}]$. H atoms are omitted for clarity. (b) Positive-mode ESI mass spectrum of $[Fe_{55}]$.

$[Ni_{13}]$ was synthesized by reacting $[Li(THF)_x][Ni\{N(SiMe_3)_2\}_3]$ (x = 4.5−5) and HBpin. Single-crystal X-ray diffraction analysis revealed that $[Ni_{13}]$ has an icosahedral core protected by twelve Bpin, which are located on twelve vertices of the icosahedron (Fig. 2). Eight Li atoms are placed on the Ni_{13} icosahedron through the coordination with three adjacent O atoms of neighboring Bpin ligands, making up a cubic cage. The $[Ni_{13}]$ crystallizes with a $[Ni\{N(SiMe_3)_2\}_3]$ and forms an ion pair. Detailed structural analysis was performed based on the crystal structure.

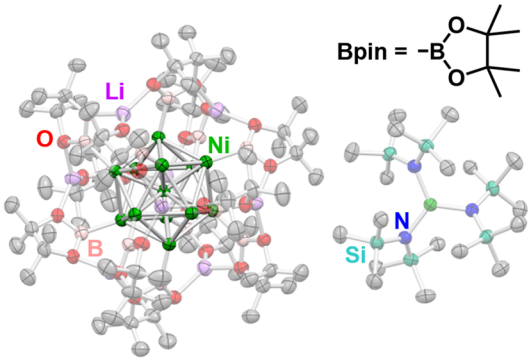

Fig. 2. Crystal structure of $[Ni_{13}]$. H atoms are omitted for clarity.

1) R. Araake, K. Sakadani, M. Tada, Y. Sakai, Y. Ohki, *J. Am. Chem. Soc*. **2017**, *139*, 5596. 2) Y. Ohki *et al*., *Angew. Chem., Int. Ed*. **2016**, *55*, 15821.

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遠心エバポレーターを用いた溶媒揮発に伴う自己組織化とメソポーラスアルミナ粉体の合成

（産総研）〇若林 隆太郎・木村辰雄

Self-assembly with the evaporation of solvents by using a centrifugal evaporator for synthesizing mesoporous alumina powders (*National Institute of Advanced Industrial Science and Technology, AIST-Chubu*) 〇Ryutaro Wakabayashi, Tatsuo Kimura

The evaporation-induced self-assembly (EISA) process is generally applied for synthesizing surfactant-assisted mesoporous materials. However, recovery of ordered mesoporous alumina is quite limited as its powder form because the formation of a mesostructure is strongly affected by the evaporation conditions of solvents. Accordingly, we have challenged to regulate the evaporation process by using a spray-dryer for the preparation of high-quality mesoporous alumina powders. In this presentation, we demonstrate uniqueness of a centrifugal evaporation process applied for preparing surfactant-assisted mesoporous alumina. Unlike a common rotary evaporation process, the centrifugal force is helpful for avoiding a vigorous boiling of solvents (e.g., ethanol and water). After removing the solvents completely under vacuum, the resultant solid was calcined at 400 °C. Although chemical composition of the precursor solution was optimized for our spray-drying process with the formation of surfactant-assisted spherical mesopores, the formation of tubular mesopores was confirmed by TEM and SEM. The difference in periodicity would be arising from the interface during the evaporation process. In the case using the centrifugal evaporator, tubular mesopores would be preferential to be formed at the flat vapor-liquid interface through the EISA process.

Keywords : Alumina; Mesoporous; Self-Assembly; Centrifugal Evaporation

溶媒揮発により誘起される自己組織化プロセスは界面活性剤を用いたメソポーラス材料の合成によく利用される。しかしながら、溶媒揮発の条件がメソ構造の生成に大きく影響するため、粉体として規則性メソポーラスアルミナを回収することは極めて限られる。そのため、我々は、高品質なメソポーラスアルミナの合成を目指し、スプレードライヤーを利用して溶媒揮発過程を規定することに取り組んできた。

本発表では、界面活性剤を用いたメソポーラスアルミナの合成に適用した遠心力をかけながら減圧乾燥する遠心エバポレーターの特徴を説明する。通常のロータリーエバポレーターとは異なり、溶媒の激しい突沸を避けるのに遠心力が役立つ。減圧下で溶媒を完全に除去して回収される固形物を 400℃で焼成した結果、前駆溶液の化学組成は界面活性剤を用いて球状メソ孔が生成するようにスプレードライ法で最適化したが、チューブ状メソ孔の生成が TEM 及び SEM により確認された。周期構造の差は溶媒揮発過程に於ける界面から生じるだろう。遠心エバポレーターを用いた場合、溶媒揮発による自己組織化プロセスを通じ、フラットな気液界面ではチューブ状メソ孔の生成が好ましいのだろう。

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大型ナノシート複合積層膜の作製と電気化学測定によるイオン拡散挙動の解析

(信州大工[1]・信州大 RISM 研[2]・岡山大 RCIS[3]) ○林 文隆[1]・小木曽 寿樹[1]・田中 厚志[2]・仁科 勇太[3]・山田 哲也[1,2]・手嶋 勝弥[1,2]

Preparation of laminar composite membranes consisting of large niobate and graphene oxide nanosheets and electrochemical analysis of ion diffusion behaviors

([1]*Faculty of Engineering,* [2]*RISM, Shinshu University,* [3]*RCIS, Okayama University*) ○Fumitaka Hayashi,[1] Hisaki Ogiso,[1] Atsushi Tanaka,[2] Yuta Nishina,[3] Tetsuya Yamada,[2] Katsuya Teshima[1,2]

Two-dimensional laminar composite membranes consisting of nanosheets have attracted great attention of chemists for application to ionic and molecular-sieving membranes owing to their robustness and unique separation properties. Herein we demonstrate preparation of two-dimensional laminar composite membranes by filtering colloidal solution containing large NbO_x and graphene oxide nanosheets onto a support membrane. The salt removal degree and permeability of the composite membranes are higher than those of the membranes consisting of NbO_x or graphene oxide nanosheets alone. The diffusion behaviors of ions in the channels of laminar composite membranes were analyzed by electrical impedance spectroscopy.

Keywords: Layered material; Ion separation; Laminar composite membrane; Nanosheet

分離膜による水溶液からのイオン分離は，資源や汚染水問題を解決する重要技術である。二次元ナノチャネルを移動するイオンは，水溶液中とは異なる挙動を示すため，ナノシートを積み重ねた二次元積層膜に注目が集まっている。酸化物ナノシートは層状結晶を剥離して得られる二次元結晶であり，フラックス法を用いると 10^4 を超える大きな異方性比と最大 100 μm に達するシートを調製できる。本研究では，高い透水性とイオン選択性を併せもつ積層膜を目指し，大型酸化物ナノシートと酸化グラフェンの比率を変化させ，吸引濾過法により 3 種の二次元積層膜（GO，NbN，GO/NbN）を作製した。断面 SEM 観察から，いずれも 3 種の積層膜の活性層厚みは~100 nm であり，湿潤状態で XRD 分析すると，GO，NbN および GO/NbN の繰り返し構造はそれぞれ 1.53，1.29 および 1.19 nm であった。複合膜の塩除去率を評価すると，異種ナノシートを組み合わせた GO/NbN は GO や NbN に比べて高い塩除去特性を示した（Fig. 1）。当日は，電気化学測定の結果と併せて，イオン伝導特性と膜性能・構造の関係について議論する。

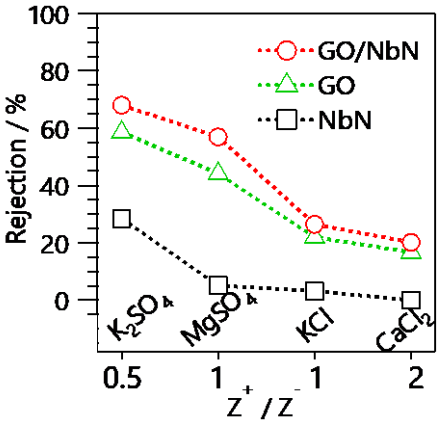

Fig. 1 Comparison of the separation performance of the GO, NbN, GO/NbN. Solute conc., 10 mM; Press., 0.5 MPa; Flow rate, 100 mL·min^{-1}; time, 24 h; temp., room temperature.

謝辞：本研究の一部は，科研費（Grant No. 22H00568，20K05074）の支援をうけた。

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

[K506-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Manabu Nakaya, Ryo Inoue

Fri. Mar 24, 2023 9:00 AM - 10:20 AM K506 (K506, Lecture Hall Bldg. [5F])

[K506-3am-01] Synthesis of two-dimensional layer-structured coordination polymer ELM-12/3 and gate-opening adsorption properties

○Hiroki Miura[1], Atsushi Kondo[2], Hirofumi Kanoh[3], Hiroshi Kajiro[1] （1. Nippon Steel Corporation, 2. Oita University, 3. Chiba University）

9:00 AM - 9:20 AM

[K506-3am-02] Helical Induction, Chiroptical Properties, and Quantitative Prediction of Dissymmetry Factor on the Circularly Polarized Phosphorescence of Iminopyrrolyl Platinum(II) Complexes

○Ryo Inoue[1], Riki Kondo[1], Yasuhiro Morisaki[1] （1. Kwansei Gakuin University）

9:20 AM - 9:40 AM

[K506-3am-03] pH effect on hydrothermal synthesis of the copper organodiphosphonate polymers: Investigation of luminescence and magnetic properties

○BURAK AY[1,2], TAKAYUKI ISHIDA[1] （1. The University of Electro-Communications, 2. Çukurova University）

9:40 AM - 10:00 AM

[K506-3am-04] External-stimuli responsiveness in luminescence properties of salophene-type platinum(II) complexes with carboxy substituents

○Shun Fujii[1], Manabu Nakaya[1] （1. Josai University）

10:00 AM - 10:20 AM

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二次元層状配位高分子 ELM-12/3 の合成とゲート型吸着特性

（日本製鉄[1]・大分大院理工[2]・千葉大院理[3]）○三浦 大樹[1]・近藤 篤[2]・加納 博文[3]・上代 洋[1]

Synthesis and gate adsorption properties of two-dimensional layer-structured coordination polymer, ELM-12/3 ([1]*Nippon Steel Corporation,* [2]*Graduate School of Science and Technology, Oita University*, [3]*Graduate School of Science, Chiba University*) ○Hiroki Miura,[1] Atsushi Kondo,[2] Hirofumi Kanoh,[3] Hiroshi Kajiro[1]

ELM-type PCP (ELM = Elastic Layer-structured Metal-organic framework, PCP = Porous Coordination Polymer) has a two-dimensional layered network structure consisting of M^{2+} ions, 4,4′-bipyridine ligands, and anions coordinating to M^{2+} at axial positions. ELM-type PCP shows crystal structural change at a certain threshold pressure in gas adsorption. The structure-change induced sudden gas adsorption behavior. The unique gas adsorption behavior is called "gate adsorption".

Gas adsorption properties can be controlled by using a solid solution technique with multiple types of metal ions and counter ions. In this study, we synthesized ELM-12/3 ([Cu-(bpy)$_2$(CF_3SO_3)(CF_3BF_3)]), and its gas adsorption properties were investigated. As a results, nitrogen adsorption isotherm at 77 K shows two-step adsorption, where the first and second step were considered to be micropore adsorption and following gate adsorption with structural changes, respectively. The N_2 adsorption isotherm on ELM-12 containing only $CF_3SO_3^-$ ions is two-step as well as that on ELM-12/3. On the other hand, in the case of ELM-13 containing only $CF_3BF_3^-$, the adsorption isotherm is one-step. Structure, adsorption properties, and other physical properties on ELM-12/3 are reported in comparison to ELM-12 and ELM-13.

Keywords: Porous Coordination Polymer; Metal-organic framework; Gate adsorption; Solid solution

ELM 型 PCP (ELM = Elastic Layer-structured Metal-organic framework, PCP = Porous Coordination Polymer)は、M^{2+}イオンと bpy 配位子からなる二次元層状のネットワーク構造を有し、M^{2+}の軸位にアニオンが配位している。また、そのガス吸着において、ある閾値圧になると結晶構造変化に伴った急激なガス吸着挙動を示す構造変化型 PCP であり、その特異なガス吸着挙動はゲート吸着と呼ばれている。

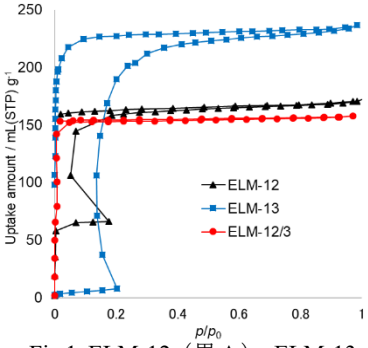

Fig 1. ELM-12（黒▲）、ELM-13（青■）および ELM-12/3（赤●）の N_2 吸着等温線(77 K)

複数種の金属イオンや複数種の対イオン等を利用し、固溶体化する手法でガス吸着特性を制御出来る事が知られており、今回我々は $CF_3SO_3^-$と $CF_3BF_3^-$を有する ELM-12/3 ([Cu(bpy)$_2$(CF_3SO_3)(CF_3BF_3)])を合成し、ガス吸着特性を調べた[1)]。77 K における N_2 吸着等温線では、1 段目がミクロ細孔への吸着、2 段目が構造変化によるゲート吸着と考えられる 2 段階吸着を示した（図 1）。$CF_3SO_3^-$イオンのみを含有し、N_2 吸着で 2 段の吸着を示す ELM-12、および $CF_3BF_3^-$のみを含有し、1 段吸着を示す ELM-13 との構造、吸着特性等の物性の違いを報告する。

1) H. Kajiro, A. Kondo, K. Kaneko, H. Kanoh, *Int. J. Mol. Sci.* **2010**, *11*, 3803.

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らせん状白金錯体の合成と円偏光リン光特性、及びリン光異方性因子の基礎理論開拓

（関西学院大院理工）○井上 僚・近藤　利樹・森崎 泰弘

Helical Induction, Chiroptical Properties, and Quantitative Prediction of Dissymmetry Factor on the Circularly Polarized Phosphorescence of Iminopyrrolyl Platinum(II) Complexes

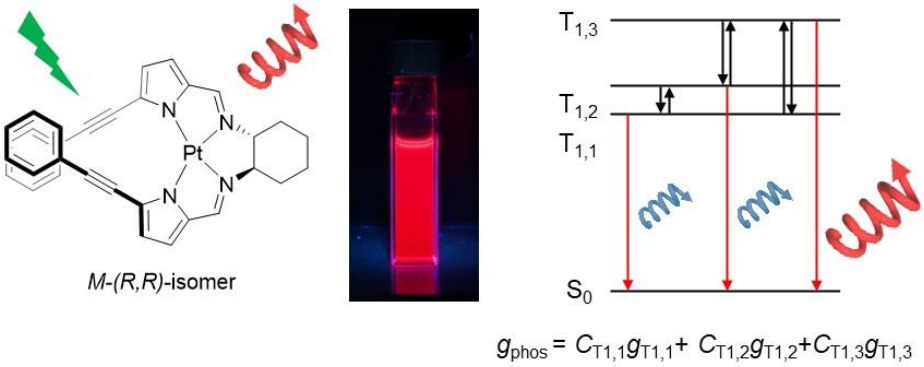
(*Graduate School of Science and Technology, Kwansei Gakuin University*)
○Ryo Inoue, Riki Kondo, Yasuhiro Morisaki

Chiral transition metal complexes have attracted significant attention for the development of optoelectrical materials, such as circularly polarized phosphorescence (CPP)-emitting devices. In this presentation, we report the helicity induction of d-π-conjugated platinum(II) complexes by the point chirality of 1,2-diaminocyclohexane and their CPP properties. The obtained *C*2-helical complexes exhibited excellent chiroptical properties with high dissymmetry factors (circular dichroism: $g_{abs} = 1.2 \times 10^{-2}$, CPP: $g_{phos} = 3.2 \times 10^{-3}$). Moreover, we conducted a theoretical investigation of the dissymmetry factor of CPP, $g_{phos,calc}$, using a kinetic model of triplet state sublevels. The *ab initio* calculations represented the experimental g_{phos} values, as well as the impact of helical chirality on the CPP.

Keywords : Platinum Complex; Circularly Polarized Phosphorescence; Helicity

円偏光リン光を示す光学活性な金属錯体は、高効率な有機 EL デバイスの開発に有用であるため、近年活発に研究されている。しかしながら、円偏光リン光は三重項状態が複雑であるため、その機構はほとんど未解明の状態であった。

本発表では、1,4-ジアミノシクロヘキサンをキラル源とした螺旋状白金錯体の合成と円偏光リン光特性について報告する。得られた錯体は優れたキロプティカル特性を示した[1)]。さらに、三重項の速度論から円偏光リン光の *g* 値の理論式を導出することに成功した。当該理論式を基にした計算により、らせん不斉が円偏光リン光に与える影響を明らかにした。



1) R. Inoue, R. Kondo, Y. Morisaki, *Chem. Mater.* **2022**, *34*, 7959-7970.

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pH effect on hydrothermal synthesis of the copper organodiphosphonate polymers: Investigation of luminescence and magnetic properties

([1]*The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan;* [2]*Çukurova University, 01330, Adana, Turkey*) ○Burak AY [1,2], Takayuki Ishida [1]

Keywords: Hydrothermal synthesis; Copper organodiphosphonate; Magnetism

The synthesis of metal organic frameworks (MOFs) under hydrothermal condition is of great interest. This synthetic method not only affords the opportunity to prepare coordination compounds with novel structures and properties but also provides an environmentally friendly approach for the construction of MOFs through crystal engineering. Synthesis of MOFs depends on different parameters such as the metal or ligand type, pH value, stoichiometric ratio, mineralizing agent, reaction temperature and time.[1] In this study, pH effect of the solution on polymer formation under subcritical conditions was investigated. Multifunctional 1,2-phenylenebis(methylene))bis(phosphonic acid (HL_4) and 4,4'-bipyridine (bpy) were selected as ligands due to the potential coordination sites. Three MOFs, $[Cu^{2+}_3(HL^{3-})_2]_n$ (**1**),[2] $[Cu^{2+}_4(L^{4-})_2(OH_2)_4]_n{\cdot}H_2O$ (**2**) and $[Cu^{2+}_4(bpy)(HL^{3-})_2(OH^-)_2]_n{\cdot}2H_2O$ (**3**) were synthesized as a result of changing the pH values (Initial pH: 2.20, 3.50 and 6.00 to 3.50, respectively). Single crystal X-ray analysis (Fig. 1, top) showed that while the copper atoms in **1** have four and six coordination numbers (CNs), **2** and **3** showed five CNs. From the analysis of magnetic susceptibility measurements (Fig. 1, bottom), all the Cu valences were confirmed to be +2, and antiferromagnetic interactions were characterized.

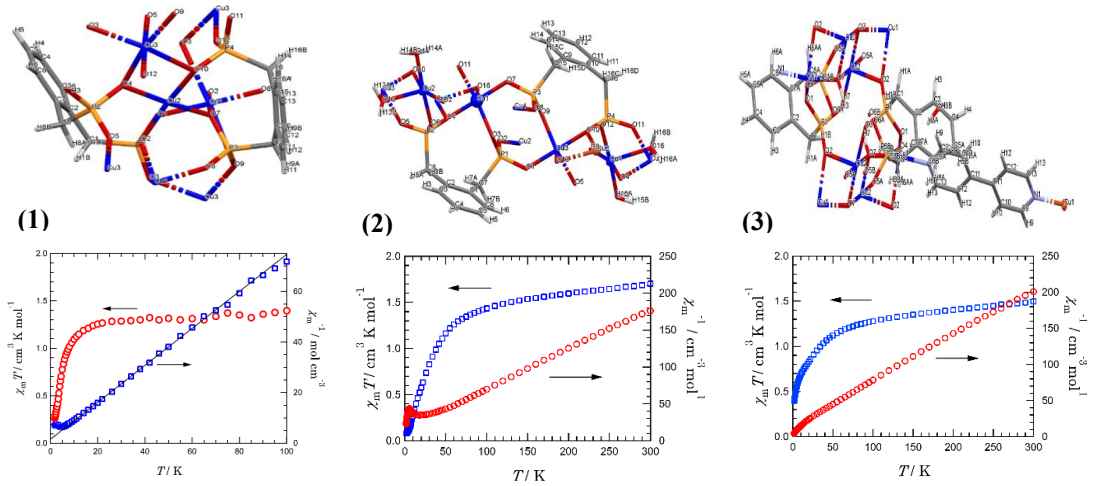

Figure 1. Crystal structures (Colour codes: Cu, blue; P, orange; O, red; N, light blue; C, gray; H, white) and temperature dependence of $\chi_m T$ and χ_m^{-1} for **1** - **3** on the formula basis.

1) P.J. Ollivier, J.R.D. DeBoard, P.J. Zapf, J. Zubieta, J. Mol. Struct. 470 (1998) 49-60.
2) B. Ay, R. Takano, T. Ishida, E. Yildiz, Polyhedron 225 (2022) 116038.

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カルボン酸置換基を有するサロフェン型白金(II)錯体の外部刺激に応答した発光特性

（城西大院理）〇藤井 駿・仲谷 学

External-stimuli responsiveness in luminescence properties of salophen-type platinum(II) complexes with carboxy substituents (*Graduate School of Science, josai University*) 〇Shun Fujii , Manabu Nakaya

Salophen-type complexes have been widely studied because of various functions based on the coordinating metal ions and their easy modification. In deed, their platinum(II) complexes have attracted much attention due to the variety of the luminescence properties. In this work, platinum(II) complexes with regioselectivity introduced carboxylic acid substituents were synthesized (Fig. 1), and their optical properties were investigated under various condition. At first, X-ray structure analysis revealed that complex **1** assembled by the intermolecular interaction through the carboxylic acid substituents. On the other hand, complex 3 accumulated by π-π interactions with formation of hexagonal pore. In DMSO solution, each complex exhibited systematic UV- and luminescence properties depending on the number of carboxylic group (Fig. 2). As further experiments, pH dependency and the effect of addition of small organic molecules on the luminescence property were discussed. The detailed discussion will be conducted in the presentation.

Keywords : Platinum(II) complex ; Salophen type complex ; Luminescence

サロフェン型錯体は、置換基の導入が容易であり、金属種に応じた多彩な機能性を持つことから、これまでに多くの研究が行われている。[1] 本研究では、カルボン酸置換基を位置選択的に導入したサロフェン型白金(II)錯体１－３を合成した（図１）。X 線構造解析結果より、錯体１はカルボン酸相互作用によって集積し白金間相互作用を形成し集積していた。錯体３は π–π 相互作用によってカルボン酸を中心にヘキサゴナルに集積し細孔を形成していた。細孔内部には一次元に水分子を包摂していた。各錯体の DMSO 溶液は、置換基の数に応じた系統的なスペクトル変化を示した（図２）。また、pH 変調によるプロトン化・脱プロトン化や、有機小分子の添加など、様々な条件において分光学的性質を評価した。溶液中において、DMSO/水混合溶媒の水の割合、pH 変調を行うと塩基性の時に各錯体は凝集誘起発光（AIE）を示した。また有機小分子を添加した際もカルボン酸の位置や数に応じて発光特性を変化させることが明らかとなった。詳細は当日述べる予定である。

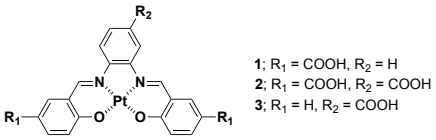

図１　錯体１－３の分子構造

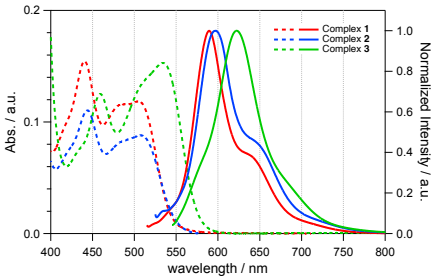

図２　錯体１－３の DMSO 溶液での吸収および発光スペクトル

1) J. Cheng, X. Ma, Y. Zhang, J. Liu, X. Zhou, H. Xiang, *Inorg. Chem.* **2014**, *53*, 3210-3219.

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

[K504-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kentaro Kadota, Shinya Takaishi

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K504 (K504, Lecture Hall Bldg. [5F])

[K504-3pm-01] Investigation of thermodynamics in melting Cu^{2+}-based 1D coordination polymers

○Yuki Ohara[1], Taichi Nishiguchi[1], Shin-ichiro Noro[3], Daniel Packwood[2], Satoshi Horike[1,2]
（1. Graduate School of Engineering, Kyoto University, 2. Institute for Advanced Study, Kyoto University, 3. Faculty of Environmental Earth Science, Hokkaido University）

1:10 PM - 1:30 PM

[K504-3pm-02] Spatially Controlled Hybridization of Porous Metal-Organic Crystals

○Kunyi Leng[1,2], Takuzo Aida[1,2], Hiroshi Sato[2,3] （1. The University of Tokyo, 2. RIKEN Center for Emergent Matter Science, 3. JST-PRESTO）

1:30 PM - 1:50 PM

[K504-3pm-03] Three-dimensional van der Waals frameworks assembled from octahedral metal-organic polyhedra

○Shun Tokuda[1], Shuhei Furukawa[1] （1. iCeMS, Kyoto University）

1:50 PM - 2:10 PM

[K504-3pm-04] Recognition of Copolymer Sequence via Gated Inclusion in Flexible Metal-Organic Frameworks

○Nobuhiko Hosono[1], Biplab Manna[2], Mizuki Asami[2], Takashi Uemura[1] （1. Grad. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Frontier Sci., The Univ. of Tokyo）

2:10 PM - 2:30 PM

[K504-3pm-05] Structural and property evaluation of cyano-bridged coordination polymers exhibiting anisotropic thermal expansion

○Ryota Kosuge[1], Takashi KOSONE[1,2], Naoya ADACHI[1,2] （1. Graduate School of Tokyo Denki University, 2. Tokyo Denki University）

2:40 PM - 3:00 PM

[K504-3pm-06] Consideration on Gated CO_2 Adsorption Behavior in One-Dimensional Porous Coordination Polymers of Phenazine-Linked Paddlewheel diruthenium complex

○Wataru Kosaka[1], Jun Zhang[2], Hitoshi Miyasaka[1] （1. IMR, Tohoku Univ., 2. FRIS, Tohoku Univ.）

3:00 PM - 3:20 PM

[K504-3pm-07] Quinoid-Based Three-Dimensional Metal-Organic Framework, $Fe_2(dhbq)_3$: Porosity, Electrical Conductivity and Solid-State Redox Properties

○Shraddha Gupta[1], Haruki Tanaka[1], Shinya Takaishi[1] （1. Tohoku University）

3:20 PM - 3:40 PM

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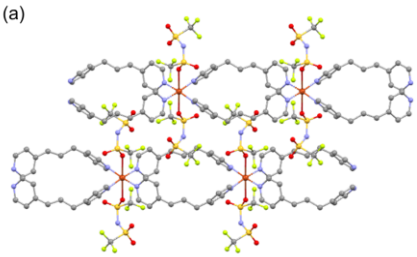
Investigation of thermodynamics in melting Cu^{2+}-based 1D coordination polymers

([1]*Graduate School of Engineering, Kyoto University*, [2]*Institute for Advanced Study, Kyoto University*, [3]*Faculty of Environmental Earth Science, Hokkaido University*,)
○Yuki Ohara,[1] Taichi Nishiguchi,[1] Shin-ichiro Noro,[3] Daniel Packwood,[2] Satoshi Horike[1,2]
Keywords: Coordination polymer; Melting; Crystal structures; Thermodynamics; Entropy

Liquid and glassy states of coordination polymers (CPs) or metal-organic frameworks (MOFs) have gained attention as a new class of amorphous materials.[1] To expand the structural libraries and functions, design principles for crystal structures with low melting points (T_m) before reaching decomposition is desired. T_m can be predicted by analyzing thermodynamic parameters described by enthalpy of fusion (ΔH) and entropy of fusion (ΔS) according to the equation $T_m = \Delta H/\Delta S$. Recent studies in ionic liquids have revealed that a large ΔS deriving from conformational and configurational entropy is critical for decreasing T_m.[2] However, for CPs it has been challenging to estimate T_m from thermodynamic parameters, especially for ΔS because of their complex, extended natures and the uncertainty of the liquid structures.

We observed molecular structure-dependent differences in melting behaviors of 1D ribbon-chain CPs, which consist of Cu^{2+}, bipyridine derivative linkers and monovalent anions (Fig).[3] The observed tendency of melting and non-melting structures indicates that the melting behaviors are governed by increasing ΔS deriving from conformational entropy, which is expected from the molecular structures of the linkers and anions. A further decrease in T_m was observed when the $-CF_3$ groups in bis(trifluoromethylsulfonyl)imide anion ($TFSI^-$) was changed to $-CH_3$ groups (Ms_2N^-). DFT calculations indicate that the latter compound has stronger interaction between 1D chains, which enlarges ΔS by suppressing the kinetic entropy in crystalline state. These studies suggest that ΔS in terms not only of multiple conformation of molecules but also of dynamics of crystals is important for understanding the melting of CPs.

(a)



(b)

Compounds	$Cu(TFSI)_2(bpp)_2$	$Cu(Ms_2N)_2(bpp)_2$	$Cu(BF_4)_2(bpp)_2$	$Cu(TFSI)_2(bpe)_2$
Linker (L)	bpp	bpp	bpp	bpe
Anion (A)	$TFSI^-$	Ms_2N^-	BF_4^-	$TFSI^-$
T_m / °C	196	171	No melting	No melting
ΔH / kJ mol^{-1}	44.6	44.0	--	--
ΔS/ J mol^{-1} K^{-1}	95.1	99.2	--	--

Fig. (a) The crystal structure of the representative 1D ribbon-chain CP $Cu(TFSI)_2(bpp)_2$ (b) T_m, ΔH, and ΔS of four isostructures measured in differential scanning calorimetry (DSC).

1) S. Horike *et al.*, *Chem. Rev.* **2022**, *122*, 4163.
2) T. Endo *et al.*, *Chem. Sci.* **2022**, *13*, 7560.
3) a) S. Noro *et al.*, *Commun. Chem.* **2020**, *3*, 143. b) K. Maeda *et al.*, *J. Phys. Chem. C.* **2013**, *78*, 12090.

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Spatially Controlled Hybridization of Porous Metal–Organic Crystals

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

Keywords: Metal–Organic Framework; Crystal Engineering; Hybrid Materials; Photochemistry; Porous Materials

Hybrid materials with two or more distinct chemical components integrated into a single platform hold enriched diversity, versatility, and functionality, in comparison with conventional unitary materials.[1] Metal-organic frameworks (MOFs), as crystalline porous materials, have attracted extensive attention. Their physicochemical properties are highly dependent on the composition and architectures. Although the hybridization of multiple MOF crystals has emerged as a powerful tool for modifying porous properties,[2] it remains challenging but very attractive to develop a strategy for spatially controlled arrangement and hybridization of different types of MOF crystals.

Recently, we reported a photochemically crushable and regenerative MOF (**MOF$_1$**) using a dithienylethene-based ligand (L_1, Fig. 1a).[3] **MOF$_1$** crystals can be dissolved in a solvent by UV light and subsequently regenerated by visible light. This unique property inspired us to come up with a photochemical surgery approach to realize hybrid MOF crystals by the destruction of a targeted portion of MOF crystals by UV light and then selectively crystallizing new MOF crystals at the destructed location (Fig. 1b). **MOF$_2$** crystal composed of another photoreactive ligand (L_2, Fig. 1a) was successfully hybridized with the **MOF$_1$** crystal. We also report on the hybridization of MOF crystals with different types of ligands as well as with MOF crystals composed of different metal ions.

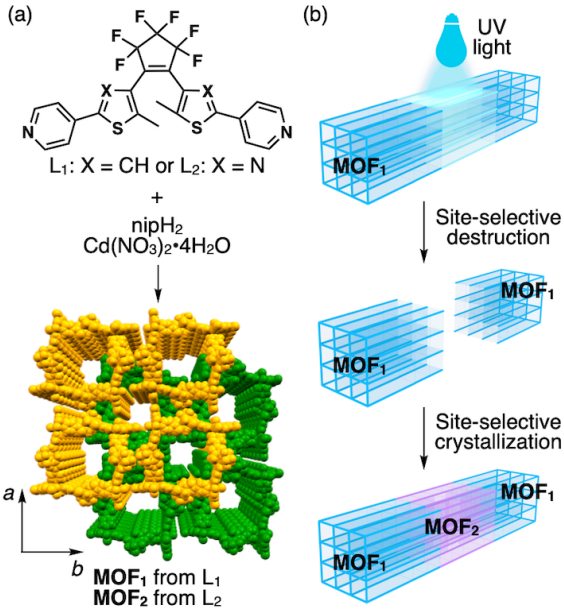

Fig. 1 (a) Structures of photoreactive ligands (L_1 and L_2), **MOF$_1$**, and **MOF$_2$**. nipH$_2$: 5-nitroisophthalic acid. (b) Photochemical surgery for hybridization of multiple MOF crystals.

1) E. Katz, I. Willner, *Angew. Chem. Int. Ed.* **2004**, *43*, 6042. 2) L. Feng, K.Y. Liang, J. Powell, H.C. Zhou, *Matter* **2019**, *1*, 801. 3) H. Sato, T. Matsui, Z.Y. Chen, J. Pirillo, Y. Hijikata, T. Aida, *J. Am. Chem. Soc.* **2020**, *142*, 14069.

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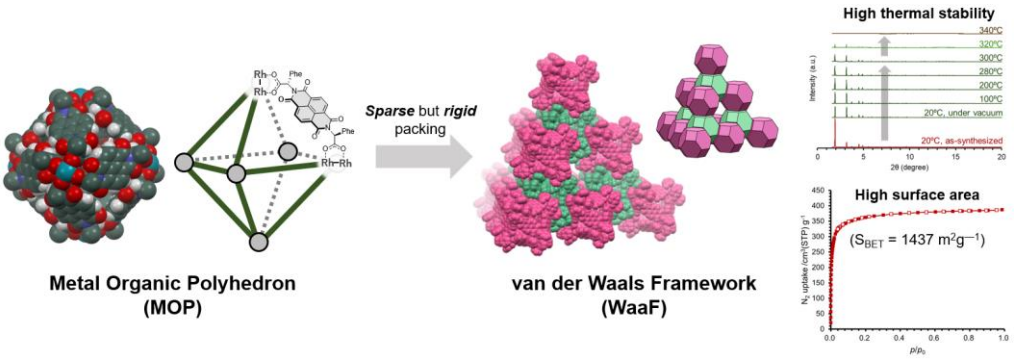
Three-Dimensional van der Waals Frameworks Assembled from Octahedral Metal-Organic Polyhedra

([1]*Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*,)
○Shun Tokuda,[1,2] Shuhei Furukawa[1,2]

Keywords: Metal-Organic Polyhedra; Self-Assembly; Porous Framework Materials; van der Waals Interaction; Naphthalenediimide

Highly directional, strong intermolecular interactions are believed to be essential to synthesize porous framework materials. For instance, coordination, covalent, and hydrogen bonds are used to assemble molecular components to form MOFs, COFs, and HOFs, respectively. On the contrary, van der Waals (vdW) interaction, one of the most ubiquitous intermolecular interactions, is known as a non-directional, weak interaction. Due to the less controllable nature, vdW interaction has been barely used to construct porous frameworks.

In this study, we demonstrate that vdW interaction drives the assembly of a porous framework from supramolecular building blocks, so-called metal-organic polyhedra (MOPs), a group of cage-shaped metal complexes with high structural modularity.[1] We synthesized a novel octahedral MOP from Rh(II) ions and naphthelenediimide (NDI) derivatives. X-ray diffraction experiments revealed that twelve NDI moieties as edges are connected by six Rh_2 paddlewheel vertices, leading to the formation of triangle faces with large NDI moieties. The face-to-face vdW interactions between MOPs generate diamond-like packing structure of MOPs in a crystalline phase, with a huge void space in the network (~36%, calculated from the X-ray structure). This porous framework built with vdW interactions, named as van der Waals framework (WaaF), showed outstanding porosity (BET surface area: 1437 m^2g^{-1}) and high thermal stability (crystallinity retained up to 320 ºC) even after the removal of guest molecules. This work highlights an overlooked potential of less directional/weak vdW interactions toward the design of porous framework materials.



1) T. Tateishi, M. Yoshimura, S. Tokuda, F. Matsuda, D. Fujita, S. Furukawa, *Coord. Chem. Rev.* **2022**, *467*, 214612.

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柔軟性 MOF による共重合体のモノマー配列認識

（東大院工 [1]・東大院新領域 [2]）○細野暢彦 [1]・Biplab Manna[2]・浅見美月 [2]・植村卓史 [1]
Recognition of Copolymer Sequence via Gated Inclusion in Flexible Metal-Organic Frameworks ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Frontier Sciences, The University of Tokyo*) ○Nobuhiko Hosono,[1] Biplab Manna,[2] Mizuki Asami,[2] Takashi Uemura[1]

The monomer sequence is very important parameter of polymers because it not only affects the material properties but also can be considered as molecular information (i.e. data).[1)] However, decoding the monomer sequence of synthetic polymers remains a formidable challenge because no rational and universal method to access the sequential information has been discovered. In this study, we developed a new approach to directly recognize monomer structure, composition, and sequence of synthetic copolymers by using a flexible nanoporous crystals of metal-organic frameworks (MOFs).[1)] We found that the flexible MOF can decode the monomer composition and local monomer sequence of random copolymers, and selectively incorporate the copolymers with specific monomer sequences into the nanopores. This enables to sort and separate polymer chains with monomer sequence information from a chaotic mixture of many possible structures.
Keywords : Molecular Recognition; Monomer Sequence; Porous Crystals; Metal-Organic Framework; Separation

共重合体中のモノマー配列は、高分子の物性や機能に影響するだけでなく、配列自体が分子情報として捉えることのできる非常に重要なパラメーターである [1)]。しかし、高分子鎖上のモノマー配列情報を認識する分子システムの設計は困難を極め、これまで合理的な手法が見いだされてこなかった。本研究で我々は、ある柔軟な骨格を有する多孔性金属錯体（Metal-Organic Framework: MOF）のナノ細孔に高分子鎖が浸入する現象に着目し、結晶性細孔構造をテンプレートとしたモノマー配列認識を検討した。結果、MOF 細孔内に規則的に配列した金属配位不飽和サイトと、共重合体中のモノマーとの相互作用により、ある特定のモノマー組成および局所モノマー配列を有する高分子鎖が認識され、MOF のナノ細孔へ選択的に取り込まれることを見出した（Figure 1）[2)]。本原理により、混合物から特定のモノマー配列を有する高分子鎖を選別し分離することに成功した。

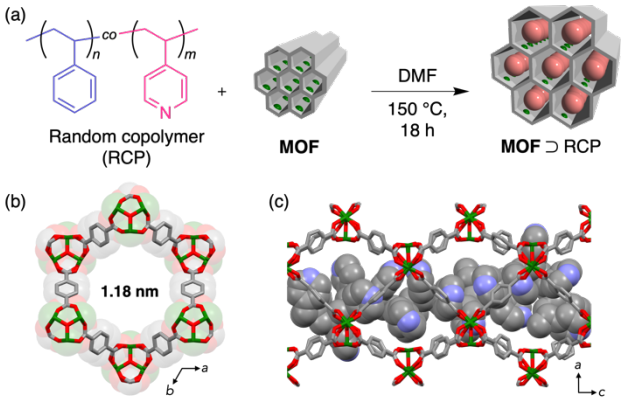

Figure 1: (a) Schematic diagram of copolymer insertion into the MOF pores. (b) Crystal structure of the MOF. (c) Modeled structure of the MOF including the polymer chain in the pore.

1) J. F. Lutz, *et. al.*, *Nat. Rev. Mater.* **2016**, *1*, 16024.
2) B. Manna, M. Asami, N. Hosono, T. Uemura, *submitted*.

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異方的な熱膨張を示す新規シアノ架橋配位高分子の構造及び物性評価

（電機大院理工 [1]・電機大理工 [2]）○小管 亮太 [1]・小曽根 崇 [1,2]・足立 直也 [1,2]

Structural and property evaluation of cyano-bridged coordination polymers exhibiting anisotropic thermal expansion

([1]*Graduate school of Tokyo Denki University,* [2]*Tokyo Denki University*) ○Ryota Kosuge,[1] Takashi Kosone,[1,2] Naoya Adachi,[1,2]

Negative thermal expansion (NTE), in which lattice parameter increases with decreasing temperature for cyano-bridged coordination polymers was studied. We investigated the temperature dependence of lattice constants for one-dimensional structures $Fe(XIm)_4[Ni(CN)_4]$ (X = 1-Isopropyl, 1-Allyl, 1-Benzyl) and two dimensional structures $Fe(YIm)_2[Ni(CN)_4]$ (Y = 1-H, 1-Methyl, 1-Vinyl, 1-Propyl) by using single X-ray and powder X-ray diffraction analysis at various temperature. In this study, we discussed the correlation between the crystal structure and NTE.

Keywords : Hofmann-like coordination polymer; Negative thermal expansion

シアノ架橋配位高分子では，温度減少とともに格子定数の増大する負の熱膨張現象 (Negative Thermal Expansion : NTE) が観測される。 NTE が観測されるシアノ架橋配位高分子の代表的な例としてプルシアンブルー類縁体があげられ [1)]，その原因は温度の上昇によりシアノ基の振動が大きくなることが原因とされている [2)]。一方，シアノ架橋による二次元層状構造を有した Hofmann 型配位高分子においても NTE が確認されている。二次元層状構造における層間の分子間相互作用や二次元シートの歪みなどの観点から NTE と構造の相関関係の検討がなされている [3)]。本研究では，一次元構造を有する新規シアノ架橋配位高分子 $Fe(XIm)_4[Ni(CN)_4]$ (X = 1-Isopropyl, 1-Allyl, 1-Benzyl) および二次元構造を有する $Fe(YIm)_2[Ni(CN)_4]$ (Y = 1-H, 1-Methyl, 1-Ethyl, 1-Vinyl, 1-Propyl) における格子定数変化の温度依存性について単結晶 X 線構造解析および粉末 X 線構造解析によって調べた。発表では，結晶構造と NTE の相関関係についての検討を報告する。

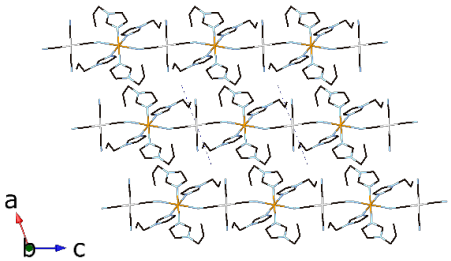

Fig.1 $Fe(1\text{-}AllylIm)_4[Ni(CN)_4]$の結晶構造

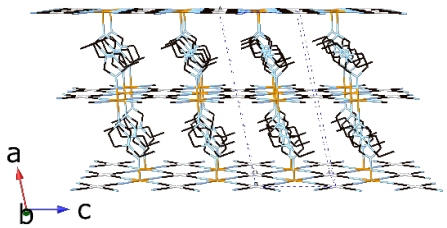

Fig.2 $Fe(1\text{-}EthylIm)_2[Ni(CN)_4]$の結晶構造

1) Qilong Gao *et al Angew. Chem. Int. Ed.* **2017,** *56, 9023-9028*
2) Andrew L. Goodwin *et al Phys. Rev. B Condens. Matter Mater. Phys.* **2005,** *71,* 140301
3) Ryo Ohtani *et al* Inorg. Chem. **2022,** 61, 21123-21130

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Consideration on Gated CO_2 Adsorption Behavior in One-Dimensional Porous Coordination Polymers of Phenazine-Linked Paddlewheel Diruthenium Complex

([1]*Institute for Materials Research, Tohoku University*, [2]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University*) ○Wataru Kosaka,[1] Jun Zhang,[2] Hitoshi Miyasaka[1]

Keywords: Gated adsorption; Paddlewheel-type diruthenium complexes; Metal−organic Framework

Low-dimensional coordination polymers such as one-dimensional (1-D) chains often exhibit gated guest sorption accompanying structural transition at a temperature (T_G),[1,2] which is associated with an external pressure of the guest (P_G) characteristic to the material and guest used. This phenomenon can be evaluated in the Clausius–Clapeyron (CC) equation of $d(\ln P_G)/d(1/T_G) = \Delta H_G/R$, where ΔH_G and R are the transition enthalpy and gas constant, respectively. In this study, gated CO_2 adsorption was investigated in a 1-D chain based on a benzoate-bridged paddlewheel diruthenium(II,II) complex with a phenazine (phz) linker, $[Ru_2(p\text{-MeOPhCO}_2)_4(phz)]$ (**1**; p-$MeOPhCO_2^-$ = p-anisate).[3]

Surprisingly, **1** underwent gate-opening (GO)/-closing (GC) at a much higher T_{GC} = 385 K under P_{CO2} = 100 kPa (Fig. 1a) than those previously reported for such chain compounds, which usually appeared in the temperature range of 200–270 K.[1,2] CC analyses gave a similar ΔH_G value for these compounds (inset of Fig. 1a), indicating that the transition entropy ΔS_G in each system plays a key role in shifting T_G; **1** results in a much smaller $|\Delta S_G|$ in the series. The crystal structure of the CO_2-accommodated phase (**1⊃CO₂**, Fig. 1b) revealed that Only **1** produced a CO_2-accessible 2-D topological pore in its CO_2-adsorbed phase **1⊃CO₂** (Fig. 1c). whereas the others reported previously produced 1-D or discrete (0-D) topological pores for CO_2 accommodation. These findings strongly reflect the degree of freedom of CO_2 molecules in pores, which is related to ΔS_G.

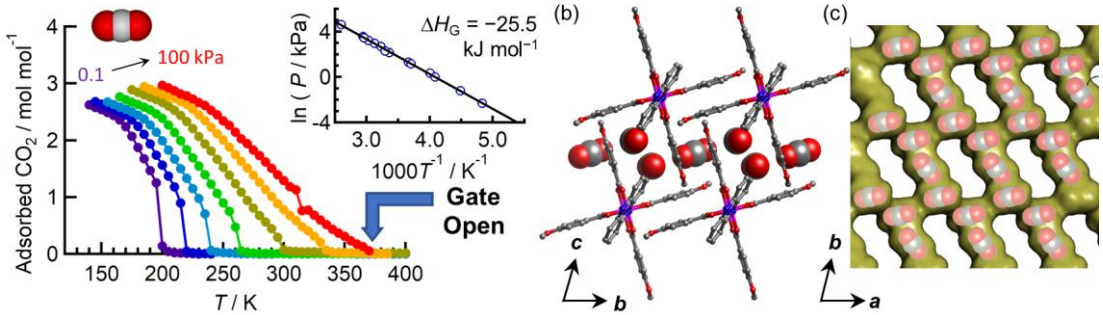

Fig. 1 (a) CO_2 adsorption isobar. (b) Structure of **1⊃CO₂**. (c) Connolly surface of micropore for **1⊃CO₂**.

1) W. Kosaka et al., *J. Am. Chem. Soc.* **2014**, *136*, 12304. 2) C. Dou et al., *Chem. Lett.* **2017**, *46*, 1288. 3) W. Kosaka et al., *Inorg. Chem.* **2022**, *61*, 12698.

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Quinoid-Based Three-Dimensional Metal-Organic Framework, $Fe_2(dhbq)_3$: Porosity, Electrical Conductivity and Solid-State Redox Property

([1]*Graduate School of Science, Tohoku University*, [2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○ Shraddha Gupta,[a]* Haruki Tanaka,[a] Kentaro Fuku,[a] Hiroaki Iguchi,[a] Ryota Sakamoto,[a] Hiroaki Kobayashi,[b] Yoshiyuki Gambe,[b] Itaru Honma,[b] Shinya Takaishi [a]*

Keywords: Metal-Organic Framework; 2,5-dihydroxy-1,4- benzoquinone; Redox-Active; Lithium-ion Battery

Coordination polymers of iron and 2,5-dihydroxy-1,4- benzoquinone based ligands have been emerging out as a new exciting material because of its appealing features of exhibiting redox activity and possessing high electrical conductivity which also make them potent candidate to be incorporated as a cathode in LIB. The specific capacity of the material is further limited by redox inactivity of iron in case of Fe^{2+}containing MOF ($Fe^{2+} \rightarrow Fe^0$ does not proceed in the cathode reaction).[1] Although Fe redox can be used with Fe^{3+} containing MOFs, it is generally difficult to proceed with the cation insertion reaction in Fe^{3+} MOFs because the pore is occupied by a bulky cation that is difficult to desorb.[2]

In this study, we synthesized a microporous [$Fe_2(dhbq)_3$] MOF containing Fe^{3+} without incorporating extra cations. The MOF is buildup of Fe(III) and $dhbq^{2-}$ ligand which exhibits redox activity based on metal and ligand with a theoretical capacity of 408 mAh /g. Upon incorporating as a cathode, it exhibited a first discharge capacity of 322 mAh /g stem from metal and ligand-based redox activity. As a result of strong d-π conjugation in a three-dimensional network., it showed relatively high electrical conductivity of 1.2×10^{-2} S cm^{-1}.

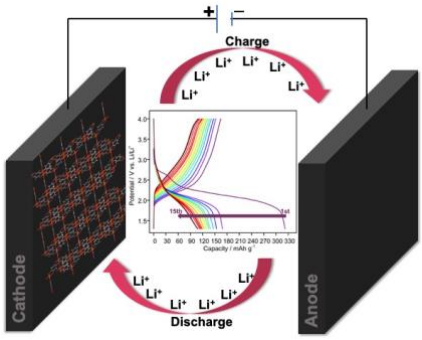

Figure 1. Schematical representation of lithium insertion and desertion.

1) Kon, K., *ACS Appl. Mater. Interfaces* **2021**, *13* (32), 38188–38193. 2) Ziebel, M. E., *J. Am. Chem. Soc.* **2020**, *142* (5), 2653–2664. 3) Murase, R., *Inorg. Chem.* **2017**, *56* (15), 9025–9035. 4) Darago, L. E., *J. Am. Chem. Soc.* **2015**, *137* (50), 15703–15711.

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

[K505-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kazuhiro Uemura, Masaki Yoshida

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-3pm-01] Synthesis and Properties of Mixed-Valence Mn-oxo Clusters Ligated with Rigid Triptycene-Based Ligands

○Mikiya Kato[1,2], Tomoya Fukui[1,2], Ryosuke Takehara[1,2], Yoshiaki Shoji[1,2], Fukushima Takanori[1,2] （1. CLS, Tokyo Tech., 2. Sch. Mater. Chem. Tech., Tokyo Tech.）

1:10 PM - 1:30 PM

[K505-3pm-02] Near-infrared emission in Ag_{29} nanoclusters induced by the modification with metal complexes

○Wataru Ishii[1], Yoshinori Okayasu[2], Yoichi Kobayashi[2], Kawai Tsuyoshi[3], Takuya Nakashima[1] （1. Osaka Metropolitan University, 2. Ritsumeikan University, 3. Nara Institute of Science and Technology）

1:30 PM - 1:50 PM

[K505-3pm-03] Magnetic properties of paramagnetic one-dimensional chains where first transition metals are infinitely aligned with metal– metal bonds

○Atsushi Takamori[1], Kazuhiro Uemura[2] （1. Graduate School of Engineering, Gifu University, 2. Faculty of Engineering, Gifu University）

1:50 PM - 2:10 PM

[K505-3pm-04] Vapor, mechanical, and piezochromic multicolor switching of a carbon-centered hexagold(I) cluster with flexible N-heterocyclic carbene ligands

○Leonardo Hayato Takeshige[1], Xiao-Li Pei[1], Hitoshi Ube[1], Zhen Lei[1], Hiroki Kobayashi[2], Kazuki Komatsu[2], Hiroyuki Kagi[2], Mitsuhiko Shionoya[1] （1. Department of Chemistry, Grad. Sch. Sci, The Univ. of Tokyo, 2. Geochemical Research Center, Grad. Sch. Sci, The Univ. of Tokyo）

2:10 PM - 2:30 PM

[K505-3pm-05] Regioselective deprotonation of twisted trinuclear macrocycles to control the rate of helicity inversion

○Tomoki NAKAJIMA[1], Shohei TASHIRO[1], Masahiro EHARA[2], Mitsuhiko SHIONOYA[1] （1. Grad. Sch. of Sci.; The Univ. of Tokyo, 2. IMS）

2:40 PM - 3:00 PM

[K505-3pm-06] Stability Control and Luminescence of Porous Crystals of Self-assembled Platinum(II) Complexes Based on the Electronic Tuning of Ligands

○Masaki Yoshida[1], Takanari Mochizuki[2], Atsushi Kobayashi[2], Masako Kato[1] （1. Kwansei Gakuin Univ., 2. Hokkaido Univ.）

3:00 PM - 3:20 PM

[K505-3pm-07] Multi-step conversion of protonation state based on the coupling of proton, spin and molecular orientation

○Takumi Nakanishi[1], Osamu Sato[1] （1. Kyushu University）

3:20 PM - 3:40 PM

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剛直なトリプチセン多座配位子を用いた混合原子価マンガン酸化物クラスターの合成と機能

（東工大化生研 [1]・東工大物質理工 [2]）○嘉藤 幹也 [1,2]・福井 智也 [1,2]・竹原 陵介 [1,2]・庄子 良晃 [1,2]・福島 孝典 [1,2]

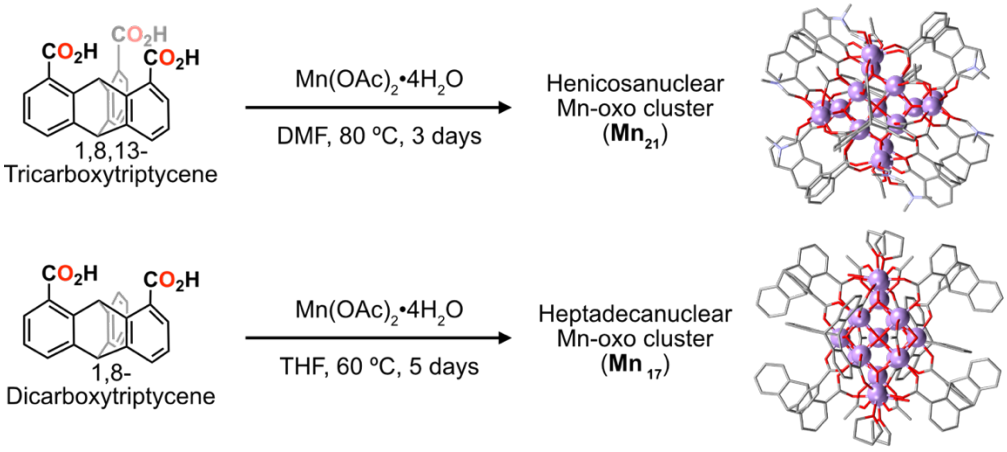
Synthesis and Properties of Mixed-Valence Mn-oxo Clusters Ligated with Rigid Triptycene-Based Ligands

([1]*Lab. Chem. Life Sci., Tokyo Tech.*, [2]*Sch. Mater. and Chem. Tech., Tokyo Tech.*)
○ Mikiya Kato,[1,2] Tomoya Fukui,[1,2] Ryosuke Takehara,[1,2] Yoshiaki Shoji,[1,2] Takanori Fukushima[1,2]

We have reported the selective construction of a decanuclear zinc-oxo cluster upon complexation of 1,8,13-tricarboxytriptycene with zinc acetate dihydrate[1)]. In this work, we investigated the complexation of 1,8,13-tricarboxytriptycene or 1,8-dicarboxytriptycene with manganese acetate tetrahydrate, and obtained two types of mixed-valence manganese oxo clusters (**Mn_{21}** and **Mn_{17}**). Here we will report the synthesis, characterization, and properties of the manganese oxo clusters.

Keywords : Polynuclear complex; Multidentate ligand; Triptycene; Manganese oxide; Mixed-valence complex

金属酸化物クラスターは、光電子、磁性、酸化還元特性といった多彩な機能を発現する。最近我々は、剛直な多座配位子である 1,8,13-トリカルボキシトリプチセンと酢酸亜鉛の錯形成により、四面体状 10 核亜鉛酸化物クラスターが選択的に形成されることを報告している [1)]。本研究では、1,8,13-トリカルボキシトリプチセンおよび 1,8-ジカルボキシトリプチセンの 2 種類の配位子と、酢酸マンガン四水和物の錯形成を検討した。その結果、核数の異なる 2 種類の巨大な混合原子価マンガン酸化物クラスターが形成されることを見いだした。本発表では、新規マンガン酸化物クラスターの合成、構造、およびその物性について報告する。



1) M. Kato, T. Fukui, H. Sato, Y. Shoji, T. Fukushima, *Inorg. Chem.* **2022**, *61*, 3649.

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Near-infrared emission in Ag_{29} nanoclusters induced by the modification with metal complexes

([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*College of Life Sciences, Ritsumeikan University,* [3]*Nara Institute of Science and Technology*) ○Wataru Ishii,[1] Yoshinori Okayasu,[2] Yoichi Kobayashi,[2] Tsuyoshi Kawai,[3] Takuya Nakashima[1]

Keywords: Silver nanocluster; Near infrared emission; Excited state relaxation

Metal nanoclusters (NCs) composed of defined numbers of metal atom and ligand show structure-dependent optical properties. The property of NCs can be modulated by metal atom doping and ligand engineering. The ionic nature of NCs also affects their optical properties especially in photoluminescence (PL) property through controlling the ionic interaction with counter ions. We previously reported the accumulation of Na^+ counter ions in a local surface site of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ NC (BDT: 1,3-benzenedithiol; TPP: triphenylphosphine) resulted in the induction of intense NIR PL at 770 nm.[1] Although the use of Au-doped Au_xAg_{29-x} NCs further increased the PLQY over 45% at 800 nm in the solution state, the conjugation of NCs with Na^+ counter ions required the condition of photoirradiation which could lead to a simultaneous degradation of chemically less stable silver-based NCs.

In the present study, we found that transition metal complexes such as silver(I) complex could bound to the peripheral region of Ag_{29} NCs, leading to the strong NIR PL without light irradiation. The binding of silver(I) complexes to Ag_{29} NCs is confirmed by the single-crystal X-ray diffraction measurement, which is further supported by the ESI-MS and NMR measurements. The change of excited-state dynamics triggered by the binding of silver(I) complexes is discussed based on the results of transient absorption study as well as temperature-dependent PL study. The modification of Ag_{29} NCs with silver(I) complexes is considered to give rise to a triplet excited-state responsible for the intense NIR PL (Fig. 1).

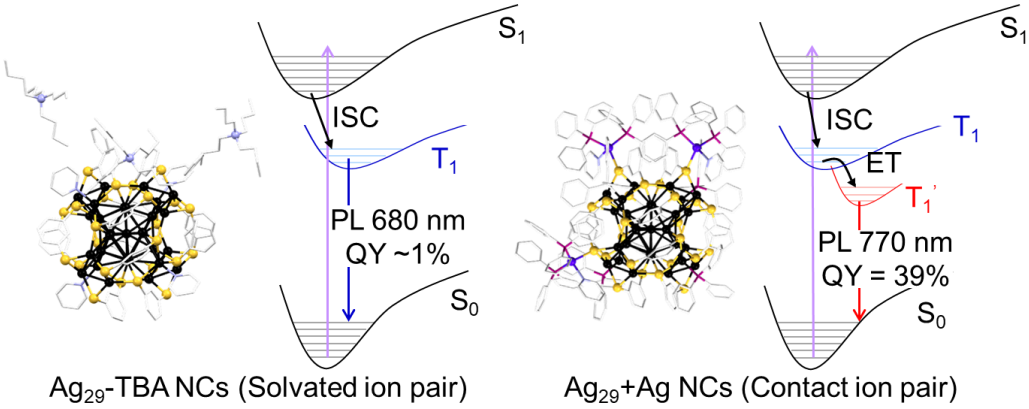

Fig. 1 Schematic diagrams of excited state relaxation for Ag_{29} NCs in the absence and presence of Ag(I) complexes.

1) W. Ishii et al., *Chem. Commun.* **2021**, *57*, 6483.

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Magnetic properties of paramagnetic one-dimensional chains where first transition metals are infinitely aligned with metal–metal bonds

([1]*Graduate School of Engineering, Gifu University*, [2]*Faculty of Engineering, Gifu University*)
○Atsushi Takamori,[1] Kazuhiro Uemura [2]

Keywords: Magnetic Behavior; One-dimensional Chain; Hetero-metal; Multinuclear Complex

Heteronuclear metal string complexes (HMSCs), where two or three metals are regularly aligned as several strings with metal–metal bonds, have been the focus of attention due to their potential applications, which are not found in extended metal atom chains comprised of homometals. The well-known synthetic approach to obtain these HMSCs is a template method utilizing multidentate ligands. In contrast, Pt-assisted extension has been the focus of attention because the combination of Pt and desired metals (= M) afforded heterometallic Pt–M complexes. Recently, we reported trinuclear complexes *trans*-$[Pt_2M(piam)_4(NH_3)_4](ClO_4)_2$ (**1-M**, piam = pivalamidate, M = Mn, Co, Ni, and Cu) are dimerized to be hexanuclear complexes Pt–M–Pt···Pt–M–Pt, showing magnetic interactions through –Pt···Pt– bonds.[1,2] Although the inner Pt atoms of Pt–M–Pt complexes metallophilic interact each other, the outer ones did not, resulted in the finite HMSCs. In this study, we will show crystal structures and physical properties for infinite one-dimensional chains aligned as ···Pt–M–Pt···Pt–M–Pt···, which were successfully obtained by changing the bridging ligand from piam to acetamidate (= acam).

Simply mixing *trans*-$[Pt(acam)_2(NH_3)_2]$, MCl_2 (M = Co, Ni, and Cu), and $NaClO_4$ in adequate solvent afforded single-crystals of *trans*-$[Pt_2M(acam)_4(NH_3)_4](ClO_4)_2$ (**2-M**). Single-crystal X-ray analyses revealed that each trinuclear complex is extended to be one-dimensional chains, with the close Pt···Pt distances of about 3.47–3.61 Å (Figure 1). Considering the chemical formulae, the formal oxidation states of M are Co(+2), Ni(+2), and Cu(+2). XPS and EPR measurements resulted in that M in **2-M** have high-spin states with unpaired electrons. Temperature dependence of magnetic susceptibilities for **2-Co** and **2-Ni** showed antiferromagnetic behaviors through –Pt···Pt– bonds separated by about 8.8 Å, with $J = -9.5$ (**2-Co**) and -13.5 (**2-Ni**) cm^{-1}. In contrast, **1-Cu** showed weak ferromagnetic behavior with $J = 0.14$ cm^{-1}.

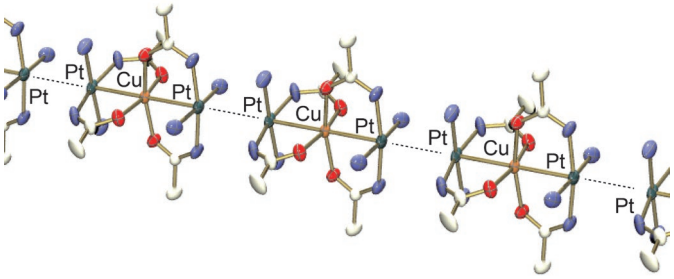

Figure 1. Crystal structure of **2-Cu**.

1) Takamori, A.; Uemura, K. *Inorg. Chem.*, **2022**, *61*, 5762–5778. 2) Uemura, K.; Takamori, A. *Coord. Chem. Rev.*, **2022**, *471*, 214736.

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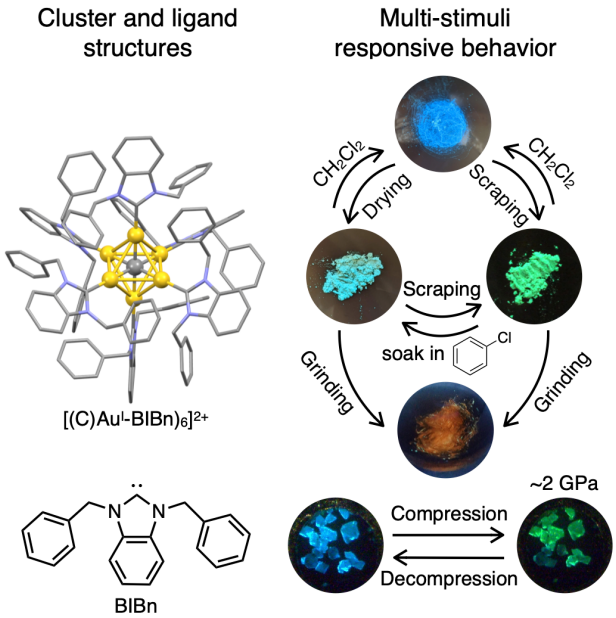
Vapor, mechanical, and piezochromic multicolor switching of a carbon-centered hexagold(I) cluster with flexible *N*-heterocyclic carbene ligands

([1]*Department of Chemistry, Graduate School of Science, The University of Tokyo*, [2]*Geochemical Research Center*, *Graduate School of Science, The University of Tokyo*)
○ Leonardo Hayato Takeshige,[1] Xiao-Li Pei,[1] Hitoshi Ube,[1] Zhen Lei,[1] Hiroki Kobayashi,[2] Kazuki Komatsu,[2] Hiroyuki Kagi,[2] Mitsuhiko Shionoya[1]
Keywords: Gold Clusters, *N*-Heterocyclic Carbenes, Vapochromism, Mechanochromism, Piezochromism.

The discovery of multi-stimuli responsive materials is essential for the development of next-generation sensors; however, integrating multi-stimuli responses such as vapor-, mechanical-, and piezo-stimulation into a single system remains challenging. Ligand-protected gold clusters are potential candidates for such applications because their luminescence can be tuned by several parameters, including gold-gold distance, ligand orientation, and aggregated state.[1] Nevertheless, the principles governing stimuli-responsive behaviors remain to be elucidated.

In this study, the relatively flexible *N,N'*-dibenzylbenzimidazolylidene (BIBn) ligand was used to synthesize a carbon-centered hexagold(I) cluster,[2] $[(C)(Au^{I}\text{-BIBn})_6](BF_4)_2$. Two crystal pseudopolymorphs exhibiting blue and turquoise luminescence under photoirradiation at 365 nm were found to be interconvertible by the addition and removal of CH_2Cl_2. Theoretical calculations suggest that ligand orientation is important for the emission-color changes.[3] Furthermore, scraping with a spatula produced a third emission color with reduced crystallinity. These three emission colors were attributed to changes in the aggregation states. Grinding in a mortar produced a short-lived red emissive state, which then spontaneously converted to an unidentified green emissive state. In addition, the application of hydrostatic pressure increased up to about 2 GPa resulted in a continuous decrease in the unit-cell parameters accompanied by a sudden redshift of the emission at 1 GPa.



1) V. W.-W. Yam, et al. *ACS Mater. Lett.* **2019**, *1*, 277. 2) M. Shionoya, et al., *Organometallics* **2018**, *37*, 2007. 3) M. Shionoya, et al. submitted for publication.

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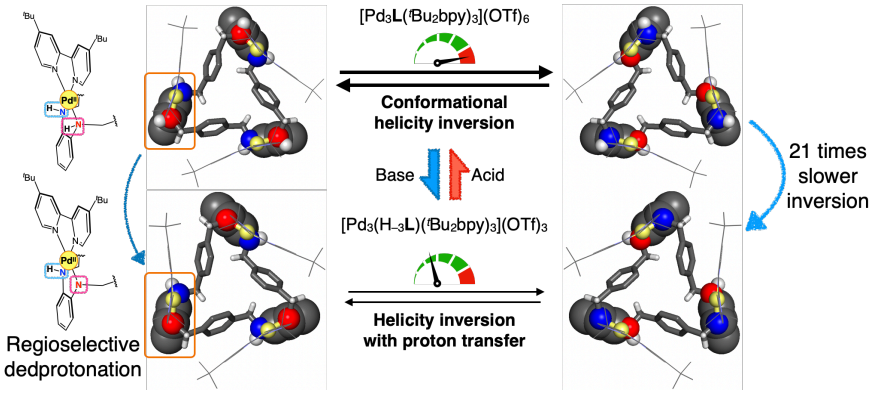
Regioselective deprotonation of twisted trinuclear macrocycles to control the rate of helicity inversion

([1]*Grad. Sch. of Sci.*; *The Univ. of Tokyo*, [2]*IMS*) ○Tomoki NAKAJIMA,[1] Shohei TASHIRO,[1] Masahiro EHARA,[2] Mitsuhiko SHIONOYA[1]

Keywords: Helicity inversion; Deprotonation; Pd complex; Multinuclear complex; Macrocyclic compound

Molecular motions including translation and rotation are controlled by various external stimuli, such as acid and base, to achieve molecular machines that work reversibly. For example, Stoddart and his co-workers demonstrated reversible translation motion of a molecular shuttle controlled by electrostatic repulsion upon addition of acid and base.[1] In this study, we aimed to control the inversion rate of a helically twisted trinuclear Pd^{II} complex, $[Pd_3\mathbf{L}(^tBu_2bpy)_3](OTf)_6$, by regioselective deprotonation. Indeed, the inversion rate of the deprotonated $[Pd_3(H_{-3}\mathbf{L})(^tBu_2bpy)_3](OTf)_3$ was significantly slowed down. Reversible conversion between the original and deprotonated Pd^{II} complexes by acid and base was also confirmed.

A trinuclear Pd^{II} complex, $[Pd_3\mathbf{L}(^tBu_2bpy)_3](OTf)_6$, was synthesized by the reaction of a macrocyclic ligand **L** with a Pd^{II} salt. Single-crystal XRD and ^{1}H NMR analyses revealed that the macrocyclic framework of the Pd^{II} complex was helically twisted by intramolecular C-H···π interactions. This Pd^{II} complex exhibited helicity inversion between (*P*)- and (*M*)-helicity, with an estimated inversion rate of 3.31 s^{-1} at 300 K in acetone-d_6 by EXSY NMR analysis. The Pd^{II} complex was then reacted with 26 equiv. of Na_2CO_3 and ^{1}H NMR analysis revealed that only three of the six amine protons of **L** were site-selectively deprotonated to $[Pd_3(H_{-3}\mathbf{L})(^tBu_2bpy)_3](OTf)_3$. Furthermore, the effect of regioselective deprotonation on the helicity inversion rate was investigated using EXSY NMR, and the inversion rate of $[Pd_3(H_{-3}\mathbf{L})(^tBu_2bpy)_3](OTf)_3$ was 0.155 s^{-1} at 300 K in acetone-d_6, which is 21 times slower than that of $[Pd_3\mathbf{L}(^tBu_2bpy)_3](OTf)_6$ due to the intramolecular proton transfer. This presentation will explain the mechanism of helicity inversion.



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Stability Control and Luminescence of Porous Crystals of Self-assembled Platinum(II) Complexes Based on the Electronic Tuning of Ligands

([1]*School of Biological and Environmental Sciences, Kwansei Gakuin University*, [2]*Faculty of Science, Hokkaido University*) ○ Masaki Yoshida,[1] Takanari Mochizuki,[2] Atsushi Kobayashi,[2] Masako Kato[1]

Keywords: Cyclometalated Pt(II) complexes; Porous molecular crystals; Luminescence; Intermolecular interactions

Porous molecular crystals (PMCs) have been actively studied as next-generation sensing and adsorption materials because of their structural/electronic flexibility and porosity. On the other hand, it is sometimes difficult to selectively obtain the desired porous structure due to the competition of weak intermolecular interactions during the crystallization. Previously, we developed a PMC built from a luminescent Pt(II) complex **1** (Fig. 1), which exhibited the assembly-induced emission owing to the Pt···Pt interactions.[1)] However, this porous structure was a kinetically trapped phase, and a thermodynamically more stable non-porous structure was favorably formed.

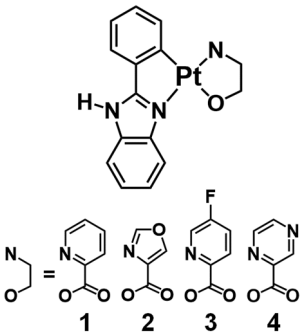

Fig. 1 Structures of **1**-**4**.

In this study, we have investigated to obtain the desired porous structure as the thermodynamically most stable phase by controlling the intermolecular interactions through ligand modification (**2**-**4** in Fig. 1). Although the complex **2** never formed the porous structure, the desired porous crystals were preferentially obtained for complexes **3** and **4** (Fig. 2) bearing the electron-deficient ligands. In contrast to the negligible Pt···Pt interactions in the non-porous crystal of **2**, the Pt···Pt interactions were enhanced by the electron-deficient ligands (d(Pt···Pt) = 3.4994(4) Å for **1**, 3.4503(4) Å for **3**, and 3.3390(3) Å for **4**). Importantly, depending on the strength of Pt···Pt interactions, these crystals exhibited distinctly different UV-vis absorption (Fig. 3) and luminescence behavior. The photophysical properties as well as the guest adsorption behavior of these crystals will be discussed.

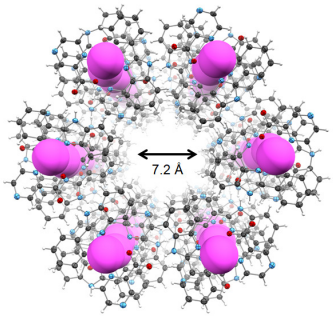

Fig. 2 Porous structure of **4**.

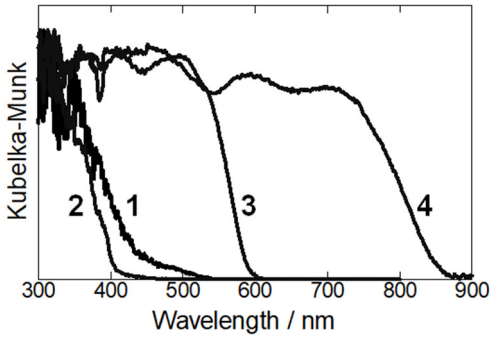

Fig. 3 UV-vis spectra of crystals **1**-**4**.

1) M. Yoshida, M. Kato, *et al.*, *Chem. Commun.* **2020**, *56*, 12989.

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プロトン、スピン、分子配向の連動に基づくプロトン化状態の多段階変換

（九大先導研 [1]）○中西　匠 [1]・佐藤　治 [1]

Multi-step conversion of protonation state based on the coupling of proton, spin and molecular orientation

([1]*Institute for Materials Chemistry and Engineering, Kyushu University*)
○Takumi Nakanishi[1] and Osamu Sato[1].

Proton transfer phenomenon controlled by external stimuli is an attractive research target for the development of functional materials. Our group have developed the iron(II) complexes exhibiting the intramolecular proton transfer coupled spin transition (PCST) to explore the unprecedented proton transfer phenomenon in crystalline system and to realize the new functions in molecular-based materials science. In this presentation, we report the iron(II) complex ([Fe(HL-F)$_2$](OTf)$_2$) exhibiting unprecedented proton transfer behaviors and transition processes based on the coupling of three kind of components (proton, spin and molecular orientation).

Keywords : Proton Transfer; Spin Transition; Hydrogen Bond; Multi Stability; Hydrazone Complex

プロトン移動現象は水素結合を形成する分子の電子状態および結合の変化を引き起こすことから、外場によるプロトン移動の制御が可能な物質の開拓は強誘電体や蛍光材料、磁性や伝導性、光学特性等の制御が可能な機能性材料の開発に応用出来ると期待される。当研究グループでは固体中における新たなプロトン移動現象や外場誘起プロトン移動に基づく新規機能の開拓を目的に、プロトン移動現象とスピン転移現象が連動して発現する鉄二価錯体（プロトン結合スピン転移錯体）の開発を行っている。当グループでは以前にプロトン移動とスピン転移に加え、極性アニオンの回転が連動する錯体[Fe(HL-F)$_2$](OTf)$_2$を開発し、この錯体が結晶中において多様なプロトン化状態、プロトン移動現象を示すことを報告した[1]。最近、本錯体の磁性測定結果を基に単結晶 X 線回折測定を行った結果、これまでに観測されていた 3 種の相に加え、新たな中間相(INT2 相)が存在することが確認された（図 1）。本発表では、新たな中間相の構造を基に明らかとなった、新規プロトン移動現象およびプロトン移動過程の発現ついて報告する（図 2）。

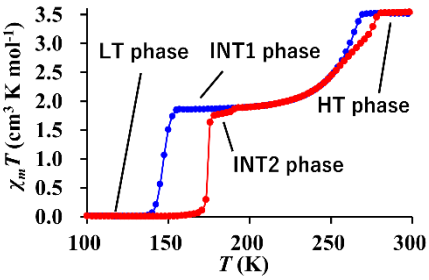

図 1 [Fe(HL-F)$_2$](OTf)$_2$ の磁性および結晶構造解析により確認された 4 種の相。

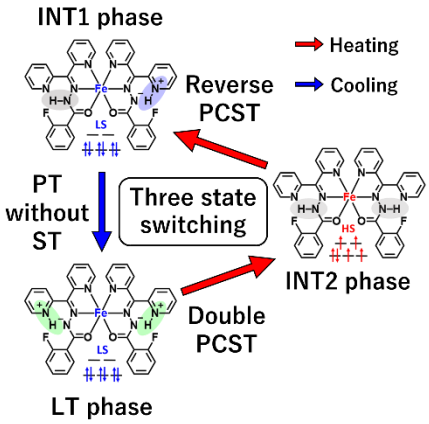

図 2 観測されたプロトン移動挙動およびプロトン移動過程。

1) 中西匠、堀優太、塩田淑仁、吉澤一成、佐藤　治　第 15 回分子科学討論会、3D14 (2021).

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

[K505-3vn] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Hironobu Ozawa, Yoshimasa Wada

Fri. Mar 24, 2023 4:10 PM - 6:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-3vn-01] Mechanistic Study on Chromium-catalyzed Ring-opening Arylation of 7-Oxabenzonorbornadiene Derivatives with Aryl Grignard Reagents

○Kohei Nishi[1], Hayato Tsurugi[1], Kazushi Mashima[2] （1. Graduate School of Engineering Science, Osaka University, 2. Graduate School of Pharmaceutical Sciences, Osaka University）

4:10 PM - 4:30 PM

[K505-3vn-02] [2+2+1]-Cycloaddition Reaction of Azobenzenes and Diarylacetylenes Catalyzed by Early Transition Metal Imido Complexes

○Takuya Akiyama[1], Yuya Kakiuchi[1], Ian A. Tonks[2], Hayato Tsurugi[1], Kazushi Mashima[3] （1. Graduate School of Engineering Science, Osaka University, 2. University of Minnesota, 3. Graduate School of Pharmaceutical Science, Osaka University）

4:30 PM - 4:50 PM

[K505-3vn-03] Mechanistic study of photocatalytic CO_2 reduction by a Ru(II)-Re(I) supramolecular photocatalyst

○Kei Kamogawa[1], Yuki Kato[2], Yuushi Shimoda[3], Kiyoshi Miyata[3], Ken Onda[3], Takumi Noguchi[2], Yusuke Tamaki[1], Osamu Ishitani[1,4] （1. Tokyo Institute of Technology, 2. Nagoya University, 3. Kyushu University, 4. Hiroshima University）

4:50 PM - 5:10 PM

[K505-3vn-04] Improvement of formation quantum yields of one-electron reduced species of Re(I)-complex photosensitizers and its utilization

○Naoki Hosokawa[1], Yusuke Tamaki[1], Osamu Ishitani[1,2] （1. Tokyo institute of technology, 2. Hiroshima University）

5:10 PM - 5:30 PM

[K505-3vn-05] Supramolecular Framework Catalyst Constructed by Iron Porphyrin Complexes for Photochemical CO_2 Reudction

○Kento Kosugi[1], Chiharu Akatsuka[1], Mio Kondo[1,2], Shigeyuki Masaoka[1] （1. Osaka University, 2. JST PRESTO）

5:40 PM - 6:00 PM

[K505-3vn-06] Iron-catalyzed ring-opening metathesis polymerization of olefins

○Satoshi Takebayashi[1], David Milstein[2] （1. Okinawa Institute of Science and Technology Graduate University, 2. Weizmann Institute of Science）

6:00 PM - 6:20 PM

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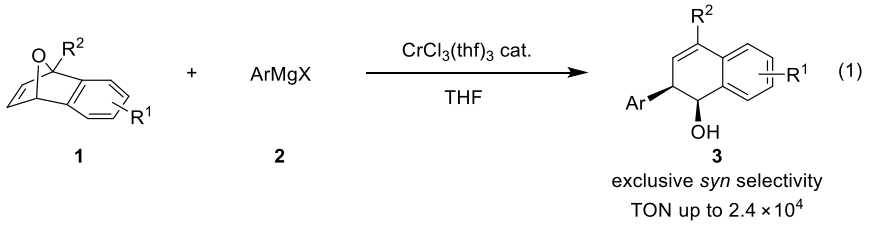
Mechanistic Study on Chromium-catalyzed Ring-opening Arylation of 7-Oxabenzonorbornadiene Derivatives with Aryl Grignard Reagents

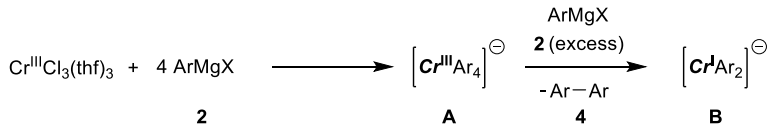
([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Pharmaceutical Sciences, Osaka University*) ○Kohei Nishi,[1] Hayato Tsurugi,[1] Kazushi Mashima[2]

Keywords: Chromium catalyst; Aryl Grignard reagent; 7-Oxabenzonorbornadiene derivatives; C–O bond cleavage; Ring-opening

Stereoselective synthesis of multi-functionalized 1,2-dihydronaphthalen-1-ols has attracted interest due to their intrinsic applicability as building blocks for derivatizing to biologically active compounds.[1] Ring-opening of 7-oxabenzonorbornadiene derivatives with organometallic reagents in the presence of suitable transition metal catalysts is one of the straightforward methods to obtain the 1,2-dihydronaphthalen-1-ol skeleton.[2] Herein, we report chromium-catalyzed *syn*-selective ring-opening arylation of 7-oxabenzonorbornadiene derivatives **1** with aryl Grignard reagents **2**, giving *syn*-2-ary-1,2-dihydronaphthalen-1-ols **3** under ligand-free conditions (eq. 1). Several control experiments were carried out to clarify the active species for this ring-opening arylation starting from commercially available $CrCl_3(thf)_3$. In the initial step, tetraarylchromate(III) species **A** is generated by the reaction of $CrCl_3(thf)_3$ and 4 equiv. of aryl Grignard reagent **2**, and subsequent two-electron reduction of **A** *via* reductive elimination of one equiv. of biaryl **4** affords diarylchromate(I) species **B** (Scheme 1), in which excess amounts of **2** are indispensable for the reduction of **A**. In addition, *in situ*-generated Cr(I) species **B** showed high activity at –20 °C, whereas the Cr(III) species **A** was inactive under the same reaction conditions.



Scheme 1. Proposed Mechanism for Generation of Catalytically Active Diarylchromate(I) Species **B**



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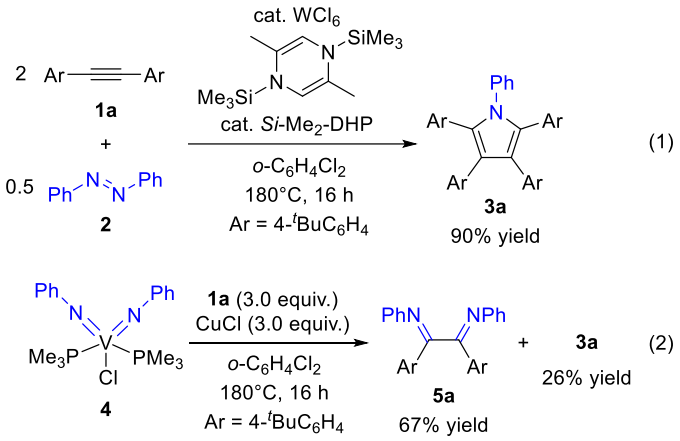
[2+2+1]-Cycloaddition Reaction of Azobenzene and Diaryl-acetylenes Catalyzed by Early Transition Metal Imido Complexes

([1]*Graduate School of Engineering Science, Osaka University*, [2]*University of Minnesota,* [3]*Graduate School of Pharmaceutical Science, Osaka University*) ○Takuya Akiyama,[1] Yuya Kakiuchi,[1] Ian A. Tonks,[2] Hayato Tsurugi,[1] Kazushi Mashima[3]

Keywords: Early transition metal; Imido complex; Pyrrole; Cycloaddition; DFT calculation

Reactivity of an early transition metal-nitrogen double bond involved in imidometal complexes with unsaturated organic compounds has been extensively investigated as a key step for synthesizing a variety of *N*-containing organic molecules. Catalytic [2+2+1]-cycloaddition reaction of the metal-nitrogen double bond with two equiv. of alkynes is a straightforward method in preparing synthetically valuable multi-substituted pyrrole derivatives. We previously reported that imido complexes of titanium and vanadium served as efficient catalysts to obtain alkyl-substituted pyrroles in one-pot manner; however, these catalysts were ineffective for incorporating diarylacetylenes.[1] Herein, we report that an *in situ*-generated bis(imido)tungsten species from WCl_6 and organosilicon reductant, *Si*-Me_2-DHP, exhibits superior catalytic activity among group 4-6 transition metal imido complexes for the [2+2+1]-cycloaddition of diarylacetylene **1a** with azobenzene (**2**), giving pyrrole **3a** in 90% yield (eq. 1). DFT calculations on the reaction sequences revealed that bis(imido)tungsten species possesses the lowest activation barrier for the rate-determining initial incorporation of **1a** to one of two imido moieties of *in situ*-generated bis(imido)tungsten among the structurally related Mo, Nb, and Ta derivatives. In addition, low catalytic activity of bis(imido)vanadium species for the formation of **3a** is ascribed to the generation of energetically accessible and unreactive (α-diimine)vanadium species; in fact, formation of the α-diimine **5a** from the bis(imido)vanadium complex **4** and **1a** was confirmed by the control experiment (eq. 2). Further details on the difference of W and Ti-catalyzed multi-arylated pyrrole formation are disclosed in this presentation.



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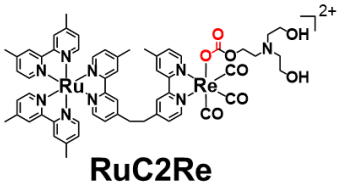
Mechanistic study of photocatalytic CO_2 reduction by a Ru(II)-Re(I) supramolecular photocatalyst

([1]*School of Science, Tokyo Institute of Technology*, [2]*Graduate School of Science, Nagoya University*, [3]*Graduate School of Science, Kyushu University*, [4]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kei Kamogawa[1], Yuki Kato[2], Yuushi Shimoda[3], Kiyoshi Miyata[3], Ken Onda[3], Takumi Noguchi[2], Yusuke Tamaki[1], Osamu Ishitani[1,4]
Keywords: Carbon dioxide reduction; Photocatalyst; Reaction mechanism

Photocatalytic CO_2 reduction using visible light as an energy source potentially gives a solution to the energy shortage and global warming problems. Although many researchers have intensively been working on developing CO_2 reduction photocatalysts, one of the significant problems in this field is the insufficiency of mechanistic insights into photocatalysis.



RuC2Re

Fig. 1 Structure of **RuC2Re**

A Ru(II)-Re(I) supramolecular photocatalyst (**RuC2Re,** Fig. 1) consisting of $[Ru(diimine)_3]^{2+}$ redox photosensitizer and *fac*-$[Re(diimine)(CO)_3(OC(O)OC_2H_4NR_2)]$ catalyst can efficiently capture CO_2 and reduce CO_2 to CO with high durability and selectivity.[1] Recently, our group has reported the formation processes of one-electron reduced species (OERS) of the Re unit of **RuC2Re** (**RuC2(Re)**$^-$), which is a crucial intermediate in the initial stage of photocatalytic CO_2 reduction, in detail.[2] However, the mechanism of the subsequent processes after the formation of **RuC2(Re)**$^-$ was still unclear.

In this work, we investigated the unknown mechanism of the subsequent processes of **RuC2(Re)**$^-$, utilizing various methods such as FT-IR spectroscopy and liquid chromatography analysis of photocatalytic reaction solution. The carboxylate complex **RuC2Re(COOH)** with a *fac*-Re(diimine)$(CO)_3$(COOH) unit was successfully detected as a subsequent intermediate of **RuC2(Re)**$^-$ by using time-resolved infrared spectroscopy combining laser flash photolysis and rapid-scan FT-IR method. This important intermediate was also detected by FT-IR measurements of photocatalytic reaction solution during steady-state light irradiation. Furthermore, it has been clarified that **RuC2Re(COOH)** eventually releases CO and OH^- and turns into the starting complex **RuC2Re**. In the presentation, the mechanism of these reactions, including the source of the second electron and the kinetics of each process, will be discussed in detail.

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Improvement of formation quantum yields of one-electron reduced species of Re(I)-complex photosensitizers and its utilization

([1]*School of Science, Tokyo institute of technology*, [2]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Naoki Hosokawa,[1] Yusuke Tamaki,[1] Osamu Ishitani[2]

Keywords: Redox photosensitized reaction; One-electron reduced species of photosensitizers; Quantum yield

Redox photocatalytic reactions using redox photosensitizers are utilized in various research fields. Quantum yields of the photochemical formation of one-electron reduced species (OERS) of the photosensitizers (Φ_{OERS}), which is an initiation process of the photocatalytic redox reactions, potentially affects the quantum yields of the overall redox photocatalytic reactions. We previously demonstrated that Φ_{OERS} of some Re(I)-complex photosensitizers (Fig. 1) using 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) or triethanolamine (TEOA) as reductants were much higher compared to the Ru(II)- and Os(II)-complex photosensitizers.[1-3] However, Φ_{OERS}s were suppressed by addition of both BIH and TEOA that has been frequently used as an additives for photocatalytic CO_2 reduction.

In this presentation, we clarify how TEOA affects the formation process of OERS of the Re(I)-complexes. Transient absorption spectra were measured of the Re(I) complexes in reaction solutions including BIH and/or TEOA for tracing OERS formation processes on ns and μs time scales. The result indicates that TEOA promotes back electron transfer process from OERS to one-electron oxidized species of BIH and decrease Φ_{OERS}.

We will also discuss about relationships between the efficiencies of the OERS formation and the photocatalytic reaction for CO_2 reduction, and effects of TEOA to the photocatalytic reactions.

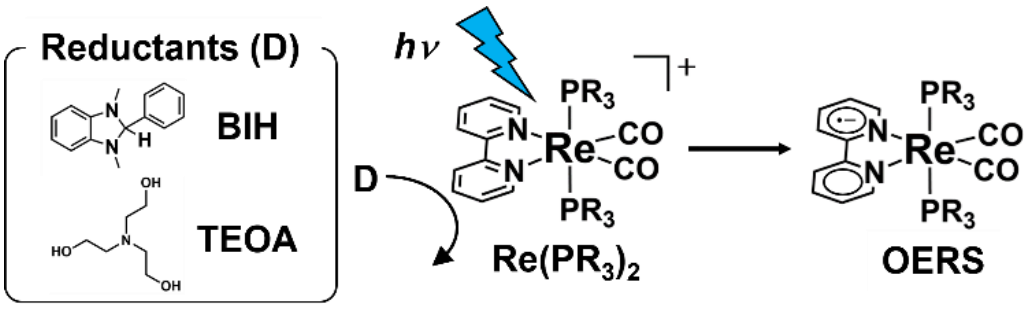

Figure 1. Photochemical reduction of Re(I)-complex

[References]

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Supramolecular Framework Catalyst Constructed by Iron Porphyrin Complexes for Photochemical CO_2 Reduction

([1]*Graduate School of Engineering, Osaka University*, [2]*JST PRESTO*) ○Kento Kosugi,[1] Chiharu Akatsuka,[1] Mio Kondo,[1,2] Shigeyuki Masaoka[1]

Keywords: CO_2 Reduction; Supramolecular Framework Catalyst; Photochemistry; Reaction Field; Porphyrin

Molecule-based porous crystalline photocatalysts without noble metals are one of the most attractive systems for visible-light-driven CO_2 reduction. However, reports on this class of photocatalysts are still limited and their activities are quite low compared to those containing noble metals. Here, we report an iron-complex-based porous crystalline photocatalyst for CO_2 reduction with high activity, selectivity, and stability.

A key to our success is the introduction of the concept of supramolecular framework catalyst,[1] which are constructed by the self-assembly of discrete catalyst modules bearing catalytic site and intermolecular interaction sites via noncovalent interactions. Important feature of supramolecular framework catalysts is that three essential components for light-driven CO_2 reduction, (i) photosensitizer, (ii) reaction field, and (iii) catalytic sites, can easily be incorporated into their structures in ordered fashion. In this study, we employed **FeBPPy** as a molecular module (Figure 1). **FeBPPy** contains an iron porphyrin scaffold, which can function as a catalytic site for CO_2 reduction, with pyrene moieties, which serve as both light-harvesting units and non-covalent interaction sites, at the *meso* positions. By a simple recrystallization technique, **FeBPPy** are self-assembled into the supramolecular framework catalyst (**FC1**).[2]

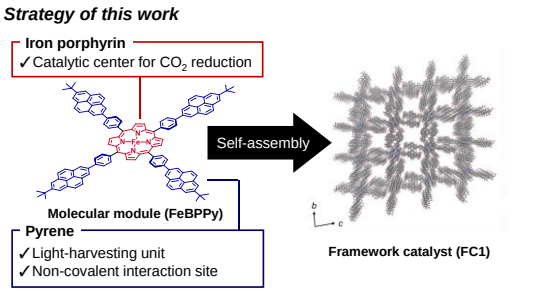

Figure 1. Structure and features of **FeBPPy** and **FC1**.

Photocatalytic CO_2 reduction of **FC1** was conducted under visible-light irradiation ($400 \leq \lambda \leq 750$ nm) in a CO_2 saturated MeCN containing the suspension of **FC1** as a photocatalyst, 0.2 M TFE as a proton source and 0.2 M BIH as a sacrificial electron donor. After 24 h, the formation of CO (697.3 mmol g^{-1}, selectivity 99.9%) was confirmed. The production rate was 29,100 μmol g^{-1} h^{-1}, which is more than 100 times higher than those of current best-in-class porous-crystalline-solid-based photocatalysts without noble metals. The performance of the **FC1** is also excellent in terms of apparent quantum yield for CO production (0.596% at 400 nm) and stability (up to 96 h).[3] The details of the control experiment, durability test, and mechanistic investigation will be discussed in the presentation.

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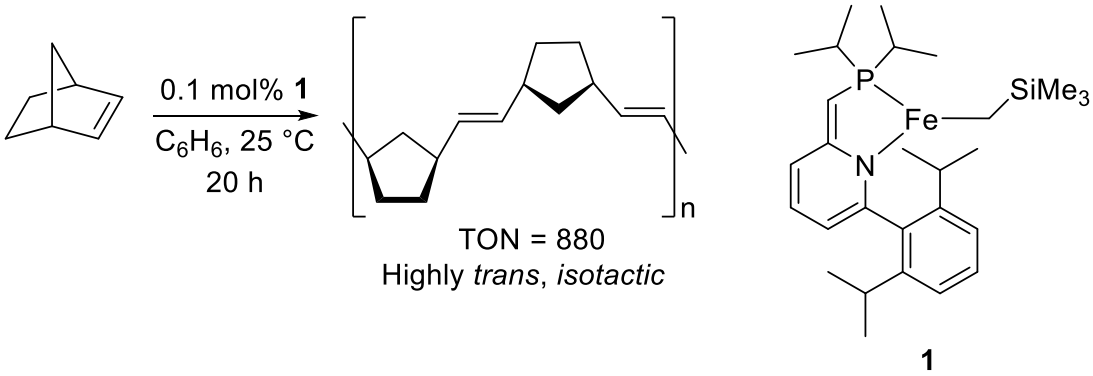
Iron-catalyzed ring-opening metathesis polymerization of olefins

([1]*Okinawa Institute of Science and Technology Graduate University*, [2]Weizmann Institute of Science and Technology) ○Satoshi Takebayashi,[1] David Milstein[2]

Keywords: Olefin Metathesis; Iron Catalysts; Mechanism; ROMP

The olefin metathesis reaction is among the most widely applicable catalytic reactions for carbon-carbon double bond formation. Currently, Mo- and Ru-carbene catalysts are the most common choices for this reaction. It has been suggested that an iron-based catalyst would be a desirable economical and biocompatible substitute of the Ru-catalysts;[1] however, practical solutions in this regard are still lacking.[2] **Here, we report the discovery and mechanistic studies of three-coordinate iron (II) catalysts for ring opening metathesis polymerization (ROMP) of olefins.** Moreover, the iron catalysts enabled the formation of polynorbornene with stereoregularity and high molecular weight (>10^7 g/mol). The polymerization in the presence of styrene revealed cross metathesis reactivity with an iron catalyst. Mechanistic studies suggest the possible role of metal-ligand cooperation in formation of the productive catalyst. This work opens the door to the development of iron-complexes that can be economical and biocompatible catalysts for olefin metathesis reactions.[3]



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

[K506-3vn] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Atsushi KOBAYASHI, Yohei Ogiwara

Fri. Mar 24, 2023 4:10 PM - 6:40 PM K506 (K506, Lecture Hall Bldg. [5F])

[K506-3vn-01] Effect of a Sulfur Atom in the Benzylidene Ligand of Hoveyda-Grubbs-type Complexes on Their Catalytic Activities

○Tsubasa Kinugawa[1], Shun Hirota[1], Takashi Matsuo[1] （1. Division of Materials Science, Nara Institute of Science and Technology）

4:10 PM - 4:30 PM

[K506-3vn-02] Multi-potential-step chronocoulospectrometry for electrocatalytic proton reduction by mononuclear ruthenium complexes

○Yuta Tsubonouchi[1], Norihisa Hoshino[1], Debraj Chandra[1], Zaki Zahran[1], Masayuki Yagi[1] （1. Grad. School of Sci. and Tech., Niigata univ.）

4:30 PM - 4:50 PM

[K506-3vn-03] A Highly Stable Molecular-based TiO_2 Photoanode for Photoelectrochemical Water Splitting Achieved by Pyridyl Anchoring Technique

○Xin Yan[1], Ken Sakai[1], Hironobu Ozawa[1] （1. Dept. Chem. Kyushu Univ.）

4:50 PM - 5:10 PM

[K506-3vn-04] Photochemical Reduction of Carbon Dioxde Catalyzed by Ru-Pd Bimetallic Complexes

○Siteng Yang[1], Nobuharu Iwasawa[1], Jun Takaya[1] （1. Titech）

5:20 PM - 5:40 PM

[K506-3vn-05] Photo-induced pentafluoroethylation mediated by cobalt(III) complexes supported by naphthyridine-based ligands

○Hoan Minh Dinh[1], Julia R. Khusnutdinova[1] （1. Okinawa Institute of Science and Technology）

5:40 PM - 6:00 PM

[K506-3vn-06] Molecular Catalysis of Co-NHC Complexes in Hydrogen Evolution from Water

○Kosei Yamauchi[1], Yasunobu Wakafuji[1], Kaori Kawamura[1], Masanori Kan[1], Ken Sakai[1] （1. Kyushu University）

6:00 PM - 6:20 PM

[K506-3vn-07] Mechanistic Investigation of Electrochemical Hydrogen Evolution from Water Catalyzed by a Co-NHC Complex

○Masanori Kan[1], Kosei Yamauchi[1], Ken Sakai[1] （1. Dept. Chem. Kyushu Univ.）

6:20 PM - 6:40 PM

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Hoveyda-Grubbs 型錯体の反応性におけるベンジリデン配位子上の硫黄原子の効果

（奈良先端大・物質創成 [1]）○衣川 翼 [1]・廣田 俊 [1]・松尾 貴史 [1]

Effect of a Sulfur Atom in the Benzylidene Ligand of Hoveyda-Grubbs-type Complexes on Their Catalytic Activities

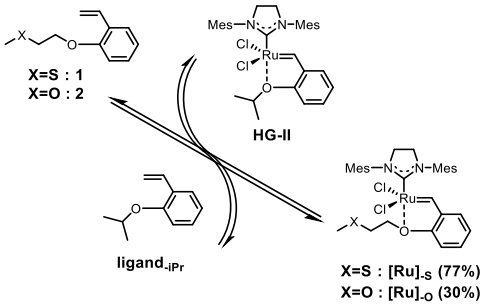
([1]*Dvision of Materials Science of Science and Technology, Nara Institute of Science and Technology*) ○Tsubasa Kinugawa,[1] Shun Hirota,[1] Takashi Matsuo.[1]

Olefin Metathesis (OM), a C-C double bond rearrangement reaction, is expected to be applicable for biomolecular chemistry because of its high functional group selectivity. To achieve efficient OM reactions in aqueous media, the structural modification of Hoveyda-Grubbs 2nd (**HG-II**) complexes has been studied. We previously reported that **HG-II**-type complex with an ethylenamide group at the terminal of a 2-alkoxybenzylidene ligand on a **HG-II**-type complex has a hydrogen bond between the amide moiety and a chlorido ligand, resulting in a high stability with a similar reacitivity to **HG-II**[1)]. Accordingly, we synthesized **HG-II**-type complexes with a chalcogen atom at the terminal of the 2-alkoxybenzylidene ligand, assuming that the chalcogen atom contributes to the compelx stability. The 1:1 ligand exchange reaction between **HG-II** and **1** showed 77% conversion, indicating that **[Ru]**$_{\text{-S}}$ is more stable than **HG-II**. The catalytic activity of **[Ru]**$_{\text{-S}}$ was found to be similar to that of the previously reported **HG-II**-type complex with an amide moiety.

Keywords : Olefin Metathesis; Ligand Exchange; Chalcogen Atom

オレフィンメタセシスは、C-C 二重結合の組み換え反応であり、その高い官能基選択性から、生体分子化学分野での適用も試みられ、水中で効率よくオレフィンメタセシスを進行させるため、Hoveyda-Grubbs 第 2 世代錯体 (**HG-II**)の構造修飾が行われている。我々は、2-アルコキシベンジリデン配位子末端にエチレンアミド基を有する錯体が NH•••Cl 水素結合を形成により、触媒活性を保ちつつ **HG-II** 錯体よりも安定な錯体であることを報告した [1)]。しかし、水中における NH•••Cl 水素結合の効果の有無が懸念された。そこで本研究では、水素結合に代わって錯体の安定性を向上と触媒活性を有する錯体を得るため、16 族元素を導入した配位子 **1**, **2** 及び錯体**[Ru]**$_{\text{-S}}$, **[Ru]**$_{\text{-O}}$ の合成を行った。

配位子 **1** と **HG-II** 錯体を 1:1 に混合して配位子交換反応を行ったところ、硫黄原子を有する**[Ru]**$_{\text{-S}}$ が収率 77%で生成し、50%を超える収率であることから、**[Ru]**$_{\text{-S}}$ は **HG-II** 錯体よりも安定であることが分かった。また、N-tosyldiallylamine の閉環メタセシス反応活性は、エチレンアミド基を有する錯体と同等の触媒活性であった。このことから、**[Ru]**$_{\text{-S}}$ は触媒活性を保ちつつ安定性が高い錯体であることが明らかになった。



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Multi-potential-step chronocoulospectrometry for electrocatalytic proton reduction by mononuclear ruthenium complexes

(*Grad. School of Sci. and Tech., Niigata Univ.*) ○Yuta Tsubonouchi, Norihisa Hoshino, Debraj Chandra, Zaki Zahran, Masayuki Yagi

Keywords: Artificial photosynthesis; Proton reduction; Spectroelectrochemical measurements; Molecular catalysts; Ruthenium complexes

Electrocatalytic proton reduction to H_2 is a topic of worldwide interest as the need to solve energy and environmental issues. Molecular metal complexes are promising candidates for proton reduction catalysts, since their catalytic activity can be tuned via rational ligand design. An understanding of the redox reactions and catalytic aspects of the molecular catalysts is essential for improving their catalytic performance for proton reduction. A spectroelectrochemical technique is useful to directly observe the real change in the molecular catalysts in addition to the electrochemical data for current or charge for monitoring the reactions of molecular catalysts.[1)] In this study, we investigated electrocatalytic activities of *distal*-/*proximal*-$[Ru(tpy)(L)(OH_2)]^{2+}$ isomers[2)] (tpy = 2,2':6',2''-terpyridine, L = 5-phenyl-2,8-di(2-pyridyl)-1,9,10-anthyridine) for proton reduction (Fig 1). Moreover, the catalytic mechanisms of both isomers were studied using a multi-potential-step chronocoulospectrometric (MPSCCS) technique (Fig 1).

UV-visible spectroscopic analysis of *distal*-/*proximal*-$[Ru(tpy)(L)(OH_2)]^{2+}$ in acetonitrile (AN) showed that both isomers are stoichiometrically converted to *distal*-/*proximal*-$[Ru(tpy)(L)(AN)]^{2+}$ by exchange of the aqua ligand with solvent AN. The observed rate constants for the formation of *distal*-/*proximal*-$[Ru(tpy)(L)(AN)]^{2+}$ were estimated to be 2.8 x 10^{-2} and 5.4 x 10^{-2} min^{-1}, respectively. Cyclic voltammograms (CVs) of *distal*-/*proximal*-$[Ru(tpy)(L)(AN)]^{2+}$ in dry AN under Ar exhibited three reversible reduction waves, assigned to three sequential one-electron reduction processes for both isomers. Addition of water changed the profile of the CVs for both isomers: large catalytic currents for proton reduction appeared. In the presentation, the proton reduction mechanisms of both isomers will be discussed based on the results obtained from the MPSCCS analysis.

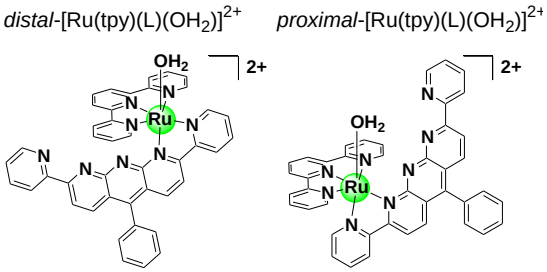

Fig 1. Structures of *distal* and *proximal* isomers of mononuclear Ru aquo complexes.

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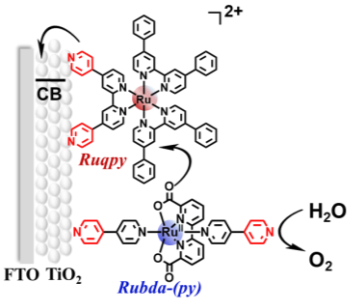
A Highly Stable Molecular-based TiO_2 Photoanode for Photoelectrochemical Water Splitting Achieved by Pyridyl Anchoring Technique

(Department of Chemistry, *Kyushu University*) ○Xin Yan,[1] Ken Sakai,[1] Hironobu Ozawa[1]

Keywords: water splitting; water oxidation catalyst; photosensitizer; TiO_2; pyridyl anchor

Recently, overall water splitting by a molecular-based photoelectrochemical cell has attracted considerable attention because it is regarded as one of the promising methods for solar-to-hydrogen conversion. In this context, extensive efforts have been thus far devoted to develop a highly efficient and stable molecular-based photoanode for water oxidation by modification of semiconductors with both a photosensitizer and a water oxidation catalyst (WOC). However, the poor stability of the molecular-based photoanodes in aqueous media due to the detachment of such functional molecules from the semiconductor surfaces is still one of the most serious problems to achieve such photoanodes. On the other hand, we previously demonstrated that the mesoporous TiO_2 electrode modified with Ru-qpy photosensitizer can act as a highly stable and efficient photoanode for solar driven hydrogen production in the presence of sacrificial electron donor (EDTA) since the chemisorption of Ru-qpy by pyridyl anchors is highly stable even in aqueous media.[1]



In this study, Ru(bda)-py WOC[2] is incorporated to the Ru-qpy-modified TiO_2 electrode to develop a highly stable molecular-based photoanode because this WOC is expected to strongly chemisorb to the TiO_2 surfaces by using one of the two pyridyl rings. The molecular-based photoanodes were prepared by the stepwise adsorption of Ru-qpy and Ru(bda)-py in this order, and the amounts of adsorbed molecules were estimated to be 0.16 and 0.02 μmol/cm^2, respectively. This photoanode generates the steady anodic photocurrent density about 90 μA/cm^2 under intermittent visible light irradiation in an acetate buffer (pH 5.0), strongly suggesting that photoelectrochemical water oxidation promotes at the surfaces of the photoanode. As expected, O_2 production is confirmed to proceed with over 90% Faradaic efficiency by the controlled potential electrolysis (CPE) under continuous irradiation when the electrode potential is held at 0.05 V vs. SCE. More importantly, the catalytic performance of this photoanode maintains over 3 h, demonstrating that the stability of molecular-based photoanode can be effectively improved by the pyridyl anchoring technique invented by our group. It is further confirmed that overall water splitting also proceeds with over 90% Faradaic efficiency for both O_2 and H_2 production when a small electrical bias (0.4 V vs. cathode) is applied, and relatively large solar-to-hydrogen conversion efficiency (0.07%) is obtained in our molecular-based photoelectrochemical cell.

[1] K. Morita, K. Sakai, H. Ozawa, *ACS Appl. Energy Mater.*, **2019**, *2*, 987.
[2] Y. Jiang, F. Li, F. Huang, B. Zhang, L. Sun, *Chinese J. Catal.*, **2013**, *34*, 1489.

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Photochemical Reduction of Carbon Dioxide Catalyzed by Ru-Pd Bimetallic Complexes

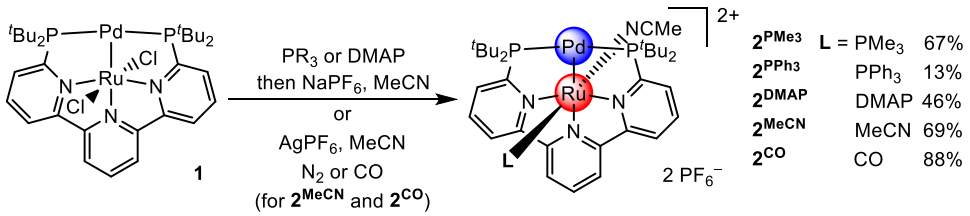
(*Department of Chemistry, Tokyo Institute of Technology*) ○Siteng Yang, Nobuharu Iwasawa, Jun Takaya

Keywords: Carbon Dioxide, Photoreduction, Bimetallic Complex, Artificial Photosynthesis

Development of single catalyst systems, which realize efficient photochemical reduction of CO_2 to useful C1 sources without external photosensitizers, has been one of challenges in artificial photosynthesis aiming to achieve high efficiency in catalytic activity and photoenergy conversion. However, such single catalyst systems reported so far have usually suffered from low catalyst efficiency. Meanwhile, our group has developed 6,6”-bis(phosphino)terpyridine derivatives as efficient scaffolds for various metal-metal bonds including a combination of Ru and Pd. In this presentation, we report the synthesis of various Ru–Pd bimetallic complexes that act as highly efficient single catalysts for photo-reduction of CO_2 to CO.

We have successfully synthesized dicationic Ru–Pd bimetallic complexes **2** having various supporting ligands L on Ru via ligand exchange reactions of a neutral complex **1** (**Scheme 1**). These dicationic Ru–Pd complexes were found to be active catalysts for photo-reduction of atmospheric pressure of CO_2 to CO in dehydrated DMA with BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole, 0.1 M) as a sacrificial reductant under visible light irradiation (425 nm LED). The PPh_3-coordinated Ru–Pd complex $\mathbf{2^{PPh3}}$ exhibited the best catalytic activity among tested to generate CO selectively, achieving the TON of 389 (2 h) and the TOF of 194 h^{-1} (**Scheme 2**). These results demonstrate that dicationic Ru-Pd bimetallic complexes act as highly efficient single catalysts that furnish both functions of photosensitizer and CO_2 reduction, providing new design of molecular catalysts for CO_2 fixation reactions using photoenergy.

Scheme 1.



Scheme 2.

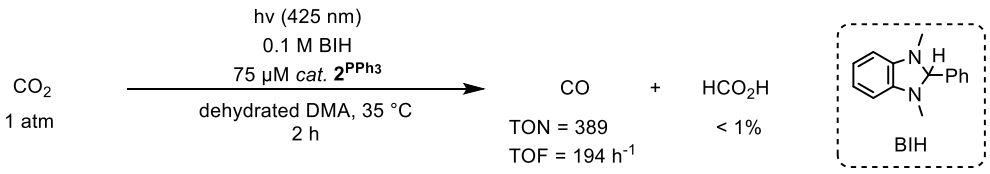


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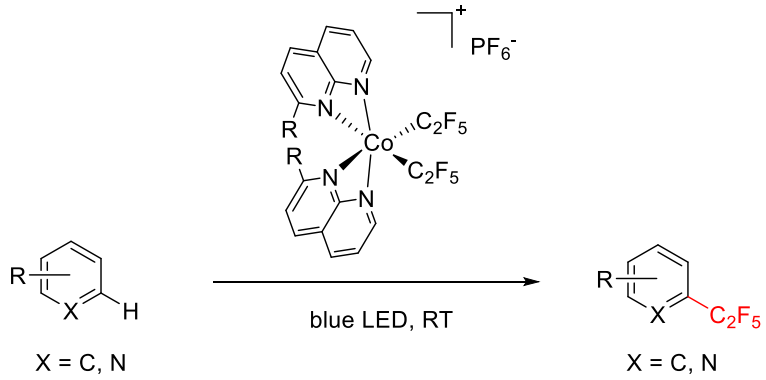
Photo-induced pentafluoroethylation mediated by cobalt(III) complexes supported by naphthyridine-based ligands

([1]*Okinawa Institute of Science and Technology*) ○Hoan Minh Dinh[1], Julia R. Khusnutdinova[1]
Keywords: cobalt complex, pentafluoroethylation, photo-induced bond homolysis

Incorporating fluoroalkyl groups into drug molecules has attracted great attention recently as a powerful tool to modulate metabolic stability and biological activity of pharmaceuticals. While radical trifluoromethylation mediated by first-row base metal has been widely applied in medicinal chemistry, the analogous strategy to introduce pentafluoroethyl or longer-chain fluoroalkyl group is relatively rare, even though the extra CF_2 group may cause a significant change in steric demand, dipole moment and lipophilicity.[1] Among the base metal, nickel has emerged as a powerful, cheap alternative to precious second and third-row transition metals for radical perfluoroalkylation.[2] Cobalt complexes, on the other hand, have gained less attention since they are considered relatively less active in trifluoromethylation than nickel complexes.

Recently, our group reported photoinduced protocols for trifluoromethylation of arenes and heteroarenes catalyzed by high-valent nickel(III) complexes supported by simple dimethylnaphthyridine ligands.[3] This report has shown that even the simple naphthyridine ligand can promote photo-induced CF_3 radical formation from nickel complexes. Considering the easy accessibility of cobalt precursors with longer fluoroalkyl chains, in this study, we use the simple naphthyridine-based ligands to support the formation of cobalt-pentafluoroethyl complexes. Under blue LED irradiation, these cobalt complexes exhibit facile cobalt-pentafluoroethyl bond homolysis and the release of a C_2F_5 radical, which can be trapped by TEMPO. Those complexes are also competent in stoichiometric C(sp^2)-H pentafluoroethylation in arenes and heteroarene under blue LED visible light irradiation.



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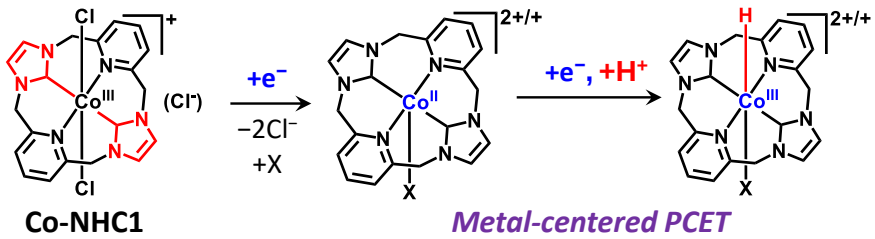
Molecular Catalysis of Co-NHC Complexes in Hydrogen Evolution from Water

([1]*Department of Chemistry, Kyushu University*) ○Kosei Yamauchi,[1] Yasunobu Wakafuji,[1] Kaori Kawamura,[1] Masanori Kan,[1] Ken Sakai[1]

Keywords: Co-NHC; Artificial Photosynthesis; Hydrogen Evolution; Water Splitting; Molecular Catalyst

Artificial photosynthesis based on splitting water into H_2 and O_2 with solar energy has attracted recent years. In order to realize the overall water-splitting reaction based on molecular systems, it is crucial to develop highly active molecular catalysts for both hydrogen and oxygen evolution reactions (HER and OER). In this context, we have focused on molecular catalysis for H_2 evolution from water by employing a photochemical system comprising of EDTA, $[Ru(bpy)_3]^{2+}$, electron relay and the catalyst, where one-electron-reduced species of methylviologen MV^{2+} (i.e., MV^{+}•) only has a driving force (DF) of 150 meV for HER at pH 5.0. Within these studies, we succeeded in demonstrating that a macrocyclic cobalt-NHC complex **Co-NHC1** serves as a catalyst for HER using MV^{+}• as a reductant via the metal-centered PCET process.[1] This is the first example of the 1st row transition metal complex showing the catalysis in this system. Upon changing the electron mediator, we have improved the photosystem which shows 70 times higher rate of HER compared with that of MV^{2+}.[2] On the other hand, we have recently conducted the detailed analyses on the homogeneous electrocatalysis of **Co-NHC1** in aqueous media. Importantly, the turnover frequency (TOF) of HER catalyzed by **Co-NHC1** has turned out to be extremely high even in neutral media, in which some other cobalt-based molecular catalysts have been previously examined under the similar conditions.[3] Our recent finding includes the development of the highly efficient molecular system based on new cobalt-NHC complexes in photochemical H_2 evolution from alkaline water, which will be discussed in the presentation.



1) Kawano, K.; Yamauchi, K.*; Sakai, K.*, *Chem. Commun.* **2014**, *50*, 9872-9875. 2) Yatsuzuka, K.; Yamauchi, K.*; Kawano, K.; Ozawa. H.*; Sakai, K.*, *Sustainable Energy Fuels* **2021**, *5*, 740-749. 3) Wang, J.-W.; Yamauchi, K.; Huang, H.-H.; Sun, J.-K.; Luo, Z.-M.; Zhong, D.-C.*; Lu, T.-B.*; Sakai, K.*, *Angew. Chem. Int. Ed.* **2019**, *58*, 10923-10927.

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Mechanistic Investigation of Electrochemical Hydrogen Evolution from Water Catalyzed by a Co-NHC Complex

(*Department of Chemistry, Kyushu University*) ○Masanori Kan, Kosei Yamauchi, Ken Sakai

Keywords: Hydrogen Evolution; Turnover Frequency (TOF); Electrochemistry; Homogeneous Catalysis; N-Heterocyclic Carbene (NHC)

Hydrogen production based on water splitting using solar energy has attracted much attention. Our laboratory previously reported that an N-heterocyclic carbene cobalt complex, **Co-NHC1**, promotes photochemical hydrogen evolution from water with low driving force.[1,2] In this study, mechanistic studies on hydrogen evolution reaction (HER) by **Co-NHC1** were carried out through the advanced electrochemical analyses.

The concentration dependence of the phosphate buffer solution was evaluated by conducting linear sweep voltammogram (LSV) measurement at pH = 7 (Figure 1). As a result, it was found that one $H_2PO_4^-$ molecule is involved as a proton mediator during the PCET-based (proton-coupled electron transfer) reduction process towards Co(II), which is considered as the rate-limiting step. Importantly, the turnover frequency of HER catalyzed by **Co-NHC1** was estimated to be 25,000,000 s^{-1}, showing that **Co-NHC1** has exceptionally high catalytic activity of HER. Next, kinetic isotope effect (KIE) was evaluated, where the KIE was estimated to be 13.7. It strongly indicates that the Co(III)-H formation process proceeds via the CPET (concerted proton-electron transfer) process. More importantly, a linear correlation was observed between the maximum catalytic current ($i_{cat,max}$) and the concentration of **Co-NHC1** (Figure 2), where $i_{cat,max}$ values were determined from the plateau-shaped currents obtained by increasing the scan rate. Therefore, it can be concluded that the HER catalyzed by **Co-NHC1** proceeds via a unimolecular pathway.

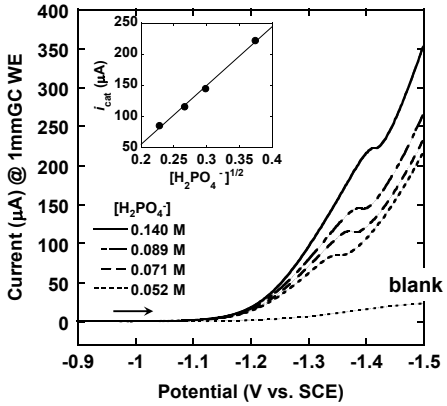

Figure 1. LSVs for the aqueous phosphate buffer solutions (pH = 7; [$H_2PO_4^-$] =0.052-0.14 M) of 18 μM **Co-NHC1** (WE: GC, CE: GC, RE: SCE, Scan rate: 0.1 V/s).

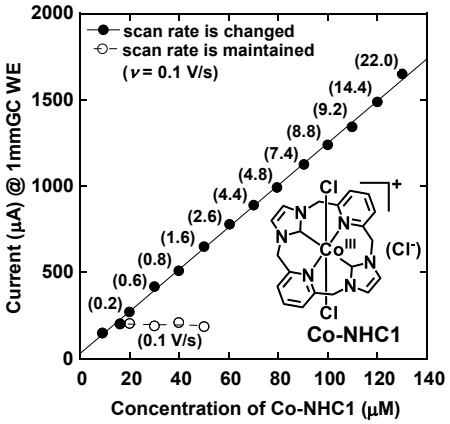

Figure 2. Concentration dependence of $i_{cat,max}$ values for the LSVs using aqueous phosphate buffer solutions (0.4 M, pH = 7.0) of **Co-NHC1** (10-130 μM).

1) K. Kawano, K. Yamauchi, K. Sakai, *Chem. Commun*. **2014**, *50*, 9872. 2) K. Yatsuzuka, K. Yamauchi, K. Kawano, H. Ozawa, K. Sakai, *Sustainable Energy Fuels* **2021**, *5*, 740.

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

[K404-3am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kenichi Michigami, Taiga Yurino

Fri. Mar 24, 2023 9:00 AM - 11:20 AM K404 (K404, Lecture Hall Bldg. [4F])

[K404-3am-01] Asymmetric Hydrogenation of α-Amino Esters through Dynamic Kinetic Resolution Catalyzed by Ruthenabicyclic Complexes (RUCY)

○Hiroki Ishikawa[1], Taiga Yurino[2,3], Ryo Komatsu[2], Ming-Yuan Gao[2], Noriyoshi Arai[2], Taichiro Touge[1], Kazuhiko Matsumura[1], Takeshi Ohkuma[2,3] (1. Takasago International corporation, 2. Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center, Hokkaido University)

9:00 AM - 9:20 AM

[K404-3am-02] Synthesis of Fused Cyclopentadienes and Cycloheptatrienes via Direct Carbon– Carbon Double Bond Cleavage of Cyclopropene Enabled by Ruthenium Catalysis

○Tomohiro Kikuchi[1], Takeshi Yasui[1], Yoshihiko Yamamoto[1] (1. Grad. Sch. Pharm. Sci., Nagoya Univ.)

9:20 AM - 9:40 AM

[K404-3am-03] 7-*Exo-dig* Hydrocarboxylation of Alkyne-Tethered Carboxylic Acids with Gold-Zinc Cooperative Catalysis

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

9:40 AM - 10:00 AM

[K404-3am-04] Chiral phosphoric acid-Au(I) hybrid complex catalyzed asymmetric synthesis of indole fused seven-membered ring compounds

○Naoya Taniguchi[1], Mitsuhiro Ueda[1,2], Kenichi Michigami[1,2], Masato Ohashi[1,2] (1. Osaka Prefecture Univ., 2. Osaka Metropolitan Univ.)

10:20 AM - 10:40 AM

[K404-3am-05] Synthesis of SGLT2 Inhibitors by Means of Copper-Mediated Coupling Reactions with Grignard Reagents

○Sandeep Rameshrao Tapkir[1], N. Maheshwara Reddy[1], Shaheen Kasim Mulani[1], Masahiko Seki[1,2], Kazushi Mashima[1] (1. Graduate School of Pharmaceutical Science, Osaka University, Suita, Osaka 565-0871, Japan, 2. Marketting Group, Tokuyama Corporation, Tsukuba, Ibaraki 300-4247, Japan)

10:40 AM - 11:00 AM

[K404-3am-06] A Novel General Method for Preparation of Thioesters: In Quest of Direct Conversion of Esters to Aldehydes and Ketones

○Shaheen Kasim Mulani[1], Akinari Uchibayashi[1], Sandeep Ramesharao Tapkir[1], N. Maheshwara Reddy[1], Masahiko Seki[1,2], Kazushi Mashima[1] (1. Graduate School and School of pharmaceutical Sciences, Osaka University, 2. Tokuyama Corporation, Tsukuba)

11:00 AM - 11:20 AM

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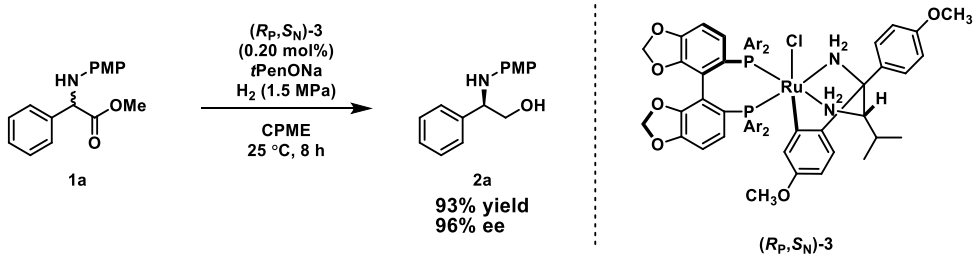
Asymmetric Hydrogenation of α-Amino Esters through Dynamic Kinetic Resolution Catalyzed by Ruthenabicyclic Complexes (RUCY®)

([1]*Takasago International Corporation,* [2]*Division of Applied Chemistry, Faculty of Engineering, Hokkaido University,* [3]*Frontier Chemistry Center, Hokkaido University*)
○ Hiroki Ishikawa,[1] Taiga Yurino,[2,3] Ryo Komatsu,[2] Ming-Yuan Gao,[2] Noriyoshi Arai,[2] Taichiro Touge,[1] Kazuhiko Matsumura,[1] Takeshi Ohkuma[2,3]
Keywords: Ruthenium Complexes; Asymmetric Hydrogenation; Dynamic Kinetic Resolution, Aminoesters; Optically Active Aminoalcohols

Optically active β-substituted β-aminoethanols have been frequently utilized in the synthesis of a wide variety of bioactive compounds, including natural products, medicines, and agrochemicals. Reduction of enantiomerically enriched α-amino esters into the β-amino alcohols with maintenance of the enantiopurity by metal hydride reagent or transition metal catalyst is well-known methods. [1] However, these procedures are required to prepare the corresponding enantiomerically enriched α-amino esters in advance. We herein report asymmetric hydrogenation of racemic α-substituted α-amino esters into the enantiomerically enriched β-amino alcohols through dynamic kinetic resolution with chiral ruthenabicyclic complexes (RUCY®). [2]

N-PMP (PMP = *p*-methoxyphenyl) protected phenylglycine methyl ester **1a** was selected as a substrate for optimization of catalyst structure and reaction conditions, and the RuCl[(*S*)-daipena][(*R*)-dm-segphos] (R_P,S_N)-**3**/*t*PenONa system was successfully catalyzed the hydrogenation of **1a** to give **2a** in 96% ee. The scope of the reaction was also examined, and a variety of β-aryl- and β-heteroaryl-substituted β-aminoethanols was obtained in high ee (up to 97%). The mechanistic deuteration experiments suggested that the reaction is not a simple ester hydrogenation, but proceeds with 1,2-hydride migration of the α-amino acetalate intermediate into the α-hydroxy imine.



1) See for example: (a) W. Kuriyama *et al.*, *Adv. Synth. Catal*. **2010**, *352*, 92–96. (b) B. M. Widegren *et al.*, *Org. Lett*. **2018**, *20*, 2654–2658.
2) K. Matsumura *et al. J. Am. Chem. Soc*. **2011**, *133*, 10696–10699.

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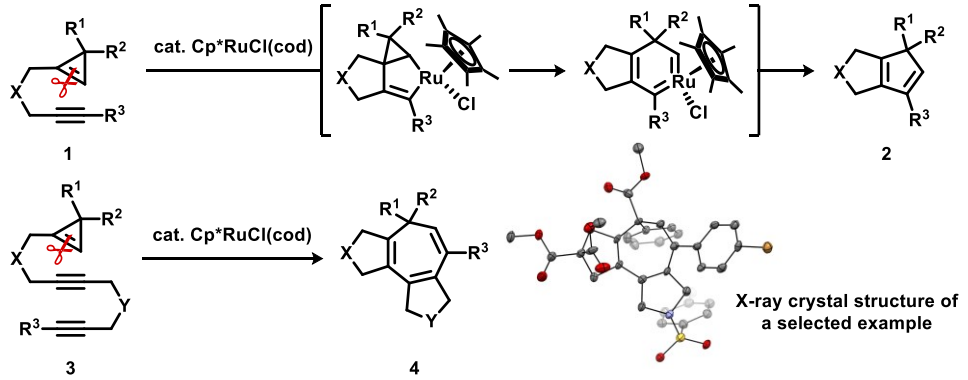
Synthesis of Fused Cyclopentadienes and Cycloheptatrienes via Direct Carbon–Carbon Double Bond Cleavage of Cyclopropene Enabled by Ruthenium Catalysis

([1]*Graduate School of Pharmaceutical Sciences, Nagoya University*)
○Tomohiro Kikuchi,[1] Takeshi Yasui,[1] Yoshihiko Yamamoto[1]
Keywords: Ruthenium Catalysis; Cycloisomerization; Cyclopropene; Cyclopentadiene; Cycloheptatriene

It is widely known that the transition-metal-mediated carbon–carbon single bond cleavage of a cyclopropene ring readily proceeds.[1] On the other hand, the ring opening of cyclopropenes via direct and selective carbon–carbon double bond cleavage of the cyclopropene ring is a formidable challenge.

Transition-metal-catalyzed cycloaddition reactions provide us with an opportunity to construct a variety of complex ring scaffolds in a single operation. In particular, η^5-cyclopentadienyl ruthenium complexes and 1,6-diynes generate five-membered cyclic biscarbenoids, which can lead to formation of various aromatic compounds in the presence of appropriate reactants.[2] Given the similarity of cyclopropenes and alkynes,[3] we hypothesized that the reaction of cyclopropene-ynes **1** with the ruthenium catalyst could form cyclopropane-fused ruthenacycles, which can be key intermediates for the formation of non-aromatic carbocycles. Herein, we report the ruthenium-catalyzed cycloaddition of **1** via carbon–carbon double bond cleavage of the cyclopropene ring to provide fused cyclopentadienes **2**. The density functional theory calculations indicate that the reaction proceeds via cyclopropane-fused ruthenacycles, which undergoes ring expansion to generate six-membered cyclic biscarbenoids. We also demonstrated a synthesis of fused cycloheptatrienes **4** via the cycloaddition of cyclopropene-diynes **3**.



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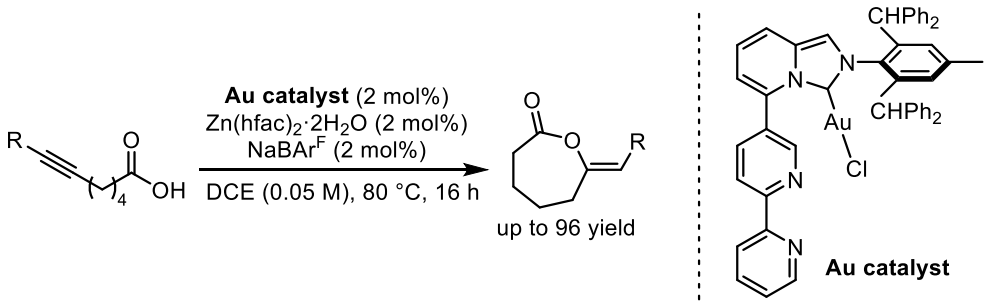
7-*Exo-dig* Hydrocarboxylation of Alkyne-Tethered Carboxylic Acids with Gold-Zinc Cooperative Catalysis

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

Keywords: Cooperative Catalysis; Gold Catalyst; Nucleophilic Addition; *N*-heterocyclic carbene; Lactone Synthesis

Lactones are abundant skeletons in natural products and pharmaceutical molecules.[1] Cyclization of alkyne-tethered carboxylic acids is one of the most straightforward methods for preparing synthetically important *exo*-alkylidethylene-type enol lactones.[2] However, the synthesis of seven-membered ring lactones named ε-lactones through the alkyne cyclization has been limited in substrate scope due to difficulty of seven-membered ring forming reaction between the two remote reaction sites. Earlier, we have developed gold-zinc heterobimetallic catalysis for nucleophilic addition of carboxylic acids towards non-activated alkynes, in which nucleophilic addition is promoted through cooperative action of the Lewis acidic gold atom for activating alkynes and the basic zinc atom for activating carboxylic acids through deprotonation.[3] In this contribution, we utilized the gold-zinc cooperative catalysis for cyclization of alkyne-tethered carboxylic acids including non-activated internal alkynes for preparing 7-membered lactones.

In the initial study, we found that formation of oligomers through intermolecular reaction is a main problem. Hence, for preventing such side-reactions, we introduced bulky substituents at the ortho-position of an *N*-aryl substituent on NHC ligands, expecting that a bulky substituent possibly facilitate the cyclization through bending the long-chain substrates. Additionally, a basic anion ligand bound to the zinc atom appeared to be important for high efficiency of the catalyst. Specifically, the optimized conditions employed weakly basic hexafluoroacethylacetonate (hfac). The resulting cooperative systems showed high performance toward 7-*exo-dig* cyclization with excellent functional group tolerance. A reaction mechanism was investigated by DFT calculations.



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2) (a) J. Francos, V. Cadierno, *Catalysts* **2017**, *7*, 328. (b) V. Cadierno, *Catalysts* **2020**, *10*, 1206.
3) V. K. Rawat, K. Higashida, M. Sawamura, *ACS.Catal.* **2022**, *12*, 8325.

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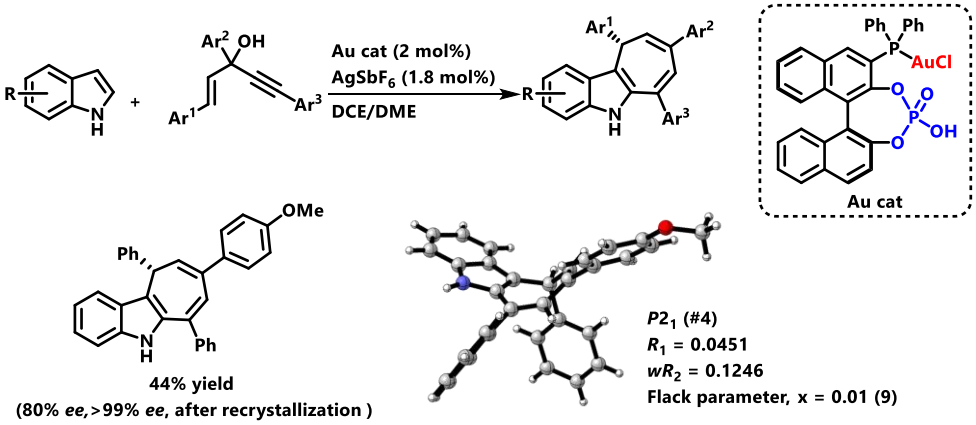
Chiral phosphoric acid-Au(I) hybrid complex catalyzed asymmetric synthesis of indole fused seven-membered ring compounds

([1]*Department of Chemistry, Graduate School of Science, Osaka Prefecture University*, [2]*Department of Chemistry, Graduate School of Science, Osaka Metropolitan University*)
○Naoya Taniguchi,[1] Mitsuhiro Ueda,[1,2] Kenichi Michigami,[1,2] Masato Ohashi[1,2]
Keywords: Asymmetric synthesis; Gold catalyst; Chiral phosphoric acid; Indole derivative

Au(I) complexes are well known as a useful catalyst for the construction of polycyclic compounds via cyclization triggered by the π-activation of alkynes. In the pharmaceutical science, the development of synthetic method of chiral polycyclic compounds is one of the important researches. In spite of the tremendous efforts to develop the Au(I)-catalyzed enantioselective cyclization reactions, the asymmetric activation of alkynes still represents a great challenge.

Recently, we developed an Au(I) complex bearing the hybrid phosphine ligand endowed with an acid-base bifunctional chiral phosphoric acid, and we found that the Au(I) complex showed the catalytic activity for the indole-fused seven-membered rings formation reaction[1)] with moderate enantioselectivity (up to 61% *ee*) [2)]. We herein report the recent progress in the chiral Au(I)-catalyzed asymmetric construction of indole fused seven-membered ring compounds, including the expansion of the scope and limitation of the substrates as well as the determination of the absolute configuration of the reaction product by means of X-ray diffraction study. In addition, the enantio-determining step in this reaction, inferred from density functional theory (DFT) calculations, will also be discussed.



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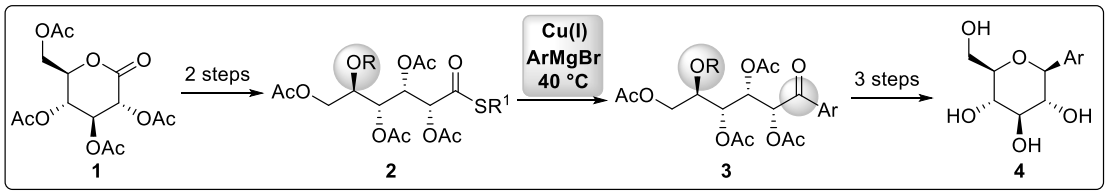
Synthesis of SGLT2 Inhibitors by Means of Copper-Mediated Coupling Reactions with Grignard Reagents

([1]*Graduate School of Pharmaceutical Science, Osaka University, Suita, Osaka 565-0871, Japan,* [2]*Marketting Group, Tokuyama Corporation, Tsukuba, Ibaraki 300-4247, Japan*) ○ Sandeep Rameshrao Tapkir,[1] N. Maheshwara Reddy,[1] Shaheen Kasim Mulani,[1] Masahiko Seki,[1,2] Kazushi Mashima[1]

Keywords: SGLT2 inhibitor; C-arylglycoside; C-glycosidation, diarylcuprate; Grignard reagent.

SGLT2 inhibitors such as canagliflozin (Invokana®), dapagliflozin (Farxiga®), and empagliflozin (Jardiance®) have received considerable attention as an anti-diabetes drug.[1] They have β-*C*-arylglycoside as the key structural motif. Several approaches have been devised especially for carbon−carbon bond formation to construct a β-*C*-arylglycoside skeleton. However, they suffer from drawbacks of such as need of cryogenic conditions, expensive and/or hazardous reagents and poor functional group compatibility which restricted their application to industrial large-scale production.[2] In our previous studies, improved synthesis of SGLT2 inhibitors based on ketone synthesis employing Grignard reagents and copper(I) salts has been reported.[3] Even though it can be conducted under mild reaction conditions, use of benzyl protecting group was a major drawback in terms of high cost and less atom economy for deprotection step.

To address the challenge, the present study was planned to use easily cleavable acetyl protected intermediates. Synthesis of acetyl protected thioester **2** was achieved by treatment of tetra-*O*-Ac-D-gluconolactone **1** with thiol and ^{i}PrMgCl. Then, compound **2** was treated with diarylcuprates generated in situ from copper(I) salts and aryl Grignard reagents to give ketone **3**. From **3**, deprotection, cyclization and silane reduction provided desired SGLT2 inhibitors **4**.



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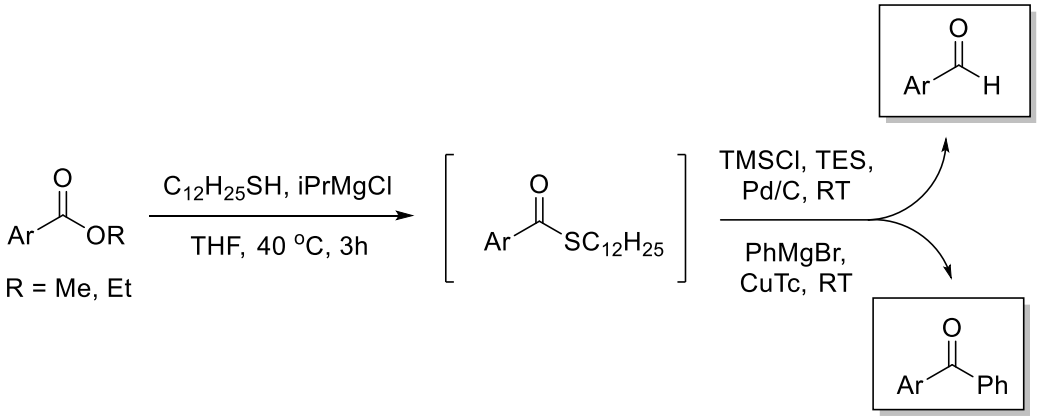
A Novel and General Method for Preparation of Thioesters: In Quest of Direct Conversion of Esters to Aldehydes and Ketones

([1]*Graduate School of Pharmaceutical Sciences, Osaka University*, [2]*Tokuyama Corporation*)
○Shaheen Kasim Mulani,[1] Akinari Uchibayashi,[1] Sandeep Ramesharao Tapkir, [1] N. Maheshwara Reddy,[1] Masahiko Seki[1,2] and Kazushi Mashima[1]

Thioesters are versatile and key intermediates for preparing various useful carbonyl compounds such as ketones, aldehydes, and so on. Although thioesters have been derived in various synthetic routes, we recently developed a new protocol by treating the corresponding esters with thiols in the presence of ^{i}PrMgCl.[1] Herein, we report a direct one pot conversions of esters to aldehydes and ketones: the reaction of the in situ generated thioesters with TMSCl (thiol scavenger) followed by reduction (triethylsilane and Pd/C) afforded the corresponding aldehydes,[2,3] while one pot reaction of the in situ generated thioesters with Grignard reagents and CuTC produced the corresponding ketones.



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

[K603-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Makoto Yamashita, Yoshiaki Shoji

Fri. Mar 24, 2023 9:00 AM - 10:50 AM K603 (K603, Lecture Hall Bldg. [6F])

[K603-3am-01] Substituents on Boron of Organoboron Complexes Modulates Luminescent Properties via Excited Triplet States

○Shunichiro Ito[1], Keisuke Suwa[1], Kazuo Tanaka[1], Yoshiki Chujo[1] (1. Kyoto University)

9:00 AM - 9:20 AM

[K603-3am-02] Reactivity of diborylcarbenoid and properties as an equivalent to diborylcarbene

○Yuki Shibutani[1], Shuhei Kusumoto[1], Kyoko Nozaki[1] (1. The University of Tokyo)

9:20 AM - 9:40 AM

[K603-3am-03] Near-infrared Emissive Properties and Their Stimuli-responsiveness of π-Conjugated Polymers Based on Flexible Boron Complexes

○Masashi Nakamura[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Graduate School of Engineering, Kyoto University)

9:40 AM - 10:00 AM

[K603-3am-04] Evaluation of Stimulus Responsiveness by Hypervalent Bismuth Compounds with π-Conjugated Scaffolds

○Kazuya Tanimura[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Grad. Sch. of Eng., Kyoto Univ.)

10:10 AM - 10:30 AM

[K603-3am-05] Novel Template Synthesis for Disilacycloalkanes Utilizing Reactivity of a Siloxane Bond

○Tu Yuyang[1], Inagaki Yusuke[1], Setaka Wataru[1] (1. Tokyo Metropolitan University)

10:30 AM - 10:50 AM

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Substituents on Boron of Organoboron Complexes Modulates Luminescent Properties via Excited Triplet States

(*Graduate School of Engineering, Kyoto University*) ○Shunichiro ITO, Keisuke SUWA, Kazuo TANAKA, Yoshiki CHUJO

Keywords: *Organoboron Complex; Phosphorescence; Delayed fluorescence; Solid-state emission*

Abstract

Organoboron complexes have attracted attention because of their electron-accepting character and remarkable luminescent properties. Recently, we have synthesized *β*-diketiminate boron complexes that exhibit functional luminescence in solid states. Furthermore, these boron complexes exhibit phosphorescence with long lifetime (~1 sec) at 77 K as well as fluorescence.[1] This fact indicates that the intersystem crossing from the singlet excited states to triplet ones is fast enough to compete with fluorescence. However, the detailed mechanism of such a fast intersystem crossing of this class of compounds is unclear. Herein, we demonstrate that substituents on their boron atom modulate their luminescent properties via excited triplet states, *i.e.* phosphorescence and delayed fluorescence. We will describe their synthesis and photophysical properties.

Results and Discussion

We synthesized boron complexes with different substituents at the boron center. The typical examples of the obtained compounds were shown in Figure 1. Interestingly, their photophysical properties highly depended on the substituents on the boron atom. Biphenyl-substituted complex **BBiph** exhibited room-temperature phosphorescence, while phenyl substituted one **BPh** showed thermally activated delayed fluorescence. Density functional theory calculations suggested that the intersystem crossing would occur between locally excited (LE) and charge transfer (CT) excited states. The relative location of the LE and CT states could be modulated by the substituents. We will describe the detailed mechanisms of these photoluminescence properties and demonstrate further functionalization of these complexes.

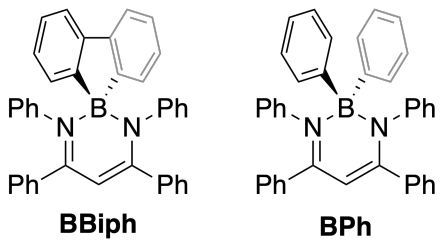

Figure 1. Chemical structures of synthesized organoboron complexes.

Reference

[1] (a) Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2014**, *136*, 18131; (b) Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2014**, *20*, 8320; (c) Yamaguchi, M.; Ito, S.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Mater. Chem. C* **2016**, *4*, 5314; (d) Ito, S.; Yaegashi, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, *27*, 9302.

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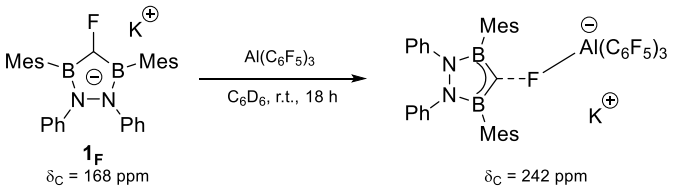
Reactivity of diborylcarbenoid and properties as an equivalent to diborylcarbene

([1]*Graduate School of Engineering, The University of Tokyo*) ○Yuki Shibutani[1], Shuhei Kusumoto[1], Kyoko Nozaki[1]

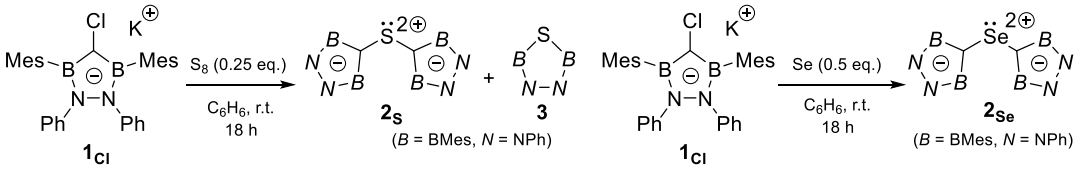
Keywords: Carbene, Diborylcarbene, Carbenoid, Chalcogen

Carbene is a neutral divalent carbon species possessing six valence electrons. Singlet carbene can exhibit both Lewis basicity and acidity. Looking at the chemistry of carbene, although various persistent carbenes have been studied, they are known to be strongly Lewis basic because they all have π-donating substituent(s) on the carbene carbon to stabilize the p-type vacant orbital. In a sharp contrast, diborylcarbene (DBC) where the carbene carbon is substituted by two boryl groups has long been discussed as a Lewis acidic carbene. However, its property has never been explored except for theoretical studies and trapping reactions.[1]

In this work, we synthesized K/X-diborylcarbenoids $\mathbf{1_X}$ (X = F, Cl) as stable equivalents to DBC, and studied their reactivities. When $\mathbf{1_F}$ reacted with $Al(C_6F_5)_3$ in benzene-d_6, the ^{13}C NMR chemical shift of the carbenoid carbon shifted from 168 ppm to 242 ppm (Scheme 1). ESI(+)-TOFMS spectrum of this reaction solution showed peaks corresponding to the DBC-proton or potassium cation adducts, which were not found in the absence of $Al(C_6F_5)_3$. These observations strongly suggest the interaction between aluminum atom and fluorine atom on the carbenoid carbon. We also examined the reactivity of synthesized diborylcarbenoid $\mathbf{1_{Cl}}$ toward elemental chalcogens (Scheme 2). When $\mathbf{1_{Cl}}$ reacted with elemental sulfur at ambient temperature in benzene, two kinds of products $\mathbf{2_S}$ and **3** were obtained. Both $\mathbf{2_S}$ and **3** were characterized by single crystal X-ray diffraction analysis. Reaction of $\mathbf{1_{Cl}}$ with elemental selenium also gave C–Ch–C type compound $\mathbf{2_{Se}}$.



Scheme 1. F atom abstraction from $\mathbf{1_F}$ with $Al(C_6F_5)_3$.



Scheme 2. Reactions of $\mathbf{1_{Cl}}$ with elemental chalcogens (S, Se).

[1] D. Bourissou, O. Guerret, F. P. Gabbai, and G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

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Near-infrared Emissive Properties and Their Stimuli-responsiveness of π-Conjugated Polymers Based on Flexible Boron Complexes

([1]*Graduate School of Engineering, Kyoto University*)
○Masashi Nakamura,[1] Masayuki Gon,[1] Kazuo Tanaka[1]

Keywords: Boron; Conjugated polymer; Near-infrared emission; Donor–Acceptor; Stimuli-responsiveness

The stimuli-responsive luminescent properties are useful as chemical sensors. Especially, near-infrared (NIR) light-emitting materials can be high-sensitive sensors because of the possibility to convert small energy changes into large wavelength ones. To endow some stimuli-responsiveness, one of the promising properties is aggregation-induced emission (AIE), proposed by Tang.[1)] AIE luminogens (AIEgens) exhibit no or weak emission in solution but become highly emissive in aggregation or solid state. Recently, turn-on type NIR AIEgens have reported.[2)] However, the wavelength changes were limited due to the twisted structures which isolated the fluorophores. On the other hand, we have developed novel AIEgen boron-fused azobenzene complexes. Unlike common AIEgens, the π-conjugated system can be expanded, and drastic fluorescence wavelength changes are expected. In contrast, the copolymer constructed by the boron complex and a strong donor unit showed NIR emission in solution while the fluorescence drastically weakened in film, which phenomenon is called aggregation-caused quenching (ACQ).[3)]

In this work, we successfully developed AIE-active NIR emissive π-conjugated polymer **P-Me-BT** by introducing methyl group at boron. Comparing with conventional ACQ polymer **P-F-BT**, their photophysical properties were evaluated (Figure 1). Furthermore, their temperature-responsive luminescent properties were clarified (Figure 2). As the temperature decreased, both polymers aggregated and exhibited different changes of emission wavelength and intensity reflecting the difference of AIE and ACQ properties.

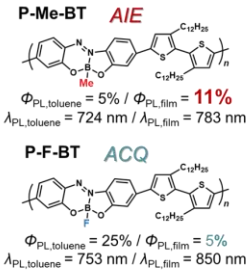

Figure 1. Chemical structures and photophysical properties of **P-Me-BT** and **P-F-BT**.

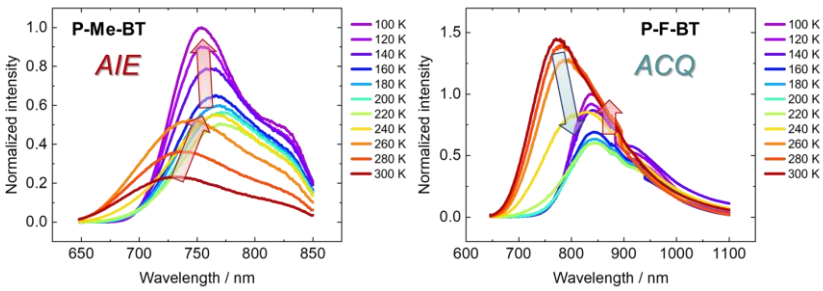

Figure 2. Variable temperature photoluminescence of **P-Me-BT** and **P-F-BT** in 2-methyltetrahydrofuran (1.0×10^{-5} M per repeating unit) at the condition from 300 to 100 K in 20 K increments, excited at wavelengths of absorption maxima.

1) Tang, B. Z. *et al. Chem. Commun.* **2001**, 1740. 2) Ding, D. and Tang, B. Z. *et al. J. Am. Chem. Soc.* **2020**, *142*, 15146. 3) Chujo, Y. *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 6546.

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Evaluation of Stimulus Responsiveness by Hypervalent Bismuth Compounds with π-Conjugated Scaffolds

(*Graduate School of Engineering, Kyoto University*)
○ Kazuya Tanimura, Masayuki Gon, Kazuo Tanaka

Keywords: Bismuth; Hypervalent state; Conjugated molecule; Stimulus responsiveness; Optical properties

Organic molecules have been widely used in the development of OLEDs and OPVs. Among them, π-conjugated molecules have attracted much attention due to their high stability, electrical conductivity, and unique optical properties. In addition, they have also been expected to develop the sensing function to visualize stimuli in various environments. Since the sensing function of such π-conjugated polymers is challenging to achieve with only a carbon skeleton, introducing heteroatoms is one of the effective strategies.

This research focuses on hypervalent states of heavy elements to develop new molecular designs and sensing functions for response to various environments. Bismuth, a group 15 element of period 6, has Lewis acidity. We created a new sensing material using the interaction of Lewis acidity with functional groups by combining hypervalent bismuth with π-conjugated molecules.

To investigate stimulus responsiveness, we synthesized bismuth compounds using azobenzene tridentate ligands (Figure 1). We focused on acid responsiveness. In **BiAz**, the absorption spectrum changed in response to the addition of trifluoroacetic acid (TFA) (Figure 2a), and then the addition of triethylamine (Et_3N) recovered its original state. The Lewis acidity of hypervalent bismuth causes it to interact with Lewis basic molecules and to change its interaction with π-conjugated scaffolds. It was found that the response was more acute after the addition of dimethyl sulfoxide (DMSO) than before (Figure 2b). In this presentation, we will discuss the detailed mechanism and evaluation of the response.

Figure 1. Hypervalent bismuth compounds, **BiAz** (R = Ph).

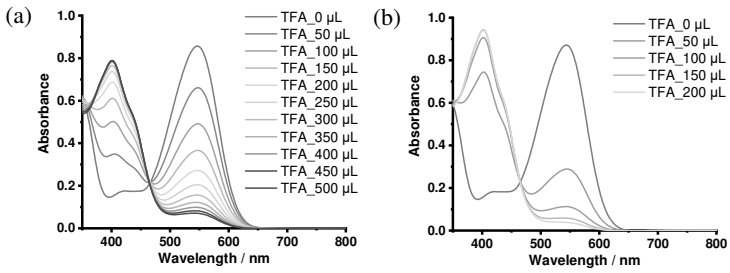

Figure 2. UV–vis absorption spectra of the mixtures containing (a) **BiAz** (5.0×10^{-5} M in THF), and (b) **BiAz** (5.0×10^{-5} M in THF/DMSO = 99/1 v/v) with each amount of TFA solution (1.0×10^{-3} M in THF).

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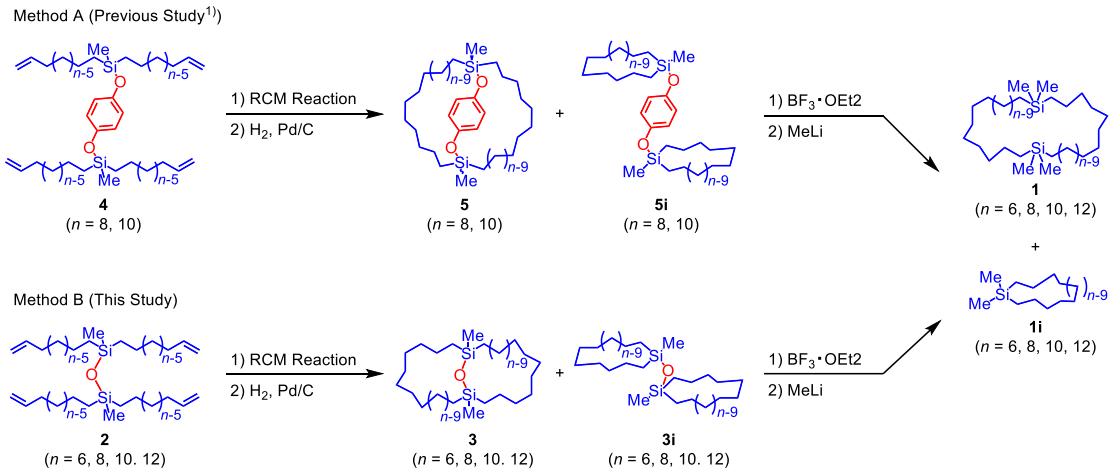
Novel Template Synthesis for Disilacycloalkanes Utilizing Reactivity of a Siloxane Bond

(*Graduate School of Urban Environmental Science, Tokyo Metropolitan University*)
○Yuyang Tu, Yusuke Inagaki, Wataru Setaka

Keywords: Macrocyclic compounds, Template Synthesis, Siloxane bonds, Ring-closing metathesis reactions, Silicon compounds

Macrocyclic compounds with flexible structures are generally much more difficult to synthesize than those with rigid structures. Previously, we reported the synthesis of two kinds of disilacycloalkanes **1**, starting from dihydroxybenzene templated compounds **4** with two different lengths of alkene chains **C8** and **C10** (Method A).[1] Their structures in both solution and solid-state were also discussed. However, there were three issues that make low yields of the target compounds **1**.[1] Intermediate compounds **5** and **5i** were easily decomposed because of the chemically liable Si-O bonds. Synthesis of a smaller size (**C6**) derivatives are difficult due to large size of the template. The selectivity of the ring-closing metathesis (RCM) reactions was particularly unsatisfactory making the yield of the disilacycloalkanes lower.

Herein, we developed a more efficient and selective method for the synthesis of disilacycloalkanes utilizing the reactivity of a siloxane bond (Method B). Particularly, this novel method showed high selectivity for desired cyclic compounds **3**. Also, siloxane-based compounds were extremely stable which make us successfully synthesize compound **1** with larger and smaller sizes (**C6** and **C12**). In this talk, the details of the synthesis and properties of the final compounds and intermediates will be discussed.



1) Tu, Y.; Inagaki, Y.; Kwon, E.; Setaka, W. *Chem. Lett.* **2021**, *50* (7), 1397–1399.

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

[K603-3pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Manabu Abe, Yutaka Ie

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K603 (K603, Lecture Hall Bldg. [6F])

[K603-3pm-01] Charge transporting properties of cationic diazulenomethenes

○Satoshi Takahashi[1], Masahito Murai[1], Yusuke Hattori[2], Shu Seki[2], Takeshi Yanai[1,3], Shigehiro Yamaguchi[1,3] （1. Nagoya University, Graduate School of Science, 2. Kyoto University, Graduate School of Engineering, 3. Nagoya University, ITbM）

1:10 PM - 1:30 PM

[K603-3pm-02] Development of Electroswitchable Organic π-Systems with Near-Infrared (NIR) Absorptions: Control of HOMO/LUMO Levels Based on Unique Structures

○Takashi Harimoto[1], Takanori Suzuki[2], Yusuke Ishigaki[2] （1. Graduate School of Chemical and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University）

1:30 PM - 1:50 PM

[K603-3pm-03] $S = 1$ Antiferromagnetic 1-D Heisenberg Chain of Verdazyl-Nitroxide Diradical with Long-Range Ordering and Haldane Gap

○Hodaka HAMAMOTO[1], Daiki SHIMIZU[1], Kenji MATSUDA[1] （1. Kyoto University）

1:50 PM - 2:10 PM

[K603-3pm-04] Quantum chemical evaluation of the effect of radical substituents on molecular open-shell characters and associated physical properties

○Tomohito Shinozuka[1], Daiki Shimizu[1], Kenji Matsuda[1] （1. Kyoto University）

2:10 PM - 2:30 PM

[K603-3pm-05] Synthesis and properties of Blatter radical oligomers showing spin-dependent photoexcitation behavior

○Daiki SHIMIZU[1], Takero AOKI[1], Kenji MATSUDA[1] （1. Graduate School of Engineering, Kyoto University）

2:40 PM - 3:00 PM

[K603-3pm-06] Stabilization by Cation-capped Orthogonal Approach: Isolation and Properties of a Series of Hydrocarbonic Dications with Multiple 14π-Aromatic Units

Yuki Hayashi[1], Shuichi Suzuki[2], Takanori Suzuki[1], ○Yusuke Ishigaki[1] （1. Faculty of Science, Hokkaido Univ., 2. Graduate School of Engineering Science, Osaka Univ.）

3:00 PM - 3:20 PM

[K603-3pm-07] 3D-shapted N-type organic semiconductors based on naphthothiophene diimide: synthesis and applications

○Masanori Sawamoto[1], Rukiya Matsidik[1], Takimiya Kazuo[1,2] （1. RIKEN, 2. Tohoku University）

3:20 PM - 3:40 PM

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Charge transporting properties of cationic diazulenomethenes

([1]*Graduate School of Science, Nagoya University*, [2]*Graduate School of Engineering, Kyoto University*, [3]*Institute of Transformative Bio-Molecules, Nagoya University*)
○Satoshi Takahashi,[1] Masahito Murai,[1] Yusuke Hattori,[2] Shu Seki,[2] Takeshi Yanai,[3] Shigehiro Yamaguchi,[1,3]

Keywords: Azulene; Sulfur; Cations; Charge-segregated accumulation; Charge-transporting properties

In ionic π-conjugated systems, the appropriate design of ion pair structures that enables controlling over intermolecular interactions would endow the π-skeleton with unusual properties. In particular, the charge-segregated assembly of cationic π-skeletons would be useful as a motif of n-type organic semiconductors. However, the charge-by-charge assembly is usually preferred to the charge-segregated assembly due to the sterically demanding peripheral substituents in the π-conjugated systems and electrostatic repulsion of charged species. We have recently reported that the diazulenylmethyl cations planarized with a silicon bridge were stable due to the effective charge delocalization and formed J-type aggregates to exhibit the near-infrared emissions up to 850 nm.[1)] In these molecules, the substituents on the silicon bridge disturb the largely overlapped π-stacking, resulting in the formation of a slipped off-set π-stacked arrangement. Herein, we synthesized a sulfur-bridged analogue of the diazulenylmethyl cations and investigated their optoelectronic properties of its condensed crystalline state. We envisioned that the replacement of the silicon with a sulfur would significantly alter the π-stacked arrangement to achieve charge-segregated columnar assembly.

Sulfur-bridged cationic diazulenomethene **1** with SbF_6^- as a counter anion formed charge-segregated assembly in the crystal packing (Figure 1a). The pair interaction energy decomposition analysis (PIEDA) revealed that the large stabilization in the dispersion term of the adjacent two molecules of $\mathbf{1}^+$ counteracts the disadvantage of the electrostatic term, and thereby the unusual charge-segregated assembly is achieved (Figure 1b). Reflecting the well-ordered assembled structure of **1** showed a high carrier mobility of 1.7 cm^2/Vs in the flash-photolysis time-resolved microwave conductivity (FP-TRMC) and photocurrent measurements (Figure 1c).

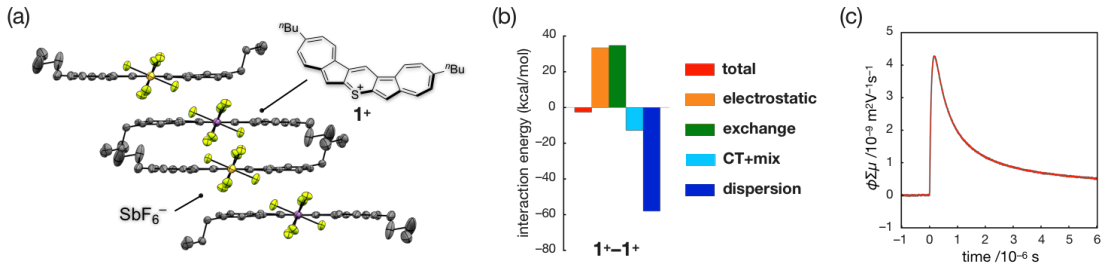

Figure 1. (a) Crystal structure of **1**, (b) PIEDA calculation results at the MP2/MCP-DZP level of theory, and (c) FP-TRMC transients of **1** upon the excitation at 355 nm pulse laser.

1) M. Murai, M. Abe, S. Ogi, S. Yamaguchi, *J. Am. Chem. Soc.* **2022**, *144*, 20385.

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Development of Electroswitchable Organic π-Systems with Near-Infrared (NIR) Absorptions: Control of HOMO/LUMO Levels Based on Unique Structures

([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Faculty of Science, Hokkaido University*) ○Takashi Harimoto,[1] Takanori Suzuki,[2] Yusuke Ishigaki[2]
Keywords: Redox System, NIR Absorption, Oligocation, Dyes and Pigments

Electrochromic systems capable of switching near-infrared (NIR) absorption are fascinating from the viewpoint of applications in the materials and life sciences, and thus the development of organic-based materials is needed to reduce the environmental impact and improve biocompatibility. Among such electrochromic systems, mono- and bisquinodimethane derivatives **1** and **2** with a folded form undergo one-stage multi-electron oxidation to produce twisted di- and tetracations with a planar acene skeleton. The HOMO of oligocations $\mathbf{1}^{2+}$ and $\mathbf{2}^{4+}$ is mainly located on the acene framework, and the corresponding LUMO is delocalized in peripheral diarylmethylium units. As a result, a NIR absorption band based on an intramolecular charge-transfer (CT) interaction from HOMO to LUMO was observed in these oligocationic dyes.[1,2] Therefore, controlling the HOMO and LUMO levels of oligocations is an effective approach for the precise modulation of longer-wavelength absorption in the NIR region.

Herein, we propose two different strategies for modulating frontier orbital levels: (i) a "π-extention strategy" that allows a red-shift of the NIR absorption band by elevating the HOMO levels of the acene core (Figure 1) and (ii) the "*ortho*-substitution strategy" that allows an enhancement of NIR-absorbing abilities by lowering the LUMO levels of the chromophores (Figure 2).[3] Under these strategies, we designed and synthesized various quinodimethane derivatives and demonstrated quantitative redox interconversion with diarylmethylium-type dyes exhibiting NIR absorption bands due to the narrower HOMO-LUMO gaps. Their properties were characterized by electrochemical, spectroscopic and theoretical studies, and the NIR absorption properties can be drastically changed by controlling the HOMO of the donor unit and the LUMO level of the acceptor unit.

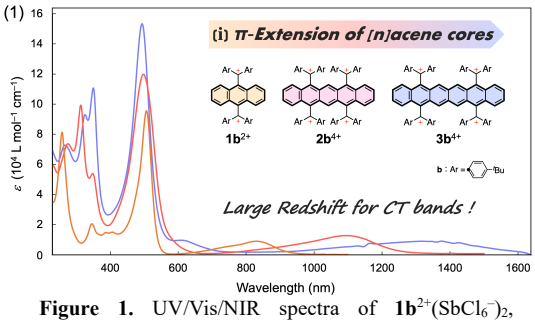

Figure 1. UV/Vis/NIR spectra of $\mathbf{1b}^{2+}(SbCl_6^-)_2$, $\mathbf{2b}^{4+}(SbCl_6^-)_4$, and $\mathbf{3b}^{4+}(SbCl_6^-)_4$ in CH_2Cl_2.

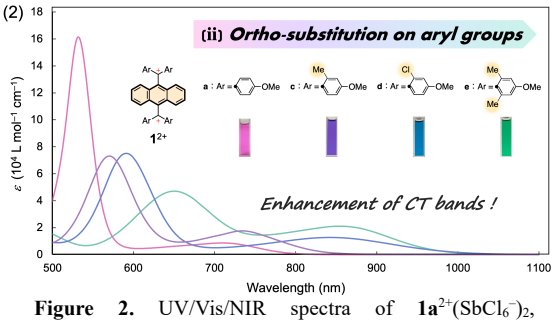

Figure 2. UV/Vis/NIR spectra of $\mathbf{1a}^{2+}(SbCl_6^-)_2$, $\mathbf{1c}^{2+}(SbCl_6^-)_2$, $\mathbf{1d}^{2+}(SbCl_6^-)_2$, and $\mathbf{1e}^{2+}(SbCl_6^-)_2$ in CH_2Cl_2.

1) Y. Ishigaki, K. Sugawara, T. Tadokoro, Y. Hayashi, T. Harimoto, T. Suzuki, *Chem. Commun.*, **2021**, 57, 7201. 2) Y. Ishigaki, T. Harimoto, K. Sugawara, T. Suzuki, *J. Am. Chem. Soc.* **2021**, *143*, 3306. 3) T. Harimoto, T. Suzuki, Y. Ishigaki, *Chem. Eur. J.* **2023**, *accepted*.

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S = 1 Antiferromagnetic 1-D Heisenberg Chain of Verdazyl-Nitroxide Diradical with Long-Range Ordering and Haldane Gap

(*Graduate School of Engineering, Kyoto University*) ○Hodaka HAMAMOTO, Daiki SHIMIZU, and Kenji MATSUDA

Keywords: 1-D antiferromagnetic chain; Organic diradical; Haldane gap; Canted antiferromagnet; Heisenberg chain

Low-dimensional magnetism has attracted interest in light of quantum phenomena that cannot be expected from the classical picture. As a representative example, Haldane predicted that the spin excitation behavior of 1-D antiferromagnetic (AFM) Heisenberg chains strongly depends on whether *S* is an integer. Namely, spin excitation occurs with an energy gap for an integer *S*, but it becomes gapless for a half-integer *S*.[1] Metal complexes have been used as models of *S* = 1 AFM Heisenberg systems, but large spin-orbit coupling often interferes with the quantum effect. Thus, organic compounds with smaller spin-orbit coupling are promising targets. However, only two organic diradicals are known to form *S* = 1 AFM Heisenberg chain,[2,3] and the existence of the Haldane gap was not confirmed.

Herein, we synthesized a new diradical, verdazyl-nitroxide diradical **1**, and studied its magnetic properties. Diradical **1** has a triplet ground state and small magnetic anisotropy ($|D/2J| = 5.5\times10^{-5}$). In the crystal, **1** was packed in a 1-D chain manner (Figure 1c). Diradical **1** showed strong intramolecular ferromagnetic interactions (J_F/k_B = 190 K) and weak intermolecular AFM interaction (J_{AF}/k_B = –2.8 K). The *M-H* curve of **1** showed a hysteresis between 0–200 Oe and a plateau between 200–4000 Oe. The narrow hysteresis is attributed to the spin canting through spin-orbit coupling, indicating the existence of long-range magnetic ordering. Furthermore, the plateau indicates the gapped spin excitation, which is the first confirmation of the Haldane gap in a purely organic crystal.

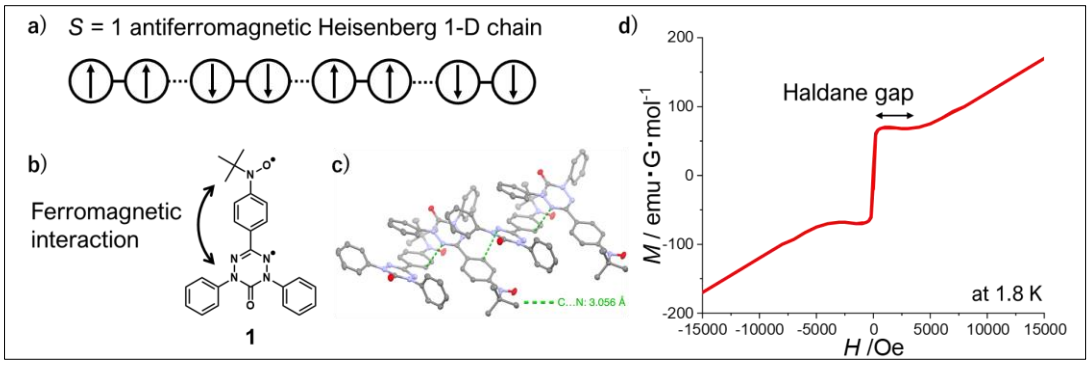

Figure 1. a) Schematic drawing of 1-D AFM Heisenberg Chain of *S* = 1 diradical, b) verdazyl-nitroxide diradical **1**, c) X-ray crystal structure of **1**, and d) *M-H* curve of **1**.

[1] F. D. M. Haldane, *Phys. Lett. A* **1983**, *93*, 464.

[2] A. Rajca, M. Takahashi, M. Pink, G. Spagnol, S. Rajca, *J. Am. Chem. Soc.* **2007**, *129*, 10159.

[3] W. Wang, C. Chen, C. Shu, S. Rajca, X. Wang, A. Rajca, *J. Am. Chem. Soc.* **2018**, *140*, 7820.

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Quantum chemical evaluation of the effect of radical substituents on molecular open-shell characters and associated physical properties

(*Graduate School of Engineering, Kyoto University*) Tomohito Shinozuka, Daiki Shimizu, Kenji Matsuda

Keywords: Open-shell character; Radical substituent; Quantum chemical calculation; Polycyclic aromatic hydrocarbon; Electron spin

Open-shell character *y* of a molecule correlates with its physical properties, such as singlet fission and nonlinear optical responses.[1] As guidelines for controlling *y*, donor-acceptor substitution, external electric field application, π-extension, and introduction of electron-rich heteroatoms have already been reported.[2,3] In this study, we investigated the effect of various radical substituents on *y*. We evaluated *y* by natural orbital occupation numbers of radical/non-radical substituted polycyclic aromatic hydrocarbons (PAHs) such as pentacene calculated at the LC-UBLYP/6-311G(d,p) level of theory. It was found that radical substituents significantly altered the *y* of PAHs compared to non-radical substituents. The calculated *y* of both radical/non-radical substituted PAHs was correlated to their HOMO–LUMO gaps. Non-radical substituents such as amino-, nitro-, and phenyl-substituted PAHs showed comparable H–L gaps. On the other hand, dicyanomethyl (DCM) substituted PAHs exhibited decreased *y* and increased H–L gap due to the interaction of the SOMO of the radical unit with the frontier orbitals of the PAHs. Contrarily, in the case of the nitronyl nitroxide (NN) substituted PAHs, the H–L gaps are narrowed by the interaction of the HOMO and LUMO of the radical (rather than SOMO) with the frontier orbitals of the PAHs, leading to the increased *y*. These results showcase the unique character of radical substituents for controlling the open-shell character *y* of PAHs. We will discuss the effect in detail from the viewpoint of the topology of molecular orbitals and also referring other properties, such as the spin-state energy gap.

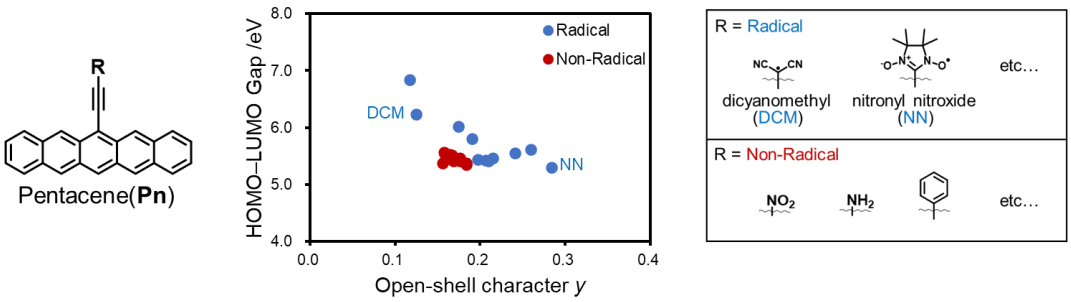

Fig. Correlation of open-shell character *y* and HOMO–LUMO gap of radical/non-radical substituted pentacenes (as an example of substituted PAHs)

1) M. Nakano *Chem. Rec.* **2017**, *17*, 27; 2) M. Nakano *et al. J. Phys. Chem. Lett.* **2011**, *2*, 1094;
3) M. M. Haley *et al. J. Phys. Org. Chem.* **2020**, *33*, 4114.

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スピン依存的な光励起挙動を示す Blatter ラジカル多量体の合成と物性

（京大院工）〇清水 大貴、青木 健朗、松田 建児

Synthesis and properties of Blatter radical oligomers showing spin-dependent photoexcitation behavior (*Graduate School of Engineering, Kyoto University*) Daiki Shimizu, Takero Aoki, Kenji Matsuda

We synthesized a triptycene-based Blatter radical dimer **1** (Fig. 1a). Magnetic measurement on **1** shows small singlet–triplet energy gap (ΔE_{ST}) of –3.0 kJ/mol, which leads to singlet/triplet population ratio of 1/1 at room temperature (Fig. 1b). Absorption spectra of **1** at room temperature exhibited characteristic NIR band which is absent for the corresponding monomer. TD-DFT calculation revealed that the NIR band was solely ascribed to **1** in the singlet state. Variable temperature study showed reinforcement of the NIR band as cooling to increasing singlet population (Fig. 1c). In this presentation, the origin of this spin-state dependent optical features and spin-selective excitation/excited-state dynamics will be discussed.
Keywords: Stable Radical, Electron Spin, Photochemistry, Excited-state Dynamics, Diradical

ジラジカル化合物は特異的に小さな一重項-三重項エネルギー差 (ΔE_{ST}) を示し、室温程度の熱で基底状態とは異なる励起スピン状態を生じることが知られている。しかし、熱エネルギー (k_BT = 2.5 kJ/mol at 298 K) 程度の相互作用では磁性以外に 2 つのスピン状態の物性に大きな違いを与えることはないと考えられてきた。実際に、小さな ΔE_{ST} を有する化合物では代表的な電子物性である吸収・発光スペクトルがほとんどスピン状態に依存しないことが報告されている。[1,2]

本研究では空間的に相互作用した Blatter ラジカル二量体 **1** を設計・合成した (Fig. 1a)。ジラジカル **1** は J/k_B = –180 K 程度の弱い相互作用を有しながら、スピン状態に大きく依存した吸収スペクトルを示すことを見出した(Fig. 1b,c)。これにより熱平衡状態で共存する２つのスピン状態の一方を選択的に光励起することが可能となる。本発表ではスピン状態と光学特性の相関を詳細に議論するほか、対応する三量体の合成と物性についても報告する。

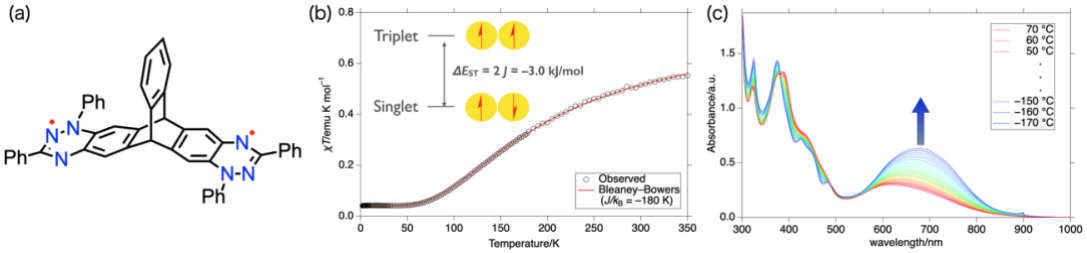

Fig. 1. (a) Structure of **1**. (b) χT–T curve of **1**. (c) VT-Absorption spectra on **1** in 2-MeTHF.

1) A. Konishi, T. Kubo *et al. J. Am. Chem. Soc.* **2013**, *135*, 1430.
2) J. Liu, S. Li, J. Huang, J. Zhang *et al. J. Am. Chem. Soc.* **2018**, *140*, 13719.

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カチオンキャッピングアプローチによる安定化：複数の 14π 芳香族ユニットから成る炭化水素ジカチオンの単離と性質

（北大院理 [1]・阪大院基礎工 [2]）林 裕貴 [1]・鈴木 修一 [2]・鈴木 孝紀 [1]・○石垣 侑祐 [1]
Stabilization by Cation-capped Orthogonal Approach: Isolation and Properties of a Series of Hydrocarbonic Dications with Multiple 14π-Aromatic Units ([1]*Faculty of Science, Hokkaido University*, [2]*Graduate School of Engineering Science, Osaka University*) Yuki Hayashi,[1] Shuichi Suzuki,[2] Takanori Suzuki,[1] ○Yusuke Ishigaki[1]

A series of six dications composed of pure hydrocarbons with one to six non-substituted 9,10-anthrylene units end-capped with two dibenzotropyliums were designed and synthesized to elucidate the electronic properties of huge oligo(9,10-anthrylene) backbones (Figure 1). Their structures were successfully determined by X-ray analyses even in the case of eight planar 14π-electron units, revealing that all dications adopt almost orthogonally twisted structures between neighboring units. Spectroscopic and voltammetric analyses show that neither the significant overlap of orbitals nor the delocalization of electrons between 14π-electron units occurs due to the orthogonally twisted geometry even in solution.
Keywords: Dibenzotropylium; Oligoanthrylene; Stimuli-Responsive Molecules; Dication; Biradical

本研究では，末端をジベンゾトロピリウムでキャッピングした一連のジカチオンを設計し，1～6 個の 9,10-アントリレンユニットを有する誘導体を合成した（図 1）。純粋な炭化水素から成るにもかかわらず，X 線結晶構造解析及び分光学的測定による調査が可能なほどにこれらのオリゴアントリレンは安定であり，一般的な有機溶媒に対し高い溶解性を示した。固体及び溶液の両状態において各 14π 芳香族ユニットは直交した構造をとることを見出し，これによりユニット間の電子的相互作用がほとんどないことが示された。その結果，さらなる酸化により多価カチオンの可逆的な形成が可能となり，アントリレンユニットと同じ数の電子の放出に対応する酸化過程が観測され，オリゴアントリレンの電子的特性を初めて明らかにした。さらに，二電子還元によって生じたビラジカルとキノジメタン構造の熱力学的安定性がユニット数に応じて異なるため，アントリレンの数によって応答挙動を変調可能なことを見出した[1]。

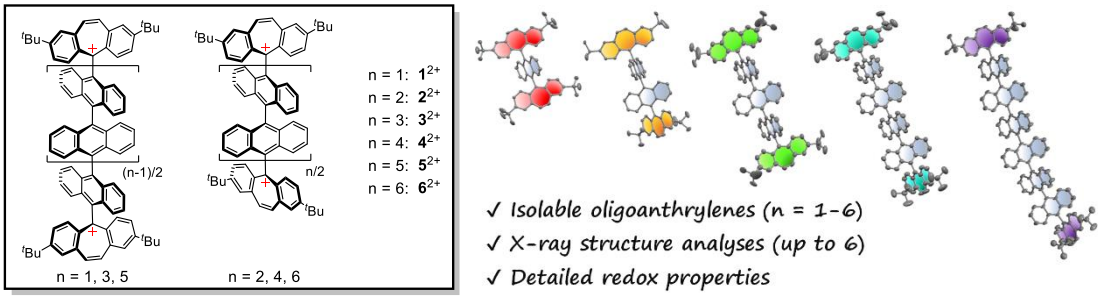

Figure 1. 本研究により新たに単離したオリゴアントリレン誘導体 $\mathbf{1}^{2+}$–$\mathbf{6}^{2+}$ と X 線構造

[1] Y. Hayashi, S. Suzuki, T. Suzuki, Y. Ishigaki,* *J. Am. Chem. Soc.* **2023**, *in press*. [DOI: 10.1021/jacs.2c12574]

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3D-shaped N-type organic semiconductors based on naphthothiophene diimide: synthesis and applications

([1]*RIKEN CEMS*, [2]*Graduate School of Science, Tohoku University*)
○Masanori Sawamoto,[1] Rukiya Matsidik,[1] Kazuo Takimiya,[1,2]

Keywords: 3D-shaped organic semiconductor, Naphthothiophene diimide (NTI), Transistor, Solar cell, Thermoelectric device

Naphthothiophene diimide (NTI), originally developed as an n-type organic semiconductor,[1)] can be utilized as terminal building units for developing n-type organic semiconductors with low-lying LUMO energy levels. Such NTI-based materials were useful as the n-type organic semiconductors in field-effect transistor (OFET) and photovoltaic (OPV) devices.[2)] We also recently found that the direct arylation reaction can proceed at the thiophene α-position of the NTI unit, which allows us to readily introduce the NTI unit on various π-conjugated frameworks.[3)] By taking advantage of these features of the NTI unit, we designed novel multi-NTI n-type organic semiconductors with three-dimensional (3D) molecular shapes; in this study, a molecule with six NTI units on a benzene ring (NTI6, **Figure 1**) is featured, and its physicochemical properties and applications in OFET and OPV devices are reported.

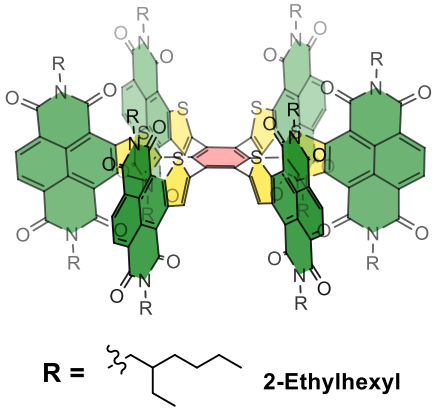

Figure 1. The structure of NTI6.

The OFET devices fabricated by the solution process showed decent n-channel FET behaviors, and the mobility extracted from the saturation regime was up to 1.9×10^{-2} cm^2/V s (**Figure 2a**). NTI6 also acted as the accepter molecule in the OPV devices combined with PCE10 as the donor material, affording a power conversion efficiency of up to 7.4% (**Figure 2b**). These results indicate that the present molecular design strategy, 3D-shaped NTI molecules, is promising for developing solution-processable novel n-type organic semiconductors.

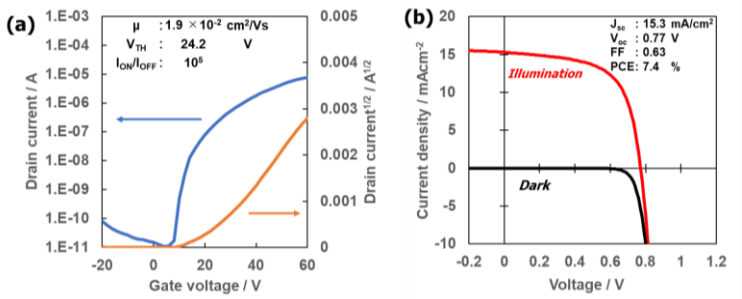

Figure 2. Results of OFET(a) and OPV(b) using NTI6.

1) W. Chen, *et al., J. Mater. Chem.* C, **2016**, *4*, 8879. 2) J. Hamonnet, *et al.*, *Chem. Mater.*, **2017**, *29*, 9618. 3) R. Matsidik, *et al.*, *Chem. Asian J.* **2019**, *14*, 1651.

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

[K606-3am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Hiroshi Katagiri, Shotaro Hayashi

Fri. Mar 24, 2023 9:00 AM - 11:40 AM K606 (K606, Lecture Hall Bldg. [6F])

[K606-3am-01] Photo-Induced Crawling Motion of Azobenzene Crystals on a Liquid-Like Surface and its Application for Object Transportation

○Makoto Saikawa[1,2], Mio Ohnuma[2], Yoshihiro Kikkawa[2], Kengo Manabe[2], Koichiro Saito[2], Yasuo Norikane[2,1] (1. Univ. of Tsukuba, 2. AIST)

9:00 AM - 9:20 AM

[K606-3am-02] Polymorphism Driven Photosalient Effect in Tetra-*ortho*-Bromo Azobenzene

○Keegan McGehee[1,2], Dennis Kwaria[1,2], Koichiro Saito[2], Rie Haruki[3], Shunsuke Nozawa[3], Ryo Fukaya[3], Yasuo Norikane[2,1] (1. Graduate School of Pure and Applied Science, University of Tsukuba, 2. Research Institute for Advanced Electronics and Photonics, National Institute of Advanced Industrial Science and Technology, 3. High Energy Accelerator Research Organization)

9:20 AM - 9:40 AM

[K606-3am-03] Reversible crystal stretching behavior of azobenzene with long alkoxy chains by thermal phase transition

○MINGHAO GAO[1,2], Dennis Kwaria[1,2], Hiroyuki Minamikawa[2], Yasuo Norikane[2,1] (1. University of Tsukuba, 2. AIST)

9:40 AM - 10:00 AM

[K606-3am-04] Machine-learning-based material design and condition optimization of generating higher force of photomechanical crystals

○Kazuki Ishizaki[1], Toru ASAHI[1], Takuya TANIGUCHI[1] (1. Waseda University)

10:00 AM - 10:20 AM

[K606-3am-05] Mechanochromic fluorescence properties and supramolecular structural changes exhibited by amphiphilic molecules with anthracene moieties

○QIMING LIU[1], yoshimitsu sagara[1] (1. Tokyo Institute of Technology)

10:20 AM - 10:40 AM

[K606-3am-06] Supramolecular polymer/supramolecular polymer transformation based on kinetic control and an external stimulus~Extended to Stacked forms

○Sukyeong Kim[1], Yusuke Kuramochi[1], Akiharu Satake[1] (1. Grad. Sch. of Sci., Tokyo Univ. of Sci.)

10:40 AM - 11:00 AM

[K606-3am-07] Organogel Actuators Consisting of Redox-Responsive Foldamers

○Taichi Ikeda[1] (1. National Institute for Materials Science)

11:00 AM - 11:20 AM

[K606-3am-08] High-Speed Actuation of Solvent Green 3 Crystals by Photothermally Induced Natural Vibration

○Shodai Hasebe[1], Yuki Hagiwara[1], Taiki Goto[1], Toru Asahi[1], Hideko Koshima[1] (1.

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Waseda Univ)
11:20 AM - 11:40 AM

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Photo-Induced Crawling Motion of Azobenzene Crystals on a Liquid-Like Surface and its Application for Object Transportation

([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*National Institute of Advanced Industrial Science and Technology (AIST)*) ○Makoto Saikawa,[1,2] Mio Ohnuma,[2] Yoshihiro Kikkawa,[2] Kengo Manabe,[2] Koichiro Saito,[2] Yasuo Norikane[2,1]

Keywords: Azobenzene; Organic Crystal; Crystal Crawling; Contact Angle Hysteresis; Object Transportation

Light is an attractive external stimulus for manipulating a motion of a material due to its non-contact and environmentally friendly features. A crystal of 3,3'-dimethylazobenzene (3,3'-DMAB, Fig. 1a) shows photo-induced crawling motion by simultaneous irradiation of UV and visible lights on solid surfaces.[1] Here we wish to report that the crystal crawls faster with maintaining its droplet-like shape. This motion can be achieved on a liquid-like surface, where a glass surface is functionalized by a mixture of alkyltrimethoxysilane and tetramethoxysilane.[2] In addition, it was found that the velocity and its shape were dependent on the irradiation intensity and the temperature of substrate. For example, upon strong visible light irradiation, the velocity was smaller than when the intensity of the visible light was much lower, and its shape deformed while crawling (Fig. 1b).

These crystals were expected to take up objects inside and carry them as they moved because the crawling motion was accompanied by liquefaction of the crystal. Monodisperse and spherical silica particles with a particle size of 2, 5, 10, and 20 μm were employed as the objects, respectively. For the particles up to 10 μm in diameter, it was successfully demonstrated that crystals picked up and transported them on the liquid-like surface (Fig. 1c). Furthermore, no significant deformation of its droplet-like shape was observed during transportation. The liquid-like surface is more suitable than the hydrophilic one for object transportation. In this presentation, we will discuss the notable crawling motion on the liquid-like surface and its application as a photo-controllable carriage vehicle in detail.

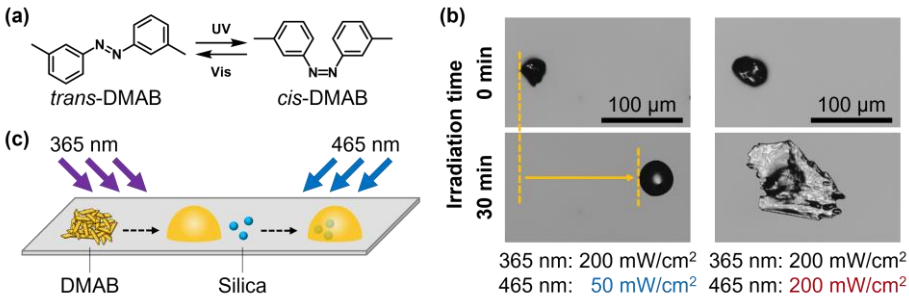

Figure 1. (a) Chemical structure of 3,3'-DMAB, (b) Photomicrographs of the crawling motion at different irradiation intensities, and (c) Schematic illustration of the crawling and object transportation.

1) E. Uchida, R. Azumi, Y. Norikane, *Nat. Commun.* **2015**, *6*, 7310. 2) C. Urata, B. Masheder, D. F. Cheng, A. Hozumi, *Langmuir.* **2012**, *28*, 17681.

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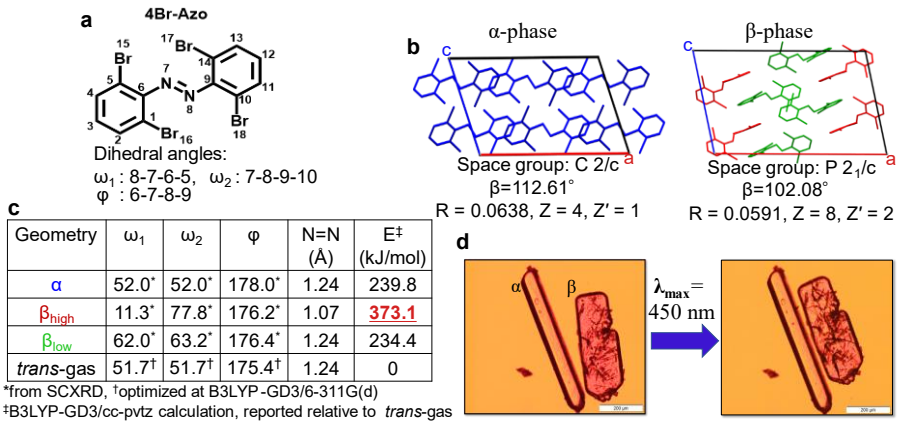
Polymorphism Driven Photosalient Effect in Tetra-*ortho*-Bromo Azobenzene

([1] *Graduate School of Science and Technology, University of Tsukuba,* [2]*National Institute of Advanced Industrial Science and Technology (AIST),* [3]*High Energy Accelerator Research Organization* (KEK)) ○Keegan McGehee[1,2], Dennis Kwaria[1,2], Koichiro Saito[2], Rie Haruki[3], Shunsuke Nozawa[3], Ryo Fukaya[3], Yasuo Norikane[2,1]

Keywords: Photomechanical Behavior, Crystal Polymorphism, X-ray Diffraction, Density Functional Theory, Azobenzene

The photosalient effect is a unique photomechanical response that is characterized by the rapid jumping motion of a crystal upon photoirradation[1]. We present here the first observation, to the best of our knowledge, of a photosalient azobenzene derivative, tetra-*ortho*-bromo azobenzene (4Br-Azo). This is an effect that is unique to one of two isolated polymorphic phases of *trans* 4Br-Azo (**Fig. 1**). The β-phase was found to exhibit cracking followed by rapid breaking and jumping when exposed to light from a filtered Hg lamp. Unlike many photomechanical crystal systems[2,3], triggering this behavior was found to be more dependent on the intensity of the light than the irradiation wavelength. In comparison to the photosalient β-phase, the α-phase of 4Br-Azo macroscopically appears to be inert to light. Thus, the precise molecular properties leading to the different light responses of these crystals is of great interest.

By analyzing data from differential scanning calorimetry (DSC), Raman, absorption spectroscopy, x-ray diffraction (XRD), and density functional theory (DFT), it was revealed that a relative instability of the β-phase due to the presence of a highly strained molecular conformation (**Fig. 1 b,c**) is the key factor to the photosalient effect of this phase. By presenting the results of this investigation, a detailed look at the molecular properties of 4Br-Azo will be shared. In addition, the proposed mechanism of the photosalient effect in this system will be discussed.



Geometry	ω_1	ω_2	φ	N=N (Å)	E‡ (kJ/mol)
α	52.0°	52.0°	178.0°	1.24	239.8
β_{high}	11.3°	77.8°	176.2°	1.07	373.1
β_{low}	62.0°	63.2°	176.4°	1.24	234.4
trans-gas	51.7†	51.7†	175.4†	1.24	0

*from SCXRD, †optimized at B3LYP-GD3/6-311G(d)
‡B3LYP-GD3/cc-pvtz calculation, reported relative to *trans*-gas

Fig. 1. a) Molecular structure of 4Br-Azo. b) Unit cells of the two 4Br-Azo phases, (010) face up. Hydrogens omitted for clarity. Colored by molecular symmetry. c) Table comparing 4Br-Azo *trans* geometries. d) Microscope image of the two types of crystals before and after irradiation. Scale bars 200 μm.

1) P. Naumov, *et al*. *Angew. Chem. Int. Ed.*, **2013**, *52*, 9990-9995. 2) E. Uchida *et al*. *Nat. Commun.* **2015**, *6*, 7310. 3) P. Naumov *et al*. *J. Am. Chem. Soc*. **2020**, *142*, 13256−13272.

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長鎖アルコキシ基を持つアゾベンゼン結晶の熱相転移による可逆伸縮挙動

（筑波大 [1]・産総研 [2]）○高 明昊 [1,2]・Dennis Kwaria[1,2]・南川 博之 [2]・則包 恭央 [2,1]

Reversible crystal stretching behavior of azobenzene with long alkoxy chains by thermal phase transition

([1]*University of Tsukuba*, [2]*AIST*) ○Minghao Gao[1,2], Dennis Kwaria[1,2], Hiroyuki Minamikawa[2], Yasuo Norikane[2,1]

Thermal- and photo-induced mechanical motion of organic crystals are expected to be used in optical devices and actuators. Here, a reversible stretching behavior in crystals of 4,4'-bis(dodecyloxy)-3,3'-dimethylazobenzene (**1**) was newly found (**Fig. 1**). The compound **1** was synthesized according to the literature.[1] The crystal shows thermal crystal-to-crystal phase transition around 58°C and prominent size change at around 9% in long axis (**Fig. 1**). By measuring differential scanning calorimetry (DSC), single crystal X-ray, and powder X-ray diffraction (p-XRD), structure and thermodynamic properties were elucidated (**Fig. 2**). We will discuss the stretching mechanism of the crystal. In addition, controlling the stretching behavior by visible light irradiation will be demonstrated as actuators and stimuli responsive soft robots.

Keywords : azobenzene crystal, mechanical motion, thermal phase transition, photomechanical effect, single crystal structure analysis

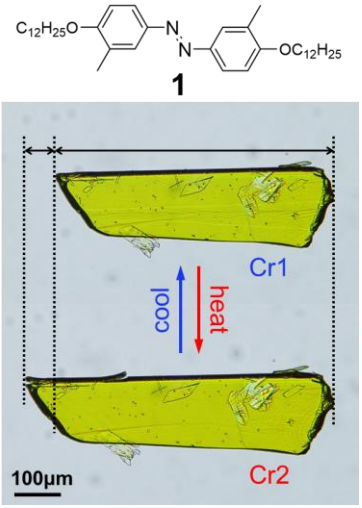

Fig. 1 Chemical structure and crystal stretching of **1**.

有機結晶において熱や光刺激で機械的な運動が誘起されることが知られている。本研究では、4,4'-ビス(ドデシルオキシ)-3,3'-ジメチルアゾベンゼン(**1**)の結晶において、可逆的な伸縮挙動を見出したので報告する。**1** は文献 [1] に従って合成した。この結晶は、加熱時に 58℃付近で結晶－結晶相転移を示し、相転移に伴って長軸方向に約 9 %伸長する(**Fig. 1**)。示差走査熱量測定、単結晶 X 線、粉末 X 線回折を測定することにより、構造と力学特性の関連を検討し、結晶の伸縮メカニズムについて議論する予定である(**Fig. 2**)。

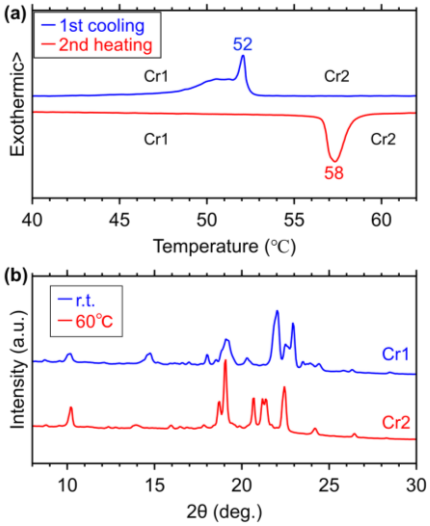

Fig. 2 (a) DSC curves and (b) p-XRD profile of **1** at room temperature and 60°C.

1) Uchida, E., Sakaki, K., Nakamura, Y., Azumi, R., Hirai, Y., Akiyama, H., Yoshida, M., Norikane, Y., *Chem. Eur. J.* **2013**, 19, 17391-17397.

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Machine-learning-based material design and condition optimization of generating higher force of photomechanical crystals

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*Center for Data Science, Waseda University*) ○Kazuki Ishizaki,[1] Toru Asahi,[1] Takuya Taniguchi[2]

Keywords: Generating force; Photomechanical crystal; Machine learning; Young's modulus

Photomechanical crystals show macroscopic motion under UV light irradiation. In our previous work, the generated force of the photomechanical salicylideneamine crystals was about 8.7 mN even under optimal conditions.[1] It is necessary to search a wide range of conditions to find the optimum conditions to increase generating force. In this study, photomechanical crystals with various Young's modulus were fabricated based on material design guidelines obtained by LASSO regression, and then conditions achieving larger generating force were explored by Bayesian optimization.

In material design, we prepared dataset including molecular structures and Young's modulus by manually collecting data from papers. LASSO regression was conducted to identify substituents correlated with Young's modulus (Fig. 1a). After fabricating some crystals, the conditions for larger generating force were searched using Bayesian optimization. Bayesian optimization suggests the next experimental conditions based on the value of the acquisition function calculated by the predictions and the uncertainty of the predictions. Generating force F was measured under the condition of the Young's modulus E, crystal size S, and light intensity I presented by Bayesian optimization (Fig. 1b). Because it is easier to change the light intensity (I) than to change the crystal samples (E, S), the optimization of the light intensity (I) was performed without changing the crystal samples (E, S). In this research, a quadratic function was optimized to find the suitable intensity which affords maximum force of a specific crystal. After optimizing the irradiation intensity (I) for a particular crystal sample (E, S), we performed the same operation for the other crystal samples (E, S) presented by Bayesian optimization (Fig. 1b).

(a)

Functional group	Coefficient of Lasso regression
Hydroxy group	1.394
Nitro group	1.013
Halogen	-0.307
Benzene ring	-1.628

(b)

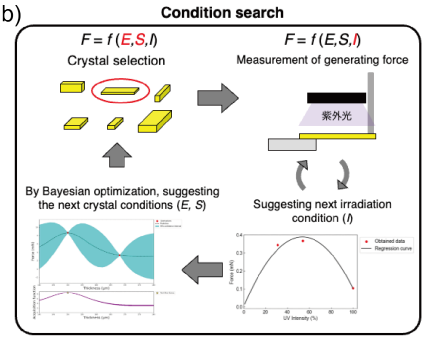

Figure1. (a) Molecular design by LASSO regression. (b) Optimization process of experimental conditions.

1) K. Ishizaki, R. Sugimoto, Y. Hagiwara, H. Koshima, T. Taniguchi, T. Asahi, *CrystEngComm,* **2021**, 23, 5839-5847.

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アントラセン部位を持つ両親媒性分子が示すメカノクロミック蛍光特性と超分子構造変化

（東工大物質理工 [1]）○QIMING LIU[1]・相良 剛光 [1]

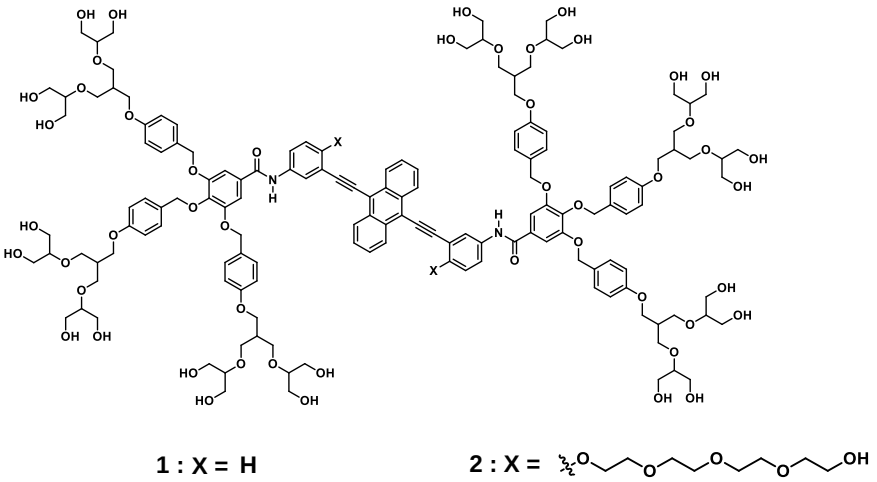
Mechanochromic fluorescence properties and supramolecular structural changes exhibited by amphiphilic molecules with anthracene moieties

([1]*Department of Materials Science and Engineering, Tokyo Institute of Technology*) ○QIMING LIU,[1] Yoshimitsu Sagara[1]

In recent years, mechanochromic materials whose fluorescence properties change due to alteration in their molecular assembled structures induced by mechanical stimuli have been extensively studied.[1,2] In this research, we aim to develop mechanochromic luminescent supramolecular fibers which can show high sensitivity to mechanical stimuli and exhibit clear fluorescence color changes. Specifically, we designed and synthesized two amphiphilic molecules with anthracene moieties. Both amphipathic molecules form supramolecular fibers and show mechanochromic fluorescence. These mechanochromic fluorescence properties are caused by changes in the molecular assembled structure induced by mechanical stimuli.

Keywords : Mechanochromic luminescence; Supramolecular fiber; AFM; Fluorescence

近年、機械的な刺激によって、分子集合構造が変化し、蛍光特性が変化するメカノクロミック材料が盛んに研究されている[1,2]。本研究では、より実用的なメカノセンサーへの応用を目的として、機械的な刺激に対する感度を大きく向上させ、大きな蛍光色変化を示すメカノクロミック超分子ファイバーの開発を目指した。具体的には、二つのアントラセン部位を持つ両親媒性分子を設計・合成した。二つの両親媒性分子はともに複数の超分子構造を形成することが観察され、また、メカノクロミック蛍光特性を示すことが確認できた。このメカノクロミック蛍光特性は、力によって分子集合構造が変化することが原因である。



1) Y. Sagara, S. Yamane, M. Mitani, C. Weder, T. Kato, *Adv. Mater.* **2016**, *28*, 1073.
2) Y. Sagara, T. Komatsu, T. Ueno, K. Hanaoka, T. Kato, T. Nagano, *J. Am. Chem. Soc.* **2014**, *136*, 4273.

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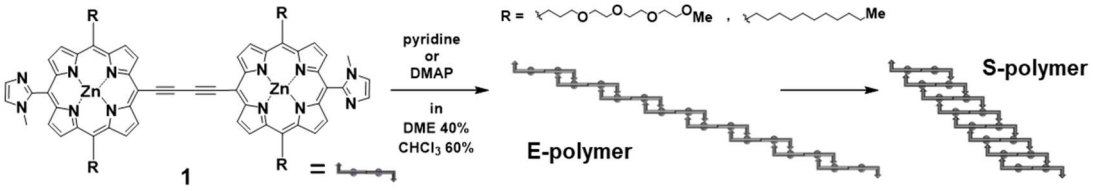
速度支配と刺激誘導を鍵とした超分子ポリマー／超分子ポリマー変換～伸長型から重なり型ポリマーへ

（東理大院理）○金 淑瑛・倉持 悠輔・佐竹 彰治

Supramolecular Polymer/Supramolecular Polymer Transformation Based on Kinetic Control and an External Stimulus～Extended to Stacked Forms (*Graduate School of Science, Tokyo University of Science*) ○Sukyeong Kim, Yusuke Kuramochi, Akiharu Satake

Supramolecular polymers are smart nanomaterials that can change their structures and functions, but the problem is how to express the structures and functions at the desired timing. We have found a unique system in which zinc porphyrin **1** interconverts between E-polymer (**E**) and S-polymer (**S**) by changing the solvent composition. In this method, the **E**/**S** ratio was thermodynamically controlled by changing the solvent composition. In this study, the transformation from **E** to **S** was controlled without changing the solvent composition. We added **1** with pyridine-ligand to a solvent system in which the **S** was dominant. Then, **E** was immediately formed under kinetic control. The **E** was converted gradually for 20min into **S** without passing through the monomer. When DMAP was used instead of pyridine, more stable **E** was formed. The **E** was immediately transformed into **S** by adding acetic acid.
Keywords : Kinetic control; non-bonding interaction; supramolecular polymer; coordination isomers; porphyrin

超分子ポリマーは環境に応じて構造と機能を変えることができるスマートナノ材料であり、どのようにして望みのタイミングで超分子構造と機能を発現させるかが課題となっている。我々は良・貧溶媒組成の変化によって亜鉛ポルフィリン **1** が伸長型(以下、E-poly)と重なり型配位超分子ポリマー (以下、S-poly)の間で相互変換するユニークな系を見出している。[1] この方法は溶媒組成を変更することによって熱力学的に E/S-poly 比を制御しているといえる。本研究では溶媒組成を変えずに E/S-poly 変換の制御を行うため、本来 S-poly が熱力学的に安定な溶媒組成において E-poly を速度論的に形成させ、任意のタイミングで S-poly への変換を開始できるような系の開発に取組んだ。その結果、**1** とピリジンを混合した溶液を 1,2-dimethoxyethane /$CHCl_3$=40/60 v/v%に添加すると E-poly が速度論的に形成することを見出した。引き続き経時変化を UV－vis スペクトルで観測するとモノマーを経由せずに熱力学的に安定な S-poly へ変化した。窒素リガンドの種類を変化させて E/S-poly 変換の初期速度を比べると亜鉛ポルフィリンとの結合定数が大きいものほど変換速度が低下することが分かった。4-(dimethylamino)pyridine (DMAP)を用いると、速度論的に E-poly が形成し、この系に酢酸を添加すると DMAP との酸塩基反応により速やかに S-poly の形成を開始できることを見出した。さらにこの E/S-poly 変換が見かけ上の 1 超分子内反応が可能であることを実証するための低濃度のマイクロ流路中での変換も行った。



[1] A. Satake, *et al.*, *Chem.Eur.J.*, **2018**, *24*, 14733.

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レドックス応答性フォルダマーからなる有機ゲルアクチュエータ

（物材機構 [1]）〇池田 太一 [1]

Organogel Actuators Consisting of Redox-Responsive Foldamers ([1]*Research Center for Functional Materials, National Institute for Materials Science*) 〇Taichi Ikeda[1]

The foldamers consisting of the alternatively connected tetrathiafulvalene (TTF, electron donor unit) and viologen (V^{2+}, electron acceptor unit) though ethylene oxide spacers were synthesized. Those foldamers showed the conformation change between the folded and extended states in response to the redox stimuli. Thermodynamic properties in the folding process and the conformation change in response to the external stimuli were analyzed.[1)] The organogel consisting of the stimuli-responsive foldamers were prepared through catalyst-free azide-alkyne cycloaddition reaction between azide-terminated foldamer and tetra-alkyne ester crosslinker. That organogel exhibited the volume change in response to the redox stimulus, and the actuation force during the contraction process was successfully measured.[2)]

Keywords: Foldamer; Stimuli-responsive materials; Gels; Supramolecular Chemistry; Actuators

テトラチアフルバレン(TTF, 電子供与性ユニット)とビオロゲン(V^{2+}, 電子受容性ユニット)がスペーサーを介して交互に連結されたフォルダマーを合成した．このフォルダマーは折りたたみ状態・伸びきり状態の間のコンホメーション変化をレドックス刺激により制御できる．折りたたみ反応の熱力学的特性や外部刺激によるコンホメーション変化を解析した.[1)] アジド基末端のフォルダマーとアルキンエステルを４つ有する架橋剤の間の無触媒アジド-アルキン環化付加反応によりフォルダマーをゲル網目に組み込んだ有機ゲルを作成した．得られたゲルはレドックス刺激に応じた体積変化を示し、収縮時のアクチュエーション力を測定することに成功した.[2)]

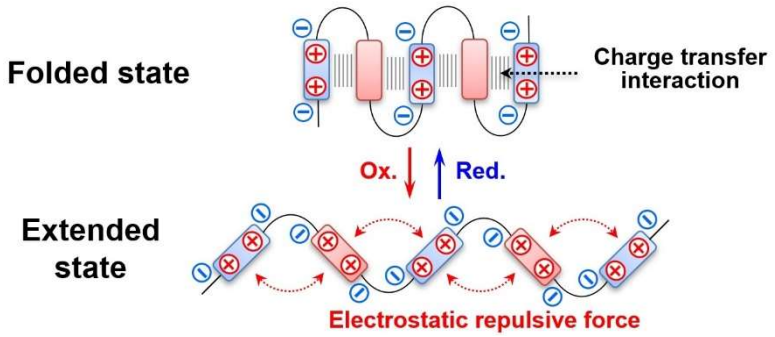

Figure. Schematic illustration of redox-responsive foldamer and its conformation change

References: 1) T. Ikeda, W. Nakanishi *Mater. Today Chem.* **24**, 100863 (2022)
2) T. Ikeda *ACS Appl. Polym. Mater.* Accepted.

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High-Speed Actuation of Solvent Green 3 Crystals by Photothermally Induced Natural Vibration

([1]*Graduate School of Advanced Science and Engineering, Waseda University,* [2]*School of Advanced Science and Engineering, Waseda University,* [3]*Research Organization for Nano & Life Innovation, Waseda University*) ○Shodai Hasebe,[1] Yuki Hagiwara,[1] Taiki Goto,[2] Toru Asahi,[1,2,3] Hideko Koshima[3]

Keywords: Natural Vibration; Photothermal Effect; Crystal Actuation; Solvent Green 3

Mechanically responsive organic materials have attracted much attention in both basic research and applications to smart actuators and soft robots.[1] We have developed many light-driven mechanical crystals (*photomechanical crystals*) over the past decade, mainly based on photoisomerization.[2,3] Recently, we reported 25 Hz high-speed bending induced by the photothermal effect—a physical phenomenon by which thermal energy (heat) is generated through nonradiative deactivation of the photoexcited state.[4] We then elucidated the bending mechanism that a nonsteady temperature gradient in the thickness direction causes photothermal-driven bending, ultimately achieving 500 Hz high-speed bending.[5] Here we report high-speed and large bending of solvent green 3 (**1**) crystals (Figure 1a) by natural vibration induced by the photothermal effect.

When a needle-shaped crystal of **1** was exposed with an ultraviolet (UV) laser at 375 nm (Figure 1b), the crystal oscillated at ~70 Hz by natural vibration accompanied by bending away motion by the photothermal effect (Figure 1c). Pulsed UV laser irradiation at the natural frequency of 70 Hz greatly increased the bending angle to 11° by resonance, achieving high-speed and large bending (Figure 1d). This high-speed bending could also be induced by visible lasers at 450, 520, and 638 nm and even by a continuous light from visible to near-infrared with a halogen lamp (400–2000 nm).

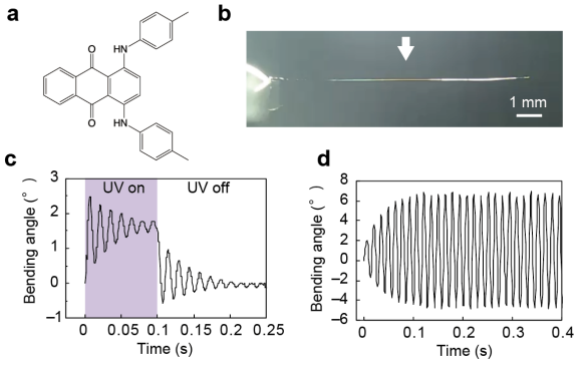

Figure 1. (a) Molecular structure of Solvent Green 3 (**1**). (b) Photograph of a needle-shaped **1** crystal viewed from the side face. (c) Photothermally driven bending upon UV irradiation for 0.1 s. (d) 70-Hz high-speed bending by photothermal-induced natural vibration upon pulsed UV irradiation at 70 Hz.

1) *Mechanically Responsive Materials for Soft Robotics*, ed. H. Koshima, Wiley-VCH, **2020**. 2) H. Koshima, N. Ojima, H. Uchimoto, *J. Am. Chem. Soc.*, **2009**, *131*, 6890–6891. 3) H. Koshima, K. Takechi, K. Uchimoto, N. Ojima, *Chem. Commun.* **2011**, *47*, 11423–11425. 4) Y. Hagiwara, T. Taniguchi, T. Asahi, H. Koshima, *J. Mater. Chem. C* **2020**, *8*, 4876–4884. 5) S. Hasebe, Y. Hagiwara, J. Komiya, M. Ryu, H. Fujisawa, J. Morikawa, T. Katayama, D. Yamanaka, A. Furube, H. Sato, T. Asahi, H. Koshima, *J. Am. Chem. Soc.* **2021**, *143*, 8866–8877.

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

[K606-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kiichi Amimoto, Yoshimitsu Sagara

Fri. Mar 24, 2023 1:40 PM - 3:40 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-3pm-01] Synthetic design of nitrogen-containing Lewis basic π-conjugated molecules toward fluorescent molecular cocrystals

○Mahiro Nakabayashi[1], Takumi Matsuo[1], Shotaro Hayashi[1] (1. Kochi University of Technology)

1:40 PM - 2:00 PM

[K606-3pm-02] Creating Flexible Molecular Inclusion Crystals and Their Thermo-Triggered Crystal-to-Crystal Phase Transition

○Yuto Hino[1], Shotaro Hayashi[1] (1. Kochi University of Technology)

2:00 PM - 2:20 PM

[K606-3pm-03] Naphtyl-appended fluoranthene crystals with two 2D topologies and their anisotropic fluorescence waveguide

○Takumi Matsuo[1], Yuto Hino[1], Shoaro Hayashi[1] (1. Kochi Univ. of Tech.)

2:20 PM - 2:40 PM

[K606-3pm-04] Synthesis and Fluorescent Properties of Sulfonylaniline Positional Isomers

○Hiroki Sato[1], Kohei Tsujimura[1], Nanami Hoshino[2], Aki Sato[2], Shota Takizawa[1], Hiroshi Katagiri[1,2] (1. Grad. Sch. of Org. Mater. Sci., Yamagata Univ., 2. Grad. Sch. of Sci. and Eng., Yamagata Univ.)

2:40 PM - 3:00 PM

[K606-3pm-05] Crystal Structures and FET Characteristics of Diiodo-substituted Asymmetric Thienoacene Isomers

○Amane Matsunaga[1], Mai Hasada[2], Kakeru Hasumi[1], Daisuke Kumaki[2], Shizuo Tokito[2], Hiroshi Katagiri[1,2] (1. Grad. Sch. of Sci. and Eng., Yamagata Univ., 2. Grad. Sch. of Org. Mater. Sci., Yamagata Univ.)

3:00 PM - 3:20 PM

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含窒素 Lewis 塩基性 π 共役系分子の合成設計に基づく多成分系分子結晶の創成と光機能

（高知工大）○中林 真宏・松尾 匠・林 正太郎

Synthetic Design of Nitrogen-containing Lewis Basic π-Conjugated Molecules toward Fluorescent Molecular Cocrystals (*Kochi University of technology*) ○Mahiro Nakabayashi, Takumi Matsuo, Shotaro Hayashi

Noncovalent synthesis is basically an important issue in the crystal engineering of organic molecules. The interactions between pyridine derivatives and iodoarenes are particularly effective in controlling molecular orientation. On the other hand, molecular design using these units is necessary to achieve functionalities such as luminescence and semiconducting. In this study, fluorescent π-conjugated molecules with multiple pyridyl groups were designed and synthesized. Co-crystallization of **1** with *p*-diiodoperfluorobenzene was performed to obtain co-crystals. The structure of the co-crystal was determined by single-crystal X-ray structure analysis. Spectral properties showed that the co-crystal has an optical waveguiding characteristic. Interestingly, anisotropic optical waveguides were achieved by molecular control of organic crystals using fluorescent π-conjugated molecules. The optical waveguiding occurred based on the transition dipole of the π-conjugated molecule.
Keywords: Pyridine; Co-crystals; Lewis Pairs; π-Conjugated Molecules

非共有結合合成はクリスタルエンジニアリングにおいて非常に重要である。特に、ピリジン環とヨードアレーンの相互作用は指向性が強いため、分子の配向性を精密に制御することが可能である。一方、適切な分子設計に基づいて構成された π 共役系分子は、発光性や半導性といった機能を実現する。近年、発光性 π 共役系分子を用いた有機結晶は、その分子配向・配列に基づいて異方的な光導波路を実現することが示された [1)]。本研究では、ピリジン環を 2 つ有する発光性 π 共役系分子を設計・合成し(**Figure 1a**)、ジヨードアレーンとの共晶化を試みた。化合物 **1** と *p*-diiodoperfluorobenzene の共結晶(**Figure 1b**)では光導波機能が発現することを調べた。得られた共結晶は単結晶 X 線構造解析によって構造を調査し、分光学的特徴を調べた(**Figure 1c**)。その結果、分子の遷移双極子モーメント方向に光導波することが示唆された。

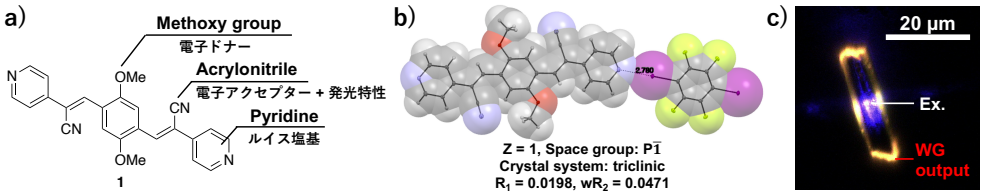

Figure 1. (a) Design of π-conjugated molecule **1**. (b) Crystal structure of **1** and *p*-diiodoperfluorobenzene cocrystal. (c) Microscope image of cocrystal focused laser beam irradiation.

1) Yong Liu, Huiping Hu, Ling Xu, Bing Qiu, Jie Liang, Fang Ding, Kang Wang, Manman Chu, Wei Zhang, Ming Ma, Bo Chen, Xinzheng Yang, and Yong Sheng Zhao, *Angew. Chem. Int. Ed.*, **2020**, *11*, 4456–4463.

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柔軟性分子包摂結晶の自在創成とその熱的結晶－結晶相転移

（高知工大院工）○樋野 優人・林 正太郎

Creating Flexible Molecular Inclusion Crystals and Their Thermo-Triggered Crystal-to-Crystal Phase Transition (*Graduate School of Engineering, Kochi University of Technology*) ○Yuto Hino, Shotaro Hayashi

Because molecular crystals are highly densely-lattice molecular packing, these are no flexibility. On the other hand, we recently achieved flexible molecular crystals by designing columnar structures with motionable layer structures from the viewpoint of free molecular motion. More recently, we found that the crystallization of 1,8-bisphenylanthracene (**1**) yields molecular inclusion crystals due to encapsulating various solvent molecules. As a result of encapsulation, the columnar structure of the crystal can be controlled by the included solvent molecules. Thus, we investigated the directional-specific flexibility of the obtained crystals. It was found that several crystals showed anisotropic brittle, plastic, and elastic deformations based on the included solvents, and crystal structure. We present herein the details of these results and unique step-wise thermo-triggered crystal-to-crystal phase transition.
Keywords : self-assembly; photoluminescence; inclusion crystal; anthracene; phase transition

稠密な分子集合体である分子結晶は、典型的な脆性材料である。一方、カラムナー構造形成とその動的な層間を生み出す分子運動の自由度（揺らぎ）を分子結晶設計指針とすることで、柔軟性材料を実現することができる[1)]。最近我々は、1,8-ビスフェニルアントラセン（**1**）[2)]の結晶化から溶媒として用いた分子の包摂が実現できることを見出した（Figure 1a）。その結果、包摂する分子により結晶のカラムナー構造およびその層間構造の制御が可能であることが明らかになった。機械変形機能の方向依存性を調査したところ、方向によって脆性、塑性、弾性変形を示した（Figure 1b）。本発表ではこれら実験の詳細や包摂結晶の結晶構造、異方性柔軟性機能に加え、熱的刺激をトリガーした多段階結晶－結晶相転移について述べる。

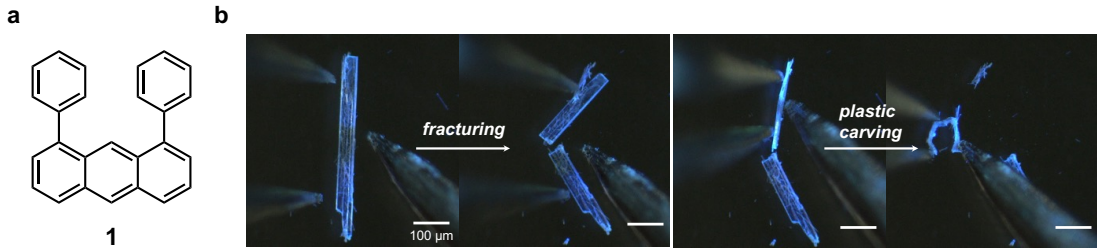

Figure 1. (a) Molecular structure of 1,8-bisphenylanthracene, **1**. (b) Photograph of the inclusion crystal of **1** under UV. Directional dependent mechanical deformation.

1）S. Hayashi, *Bull. Chem. Soc. Jpn.* **2022**, *95*, 721–727.
2）Y. Hino, S. Hayashi, *Chem. Eur. J.* **2021**, *27*, 17595–17600.

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ナフチル置換フルオランテンの結晶成長による２種類の二次元トポロジー発現とそれらの異方性蛍光導波特性

（高知工大 [1]）○松尾 匠 [1]・樋野 優人 [1]・林 正太郎 [1]

Naphtyl-appended Fluoranthene Crystals with Two 2D Topologies and Their Asymmetric Fluorescence Waveguide

([1]*Kochi University of Technology*) ○Takumi Matsuo,[1] Yuto Hino,[1] Shotaro Hayashi[1]

Novel naphthyl-appended fluoranthene that exhibits efficient fluorescence in solution and in the solid state was successively synthesized via Sonogashira cross-coupling reaction of 1,8-Dibromonapthalene. Although the obtained platelet crystals were not polymorphic, two 2D crystal topologies appeared. Fluorescence waveguide was revealed by spatially-resolved photoluminescence measurements of the crystals. Consequently, values of attenuation coefficient (dB/cm) were dramatically varied depending on the guiding directions of the fluorescence in an isolated crystal, which suggests that anisotropic fluorescence waveguide appeared in the platelet crystals.

Keywords : Fluoranthene, fluorescent molecular crystals, anisotropic fluorescence waveguide

1,8-Dibromoanthracene を原料に薗頭クロスカップリング反応によりナフチル基置換フルオランテンが新規に合成できることがわかった。この分子は溶液・固体状態ともに高い発光量子収率を示した。得られた薄板状結晶には多形が存在しなかったが、二種類の結晶トポロジー(CT-I, CT-II)が存在することがわかった。空間分解顕微蛍光スペクトル測定により蛍光導波特性を調査したところ、CT-Iにおいて結晶短軸方向への導波では 839 dB/cm, 長軸方向では 1088 dB/cm の減衰係数となり異方的に蛍光導波することがわかった。

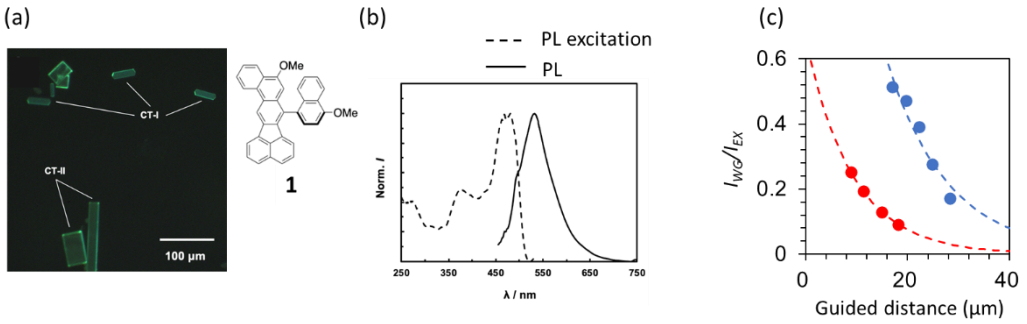

図 1 (a) 新規フルオランテンの分子構造及び CT-I, CT-IIの蛍光像, (b) 蛍光・蛍光励起スペクトル, (c) CT-Iにおける結晶短軸（赤）及び長軸方向（青）への蛍光減衰プロット及びフィッティングカーブ（点線）.

1) Y. Hino, T. Matsuo and S. Hayashi, “Unique 2D Face Topologies in Naphthyl-appended Naphtho[k]fluoranthene-based 3D Crystals for Optical Waveguide”, *Adv. Opt. Mater. in press*.

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スルホニルアニリン位置異性体の合成と蛍光特性

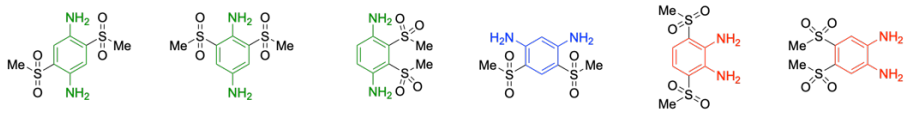
（山形大院有機[1]・山形大院理工[2]）○佐藤 大幹[1]・辻村 光平[1]・星野 七海[2]・佐藤 亜紀[2]・瀧澤 将太[1]・片桐 洋史[1,2]

Synthesis and Fluorescent Properties of Sulfonylaniline Positional Isomers ([1]*Graduate School of Organic Materials Science, Yamagata University,* [2]*Graduate School of Science and Engineering, Yamagata University*) ○Hiroki Sato,[1] Kohei Tsujimura,[1] Nanami Hoshino,[2] Aki Sato,[2] Shota Takizawa,[1] Hiroshi Katagiri[1,2]

The optical properties of organic fluorescent dyes are significantly influenced by substituent type and position. We have reported sulfonylaniline dyes in which amino and sulfonyl groups are introduced into the benzene ring[1-3]. In particular, the green-fluorescent dye **2,5-BMeS-*p*-A** exhibits high quantum yield, solid-state fluorescence, and a large Stokes shift. In this study, we investigated the correlation between molecular structure and optical properties of positional isomers of sulfonylaniline dyes and attempted to systematically understand the push-pull system (Figure 1). Comparison of the optical properties of all positional isomers in acetonitrile revealed that **2,5-BMeS-*p*-A** and **2,3-BMeS-*p*-A** have longer absorption and fluorescence wavelengths and larger Stokes shifts, and that **2,5-BMeS-*p*-A**, **2,6-BMeS-*p*-A** and **3,6-BMeS-*o*-A** have high fluorescence quantum yield. These results suggest that the para- and ortho-phenylenediamine frameworks and the proximity of amino and sulfonyl groups are advantageous for the construction of long-wavelength high-quantum-yield fluorophores.

Keywords : Fluorescent Dye, Sulfonylaniline, Push-Pull System, Positional Isomer

有機蛍光色素の光学特性は，置換基の種類や位置によって大きく影響される．これまでに，我々はベンゼン環にアミノ基とスルホニル基を導入したスルホニルアニリン系蛍光色素を報告している[1-3]．特に，緑色蛍光色素 **2,5-BMeS-*p*-A** は高い量子収率，固体蛍光，ならびに大きなストークスシフトを示す．本研究では，スルホニルアニリン位置異性体を合成することで本骨格を基盤とした Push-pull 系の体系的な理解を目的とし，スルホニルアニリン位置異性体の分子構造と光学特性の相関を調査した (Figure 1)．アセトニトリル中における全位置異性体の光学特性を比較すると，**2,5-BMeS-*p*-A** と **2,3-BMeS-*p*-A** は吸収および蛍光波長の長波長化と大きなストークスシフトが確認され，蛍光量子収率は **2,5-BMeS-*p*-A**, **2,6-BMeS-*p*-A**, **3,6-BMeS-*o*-A** が高い値を示した．これらの結果は，パラまたはオルトフェニレンジアミン骨格およびアミノ基とスルホニル基の隣接配置が長波長または高い量子収率を示す蛍光色素の構築に有利であることを示唆している．



Compounds	2,5-BMeS-*p*-A	2,6-BMeS-*p*-A	2,3-BMeS-*p*-A	4,6-BMeS-*m*-A	3,6-BMeS-*o*-A	4,5-BMeS-*o*-A
λ_{abs} [nm]	382	375	388	299	353	310
λ_{em} [nm]	492	471	491	349	435	400
Φ [-]	0.49	0.45	0.022	0.0043	0.57	0.017
Stokes shift [nm]	110	96	103	50	82	90

Figure 1. Optical properties of sulfonylaniline positional isomers in acetonitrile.

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ジヨード置換非対称チエノアセン異性体の結晶構造と FET 特性

（山形大院理工 [1]・山形大院有機 [2]）〇松永 周 [1]・羽佐田 麻衣 [2]・蓮見 翔 [1]・熊木 大介 [2]・時任 静士 [2]・片桐 洋史 [1,2]

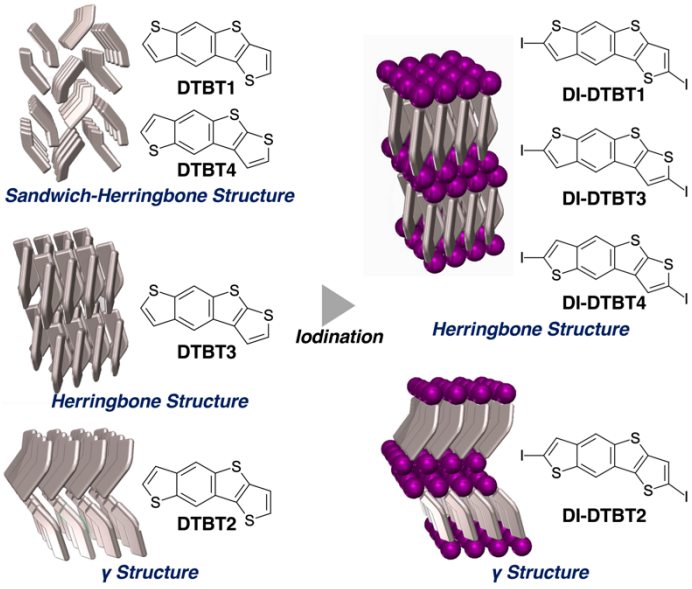
Crystal Structures and FET Characteristics of Diiodo-substituted Asymmetric Thienoacene Isomers

([1]*Graduate School of Science and Engineering, Yamagata University*, [2]*Graduate School of Organic Materials Scienece, Yamagata University*) 〇 Amane Matsunaga,[1] Mai Hasada,[2] Kakeru Hasumi,[1] Daisuke Kumaki,[2] Shizuo Tokito,[2] Hiroshi Katagiri[1,2]

In the active layer of organic field-effect transistors (OFETs), organic semiconductor materials are required to have a molecular orientation suitable for effective charge transport. We have investigated the molecular orientation control using iodine–iodine interactions.[1] In this study, we investigated the crystal structures and FET properties of four asymmetric thienoacene (DTBT) isomers and their diiodinated derivatives (DI-DTBT). It was found that DTBT1 and DTBT4 form slip-stack sandwich-herringbone structures, DTBT2 forms full-stack γ structure, and DTBT3 forms herringbone structure. On the other hand, diiodo-substituted DI-DTBT1, DI-DTBT3, and DI-DTBT4 formed herringbone structures, and DI-DTBT2 formed a full-stack γ structure. In the diiodine isomers, the iodine–iodine interaction contributed to the formation of the crystal structure favorable for charge transport.

Keywords : Organic Semiconductors, Thienoacenes, Halogen–Halogen Interactions, Dispersion Force, Iodine

有機電界効果トランジスタ(OFET)の活性層では，効率的な電荷輸送に適した有機半導体分子の配列が求められる．我々はこれまでに，ヨウ素–ヨウ素相互作用を活用した分子配向制御について調査してきた [1]．本研究では，4 種の非対称チエノアセン(DTBT)異性体，およびそれらのジヨード誘導体(DI-DTBT)の結晶構造と FET 特性を調査した. その結果, DTBT1 および DTBT4 は slip-stack 型 sandwich-herringbone 構造, DTBT2 は full-stack 型 γ 構造, DTBT3 は herringbone 構造を形成することが明らかになった．一方, ジヨード置換体では, DI-DTBT1，DI-DTBT3，DI-DTBT4 は full-stack 型 herringbone 構造，DI-DTBT2 は full-stack 型 γ 構造を形成した．さらに，ジヨード異性体ではヨウ素–ヨウ素相互作用が電荷輸送に有利な結晶構造の形成に寄与していることが明らかになった．



1) A. Matsunaga, *et al., J. Phys. Chem. Lett.* **2021**, *12*, 111–116.

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[K602-3pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Shinsuke Inagi, Yousuke Ooyama

Fri. Mar 24, 2023 1:30 PM - 3:40 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-3pm-01] Electrocatalytic CO_2 insertion into unreactive organic molecules

○Yutaka Saga[1], Nozomi Yamaguchi[1], Toshimichi Kobayashi[1], Mio Kondo[1,2], Shigeyuki Masaoka[1] (1. Osaka Univ., 2. JST PRESTO)

1:30 PM - 1:50 PM

[K602-3pm-02] Electro-Conversion Utilizing Oxygen Reduction Reaction

○Takashi Yamamoto[1], Tsuyoshi Saitoh[2], Yasuaki Einaga[1] (1. Faculty of Science and Technology, Keio Univ., 2. International Institute for Integrative Sleep Medicine, Univ. of Tsukuba)

1:50 PM - 2:10 PM

[K602-3pm-03] Electrochemical Dearomative Carboxylation of Electron-deficient Aromatic Compounds

○Vishal Kumar Rawat[1], Hiroki Hayashi[1,2], Satoshi Maeda[1,2,3], Tsuyoshi Mita[1,2] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

2:10 PM - 2:30 PM

[K602-3pm-04] Evaluation of reactivities of aryls under electrochemical conditions by using oxidation potential gap (ΔE_{ox})

○Kazuhiro Okamoto[1], Naoki Shida[1], Haruka Morizumi[2], Yoshikazu Kitano[2], Kazuhiro Chiba[2] (1. Yokohama National Univ., 2. Tokyo Univ. of Agric. and Technol.)

2:40 PM - 3:00 PM

[K602-3pm-05] Development of π-extended iodoarene mediator for electrochemical C-N coupling and its kinetics

○Naoki Shida[1], Shohei Yoshinaga[1], Mahito Atobe[1] (1. Yokohama National University)

3:00 PM - 3:20 PM

[K602-3pm-06] Electrochemical Synthesis of Hetero[7]helicenes, Dehydro-hetero[7]helicenes and Hetero[8]circulenes with Intriguing Optical Features

○Mohamed S. H. Salem[1], Md Imrul Khalid[1], Ahmed Sabri[1], Hiroaki Sasai[1], Shinobu Takizawa[1] (1. SANKEN, Osaka University, Ibaraki-shi, Osaka 567-0047, Japan)

3:20 PM - 3:40 PM

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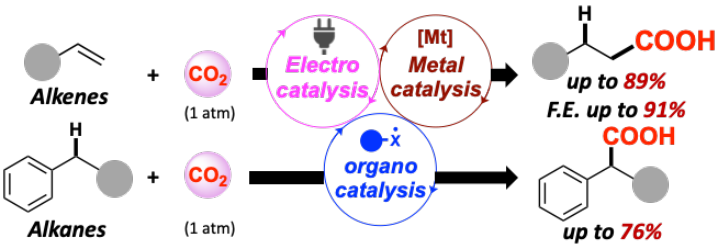
Electrocatalytic CO_2 Insertion into Unreactive Organic Molecules

([1]*Graduate School of Engineering, Osaka University*, [2]*JST PRESTO*) ○Yutaka Saga,[1] Nozomi Yamaguchi,[1] Toshimichi Kobayashi,[1] Mio Kondo,[1,2] Shigeyuki Masaoka[1]

Keywords: Unreactive Organic Molecules, Electrochemistry, CO_2 Insertion, HAT Catalyst, Metal Complex Catalyst

The utilization of CO_2 gas has attracted considerable attention as a solution to the current energy problems. Especially, the transformations to incorporate CO_2 into organic skeletons by C-C bond-forming reactions are highly attractive in terms of environmental-friendship and as a strategy to directly access various carboxylic acids. Whereas CO_2 insertion reactions into organic molecules with activated chemical bonds (e.g. carbon-halogen bonds) have been widely studied,[1] there have been only limited examples to accomplish direct CO_2 insertion reactions into unreactive organic molecules, such as alkenes and alkanes.

Herein, we achieved the electrochemical CO_2 insertion reactions into alkenes using a pentanuclear nickel complex composed of five nickel ions and six bpp$^-$ ligands (**Ni5**, Hbpp = 3,5-bis(2-pyridyl)pyrazole) as a catalyst.[2] The CO_2 insertion reaction of styrene smoothly proceeded in high yields (up to 89%) and high Faradaic efficiencies (up to 91%) at a relatively low voltage (2–3 V), which is in sharp contrast to the previously reported relevant systems.[3] To the best of our knowledge, this is the first example to realize the electrochemical CO_2 insertion into unreactive organic molecules under mild conditions at an applied voltage of 2 V. Additionally, we successfully achieved the broad substrate generalities, including styrene derivatives, di- and tri-substituted alkenes, Michael acceptor alkenes and an aliphatic alkene. Moreover, we propose a plausible catalytic cycle involving the key **Ni5**-CO_2 adduct.



Furthermore, we achieved the first electrochemical CO_2 insertion reactions into alkanes bearing unactivated benzylic C(sp^3)-H bonds by developing a new electrochemical methodology comprising a Hydrogen Atom Transfer (HAT) catalyst, a metal catalyst and CO_2 gas.[4] Reaction development, substrate generalities and detailed mechanistic studies will be given in the presentation.

1) A. Tortajada, F. Julia-Hernandez, M. Borjesson, T. Moragas, R. Martin, *Angew. Chem. Int. Ed.* **2018**, *57*, 15948.

2) N. Yamaguchi, Y. Saga, T. Akai, K. Kosugi, M. Kondo, S. Masaoka, *under revision.*

3) A. Alkayal, V. Tabas, S. Montanaro, I. A. Wright, A. V. Malkov, B. R. Buckley, *J. Am. Chem. Soc.* **2020**, *142*, 1780.

4) T. Kobayashi, Y. Saga, M. Kondo, S. Masaoka, *manuscript in preparation.*

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酸素還元反応を活用した電気化学的分子変換

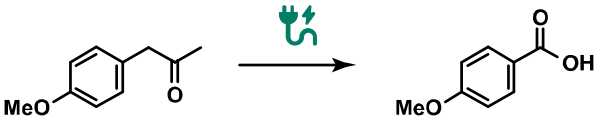
（慶大理工 [1]・筑波大学国際統合睡眠医科学研究機構 [2]）〇山本 崇史 [1]・斉藤 毅 [2]・栄長 泰明 [1]
Electro-Conversion Utilizing Oxygen Reduction Reaction ([1]*Faculty of Science and Technology, Keio University*, [2]*Institute for Integrative Sleep Medicine, University of Tsukuba,*) 〇Takashi Yamamoto,[1] Tsuyoshi Saitoh,[2] Yasuaki Einaga[1]

Electro-organic synthesis, in which electrons act as a reagent, is regarded as a cost-efficient and sustainable green method because it does not require special reagents such as metal and chiral catalysts. In electro-organic synthesis, it is necessary to pay attention not only to a desired reaction at a working electrode, but also to a counter electrode reaction that plays a significant role in ensuring selectivity and efficiency. Here, we report electro-conversions utilizing oxygen reduction reactions on a boron-doped diamond cathode. When phenylacetone was used as a substrate, a corresponding carboxylic acid was afforded through an oxidative bond cleavage reaction. Furthermore, when cumene was used as a substrate, acetophenone was afforded through generation of cumene hydroperoxide and a subsequent electrochemical reaction.
Keywords : Electro-Organic Synthesis; Diamond Electrode; Oxygen Reduction Reaction

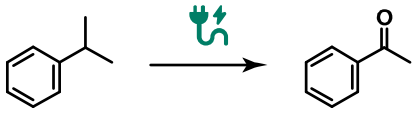
有機電解合成は電子を試薬として作用させることに加え、金属触媒などの特別な試薬を必要としないことから、低環境負荷型の合成手法として産学の両側面から大いに注目を集めている。実際に、有機電解合成では作用極で進行する所望の反応はもちろんのこと、選択性や効率を担保する役割を担う対極反応にも注意を払う必要がある [1)]。本講演では、以上のような背景を踏まえた、ホウ素ドープダイヤモンド陰極上で進行する酸素還元反応を活用する分子変換を報告する。

フェニルアセトン類を基質とした場合、対応する安息香酸が得られた [2)]。これは、ダイヤモンド陰極上での酸素還元によって生成したスーパーオキシドが活性種として作用し、アシル－炭素結合が酸化的に開裂する反応であると推定された。また、クメンを基質とした場合、アセトフェノンが得られた [3)]。これは、上述の分子変換と同様に、ダイヤモンド陰極上での酸素還元によって生成したヒドロペルオキシドアニオンが活性種として作用し、過酸化物であるクメンヒドロペルオキシドを経由する電解酸化反応であると推定された。

Ex. 1: Phenylacetone → Benzoic acid



Ex. 2: Cumene → Acetophenone



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3) M. Kitano, T. Saitoh. S. Nishiyama, Y. Einaga, T. Yamamoto, *Beilstein J. Org. Chem.* **2022**, *18*, 1154.

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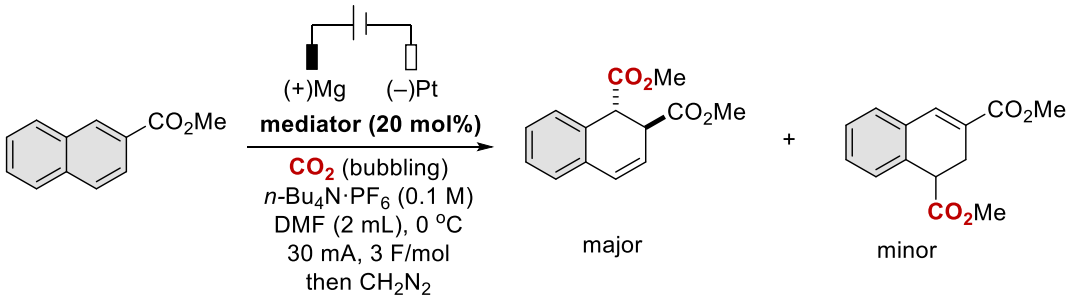
Electrochemical Dearomative Carboxylation of Electron-deficient Aromatic Compounds

([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*) ○Vishal Kumar Rawat,[1,2] Hiroki Hayashi,[1,2] Satoshi Maeda,[1,2,3] Tsuyoshi Mita[1,2]

Keywords: Carbon Dioxide; Aromatic Compounds; Electrochemical Reduction; Dearomatization; Naphthalene

Dearomative carboxylation of stable aromatic compounds from nucleophilic CO_2 radical anion species is a powerful method for producing synthetically useful carboxylic acids. This radical species could readily be prepared electrochemically or photochemically. Recently, our group reported the electrochemical method for the dearomative dicarboxylation of heteroaromatics utilizing CO_2, and the photoredox method for the analogous monocarboxylaion of heteroaromatics and electron deficient aromatic compounds by using cesium formate as a C1 source.[1,2] Encouraged by these findings, we herein describe a new methodology using electrochemical strategy for the reductive carboxylation of electron-deficient naphthalene derivatives with CO_2 that produces unprecedented *trans*-oriented carboxylic acids with respect to the electron-withdrawing group on the naphthalene ring as a major diastereomer.

Under the similar conditions for the electrochemical dearomative carboxylations of heteroaromatics,[1] the reaction of methyl 2-naphthoate furnished a complex mixture of unselectively mono- or dicarboxylated products. To improve the low chemo- and regioselectivity, a catalytic amount of a polyaromatic hydrocarbon, which could work as a mediator in redox process of electrochemical carboxylation,[3] was found to be effective in the present reaction. Reaction with 20 mol% of polyaromatic hydrocarbon was found to be effective to furnish carboxylation at C1-position selectively along with a minor regioisomer.



mediator: anthracene, napthalene, pyrene, *p*-terphenyl, etc.

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酸化電位ギャップ（ΔE_{ox}）を指標とした電解レドックス系におけるアリール類の反応性評価

（横国大院 [1]・農工大院 [2]）○岡本 一央 [1]・信田 尚毅 [1]・森住 春香 [2]・北野 克和 [2]・千葉 一裕 [2]

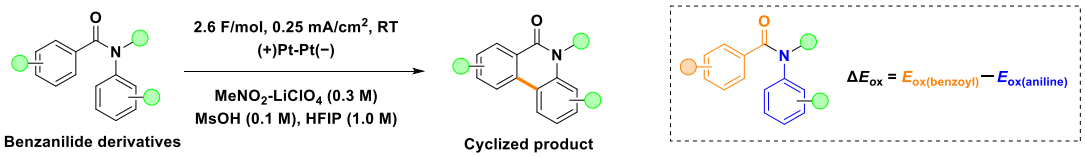
Evaluation of reactivities of aryls under electrochemical conditions by using oxidation potential gap (ΔE_{ox}) ([1]*Graduate School of Engineering, Yokohama National University*, [2]*Department of Applied Biological Science, Tokyo University of Agriculture and Technology*) ○Kazuhiro Okamoto,[1] Naoki Shida,[1] Haruka Morizumi,[2] Yoshikazu Kitano[2], Kazuhiro Chiba[2]

Oxidative cross-coupling reaction enabled direct biaryl synthesis from unactivated C-H bonds. However, reaction between electronically gapped aryl substrates generally failed. We found the efficiency of intramolecular radical cation cross-coupling reaction could be evaluated by oxidation potential gap (ΔE_{ox}). Reliability of this parameter was verified by experimental and computational analysis.

Keywords : Electrochemistry; Radical cation; Cross-coupling

極性転換により開始される芳香族ラジカルカチオンクロスカップリング反応は、ハロゲンなどの官能基を必要とせずにビアリール骨格を構築でき、合成工程の簡略化に繋がるため有用性が高い。一方で、反応の成否はカップリングパートナー間の電子状態に大きく依存し、電子不足-電子豊富アリール間のラジカルカチオンクロスカップリング反応は困難を極める。我々は、この原因が極性転換によって生じるラジカルカチオン種の SOMO と求核剤の HOMO との間のエネルギー差にあり、HOMO のイオン化ポテンシャルを反映する酸化電位値の差（酸化電位ギャップ：ΔE_{ox}）を指標としてその効率を予測できるとの仮説を立て、その妥当性の検証を行った。

ベンズアニリド誘導体の環化反応をモデル反応とし、ラジカルカチオンの求電子性を損なわない弱ドナー性電解液である $MeNO_2$-HFIP 混合溶媒系 [1] で電解酸化を行った。その結果、基質のベンゾイル部位とアニリン部位との間の ΔE_{ox} の絶対値が小さいほど環化反応の収率が高くなるという傾向が見られた。DFT 計算による反応機構解析から、ラジカルカチオン中間体が環化遷移状態を形成するための活性化エネルギー（ΔE）と ΔE_{ox} の値に相関が見られたことから、ΔE_{ox} が分子内ラジカルカチオンクロスカップリング反応の効率を予測する指標として有効であることが示された [2]。



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π拡張構造を有するヨードアレーンメディエータを用いた電気化学的 C-N カップリング反応の開発と速度論解析

（横国大院工 [1]）○信田 尚毅 [1]・吉永 昌平 [1]・跡部 真人 [1]

Development of π-extended Iodoarene Mediator for Electrochemical C-N Coupling and its Kinetics

([1]*Graduate School of Science and Engineering, Yokohama National University*) ○ Naoki Shida,[1] Shohei Yoshinaga,[1] Mahito Atobe[1]

Hypervalent iodine is a useful reagent in synthetic organic chemistry, but its large-scale use raises concerns about safety and environmental impact.[1] To establish an environmentally benign reaction system, an electrochemical mediator system has been proposed in which hypervalent iodine is generated by electrochemical oxidation of the corresponding iodoarenes.[2] In this study, novel π-extended iodoarenes (**1**) have been designed, and developed as efficient electrochemical mediators (Figure 1). Electrochemical oxidation of various *N*-Boc-2-aminobiphenyl analogues (**2**) was successfully carried out to obtain carbazole-derivatives **3** in high yield. Mechanistic study based on the electrochemical measurement and kinetic analysis using Foot-of-the-Wave Analysis (FOWA)[3] will also be discussed.[4]

Keywords : Electrosynthesis; Electrochemical Mediator; Hypervalent Iodine; C-N Coupling Reaction

超原子価ヨウ素は有機合成化学において有用な試薬であるが、その大量使用には安全性や環境負荷が付随する [1]。安全で環境調和性の高い超原子価ヨウ素反応系を確立するために、対応するヨードアレーンを電解酸化することで超原子価ヨウ素を発生させる電解メディエーター系が提案されている [2]。しかし、触媒量のヨードアレーンを用いた電極反応の成功例はいまだに限定的である。

本研究では、新規π拡張ヨードアレーン **1** を設計し、効率の良い電気化学メディエーターとして発展させた（Figure 1）。種々の *N*-Boc-2-aminobiphenyl 類縁体 **2** の電解酸化により対応するカルバゾール類 **3** を高収率で得ることに成功した。本反応では、安定な **1**$^{\bullet+}$に形成されるσ-hole が **2** との相互作用を促進していることを明らかとした。また、Foot-of-the-Wave Analysis (FOWA)[3] に基づく電気化学触媒過程の速度論的解析も行ったため併せて報告する [4]。

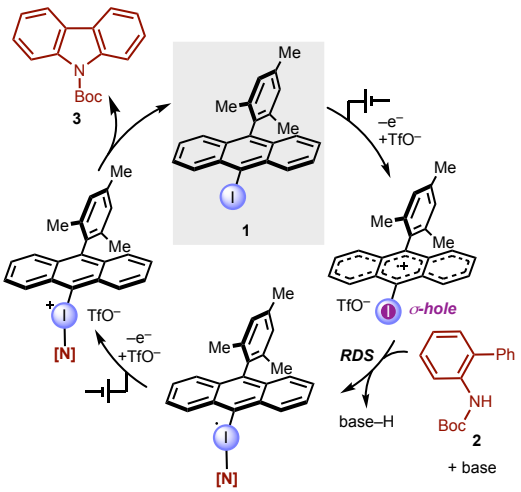

Figure 1. Plausible reaction mechanism

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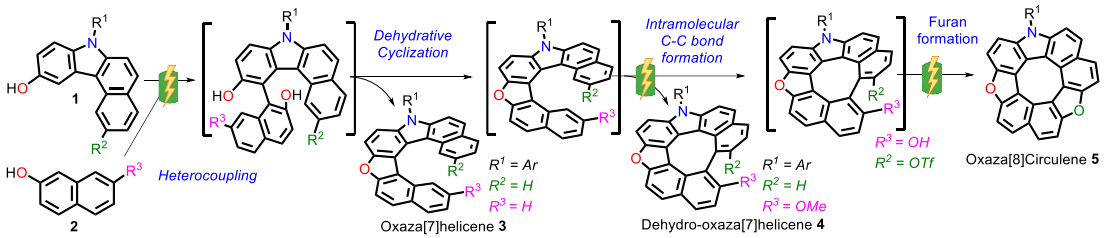
Electrochemical Synthesis of Hetero[7]helicenes, Dehydro-hetero[7]helicenes and Hetero[8]circulenes with Intriguing Optical Features

(*SANKEN, Osaka University, Ibaraki-shi, Osaka 567-0047, Japan*) ○Mohamed S. H. Salem, Md. Imrul Khalid, Ahmed Sabri, Hiroaki Sasai, Shinobu Takizawa

Keywords: Electrochemistry; Sequential Reaction; Helicenes; Dehydrohelicenes; Circularly Polarized Luminescence

Polycyclic heteroaromatic compounds (PHAs) including helicenes, dehydrohelicenes, and circulenes show unique architectures that endowed them with various desirable optical and electronic features. Although various successful strategies were introduced to afford PHAs, there are some remaining limitations related to the low total yields, harsh reaction conditions (such as high temperature), easy racemization of the synthetic intermediates, and/or overuse of oxidants (narrow functional group tolerance).[1]

In this work, we introduce the first electrochemical approach for synthesizing unsymmetrical PHAs *via* sequential transformations. The electrochemical sequence starts with the chemoselective hetero-coupling of 3-hydoxycarbazoles **1** and 2-naphthols **2**, followed by a dehydrative cyclization to afford oxaza[7]helicenes **3**.[2] We extended our protocol by re-optimizing the electrochemical parameters and varying substrate **2** to include an additional step; the intramolecular carbon-carbon bond formation giving dehydro-oxaza[7]helicenes **4**.[3] Hetero[8]circulenes **5** were prepared in good yields *via* a four-step sequence that involved the dehydrative furan formation as the final step. The chiral stability and optical features of these PHAs were studied and revealed interesting characteristics. An intense blue-colored circularly polarized luminescence CPL with $|g_{lum}| = 2.5 \times 10^{-3}$ at 433 nm was observed which is the highest among reported dehydrohelicenes.[3]



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

[K602-3vn] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Kazuhide Nakata, Satoshi Usui

Fri. Mar 24, 2023 4:10 PM - 6:00 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-3vn-01] Heterocyclic Effect on Quinoidal Character of Tetraradicals

○Takuma Miyamura[1], Jin Ayatsuka[1], Manabu Abe[1] （1. Hiroshima University）

4:10 PM - 4:30 PM

[K602-3vn-02] Substituent effects on gas-phase stabilities of phenylcyclopentyl cations

○Kazuhide Nakata[1] （1. Hosei Univ.）

4:30 PM - 4:50 PM

[K602-3vn-03] Automated Reaction Path Search for Stereospecific Pericyclic Reaction Using the AFIR Method

○Tsuyoshi Mita[1,2], Hideaki Takano[1,2], Hiroki Hayashi[1,2], Kanna Wataru[3], Yu Harabuchi[1,2,3], K N Houk[4], Satoshi Maeda[1,2,3] （1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ., 4. Univ. of California Los Angeles）

4:50 PM - 5:10 PM

[K602-3vn-04] Computational study of noncovalent interactions in Rh-catalyzed [2+2+2] cycloadditions

○Yuki Nagashima[1], Ryota Abe[1], Jin Tanaka[1], Ken Tanaka[1] （1. Tokyo Institute of Technology）

5:20 PM - 5:40 PM

[K602-3vn-05] Catalytic Olefin Aminocarboxylation with Aminium Radical Cation and CO_2: Synthesis of β-Amino Acids Based on Quantum Chemical Calculations

○Wataru Kanna[1], Yu Harabuchi[2,3,4], Hitomi Katsuyama[2,3], Hideaki Takano[2,3], Hiroki Hayashi[2,3], Tsuyoshi Mita[2,3], Satoshi Maeda[2,3,4] （1. Grad. School of Chem. Sci. and Eng, Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. JST-ERATO, 4. Fac. of Sci, Hokkaido Univ.）

5:40 PM - 6:00 PM

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テトララジカルのキノイド性に及ぼすヘテロ環効果

（広大院先進理工 [1]）○宮村 琢磨 [1]・綾塚 仁 [1]・安倍 学 [1]

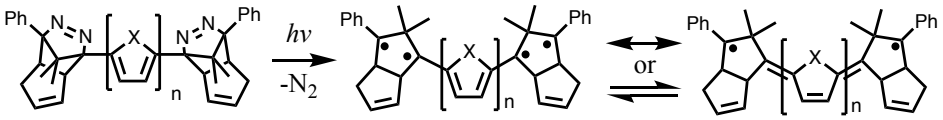
Heterocyclic Effect on Quinoidal Character of Tetraradicals

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Takuma Miyamura[1], Jin Ayatsuka[1], Manabu Abe[1]

Paraphenylene diradicaloids (PPDRs) such as Tschitschibabin's and Müller's hydrocarbons are known to possess singlet ground states to form quinoidal structures[1,2]. Conceptually, the quinoidal/open-shell singlet contribution in those hydrocarbons is determined by the balance between aromatic stabilization and closed-shell bond-formation effects. Thus, the number and degree of aromaticity of the aryls between the two radicals in PPDR determines whether the PPDR exhibits quinoidal/singlet diradical character. In this research, we investigated the influence of heterocyclic groups on the quinoidal/singlet diradical character in PPDR derivatives (X = O, S) containing oligoaryl moieties. Quinoidal structures were experimentally observed under low temperature matrix conditions after the photochemical denitrogenation of the corresponding azoalkanes. Furthermore, DFT calculations suggested that the quinoidal contribution of oligothiophene is higher than that of oligofuran.

Keywords: Radical; Quinoid; Heterocycles

Tschitschibabin や Müller 型ジラジカルなどのパラフェニレンジラジカル（PPDR）は基底開殻性一重項を示し、キノイド構造を有していることが報告されている [1,2]。PPDR のキノイド性に及ぼす芳香環の枚数効果は、ラジカル間に挟まれた芳香環の芳香族安定化とキノイドの閉殻構造を形成することによる安定化とのバランスによって決定する。本研究では、ヘテロ環を有する PPDR 誘導体(X = O, S)用い、キノイド構造に及ぼすヘテロ環効果を調査した。低温マトリックス条件下において、テトララジカルのキノイド構造由来と考えられる吸収帯を確認し、理論計算の結果からキノイド構造の安定性はオリゴチオフェン＞オリゴフランであることが示唆された。



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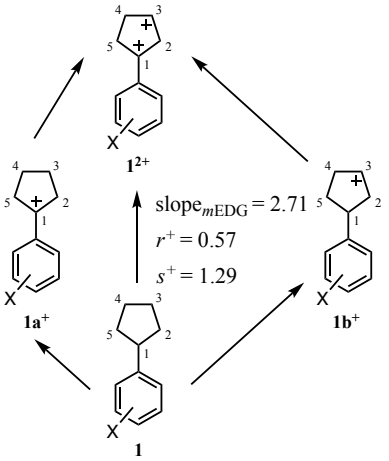
フェニルシクロペンチルカチオンの気相安定性に及ぼす置換基効果

（法大自然科学セ）○中田 和秀
Substituent effects on gas-phase stabilities of phenylcyclopentyl cations (*Science Research Center, Hosei University*) ○Kazuhide Nakata

Substituent effects of electron-deficient species are analyzed by an extended Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + s^+\Delta\bar{\sigma}_s^+)$) that implements the third term to estimate the degree of saturation effect. In the previous work, substituent effect of gas-phase dehydride reactions (1) of phenylcyclopentane (**1**) to give dication $\mathbf{1}^{2+}$ were computationally determined and compared to that of 90°-fixed α,α-dimethylbenzyl cations (**2**) that is used as the σ^0-reference system. As a result, an excellent linear correlation was observed for the plot of *meta*-EDGs with a slope of 2.71. In addition, the plots of both *para* –R groups and EWGs deviated above from the correlation line, and the degree of through-resonance and saturation effects were estimated as 0.57 and 1.29, respectively. These facts show that the ρ and s^+ values are significantly larger than those observed in benzylic cations. To explore the origin of enhanced ρ and s^+ values in $\mathbf{1}^{2+}$, reaction (1) was divided into two steps; dehydride of **1** to give mono cation $\mathbf{1a}^+$ or $\mathbf{1b}^+$ and dehydrides of $\mathbf{1a}^+$ and $\mathbf{1b}^+$ to give $\mathbf{1}^{2+}$. Substituent effects of all elementary reactions were analyzed by comparing with that of **2** to reveal that the enhancement of the ρ and s^+ values are attributed to the dehydride at the position 3 of the cyclopentane ring.
Keywords : Electron Deficient Species; Gas-Phase Stability; Substituent Effect; Extended Yukawa-Tsuno Equation; ρ value

電子不足系の置換基効果は、サチュレーション効果を相関する第三項を導入した拡張湯川−都野式（$-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + s^+\Delta\bar{\sigma}_s^+)$）によって精度良く相関される。前回、フェニルシクロペンタン(**1**)からジカチオン $\mathbf{1}^{2+}$が生成する気相反応(1)について、置換基効果を計算化学によって決定した。得られた置換基効果をσ^{0}基準系である 90°固定α,α-ジメチルベンジルカチオン(**2**)と比較したところ、*meta*-EDG のプロットは傾き 2.71 の優れた直線相関を与えた。また、*para* –R 基のおよび EWG のプロットは、この相関線から上方への片寄りを示し、直接共鳴効果およびサチュレーション効果の度合いは、それぞれ、r^+=0.57 および s^+=1.29 と評価された。この事実は、ジカチオン $\mathbf{1}^{2+}$の ρ 値および s^+値がベンジル位カチオンと比較して非常に大きいことを示す。この原因を解明する目的で、反応(1)を、**1** からモノカチオン $\mathbf{1a}^+$または $\mathbf{1b}^+$が生成する過程と、$\mathbf{1a}^+$および $\mathbf{1b}^+$から $\mathbf{1}^{2+}$が生成する過程に分解した。全ての素過程の置換基効果を **2** と比較して解析した結果、芳香環から遠位の 3 位の脱ヒドリド化の際に ρ 値および s^+値が顕著に大きくなることが明らかになった。



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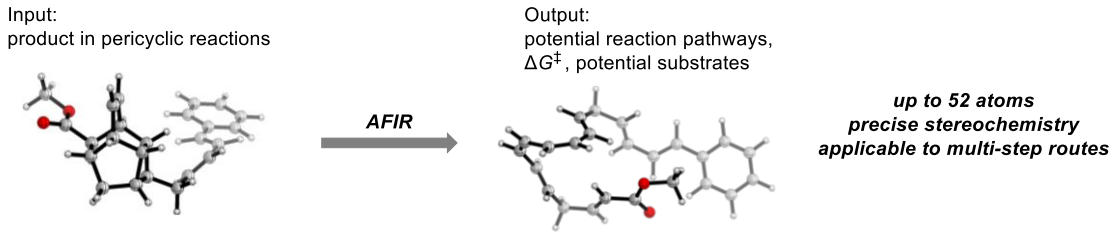
立体特異的なペリ環状反応の反応自動経路探索：AFIR 法による量子化学的逆合成

（北大 WPI-ICReDD[1]・JST-ERATO[2]・北大院理 [3]）○美多　剛 [1,2]・髙野 秀明 [1,2]・林　裕樹 [1,2]・神名　航 [3]・原渕　祐 [1,2,3]・K. N. Houk[4]・前田　理 [1,2,3]
Automated Reaction Path Search for Stereospecific Pericyclic Reaction Using the AFIR ([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*, [4]*Univ. of California Los Angeles*) ○ Tsuyoshi Mita,[1,2] Hideaki Takano,[1,2] Hiroki Hayashi,[1,2] Wataru Kanna,[3] Yu Harabuchi,[1,2,3] K. N. Houk,[4] Satoshi Maeda[1,2,3]

Pericyclic reactions, in which bond-forming and cleaving events simultaneously occur via cyclic transition states without ionic nor radical intermediates, are often seen in organic synthesis. Woodward-Hoffmann rules kinetically governs the stereospecificity of pericyclic reactions. We will present that fully automated reaction path search method (AFIR method) traces an input compound back to reasonable starting compounds through thermally allowed pericyclic reactions by product-based quantum chemistry-aided retrosynthetic analysis (QCaRA). This technology was also applied to the retrosynthetic analysis of endiandric acid C, which was synthesized by Nicolaou in 1982, leading to the access to the corresponding starting polyenes with a perfect stereospecific manner.
Keywords : Pericyclic Reaction; AFIR Method; Automated Reaction Path Search; Electrocyclic Reaction; Sigmatropic Rearrangement

AFIR 法は反応経路自動探索プログラムであり、DFT 計算等と組み合わせて用いることで、遷移状態、中間体のエネルギーを自動的に計算して反応経路を見つけ出すことができる。今回我々は、AFIR 法を基盤とした、より高エネルギーの化学構造を探索する量子化学的逆合成法を用いることで、ペリ環状反応を経由する量子化学的逆合成に成功した。ペリ環状反応は環状遷移状態を経由することが特徴であり、Woodward-Hoffmann 則によりその立体特異性が速度論的に規定されている。我々は目的物のインプット構造に対して、逆合成 AFIR 法を適用することで、化学者の事前知識を必要とせず、自動的に熱的な許容経路を通り、出発原料に逆合成されることを見出した。特に、Nicolaou が 1982 年に全合成した endiandric acid C のメチルエステル（52 原子）を検討したところ、Diels-Alder 反応と 6π/8π 電子系の電子環状反応を経由して、正しい立体化学を有する出発物質のポリエンに逆合成された [1]。



1) T. Mita, H. Takano, H. Hayashi, W. Kanna, Y. Harabuchi, K. N. Houk, S. Maeda, *J. Am. Chem. Soc.* **2022**, *144*, 22985-23000.

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ロジウム触媒を用いた[2+2+2]付加環化反応における非共有結合性相互作用の計算化学的解析

（東工大 物質理工 [1]）〇永島 佑貴 [1]・阿部 諒太 [1]・田中 仁 [1]・田中 健 [1]

Computational study of noncovalent interactions in Rh-catalyzed [2+2+2] cycloadditions

([1] *Department of Chemical Science and Engineering, Tokyo Institute of Technology*)
〇Yuki Nagashima,[1] Ryota Abe,[1] Jin Tanaka,[1] Ken Tanaka[1]

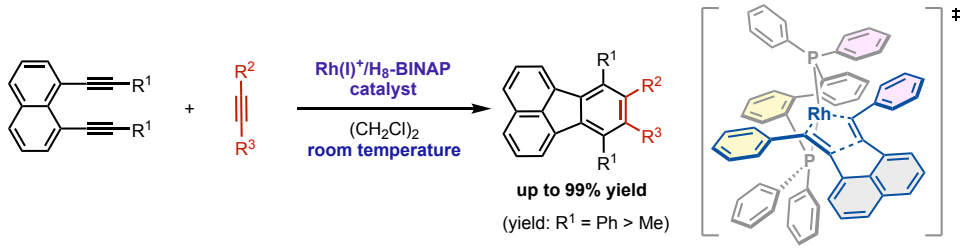
Rh-catalyzed [2+2+2] cycloadditions of alkynes are valuable methods for constructing benzene rings regarding the atom and step economy. Among these, intermolecular [2 + 2 + 2] cycloadditions using diynes and monoynes have been the most widely used in organic synthesis, and they allow diversity-oriented synthesis while limiting the number of isomers produced. During investigations of these [2+2+2] cycloadditions using diynes and monoynes, we unexpectedly noticed the importance of noncovalent interactions. Theoretical and experimental mechanistic studies have demonstrated that noncovalent interactions accelerate sterically demanding [2+2+2] cycloadditions reactions by stabilizing the transition states rather than inducing steric repulsions. We would like to show some examples of interactions in these [2+2+2] cycloadditions.

Keywords : Rhodium; [2+2+2] cycloaddition; noncovalent interaction; DFT calculation

ロジウム触媒を用いたアルキンの [2+2+2] 付加環化反応は、原子効率に優れ、一工程でベンゼン環を与える有用な手法である。特に、ジインとモノインを用いた分子間反応は、交差生成物を効率よく与えるため汎用される。

我々は、このような分子間交差 [2+2+2] 反応の反応機構を計算化学的に解析する過程において、非共有結合性相互作用が反応速度や選択性に影響を与える場合があることに気づいた。例えば、基質のアルキン上に嵩高い置換基が結合している場合、立体障害によって反応速度が低下するのが一般的であるが、特定の置換基においては反応速度がむしろ向上することを見出した。

本発表では、最近取り組んだ [2+2+2] 付加環化反応の機構解析 [1,2] に加え、下記の [2+2+2] 付加環化反応をモデルとし、金属への配位結合・π—π相互作用・C–H—π相互作用などの幅広い非共有結合性相互作用の重要性を示す [3]。



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アミニウムラジカルと二酸化炭素を用いたオレフィンのアミノカルボキシル化：量子化学計算を活用したβ-アミノ酸の新規合成法の開発

（北大院総化[1]・北大 WPI-ICReDD[2]・JST-ERATO[3]・北大院理[4]）○神名　航[1]・原渕　祐[2,3,4]・勝山　瞳[2,3]・髙野 秀明[2,3]・林　裕樹[2,3]・美多　剛[2,3]・前田　理[2,3,4]

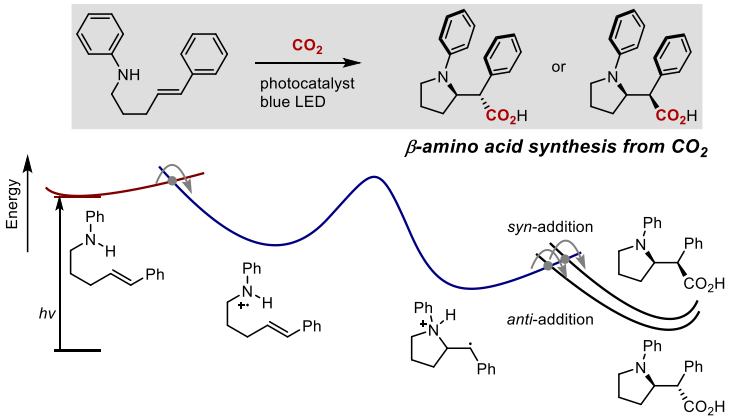
Catalytic Olefin Aminocarboxylation with Aminium Radical Cation and CO_2: Synthesis of β-Amino Acids Based on Quantum Chemical Calculations

([1] *Grad. School of Chem. Sci. and Eng., Hokkaido Univ.*, [2]*WPI-ICReDD, Hokkaido Univ.*, [3]*JST-ERATO*, [4]*Fac. of Sci., Hokkaido Univ.*) ○Wataru Kanna,[1] Yu Harabuchi,[2,3,4] Hitomi Katsuyama,[2,3] Hideaki Takano,[2,3] Hiroki Hayashi,[2,3] Tsuyoshi Mita,[2,3] Satoshi Maeda[2,3,4]

β-Amino acids are frequently found as important component in biologically active molecules such as drugs. On the other hand, CO_2 is an ideal C1 source in organic synthesis due to its abundant, inexpensive, non-toxic, and renewable properties.
In this study, we have developed a synthetic method of β-amino acids via aminocarboxylation of alkenes with aminium radical cation and CO_2 in the presence of a photoredox catalyst, based on the artificial force induced reaction (AFIR) method.[1] We have also explained the diastereoselectivity of the target β-amino acid using a new computational method developed in our group.[2] We further modified reaction conditions based on the computational results so that the yield of the targeted β-amino acid was greatly improved.
Keywords : β-amino acid; carboxylation; carbon dioxide; quantum chemical calculations; AFIR method

β-アミノ酸は医薬品などの生物活性物質に数多くみられる骨格である。一方で、CO_2は、有機合成化学の視点では安価かつ再生可能な理想的 C1 資源であり、CO_2を付加価値の高い化合物へ変換する反応の開発は重要な課題である。

我々は AFIR 法[1]を活用し、オレフィンを光電子移動触媒存在下で分子内のアミニウムラジカル及び CO_2 と反応させる β-アミノ酸の新規合成法を開発した。加えて、当研究室で開発された新規計算手法[2]により、通常では計算の難しい電子移動過程まで詳細に解析することで、生成物のジアステレオ選択性を説明した。また、計算結果に基づいて反応条件を改善し副反応を抑制した結果、目的の β-アミノ酸の収率向上に成功した。



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[K705-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Kazunobu Igawa, Keisuke Asano

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-3pm-01] Photocatalytic transfer hydrogenation from water to carbon–carbon multiple bonds of unsaturated carboxylic acids

○Farzaneh SOLEYMANIMOVAHED[1], Shogo Mori[1], Daling Lu[2], Takashi Hisatomi[2], Kazunari Domen[2], Susumu Saito[1] （1. Nagoya University, 2. Shinshu University）

1:10 PM - 1:30 PM

[K705-3pm-02] Development of Photoinduced α-Alkylation Reactions of Carbonyl Compounds with Alkenes

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

1:30 PM - 1:50 PM

[K705-3pm-03] Modular Synthesis of 1,4-Dicarbonyl Compounds via Sequential Photocatalysis Using Ambiphilic Radical Linchpin

○Akira Matsumoto[1], Keiji Maruoka[1,2] （1. Kyoto University, 2. Guangdong University of Technology）

1:50 PM - 2:10 PM

[K705-3pm-04] Development of Visible Light-Gated Bifunctional Cyclooctene Catalysts

○Tagui NAGANO[1], Keisuke ASANO[2], Daisuke URAGUCHI[2] （1. Kyoto Univ., 2. Hokkaido Univ.）

2:10 PM - 2:30 PM

[K705-3pm-05] Reduction of Nitriles, Aldehydes, and Ketones with Tetrahydroxydiborn Catalyzed by an Amphiphilic Resin-Supported Nanopalladium Catalyst

○Kaili Zhang[1,2], Aya Tazawa[1], Shintaro Okumura[1,2], Yasuhiro Uozumi[1,2] （1. Institute for Molecular Science , 2. The Graduate University for Advanced Studies）

2:40 PM - 3:00 PM

[K705-3pm-06] Electrochemical Allylation Reactions Catalyzed by Nitrogen-Doped Carbon Supported Zinc Electrodes

○Ryusuke Masuda[1], Tomohiro Yasukawa[1], Yasuhiro Yamashita[1], Shu Kobayashi[1] （1. The Univ. of Tokyo）

3:00 PM - 3:20 PM

[K705-3pm-07] Continuous-flow enantioselective hydroacylations with chiral heterogeneous Rh catalysts and sequential-flow transformations

○Yuki Saito[1], Shū Kobayashi[1] （1. The University of Tokyo）

3:20 PM - 3:40 PM

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Photocatalytic Transfer Hydrogenation from Water to Carbon–Carbon Multiple Bonds of Unsaturated Carboxylic Acids

(*[1]RCMS, Nagoya Univ., [2]IRCCS, Nagoya Univ., [3]RISM, Shinshu Univ., [4]JST PRESTO, [5]Grad. Sch. Sci., Nagoya Univ.*) ○Farzaneh Soleymani Movahed,[1] Shogo Mori,[2] Daling Lu,[3] Takashi Hisatomi,[3,4] Kazunari Domen,[3] Susumu Saito[2,5]

Keywords: *artificial photosynthesis, transfer hydrogenation, photocatalyst, semiconductor, strontium titanate*

Catalytic hydrogenation of alkenes to alkanes is considered a critical process in organic chemistry since saturated carbon–carbon bonds are present in agrochemical and pharmaceutical industries.[1] The hydrogenation of alkenes is currently available utilizing hydrogen gas; however, this long-established method suffers from harsh reaction conditions. Additionally, adequate handling and safety measurements are essential for the employment of hydrogen gas due to the enhanced risk of gas ignition.[2] Alternatively, transfer hydrogenation has emerged as a promising approach to replace hazardous hydrogen gas with safe hydrogen donors under mild conditions. Furthermore, the application of naturally abundant and eco-friendly materials including water as a hydrogen donor in transfer hydrogenation has become an indispensable topic for the sustainable development of synthetic approaches.

Our research group is working on artificial photosynthesis to enable thermodynamically endergonic organic transformations utilizing water as an electron source under solar light irradiation. In recent years, harnessing sustainable solar light to activate water molecules for valuable organic reactions has attracted much attention.[3] Herein, we disclose an example of artificial photosynthesis for the transfer hydrogenation of unsaturated carboxylic acids using water as a hydrogen source. A newly designed strontium titanate-based heterogeneous photocatalyst functions in an aqueous solution without any sacrificial organic hydrogen donors under near-UV or simulated solar light irradiation. Our thermodynamically endergonic transfer hydrogenation protocol has the potential to expand opportunities for advancements in green chemistry philosophy.

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光触媒を用いたアルケンによるカルボニル化合物のα−アルキル化反応の開発

(東大院理) ○山下恭弘・小林修

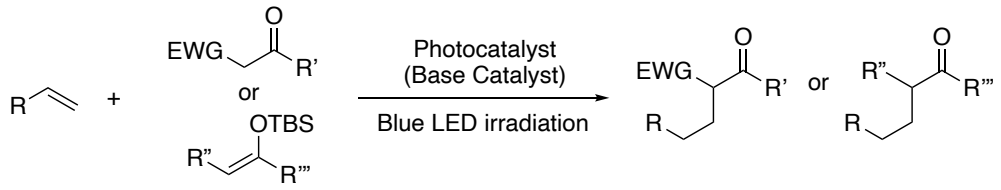
Development of Photoinduced α-Alkylation Reactions of Carbonyl Compounds with Alkenes

(School of Science, The Univ. of Tokyo) ○ Yasuhiro YAMASHITA・Shū KOBAYASHI

α-Alkylation reactions of carbonyl compounds are a fundamental methodology in carbon–carbon bond formation. Compared to allylation reactions with alkyl halides in substitution fashion, the alkylation reactions with alkenes in addition fashion are more atom economical methodology; however, available alkenes are limited to activated alkenes such as Michael acceptors. Here, we investigated photoinduced α-alkylation reactions of carbonyl compounds with alkenes as electrophiles. α-Carbonyl radicals, which were prepared from alkaline metal enolates or silicon enolates by using photocatalysts, smoothly reacted with alkenes bearing no electron-withdrawing group (EWG) under blue light irradiation to afford the desired products in good to high yields. In this presentation, we will report our recent research results on the alkylation reactions via α-carbonyl radical formation.

Keywords: Photocatalyst; Radical; Carbon–carbon Bond Formation; Carbonyl Compound; Alkene

カルボニル化合物のα位でのアルキル化反応は、有機合成化学において基本的な炭素—炭素結合生成反応である。この反応は、求電子剤としてハロゲン化アルキル等を用いる求核置換反応によって主に行われている一方で、アルケンに対する求核付加反応によるアルキル化は、高い原子効率を実現できるが電子求引基(EWG)を持たないアルケンは反応性が低いため、それを用いた反応はしばしば困難であった。演者らは、反応性の低いアルケンを求電子剤として用いる汎用的なアルキル化反応の実現を志向し、α-カルボニルラジカルを用いる反応の検討を行った。これまでに活性メチレン化合物であるマロン酸エステル等とスチレン類との反応において、触媒的に発生させたエノラートの一電子酸化によるα-カルボニルラジカルの発生の検討を行い、有機光触媒と金属塩基触媒を用いることによって、青色光照射下で目的の反応が温和な条件で進行することを明らかにしている[1)]。さらに、酸性度の低いケトンやエステルの反応も、それらのケイ素エノラートを前駆体として用いることによって進行することを見出した[2,3)]。さらに、最近、1-デセンのような不活性アルケンを用いる反応の開発も行った。本講演では、最近の成果も含めた本研究の詳細について報告する。



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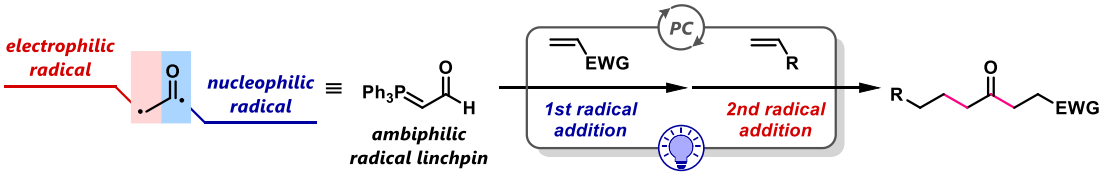
Ambiphilic ラジカル前駆体を用いた連続光触媒反応による 1,4-ジカルボニル化合物のモジュール合成

（京大院薬 [1]・広東工業大学 [2]）〇松本晃 [1]・丸岡啓二 [1,2]
Modular Synthesis of 1,4-Dicarbonyl Compounds via Sequential Photocatalysis Using Ambiphilic Radical Linchpin ([1]*Graduate School of Pharmaceutical Sciences, Kyoto University*, [2]*Guangdong University of Technology*) 〇Akira Matsumoto,[1] Keiji Maruoka[1,2]

Organic molecules that connect themselves with multiple substrates by different C−C bond-forming reactions can be utilized as linchpin reagents in multicomponent process. While they are useful in rapidly increasing the molecular complexity, the application of this method to radical chemistry has been underexplored. We recently found that a formyl-stabilized phosphorus ylide can serve both as a nucleophilic and an electrophilic carbon-centered radicals under visible-light photoredox conditions. Based on this ambiphilic character, we have developed a one-pot sequence involving two radical additions with the phosphorus ylide as a novel radical linchpin to enable the modular synthesis of 1,4-dicarbonyls from two readily available alkene fragments.
Keywords : Photoredox Catalyst; Phosphorus Ylide; 1,4-Dicarbonyl Compound; Ambiphilic Linchpin

炭素–炭素結合形成反応によって複数の基質と逐次的に連結する分子は、リンチピン試薬として多成分反応に利用される [1)]。この手法は分子骨格の複雑性を迅速に増大させる上で有用である一方、その多くは結合形成の過程で不安定な有機金属化学種を用いる必要があり、官能基許容性の低下や煩雑な実験操作を伴う。また、同様の合成戦略をラジカル反応による結合形成へ拡張する試みは未だ限られている。

最近我々は、ホルミル基によって安定化されたリンイリドが、可視光レドックス条件下において求核的ラジカルおよび求電子的ラジカルの両方の性質を有することを明らかにした。そこで、これらの性質を逐次的に発現させることで、電子的性質の異なる二種類のアルケンへの連続的なラジカル付加による多成分連結が可能であると考えた。検討の結果、一つの可視光レドックス触媒によって二種類のラジカル付加反応が駆動するワンポット連続プロセスを確立し、多様な官能基を有する 1,4-ジカルボニル化合物の迅速モジュール合成を達成した。



1) Deng, Y.; Smith, A. B., 3rd. *Acc. Chem. Res.* **2020**, *53*, 988.

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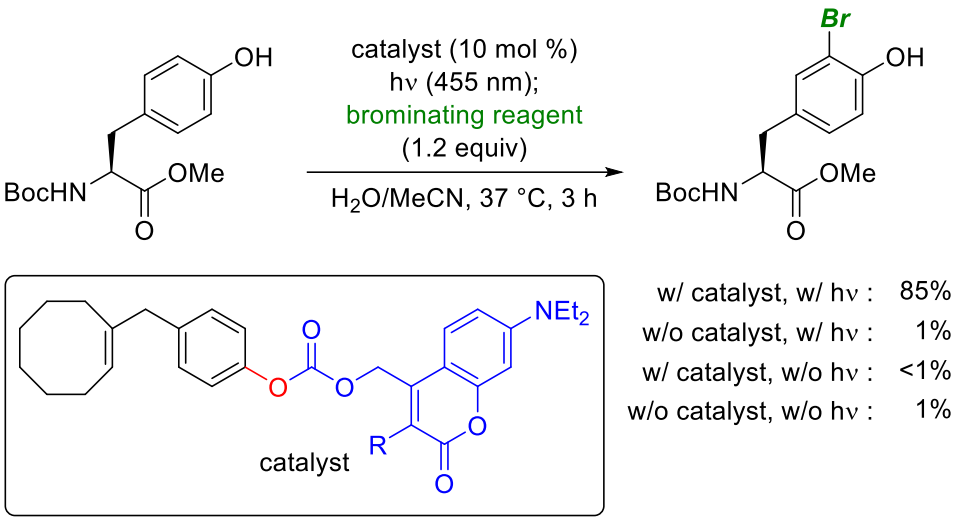
Development of Visible Light-Gated Bifunctional Cyclooctene Catalysts

([1]*Graduate School of Engineering, Kyoto University,* [2]*Institute for Catalysis, Hokkaido University*) ○Tagui Nagano,[1] Keisuke Asano,[2] Daisuke Uraguchi[2]

Keywords: Visible Light-Gated Catalyst; Cyclooctene; Bifunctional Catalyst; Halogenation

Bromination of biomolecules is significant for introduction of mass tags, which have an unusual isotopic abundance and useful for analyzing complex biomolecular systems. In this context, spatiotemporally controlled bromination of biomolecules has potentials as a powerful chemical biology tool, and for this purpose, photochemical reaction is useful. However, the methodology is underdeveloped. We recently developed bifunctional catalysts using cyclooctene derivatives, which are frequently used as click reaction tags and their biocompatibility is well-recognized,[1] and the catalytic activity is controllable through protection and deprotection of their substituents.[2] In this study, we developed light-gated bifunctional cyclooctene catalysts for bromination, which were activated in situ thorough deprotection by irradiation of ultraviolet and visible light. These catalysts were useful for bromination of tyrosine derivatives, which would be applicable to modification of peptides and proteins.



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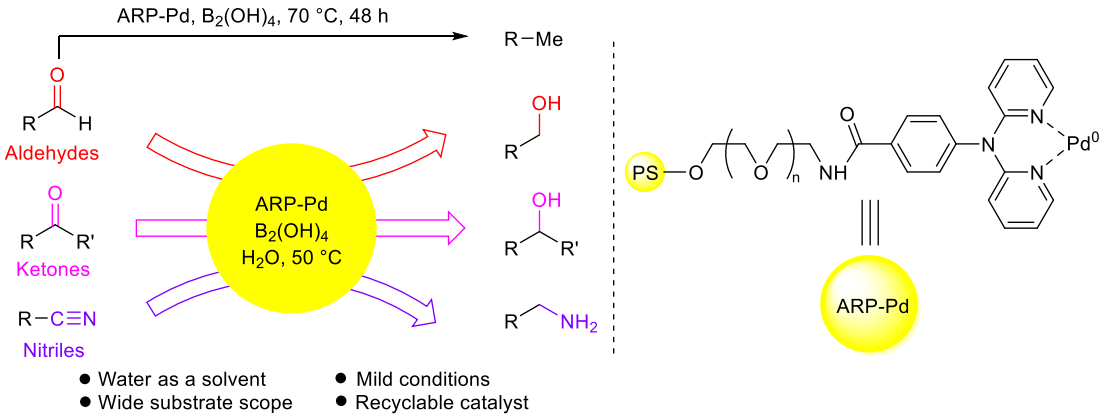
Reduction of Nitriles, Aldehydes, and Ketones with Tetrahydroxydiborn Catalyzed by an Amphiphilic Resin-Supported Nanopalladium Catalyst

([1]*Institute for Molecular Science*, [2]*The Graduate University for Advanced Studies*) ○Kaili Zhang,[1,2] Aya Tazawa,[1] Shintaro Okumura,[1,2] Yasuhiro Uozumi[1,2]

Keywords: Water; Palladium Catalysis; Tetrahydroxydiboron; Carbonyl Compounds; Nitriles

In the past few decades, tetrahydroxydiboron ($B_2(OH)_4$) has received attention as a versatile reductant. Thus, it has been reported that the combination of transition-metal catalyst and $B_2(OH)_4$ reduces various organic compounds such as alkenes, alkynes,[1] aryl halides,[2] azaarenes, and nitroarenes.[3] Herein, we report a novel reduction of aldehydes, ketones, and nitriles by $B_2(OH)_4$ with a polymer-supported palladium catalyst in water.

Amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported palladium nanoparticles (ARP-Pd) were prepared by reduction of a PS-PEG resin-supported palladium(II) complex.[4] Reduction of aldehydes and ketones with $B_2(OH)_4$ (3 equiv) was carried out in water at 50 °C for 10 min in the presence of ARP-Pd (7.5 mol%) to give the corresponding alcohols in ≤91% yield. The reduction of nitriles also proceeds with ARP-Pd (0.1-5.5 mol%), $B_2(OH)_4$ (3 equiv), and HCl (1.2 equiv) to afford the corresponding amines in up to 86% yield. Furthermore, the exhaustive reduction of aldehydes took place with $B_2(OH)_4$ and ARP-Pd at 70 °C for 48 h to give the corresponding alkyl products.



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Electrochemical Allylation Reactions Catalyzed by Nitrogen-Doped Carbon Supported Zinc Electrodes

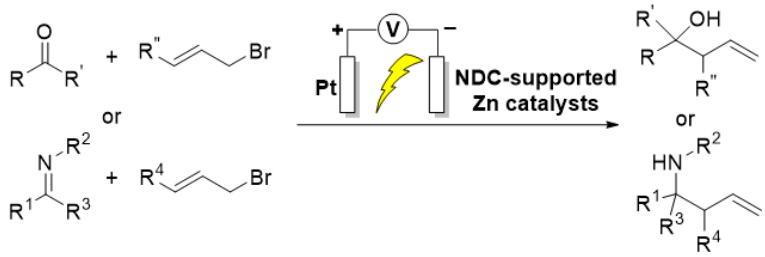
(School of Science, The Univ. of Tokyo) ○ Ryusuke MASUDA, Tomohiro YASUKAWA, Yasuhiro YAMASHITA, Shū KOBAYASHI

Keywords: Heterogeneous Catalyst; Single-Atom Catalyst; Nitrogen-Doped Carbon; Electrochemical Reaction; Allylation Reaction

Heterogeneous catalysts have great advantages over homogeneous catalysts due to their reusability, applicability to continuous-flow reactions, and reducing wastes significantly. Nitrogen-doped carbon (NDC) is an attractive support for metal nanoparticles or single-atom catalysts to stabilize metal species by strong metal-nitrogen interactions.[1] We have recently developed nitrogen-doped carbon incarcerated metal nanoparticle catalysts (NCI-M) prepared from poly(4-vinylpyridine) through a polymer-incarceration method for not only redox reactions but also carbon–carbon bond-forming reactions including asymmetric reactions.[2]

Organometallic reagents hold a special place in organic synthesis because they have widespread synthetic applications based on carbon–carbon bond formation. However, in conventional methods, stoichiometric amounts of metal reagents are required in such transformations and large amounts of metallic wastes are generated, which have hindered applications to continuous-flow systems. Therefore, catalytic carbon–carbon bond-forming reactions without metallic wastes are required significantly.

We envisioned an electrochemical approach in which catalytic amounts of metals supported on nitrogen-doped carbon-based cathode form organometallic reagents and subsequent electroreduction after the reaction regenerates metal(0) on the cathode. We developed nitrogen-doped carbon-supported zinc catalysts and used them as an electrode to achieve electrochemical allylation reactions of carbonyl compounds and imines. In contrast to conventional allylation reactions using organometallic reagents, the system not only minimized metal-derived waste but also proceeded with a catalytic amount of zinc. It was also successfully applied to electrochemical continuous-flow reactions. The detail results will be reported in this lecture.



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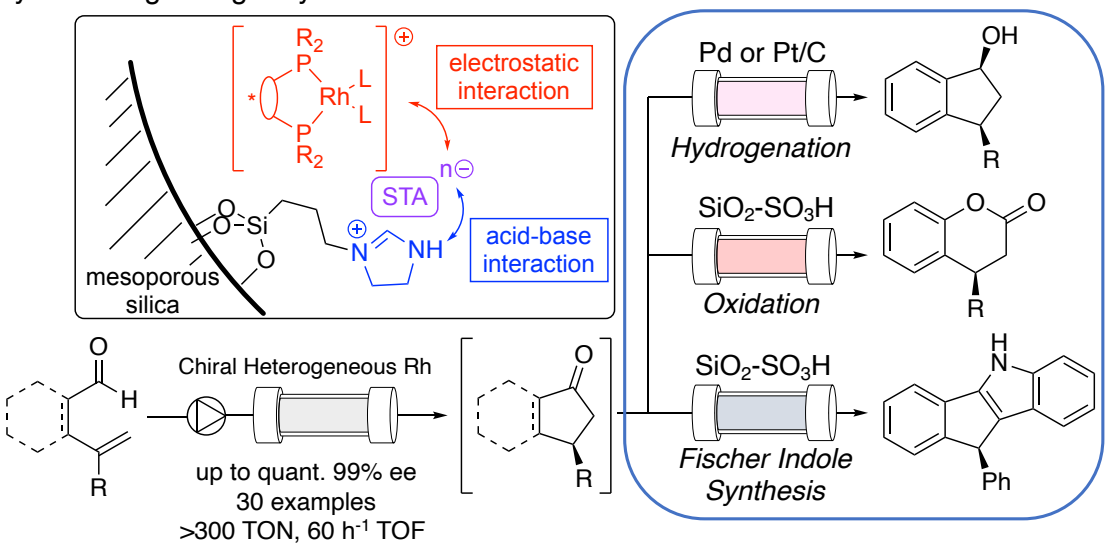
Continuous-Flow Enantioselective Hydroacylations with Chiral Heterogeneous Rh Catalysts and Sequential-Flow Transformations

(School of Science, The Univ. of Tokyo) ○ Yuki SAITO, Shū KOBAYASHI

Keywords: Heterogeneous Catalyst; Flow Reaction; Enantioselective Reaction; Rh; Hydroacylation

Transition metal-catalyzed enantioselective C−H bond functionalization has become an efficient method for synthesis of complex optically active molecules. However, heterogeneous catalysts for this chemistry have remained unexplored despite the advantages in easy catalyst separation and reuse. On the other hand, our group recently developed an efficient immobilization method of chiral metal catalysts using heteropoly acid/amine-functionalized SiO_2 composite and enantioselective flow reactions using chiral heterogeneous catalysts prepared by this approach.[1,2] Herein, we report the development of chiral heterogeneous Rh catalysts for continuous-flow enantioselective hydroacylations using this technique.

Heterogeneous catalysts were prepared by simply mixing supports and chiral Rh complexes[3], and prepared catalysts showed excellent activity to afford indanone derivatives in quantitative yield with 99% ee. It was found that the structure of amine on the surface of mesoporous SiO_2 had a significant effect on catalyst activity and selectivity. Under the optimized reaction conditions, >300 TON was achieved without leaching of Rh species. The catalysts demonstrate wide substrate scope, and sequential flow reactions combining with other heterogeneous catalyses for synthesizing biologically active molecules were realized.



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[D1443-3am] 16. Natural Products Chemistry, Chemical Biology

Chair: Atsushi Shimoyama, Daisuke Takahashi

Fri. Mar 24, 2023 9:00 AM - 10:00 AM D1443 (1443, Bldg. 14 [4F])

[D1443-3am-01] Posttranslational glycan modification in *Thermococcus kodakarensis*: discovery and synthesis of *myo*-inositol containing *N*-glycan

○Kohtaro Hirao[1], Yoshiyuki Manabe[1,2], Koichi Fukase[1,2] (1. Graduate School of Science, Osaka University, 2. Forefront Research Center, Osaka University)

9:00 AM - 9:20 AM

[D1443-3am-02] Synthesis of acetic acid bacteria *Acetobacter pasteurianus* lipid A

○Haruki Yamaura[1], Atsushi Shimoyama[1], Koichi Fukase[1] (1. Osaka university)

9:20 AM - 9:40 AM

[D1443-3am-03] Synthetic Study in Dendritic Glycosylation Contributing to Assembly of Diverse High-mannose-type Glycan Library

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

9:40 AM - 10:00 AM

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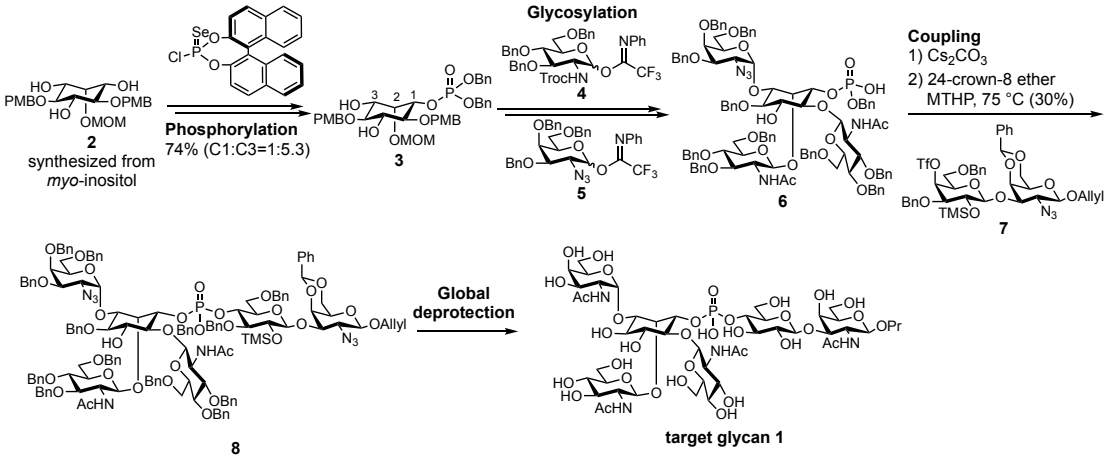
Posttranslational glycan modification in *Thermococcus kodakarensis*: discovery and synthesis of *myo*-inositol containing *N*-glycan

([1]*Graduate School of Science, Osaka University,* [2]*Forefront Research Center, Osaka University*) ○Kohtaro Hirao,[1] Yoshiyuki Manabe,[1,2] Koichi Fukase[1,2]

Keywords: Thermophilic Archaea; *N*-Glycan; Inositol; Glycosylation; Phosphoester

Archaea membrane proteins are glycosylated with asparagine-linked oligosaccharides (*N*-glycans), same as eukaryote proteins. However, their functions have not been well elucidated. To address this issue, we previously isolated *N*-glycan from the hyperthermophilic archaeon, *Thermococcus kodakarensis*, and determined its structure as **1** (scheme 1). *N*-Glycan **1** has highly glycosylated inositol, which is linked with the disaccharide via phosphate. We achieved the chemical synthesis of **1** (Scheme 1). According to our previous report,[1] **3** was synthesized via regioselective phosphorylation of **2** using an asymmetric phosphorylation reagent. Glycosylation of **3** with **4** followed by introduction of galactosamine using **5** afforded **6**. Coupling between the inositol phosphate and the disaccharide was then investigated under condensation conditions using various reagents, including CDI, DCC, PyBOP, and DIAD/PPh_3, but the reactions did not proceed. After the thorough investigation, S_N2 type reaction between cesium salt of phosphoric acid **6** and triflate **7** successfully gave the desired coupling product **8**. After global deprotection, we obtained the target glycan **1**. A comparison of the NMR data of the isolated *N*-glycan with that of synthetic **1** confirmed the structure of the *N*-glycan.



Scheme 1. Synthesis of target glycan **1**

1) Aiba, T. et al. *Chem. Eur. J.* **2017**, 23, 8304.

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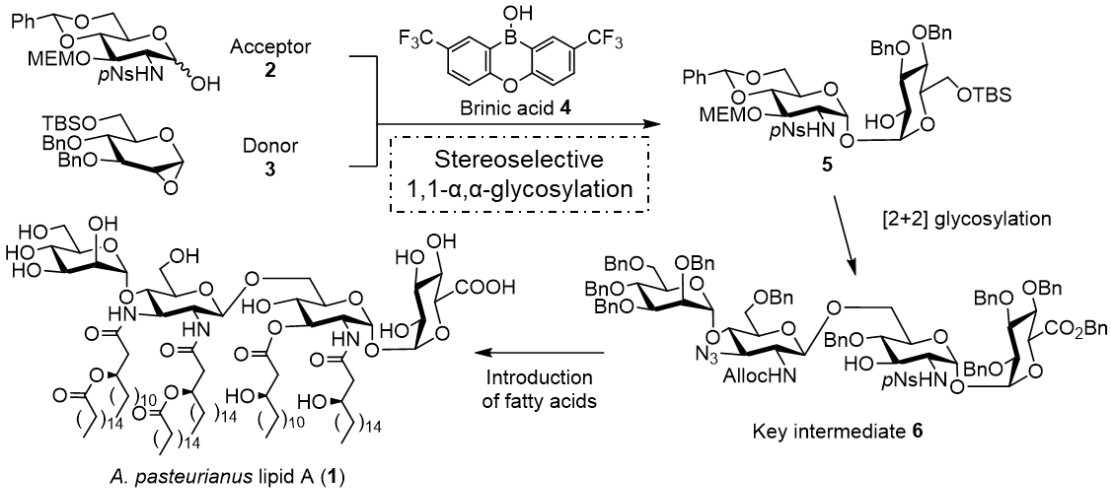
Synthesis of acetic acid bacteria *Acetobacter pasteurianus* lipid A

(*Graduate School of Science, Osaka University*) ○Haruki Yamaura, Atsushi Shimoyama, Koichi Fukase

Keywords: innate immunity; lipid A; *Acetobacter pasteurianus*; acetic acid bacteria; adjuvant

Lipopolysaccharide (LPS), one of the cell surface components of Gram-negative bacteria, activates innate immunity. LPS and its active entity lipid A are candidates for vaccine adjuvants that enhance the effectiveness of vaccine. Many bacterial LPSs such as canonical *Escherichia coli* LPS have strong immunostimulatory function but highly inflammatory effect and lethal toxicity. Therefore, it is essential to control the toxicity in order to apply LPS and lipid A to adjuvants.

In this study, we focused on an acetic acid bacteria *Acetobacter pasteurianus* lipid A (**1**)[1], which is expected to be safe through food experience, as a low-toxicity adjuvant (Scheme 1). *A. pasteurianus* lipid A (**1**) contains a unique tetrasaccharide backbone that is unprecedented in synthesis. Here, we investigated the efficient construction of 1,1-α,α-glycosidic linkage of **5** and found that 1,2-*cis*-glycosylation between **2** and **3** catalyzed by borinic acid **4**[2] afforded **5** in high yield and stereoselectivity. Next, [2+2] glycosylation was used to synthesize the key intermediate **6** with orthogonal protecting group pattern. After introduction of various fatty acids into appropriate positions of **6**, all protecting groups were removed by catalytic hydrogenolysis to achieve the first chemical synthesis of *A. pasteurianus* lipid A (**1**). Its biological activity is now under investigation.



Scheme 1. Synthesis of *A. pasteurianus* lipid A (**1**)

1) M. Hashimoto, K. Fukase, Y. Fujimoto, et al., *J. Bio. Chem.*, **2016**, *291*, 21184–21194. 2) Y. Takemoto, et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 14054–14059

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樹状型グリコシル化法による分岐鎖伸長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・栗原 大輝・戸谷 希一郎

Synthetic Study in Dendritic Glycosylation Contributing to Assembly of Diverse High-mannose-type Glycan Library (*Department of Science and Technology, Seikei University*) ○ Ruchio Usui, Megumi Kabasawa, Taiki Kuribara, Kiichiro Totani

Various high-mannose-type glycans play significant biological roles such as glycoprotein quality control. For the analysis of the biological functions, high-mannose branched isomers are the key to increasing the effectiveness of medical applications. However, there is problematic in rapid access to obtain a sufficient amount of branched library of high-mannose-type glycans. To overcome the above subject, we designed the one-pot strategy called dendritic glycosylation, contributing to their branch synthesis.

Dendritic glycosylation is a two-step process in which all branched chains are elongated simultaneously. In the first step, we elongated the triple branches of $Man_3GlcNAc_2$ (M3)-type tri-OH accepter provided by bottom-up chemical synthesis. 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. This strategy was implemented in two phases: model experiments of partial structures of target glycans and application to the synthesis of natural-type high mannose-type glycans.

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。生体機能の解析には、高マンノース型糖鎖上の多様なブランチ異性体の理解が重要だが、高マンノース型糖鎖の分岐鎖ライブラリーは、十分な量を迅速に入手することが困難である。そこで、我々は研究試料として有用な高マンノース型分岐糖鎖ライブラリー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。

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。樹状型グリコシル化は、２つの段階的フェーズから構成される。第一段階では、化学合成で得られた tri-OH を有する $Man_3GlcNAc_2$（M3）型の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、２段階目に、同様に tri-OH を有する M6 型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。

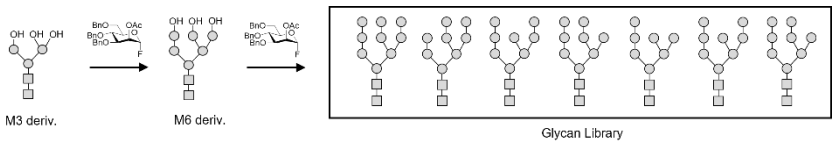

Figure 1. Dendritic Glycosylation Strategy

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

[E1661-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Shinya Ariyasu, Shun Hirota

Fri. Mar 24, 2023 9:00 AM - 11:30 AM E1661 (1611, Bldg. 16 [1F])

[E1661-3am-01] **Accumulation of Protein Cage into in-cell Protein Crystal**

○THUC TOAN PHAM[1], Koki Date[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology/ School of Life Science and Technology)

9:00 AM - 9:20 AM

[E1661-3am-02] Construction of Antifreeze protein like semi-clathrate hydrate in the ferritin cage

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

9:20 AM - 9:40 AM

[E1661-3am-03] Structure analysis of pH-responsive piston dynamics of R-body

○Koki DATE[1], Thuc Toan PHAM[1], Hyeonho LEE[1], Takayuki UCHIHASHI[2], Hironari KAMIKUBO[3], Chihong SONG[4], Kazuyoshi MURATA[4], Takafumi UENO[1] (1. School of Life Science and Technology, Tokyo Institute of Technology, 2. Graduate School of Science, Nagoya University, 3. School of Science and Technology, NAIST, MS, 4. ExCELLS/NIPS)

9:40 AM - 10:00 AM

[E1661-3am-04] Developing protein-cellulose nanocrystal hybrid films for structural coloration

○Kosuke Kikuchi[1], Bruno Frka-Petesic[2], Silvia Vignolini[2], Takafumi Ueno[1] (1. Tokyo Institute of Technology, 2. University of Cambridge)

10:00 AM - 10:20 AM

[E1661-3am-05] Construction of a stimuli-responsive cytochrome *c*-based hydrogel driven by its folding and unfolding behavior

○Kazuki Kageyama[1], Takahiro Urayama[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka university)

10:30 AM - 10:50 AM

[E1661-3am-06] Development of Myoglobin-based Artificial Metalloenzymes: Nitrile Synthesis via Dehydration of Aldoximes

○Miteki Abe[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Osaka University)

10:50 AM - 11:10 AM

[E1661-3am-07] ATP Responsive Two-Dimensional Biomaterial from Biomolecular machine GroEL

○TONMOY RAY[1,2], TAKUZO AIDA[1,2] (1. The University of Tokyo, 2. RIKEN CEMS)

11:10 AM - 11:30 AM

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Accumulation of Protein Cage into in-cell Protein Crystal

(*School of Life Science and Technology, Tokyo Institute of Technology*) ○Thuc Toan Pham, Koki Date, Satoshi Abe, Takafumi Ueno

Keywords: Protein cage, Polyhedra crystal, In-cell accumulation, ferritin

In-cell protein crystals such as polyhedra crystal (PhC) appear as a promising scaffold to construct solid material because of the high stability and advantage in preparation.[1] The original function of PhC is to encapsulate CPV viruses into cubic crystalline particles inside insect cells and then release them at higher pH. Inspired by that phenomenon, there were reports of the construction of solid materials by encapsulating target proteins into PhC *via* co-crystallization. The most-used common technique is the co-expression of PhC and a fusion protein between the target and H1 segment derived from the N-terminal of polyhedrin monomer (PhM).[2, 3] This technique has been used to encapsulate monomeric proteins. We devised an idea to establish a method to effectively encapsulate protein assemblies into PhC crystals *via* crystallization because many proteins exhibit their functions through their assembled structures.

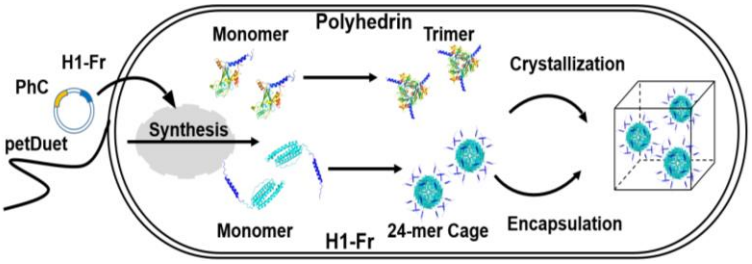

Figure 1. Encapsulation of H1-Fr cage into PhC by co-expression in *E.coli* cells.

In this work, we select the target of ferritin, a natural protein cage composed of 24 subunits. Ferritin is a high-stability protein cage and a well-known scaffold used for functionalization; therefore, accumulating ferritin cages into PhC will open more opportunities to construct solid functional materials. Furthermore, the Ferritin cage exposes the N-terminal of all subunits at the outer surface of the cage, so we fused the H1 segment derived from PhC to the N-terminal of Ferritin (**H1-Fr**). When **H1-Fr** is co-expressed with PhM in *E.coli*, 24 H1 segments are assembled on the outer surface of ferritin, and the interaction between H1 and PhC results in the synthesis of PhC encapsulating **H1-Fr**. (Figure 1). Co-expression of Fr without H1 and PhM did not encapsulate ferritin into PhC. Our data demonstrate the formation of the **H1-Fr** cage after fusing the H1 segment to ferritin and the high encapsulation of the **H1-Fr** into PhC. Furthermore, we also optimize the lengths of the H1 helix to maximize the accumulation of **H1-Fr** cages into PhC. Our results provide a promising technique for constructing solid functional materials by accumulating protein assemblies into PhC crystals.

1) Fasséli Coulibaly *et al.*, *Nature*, **2007**, 446, 97–101.
2) Tien K. Nguyen *et al., ACS Appl. Nano Mater,* **2021**, 4, 2, 1672–1681.
3) Mariko Kojima *et al.*, *Biomater. Sci.*, **2022**,10, 354-367.

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Construction of antifreeze protein like semi-clathrate hydrate in the ferritin cage

([1] *School of Life Science and Technology, Tokyo Institute of Technology*)
○ Jiaxin Tian[1], Maity Basudev[1], Satoshi Abe[1], Takafumi Ueno[1]

Keywords: ferritin, water clusters, semi-clathrate, X-ray structure

Water molecules play essential roles in protein structures and functions by forming hydrogen-bonding networks [1]. Besides such roles, the water molecules can also form polygonal water clusters such as pentagons found in some antifreeze proteins (Fig. 1a) [2] to inhibit ice growth in organisms at sub-zero temperatures [3]. This kind of water pentagonal cluster is commonly called semi-clathrate hydrates. The artificial design of semi-clathrate hydrates can extend the potential applications of antifreeze protein in cryo-technology, such as organ storage and cryo-medicine. Most current studies focused on understanding the ice-binding mechanism by antifreeze proteins. More information is needed about how semi-clathrate is formed and the artificial design. These are useful for developing artificial antifreeze proteins for practical applications.

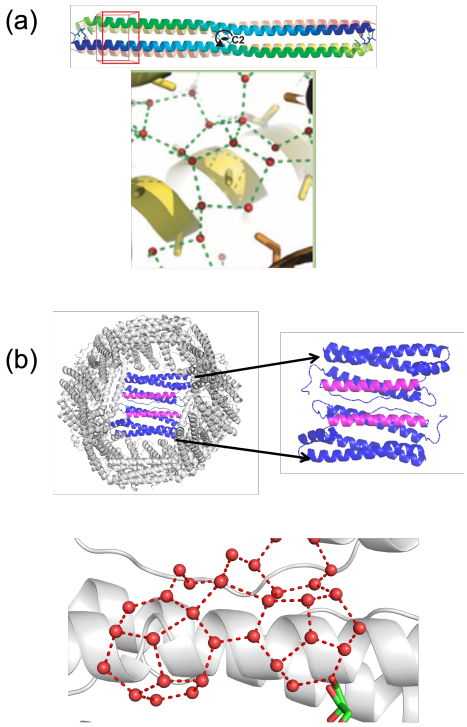

Figure 1. (a)Helices structure of type I antifreeze protein, Maxi (upper) and semi-clathrate structure (bottom). (b)The 2-fold symmetric interface of ferritin (upper). The semi-clathrate hydrate constructed in the poly-Ala mutant (bottom）.

In this presentation, we will describe the construction of artificial semi-clathrate hydrate in the ferritin cage (Fig. 1b). The ferritin cage has 2-, 3-, and 4-fold symmetrical interfaces to maintain the 24-mer assembly structure. The 24-mer assembly structure forms an internal hollow with a diameter of 8nm. Two helices are aligned with an antiparallel interface, which is considered a suitable site for forming semi-clathrates as a model of Maxi (Fig. 1b upper). We constructed poly-Ala regions at this interface. The crystal structure of the poly-Ala mutant shows that semi-clathrates are formed on the substituted alanine. (Fig. 1b bottom). The detailed X-ray crystal structure and the comparison with natural semi-clathrates in Maxi will be discussed.

Reference:
[1] J. Lee and S. H. Kim, *Protein Science*. **2009**, 18, 1370. [2] T. Sun, et al., *Science*. **2014**, 343, 795.
[3] P. L. Davies, *Trends Biochem. Sci*. **2014**, 39, 548

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pH 応答性伸縮タンパク質集合体の動的構造の解析

（東工大生命理工 [1]、名大院理 [2]、奈良先端大物質 [3]、ExCELLS・生理学研究所 [4]）○伊達弘貴 [1]・Thuc Toan PHAM[1]・Hyeonho LEE[1]・内橋貴之 [2]・上久保裕生 [3]・宋致宏 [4]・村田和義 [4]・上野隆史 [1]
Structure analysis of pH-responsive piston dynamics of R-body ([1]School of Life Science and Technology, Tokyo Institute of Technology, [2]Graduate School of Science, Nagoya University, [3]School of Science and Technology, NAIST, MS, [4]ExCELLS/NIPS) ○DATE Koki,[1] Thuc Toan PHAM,[1] Hyeonho LEE,[1] UCHIHASHI Takayuki,[2] KAMIKUBO Hironari,[3] SONG Chihong,[4] MURATA Kazuyoshi,[4] UENO Takafumi[1]

Solid materials formed by the assembly of proteins are attracting attention as soft materials because of their unique properties and shapes. We focused on the Refractile body (R-body), a molecular piston constructed in living cells.[1] This protein reversibly extends and contracts from a coiled structure with 400 nm to a tube with a 20 μm length between pH 5 and 7. (Fig. 1)[2] Although the three-dimensional structure has been observed by transmission electron microscopy in previous studies, the detailed structure has not yet been determined. (Fig. 1)[2] In this study, we analyzed the protein assembly structure using high-speed atomic force microscopy (HS-AFM). Furthermore, the result of attenuated total reflection infrared spectroscopy (ATR-IR) indicates that the α-helix is the major secondary structure component. Using these results and the predicted structure by AlphaFold2, we attempted to create an assembly structure model.
Keywords : Protein assembly; pH-responsive; Active matter; Small Angle X-ray Scattering: SAXS; High-Speed Atomic Force Microscopy: HS-AFM

タンパク質が集合化することによって形成される固体材料は，その特異な物性や形状から次世代ソフトマテリアルとして注目されている．我々はゾウリムシの細胞共生体内で発現し，伸縮により内側から細胞を破壊する Refractile body（R-body）に注目した [1]．R-body は，pH 5 と pH 7 の間で長さ 400 nm コイル構造から，長さ 20 μm のチューブ構造へと可逆的な伸縮を行う（Fig. 1）[2]．先行研究では，その三次元構造は透過型電子顕微鏡で観察できているものの，詳細な構造決定には至っていない（Fig. 1）[2]．そこで本研究では，伸縮メカニズムの解明にはタンパク質の集積構造を解明することが必要と考え，高速原子間力顕微鏡（HS-AFM）測定等を用いた構造解析を行った．HS-AFM 測定でチューブ状の R-body の内側表面および外側表面の構造を観測した．さらに，全反射赤外分光法（ATR-IR）測定から 1650 cm^{-1} 付近に Amide I の α ヘリックスに特徴的なピークが観測された．この結果から α ヘリックスが主要二次構造成分となっていることが示された．これらの結果と AlphaFold2 の予想構造を用いて集積構造モデルの作成及び，伸縮メカニズムの解明を試みた．

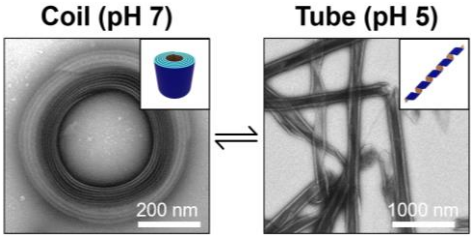

Fig. 1 TEM image of R-body.[2]

1) Pond, F. R. *et al.*, *Microbiol. Rev.* 53, 25-67, **1989**. 2) Polka, J. K. *et al.*, *ACS Synth. Biol.* 5, 303-311, **2016**.

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Developing protein-cellulose nanocrystal hybrid films for structural coloration

([1]*School of Life Science and Technology, Tokyo Institute of Technology*, [2]*Yusuf Hamied Department of Chemistry, University of Cambridge*) ○Kosuke Kikuchi,[1] Bruno Frka-Petesic,[2] Silvia Vignolini,[2] Takafumi Ueno[1]

Keywords: Protein Chemistry; Cellulose Nanocrystal; β-lactoglobulin; Structural Color; Polarized Microscopy

Modulating the adhesion, plasticity, and other properties of films is essential to improve the durability of the materials. With the demand for biocompatible and sustainable materials, it has been required to develop biopolymer-based films.

The polysaccharide cellulose is the most abundant organic compound on earth and constitutes plant cell walls.[1] Cellulose nanocrystals (CNCs), which are generally formed by chemical hydrolysis of cellulose fibers, are rod-shaped sub-micron colloids and are known to self-assemble into chiral nematic (cholesteric) structures upon drying (Figure 1a).[2] Due to its periodic Bouligand structure, the CNC films show structural color. Although CNC films have been extensively studied over decades, proteins used for the modulation of their properties were limited to polydisperse fibril assemblies such as amyloids and silk fibroins.[3,4]

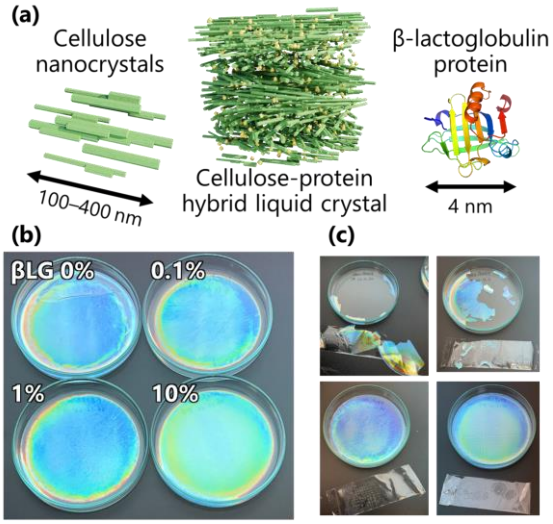

Figure 1. (a) The schematic illustration of cellulose nanocrystals (CNCs), β-lactoglobulin (βLG, PDB ID: 1BEB), and their complex. (b) βLG-CNC mixed films with varied protein mass (0, 0.2, 2.0, 20 mg) against fixed CNC dry mass (200 mg). (c) The adhesion test results for the films in (b).

In this work, we used β-lactoglobulin (βLG) protein from bovine whey to control the hydrophilicity and plasticity of the CNC film (Figure 1b). βLG is an abundant protein with a diameter of about 4 nm (Figure 1a).[5] We performed polarization microscopy observations, UV-Vis spectroscopy, and adhesion tests for the βLG-CNC hybrid films (Figure 1c). Since protein's charge and functional groups on the surface can be rationally designed by conventional protein engineering techniques, this work opens the door for highly controllable and sustainable protein-cellulose hybrid materials for optics, coating, and food industries.

[1] A. C. O'Sullivan, *Cellulose* **1997**, *4*, 173-207. [2] T. G. Parton, *et al.*, *Nat. Commun.* **2022**, *13*, 2657. [3] G. Guidetti, *et al.*, *Adv. Sustain. Syst.* **2021**, *5*, 2000272. [4] K. J. De France, *et al.*, *Biomacromolecules.* **2020**, *21*, 5139-5147. [5] S. Brownlow, *et al.*, *Structure* **1997**, *5*, 481-495.

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Construction of a stimuli-responsive cytochrome *c*-based hydrogel driven by its folding and unfolding behavior

(*Graduate School of Engineering, Osaka University*) ○Kazuki Kageyama, Takahiro Urayama, Koji Oohora, Takashi Hayashi

Keywords: Hydrogel; Cytochrome *c*; Stimuli-responsive gel; Biomaterials

Stimuli-responsive gels, which change their volume and properties in response to external stimuli, have attracted attention as unique materials for chemical sensors and actuators. As a component of new biomaterials, protein is a useful candidate. Their structure and/or physicochemical properties are expected to change with external stimuli such as pH and temperature changes. Toward a new type of biomaterials, we have focused on cytochrome *c*, an electron-transfer hemoprotein, as a building block. Heme, an iron porphyrin complex, is covalently attached to the protein matrix *via* sulfide bond, and histidine and methionine are coordinated to the iron center. The stability of the folding structure is strongly related to the S–Fe coordination bond between methionine and heme, and the unfolding event occurs after cleavage of this ligation[1]. Furthermore, the stability depends on redox state of the iron center: the folding structure of the Fe^{2+} state is more stable than that of the Fe^{3+} state[2] (Fig 1). This feature enables to monitor redox-driven folding and unfolding events.

In this study, a cytochrome *c*-based redox responsive hydrogel has been constructed by Schiff base formation *via* reaction of glutaraldehyde with amino groups on the protein surface. The Schiff base moieties were further reduced by sodium cyanoborohydride and then the iron center was oxidized to obtain the designed gel (Fig 2). This gel in the Fe^{3+} state shows the swelling behavior in the presence of 3.5 M chemical denaturant. The gel shrinks upon the addition of reductant. This redox-responsive volume change is confirmed to be reversible and would be caused by the unfolding-refolding of cytochrome *c*.

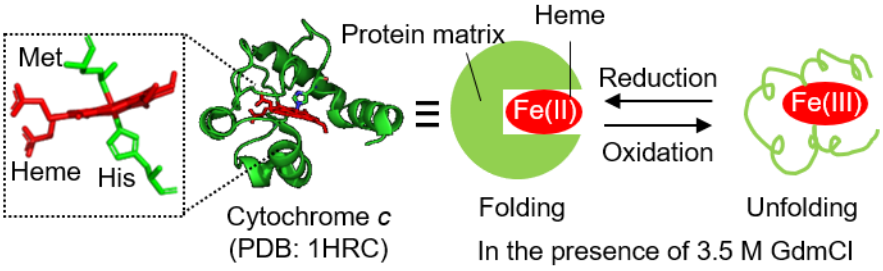

Fig. 1. Redox-dependent folding-unfolding behavior of cytochrome *c*.

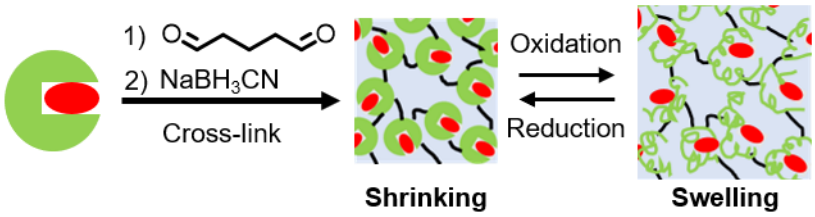

Fig. 2. Preparation of cytochrome *c*-based hydrogel.

1) D. L. Rousseau *et al.*, *J. Biol. Chem.*, **1999**, *274*, 17853. 2) H. B. Gray *et al.*, *Science*, **1996**, *271*, 1558.

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ミオグロビンを利用した人工金属酵素の開発：アルドキシム脱水反応によるニトリル合成

（阪大院工）○阿部 美笛・加藤 俊介・林 高史

Development of Myoglobin-based Artificial Metalloenzymes: Nitrile Synthesis via Dehydration of Aldoximes. (*Graduate School of Engineering, Osaka University*) ○Miteki Abe, Shunsuke Kato, Takashi Hayashi

Industrial process of nitrile synthesis requires harsh conditions (high temperature, strong basicity) and special reagents, which are of concern in the field of green chemistry. To develop a sustainable production process, we here achieved highly efficient nitrile synthesis under mild conditions using an artificial metalloenzyme (Figure 1). The artificial metalloenzyme (rMb-FePc) was prepared by replacing heme *b*, the cofactor of myoglobin (Mb), with iron porphycene (FePc). rMb-FePc showed high catalytic activity toward dehydration reaction of aldoximes to produce nitriles. Total turnover number reaches up to 5.0×10^3 under mild conditions (30 C, pH 7.0). Furthermore, introduction of an amino acid residue with a hydroxyl group in the active site enhances the initial rate of the rMb-FePc-catalyzed dehydration reaction by more than four-fold.

Keywords : Biocatalysis; Artificial Metalloenzyme; Nitrile; Myoglobin; Aldoxime dehydratase

ニトリル合成は、化学工業プロセスにおいて過酷な条件（高温、強塩基性）や、特殊な試薬を必要とし、環境負荷の大きさや官能基耐性の低さが問題となる。そこで本研究では、持続可能な生産プロセスの開発をめざし、人工金属酵素を利用することで、温和な条件下で高効率なニトリル合成を達成した。ミオグロビン（Mb）に鉄ポルフィセン（FePc）を再構成した人工金属酵素（rMb-FePc） は、アルドキシムの脱水によるニトリル合成反応に対して、温和な条件下（30 °C, pH 7.0）で、触媒回転数 5.0×10^3 の高い触媒活性を示した。さらに、rMb-FePc の活性中心近傍に水酸基(Ser, Tyr)を有するアミノ酸残基の変異導入を行ったところ、脱水反応の初速度は 4 倍以上となった。

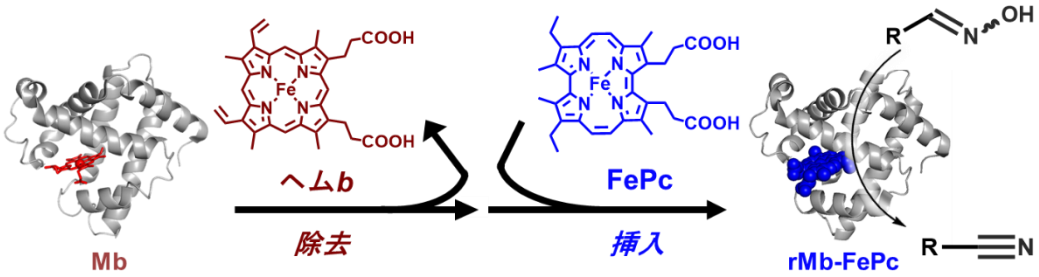

Figure 1. Nitrile synthesis catalyzed by rMb-FePc

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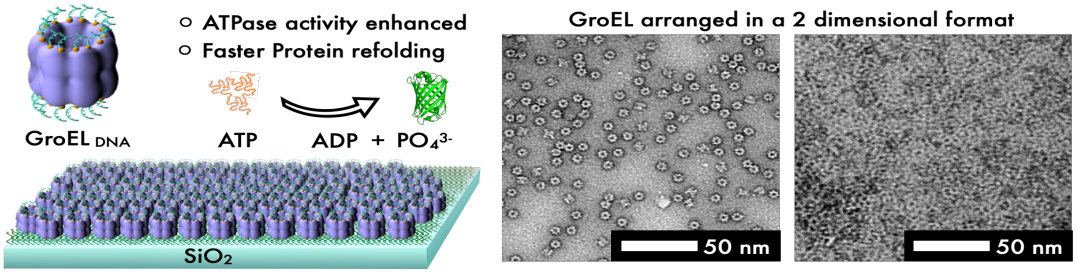
ATP Responsive two-dimensional Biomaterial from Biomolecular machine GroEL

([1]*Graduate School of Engineering, The University of Tokyo,* [2]*RIKEN Center for Emergent Matter Science*)
○Tonmoy Ray[1], Takuzo Aida[1,2*]

Keywords: Biomolecular machine; Surface immobilization; Enzyme catalysis; Porous Materials; Stimuli Responsive

Naturally occurring membranous structures are formed by the precision lateral assembly of monomeric building blocks such as lipids or proteins [1]. However, achieving two-dimensional (2D) structures of proteins is still a big synthetic challenge. Herein, we report a synthesis strategy where we utilize DNA attached GroEL as shape-persistent building blocks for the construction of an endogenous- stimuli-responsive, porous 2D sheet. Chaperonin GroEL is a biomolecular machine consisting of two stacked heptameric rings, each with a 4.6-nm cavity, with an opening at the apical domain. GroEL encapsulates denatured proteins into its cavities, facilitates refolding and releases captured proteins by adenosine triphosphate (ATP)-induced mechanical opening/closing motions. The apical domains and sidewall of GroEL are stable against enzymatic/chemical modifications. This is an advantage of using GroEL as a building block for biomaterial applications. Our lab has pioneered the use of GroEL for nanotubular supramolecular polymerization [2–6].
The current design demonstrates the structural advantage of **GroEL$_{DNA}$**, which has densely functionalized DNA motifs on its apical domain site-specifically. To support this precision 2-D lateral assembly structure a DNA coated surface was engineered. Upon annealing conditions, an excess of monomeric units preferentially hybridize and align themselves on to the substrate surface. Further the design has been optimized to crosslink the assembly and exfoliate from the surface using DNA toehold mediated mechanism. Currently the studies show a high ATPase activity and also interesting properties like guest refolding during immobilization. Next, we are curious to exploit the porous nature of this novel biomaterial for membrane applications.



[**References**]
[1] *Microbiol. Rev.* **2014**, *38*, 823. [2] *JACS* **2013**, *135*, 11509. [3] *JACS* **2015**, *137*, 4658. [4] *JACS* **2016**, *138*, 11152. [5] *JACS* **2018**, *140*, 26. [6] *JACS* **2020** 142, *31*, 13310.

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

[E1662-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Hiroshi Nonaka, Yusuke Nasu

Fri. Mar 24, 2023 9:00 AM - 11:30 AM E1662 (1612, Bldg. 16 [1F])

[E1662-3am-01] Screening of catalytic antibodies against PD-1 and PD-L1 and the features of clones obtained

Emi Hifumi[2], Tamami Nonaka[2], Hiroaki Taguchi[3], ○Taizo Uda[1,2] (1. ISIT, 2. Olta Univ., 3. Suzuka Univ. Med. Sci.)

9:00 AM - 9:20 AM

[E1662-3am-02] Generation of stable microtubule superstructures induced by Tau-derived peptide-fused tetrameric proteins

○Hiroshi Inaba[1], Yurina Sueki[1], Muneyoshi Ichikawa[2], Arif Md. Rashedul Kabir[3], Takashi Iwasaki[4], Akira Kakugo[3], Kazuki Sada[3], Kazunori Matsuura[1] (1. Graduate School of Engineering, Tottori University, 2. Graduate School of Science and Technology, Nara Institute of Science and Technology, 3. Graduate School of Science, Hokkaido University, 4. Graduate School of Agricultural Sciences, Tottori University)

9:20 AM - 9:40 AM

[E1662-3am-03] Artificial control of protein secretion using thermogenetic dissociation module

○Mizuki Endo[1], Takeaki Ozawa[1] (1. The University of Tokyo)

9:40 AM - 10:00 AM

[E1662-3am-04] Genetically encoded fluorescent biosensors for L-lactate

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

10:00 AM - 10:20 AM

[E1662-3am-05] Development of new labeling reagents for endogenous receptors in the live mouse brain and their application to multiplex imaging

○Hiroshi Nonaka[1,2], Mengchu Wang[3], Takuma Takeshi[1], Kazuki Shiraiwa[1], Seiji Sakamoto[1,2], Itaru Hamachi[1,2] (1. Graduate School of Engineering, Kyoto Univ., 2. JST, ERATO, 3. Faculty of Engineering, Kyoto Univ.)

10:30 AM - 10:50 AM

[E1662-3am-06] Photooxidation-driven proximity labeling for mapping neurotransmitter receptor interactome in live mouse brain

○Tomonori Tamura[1], Mikiko Takato[1], Seiji Sakamoto[1,2], Hiroshi Nonaka[1,2], Itaru Hamachi[1,2] (1. Kyoto University, 2. JST ERATO)

10:50 AM - 11:10 AM

[E1662-3am-07] Identification of a gene involved in lanthanide switch by analysis of the mutants isolated during the cultivation of *Methylosinus trichosporium* OB3b with glycerol

○Wataru Shiina[1], Hidehiro Ito[1], Toshiaki Kamachi[1] (1. Tokyo Institute of Technology)

11:10 AM - 11:30 AM

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PD-1 及び PD-L1 に対する各抗体酵素の探索と得られたクローンの性質

（大分大研究機構 [1]・大分大 GL 感染研 [2]・鈴鹿医療大薬 [3]・九州先端研 [4]）一二三 恵美 [1,2]・野中 玲実 [1]・田口 博明 [3]・〇宇田 泰三 [1,4]

Screening of catalytic antibody against PD-1 and PD-L1 and the features of clones obtained (*[1] Institute for Research Management, Oita University, [2] Research Center for GLOBAL/LOCAL Infectious Diseases, Oita University, [2] Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science, [2] Nanotechnology Laboratory, Institute of Systems, Information Technologies and Nanotechnologies (ISIT)*) Emi Hifumi,[1,2] Tamami Nonaka,[1] Hiroaki Taguchi,[3] 〇Taizo Uda[1,4]

The PD-1 molecule is an immune checkpoint molecule expressed on T cells and is related with the function of T cells. On the other hand, PD-L1 is a ligand for PD-1 and is expressed on cancer cells. Anti-PD-1 antibody or anti-PD-L1 antibody are currently used as antibody drugs because they inhibit the PD-1/PD-L1 interaction. In this study, catalytic antibodies destroying PD-1 and/or PD-L1 were explored to inhibit the PD-1/PD-L1 interaction instead of the antibodies. As the result of screening, it was found that H34 clone specifically degraded the PD-1 peptide, where the reaction proceeded according to Michaelis-Menten mechanism. The H34 also degraded a recombinant human PD-1. Moreover, it was confirmed that H34 inhibited the PD-1/PD-L1 interaction. In other words, the PD-1/PD-L1 interaction was inhibited in a manner different from the inhibitory mechanism by conventional antibodies. Similarly, we found catalytic antibodies capable of degrading PD-L1 peptides. We will report on these properties.

Keywords : PD-1; PD-L1;catalytic antibody; interaction

PD-1 分子は T 細胞上に発現し、その働きに関与している免疫チェックポイント分子である。一方、PD-L1 は PD-1 に対するリガンドであり、がん細胞上に発現している。PD-L1 が PD-1 と結合すると、T 細胞の抗がん作用は抑制され、がん細胞は増殖する。PD-1 あるいは PD-L1 に対する抗体は PD-1/PD-L1 相互作用を阻害するため、T 細胞の抗がん活性は維持され抗体医薬品として使用されている。ただ、奏効率は 20~30%と低い点が課題である。本研究では、抗体に代わって、PD-1 や PD-L1 分子を直接壊す事により PD-1/PD-L1 相互作用を別な機序で阻害する抗体酵素の取得を目指した。

目的とする抗体酵素はヒト型抗体軽鎖バンクをスクリーニングする事で取得した。その中で、H34 クローンが PD-1 ペプチドだけを特異的に分解し、分解反応は Michaelis-Menten 式に従って進行することを確認した。また、H34 クローンはヒト PD-1 ペプチドだけでなく recombinant human PD-1 をも分解し、かつ PD-1/PD-L1 相互作用を完全に阻止した。即ち、これまでの抗体とは別な機構で PD-1/PD-L1 相互作用を阻止した事になる。尚、H34 の酵素活性は、変異導入実験の結果、これまでに多くのケースで見られた Ser-His-Asp による触媒三ツ組残基ではなく、Thr-Arg-Gln による新しい触媒三ツ組残基と推定された [1)]。PD-L1 に対する抗体酵素の取得では、 PD-1 との結合に関与するペプチド 2 種類(aa116-132 および aa60-76)を合成し、それぞれのペプチドの N 末端に蛍光基(MCA)を、C 末端には消光基（DNP）を付加した FRET 基質を用いて、PD-1 の場合と同様にスクリーニングを実施した。その結果、PD-L1 ペプチドを分解するクローンを見出した。本発表ではこれらの性質について併せて報告する。

1) E. Hifumi, T. Nonaka, H. Taguchi, T. Uda, *Scientific Reports,* (2022) 12:19185.

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Tau 由来ペプチド融合四量体タンパク質による安定な微小管超構造体形成

（鳥取大院工 [1]・奈良先端大院 [2]・北大院理 [3]・鳥取大院農 [4]）○稲葉 央 [1]・末岐 優里菜 [1]・市川 宗厳 [2]・Arif Md. Rashedul Kabir [3]・岩崎 崇 [4]・角五 彰 [3]・佐田 和己 [3]・松浦 和則 [1]

Generation of stable microtubule superstructures induced by Tau-derived peptide-fused tetrameric proteins ([1]*Graduate School of Engineering, Tottori University,* [2]*Graduate School of Science and Technology, Nara Institute of Science and Technology,* [3]*Graduate School of Science, Hokkaido University,* [4]*Graduate School of Agricultural Sciences, Tottori University*) ○Hiroshi Inaba,[1] Yurina Sueki,[1] Muneyoshi Ichikawa,[2] Arif Md. Rashedul Kabir,[3] Takashi Iwasaki,[4] Akira Kakugo,[3] Kazuki Sada,[3] Kazunori Matsuura[1]

Microtubules, one of cytoskeletons, are generally single-walled singlet structures. In nature, complex microtubule superstructures are formed as needed. However, there are few examples of *in vitro* construction of these superstructures. We have developed a Tau-derived peptide (TP) that binds to the inner surface of microtubules and have achieved the encapsulation of various nanostructures into microtubules by using TP.[1] In this study, we successfully induced the formation of various microtubule superstructures such as doublets, branches, and asters by using TP-fused Azami-Green, a tetrameric protein (TP-AG).[2]

Keywords : Peptide; Microtubules; Superstructures; Tetrameric protein; Active matter

細胞骨格の一種である微小管は一般的に一巻きのシングレット構造を形成するが、生体内では微小管が横方向に連なったダブレットや、分岐、アスターなどの複雑な超構造体が存在する。しかし、これら超構造体を *in vitro* で構築した例はほとんど存在しなかった。我々は微小管内部に結合する Tau 由来ペプチド（TP）を開発し、様々なナノ構造体の微小管への内包を達成している [1]。本研究では、TP を四量体タンパク質 Azami-Green に融合した TP-AG を構築し、その微小管内部および外部への結合を制御することでダブレットや分岐、アスターといった様々な微小管超構造体の形成を誘起することに成功した（Fig. 1）[2]。TP-AG の微小管外部への結合によるダブレットや分岐構造の形成が電子顕微鏡観察により確認された。TP-AG の当量などを変えることで運動性を持つアスター構造や極めて長い微小管の形成を確認し、一種類の外来タンパク質で多様な微小管超構造体を創製することに成功した。

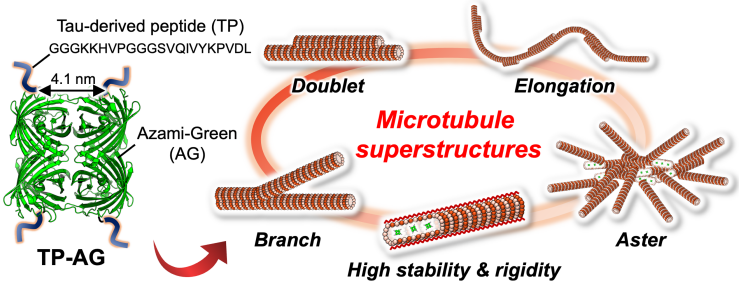

Fig. 1. Tau 由来ペプチド融合 Azami-Green（TP-AG）による微小管超構造体の形成

1) H. Inaba, K. Matsuura, *Bull. Chem. Soc. Jpn.*, **2021**, *94*, 2100. 2) H. Inaba[1], Y. Sueki[1], M. Ichikawa[1], A. M. R. Kabir, T. Iwasaki, H. Shigematsu, A. Kakugo, K. Sada, T. Tsukazaki, K. Matsuura, *Sci. Adv.*, **2022**, *8*, eabq3817 ([1]Equal contribution).

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熱遺伝学的解離モジュールによるタンパク質分泌の人為的制御

（東大院理 [1]）○遠藤 瑞己 [1]・小澤 岳昌 [1]

Artificial control of protein secretion using thermogenetic dissociation module

([1]*Graduate School of Science, The University of Tokyo*)○Mizuki Endo,[1] Takeaki Ozawa[1]

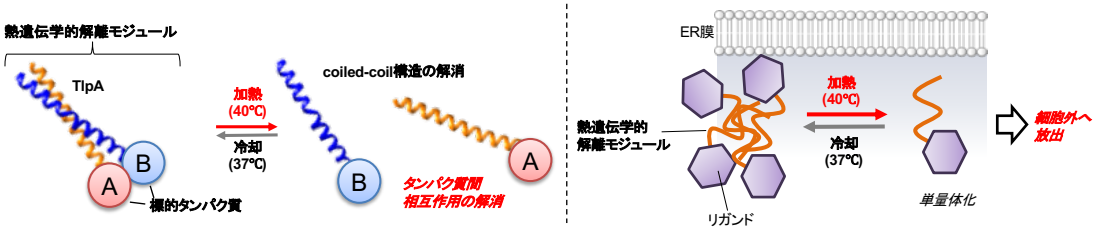
Living organisms maintain internal stability while adjusting to changing external condition through intercellular signaling mediated by secreted proteins. Recent studies have pointed out the physiological importance of the protein secretion patterns; however, the precise roles are not fully unveiled. In this study, we aimed to develop a genetically encoded system that enables artificial control of protein secretion by thermogenetic dissociation module, which could be activated by focused ultrasound heating.

In the present study, *Salmonella* thermosensing protein TlpA was selected as a thermogenetic dissociation module. The heat-induced dissociation of TlpA variants with several deletions and point mutations were examined. The screening identified homodimer or heterodimer modules with superior dissociation response upon heating to 40 °C. These modules dissociated into monomers upon local heating induced by focused ultrasound. Additionally, tandem repeat of homodimer module showed liquid-liquid phase separation in cytosol. Finally, we demonstrated that the tandem homodimer module enabled heat-induced protein secretion in cultured celles.

Keywords : Thermogenetics; Protein secretion; Ultrasound

生体内には，体外環境の変化に応じて体内環境の恒常性を維持する仕組みが備わっている．恒常性維持機構において細胞間シグナル伝達を担うタンパク質の分泌ダイナミクスが注目を集めているが，その生理的意義は完全には解明されていない．そこで本研究では，超音波による局所加熱で駆動する熱遺伝学的解離モジュールを用い，タンパク質分泌を制御することを目的とした．

本研究では熱遺伝学的解離モジュールとして加熱により coiled-coil 構造を解消するサルモネラ菌由来の転写因子 TlpA を使用した．まず， point mutation および deletion を組み合わせた候補分子を作成し，40℃に加熱した際の応答性を比較した．結果，homodimer, heterodimer ともに従来より 2-4 倍応答能の良い分子が得られた．開発した分子は超音波の局所加熱により単量体に解離することも確認された．また，homodimer の分子についてはタンデムに連結することで細胞質中で LLPS (液-液相分離)を引き起こすことも観察された．さらに，タンデムに連結した Homodimer を用いることで加熱により細胞中からのタンパク質分泌が誘導されることを確認した．



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高感度蛍光乳酸バイオセンサー -LACCO シリーズ-

（東大院理 [1], JST さきがけ [2], トロント大化 [3]）○那須 雄介 [1,2]・Giang Le[1,3]・針尾 紗彩 [1]・上條由貴 [1]・Robert E. Campbell[1]

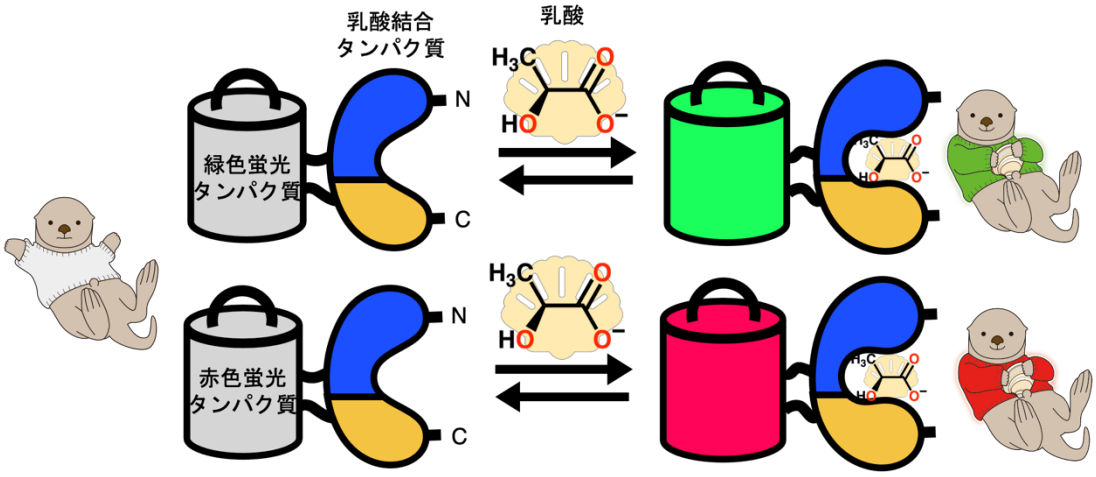
High-performance genetically encoded fluorescent L-lactate biosensors -LACCO series-

([1]*School of Science, The University of Tokyo*, [2]*PRESTO, Japan Science and Technology Agency*, [3]*Department of Chemistry, University of Toronto*) ○Yusuke Nasu,[1,2] Giang Le,[1,3] Saaya Hario,[1] Yuki Kamijo,[1] Robert E. Campbell[1]

L-Lactate, traditionally considered a metabolic waste product, is increasingly recognized as an important intra- and intercellular energy fuel and signaling molecule. To enable investigations of the emerging roles of L-lactate, we apply our protein engineering technology[1)] to develop genetically encoded L-lactate biosensors, designated LACCO series[2)–5)].

Keywords : Fluorescent protein; Biosensor; L-Lactate

これまで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，細胞内や細胞間におけるエネルギー物質やシグナル分子として，乳酸の役割が見直されつつある。ここでは，タンパク質工学 [1)]による，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）の開発 [2)–5)]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. *Nat. Chem. Biol.* **17**, 509–518 (2021).
2) **Nasu Y.**, et al. “A genetically encoded fluorescent biosensor for extracellular L-lactate”, *Nature Communications*, **12**, 7058 (2021).
3) Le and Hario et al. “High performance genetically-encoded green fluorescent biosensors for intracellular L-lactate” *bioRxiv* 2022.10.19.512892 (2022).
4) **Nasu Y.**, et al. “A red fluorescent genetically encoded biosensor for extracellular L-lactate.”, *bioRxiv* 2022.08.30.505811 (2022).
5) **Nasu Y.**, et al. “Improved genetically encoded fluorescent biosensors for monitoring of intra- and extracellular L-lactate.”, *bioRxiv* 2022.12.27.522013 (2022).

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生きたマウス脳内で機能する新規受容体ラベル化剤の開発と多重標識への展開

（京大院工 [1]・JST ERATO[2]・京大工 [3]）○野中 洋 [1,2]、王 萌初 [3]、武士 拓磨 [1]、白岩 和樹 [1]、坂本 清志 [1,2]、浜地 格 [1,2]

Development of new labeling reagents for endogenous receptors in the live mouse brain and their application to multiplex imaging

([1]*Graduate School of Engineering, Kyoto University*, [2]*ERATO, JST,* [3]*Faculty of Engineering, Kyoto University*) ○Hiroshi Nonaka[1,2], Mengchu Wang[3], Takuma Takeshi[1], Kazuki Shiraiwa[1], Seiji Sakamoto[1,2], Itaru Hamachi[1,2]

Ligand-directed acyl imidazole (LDAI) chemistry developed by Hamachi and co-workers allows the chemical labeling of endogenous proteins in a ligand recognition manner. By employing the LDAI method, we have succeeded in the chemical labeling of endogenous AMPA receptors in the live mouse brain. Given the modular feature of the acyl transfer reagent, we further applied the LDAI chemistry for other endogenous receptors by replacing the ligand moiety. We designed and synthesized new labeling reagents for multiple endogenous receptors in the live mouse brain. By using these labeling reagents, we demonstrated the multiplex imaging of target receptors.

Keywords : Ligand-directed chemistry, Endogenous receptor, Chemical labeling, Brain

脳は、数多くの神経細胞やグリア細胞によって構成されている。神経細胞同士は、多数のシナプス結合において、受容体を介した情報のやりとりを行い、脳神経ネットワークを構築している。これらの神経細胞、グリア細胞、血管などが入り組むことにより、私たちの脳は機能している。このような複雑な脳神経系では、脳そのままの環境を維持した状態で、機能解析できる手法が求められている。

我々は、これまでにタンパク質の選択的化学修飾法であるリガンド指向性化学の開発を行ってきている [1,2]。アシルイミダゾール基を反応基とするリガンド指向性化学(LDAI 化学)を用いることで、初代培養神経細胞や急性脳スライスに存在する内在性神経伝達物質受容体の選択的な化学標識に成功している [3]。昨年度の本会において、我々は、LDAI 化学を用いて、生きたマウス脳内の AMPA 型グルタミン酸受容体(AMPAR)のラベル化、及び、発達期における未知の AMPAR 動態を明らかにした。

今回、我々は生きたマウス脳内に存在する複数の内在性受容体への新規ラベル化剤を設計・合成した。それらのラベル化剤を併用して用いることで、標的受容体の多重標識や解析が可能であった。その詳細を報告する。

1)T. Tamura *et al., J. Am. Chem. Soc.,* **141**, 2782 (2019)
2)S. Fujishima *et al., J. Am. Chem. Soc.,* **134**, 3961 (2012)
3)S. Wakayama *et al., Nat. Commun.,* **8**, 14850 (2017)

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リガンド指向性 PhoxID 法による生きたマウス脳内での神経伝達物質受容体近傍ラベリング

（京大院工 [1]・JST ERATO[2]）○田村 朋則 [1]・高遠 美貴子 [1]・坂本 清志 [1,2]・野中 洋 [1,2]・浜地 格 [1,2]

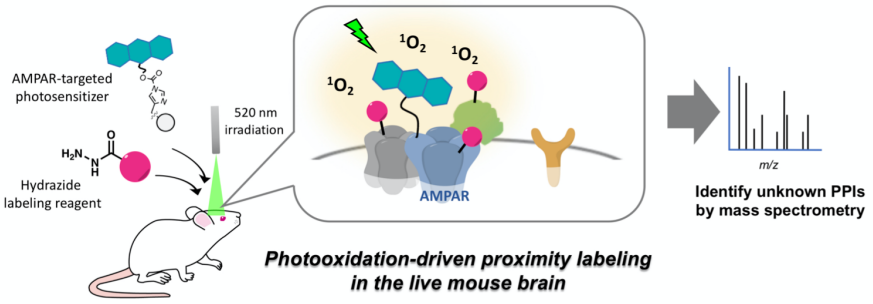
Mapping neurotransmitter receptor interactome in live mouse brain by ligand-directed PhoxID.

([1]*Graduate School of Engineering, Kyoto University*, [2]*JST ERATO*)○Tomonori Tamura,[1] Mikiko Takato,[1] Seiji Sakamoto,[1,2] Hiroshi Nonaka,[1,2] Itaru Hamachi[1,2]

An intricate network of protein-protein interactions involving neurotransmitter receptors is crucial determinants of synapse efficacy and plasticity, and thus the comprehensive characterization of the receptor interactome is a prerequisite for understanding the molecular basis of neural circuits. Here, we have established a workflow for mapping receptor interactome in the live mouse brain by LDPhoxID (ligand-directed chemistry-mediated photooxidation-driven proximity labeling for protein identification). We demonstrated the tissue and *in vivo* compatibility of LDPhoxID by identifying multiple members of the α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid-type glutamate receptor (AMPAR)- and γ-aminobutyric acid receptor ($GABA_AR$)-interactomes in the brains of live mice with just minutes of photoirradiation.

Keywords : Photo-triggered proximity labeling, Ligand-directed chemistry

シナプス形成や可塑性の発現過程において、神経伝達物質受容体は他の足場タンパク質やシナプスオーガナイザーとの相互作用を介してポストシナプス膜上に適切に局在すると考えられている。しかし、*in vivo* 環境下で特定の受容体と相互作用するタンパク質群（インタラクトーム）を網羅的に解析した例はいまだに無い。このような背景のなか、我々は時空間分解能に優れた新たな光駆動型タンパク質近傍ラベリング法として LDPhoxID (ligand-directed chemistry-mediated photooxidation-driven proximity labeling for protein identification)を開発した。本手法ではまず、我々が長年開発してきたリガンド指向性化学を用いて生きたマウス脳内の標的受容体に光増感剤を修飾する。その後、求核性プローブ存在下光照射することで、受容体周辺タンパク質を網羅的にビオチン標識し質量分析によって同定することが可能である。実際に本手法を生きたマウスの脳内の AMPAR および $GABA_AR$ に適用したところ、わずか数分の光照射で、これらの受容体の既知相互作用タンパク質を含む複数のタンパク質を同定した。



1) T. Tamura et al., *Chem. Lett*. **2020**, *49*, 145.

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Identification of a gene involved in lanthanide switch by analysis of the mutants isolated during the cultivation of *Methylosinus trichosporium* OB3b with glycerol

([1] *School of Life Science and Technology*, *Tokyo Institute of Technology*) ○Wataru Shiina,[1] Hidehiro Ito,[1] Toshiaki Kamachi[1]

Keywords: *Methanotroph, Lanthanide, Methanol dehydrogenase*

Two types of methanol dehydrogenases (MDHs), MxaFI and XoxF, have been characterized in methanotrophs like *Methylosinus trichosporium* OB3b (OB3b strain). MxaFI contains a calcium ion in its active site and XoxF contains a lanthanide (Ln) ion. In the presence of Ln ion, the expression of *mxaFI* was downregulated and that of *xoxF* was upregulated.[1] Such Ln-dependent regulation is known as the "lanthanide switch", but the detail of the regulation mechanism is not entirely understood. In this study, we isolated the OB3b mutant strains during multiple preparations of glycerol stock, which did not express XoxF in the presence of cerium ions. We aimed to reveal the genetic mechanism that XoxF was not expressed in the mutant and the environmental condition under which the mutation provides a selective advantage.[2]

Based on our whole genome analysis of the mutant strains, we focused on the mutation of the CQW49_RS02145 gene, which is orthologous to *lutH*, an Ln transporter in methylotrophs. We found that disruption of the CQW49_RS02145 gene caused the expression of MxaF and non-expression of XoxF, regardless of the presence or absence of cerium ions. The expression of XoxF was restored by the complementation of the CQW49_RS02145 gene to the disruption mutant. These results indicated that the CQW49_RS02145 gene was essential for the lanthanide switch.

We found that the supplementation of both cerium ions and glycerol to the medium had an inhibitory effect on the growth of the OB3b strain. Based on this finding, we performed an adaptive laboratory evolution of the OB3b strain in the presence of cerium ions and glycerol. After the experiment, we isolated the evolved strain, which exhibited improved cell growth in the presence of cerium ions and glycerol (Figure 1). Genotyping of the evolved strain revealed a loss-of-function mutation in the CQW49_RS02145 gene. It was suggested that residual glycerol from the frozen stock leads to a loss-of-function mutation in the CQW49_RS02145 gene.

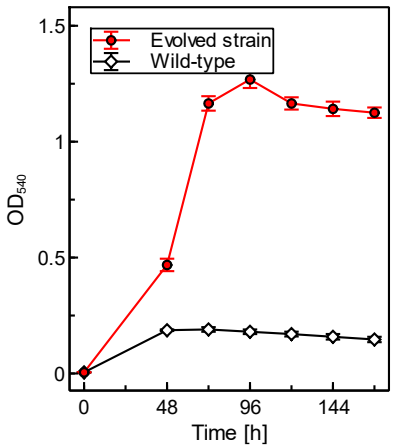

Figure 1 Growth analysis of OB3b wild-type and the evolved strain in the presence of Ce^{3+} and glycerol.

1) Farhan Ul Haque, M. *et al. Appl. Environ. Microbiol.* **2015**, *81* (21), 7546–7552.
2) Shiina, W.; Ito, H.; Kamachi, T. *Appl. Environ. Microbiol.* **2023**, in press.

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

[E1662-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Hideaki Yoshimura, Kenji Monde

Fri. Mar 24, 2023 1:10 PM - 3:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-3pm-01] Signal transduction mechanism of membrane receptors on ligand binding and cluster formation: Analysis through single-molecule imaging.

○Hideaki Yoshimura[1], Takeaki Ozawa[1] (1. The University of Tokyo)

1:10 PM - 1:30 PM

[E1662-3pm-02] Quantitative analysis of Akt isoform-specific temporal activation dynamics and downstream signaling regulation with mathematical model-aided optogenetics

○Yuka Sekine[1], Genki Kawamura[1], Takeaki Ozawa[1] (1. The University of Tokyo)

1:30 PM - 1:50 PM

[E1662-3pm-03] Dissecting the role of Akt2 in cellular metabolism by optogenetics-aided trans-omics analysis

○Genki Kawamura[1], Takeaki Ozawa[1] (1. The University of Tokyo)

1:50 PM - 2:10 PM

[E1662-3pm-04] Development of photoreactive sphingomyelin synthase 2 inhibitors and evaluation of its binding domain analysis

○Mirano Abe[1], Yuta Murai[1], Takeo Sato[1], Miho Sanagi[1], Susumu Mitsutake[2], Makoto Taniguchi[3], Kenji Monde[1] (1. Hokkaido University, 2. Saga University, 3. Kanazawa Medical University)

2:10 PM - 2:30 PM

[E1662-3pm-05] Contribution of moleculae weight of ligand functionalized poly-L-glutamates to the inhibition of cancer cell proliferation

○Masahiko Nakamoto[1], Yuki Koba[1], Michiya Matsusaki[1] (1. Osaka University)

2:40 PM - 3:00 PM

[E1662-3pm-06] Point-of-care electrochemical biosensors for measuring anti-SARS-CoV-2 neutralising IgG/sIgA antibodies and antioxidant activity in saliva

○Eiichi Tamiya[1,2], Shuto Osaki[1], Tomoko Tsuchihashi[3], Hiromi Ushijima[3], Keiichi Tsukinoki[4] (1. AIST, 2. Osaka Univ., 3. Biodevicetechnology Ltd., 4. Kanagawa Dental Univ.)

3:00 PM - 3:20 PM

[E1662-3pm-07] Determination of Permeation Kinetics of Coumarin at Lipid Bilayer of Liposomes by Using Capillary Electrophoresis with Moment Analysis Theory

○Kanji Miyabe[1], Shunta Inaba[1], Momoko Umeda[1] (1. Rikkyo University)

3:20 PM - 3:40 PM

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Signal transduction mechanism of membrane receptors on ligand binding and cluster formation: Analysis through single-molecule imaging.

([1]*School of Science, The University of Tokyo*) ○Hideaki Yoshimura,[1] Takeaki Ozawa,[1]
Keywords: Bioimaging; G protein-coupled receptor; Single-molecule imaging; Signal transduction

Living cells can be regarded as an assembly of such biomolecules as proteins, nucleic acids, and lipids, but just the coexistence of the molecules alone does not produce living cells. Investigating the localization and dynamics of the molecules of interest in living cells is essential for understanding the mechanism of cellular physiological function from the view of molecular science. A microscopic approach is a direct method to monitor the localization and dynamics of molecules in live cells. Therefore, this approach will provide crucial information on the mechanisms under chemical reactions unique to living cells, such as signal transduction. Signal transduction in living cells is a finely regulated physiological function that an artificial molecular assembly system cannot realize. This study conducted single-molecule imaging of receptor molecules and their downstream molecules to understand the molecular mechanisms under signaling regulation in living cells. We monitored the dynamics and assembly of a G protein-coupled receptor FPR1, G protein α subunit (Gα), and ligand for FPR1 in living cells. We labeled the ligand with tetramethyl rhodamine to distinguish ligand-bound FPR1 from ligand-unbound ones. In addition, we used Halo-tag conjugated Gα protein and stained it with R110. Using these tools, we performed triple-color single-molecule imaging in living cells. In this observation, fluorescent spots of FPR1 in the plasma membrane were visualized. The intensity of the spots represented the number of labeled FPR1 in each spot. Based on the intensity analysis, the FPR1 spots were classified into two states: small oligomer and large oligomer. In addition, based on the colocalization of FPR1 spots with that of the ligand, we distinguished ligand-bound FPR1 and unbound one. Thus, the states of FPR1 were categorized into four; ligand-unbound small oligomer, ligand-unbound large oligomer, ligand-bound small oligomer, and ligand-bound large oligomer. Then we analyzed the dwell time of Gα-FPR1 colocalization on individual FPR1 spots. As a result, the ligand-bound large oligomer showed a significantly longer dwell time than in the other three states. Based on this result, we propose an “AND gate” model of signal induction through FPR1, which would contribute to precise signal transduction.

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Quantitative analysis of Akt isoform-specific temporal activation dynamics and downstream signaling regulation with mathematical model-aided optogenetics

([1]*School of Science, The University of Tokyo*) ○Yuka Sekine,[1] Genki Kawamura,[1] Takeaki Ozawa[1]

Keywords: Optogenetics; mathematical model; Akt isoform; cellular signal transduction; temporal dynamics

Ser/Thr kinase Akt plays important roles in protein signal transduction pathway that induces various cellular responses. There exist three Akt isoforms; Akt1/2/3. It is suggested that when cells are stimulated by extracellular ligands, each Akt isoform exhibits its specific temporal activation pattern that selectively regulates its downstream signaling.[1-3] However, details of the temporal dynamics of three Akt isoforms remain elusive due to the lack of methods that enables quantitative analysis of its activation kinetics. The purpose of this research is to quantitatively examine the Akt isoform-specific temporal dynamics and their selective downstream signaling regulation.

To induce Akt activation, we used an optogenetic method, photoactivatable Akt (PA-Akt) system, which enables us to activate Akt by utilizing photo-induced heterodimerization of photoreceptors CRY2/CIBN (**Fig. 1a**).[4] We newly applied this system to construct PA-Akt2/3. To quantitatively analyze differences in temporal dynamics among the Akt isoforms, we employed mathematical models describing Akt activation kinetics.

We quantified CRY2-Akt isoforms' activation (phosphorylation) level changes on PA-Akt1/2/3 expressing cells. As a result, CRY2-Akt isoforms showed different de-phosphorylation patterns when transiently activated by light. Additionally, we found that Akt and its downstream molecules re-phosphorylated at least within 4 hours. By fitting the obtained Akt isoforms' activation dynamics with mathematical models (**Fig. 1b**), quantitative information on the Akt isoform-specific signaling regulation is investigated in a wide time scale.

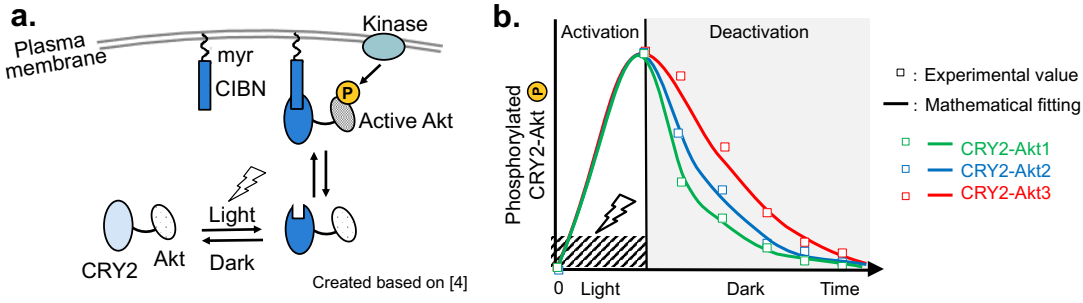

Fig 1. Analysis of Akt isoform-specific temporal dynamics. **a**. PA-Akt system. **b**. Schematic of mathematical fitting of the Akt isoforms' temporal activation patterns.

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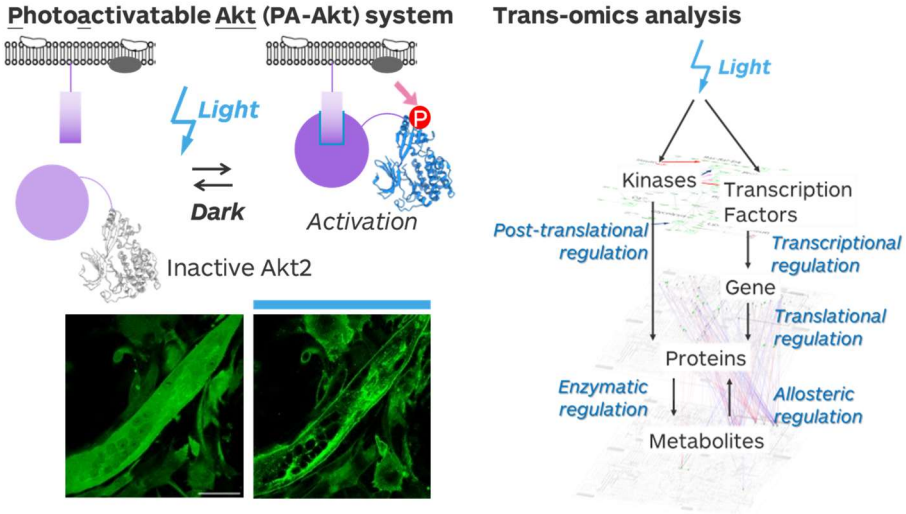
Dissecting the role of Akt2 in cellular metabolism by optogenetics-aided trans-omics analysis

(*Graduate School of Science, The University of Tokyo*) ○Genki Kawamura, Takeaki Ozawa
Keywords: Optogenetics, Akt, Insulin, Cellular signal transduction, Omics analysis

Insulin is a hormone secreted during feeding that promotes cellular metabolism. Insulin initiates cellular metabolism by activating relevant signaling pathways, including the Akt pathway. Different temporal patterns of insulin secretion are known to produce corresponding patterns of Akt activation and selectively induce various metabolic pathways.[1,2] However, there is little direct evidence for Akt-mediated regulation of metabolic pathways. In this study, we aimed to elucidate the role of Akt2 in cellular metabolism by combining optogenetics and trans-omics analysis.

To selectively regulate Akt2 activity, we used the concept of a light-activated Akt system,[3] resulting in light-dependent selective activation of Akt2. Since the regulation of metabolic reactions is influenced by a variety of factors, we performed a comprehensive analysis of intracellular molecular species by RNA-seq, LC-MS, and Western blotting. To elucidate metabolic regulation among biomolecules, we integrated the observed omics data and constructed a signaling network induced via Akt2-specific activation. The constructed network depicts Akt2-dependent metabolic regulation in cells; Akt2 activates cellular metabolism by regulating the function of metabolic enzymes both translationally and post-translationally. The findings obtained by "trans-omics analysis by optogenetics" provide new insights into the molecular mechanisms of Akt2-mediated regulation of metabolic pathways.



References: 1) Kubota et al., *Mol. Cell*, 46, 820 (2012). 2) Kubota et al. Cell Systems, 7, 118–128 (2018). 3) Katsura et al. *Sci. Rep.*, 5, 14589 (2015).

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Development of photoreactive sphingomyelin synthase 2 inhibitors and evaluation of its binding domain analysis

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Keywords : Sphingomyelin synthase, Photoaffinity labeling, Inhibitor, Obesity, Tumorigenesis

Sphingomyelin synthase (SMS) exhibits sphingomyelin synthesis activity. SMS2 is one of the three type SMS isoforms, implicated in the regulation of transmembrane signaling. Recent studies have reported to SMS2 knock out (down) mice are resistant to tumorigenesis, diet induced obesity, and decrease levels of plasma inflammatory cytokines[1,2]. Therefore, regulation of SMS2 could be a promising drug target for the diseases mentioned above to enhance the discovery of SMS2 inhibitors. However, the 3D structure model of SMS2 has not been revealed. Although the 3D structure model has also been predicted by artificial intelligence program such as AlphaFold2, the validity of this constructed model is not experimentally demonstrated and the interaction between SMS2 and its inhibitors still remain unclear due to the low sequence similarities between the homologous protein.

Photoaffinity labeling (PAL) is an effective chemical tool and is widely used in drug discovery for target identification to probe the location and structure of the binding site. Thus, as an alternative method, we adopted the PAL strategy to design and synthesize the two kinds of photoaffinity probes targeting SMS2[3] (Figure 1). The molar concentrations for 50 % inhibition (IC_{50}) of both probe indicated 150 nM for probe (1) and 100 nM for probe (2). Furthermore, we evaluated the photoaffinity labeling with SMS2 by using these PAL probes. In this presentation, we will describe the total synthesis of the both PAL probe and the result of PAL experiments.

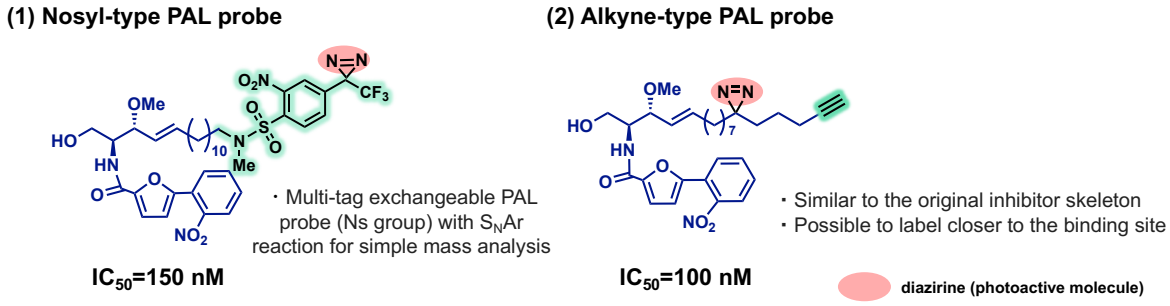

Figure1

1) Mitsutake, S. et. al. *J. Biol. Chem.* **2011**, *286*, 28544−28555. 2) Ohnishi, T. et. al. *FASEB J.* **2017**, *31*, 3816−3830. 3) Suhaily Saaidin, A. et al. *Eur. J. Org. Chem.* **2019**, 7563−7567.

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がん細胞増殖阻害能に与えるリガンド修飾ポリグルタミン酸の分子量の影響

（阪大院工 [1]）○仲本 正彦 [1]・木場勇希 [1]・松崎 典弥 [1]
Contribution of molecular weight of ligand functionalized poly-L-glutamates to the inhibition of cancer cell proliferation ([1]*Graduate School of Engineering, Osaka University*) ○Masahiko Nakamoto,[1] Yuki Koba,[1] Michiya Matsusaki[1]

The simultaneous inhibition of some biological pathways with proper metabolic relationship mechanisms using the combination of drugs has been an attractive strategy to improve therapeutic efficacy. We recently have reported the poly-L-glutamate functionalized with hetero ligands of proximal enzymes on cancer cells, carbonic anhydrase IX and matrix metalloproteinase14 (PGA-UT), that inhibits the cancer cell proliferation in a synergic manner. Here, we report the contribution of the molecular weight and ligand density of PGA-UT to the efficacy.

Keywords : Polymer inhibitor, cancer cell, enzyme inhibition. Carbonic anhydrase IX, matrix metalloproteinase

分子標的部位を高分子構造に多価的に集積することによる標的細胞認識能の向上は、がん細胞選択的なターゲティング能を有する高分子薬剤や薬物送達キャリアの設計のための重要な戦略として幅広く研究されてきた。一方で、正常細胞機能の阻害により生じる副作用は依然として大きな課題である。我々は最近、低酸素状態のがん細胞において過剰発現する炭酸脱水酵素 IX（CAIX）および膜型マトリックスメタロプロテアーゼ（MMP14）からなる近接酵素群（**Figure 1A**）を標的として相乗的に細胞増殖を阻害するリガンド修飾ポリグルタミン酸を報告した（**Figure 1B**）[1]。本発表では様々な分子量、リガンド密度を有する高分子ライブラリの細胞増殖阻害能を網羅的に解析することで明らかになった、高分子鎖の分子量が細胞増殖阻害能に与える影響を報告する（**Figure 1C**）。併せて低分子リガンド混合物と高分子の比較から、高分子化による相乗的阻害能の増幅についても議論する。本研究は近接酵素群を標的とした高分子医薬や薬剤送達キャリアとしての応用が期待される。

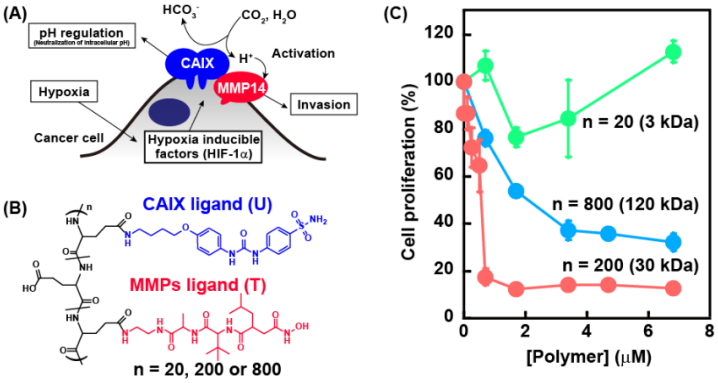

Figure 1. (A) Biological functions of proximal CAIX and MMP14 on the cancer cell under hypoxia condition. (B) Chemical structure of polymer inhibitor with ligands of CAIX and MMPs. (C) Cancer cell (MDA-MB-231) proliferative inhibition by polymers with 10% U and 10% T. Degree of polymerization are 20 (green), 200 (red) and 800 (blue), respectively.

1) Y. Koba, M. Nakamoto, M. Matsusaki, *ACS Appl. Mater. Interfaces* **2022**, 14, 51790.

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唾液中の抗 SARS-CoV-2 中和活性抗体(IgG/sIgA)と抗酸化活性を測定するポイントオブケア電気化学バイオセンサー

（産総研フォトバイオ OIL[1]・阪大産研[2]・阪大工[3]・バイオデバイステクノロジー社[4]・神奈川歯科大[5]）○民谷栄一[1,2] 大崎脩仁[1,3], 土橋朋子[4]、牛島ひろみ[4], 槻木恵一[5]
(*AIST PhotoBio OIL[1], Osaka Univ. SANKEN[2], Osaka Univ. School of Eng.[3] Biodevicetechnology Ltd.[4], Kanagawa Dental Univ.[5]*) ○ Eiichi Tamiya[1,2], Shuto Osaki[1,3], Tomoko Tsuchihashi[4], Hiromi Ushijima[4], Kei-ichi Tsukinoki[5]

The gold-linked electrochemical immunoassay and antioxidant activity measurement based on luminol electrochemiluminecence (ECL) can be performed in portable devices, which would prove useful for individual-based diagnosis using saliva samples. We analyzed the titers of neutralizing antibodies, IgG and secretory IgA (sIgA), in response to SARS-CoV-2 vaccine. 19 saliva samples were collected over a 10-month period. The range of antibody concentrations post vaccination were: serum IgG: 81–15000 U/mL, salivary IgG: 3.4–330 U/mL, salivary IgA: 58–870 ng/mL. A sharp increase in salivary IgG levels was observed after the second vaccination. sIgA levels also showed an increasing trend. A correlation with trends in serum IgG levels was observed, indicating the possibility of using saliva to routinely assess vaccine efficacy. Any correlation between antioxidant activity and protein concentration was also considered useful as a reflection of individual physical characteristics.
Keywords: Salivary biomarkers, Gold-linked electrochemical immunosensor, Electrochemi-luminescence, Anti-SARS-CoV-2 neutralizing antibodies, Antioxidant activity

バイオマーカーのモニタリングは、日々の体調を把握するのに有効な手段であり、血液サンプルの代わりに唾液を用いることで、プロセスが簡便になり、個人で検査できる利点がある。本研究では、金ナノ粒子修飾抗体を用いた電気化学イムノセンサーとルミノール電気化学発光（ECL）に基づく抗酸化活性測定法を用いた。この方法は、演者らが独自に開発したもので[1,2]、携帯機器での測定が可能であり、ここでは、SARS-CoV-2 ワクチンに対する中和活性抗体として IgG および分泌型 IgA（sIgA）を測定した。19 人の唾液試料と血清試料を定期的に採取した。特に、1 回目のワクチン接種から 3 週間後、2 回目のワクチン接種から 8 ヶ月後、3 回目のワクチン接種から 1 ヶ月後の計 10 ヶ月間に、唾液と血清を採取した。ワクチン接種後の抗体濃度の範囲は、血清 IgG: 81-15000 U/mL、唾液 IgG: 3.4-330 U/mL、唾液 IgA: 58-870 ng/mL であった。唾液中 IgG 値は 2 回目のワクチン接種後に急増し，sIgA 値も増加傾向を示した．血清 IgG 値の推移と相関があり，唾液を用いたワクチン効果の評価の可能性を示唆するものであった．また、同時に抗酸化活性を測定した。中和抗体活性との相関は認められなかったが、各個人の特性を示すものと考えられた。

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キャピラリー電気泳動とモーメント解析理論の組合せによるリポソーム脂質二分子膜におけるクマリンの透過速度の測定

（立教大理）〇宮部寛志・稲葉隼汰・梅田萌々子

Determination of Permeation Kinetics of Coumarin at Lipid Bilayer of Liposomes by Using Capillary Electrophoresis with Moment Analysis Theory (*Faculty of Science, Rikkyo University*) 〇Kanji Miyabe, Shunta Inaba, Momoko Umeda

A moment analysis method was developed for the determination of lipid membrane permeability. As a concrete example, permeation rate constants of coumarin across the lipid bilayer of liposomes consisting of 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) and phosphatidylserine (PS) were determined by analyzing the first absolute and second central moments of elution peaks of coumarin measured by liposome electrokinetic chromatography with moment equations. It seems that lipid membrane permeability of coumarin at the lipid bilayer of POPC/PS liposomes can be determined because previous permeability measurements using parallel artificial membrane permeability assay and Caco-2 cells indicated that coumarin is permeable across lipid bilayer.
Keywords : Moment Theory; Lipid Membrane Permeability; Liposome Interfacial Permeation; Lipid Bilayer; Liposome Electrokinetic Chromatography

リポソームは薬物輸送システム（DDS）の薬物キャリアとして利用されている。DDSの重要な機能の一つは薬物徐放であり、リポソーム界面の薬物透過現象は薬物徐放性能に関連する。このため、リポソーム界面における物質透過現象の詳細な究明が求められる。また、リポソームは人工細胞のモデル物質としても利用されており、その界面における物質透過速度の解析は脂質二分子膜や細胞膜を通しての物質移動や情報伝達の機構解明等に関する研究の進展にも寄与するものと期待される。

そこで本研究では、リポソーム界面の物質透過速度を測定するためのモーメント解析法を開発した。リポソームを擬似固定相として使用するリポソーム動電クロマトグラフィー（LEKC）系における溶質ピークの一次絶対および二次中央モーメントをモーメント理論に基づき解析して脂質二分子膜の溶質透過性を評価した。リポソームは1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine（POPC）と phosphatidylserine（PS）を混合して調製した（80/20 mol%）。その界面におけるクマリン（溶質）の透過速度定数を求め、本法の有用性を実証した[1)]。なお、クマリンが脂質二分子膜を透過することは parallel artificial membrane permeability assay（PAMPA）や Caco-2 細胞を用いる膜透過性試験で確認されている。

リポソームはリン脂質モノマーが化学的に弱い相互作用によって自己集合した動的なシステムであるため、その界面における物質透過現象の解析はリポソームに何等かの化学修飾や物理的作用を加えることなく、リポソームが本来あるべき状態で行う必要がある。本法では、LEKC 実験の際に溶質やリポソームの固定化や化学修飾（蛍光標識化）が不要で、両者は化学的に未修飾の遊離した本来の状態で相互作用する。また、本法ではリポソームそのものを LEKC 系の擬似固定相として使用しており、人工膜を使用する PAMPA とは異なる。本法では、本来の状態におけるリポソームの界面そのものを観測場とする in-situ 条件下での実験データの測定が可能である。さらにデータ解析については、curve-fitting 等の試行錯誤的な方法ではなく、モーメント理論の適用により LEKC データから界面透過速度定数を解析的に求めることができる。

1) K. Miyabe, S. Inaba, M. Umeda, *J. Chromatogr. A* **2023**, *1687*, 463691.

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

[E1661-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Hisae Tateishi-Karimata, Yousuke Katsuda

Fri. Mar 24, 2023 1:30 PM - 3:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-3pm-01] Exploring new methods in regulating circular RNA production using cellular model

○Lu Ni[1], Takeshi Yamada[1], Kazuhiko Nakatani[1] (1. Osaka University)

1:30 PM - 1:50 PM

[E1661-3pm-02] Synthesis of Hoechst-modified DNA that accumulated in the cell nucleus and its application.

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

1:50 PM - 2:10 PM

[E1661-3pm-03] A nucleic acid medicine that suppresses target gene expression based on RNA structure hacking

○Takuto Kamura[1], Yousuke Katsuda[1], Taishi Nakamura[2,3], Kenichi Tsujita[3], Yusuke Kitamura[1], Masaki Hagihara[4], Shin-ichi Sato[5], Toshihiro Ihara[1] (1. Faculty of Advanced Science and Technology, Kumamoto University, 2. Department of Medical Information Sciences and Administration Planning, Kumamoto University Hospital, 3. Department of Cardiovascular Medicine, Faculty of Life Sciences, Kumamoto University, 4. Faculty of Science and Technology, Hirosaki University, 5. Institute for Chemical Research, Kyoto University)

2:10 PM - 2:30 PM

[E1661-3pm-04] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (88): Mechanism of C-quadruplexes formations in response to environmental changes in cancer cells

○Hisae Tateishi-Karimata[1], Keiko Kawauchi[2], 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), Konan University)

2:40 PM - 3:00 PM

[E1661-3pm-05] Epigenetic methylations suppress droplet formation of DNA G-quadruplex and Arg-rich peptide

○Mitsuki Tsuruta[1], Keiko Kawauchi[1], Naoki Sugimoto[1,2], Daisuke Miyoshi[1] (1. Konan university, FIRST, 2. Konan university, FIBER)

3:00 PM - 3:20 PM

[E1661-3pm-06] Effect of structural selective G4 ligand on telomere length and TERRA expression level

○Yoshiki Hashimoto[1], Takeru Torii[1], Natsuki kinoshita[1], Keiko Kawauchi[1], Hisae Tateishi-Karimata[2], Naoki Sugimotgo[1,2], Daisuke Miyoshi[1] (1. FIRST, Konan University, 2. FIBER, Konan University)

3:20 PM - 3:40 PM

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Exploring new methods in regulating circular RNA production using a cellular model

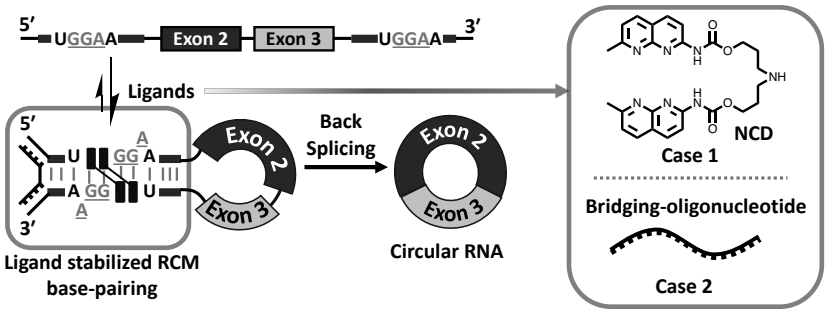
(*[1]SANKEN (The Institute of Scientific and Industrial Research), Osaka University*)
○LU Ni,[1] TAKESHI Yamada,[1] KAZUHIKO Nakatani[1]

Keywords: circular RNAs; alternative RNA splicing; back-splicing; small molecules; oligonucleotides

Circular RNAs (circRNAs) are a class of non-coding RNA, which are covalently closed loop RNA molecules. They have recently seen an increase in interest, with recent literature uncovering their pivotal roles in regulating various aspects of cell function and disease progression. Developing ligands capable of regulating circRNAs and, eventually, modulating disease progression would be particularly interesting. However, there have yet to be an established theoretical basis on how such feat could be achieved.

CircRNA's most notable feature lies in the mechanism of its biogenesis involving back splicing. Whereby interactions between introns flanking the circularizing exon, such as base-pairing between reverse complementary sequences (RCSs), are suggested to facilitate back-splicing via the formation of a prerequisite hairpin structure. The stability of which was shown to impact the efficiency of circRNA production.

Thus, based on the above mechanism, we explored the feasibility of stabilizing the said prerequisite hairpin structure formed by RCSs via externally introduced ligands, such as small molecules and oligonucleotides, to promote the production of circRNA in cells. To this end, we conducted two case studies utilizing a previously reported pre-mRNA model construct for expression of circZKSCAN1, consisting of exon 2 and 3 of gene ZKSCAN1 flanked by a pair of 36-nt RCSs. In the first case, we demonstrate an RNA binding small molecule, naphthyridine carbamate dimer (NCD), selectively upregulating the production of circZKSCAN1 when its binding site was present in the RCSs. In the second case, we demonstrate a specially designed bridging-oligonucleotide upregulating the production of circZKSCAN1 regardless of the presence of specific binding motifs. Whereby the oligonucleotide was designed to stabilize the secondary structure via physically bridging the sequences flanking the RCSs. The experimental results will be discussed in this presentation.



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細胞核に蓄積する Hoechst 修飾 DNA の合成とその応用

（青学大院理工）〇蒔苗 宏紀・西原 達哉・田邉 一仁

Synthesis of Hoechst-modified DNA that accumulated in the cell nucleus and its application

(*Graduate School of Engineering, Aoyama Gakuin University*) 〇Hiroki Makanai. Tatsuya Nishihara, Kazuhito Tanabe

Artificial nucleic acids are known as molecules with diverse functions, not only nucleic acid medicines but also in the capture and regulation of biomolecules in cells. So far, various artificial nucleic acids that tracked biomolecules and carried drugs have been developed. However, most of them functioned in cytoplasm, which limited their versatility. In this study, we developed Hoe-ODN by modifying the Hoechst molecule that accumulates in the cell nucleus with DNA to improve the versatility of artificial nucleic acids. After the synthesis, We evaluated the properties of Hoe-ODN in the cells. Hoe-ODN was administrated into cells after duplex formation with fluorophore-labeled complementary DNA. As a result, strong FAM-derived fluorescence was observed from the cell nucleus, suggesting that Hoe-ODN accumulated in the cell nucleus. At present, evaluation of the antisense activity of Hoe-ODN is in progress.

Keywords ： Artificial nucleic acids, Hoechst, cell nucleus

人工核酸は核酸医薬品として機能するだけでなく、細胞内において生体内因子との結合、捕捉、機能制御など多様な特性を示す機能分子として駆動することが知られる。これまでに、生体分子イメージングに資する人工核酸、薬剤を運搬する人工核酸などが開発され、その多様性・多機能性が示されてきた。このように、細胞内で駆動する人工核酸が多数開発されているが、そのほとんどは細胞質内で駆動するものであり、その汎用性は制限される。そこで本研究では人工核酸の汎用性向上を目的に、細胞核へ集積する Hoechst を DNA に修飾した Hoe-ODN を開発した。実際に Hoe-ODN の細胞核への蓄積能を評価するために、相補的な配列をもつ FAM 修飾 DNA と二重鎖形成させた後、Hoe-ODN を細胞内へ導入した。その結果、FAM 由来の強い蛍光が細胞核から観測され、Hoe-ODN が細胞核内へ蓄積していることが示唆された。現在、Hoe-ODN のアンチセンス活性を評価しており、併せて報告する。

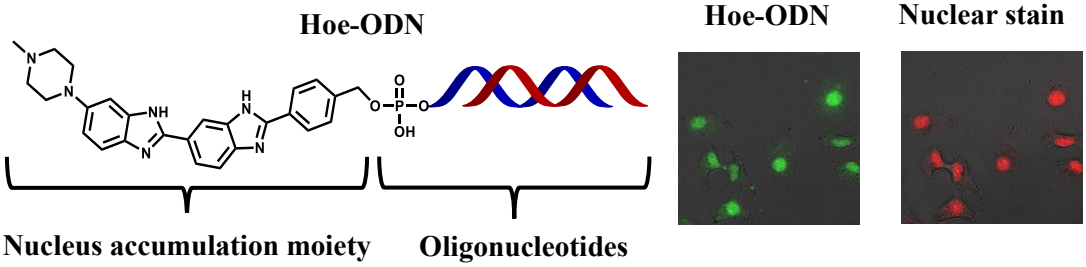

Figure 1. Chemical structure of Hoe-ODN and its accumulation in the cell nucleus.

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A nucleic acid medicine that suppresses target gene expression based on RNA structure hacking

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Keywords: RNA hacking technology (RNAh); Staple Oligomer; Suppression of gene expression; Nucleic acid medicines

Nucleic acid medicines such as small interfering RNAs (siRNAs) are promising therapeutic strategies against a large number of diseases caused by the aberrant gene expression since they can repress target gene expression in a sequence-specific manner. Generally, we need to use xeno nucleic acids (XNAs) in these medicines to enhance the nuclease resistance and the binding affinity. Although various XNAs with superior properties have been developed, the use of them in the design of siRNA medicines is limited because siRNAs containing XNAs could be excluded from RNA-induced silencing complex (RISC), which would result in the loss of suppression activity.

Therefore, we developed a method to suppress gene expression based on RNA hacking technology (RNAh) that changes the structure of target mRNA using a short nucleic acid named Staple Oligomer (DNA, RNA and XNAs). To suppress gene expression, Staple Oligomer induces the construction of RNA G-quadruplex (RGq) that inhibits protein translation (**Fig. 1**). In previous work, we succeeded in significantly suppressing the expression of TRPC6 gene, involved in cardiac hypertrophy, *in vitro* and *in cell* using Staple Oligomer. In this presentation, we report the results of the suppression efficiency and off-target effects of Staple Oligomer *in vivo* and phenotypic analysis of cardiac hypertrophy model mouse.

In the future, we are going to evaluate the distribution in mouse, the metabolic status and the toxicity of Staple Oligomer composed of XNAs (XNAs Staple) in order to apply this technique to clinical trials.

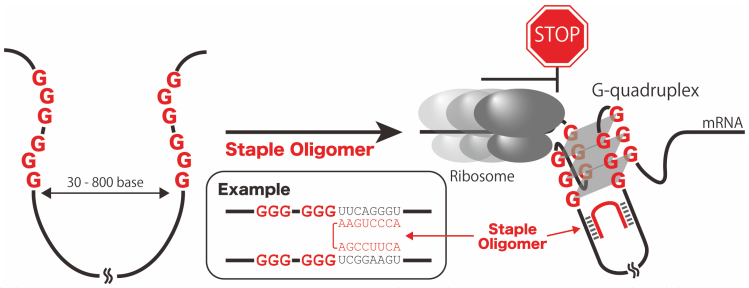

Fig. 1 Scheme of the strategy to suppress gene expression based on RNA structure hacking. RNA G-quadruplex (RGq) inhibits protein translation by blocking the progression of ribosomes.

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Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (88): Mechanism of C-quadruplex formations in response to environmental changes in cancer cells

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Keywords: molecular crowding transcript mutation; cancer cell; malignant alteration; C-quadruplex; transcript mutation

Many diseases are caused by genetic and environmental factors. Recent studies have indicated that transient, non-canonical structural changes in nucleic acids in response to the environment can regulate the expression of disease-related genes through transcription and translation.[1,2] Especially in cancer, the intracellular environment changes drastically with the onset and progression (Figure 1). We found that transcription level from the templates with G-quadruplexes were increased in highly metastatic breast cancer cells than in mild cancer and the normal cells.[3] Our results suggest that structural changes of nucleic acids in cancer cells are important for understanding the mechanism of cancer progression. However, systematic analysis of the changes in various nucleic acid structures in cancer cells has not been performed.

In this study, we investigated the effects of the intracellular environment associated with cancer malignancy on the structures of nucleic acids such as G-quadruplexes and C-quadruplexes. First, we observed how the intracellular environment was altered by malignant transformation of cancer cells using confocal microscopy. As results, the higher the malignancy of the cancer cells, the behavior of the cytoskeleton, which creates an intracellular crowding condition, was modulated upon cancer progression. Interestingly, C-quadruplexes consisting of cytosine (i-motifs) were shown to form in malignant cancer cells but not in normal cells. In the presentation, we will explain the effects of C-quadruplexes on transcriptional mutation.

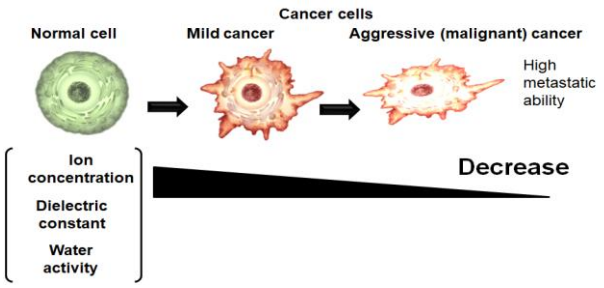

Figure 1. Chemical environments in cells are changed by tumor progressions

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.

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エピジェネティック修飾のメチル化は DNA グアニン四重鎖とアルギニンリッチなペプチドによる液滴形成を抑制する

（甲南大院 FIRST[1]・甲南大 FIBER[2]）〇鶴田充生[1]・川内敬子[1]・杉本直己[1,2]・三好大輔[1]

Epigenetic methylations suppress droplet formation of DNA G-quadruplex and Arg-rich peptide ([1]*Graduate school of faculty of Frontiers of Innovative Research in Science and Technology (FIRST),* [2]*Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University*) 〇Mitsuki Tsuruta, Keiko Kawauchi, Naoki Sugimoto, Daisuke Miyoshi

Biomolecular droplets formed via liquid-liquid phase separation is now attracting attention as a novel biological phenomenon. The droplet regulates various intracellular functions such as transcription, RNA processing, and translation. Although there is wide variety of chemical modifications to biomacromolecules, little is known about the relationship between droplet formation and chemical modifications including methylation, acetylation, and phosphorylation of DNA and proteins[1)]. Here, we investigated effect of methylation of DNA cytosine and peptide arginine on droplet formation of G-quadruplex-forming DNA and Arg- rich peptides[2)]. It was found that the ability of droplet formation was decreased by methylation of cytosine bases and arginine residues.

Keywords : Liquid-liquid phase separation, DNA, Methylation, Cytosine, Arginine

細胞内で形成される生体高分子の液滴は、転写や RNA スプライシングなどの反応を制御する新たな現象として多くの研究者からの注目を集めている[1)]。生体高分子に対するメチル化などのエピジェネティックな化学修飾も液滴形成に関与していると考えられるが、そのほとんどが明らかとされていない。そのため本研究では、液滴を形成可能なグアニン四重らせん構造（G4）に含まれるシトシンと G4 に結合するカチオン性ペプチド内のアルギニンに対するメチル化が液滴の形成に及ぼす影響を検討した（図 1）[2)]。その結果、DNA とペプチドに対するメチル化修飾により液滴形成が抑制されることが明らかとなった。

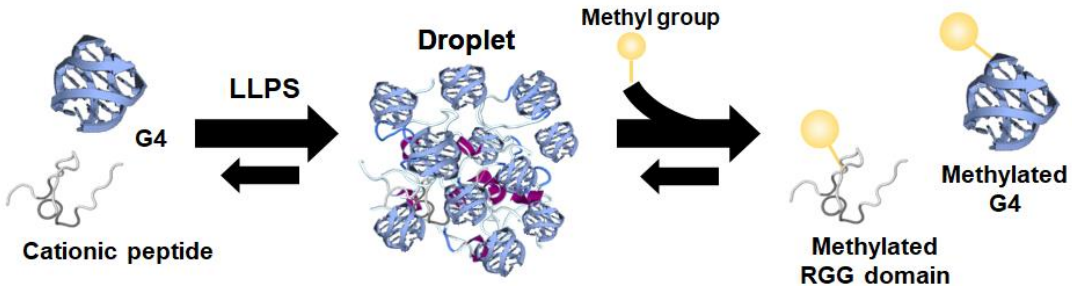

Fig. 1 Droplet formation of G4 DNA and cationic peptide and methylation effects

1) R. L. Kan *et al., Trends. Genet.* **2022**, 38, 182.
2) M. Tsuruta et al., Chem. Commun. **2022**, 58, 12931.

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G4 リガンドのテロメア長と TERRA 発現量に対する効果

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Effects of structural selective G4 ligand on telomere length and TERRA expression level

([1]*Graduate School of Frontiers of Innovative research in Science and Technology*, *Konan University* [2]*Faculty of Frontier Institute for Biomolecular Engineering Research, Konan University*) ○Yoshiki Hashimoto,[1] Takeru Torii, [1] Natsuki Kinoshita, [1] Keiko Kawauchi, [1] Hisae Tateishi-Karimata, [2] Naoki Sugimoto, [1,2] Daisuke Miyoshi[1]

Telomeres are nucleoprotein complexes, located at the ends of linear eukaryotic chromosomes, playing an essential role in the maintenance of chromosome integrity. The telomere length is maintained by the specialized enzyme, telomerase. Although telomeric repeat-containing RNA (TERRA) is one of the telomere length regulators, TERRA expression is regulated by telomere length. Telomere and TERRA consist of guanine-rich sequence which can fold into a G-quadruplex (G4). The G4 has been reported to be involved in transcription ant telomere elongation, suggesting that G4 regulates a relationship between TERRA expression level and telomere length. However, it is still unclear roles of G4 in telomere length regulation. In this study, we investigated effects of G4 ligands on telomere elongation and TERRA expression.

Keywords ：G-quadruplex; Telomere; TERRA; G-quadruplex ligand; Cancer

テロメアは染色体末端上に存在する核酸配列で細胞の分裂に関与し、その長さはテロメラーゼによって維持される。テロメラーゼによるテロメア伸長制御にはテロメア DNA より転写される TERRA が関与する。テロメアの伸長と TERRA の発現量は相互に制御し合うことが明らかになっている。テロメア及び TERRA はグアニンに富んだ核酸配列を含み、これらの配列はグアニン四重らせん構造（G4）を形成できる [1)]。G4 は転写やテロメア伸長などの様々な生物学的プロセスに関与することが報告されており [2)]、TERRA 発現量-テロメア伸長制御にも関与することが考えられる。しかしながらこれらの制御における G4 の役割はあきらかにされていない。そこで本研究では構造選択的 G4 リガンドを用いて、がん細胞における TERRA 発現量とテロメア長の相関を検討したその結果、G4 リガンドは TERRA 発現量とテロメア長に影響することが示された。

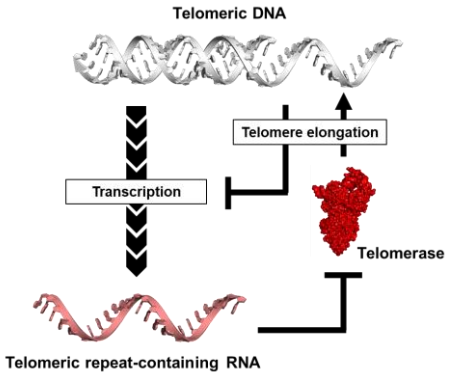

Fig. Schematic illustration of interregulation between TERRA expression and telomere elongation.

1) H. Martadinata, B. Heddi, K. W. Lim, A. T. Phan, *Biochemistry* **2011**, *50*, 6455.
2) D. Rhodes, H. J. Lipps, *Nucleic Acids Res.* **2015**, *43*, 8627.

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

[E1661-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Hidetaka Torigoe, Yuichiro Aiba

Fri. Mar 24, 2023 4:10 PM - 6:30 PM E1661 (1611, Bldg. 16 [1F])

[E1661-3vn-01] The first detection of the formation of DNA triplex structure in living human cells and an analysis of base pair dynamics under molecular crowding environment

○Tomoki Sakamoto[1,2], Yudai Yamaoki[1,2], Takashi Nagata[1,2], Masato Katahira[1,2] (1. Institute of Advanced Energy, 2. Graduate School of Energy Science, Kyoto University)

4:10 PM - 4:30 PM

[E1661-3vn-02] Investigation of parallel-stranded PNAs for the formation of an invasion complex with double-stranded DNA

○Masanari Shibata[1], Yuichiro Aiba[1], Masaki Hibino[1], Osami Shoji[1] (1. Nagoya University)

4:30 PM - 4:50 PM

[E1661-3vn-03] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (81) : Stability prediction of RNA duplexes under various molecular crowding in vitro and in cell

○Saptarshi Ghosh[1], Shuntaro Takahashi[1], Dipanwita Banerjee[1], Tatsuya Ohyama[1], Tamaki Endoh[1], Hisae Tateishi-Karimata[1], Naoki Sugimoto[1,2] (1. FIBER, Konan University, 2. FIRST, Konan University)

4:50 PM - 5:10 PM

[E1661-3vn-04] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (82) : Applications of nearest-neighbor parameters for RNA/DNA hybrid duplexes in the advancement of therapeutics

○Dipanwita Banerjee[1], Hisae Tateishi-Karimata[1], Saptarshi Ghosh[1], Shuntaro Takahashi[1], Tatsuya Ohyama[1], Tamaki Endoh[1], Maria Toplishek[2], Marko Trajkovski [2], Janez Plavec [2,3,4], Naoki Sugimoto[1,5] (1. FIBER, Konan University, 2. Slovenian NMR Centre, National Institute of Chemistry, 3. EN→FIST Centre of Excellence, 4. Faculty of Chemistry and Chemical Technology, University of Ljubljana, 5. FIRST, Konan University)

5:10 PM - 5:30 PM

[E1661-3vn-05] Development of single nucleotide polymorphism detection method based on the specific formation of T-Hg-T and C-Ag-C metal-mediated base pair

Kohsei Sekiya[1], Akira Ono[2], ○Hidetaka Torigoe[1] (1. Tokyo University of Science, 2. Kanagawa University)

5:30 PM - 5:50 PM

[E1661-3vn-06] Photosensitized oxidation of NADH analogue by hydrophobic phosphorus(V) porphyrins

○Hiroko Hasegawa[1], Kazutaka Hirakawa[1,2] (1. Department of Optoelectronics and Nanostructure Science, Graduate School of Science and Technology, Shizuoka University, 2. Applied Chemistry and Biochemical Engineering Course, Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University)

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5:50 PM - 6:10 PM

[E1661-3vn-07] Pore-wall modification of platinum porphyrin co-condensed mesoporous silica nanoparticles and their application to intracellular oxygen concentration imaging

○Shunsuke Odai[1], Junpei Noguchi[1], Arisa Yamauchi[1], Hidehiro Ito[1], Masaki Okamoto[2], Toshiaki Kamachi[1] (1. Tokyo institute of technology, 2. Keio University)

6:10 PM - 6:30 PM

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ヒト生細胞内における DNA 三重鎖構造形成の初観測および分子込み合い環境下における DNA 三重鎖構造の塩基対開閉ダイナミクスの解析

（京大エネ研 [1]・京大院エネ科 [2]）○阪本 知樹 [1,2]・山置 佑大 [1,2]・永田 崇 [1,2]・片平 正人 [1, 2]

The first detection of the formation of DNA triplex structure in living human cells and an analysis of base pair dynamics under molecular crowding environment

([1]*Institute of Advanced Energy,* [2]*Graduate School of Energy Science, Kyoto University*) ○Tomoki Sakamoto[1,2], Yudai Yamaoki[1,2], Takashi Nagata[1,2], Masato Katahira[1,2]

The intracellular environment in which nucleic acids actually work is a molecular crowding environment. It has been expected that the structure and dynamics of nucleic acids under such environment differ from those under a dilute solution environment *in vitro*. It has been reported that the DNA triplex structure, a type of non-canonical structures of nucleic acids, is associated with Friedreich's ataxia. However, there was no direct evidence for the formation of the triplex structure in living human cells. Here, we demonstrated for the first time that both parallel and antiparallel types of the DNA triplex structures can be formed in living human cells using in-cell NMR method[1-3),4)]. Furthermore, NMR relaxation dispersion experiment that can detect micro to millisecond dynamics of base pairs revealed that open/close dynamics of base pairs of the triplex structures in the solutions mimicking intracellular molecular crowding environments differ from those in dilute solution environments.

核酸が実際に働く生細胞内は分子混み合い環境であり、分子混み合い環境下と試験管内の希薄溶液環境下とでは核酸構造やその挙動が異なると考えられてきた。核酸の非標準構造の一種である DNA 三重鎖構造はフリードライヒ運動失調症と密接に関連していることが指摘されている。しかしながら、DNA 三重鎖構造が分子込み合い環境である生細胞内で実際に形成可能であることを示す直接的な証拠はこれまでに報告されていなかった。我々は生きた細胞をそのまま NMR 試料として生細胞内の標的分子の NMR シグナルを直接捉える in-cell NMR 法 [1-3)]を用いて、ヒト生細胞内において DNA 三重鎖構造の平行型・逆平行型の両型が形成可能であることを初めて証明した [4)]。さらに、マイクロ～ミリ秒範囲のダイナミクス過程を捉えることができる NMR 緩和分散法により、三重鎖構造中の塩基対の開閉ダイナミクスが、細胞内分子混み合い環境を模倣した系では、従来の希薄溶液環境とは異なることを明らかにした。

1) Recent progress of in-cell NMR of nucleic acids in living human cells. Y. Yamaoki, T. Nagata, T. Sakamoto, M. Katahira, *Biophys. Rev.*, **2020**, **12**, 411-417.
2) Shedding light on the base-pair opening dynamics of nucleic acids in living human cells, Y. Yamaoki, T. Nagata, K. Kondo, T. Sakamoto, S. Takami, M. Katahira, *Nat. Commun.*, **2022**, **13**, 7143.
3) Detection of interaction between an RNA aptamer and its target compound in living human cells using 2D in-cell NMR. O. Eladl, Y. Yamaoki, K. Kondo, T. Nagata, M. Katahira, *Chem. Commun.*, **2022**, **22**, 102-105.
4) Detection of parallel and antiparallel DNA triplex structures in living human cells using in-cell NMR. T. Sakamoto, Y. Yamaoki, T. Nagata, M. Katahira, *Chem. Commun.*, **2021**, **57**, 6364-6367.

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Investigation of parallel-stranded PNAs for the formation of an invasion complex with double-stranded DNA

([1]*Graduate School of Science, Nagoya University*) ○Masanari Shibata,[1] Yuichiro Aiba,[1] Masaki Hibino,[1] Osami Shoji[1]

Keywords: peptide nucleic acids; dsDNA; double-duplex invasion; parallel orientation

Artificial nucleic acids are attractive tools for sequence-specific recognition of natural nucleic acids owing to their complementarity based on base pairing. Peptide nucleic acid (PNA)[1] is one of the DNA analogs with an electrostatically neutral backbone (Fig.1a). Due to the absence of electrostatic repulsion between PNA and DNA, PNA has a high binding affinity to DNA. Furthermore, PNA has been utilized to direct recognize sequences in double-stranded DNA (dsDNA) via the formation of a unique invasion complex.[2] For high invasion efficiency, introducing pseudo-complementary nucleobases to PNAs is required to suppress the PNA/PNA duplex formation.

Recently, our research group has succeeded in efficiently recognizing target sequences in dsDNA by using parallel-stranded PNAs without nucleobase modification (Fig.1b).[3] Melting temperature measurements indicated that this parallel-stranded design of PNA pairs efficiently suppressed undesirable PNA/PNA duplex formation. Herein, we have conducted a more detailed investigation about invasion complex formation. The efficiency of invasion complex formation can be measured by electrophoretic mobility shift assay (EMSA). Also, we evaluated mismatch discrimination ability of parallel-stranded PNA invasion using PNAs with a single mismatch. As the result of EMSA, it was observed a significant reduction in invasion complex formation with PNAs including the mismatch, meaning their high sequence selectivity. Additionally, we synthesized several PNAs with different lengths and optimized PNA length for efficient recognition of dsDNA.

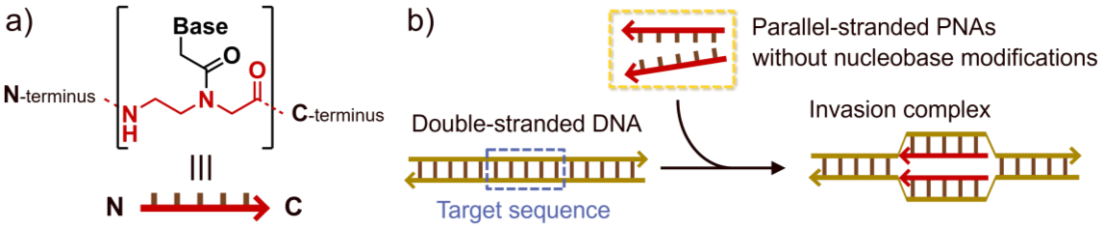

Fig. 1 (a) Chemical structure and arrow notation of PNA (from N- to C-terminus). (b) Double-stranded DNA recognition via the formation of an invasion complex by parallel-stranded PNAs.

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*., *ChemRxiv*. **2022**.

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Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (81): Stability prediction of RNA duplexes under various molecular crowding in vitro and in cell

([1]*FIBER, Konan University*, [2]*FIRST, Konan University*) ○ Saptarshi Ghosh,[1] Shuntaro Takahashi,[1] Dipanwita Banerjee,[1] Tatsuya Ohyama,[1] Tamaki Endoh,[1] Hisae Tateishi-Karimata,[1] Naoki Sugimoto[1,2]

Keywords: RNA duplex; Stability prediction; Nearest-neighbor model; Molecular crowding; In-cell condition

RNA forms various inter- or intramolecular secondary structures, in majority of which are double helices formed by the Watson-Crick base pairing and loop structures. These secondary structures affect the kinetics and yield of the transcription and translation reactions significantly depending on their stabilities.[1] Therefore, prediction of RNA duplex stability in heterogeneously crowded intracellular environments will be beneficial for regulating gene expression. Nearest-neighbor (NN) model has been widely used for predicting duplex stability from the base sequence of the duplex.[2] Here, we have developed NN parameters for RNA duplex formation under diverse crowding conditions.

We analyzed the thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°_{37}$) of 45 RNA duplexes of varying length and base composition in a crowding condition of 40 wt% polyethylene glycol 200 (PEG 200) with 100 mM NaCl. From the measured data, we derived new NN parameters for 10 propagating pairs and terminal pairs using linear least square analysis, that accurately predicted stability of plenty of RNA duplexes in crowding conditions even in a solution having exact intracellular cation composition.[3] Moreover, to obtain NN parameters applicable in any cation and crowder conditions, we separated the individual contributions of physical properties of solution for each NN base pair. The obtained parameters were shown to predict RNA duplex stability in diverse *in vitro* and localized cellular conditions (Figure 1), which will be helpful for predicting RNA structures in cell and designing RNA-based therapeutics.

Figure 1. Schematic illustration for predicting RNA duplex stability in diverse crowding conditions.

1) a) H. Tateishi-Karimata, N. Sugimoto, *Chem. Commun.*, **2020**, *56*, 2379. 2) a) S. Ghosh, S. Takahashi, T. Ohyama, T. Endoh, H. Tateishi-Karimata, N. Sugimoto, *PNAS*, **2020**, *117*, 14194. b) S. Takahashi, N. Sugimoto, *Chem. Soc. Rev.*, **2020**, *49*, 8439. 3) S. Ghosh, S. Takahashi, D. Banerjee, T. Ohyama, T. Endoh, H. Tateishi-Karimata, N. Sugimoto, *Nucleic Acids Res.*, **2023**, (just accepted).

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Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (82): Applications of nearest-neighbor parameters for RNA/DNA hybrid duplexes in the advancement of therapeutics

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Keywords: RNA/DNA hybrid duplex, Molecular crowding, Stability prediction, Nearest-neighbor model, CRISPR-Cas9

RNA/DNA hybrid duplexes form everywhere in living cells. The hybrid duplex regulates important biological reactions such as replication and transcription and also therapeutic techniques like gene modifying ASO (Antisense Oligonucleotide) and gene editing CRISPR (Clustered Regularly Interspaced Short Palindromic Repeats)-Cas9. Thus, the stability prediction for hybrid duplex in cellular conditions is essential for understanding the biological reactions and developing therapeutic techniques in cell. Previous parameters for hybrid duplex based on the nearest neighbor model were derived in 1 M NaCl solution that can predict well the stability of hybrid duplex.[1] However, the cellular environments contains low salt concentration (~100 mM) and large amount of biomolecules inducing molecular crowding, which can affect duplex stability significantly. Therefore, we derived new parameters under diverse molecular crowding conditions containing different concentrations of cations and cosolutes that predicted well the stability of hybrid duplex under diverse *in vitro* and in cell conditions. Among all applications, here we displayed the use of our new parameters for developing therapeutics by CRISPR-Cas9. Our derived parameters can estimate knockout efficiency of CRISPR-Cas9 (Figure 1). The estimation of CRISPR efficiency for different target sites will help to shorten length of guide RNA, which will be useful for improving target specificity also by decreasing off-target binding probability.[2]

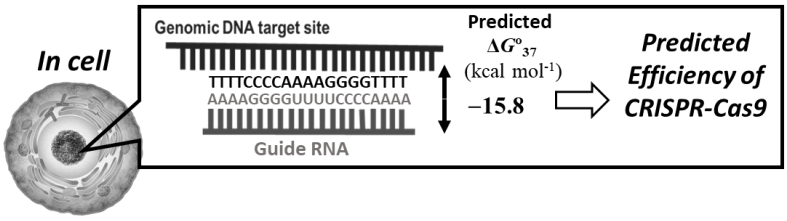

Figure 1. Schematic representation how derived parameters for stability prediction of hybrid duplex in a cellular condition can help in the development of CRISPR-Cas9.

1) N. Sugimoto, S. Nakano, M. Katoh, A. Matsumura, H. Nakamuta, T. Ohmichi, M. Yoneyama, M. Sasaki, *Biochemistry* **1995**, *34*, 11211. 2) D. Banerjee, H. Tateishi-Karimata, T. Ohyama, S. Ghosh, T. Endoh, S. Takahashi, N. Sugimoto, *Nucleic Acids Res*. **2021**, *49*, 10796.

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T-Hg-T および C-Ag-C 金属イオン含有塩基対形成に基づく一塩基多型検出法の開発

（東京理大理 [1]・神奈川大工 [2]）関谷 洸星 [1]・小野 晶 [2]・○鳥越 秀峰 [1]

Development of single nucleotide polymorphism detection method based on the specific formation of T–Hg–T and C–Ag–C metal-mediated base pair

([1]*Faculty of Science, Tokyo University of Science*, [2]*Faculty of Engineering, Kanagawa University*) Kohsei Sekiya,[1] Akira Ono,[2] ○Hidetaka Torigoe[1]

We have already found that T–T and C–C mismatched base pairs in duplex DNA specifically bind to Hg^{2+} and Ag^{+}, respectively. In this study, we have developed a single nucleotide polymorphism detection method based on these specific metal-mediated base pair formation. In this method, probes were labeled with fluorophore, carboxyfluorescein (FAM), at the 5' terminus and quencher, tetramethylrhodamine (TAMRA), at the 3' terminus to recognize the target base. When the target base was only T, fluorescence intensity of the probe to detect the target T base was significantly increased by T–Hg–T base pair formation upon Hg^{2+} addition. When the target base was only C, fluorescence intensity of the probe to detect the target C base was significantly increased by C–Ag–C base pair formation upon Ag^{+} addition.

Keywords : Single Nucleotide Polymorphism; Mismatched Base Pair; Mercury Ion; Silver Ion; Fluorescence Intensity

2 本鎖 DNA の T–T ミスマッチ塩基対に Hg^{2+}が、C–C ミスマッチ塩基対に Ag^{+}が特異的に結合する [1),2)]。本研究は、この特異的塩基対形成を用いて一塩基多型(SNP)検出法を開発した。標的配列として 5'-d(CTCAGATCCTGC**X**CTTCAAAAACAA)-3' (**X**=A, C, G, T)、5'末端を蛍光色素 FAM で、3'末端を消光色素 TAMRA で標識した T プローブ: 5'-FAM-d(<u>GGGAAA</u>AA*TGAAG**T**GCAGGA*<u>TTTCCC</u>)-TAMRA-3'、C プローブ: 5'-FAM-d(<u>GGAAA</u>AA*TGAAG**C**GCAGGA*<u>TTTCC</u>)-TAMRA-3'を調製した。斜線部は標的配列と結合し、標的配列の **X** とプローブの ***T***, ***C*** が塩基対を形成する。下線部は自己相補的であるため、プローブ単独ではヘアピンを形成し、TAMRA の消光で FAM の蛍光強度は低かった。**X**=A で T プローブが強く結合するため、ヘアピンが解消し、蛍光強度は増加したが、Hg^{2+}を添加しても蛍光強度は変化しなかった。**X**=C, G, T で T プローブが結合しないため、蛍光強度は低かった。Hg^{2+}を添加しても **X**=C, G で蛍光強度は低かったが、**X**=T では T–Hg–T 形成で T プローブが強く結合するため、ヘアピンが解消し、蛍光強度は増加した。一方、**X**=G で C プローブが強く結合するため、ヘアピンが解消し、蛍光強度は増加したが、Ag^{+}を添加しても蛍光強度は変化しなかった。**X**=A, C, T で C プローブが結合しないため、蛍光強度は低かった。Ag^{+}を添加しても **X**=A, T で蛍光強度は低かったが、**X**=C では C–Ag–C 形成で C プローブが強く結合するため、ヘアピンが解消し、蛍光強度は増加した。以上のように、T プローブで Hg^{2+}添加時に **X**=T を、C プローブで Ag^{+}添加時に **X**=C を特異的に検出できた。

1) H. Torigoe, A. Ono, T. Kozasa, *Chem. Eur. J.*, **2010**, *16*, 13218-13225.
2) H. Torigoe, I. Okamoto, T. Dairaku, Y. Tanaka, A. Ono, T. Kozasa, *Biochimie*, **2012**, *94,* 2431-2440.

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疎水性 P(V)ポルフィリンによる NADH 誘導体の光酸化機構

（静岡大創造院 [1]・静岡大工 [2]）・○長谷川 仁子 [1]・平川 和貴 [1,2]

Photosensitized Oxidation of NADH Analogue by Hydrophobic Phosphorus(V)porphyrins

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In photodynamic therapy (PDT) of cancer, oxygen-independent mechanisms are known to improve the treatment effect. Phosphorus(V) porphyrins can oxidize protein and DNA through electron transfer mechanism as singlet oxygen production mechanism does. In general, water-solubility of phosphorus(V) porphyrin is low. Therefore, 1-benzyl-1,4-dihydronicotinamide (BNADH), an NADH derivative was used as a target biomolecule in ethanol solution. The photosensitizing activity was evaluated using four phosphorus(V) porphyrins with hydrophobic alkoxyphenyl groups as photosensitizing agents. Photoexcited phosphorus(V) porphyrins effectively oxidized BNADH, and the analysis of photodamaging mechanism indicated that the electron transfer mechanism is main. The radical chain reaction was also confirmed in the electron transfer-mediated photooxidation of BNADH. This study showed that the photodynamic activity of hydrophobic porphyrins can be evaluated by using BNADH.

Keywords : Phosphorus(V) Porphyrin; Photodynamic Therapy; Electron Transfer; Singlet Oxygen; Nicotinamide Analogue

がんの光線力学的療法（PDT）では、酸素に依存しないメカニズムが低酸素状態の腫瘍に対する治療効果の向上につながる。光励起状態の P(V)ポルフィリンは、高い一重項酸素（$^1O_2$）生成量子収率を示し、さらにタンパク質や DNA 等の生体分子を電子移動機構で酸化損傷できる。一般に P(V)ポルフィリンの水溶性は低いため、水溶液中で生体分子の光酸化損傷性を評価することは困難な場合もある。そこで、本研究では、P(V)ポルフィリンの溶解度が高いエタノールに可溶な NADH 誘導体である 1-ベンジル-1,4-ジヒドロニコチンアミド（BNADH）を生体分子モデルとして用い、疎水性のアルコキシフェニル基をもつ 4 種類の P(V)ポルフィリンの光増感反応を評価した。

P(V)ポルフィリンを含むエタノール溶液に発光ダイオードを用いて可視光照射（中心波長: 585 nm）すると主に電子移動により BNADH が酸化され、加えて $^1O_2$ 生成による酸化機構の関与を確認した。また BNADH の電子移動酸化反応における量子収率が 1 を大きく超えたことから、既報 [1] による NADH の光酸化反応と同様に連鎖反応が示された。また、電子移動機構における BNADH の酸化量子収率と電子移動ギブズエネルギー（$-\Delta G$）には負の相関が見られた。電子移動速度定数と$-\Delta G$ は、正に相関したことから、$-\Delta G$ が増大すると逆電子移動も促進され、酸化量子収率が低下すると考えられる。一方、$^1O_2$ による酸化量子収率と $^1O_2$ 生成量子収率においては正の相関が認められた。以上から、BNADH の酸化反応を観測することで、疎水性光増感剤の活性やメカニズムを溶液反応で評価および解析可能なことが明らかになった。

1）K. Hirakawa, A. Murata, *Spectrochim. Acta A* **2018**, *188*, 640.

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白金ポルフィリン共縮合メソポーラスシリカナノ粒子への細孔壁修飾と細胞内酸素濃度イメージングへの応用

（東工大生命理工[1]・慶応大文[2]）○尾台 俊亮[1]・野口 純平[1]・山内 杏里彩[1]・伊藤 栄紘[1]・岡本 昌樹[2]・蒲池 利章[1]

Pore-wall modification of platinum porphyrin co-condensed mesoporous silica nanoparticles and their application to intracellular oxygen concentration imaging

([1]*School of Life Science and Technology, Tokyo institute of technology*, [2]*Faculty of Letters, Keio University*)
○Shunsuke Odai[1], Junpei Noguchi[1], Arisa Yamauchi[1], Hidehiro Ito[1], Masaki Okamoto[2], Toshiaki Kamachi[1]

Oxygen is essential for aerobic organisms and various methods have been developed to measure oxygen concentration in tissues and cells, including microelectrodes and optical methods. In terms of the monitoring of oxygen concentration in living cells, optical methods are better than other methods because they use only light and luminescence dye. However, intracellular oxygen concentration imaging using phosphorescent compounds has an intrinsic problem of oxidative damage caused by singlet oxygen. In previous study, mesoporous silica nanoparticles (MSNs) tethered phosphorescent Pt-porphyrins inside their pores were developed to overcome this problem. In this study, Pt-porphyrins co-condensed MSNs (PtP@cMSN) were synthesized, and their surface was modified to improve oxygen sensing properties. The application to intracellular oxygen concentration imaging is also described.

Keywords : Intracellular oxygen sensor, mesoporous silica nanoparticles, Phosphorescence

好気性生物において酸素は、電子伝達系やシグナル伝達といった重要な生体内反応に利用されている。このため、酸素の分布や動態の観測法が研究・開発されている。生細胞の酸素動態観測では、電極法などと比べて細胞侵襲性が低いリン光を利用した測定法が適している。しかし、酸素によるリン光の消光で生成する一重項酸素が生体反応に影響する可能性があるという課題が残されている。これまでに当研究室では、細孔内部のみに白金ポルフィリンを修飾したメソポーラスシリカナノ粒子を開発し、一重項酸素による細胞障害を低減したリン光を利用した細胞内酸素濃度測定を達成した。

本研究では、新たに共縮合法を用いて白金ポルフィリン修飾メソポーラスシリカナノ粒子を合成した。さらに表面修飾した白金ポルフィリン修飾メソポーラスシリカナノ粒子を用いて細胞内酸素濃度イメージングを行い、その機能を評価した。

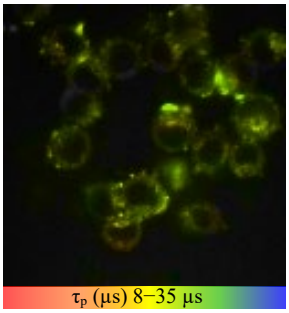

Fig. Intracellular oxygen concentration image of MKN45 cells stained with PtP@cMSN. Color bar indicates phosphorescence lifetime

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

[K304-3am] 18. Polymer

Chair: Takashi Miyata, Toshikazu Ono

Fri. Mar 24, 2023 9:00 AM - 11:20 AM K304 (K304, Lecture Hall Bldg. [3F])

[K304-3am-01] Mechanochromic elastomer showing optical property modulation by planarization and aggregation of bent boron complexes

○Toshikazu Ono Ono[1,2], Momoka Maeda[1], Luxia Cui[1], Shimakoshi Hisashi[1], Hoshino Yu[1]
（1. Graduate School of Engineering, Kyushu University, 2. Center for Molecular Systems (CMS), Kyushu University）

9:00 AM - 9:20 AM

[K304-3am-02] Thermoelectric conversion and electrochemical refrigeration using a coil– globule phase transition

○Hongyao Zhou[1], Fumitoshi Matoba[1], Ryohei Matsuno[1], Yusuke Wakayama[1], Teppei Yamada[1] （1. The University of Tokyo）

9:20 AM - 9:40 AM

[K304-3am-03] Supramolecular Miktoarm Star Copolymer with a Zinc Phthalocyanine Core for Organic Transistor Memory

○XINHAO ZHONG[1,2], JUNKO AIMI[2], MASAYUKI TAKEUCHI[1,2] （1. University of Tsukuba, 2. National Institute for Materials Science）

9:40 AM - 10:00 AM

[K304-3am-04] Interplay Between π-Conjugated Polymer Donors and Acceptors Determines Crystalline Order of Their Blends and Photovoltaic Performance

○Kodai Yamanaka[1], Masahiko Saito[1], Itaru Osaka[1] （1. The Univ. of Hiroshima）

10:00 AM - 10:20 AM

[K304-3am-05] Development of the new high metallic waterborn paint which cellulose nano fiber is used for as a viscosity agent

○Takao Tsukimori[1] （1. Toyota Motor Corporation）

10:20 AM - 10:40 AM

[K304-3am-06] Design of aromatic polyesters having sulfobetaine structure and their surface properties

○Akifumi Kawamura[1,2], Rika Itomitsu[1], Takashi Miyata[1,2] （1. Fac. Chem. Materials, Bioeng., Kansai Univ., 2. ORDIST, Kansai Univ.）

10:40 AM - 11:00 AM

[K304-3am-07] Design of Stimuli-responsive Polymers with Cyclodextrins and Detection of Denatured Proteins

○Takashi Miyata[1], Kanoko Murayama[1], Akifumi Kawamura[1] （1. Kansai Univ.）

11:00 AM - 11:20 AM

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屈曲型ホウ素錯体の平面化と凝集により光学特性変調を示すメカノクロミックエラストマー

（九大院工 [1]・九大 CMS[2]）○小野 利和 [1,2]・前田 桃花 [1]・崔 潞霞 [1]・嶌越 恒 [1]・星野 友 [2]

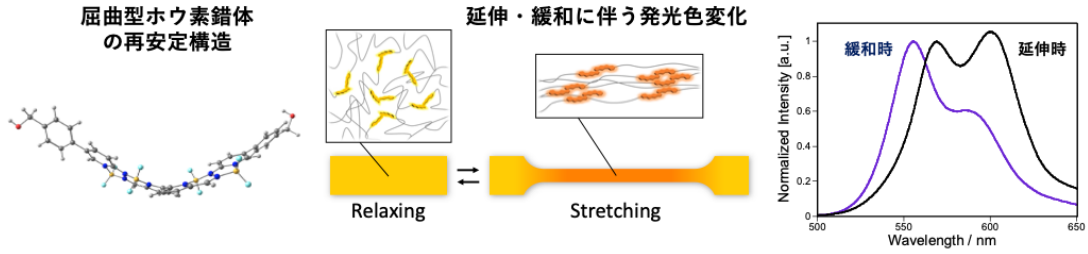
Mechanochromic elastomer showing optical property modulation by planarization and aggregation of bent boron complexes

([1]*Graduate School of Engineering, Kyushu University*, [2]*Center for Molecular Systems (CMS), Kyushu University*) ○Toshikazu Ono,[1,2] Momoka Maeda,[1] Luxia Cui,[1] Hisashi Shimakoshi,[1] Yu Hoshino[1]

Recently, functional dyes (mechanophores) that change their apparent color or emission color in response to external stresses has been attracting attention. In this study, we focused on a recently developed bent boron complex as a new mechanophore. We synthesized an elastomer material incorporating this complex covalently attached to polyurethane and evaluated its optical properties during stretching and relaxation. As a result, we found that the elastomer exhibits a large color change in response to stretching due to (1) a decrease in the HOMO-LUMO gap caused by the planarization of the boron complex and (2) an increase in optical absorption and emission at longer wavelengths due to the enhancement of dye aggregation. The details will be presented in this presentation.

Keywords : Boron Complex; Mechanophore; Polyurethane; Elastomer;

近年、高分子材料にかかる外部応力等のストレスに応答して呈色や発光色変化を生ずる機能性色素（メカノフォア）の合成が注目を集めている。[1] しかしその多くは、分子骨格内の共有結合の切断を用いたものに注力が注がれており、不可逆な応答を示すものが多く、可逆的な応答を示すメカノフォアの創製は発展途上にある。本研究では、新たなメカノフォアとして、近年我々が開発した屈曲型ホウ素錯体に着目した。[2] これをポリウレタンに共有結合で組み込んだエラストマー材料の合成を行い、延伸・緩和時における光学特性評価を行った。結果として、エラストマーの延伸に応答して、ホウ素錯体の平面化に伴う(1) HOMO-LUMO ギャップの減少と(2)色素凝集の促進に伴う光吸収・発光の長波長化が相まって、大きな呈色・発光色変化を示すメカノフォアとして機能することを見出した。その詳細について本発表で紹介する。



1) R. P. Sijbesma et al., *Chem. Soc. Rev.* **2021**, *50*, 4100-4140.
2) T. Ono *et al*., *Angew. Chem. Int. Ed.*, **2022**, *61*, e202204358.

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Thermoelectric conversion and electrochemical refrigeration using a coil–globule phase transition

([1]*Graduate School of Science, Department of Chemistry, The University of Tokyo*)
○ Hongyao Zhou,[1] Fumitoshi Matoba,[1] Ryohei Matsuno,[1] Yusuke Wakayama,[1] Teppei Yamada[1]

Keywords: Coil–Globule Phase Transition; Thermoelectric Conversion; Electrochemical Refrigeration; Entropy; Redox-responsive Polymer

Thermocell generates thermoelectric voltage (ΔV) by applying a temperature difference (ΔT) between a pair of electrodes. Seebeck coefficient ($S_e = \Delta V/\Delta T$) of thermocells is known to be proportional to entropy change of the redox reaction ($S_e = \Delta S/nF$; ΔS, entropy change; n, number of electrons; F, Faraday constant).[1] Therefore, a redox system exhibiting a large ΔS can increase the S_e value and thus expected to improve its thermoelectric efficiency.

In this study, we focused on using the large ΔS released at the coil–globule phase transition of redox polymers in aqueous media. We synthesized poly(*N*-isopropyl acrylamide-*co*-*N*-(2-acrylamide ethyl-*N'*-propylviologen)[2] (noted as PNV) and evaluated the phase transition temperature by both turbidimetry and differential scanning calorimetry (DSC). The transition temperature of the dicationic form (PNV^{2+}) was 40 °C, while that of the radical cationic form (PNV^{+}) decreased to 22 °C. The ΔS of PNV^{+} at the coil–globule transition was evaluated as 0.12 kJ K^{-1} per mole of viologen unit by DSC. The S_e of $PNV^{2+/+}$ thermocell showed a drastic increase from +0.09 to +2.1 mV K^{-1}at the phase transition temperature, which corresponds to the ΔS of 0.19 kJ K^{-1} mol^{-1} and agrees with the result from the DSC analysis. Moreover, a small temperature drop was observed when the cell temperature was increased above the transition temperature (T > 25 °C, Figure 1a). This result shows the coil–globule phase transition can induce an electrochemical refrigeration (i.e., Peltier effect) (Figure 1b).

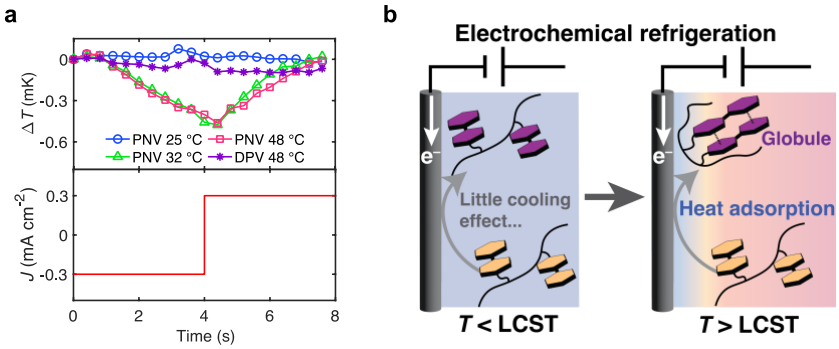

Figure 1. a) Temperature change of one of the electrodes in response to the applied current. b) A schematic showing that the coil–globule phase transition induces an electrochemical refrigeration.

1) H. Zhou, H. Inoue, M. Ujita, T. Yamada, *Angew. Chem. Int. Ed.* **2022**, 10.1002/ange.202213449 (in press). 2) K. Okeyoshi, R. Yoshida, *ibid.* **2019**, 58, 7304.

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Supramolecular Miktoarm Star Copolymer with a Zinc Phthalocyanine Core for Organic Transistor Memory

([1]*Graduate School of Pure and Applied Science, University of Tsukuba*, [2]*National Institute for Materials Science*) ○Xinhao Zhong,[1,2] Junko Aimi,[2] Masayuki Takeuchi[1,2]

Keywords: Miktoarm star copolymer; Organic transistor memory; Supramolecular; Thin film morphology

Non-volatile organic field-effect transistor (OFET) memory is an emerging and promising technology for possible use in wearable data storage since it has a non-destructive read-out memory cell system with multi-bit storage and an easily integrated structure. OFET memory possesses a memory layer between the organic semiconductors and the control gates, which can store and release charges during the writing and erasing processes. Various materials, including ferroelectric material, polymer electrets, and nano floating gates have been demonstrated to show memory characteristics in OFET device structures. We recently demonstrated non-volatile OFET memory that utilizes a star-shaped polymer with a metallo phthalocyanine (MPc) core as the memory layer. The star polymer has distinct charge trapping sites in the MPc core surrounded by dielectric polystyrene arms, enabling to store and release hole charges like nano floating gates, resulting in high performance memory characteristics.[1]

Here we prepared a new memory material, supramolecular miktoarm star copolymer with a zinc phthalocyanine core (ZnPc), which is constructed by metal-ligand coordination between ZnPc-cored star polystyrene (ZnSP) and poly(methyl methacrylate) with a pyridyl end-group (pyCTA-PMMA) as shown in Figure 1.[2] The OFET memory with the supramolecular miktoarm star copolymer as memory layer was fabricated using 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) as p-type organic semiconductor. The device performance as well as the influence of the polymer morphology on memory characteristics will be discussed.

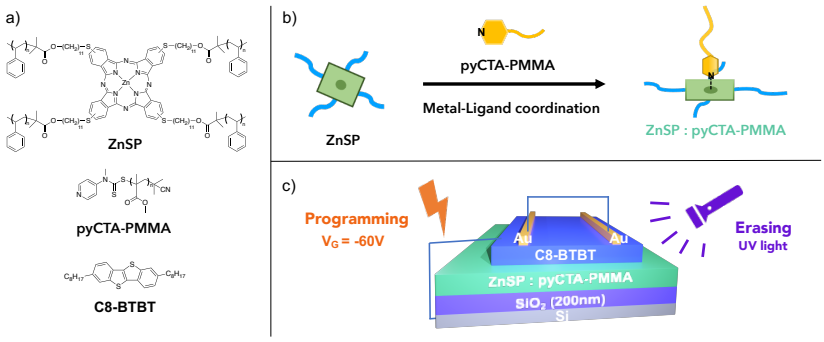

Figure 1. a) Chemical structure of ZnSP, pyCTA-PMMA and C8-BTBT. b) Formation of supramolecular miktoarm star copolymer with ZnSP and pyCTA-PMMA. c) Schematic configuration of the OFET memory device.

[1] a) J. Aimi, C. T. Lo, H. C. Wu, C. F. Huang, T. Nakanishi, M. Takeuchi W. C. Chen, *Adv. Electron. Mater.* **2016**, 2, 1500300. b) J. Aimi, P. H. Wang, C. C. Shih, C. F. Huang, T. Nakanishi, M. Takeuchi, H. Y. Hsueh and W. C. Chen, *J. Mater. Chem. C*, **2018**, 6, 2724-2732. [2] X. Zhong, A. Nagai, M. Takeuchi, J. Aimi, *Macromol Rapid Commun*, **2022**, 2200666.

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Interplay Between π-Conjugated Polymer Donors and Acceptors Determines Crystalline Order of Their Blends and Photovoltaic Performance

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kodai Yamanaka[1], Masahiko Saito[1], Itaru Osaka[1]

Keywords: *Organic photovoltaics, π-Conjugated polymer, Crystallinity, Fullerene, Non-fullerene*

Organic photovoltaics (OPVs) have been paid significant attention because they allow us to produce them on flexible and lightweight plastic substrates through the solution process. The development of new semiconducting materials has markedly improved the efficiencies of OPVs such as over 18%. Although fullerene derivatives have long been used as the n-type semiconducting (acceptor) material, nonfullerene compounds (NFAs) have recently been mainly used as the acceptor material. Whereas, for fullerene-based cells, high-crystalline π-conjugated polymers are typically used as the p-type semiconducting (donor) materials,[1)] NFA-based cells, low-crystalline polymers typically provide better efficiencies.[2)] However, we envisage that if higher crystalline polymers can function well in NFA-based cells, further improvement in efficiency could be realized.

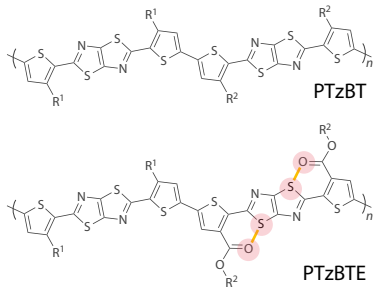

Figure 1. Chemical structures of thiophene-thiazolothiazole copolymer.

In this work, we prepared a series of thiazolothiazole (TzTz)–thiophene copolymers named PTzBT and PTzBTE (Figure 1) and systematically studied how the polymer crystallinity and aggregation properties impact the performance of OPV cells based on NFAs such as IT-4F, Y6, and Y12 as well as a fullerene material $PC_{71}BM$ as the acceptor (Figure 2). PTzBT has alkyl groups (2-butyloctyl and 2-hexyldecyl groups) as the side chains, whereas PTzBTE has alkyl (2-butyloctyl) and ester (2-hexyldecyl ester) groups as the side chains. In PTzBTE, the sulfur atom in the TzTz ring and the carbonyl oxygen can induce a noncovalent intramolecular interaction (S···O interaction) to interlock the linkage between the ester-substituted thiophene and TzTz rings, suppressing the backbone torsion.

Interestingly, whereas PTzBTE exhibited crystalline structures in the blend film regardless of the acceptor materials, PTzBT exhibited crystalline structures only when blended with acceptors showing relatively high aggregation properties and crystalline order. Notably, such crystalline order in the blend films was correlated closely with the OPV performance. This study demonstrates how the interplay between the polymer donor and acceptor plays a crucial role in determining the crystalline order in the bulk heterojunction systems and thereby high photovoltaic performance.

Reference

1) *Nat. Photon.* **2015**, *9*, 403. 2) *Joule* **2019**, *3*, 1140.

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セルロースナノファイバーを粘性剤として用いた新型高金属調水性塗料の開発

（トヨタ自動車株式会社[1]・関西ペイント株式会社[2]）○月森　隆雄[1]・小川　淳也[1]・伊藤　政之[2]

Development of the new high metallic water born paint which cellulose nanofiber is used for as a viscosity agent

（[1]*Toyota motor corporation*、[2]*Kansai Paint Co., Ltd.*）○Takao Tsukimori[1], Junya Ogawa[1], Masayuki Ito[2]

The metallic silver using thin and smooth surface aluminum flake pigment is placed as the luxury grade in each car manufacturer. But it has some technical difficulties, the color mottling by unevenness of the pigment distribution etc. Therefore, the silver color design that we could reach had a limit. We have continued developing and breakthrough technology. The new type of water borne paint system using cellulose nanofiber (CNF) as a viscosity control agent was developed and the new high metallic silver was released from 2020. Normal CNF have low transparency and viscosity control property. We applied the defibrate type of CNF that have high transparency and high viscosity control property. The characteristic of CNF makes it possible to produce high viscosity paint in low solid content. We report the rheology change of the paint using some type of CNF in this article.

Keywords : CNF; Celluloses nanofiber; silver; viscosity control agent; paint

自動車ボデーの塗装として薄膜平滑なアルミフレーク光輝材を均一に塗装した高金属調シルバーは自動車メーカー各社で最高級グレードの意匠として位置づけられている。ただし技術難度が高く、光輝材分散不良によるムラや他の作業性問題が起きやすい。そのため到達色域には限界があったが、技術検討を続けブレークスルーを達成、超高金属調意匠を達成したセルロースナノファイバー(CNF)を粘性剤として用いた超低固形分の新型水性塗料を開発[1)]。2020 年に塗色として市場に販売した。CNF は一般的なものは透明性が低く、粘性制御能力も低いが、高解繊タイプの CNF は、高い透明性と高粘性制御能力を有し低固形分で高粘性の塗料を製造する事が可能となる。本稿ではいくつかのタイプの CNF を用い塗料の粘性変化を調査した結果を報告する。

1) Development of high metallic silver water borne paint using next generation paint for car Takao Tsukimori,　自動車技術会論文集　Vol.to,No.2, March 2019

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スルホベタイン構造を有する芳香族ポリエステルの合成とその表面特性

（[1]関西大化学生命工・[2]関西大 ORDIST）○河村 暁文[1,2]・糸満 璃香[1]・宮田 隆志[1]

Design of Aromatic Polyester Having Sulfobetaine Structure and Their Surface Properties

([1]*Faculty of Chemistry, Materials and Bioengineering, and* [2]*ORDIST, Kansai University*)
○Akifumi Kawamura,[1,2] Rika Itomitsu,[1] Takashi Miyata[1,2]

Zwitterionic polymers show high hydrophilicity and oil repellency in water. Differing from the conventional sulfobetaine polymers composed of poly(meth)acrylate main chain, this paper describes the synthesis of zwitterionic polyester, poly(diethyl sulfobetaine terephthalate) (PDSBT). The PDSBT was synthesized by the reaction of poly(*N*-methyldiethylamino terephthalate) with 1,3-propanesultone. The sulfobetaine contents of PDSBTs were controlled between 0 and 98%. The PDSBT film having 83% of sulfobetaine contents showed high contact angle of a hexadecane droplet in water. In addition, hexadecane did not adsorb onto the PDSBT film containing 98% of sulfobetaine in water. In addition, the polycarbonate substrates adhered with PDSBT detached by acidic water treatment owing to the dissolution of PDSBT acting as adhesive.

Keywords : Zwitterionic polymer; Sulfobetaine polymer; Polyester; Oil repellency

双性イオンポリマーは，優れた親水性と水中撥油性とを有する。本研究では，従来のポリ（メタ）アクリレート系とは異なり，ポリエステル型のスルホベタインである poly(diethylsulfobetaine terephthalate)（PDSBT）を合成し，その表面特性を評価した。3 級アミノ基を有するポリエステルである poly(*N*-methyldiethylamino terephthalate)に 1,3-propanesultone を付加させ, PDSBT を得た。PDSBT のスルホベタイン導入率は 1,3-propanesultone の添加量により制御でき，最大 98%のスルホベタイン導入率を有する PDSBT が得られることがわかった。得られた PDSBT を用いて薄膜を調製し，空気中での水の接触角および水中でのヘキサデカンの接触角を測定したところ, スルホベタイン導入率 83%以上において水の接触角が減少し，水中でのヘキサデカンの接触角が増大した。また，スルホベタイン導入率 98%の PDSBT にはヘキサデカンが吸着しないことがわかった。これは，スルホベタイン構造により PDSBT 薄膜表面に水和層が形成しているためと推察される。

本研究は，（独）環境再生保全機構の環境研究総合推進費（JPMEERF20203R01）により実施した。

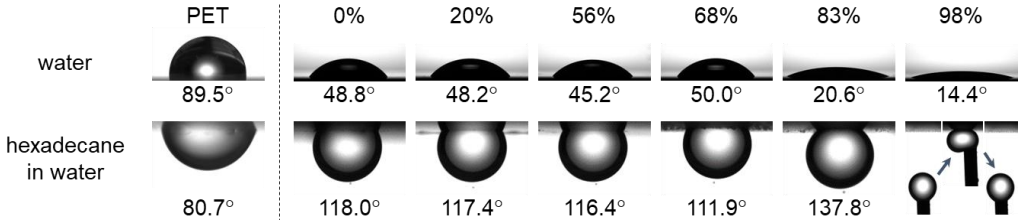

Fig. Photographs and contact angles of water droplet in air and hexadecane droplet in water on PET and PDSBTs.

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シクロデキストリンを有する刺激応答性ポリマーの設計と変性タンパク質の検出挙動

（関西大化学生命工 [1]，関西大 ORDIST[2]）○宮田隆志 [1,2]，村山果子 [1]，河村暁文 [1,2]
Design of Stimuli-responsive Polymers with Cyclodextrins and Detection of Denatured Proteins ([1]*Faculty of Chemistry, Materials and Bioengineering*, [2]*ORDIST, Kansai University*)
○Takashi Miyata[1, 2], Kanoko Murayama[1], Akifumi Kawamura[1, 2]

Stimuli-responsive polymers for detecting conformational changes of proteins are required as their denaturation causes protein-folding diseases. In this study, stimuli-responsive polymers that detected denatured proteins were designed by introducing β-cyclodextrins (CDs) as protein recognition sites to temperature-responsive polymers with a lower critical solution temperature. The addition of mixtures of native proteins (ribonuclease A, lysozyme) resulted in no change in the transmittance of a buffer solution with the resulting polymers. However, the transmittance of a buffer solution with the polymer decreased dramatically by the addition of a mixture of native and denature proteins. The complex formation between CD and the denatured protein made the polymer chains more hydrophobic because the denatured protein is more hydrophobic than the native protein, followed by the formation of precipitation.
Keywords : Stimuli-Responsive Polymer; Cyclodextrin, Molecular Recognition; Lower Critical Solution Temperature; Denatured Protein

タンパク質は特定のコンフォメーションを形成することにより様々な機能を発現する。しかし，そのコンフォメーションが変化して変性状態になるとフォールディング病などの問題を引き起こす。そのため，タンパク質のコンフォメーション変化を検出できる材料システムの開発が望まれている。本研究では，下限臨界溶液温度（LCST）を有する温度応答性ポリマーにタンパク質認識部位として β-シクロデキストリン（CD）を導入した新規な三元共重合体（P(CD-*co*-NIPAAm-*co*-OEGMA)）を合成した。Fig. 1 には，P(CD-*co*-NIPAAm-*co*-OEGMA)を溶解させたリン酸緩衝液に，ネイティブタンパク質（リボヌクレアーゼ A，リゾチーム）混合液およびそれに変性リゾチームを加えたネイティブ・変性タンパク質混合液を添加した際の濁度測定の結果を示した。図より，ネイティブタンパク質添加の有無に関わらず，ポリマー水溶液の透過率は約 100 %で一定であり，測定温度範囲で LCST を示さなかった。しかし，変性リゾチームを含むタンパク質混合液を添加すると明確な沈殿が生じた。これは，コンフォメーション変化により疎水性が増加した変性タンパク質が P(CD-*co*-NIPAAm-*co*-OEGMA) の CD と複合体を形成し，測定範囲の温度以下に LCST が低下してポリマーが不溶化するためと考えられる。したがって，P(CD-*co*-NIPAAm-*co*-OEGMA)はタンパク質混合液中の変性タンパク質にのみ応答することから，タンパク質コンフォメーション変化の検出への応用が期待できる。

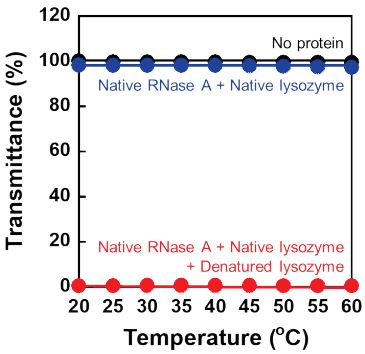

Fig. 1. Effect of temperature on transmittance (650 nm) of P(CD-*co*-NIPAAm-*co*-OEGMA) in a phosphate buffer solution (pH 7.4, 50 mM) without and with various native and denatured protein. Polymer and protein concentrations were 2.0 and 5.0 mg/mL.

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

[K301-3pm] 18. Polymer

Chair: Kohsuke Kawabata, Tsuyoshi Nishikawa

Fri. Mar 24, 2023 1:20 PM - 3:40 PM K301 (K301, Lecture Hall Bldg. [3F])

[K301-3pm-01] Polymer Degradation Unlocked by Synergistic Dual Stimuli: Base Interaction and Photocatalysis on Boryl Pendants Leading to Main-Chain Scission

○Hiroshi Makino Makino[1], Tsuyoshi Nishikawa[1], Makoto Ouchi[1] （1. Grad. Sch. of Eng., Kyoto Univ.）

1:20 PM - 1:40 PM

[K301-3pm-02] Synthesis of Self-Healing Elastomers by Scandium-Catalyzed Terpolymerization of Ethylene, Styrene and Dimethylaminophenyl-Substituted Propylene

○Haoran Zhang[1,2], Xia Wu[2], Lin Huang[2], Masayoshi Nishiura[2], Tetsuro Murahashi[1], Zhaomin Hou[2] （1. Tokyo Tech, 2. RIKEN）

1:40 PM - 2:00 PM

[K301-3pm-03] Polymers containing ester and ketone groups in chains: synthesis and their biodegradability

○Haobo Yuan[1], Kohei Takahashi[1], Shinya Hayashi[1], Chifeng Li[2], Kazuya Yamaguchi[2], Miwa Suzuki[3], Kenichi Kasuya[3,4], Kyoko Nozaki[1] （1. Grad. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Applied Chem., The Univ. of Tokyo, 3. GUCFW, 4. Grad. Sch. of Sci. Tech., Gunma Univ.）

2:00 PM - 2:20 PM

[K301-3pm-04] Synthesis of self-healing elastomers by scandium-catalyzed copolymerization of ethylene with thioether substituted propylenes

○Mingjun Chi[1,2], Hao Wang[2], Lin Huang[2], Haoran Zhang[2], Xiaobin Lin[2], Masayoshi Nishiura[2], Zhaomin Hou[2] （1. Saitama University, 2. RIKEN）

2:20 PM - 2:40 PM

[K301-3pm-05] Designing Thermally Stable Organocatalysts for Poly(ethylene terephthalate) Synthesis: Toward a One-Pot, Closed-Loop Chemical Recycling System for PET

○Shu Kaiho[1,2], Ali Al Rida Hmayed[2], Kayla R. Delle Chiaie[2], Joshua C. Worch[2], Andrew P. Dove[2] （1. Toray Industries, Inc., 2. University of Birmingham）

2:40 PM - 3:00 PM

[K301-3pm-06] Self-assembled Structure of Amphiphilic Polythiophenes with Asymmetric Electronic Structures and its Photovoltaic Properties

○Kohsuke Kawabata[1,2], Kazuo Takimiya[1,2] （1. Tohoku Univ., 2. RIKEN）

3:00 PM - 3:20 PM

[K301-3pm-07] Pathway complexity in the self-assembly process of platinum complexes possessing TEG chains

○Takehiro Hirao[1], Masaya Yoshida[1], Takeharu Haino[1,2] （1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM2, Hiroshima University）

3:20 PM - 3:40 PM

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Polymethacrylate Degradation Unlocked by Synergistic Dual Stimuli: Base Interaction and Photocatalysis on Boryl Pendants Leading to Main-Chain Scission

(*Graduate School of Engineering, Kyoto University*) ○Hiroshi Makino, Tsuyoshi Nishikawa, Makoto Ouchi

Keywords: Boron; Methacrylate Polymer; Photoreaction; Metal-free; Polymer Degradation

The development of degradable polymers collects increasing attention due to the social concerns about environmental pollution problems derived from remaining polymer debris for the long term. The incorporation of degradable trigger into the main chain is one of the typical approaches for making commodity polymers degradable. However, such triggers usually respond to a single stimulus, which could cause undesired degradation of the polymers in use. Therefore, the design of programmed degradation unlocked by synergistic dual stimuli should be useful for both stability and degradability.

Recently, we revealed that a boron pendant on the polymer main chain was usable as the trigger for the degradation of polymethacrylates via β-scission triggered by an excess amount of manganese oxidant in conjunction with a base.[1] Given the recent progress in photocatalytic carbon-boron bond homolysis[2], we came up with an idea that the boron trigger is available for programmed degradation by synergistic stimuli using photocatalysis. In this work, sodium methoxide (MeONa) was combined with 4CzIPN as a photocatalyst for backbone degradation of polymethacrylates under irradiation of blue light at room temperature (Figure 1). No degradation was observed in the absence of MeONa or photoirradiation, indicating that both base and photocatalyst were essential. Main-chain scission probably took place via photo-induced C–B bond homolysis of borates (boron-methoxide complex) and the subsequent β-scission. Thus, dual stimuli-induced degradation was achieved by taking advantage of the reactivity of boron.

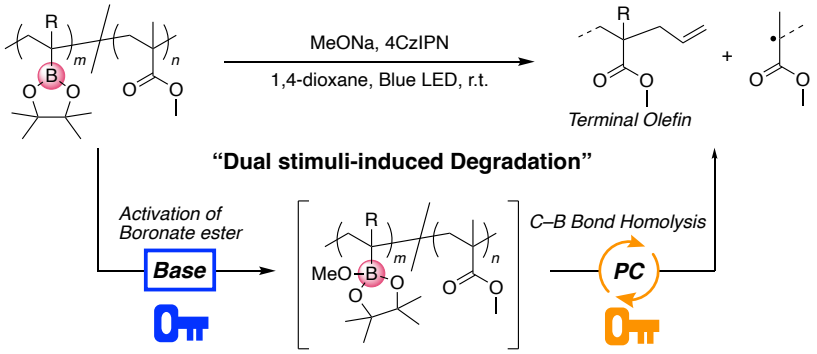

Figure 1. Synergistic dual stimuli-induced degradation of polymethacrylates bearing boronate esters.

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2) Duret, G.; Quinlan, R.; Bisseret, P.; Blanchard, N. *Chem. Sci.* **2015**, 6, 5366.

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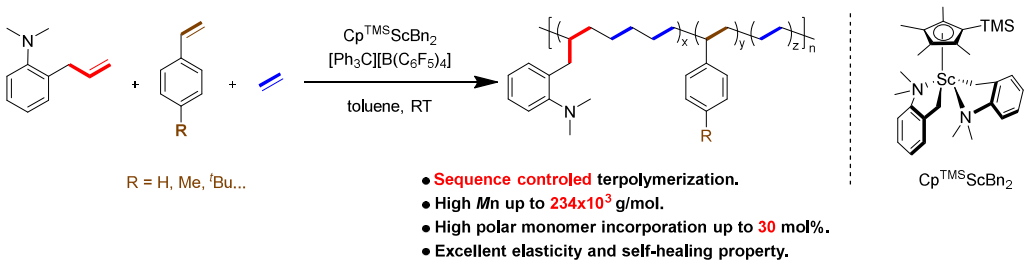
Synthesis of Self-Healing Elastomers by Scandium-Catalyzed Terpolymerization of Ethylene, Styrene and Dimethylaminophenyl-Substituted Propylene

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science;* [2]*School of Materials and Chemical Technology, Tokyo Institute of Technology*.) ○Haoran Zhang,[1,2] Xia Wu,[1] Lin Huang,[1] Masayoshi Nishiura,[1] Tetsuro Murahashi,[2] Zhaomin Hou[1]

Keywords: Scandium Catalysts; Terpolymerization; Self-Healing Property; Aminophenyl Propylene

The copolymerization of nonpolar and polar olefins in a controlled fashion is of great interest and importance but has remained much underexplored to date. We recently found that the copolymerization of ethylene (**E**) and anisyl-substituted propylenes (**AP**) by a sterically demanding half-sandwich scandium catalyst afforded unique multiblock copolymers composed of relatively long **E**-*alt*-**AP** sequences and short E-E sequences, which exhibited excellent elasticity and self-healing properties because of the microphase separation of nanodomains of the crystalline E-E segments from a flexible **E**-*alt*-**AP** matrix.[1,2] To explore the influences of heteroatom functional groups on the copolymerization and the mechanical and self-healing properties of the resulting copolymers, we examined the analogous copolymerization reactions by using dimethylaminophenylpropylene (**AMP**) instead of anisylpropylene. Herein we report that the scandium-catalyzed terpolymerization of ethylene (**E**), dimethylaminophenylpropylene (**AMP**) and styrene (**St**) gave multiblock copolymers composed of relatively long **AMP-E-E** sequences, short **E-E** blocks and short **St-St** blocks. The terpolymer showed excellent elasticity and remarkable self-healing property, as a result of microphase separation of nanodomains of the crystalline **E-E** segments and the hard amorphous **St-St** segments from a very flexible **AMP-E-E** matrix.



1) H. Wang, Y. Zhao, M. Nishiura, Y. Yang, G. Luo, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **2019**, *141*, 12624;
2) Y. Yang, H. Wang, L. Huang, M. Nishiura, Y. Higaki, Z. Hou, *Angew. Chem. Int. Ed.* **2021**, *60*, 26192.

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Polymers containing ester and ketone groups in chains: synthesis and their biodegradability

Haobo Yuan[1], Kohei Takahashi[1], Shinya Hayashi[1], Chifeng Li[2], Kazuya Yamaguchi[2], Miwa Suzuki[3], Kenichi Kasuya[3,4], Kyoko Nozaki[1]
([1]Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan [2] Graduate School of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan [3] Gunma University Center for Food Science and Wellness, 4-2 Aramakimachi, Maebashi, Gunma 371-0044, Japan [4] Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjincho, Kiryu, Gunma 376-0052, Japan)
[1]Tel: +03-5841-7264, E-mail: yuanhb@g.ecc.u-tokyo.ac.jp

One way to solve the increasingly serious white pollution problem is to use biodegradable plastics. Polyhydroxyalkanoates (PHAs) including poly-3-hydroxybutyrate (P3HB) are highly biodegradable materials. P3HB can be produced biologically from microorganisms or chemically by ring opening polymerization of lactones, however, these methods either is difficult to be scaled up or has high producing cost.

Our group previously synthesized *S*-isotactic propylene/carbon monoxide alternating copolymer (*S*-poly(P-*alt*-CO)) from the cheap propylene and CO gasses using a chiral palladium catalyst. Further oxidation by Baeyer-Villiger oxidation reaction (B-V oxidation) would give polymers containing the same unit with P3HB. However, in our previous work, by using *m*-chloroperbenzoic acid (*m*CPBA) as an oxidizing agent (Fig. 1 (a))[1] the obtained polymers contained only up to 18 mol% of ester groups.

In this work, a suitable reaction condition was found for the synthesis of polymers containing ester and ketone groups in chains from *R*-poly(P-*alt*-CO) [2] by the B-V oxidation with the cheap H_2O_2 (30 wt.% in water) as an oxidizing agent in HFIP under 0 °C (Fig. 1 (b)). Especially when $AlCl_3$ was used as an additive[3], polymers containing ester units more than 30 mol% (^{1}H NMR) were obtained in 1 hour. Two types of ester groups were detected in those polymers by ^{1}H NMR, the formation of which was caused by the two insertion sites of an oxygen atom, and over 80% of the ester groups in the polymers had the same structure as those in the P3HB. Only a very small amount of six-member-ring peroxide groups,[4] which is a notorious side product in B-V oxidation of aliphatic ketone was formed, based on the TG/DTA and ^{13}C NMR analyses. At last, the biodegradability of the polymers was examined by the biochemical oxygen demand test (BOD test) and moderate biodegradability has been detected.

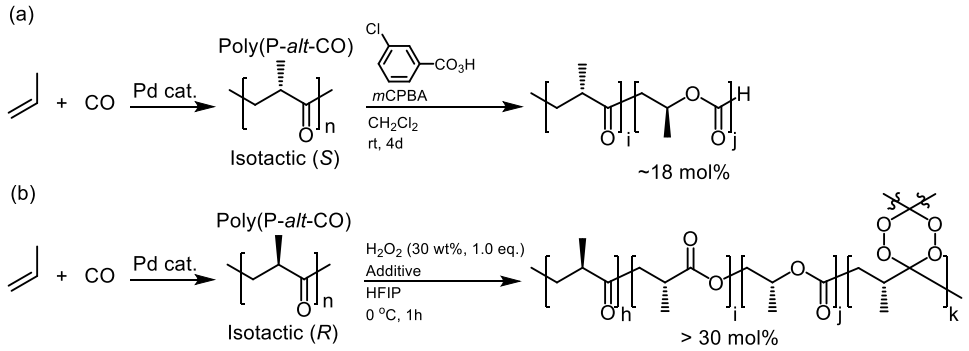

Fig. 1 Synthesis of polymers containing ester groups in chains, (a) previous work; (b) this work.

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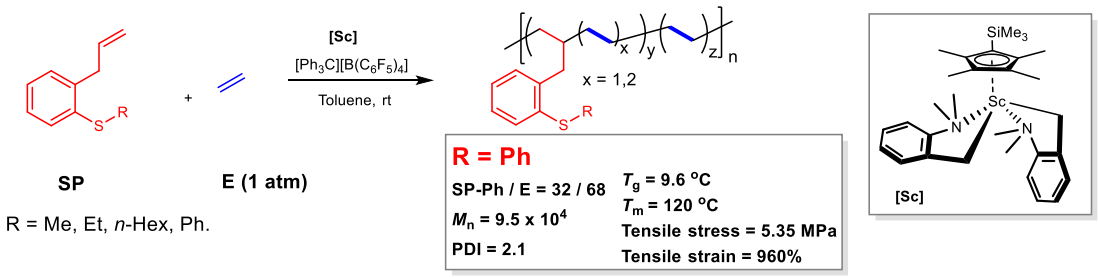
Synthesis of Self-Healing Elastomers by Scandium-Catalyzed Copolymerization of Ethylene with Thioether-Substituted Propylenes

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science;* [2]*Saitama University*) ○Mingjun Chi,[1,2] Hao Wang,[1] Lin Huang,[1] Haoran Zhang,[1] Xiaobin Lin,[1] Masayoshi Nishiura,[1] Zhaomin Hou[1,2]

Keywords: self-healing polymer; copolymerization; polar propylene; scandium catalyst

The copolymerization of nonpolar and polar olefins in a controlled fashion is of great interest and importance. We recently reported the sequence-controlled copolymerization of ethylene (**E**) and anisyl-substituted propylenes (**AP**) by a half-sandwich scandium catalyst, which afforded unique multiblock copolymers composed of relatively long **E**-*alt*-**AP** sequences and short **E-E** sequences.[1,2] Such microstructure-regulated polymers exhibited excellent elasticity and self-healing properties because of the microphase separation of nanodomains of the crystalline **E-E** segments from a flexible **E**-*alt*-**AP** matrix. To further investigate the influences of heteroatom functional groups on the copolymerization and the mechanical and self-healing properties of the resulting copolymers, we then examined the analogous copolymerizations by using various heteroatom-functionalized propylenes.

Herein we report the scandium-catalyzed copolymerization of ethylene (**E**) with thioether-substituted propylenes (**SP**) having different substituents (Me, Et, *n*-Hex, Ph) at the sulfur atom. The copolymerization afforded unique multi-block copolymers with relatively long alternating **E**-*alt*-**SP** and **E-E-SP** sequences and short **E−E** blocks. The copolymers with phenylthio substituent (**SP-Ph**) exhibited excellent elasticity and remarkable self-healing property, because of the microphase separation of nanodomains of the crystalline **E-E** segments from very flexible **E**-*alt*-**SP-Ph** and **E-E-SP-Ph** matrices.



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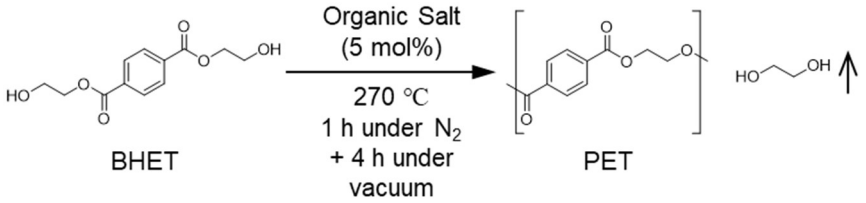
Designing Thermally Stable Organocatalysts for Poly(ethylene terephthalate) Synthesis: Toward a One-Pot, Closed-Loop Chemical Recycling System for PET

([1]*Chemicals Research Laboratories, Toray Industries, Inc.*, [2] *School of Chemistry, University of Birmingham*) ○Shu Kaiho,[1,2] Ali Al Rida Hmayed,[2] Kayla R. Delle Chiaie,[2] Joshua C. Worch,[2] Andrew P. Dove[2]

Keywords: Organocatalysts; Organic salts; Polymer synthesis; Chemical recycling; Polyesters

Organocatalysis provides robust methodology to provide 'greener' routes to polymer synthesis. However, the application towards the synthesis of aromatic polymers *via* step-growth polymerization is an area that justifies more investigation, as a consequence of the poor thermal stability of many organic catalysts and the high reaction temperatures commonly required.

In this study, thermally stable organic salts consisting of an organic base and an organic acid were explored to understand key elements required for the bulk synthesis of polyethylene terephthalate (PET) at 270 °C.[1] The ΔpK_a values of the salts played an important role in the thermal stability such that the salts with higher ΔpK_a values showed higher stability because of the strong acid-base interactions. The 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) salts with high ΔpK_a values ($\geq$ 16.9) showed the best catalytic activity among the investigated salts both in terms of low amounts of side reaction and discoloration. The thermal and chemical stability of the salts also affected the polymer properties. Dimerization side reactions that lead to defects in the polymer backbone were found to occur more readily in salts containing strong acids as components, particularly as the ΔpK_a between the acid-base components decreased. The discoloration of the PET sample was also correlated to the thermal stability of the organic salt catalyst, with a lower stability generally leading to enhanced discoloration likely due to decomposition of base components. Polymerization-depolymerization cycles were also investigated with the TBD:*p*-toluenesulfonic acid (TSA) salt and the feasibility of simple, closed-loop recycling of PET with the system was established.



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Self-assembled Structure of Amphiphilic Polythiophenes with Asymmetric Electronic Structures and its Photovoltaic Properties

([1]*Graduate School of Science, Tohoku University*, [2]*RIKEN CEMS,* [3]*Tohoku University AIMR*) ○Kohsuke Kawabata,[1,2] Kazuo Takimiya,[1,2,3]

Keywords: polythiophene; amphiphilic; block copolymer; photoelectric conversion

Creating an energy gradient or cascade structure at the donor/acceptor interface is important for efficient photocurrent generation in organic photovoltaic devices.[1,2] For this purpose, the self-assembly of all-conjugated block copolymers is one of the intriguing approaches.[3] In this study, we synthesized an amphiphilic polythiophene-based diblock-copolymer consisting of a hydrophobic hexylthiophene block and a hydrophilic oligoether-substituted fluorinated thiophene block with a 10:1 ratio (**BP12** in Fig. 1). We also investigated its self-assembly, solid-state properties, and electronic structures in comparison with the homopolymers **P1** and **P2** and a random copolymer **RP12**.

A drop of a solution of **BP12** smoothly spread on the water surface and afforded a thin film after evaporation of the solvent. In contrast, such spreading behavior was not observed for **RP12**, suggesting that the diblock structure is essential for the amphiphilicity of **BP12**. Contact angle measurements suggest that the thin film formed a hydrophobic surface on one side and a hydrophilic surface on the other due to amphiphilic self-assembly at the air/water interface. XPS analysis revealed that the hydrophilic side has a higher fluorine density and thus has a higher ionization potential by 0.2 eV than the hydrophobic side. Due to the asymmetric electronic structure of the thin film, planar heterojunction devices based on the film and $PC_{61}BM$ showed significantly different photovoltaic characteristics depending on the direction of the film. These results highlight the applicability of all-conjugated block copolymers for engineering donor-acceptor interfaces.

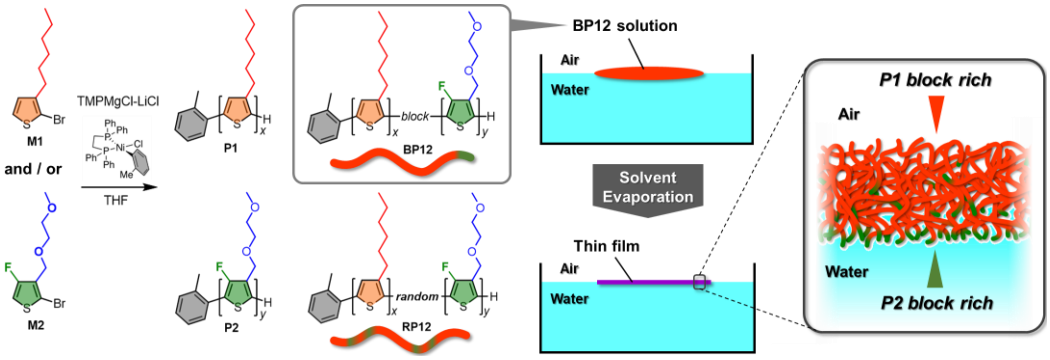

Fig. 1 Synthesis of homopolymers and block and random copolymers and schematic illustration of thin-film fabrication by the on-water-spreading method.

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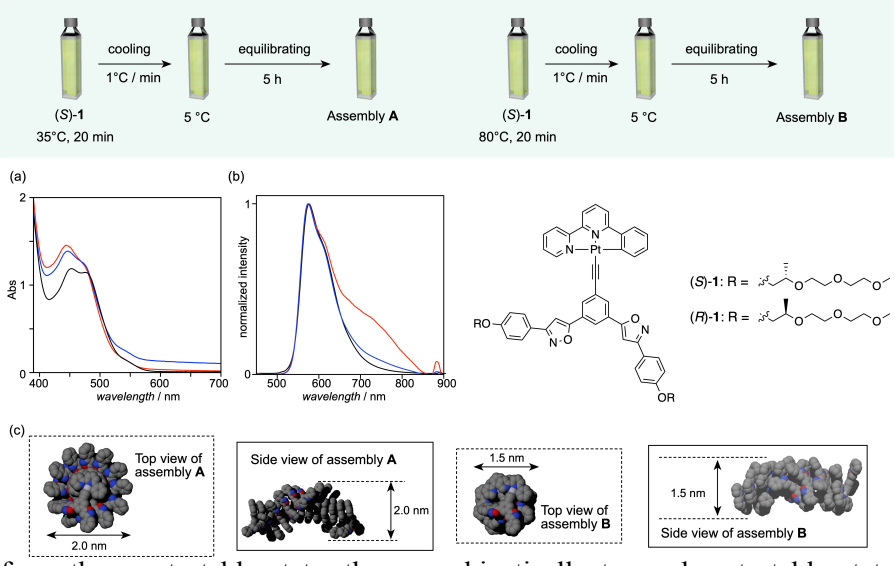
Pathway complexity in the self-assembly process of platinum complexes possessing TEG chains

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*, [2]*WPI-Knotted Chiral Meta Matter (SKCM[2]), Hiroshima University*)
○Takehiro Hirao,[1] Masaya Yoshida,[1] Takeharu Haino[1,2]



Aside from the most stable state, there are kinetically trapped metastable states in the supramolecular polymerization process, which is coined to be pathway complexity. Particular supramolecular polymers, which are commonly supramolecular polymers assembled in cooperative fashion, can be detected the metastable states as well as the most stable state. The pathway is determined by the preparation conditions, such as solvent, temperature, and concentration. Thus, two or more individually organized supramolecular assemblies can be prepared from one type of monomer molecules by varying the preparation conditions, which leads to information-rich functional materials. We have demonstrated that neutral platinum complexes with chiral TEG chains self-assembled to form helically stacked constructs in a cooperative fashion. We thus sought to gain the detailed insight into the self-assembly behavior of the platinum complexes (*S*)- and (*R*)-**1**.[1]

Supramolecular assemblies of (*S*)-**1** were prepared under two different conditions (Fig. 1 top). Both of the specimens exhibited blue-shifted peak in the absorption spectra, indicating assembled (*S*)-**1** was formed in the solutions (Fig. 1a), where we defined the two assemblies as assembly **A** and assembly **B**, respectively. Clear MMLCT band was seen in the emission spectra of assembly **A** whereas relatively weak MMLCT band was observed in the solution of assembly **B** (Fig. 1b). The discernible difference between the emission spectra indicates that assembly **A** was formed primarily by Pt–Pt interactions, while assembly **B** was formed by π–π and dipole–dipole inter-actions (Fig. 1c).

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

[B444-3pm] 19. Colloid and Interface Chemistry

Chair: Taisuke Banno, Yusuke Yonamine

Fri. Mar 24, 2023 1:30 PM - 3:40 PM B444 (444, Bldg. 4 [4F])

[B444-3pm-01] Challenges and recent progresses in experimental quantification of materials optical properties

○Dongmao Zhang[1] (1. Mississippi State University)

1:30 PM - 1:50 PM

[B444-3pm-02] Glycolipid-Type Amphiphiles with An Anilinochloromaleimide-Based Luminogen Exhibiting Aggregation-Induced Emission

Naoki Tsutsumi[1], Akitaka Ito[2], Yosuke Niko[1], Yui Bando[1], Kiyonori Takahashi[3], Masato Ikeda[4], Takayoshi Nakamura[3], Masayuki Izumi[1], ○Rika Ochi[1] (1. Kochi Univ., 2. Kochi Univ. of Tech., 3. Hokkaido Univ., 4. Gifu Univ.)

1:50 PM - 2:10 PM

[B444-3pm-03] Aggregation behavior and thickening ability of nonionic low molecular amphiphiles having CO_2-philic trimethylsilyl and CO_2-phobic hydrocarbon groups in supercritical CO_2

○Kosuke Sato[1], Atsushi Yshizawa[1], Shirin Alexander[2], Julian Eastoe[3], Masanobu Sagisaka[1] (1. Graduate School of Science and Technology, Hirosaki University, 2. Energy Safety Research Institute (ESRI), Swansea University, 3. School of Chemistry, University of Bristol)

2:10 PM - 2:30 PM

[B444-3pm-05] Formation of organic-inorganic hybrid cubic phase by the self-assembly of a synthetic lipid with alkoxysilyl groups.

○Miki Kariya[1], Kenichiro Omoto[1], Gwénaël Rapenne[1], Kazuma Yasuhara[1] (1. Nara Institute of Science and Technology)

3:00 PM - 3:20 PM

[B444-3pm-06] Clarification of the relationship between the lipid membrane properties and membrane deformation

○Yukihiro Okamoto[1,2], Zach Nicolella[1], Yoichiro Hasunuma[1], Nobuyuki Yoshioka[1], Nozomi Watanabe[1], Hiroshi Umakoshi[1] (1. Graduated School of Engineering Science, Osaka University, 2. Graduated School of Engineering Science, the Multidisciplinary Research Laboratory System at Osaka University)

3:20 PM - 3:40 PM

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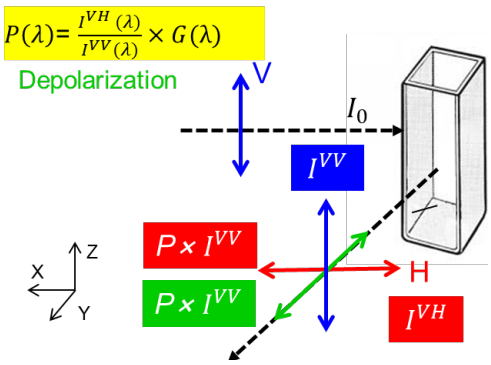
Challenges and recent progresses in experimental quantification of materials optical properties

([1]*Department of Chemistry, Mississippi State University*) ○Dongmao Zhang,[1]

Keywords: Scattering; Absorption; Emission; Depolarization; Spectroscopy

Optical spectroscopic methods that exploit light/matter interactions including absorption, scattering, and fluorescence emission have remained the most applied tools for studying the structures and properties of macromolecular, supramolecular, and nanoscale (MSN) materials. However, existing measurement techniques are inadequate to resolve the complex interplays among the materials light absorption, scattering, and fluorescence emission that can concurrently occurs in many MSN samples. As examples, UV-vis measures only the intensity attenuation of light passing through the samples but offers no insights to the origins of the signal attenuation and the photons reaching the detector. Current light scattering techniques for fluorescence MSN materials suffers from interference by both light absorption and on-resonance-fluorescence (ORF) that is inevitable in the wavelength region where the material fluorescence excitation and emission spectral overlooks. Indeed, there are numerous problematic data interpretations and analyses in literatures, including these published in leading chemical science journals. One key limitation in

Introduced in this talk several new optical spectroscopic methods we have recently developed for studying materials light absorption, scattering, and emission properties. Special emphases will be given to theory and a series of representative applications of the linearly polarized and the integrating-sphere-assisted resonance synchronous (LPRS and ISARS, respectively) spectroscopic methods.[1-4] The prospects of these LPRS and ISARS techniques for agricultural, environmental, biological, and materials research will also be discussed.



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凝集誘起発光特性を示すアニリノクロロマレイミド型蛍光団を有する糖脂質型両親媒性分子

（高知大院総合 [1]・高知工大院工 [2]・北大電子研 [3]・岐阜大工 [4]・岐阜大 iGCORE[5]）
堤 尚輝 [1]・伊藤 亮孝 [2]・仁子 陽輔 [1]・板東 佑依 [1]・高橋 仁徳 [3]・池田 将 [4,5]・中村 貴義 [3]・和泉 雅之 [1]・〇越智 里香 [1]

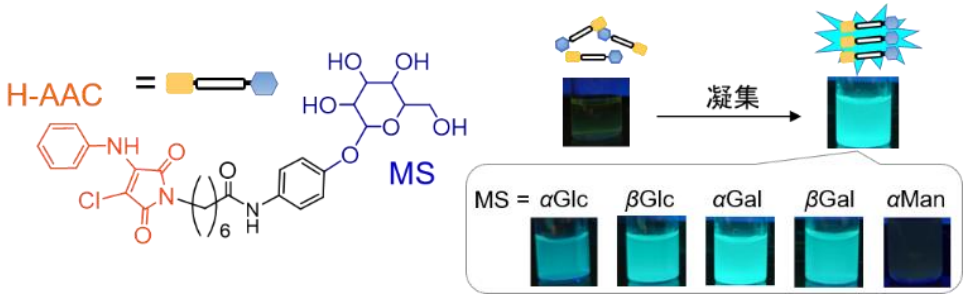
Glycolipid-Type Amphiphiles with An Anilinochloromaleimide-Based Luminogen Exhibiting Aggregation-Induced Emission

([1]*Graduate School of Integrated Arts and Sciences, Kochi University,* [2]*Graduate School of Engineering, Kochi University of Technology,* [3]*Research Institute for Electronic Science, Hokkaido University,* [4]*Faculty of Technology, Gifu University,* [5]*iGCORE, Gifu University*) Naoki Tsutsumi,[1] Akitaka Ito,[2] Yosuke Niko,[1] Yui Bando,[1] Kiyonori Takahashi,[3] Masato Ikeda,[4,5] Takayoshi Nakamura,[3] Masayuki Izumi,[1] 〇Rika Ochi[1]

Aggregation-Induced Emission (AIE) is a photophysical phenomenon found in luminogens that are non-fluorescence in dispersion state but are highly emissive in aggregate or solid state[1)]. We developed glycolipid-type amphiphiles **H-AAC-C6-Ph-MS** (MS = *α* or *β*-D-glucose (Glc), *α* or *β*-D-galactose (Gal), or *α*-D-mannose (Man)) with a luminogen (H-AAC), exhibiting AIE characteristics[2)]. Interestingly, the AIE properties of the amphiphiles rely on the epimerism of the MS moiety. The results strongly suggest that the design of molecular packing is important to control the AIE features.

Keywords : Supramolecule; Aggregation-Induced Emission; Glycolipid; Iodine; Amphiphile

凝集誘起発光（Aggregation-Induced Emission; AIE）とは、分散状態では非蛍光性であるのに対して凝集状態となることで蛍光性となる光物理現象である [1)]。本研究では、当研究室で見出した AIE 特性を示す蛍光色素骨格 H-AAC を導入した糖脂質型両親媒性分子 **H-AAC-C6-Ph-MS**（MS = *α* or *β*-D-glucose (Glc), *α* or *β*-D-galactose (Gal), or *α*-D-mannose (Man)）を合成し、糖残基の立体異性が発光特性に与える影響を評価した [2)]。各分子について物性評価をおこなったところ、糖残基の立体異性に依存して凝集状態における発光特性が異なることが明らかとなった（図）。この結果は、糖残基の立体異性が分子集合状態ならびに発光特性に影響を与えることを示唆するものである。



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Aggregation behavior and thickening ability of nonionic low molecular amphiphiles having CO_2-philic trimethylsilyl and CO_2-phobic hydrocarbon groups in supercritical CO_2

○Kosuke Sato[1], Atsushi Yshizawa[1], Shirin Alexander[2], Julian Eastoe[3], Masanobu Sagisaka[1] (*1. Graduate School of Science and Technology, Hirosaki University, 2. Energy Safety Research Institute (ESRI), Swansea University, 3. School of Chemistry, University of Bristol*)

Enhanced oil recovery technology using CO_2 (CO_2-EOR) has been not efficient so far due to very low viscosity of CO_2 compared with crude oils. To overcome this issue, enhancement of CO_2 viscosity has been tried with fluorinated thickeners being expensive and environmental burdensome. Aiming to develop an efficient fluorine-free CO_2-thickener, this study synthesized polymers and amphiphiles having CO_2-philic trimethylsilyl (TMS) groups and examined their CO_2-thickening ability by the EMS viscometer and formation of shape-anisotropic aggregates by SANS technique. These results suggested amphiphiles having two TMS groups to form ellipsoidal aggregates at various temperatures and 300 bar condition(Table 1).

Keywords : Supercritical CO2, Molecule Assembly, Nonionic Amphiphile, Thickener

CO_2 を用いた原油増進回収法（CO_2-EOR）は、CO_2 の粘度が原油に比べて、非常に低いため、効率が悪い。この問題の解決のため、高価で環境毒性の高い、フッ素系の増粘剤による CO_2 の増粘が試みられてきた。本研究では、フッ素フリーの効率的な CO_2 増粘剤の開発を目指し、親 CO_2 性トリメチルシリル基（TMS）を有する両親媒性物質とポリマーを合成し、EMS 型粘度計により CO_2 の増粘効果と SANS 測定により形状異方性分子集合体の形成について検討した。解析の結果、TMS を 2 つ持つ両親媒性物質が、300bar 条件の様々な温度で楕円体状の分子集合体を形成することが示された（Table 1）。

Table 1 Shape parameters* obtained by SANS data and fitting curves for the 50 mM TMS2AH8/CO_2 mixture at various temperature and pressure conditions. Specific viscosity was estimated from the shape parameters.

Temp. / °C	Press. / bar	$R_{f\text{-}sph}$ / Å	$R_{f\text{-}eq}$ / Å	$R_{f\text{-}pol}$ / Å	Aspect Ratio	Specific viscosity
55	300		18.20	163.33	9.0	1.30
75	300		17.34	170.42	9.8	1.30
75	200	18.5				

* $R_{f\text{-}sph}$ is radius of spherical aggregates, $R_{f\text{-}eq}$ and $R_{f\text{-}pol}$ is equatorial and polar radius of ellipsoidal aggregates, respectively.

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アルコキシシリル基を有する脂質の自己組織化による有機-無機ハイブリッド脂質キュービック相の形成

(奈良先端科学技術大学院大学 [1]・トゥールーズ大学 [2]) ○刈谷 未来 [1]・尾本 賢一郎 [1]・Gwénaël Rapenne[1,2]・安原 主馬 [1]

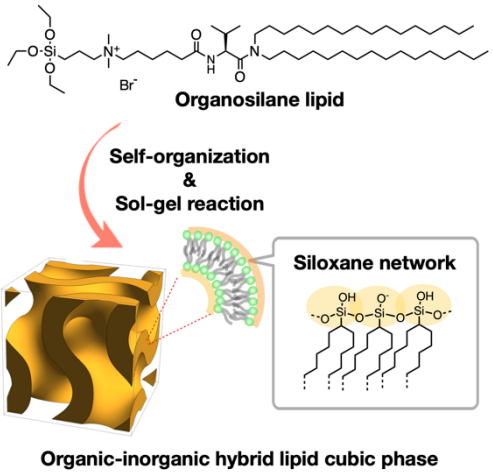
Formation of organic-inorganic hybrid cubic phase by the self-assembly of a synthetic lipid with alkoxysilyl groups

([1]*Nara Institute of Science and Technology,* [2]*University of Toulouse*)
○Miki Kariya,[1] Kenichiro Omoto,[1] Gwénaël Rapenne,[1,2] Kazuma Yasuhara[1]

Lipid cubic phases, non-lamellar lipid assemblies with a regularly arranged structure of lipid bilayers and water channels, are known to play important roles in biological systems. The use of synthetic lipids as the building block of lipid cubic phases will contribute to clarifying the principle of molecular design for the modulation of their structures and properties. In this study, we have investigated the formation of an organic-inorganic hybrid lipid cubic phase with lipid bilayers encompassing siloxane networks through the sol-gel reaction of a synthetic lipid with an organosilane moiety on its headgroup. [1] Evaluation of the lipid/water mixture using small-angle X-ray scattering and polarized optical microscopy revealed that a lipid cubic phase with a double gyroid structure was formed in a time-evolving manner by spontaneous oligomerization of lipid molecules through sol-gel reaction of alkoxysilyl groups. In this presentation, we will discuss the mechanism of the lipid cubic phase formation based on the modulation of the spontaneous curvature of the lipid membrane induced by the sol-gel reaction.

Keywords: Lipid bilayer; Lipid cubic phase; Synthetic lipid; Sol-gel reaction; Organic-inorganic hybrid

脂質キュービック相は脂質二分子膜と水チャネルが秩序的に入り組んだ構造を持つ非ラメラ状の脂質集合体の一つである。合成脂質を用いて脂質キュービック相を形成することで、人工的な構造・物性の変調および機能化が可能になる。本研究ではアルコキシシリル基を親水性頭部に有する有機ケイ素脂質を用いて、ゾル–ゲル反応により縮合させることで、シロキサンネットワークにより被覆された脂質二分子膜を有する有機-無機ハイブリッド脂質キュービック相を構築した。[1]脂質/水の混合物において、アルコキシシリル基の加水分解と重縮合による脂質分子の自発的なオリゴマー化が進行することで、ダブルジャイロイド構造を持つ脂質キュービック相が時間発展的に生成することが小角 X 線散および偏光顕微鏡観察から明らかになった。本発表では、この脂質キュービック相の形成メカニズムについて、ゾル–ゲル反応により誘起される脂質膜の自発曲率の変化に着目して議論する。



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脂質小胞体の膜変形と膜特性の相関解析

（阪大院基礎工[1]・阪大院基礎工未来ラボ[2]）○岡本 行広[1,2]・Zach Nicolella[1]・蓮沼 陽一郎[1]・吉岡 信幸[1]・渡邊 望美[1] ・馬越 大[1]

Clarification of the relationship between the lipid membrane properties and membrane deformation

([1]*Graduated School of Engineering Science, Osaka University,* [2]*Graduated School of Engineering Science, the Multidisciplinary Research Laboratory System at Osaka University*) ○Yukihiro Okamoto[1,2], Zach Nicolella[1], Yoichiro Hasunuma[1], Nobuyuki Yoshioka[1], Nozomi Watanabe[1], Hiroshi Umakosh[1]

Cell membrane deformation is significant phenomena in the cell life events such as cell migration, uptake of nutrients, infection of viruses *etc*. It has been reported that this deformation is caused by various membrane proteins and cytoskeletal proteins. In addition, the role of lipid membrane in the deformation has been also studied based on the physical constant such as elasticity. On the other hand, there is a few studies about the relationship between membrane properties such as hydrophilicity and fluidity, and lipid molecules behaviors. Thus, this paper studied the deformation of the giant unilamella vesicles (GUVs) by the thermal and electric stimulation. The thermal stimuli caused the budding and the formation of pores and these phenomena was related to the hydrophilicity and size of GUVs. In addition, the electric stimuli induced the change of the phase state, but not budding and pores. Now we are attempting to deduce the effect of hydration and fluidity on the deformation.

Keywords : Giant unilamella vesicle; deformation; thermal stimulation; AC electric field

細胞移動，物質取り込み，ウィルス感染を始めとする各種の生命現象において細胞膜の変形が観測される．この変形には，様々な膜タンパク質や細胞骨格タンパク質の関与が報告されている．一方で，脂質分子/脂質膜自体が膜変形に果たす役割に関しては，温度・電場・磁場といった外部刺激を印加し，機械的および物理的な側面から研究した例が多い．このため，膜変形と水和度などの膜特性，ならびに脂質分子自体の挙動の相関関係には未知な点が多い．

そこで，本研究では，熱ならびに電場により膜変形を誘起し，その結果，生じる現象と水和度を始めとする膜特性との関連性を明らかとすることを目的とした．細胞サイズの giant unilamella vesicle (GUV)を電気的作製法により調製した．この GUV に対して，室温付近から 50℃付近で昇温・冷却を行った結果，小さな小胞体の形成，ポアの形成が確認された．この挙動に関して，GUV 自体のサイズ依存性はもちろん，膜の水和度が大きく関与する結果となった．一方，電場印加に関して，電場印加後，直ちに形状が楕円状に変化した．この際，測定条件下では小胞体の形成やポアの形成は確認されなかったが，相分離系の GUV に対しては相状態の変化が観測された．この様に，脂質膜の特性と変形および変形から生じる膜構造の変化がお互いに影響を及ぼすことを明らかとした．

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

[K206-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Kazu Okumura, Tsukasa Torimoto

Fri. Mar 24, 2023 1:30 PM - 3:40 PM K206 (K206, Lecture Hall Bldg. [2F])

[K206-3pm-01] Evaluation of Photostability and Photodegradation Reaction in Lanthanide Complex

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

1:30 PM - 1:50 PM

[K206-3pm-02] Mechano-Bactericidal Effect in Water Synthesis and Functional Evaluation of TiO_2 Nanopillars

○Tomoya Shirasaka[1,2], Kaoru Igarashi[1], Yukari Miyazaki[2], Nobuaki Negishi[2] (1. ChibaTech., 2. AIST)

1:50 PM - 2:10 PM

[K206-3pm-03] In Operando XAFS on Local Structure and Electronic State of Tungsten Oxide Nanoparticles with Different Crystal Structure under Electrochromism

○Mari Takahashi[1], Yuki Kitazaki[1], Masafumi Harada[2], Shinya Maenosono[1] (1. Japan Advanced Institute of Science and Technology, 2. Nara Women's University)

2:10 PM - 2:30 PM

[K206-3pm-04] *ortho*-Substituent Structure Effects of Aryldiazonium Salts on Defect Photoluminescence Generation in Locally Functionalized Single-walled Carbon Nanotubes

○Tomohiro Shiraki[1,2], Sadahito Naka[1], Boda Yu[1], Tsuyohiko Fujigaya[1,2,3] (1. Grad. School of Eng., Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)

2:40 PM - 3:00 PM

[K206-3pm-05] Photoinduced electron doping of single-walled carbon nanotubes

○Naoki Tanaka[1,2], Taiki Ishii[1], Tsuyohiko Fujigaya[1,2,3] (1. Department of Applied Chemistry, Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. CMS, Kyushu Univ.)

3:00 PM - 3:20 PM

[K206-3pm-06] Flash Lamp Annealing Synthesis of Platinum Group High-Entropy Alloy Nanoparticles

○Yuji Shinkai[1], Tetsu Yonezawa[1] (1. Hokkaido University)

3:20 PM - 3:40 PM

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希土類錯体における光耐久性と光分解反応の評価

（立命館大[1]・JST さきがけ[2]）岡安 祥徳[1]・小林 洋一[1,2]
Evaluation of Photostability and Photodegradation Reaction in Lanthanide Complex
([1]*Ritsumeikan University*, [2]*PRESTO JST*)〇Yoshinori Okayasu,[1] Yoichi Kobayashi[1,2]

The molecular guidelines of luminescent materials have already been established. Among such luminescent materials, lanthanide complexes are known to exhibit high color purity and long emission lifetime. On the other hand, analysis of the durability and decomposition reactions of these luminescent materials requires detailed analysis of the excited states. However, since it is difficult to observe them with common spectroscopic instruments, molecular design of high durability and detailed understanding of the mechanism are not sufficient.

In this study, a mononuclear complex ($Eu(Ph\text{-}DK)_3$) and a dinuclear lanthanide complex ($Eu_2(BTP)_3$) have been synthesized. After 60 min of light irradiation, the absorption band derived from the ligand of $Eu(Ph\text{-}DK)_3$ decreased, whereas the absorbance change of $Eu_2(BTP)_3$ was small, indicating that it shows higher photodurability than $Eu(Ph\text{-}DK)_3$.

Keywords : lanthanide complex; β-diketonate ligand; photostability; photodegradation; Time-resolved spectroscopy

高い発光輝度を示す発光材料は、多様な分子ライブラリーによる合理的な設計指針がすでに構築されている。そうした発光性材料の中でも、希土類錯体は色純度の高い発光や、ミリ秒程度の発光寿命を示すことが知られている。一方で、これらの発光材料の耐久性や分解反応の解析は、ピコ秒やナノ秒程度で存在する励起状態を詳細に解析する必要がある。しかしながら、一般的な分光装置で観測することは困難であるために、高い光耐久性を有する分子設計や詳細なメカニズムの理解は十分ではない。

本研究では、高い光耐久性を示す分子設計を確立することを目的に、複核の希土類錯体($Eu_2(BTP)_3$)が単核錯体($Eu(Ph\text{-}DK)_3$)を合成し、光耐久性や光学特性を評価した。

それぞれの錯体に紫外光を照射し、光照射前後での吸収スペクトル変化をプロットすると、光照射 60 分後には、$Eu(Ph\text{-}DK)_3$ の配位子に由来する吸収帯は減少したのに対して、($Eu_2(BTP)_3$ は吸光度変化が小さく、$Eu(Ph\text{-}DK)_3$ よりも高い光耐久性を示すことが明らかになった。詳細は発表で述べる。

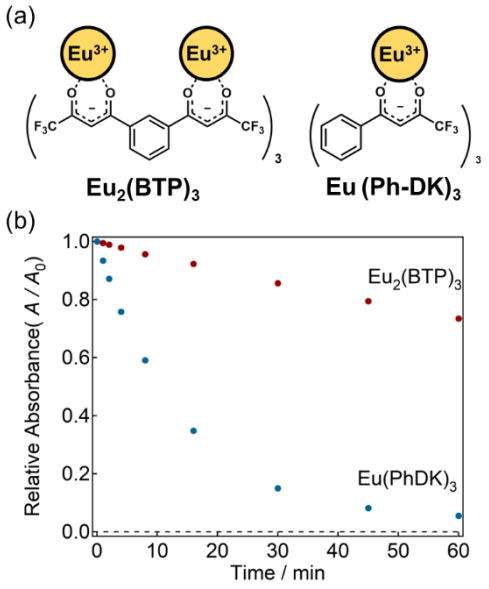

Fig. 1(a) Chemical structure of the Eu complexes. (b) Plots of relative absorbance vs time under light irradiation (365 nm, 460 mW/cm^2) of $Eu_2(BTP)_3$ (10 μM) and $Eu(Ph\text{-}DK)_3$ (24 μM) in acetonitrile.

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水中メカノ殺菌効果を発現する TiO_2 ナノピラーの合成と機能評価

（千葉工大院 [1]・産総研 [2]）○白坂 知也 [1,2]・五十嵐 香 [1]・宮崎 ゆかり [2]・根岸 信彰 [2]

Mechano-Bactericidal Effect in Water Synthesis and Functional Evaluation of TiO_2 Nanopillars

([1]*Graduate School of Engineering, Chiba Institute of Technology*, [2]*National Institute of Advanced Industrial Science and Technology*) ○Tomoya Shirasaka,[1,2] Kaoru Igarashi,[1] Yukari Miyazaki,[2] Nobuaki Negishi[2]

Lack access to safely water is a global problem. Titanium dioxide photocatalyst, which is inexpensive, safe, and easy to maintain, has been proposed for drinking water treatment as one way to deal with this problem. However, photocatalyst has the disadvantage that is inactivated under low-illuminance conditions such as rainy and night. Therefore, we tried to investigate the possibility of supplementing the disadvantages by combining photocatalyst with mechano-bactericidal effect[1)] in water, which has not yet been investigated. In this study, we controlled the shape of the TiO_2 nanoneedle (nanopillar) on photocatalyst substrate and investigated the effect of the difference of their shape to the bactericidal performance.

The various shapes of TiO_2 nanoneedles were generated onto TiO_2 substrates (PSB-01) by hydrothermal synthesis using $TiCl_4$ in the range of 0.2 M to 4.0 M. Upright needles with respect to the substrate were formed from 0.2 M to 2.0 M, and multi-directional needles with respect to the substrate were formed from 2.4 M to 4.0 M of $TiCl_4$ concentration. The sterilization efficiency of these needles was investigated, and higher sterilization efficiency was obtained regardless of needle shape than the PSB-01.

Keywords : Water Purification; Photocatalyst; Mechano-bactericidal effect; Nanostructure

安全な水へのアクセスができない問題は国際的な問題である。解決の方法の１つとして、安全・安価かつ易メンテナンスな酸化チタン（TiO_2）光触媒による水処理が提案されている。しかし、光触媒は低照度時の活性低下が問題である。そこで、我々は検討例の少ない水中におけるメカノ殺菌効果[1)]を光触媒に組み合わせることで、光触媒殺菌効果の低照度時における補完が可能か否か検討した。本研究では、TiO_2 基材表面にナノニードルを合成し、形状の差による殺菌性能の違いの有無を観察した。

ナノニードルは 0.2 M から 4.0 M の濃度範囲の $TiCl_4$ を用いて TiO_2 基材(PSB-01)上に水熱合成した。0.2 M から 2.0 M までは基材に対して直立、2.4 M から 4.0 M までは基材上でランダムな針が成長した。これらの殺菌効率を測定したところ、全ての針形状において PSB-01 よりも高い殺菌効果が得られた。

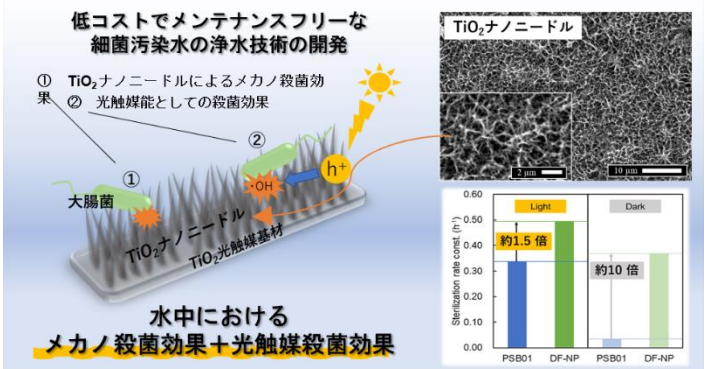

図 1 殺菌メカニズムの模式図と合成試料の SEM 像及び殺菌効率の比較

1) E. P. Ivanova, et al., *Small*, **2012**, *8*, 2489-2494.

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In Operando XAFS on Local Structure and Electronic State of Tungsten Oxide Nanoparticles with Different Crystal Structure under Electrochromism

([1]*School of Materials Science, JAIST*, [2]*Nara Women's University*) ○Mari Takahashi,[1] Yuki Kitazaki,[1] Masafumi Harada,[2] Shinya Maenosono[1]

Keywords: Tungsten oxide, Nanoparticles, Crystal structure, Electrochromism, XAFS

The electrochromism of tungsten oxide (WO_{3-x}) is known to depend on its crystal structure.[1] However, detailed information on the correlation between color, electronic and local structural change in WO_{3-x} with different crystal structures was missing. In this study, WO_{3-x} nanoparticles with different crystal structure (*i.e.* monoclinic $W_{18}O_{49}$ or hexagonal $(NH_4)_{0.75}W_3O_9$) were chemically synthesized (Fig. 1a and b) and used to make films (m-Film or h-Film) for the investigation and comparison of their electrochromic behaviour based on *in operando* X-ray absorption fine structure (XAFS). Based on color analysis, the h-Film was found to have a higher reversibility in color change than the m-Film. W L_3-edge X-ray absorption near edge structure (XANES) spectra were deconvoluted to obtain the peak positions of t_{2g} and e_g energy levels (Fig. 1c). The results showed periodic changes of the t_{2g} and e_g energy levels under repeated coloring/bleaching cycles, which was caused by the ligand field change upon Li^+ intercalation/deintercalation. An irreversible increase in the e_g level, decrease of the area intensity and increase of W-O bond distance in the first shell after repeated cycles were observed in the m-Film but not the h-Film, which suggested distortions were accumulated in the local structure of the m-Film resulting in color deterioration. In the case of the h-Film, the reason for the color deterioration was explained by the trapping of Li^+ in the optically inactive trigonal cavities. These results clearly indicate that different crystal structures have different color deterioration mechanisms.

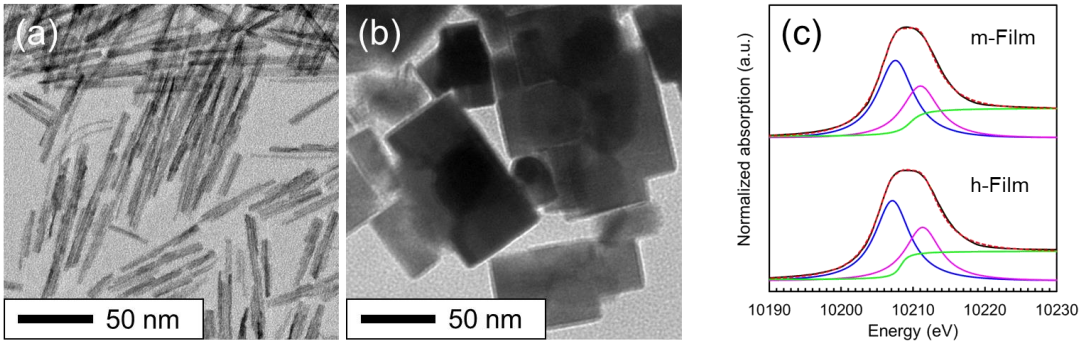

Fig. 1 TEM images of (a) $W_{18}O_{49}$ and (b) $(NH_4)_{0.75}W_3O_9$ nanoparticles. (c) W L_3-edge XANES spectra of m-Film and h-Film. Black and green lines are experimental data and background, respectively. Blue and pink lines represent t_{2g} and e_g transitions, respectively. Red dashed lines are sums of all components (background, t_{2g} and e_g transitions).

1) S. Adhikari, D. Sarkar, *J. Electrochem. Soc.* **2015**, *162*, H58.

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ortho-Substituent Structure Effects of Aryldiazonium Salts on Defect Photoluminescence Generation in Locally Functionalized Single-walled Carbon Nanotubes

([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], Sadahito Naka[1], Boda Yu[1], Tsuyohiko Fujigaya[1,2,3]
Keywords: Carbon Nanotubes; Near-infrared; Photoluminescence; Defects; Substituents

Single-walled carbon nanotubes (SWCNTs) with semiconducting features show near infrared (NIR) photoluminescence (PL), which is applicable to bioimaging and telecom technologies. Locally functionalized SWCNTs (lf-SWCNTs), which are synthesized by a slight amount of chemical modification to the tube walls, have been reported to show defect PL with red-shifted wavelengths and enhanced quantum yields (E_{11}* PL) compared to original PL (E_{11} PL) of pristine SWCNTs.[1-3] The chemical modification is used for sp^3 carbon defect introduction in the sp^2 carbon network of SWCNTs via covalent molecular attachment, forming defect sites with narrower band gaps and exciton trapping features. Aryldiazonium salts (ADs) with functional substituents have been used for the lf-SWCNT synthesis, by which defect PL wavelength modulation and NIR PL sensing system creation[4] have been performed.

Recently, we have reported that selective generation of more red-shifted defect PL (E_{11}^{*-} PL) for lf-SWCNTs synthesized by using *ortho*-substituted ADs (*o*ADs) with π-conjugated groups such as phenyl and acetylene moieties.[5] In this study, we change substituent structures in *o*ADs to examine the *ortho*-substituent effects on the defect PL property variation of lf-SWCNTs. As an example, *o*ADs with an iodine (I) group (*o*I-AD) was synthesized and reacted with SWCNTs (CoMoCAT, (6,5) chirality-rich) solubilized in D_2O containing a surfactant to synthesize lf-SWCNTs (lf-SWCNTs-*o*I). Figure 1 shows a PL spectrum of lf-SWCNTs-*o*I. PL peaks were observed at 983 and 1253 nm. The former PL signal was also observed for non-modified SWCNTs, and was assigned to E_{11} PL from the non-modified sites of lf-SWCNTs-*o*I. The latter one was newly observed after the chemical modification using *o*I-AD, and appeared in a longer wavelength region than typical E_{11}* PL (~1100 nm). Therefore, the I group was found to contribute to the E_{11}^{*-} PL generation for lf-SWCNTs, in which molecular interaction and strain effects of the substituent could be considered as an important factor based on obtained results using other halogen substituents.

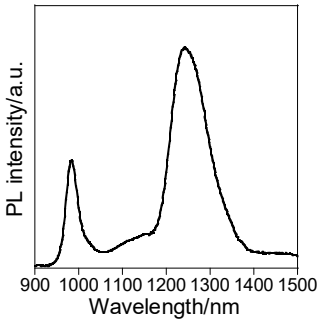

Figure 1. PL spectrum of lf-SWCNTs-*o*I. λ_{ex} = 570 nm.

1) T. Shiraki, *Chem. Lett.* **2021**, *50*, 397. 1) T. Shiraki et al., *Acc. Chem. Res.* **2020**, *53*, 1846. 3) Y. Wang et al., *Nat. Rev. Chem.* **2019**, *3*, 375. 4) T. Shiraki et al., *Nanoscale* **2022**, *14*, 13090. 5) T. Shiraki et al., *ACS Nano* **2022**, *in press*, DOI: 10.1021/acsnano.2c09897.

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光誘起ドーピングによる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]・石井 大貴 [2]・藤ヶ谷 剛彦 [1,2,3]

Photoinduced electron doping of single-walled carbon nanotubes

([1]*Department of Applied Chemistry, Kyushu University*, [2]*WPI-I2CNER, Kyushu University,* [3]*CMS, Kyushu University*)
○Naoki Tanaka,[1] Taiki Ishii,[1] Tsuyohiko Fujigaya,[1,2,3]

1,3-dimethyl-2-arylbenzimidazole (DMBI) derivatives act as good electron dopants for semiconductors and form DMBI cation ($DMBI^+$). However, in the presence of oxygen, inactive oxygen adducts (DMBI-Ox) are produced by the reaction of DMBI radicals with oxygen molecules, which decreases the doping efficiency[1]. Recently, we found that UV-irradiation of DMBI-Ox generates $DMBI^+$ and hydroxy ion that acts as electron dopant for single-walled carbon nanotubes (SWCNTs) (**Fig. 1a**). In this study, we evaluated the thermoelectric properties of photoinduced electron-doped SWCNT films and fabricated thermoelectric devices using p-n patterned SWCNT films (**Fig. 1b**). The open-circuit voltage and power output were 0.68 mV and 0.504 nW, respectively[2].

Keywords : Single-walled carbon nanotube; Thermoelectric generation; Photocyclization; Electron doping; Electron transfer

1,3-ジメチル-2-アリールベンズイミダゾール (DMBI) 誘導体は、C–H 結合開裂により発生する DMBI ラジカル ($DMBI^{\bullet}$) が有機半導体の電子ドーパントとして作用し、ドープ後は半導体の対カチオンとして $DMBI^+$を形成する。しかし酸素雰囲気下では、$DMBI^{\bullet}$と酸素との反応により酸素付加物 (DMBI-Ox) が生成し、ドーピング効率を低下させる[1]。最近我々は DMBI-Ox の新しい活用法として、DMBI-Ox の紫外線照射による分子内光閉環反応およびヒドロキシイオン発生に基づく単層カーボンナノチューブ (SWCNT) の光誘起電子ドーピングを達成した (**Fig. 1**)[2]。本研究では、本手法で得られた n 型 SWCNT の熱電特性および熱電発電デバイス性能を評価した。

DMBI-Ox 溶液に SWCNT 膜を 10 分間含浸した後、減圧乾燥を行った。得られた SWCNT 膜のゼーベック係数は正の値であったが、光照射後は負の値に変化したことから、光照射による電子ドーピングの進行を明らかにした。本手法により作製した pn パターニング SWCNT 膜を用いて熱電発電デバイスを作製したところ、温調ステージの温度差が 35 °C の時、0.68 mV の開放電圧と 0.504 nW の出力が得られた。

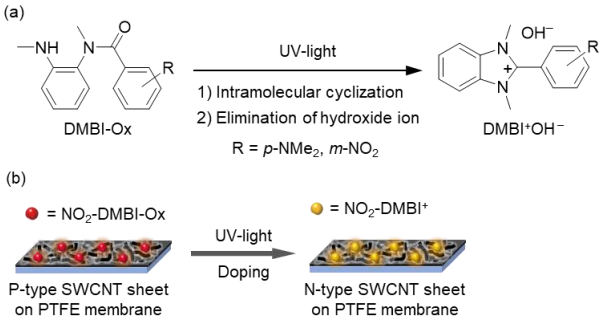

Fig. 1 (a) Intramolecular cyclization reaction of DMBI-Ox by UV-irradiation. (b) Photoinduced doping of SWCNT sheets using DMBI-Ox.

[1] O. Bardagot and R. Demadrille et al., *Appl. Phys. Lett.* **2021**, *118*, 203904.
[2] N. Tanaka, T. Ishii, I. Yamaguchi, A. Hamasuna, T. Fujigaya, *J. Mater. Chem. A* **2022**, *submitted*.

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白金族高エントロピー合金ナノ粒子のフラシュランプアニール合成

（北大院工 [1]）○新開 裕二 [1]・米澤 徹 [1]

Flash lamp annealing synthesis of platinum group high entropy alloy nanoparticles

([1]*Graduate School of Engineering, Hokkaido University*) ○Yuji Shinkai,[1] Tetsu Yonezawa[1]

Platinum group metals are known to be highly active in specific elementary reactions, and their alloy nanoparticles have a variety of adsorption sites on the particle surface. Thereby, they are attracting attention for their ability to create optimal catalysts for complex reactions involving multiple reactants and intermediates, and for multi-step reactions [1]. On the other hand, the flash lamp used in this study is capable of ultrarapid heating and cooling, which is expected to instantly reduce all metal ions and nonequilibrium aggregation of metal atoms to form nanoparticles. In this study, we propose a method for synthesizing solid solution structure Ru-Rh-Pd-Ir-Pt alloy nanoparticles in which the constituent metals are well solubilized at the atomic level by flash lamp annealing.

Figure.1 shows the results of STEM-EDS mapping of the synthesized Ru-Rh-Pd-Ir-Pt alloy nanoparticles. The distribution of each element can be confirmed without significant segregation, and it was found that they formed a solid solution with almost equal atomic weight. This indicates that Ru-Rh-Pd-Ir-Pt alloy nanoparticles were successfully synthesized.

Keywords：High-entropy alloy, Nanoparticle, Nonequilibrium, Agglomeration, Reduction

白金族金属は、それぞれ特異な素反応に対して高活性を示すことが知られており、その合金ナノ粒子は粒子表面に多彩な吸着サイトを有し、複数の反応物や中間体が関与する複雑な反応や、多段階の反応に最適な触媒を作り出すことができる点において注目を集めている。本研究ではフラッシュランプアニールによる急速加熱・急速冷却を利用した非平衡的合成により構成金属が原子レベルでよく固溶された Ru-Rh-Pd-Ir-Pt 高エントロピー合金ナノ粒子の合成法を提案する。

図 1 に合成した Ru-Rh-Pd-Ir-Pt 合金ナノ粒子の STEM-EDS マッピングの結果を示す。各元素が顕著な偏析なく分布している様子を確認でき、ほぼ等原子量で固溶体を形成していることから Ru-Rh-Pd-Ir-Pt 合金ナノ粒子の合成に成功したことが分かった。

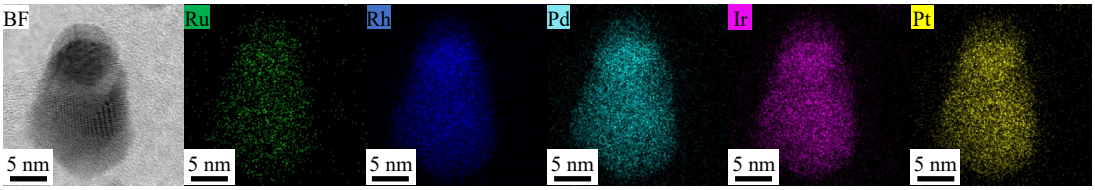

Fig.1 STEM-EDS elemental mapping of RuRhPdIrPt nanoparticles

[1] D. Wu, K. Kusada, T. Yamamoto, T. Toriyama, S. Matsumura, S. Kawaguchi, Y. Kubota, H. Kitagawa, *J. Am. Chem. Soc.*, 2020, **142(32)**, 13833–13838.

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

[K303-3pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Ryoichi Tatara, Takane Imaoka

Fri. Mar 24, 2023 1:30 PM - 3:40 PM K303 (K303, Lecture Hall Bldg. [3F])

[K303-3pm-01] Gas-fed liquid-covered cathode electrodes used for direct electrochemical reduction of dilute CO_2 in a flue gas

○Yasuhiko Takeda[1], Shintaro Mizuno[1], Ryuichi Iwata[1], Takeshi Morikawa[1], Naohiko Kato[1] （1. Toyota Central Research and Development Laboratories, Inc.）

1:30 PM - 1:50 PM

[K303-3pm-02] Composition dependence of sub-nanoparticle catalysts in electrocatalytic reactions

○Tadatoshi Iitsuka[1], Kana Shimizu, Takane Imaoka[1], Kimihisa Ymamoto[1] （1. Lab. Chem. Life Sci., Tokyo Tech.）

1:50 PM - 2:10 PM

[K303-3pm-03] Reduced Graphene Oxide Supported Transition Metal Oxide Electrocatalysts for Zinc-Air and Zinc-Air Flow Batteries

○Wei Jian Sim[1], Mai Thanh Nguyen[1], Tetsu Yonezawa[1] （1. Hokkaido University）

2:10 PM - 2:30 PM

[K303-3pm-04] Application of Sulfolane-based Concentrated Electrolytes to Potassium-ion Battery

○Ryoichi Tatara[1], Daisuke Igarashi[1], Tomooki Hosaka[1], Shinichi Komaba[1] （1. Tokyo University of Science）

2:40 PM - 3:00 PM

[K303-3pm-05] Li and Na organic batteries with porphyrinoid electrodes

○Ji-Young Shin[1], Jikwang Hwang[2] （1. Nagoya Univerity, 2. Kyoto University）

3:00 PM - 3:20 PM

[K303-3pm-06] Study of Cathodic Reaction for Lithium-O_2 Battery by Opelando XRD Measurements

○Makoto Aoki[1], Dilinigeer Dilixiati[1], Minako Ushijima[1], Suzumi Yamada[1], Toshihiro Kondo[1] （1. Ochanomizu university）

3:20 PM - 3:40 PM

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液膜被覆ガス供給カソード電極を用いた排ガス中希薄 CO_2 の直接電気化学還元

（豊田中研）○竹田 康彦・水野 真太郎・岩田 隆一・森川 健志・加藤 直彦

Gas-fed liquid-covered cathode electrodes used for direct electrochemical reduction of dilute CO_2 in a flue gas

(*Toyota Central R&D Labs., Inc.*) ○Yasuhiko Takeda, Shintaro Mizuno, Ryuichi Iwata, Takeshi Morikawa, Naohiko Kato

We are developing highly efficient large-sized artificial photosynthetic cells that reduce CO_2 to organic valuables. The newly designed 1 m^2-sized cell consisting of an electrochemical reactor and crystalline silicon solar cells converted CO_2 of 100% concentration to formate with a high conversion efficiency of 10.5%[1,2]. Thus, the next challenges are long-term durability[3] and direct conversion of CO_2 in a flue gas[4]. As for the latter, a low CO_2 concentration and a high O_2 concentration degrade the performance. Although a gas-diffusion electrode secures sufficient CO_2 supply even at a low concentration, O_2 affects fatally. By contrast, an electrode immersed in an electrolyte suffers from CO_2 depletion, whereas a low O_2 solubility mitigates the detriment. To exploit both advantages of these configurations, we developed a cathode electrode covered with a thin electrolyte layer, which is fed with a reaction gas (Fig. 1). In addition, monoethanolamine that is often used for CO_2 capture was added in the electrolyte for more CO_2 supply. Thus, we achieved Faradaic efficiencies of formate production as high as around 70% even under direct feeding of a simulated flue gas (15% CO_2, 4% O_2, N_2 81% (v/v)).
Keywords : Artificial photosynthesis; CO_2 reduction; flue gas; monoethanolamine

CO_2 を還元して有価物に変換する人工光合成セルの高効率化と大型化の両立に取り組んでいる。電気化学リアクターと結晶シリコン太陽電池を組み合わせた最新の 1 m^2 サイズのセルは、濃度 100%の CO_2 を 10.5%の高い効率でギ酸に変換した [1,2]。次の課題は、耐久性の向上と [3]、排ガス中の CO_2 の直接変換である [4]。後者については、低濃度の CO_2 と高濃度の O_2 が高効率化を妨げる。ガス拡散電極は低濃度であっても十分な CO_2 供給量を確保するものの、O_2 の悪影響が致命的となる。逆に、電解液に浸漬された電極は溶解度が低い O_2 の悪影響を受けにくいが、CO_2 の供給不足となる。これらの構成の両方の長所を組み合わせた、薄い電解液層にて覆われた触媒層に反応ガスが供給される構成を考案した（Fig. 1）[4]。CO_2 供給を更に促進するため、CO_2 回収に用いられるモノエタノールアミンを電解液に添加した。これらの結果、疑似排ガス（15% CO_2, 4% O_2, N_2 81% (v/v)）供給であっても、約 70%の高いギ酸生成ファラデー効率を実現した。

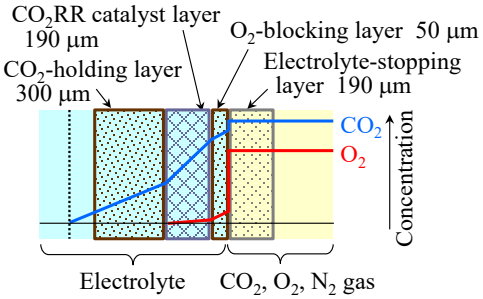

Fig. 1 Multilayered structure of gas-fed liquid-covered cathode electrode, and CO_2 and O_2 concentrations in and around the electrode.

1) N. Kato, et al., *Joule* **2021**, *5*, 687. 2) N. Kato, et al., *ACS Sustain. Chem. Eng.* **2021**, *9*, 16031.
3) M. Shiozawa, et al., *Electrocatalysis* **2022**, *13*, 30.
4) Y. Takeda, et al., submitted.

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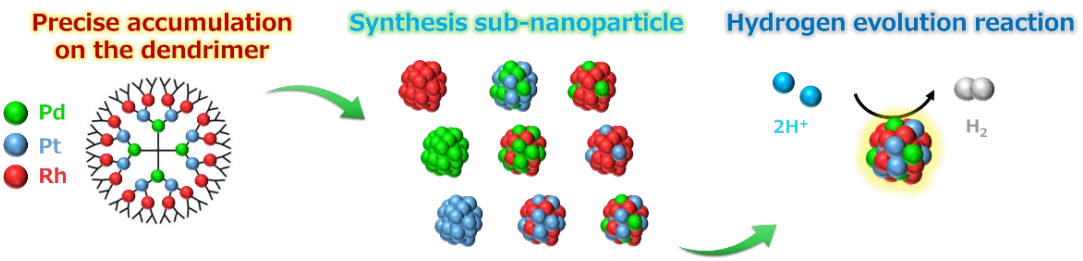
Coposition dependence of sub-nanoparticle catalysts in electrocatalytic reactions

(Lab. Chem. Life Sci., Tokyo Tech.) ○Tadatoshi Iitsuka, Kana Shimizu, Takane Imaoka, Kimihisa Yamamoto

Keywords: *cluster catalyst; hydrogen evolution reaction; alloy particle*

Crystalline bulk and nanoparticles with a grain size larger than 2 nm are crystalline, so their atoms do not mix uniformly and are phase-separated. However, sub-nanoparticles with a particle size of about 1 nm are non-crystalline, so the atoms mix uniformly, and they also exhibit atomic fluidity not seen in nanoparticles or bulk[1,2]. The catalytic activity of sub-nanoparticles can vary greatly by a single atom, and they can perform much better than bulk or nanoparticles[3]. However, synthesis of sub-nanoparticles with a precisely defined number of constituent atoms is extremely difficult, and the relationship between the unique catalytic properties of sub-nanoparticles and their composition and structure has been elucidated only piecemeal, necessitating a systematic evaluation. This study aims to synthesize metal sub-nanoparticles with a precisely defined number of atoms using phenylazomethine dendrimer (DPA-G4) as a template and to systematically evaluate their atomic composition dependence in electrochemical catalytic reactions such as hydrogen generation reactions.

DPA-G4 has a special potential gradient due to the conjugated structure of aromatic rings and imine, which results in different complexation constants for each generation. Therefore, metal salts accumulate in order from the inner layer. Taking advantage of this property, metal salt accumulation in DPA-G4 was carried out by adding 4, 8, and 16 equivalents of palladium, platinum, and rhodium metal salts, respectively, to DPA-G4. The metal salts accumulated on DPA-G4 were then reduced and loaded on a carbon carrier, Ketjen black, and HAADF-STEM observation showed palladium, platinum, and rhodium ternary alloy subnanoparticles with a particle size of about 1 nm, in which atoms were homogeneously intermixed. Hydrogen evolution reaction using the synthesized metal-alloy subnanoparticle catalysts revealed that the catalytic activity was enhanced by alloying in the case of platinum-based subnanoparticles.



1) T. Tsukamoto *et al*., *Nat. commun*, **2018**, *9*, 3873. 2) T. Imaoka *et al*., *Chem. Commun*, **2019**, *55*, 4573.

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Reduced Graphene Oxide Supported Transition Metal Oxide Electrocatalysts for Zinc-Air and Zinc-Air Flow Batteries

([1]*Hokkaido University*) ○Wei Jian Sim,[1] Mai Thanh Nguyen,[1] Tetsu Yonezawa[1]

Keywords: *zinc-air battery; electrocatalyst; graphene oxide; transition metal oxide; flow battery*

Due to the high abundance of zinc and non-flammable aqueous electrolyte, zinc-air batteries (ZABs) are an economical and safe grid-scale energy storage solution for renewable energy generation plants situated in remote locations. Efficiency of metal-air batteries are limited by the overpotentials of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), for which noble metals such as Pt and IrO_2 are benchmark electrocatalysts.[1] Transition metal oxides (TMOs) are being studied as possible substitutes for scarce and expensive noble metals.[2] In our recent work, bimetallic TMOs based on Fe/Co and Co/Ni are finely dispersed on reduced graphene oxide to achieve high catalyst activation for high current density operations of zinc-air batteries.

Bimetallic oxides (Fe/Co and Ni/Co) in various ratios were synthesized by dispersing their respective nitrate precursors and graphene oxide (GO) in water, drying the suspension, and calcining the residue at 350°C for 4 h. Upon heat treatment, GO partially loses oxygen functional groups to form electrically conductive rGO. The remaining oxygen functional groups on rGO were found to homogeneously disperse the metal oxides across the surface of the rGO particle which greatly activated the metal oxide for electrocatalytic reactions.

The FeCo-rGO and NiCo-rGO catalysts were loaded on nickel foam and assembled into the air cathodes of ZABs. Hybridization with rGO was found to be key in activating the catalysts for practical ZAB operations at high current density of 100 mA·cm^{-2} despite showing similar performance in electrochemical tests which are typically carried out at low current densities (<1 mA·cm^{-2}). Similar trends were also found for NiCo-rGO. Possible industrial application was demonstrated with the application of rGO supported Fe/Co catalysts in a zinc-air flow battery.

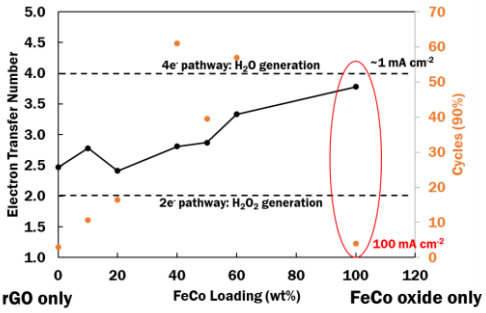

Figure 1. Inadequacy of electrochemical test results in predicting battery cyclability at high current density operations (100 mA·cm^{-2}). Fe/Co loading on rGO is varied from 0 to 100 wt%. Solid line: Electron Transfer Number calculated from electrochemical test. Orange dots: Battery cycles assessed at 90% current capacity.

1) a) S. Jung, *et al.*, *J. Mater. Chem. A.* **2015**, *4*, 3068-3076. b) R. Yoo, *et al.*, *J. Electrochem. Soc.* **2022**, *169*, 063513. 2) a) W. J. Sim, *et al.*, *Nanoscale* **2022**, *14*, 8012-8022. b) Z. Huang, *et al.*, *Sustain. Energy Fuels* **2022**, *6*, 3931-3943.

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スルホラン系濃厚電解液のカリウムイオン電池への適用

（東理大理）〇多々良 涼一・五十嵐 大輔・保坂 知宙・駒場 慎一

Application of Sulfolane-based Concentrated Electrolytes to Potassium-ion Battery (*Tokyo University of Science*) 〇Ryoichi Tatara, Daisuke Igarashi, Tomooki Hosaka, Shinichi Komaba

Concentrated electrolytes composed of sulfolane and lithium salts are well known to exhibit high cation transference number. Thus, they have attracted increasing attention as electrolytes for various lithium-ion batteries. Besides, a far higher cation transference number is expected by replacing Li^+ with K^+, which has smaller ion-solvent interaction. In this study, we investigated the solution properties of potassium salt/sulfolane mixtures and examined their applicability to potassium-ion batteries.

Keywords : Potassium-ion Batteries, Concentrated Electrolytes, Sulfolane

スルホラン(SL)とリチウム塩からなる濃厚電解液は高いカチオン輸率を示すことで知られ、各種リチウム系二次電池の電解液として注目されている [1)]。一方でカリウムイオンはリチウムイオンよりもイオン半径が大きく電荷密度が低いため、イオン－配位子間の相互作用が弱く、高速なイオン輸送が期待される [2)]。本研究では SL とカリウムビス(フルオロスルホニル)アミド塩(KFSA)から成る溶液の基礎物性を調査し、カリウムイオン電池への適合性を検討した。また同じくカリウムイオン電池用濃厚電解液として実績のある KFSA/ Triglyme (G3)系 [3)]との比較を行った。

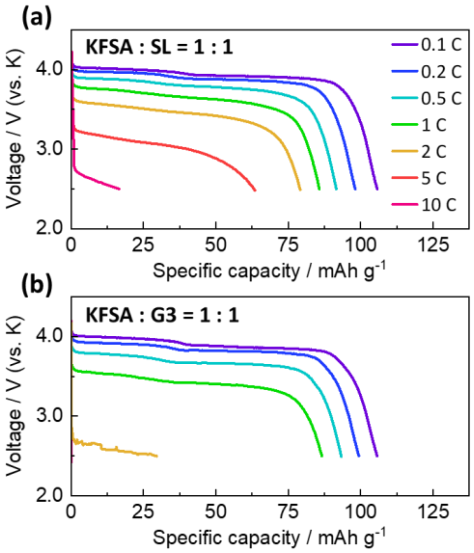

Figure Galvanostatic discharge curves of $K_2Mn[Fe(CN)_6]$ electrodes at different current density in (a) KFSA : SL = 1 : 1 and (b) KFSA : G3 = 1 : 1 electrolytes. The C rate is defined as 1 C = 155 mA g^{-1}.

Figure に (a) KFSA:SL = 1:1 及び(b) KFSA : G3 = 1 : 1 電解液中で異なる電流密度で放電した $K_2Mn[Fe(CN)_6]$電極の放電曲線を示す。高レート(> 2 C)の場合に KFSA:G3 = 1:1 電解液中では殆ど容量が得られなくなったのに対し、KFSA:SL = 1:1 電解液中では高レートで放電した場合も一定の可逆容量を示し、良好な出力特性が得られた。これは SL 系濃厚電解液中において特異な架橋構造(K^+−SL−K^+ / K^+−FSA^-−K^+)が形成される [4)]ことで K^+のホッピング伝導が促進され、濃度分極が抑制されたためだと考えられる。

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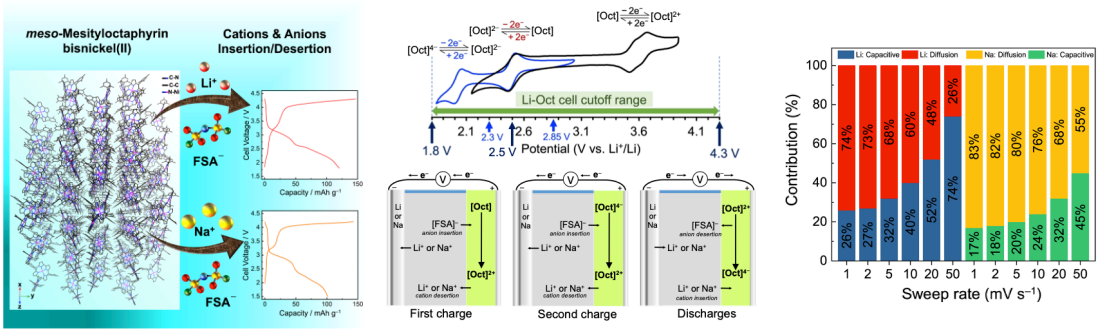
Li and Na Organic Batteries with Porphyrinoid Electrodes

([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Energy Science, Kyoto University*) ○Ji-Young Shin,[1] Jinkwang Hwang,[2]

Keywords: Electrochemical Kinetics; Electrochemical Behaviors; Porphyrinoid

A recent demand to accomplish superior rechargeable batteries is to seize efficient organic electrode materials for conserved and producible cell performances. In the spotlight on structural diversity, tunability, and persistency of organic electrode materials, specific π-conjugation platforms comprising multiple oxidation states have been explored in the current study to induce electromagnetic variability/compatibility.

Our first organic battery derived from nickel(II) norcorrole (NiNc), the smallest stable antiaromatic porphyrinoid enabling gram-scale preparation, has precisely exposed significant potentials for both lithium electrode-cooperated Li-NiNc batteries and lithium electrode-dissociated NiNc-NiNc batteries.[1] The organic batteries fabricated with an inexpensive alkali metal, Na, were subsequently investigated to enhance the inherent battery potentiality in enabling efficient dual ionic charge/discharge behaviors.[2] Furthermore, we comprehend hollow spheres in variable molecular alignment derived from specific substituents onto the main skeleton influencing the kinetic quantity of the dual-ion mobility.[3] Li-organic batteries compromising immensely elongated pai-conjugated expanded porphyrinoids were investigated with [28]hexaphyrin(1.1.1.1.1.1) persuading attractive electrochemistry,[4] and the sequential electrophysical contributions of pseudo-capacitive processes over diffusion-controlled processes preceding in Li and Na organic cells were determined using ocatphyrin(1.0.1.0.1.0.1.0).[5] The Li- and Na-Oct cells induced precisely fast charge/discharge performances and long-term cyclabilities.



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オペランド XRD 追跡によるリチウム空気電池の正極反応の解析

(お茶大 [1]) ○青木 誠 [1]・Dilinigeer Dilixiati[1]・牛島 美奈子 [1]・山田 涼美 [1]・近藤 敏啓 [1]

Study of Cathodic Reaction for Lithium-O2 Battery by Operando XRD Measurements

([1]*Ochanomizu University*) ○Makoto Aoki,[1] Dilinigeer Dilixiati,[1] Minako Ushijima,[1] Suzumi Yamada, [1] Toshihiro Kondo[1]

Lithium-O_2 batteries have been attracting much interest as one of the candidates for next generation batteries because they have a higher specific energy density in comparison to that of lithium-ion batteries. However, high overpotential associated with the decomposition of discharging products during charging has been a major issue for practical application. In order to correctly understand the battery reaction (charge/discharge reaction) and improve the performance, it is necessary to observe the charge/discharge reaction during the battery operating. In this study, we performed operando XRD measurements of the cathode during the battery operating by using a newly designed and constructed electrochemical cell. We successfully observed the formation of discharge products during discharging and the decomposition of the products during charging.

Keywords : Lithium-O_2 Battery; Operando XRD Measurements; Cathodic Reaction

蓄電池の高性能化が求められている現在、高いエネルギー密度を有し、究極の蓄電池と呼ばれているリチウム空気電池の実用化が急務となっている。しかしながら、リチウム空気電池の正極での充放電反応メカニズムは未だ解明されていない。また、充電時には過電圧が上昇し電池性能の劣化が引き起こされる。これらのことが実用化に向けた大きな課題となっている。電池反応（充放電反応）を正しく理解し、反応メカニズムを把握して電池を高性能化させるためには、電池を解体することなく充放電反応が起こっている「その場」で反応を観測する必要がある。本研究では、充放電をさせながらオペランド XRD 測定を行い、正極反応のその場追跡を試みた。

新たに設計・作製した電気化学セルを使用し、充放電をさせながらオペランド XRD 測定を行った。放電の進行にともない放電生成物が成長し（図１）、充電時に分解していく様子を観測することに成功した。

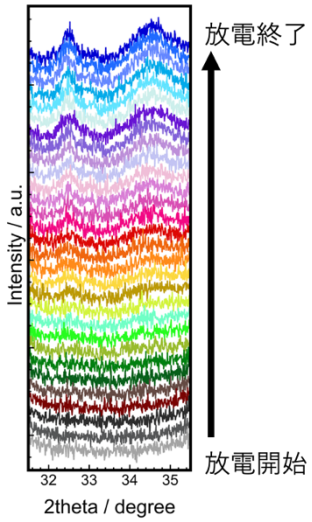

図 1 放電反応中のその場 XRD プロファイル．放電生成物由来のピークが成長していく様子が観測された．

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Academic Program [Oral B] | 22. Resources Utilization Chemistry, Environmental and Green Chemistry | Oral B

[K207-3pm] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Chair: Kenji Kitayama, Seiji Yamazoe

Fri. Mar 24, 2023 1:10 PM - 3:40 PM K207 (K207, Lecture Hall Bldg. [2F])

[K207-3pm-01] Catalytic terpolymerization of CO_2, epoxides and heteroallenes (2)

○Koichi Nakaoka[1], Satoshi Muranaka[1], Io Yamamoto[1], Chihiro Maeda[1], Kazuto Takaishi[1], Tadashi Ema[1] （1. Grad. Sch. Nat. Sci. Technol., Okayama Univ.）

1:10 PM - 1:30 PM

[K207-3pm-02] Formic acid formation from supercritical CO_2 catalyzed by Ir complexes

○Seo Ono[1,2], Ryoichi Kanega[2], Hajime Kawanami[2] （1. University of Tsukuba, 2. AIST）

1:30 PM - 1:50 PM

[K207-3pm-03] Synthesis of Glyoxal by Oxidation of Glycolaldehyde Using Ruthenium Complex Catalysts

○Takuya Sagawa[1], Atsushi Kondo[1], Mineo Hashizume[1] （1. Tokyo University of Science）

1:50 PM - 2:10 PM

[K207-3pm-04] Black coloration of wool fibers using inositol oxides

○Takeru Ohe[1], Yurika Yoshimura[1] （1. Osaka Research Institute of Industrial Science and Technology）

2:10 PM - 2:30 PM

[K207-3pm-05] Fabrication of amine immobilized silica with high amine density for capturing low-concentration CO_2

○Soichi Kikkawa[1], Miori Kataoka[1], Seiji Yamazoe[1,2] （1. Tokyo Metropolitan Univ., 2. PREST, JST）

2:40 PM - 3:00 PM

[K207-3pm-06] Development of Direct Air Capture system using liquid-Solid Phase Separation

○Seiji Yamazoe[1,2,3], Soichi Kikkawa[1,3], Kazushi Amamoto[1], Yu Fujiki[1], Jun Hirayama[1,3], Gen Kato[1], Hiroki Miura[1,3], Tetsuya Shishido[1,3] （1. Tokyo Metropolitan University, 2. PRESTO, 3. ESICB, Kyoto University）

3:00 PM - 3:20 PM

[K207-3pm-07] Solubilization of lignocelluloses in organic acid and structural characterization of biomass film

○Naoko Kobayashi[1,2], Tomohiro Hashizume[1,3], Keiko Kondo[1,4], Masato Katahira[1,4], Kenji Kitayama[1,3], Takashi Watanabe[1,2] （1. Biomass Product Tree Industry-Academia Collaborative Research Laboratory, 2. Research Institute for Sustainable Humanosphere, 3. Daicel Corporation, 4. Institute of Advanced Energy）

3:20 PM - 3:40 PM

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Catalytic terpolymerization of CO_2, epoxides, and heteroallenes (2)

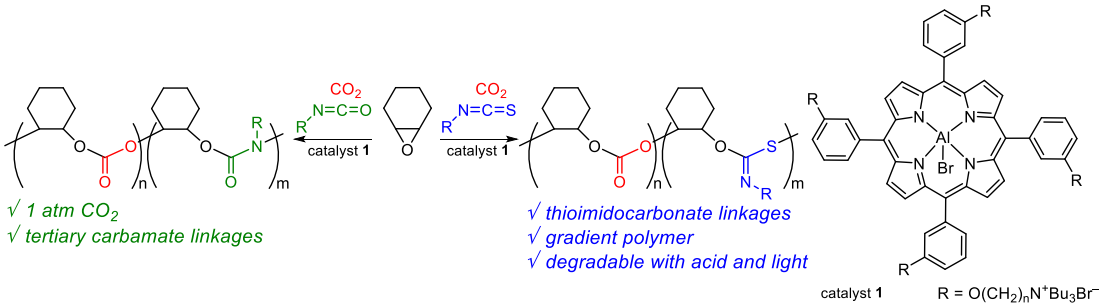
(*Graduate School of Natural Science and Technology, Okayama University*) ○Koichi Nakaoka, Satoshi Muranaka, Io Yamamoto, Chihiro Maeda, Kazuto Takaishi, Tadashi Ema

Keywords: CO_2 fixation; Polycarboates; Porphyrin; Ring-opening copolymerization; Terpolymerization

The ring-opening copolymerization of epoxides and CO_2 for the synthesis of aliphatic polycarbonates is a green sustainable synthetic technology with excellent atom economy. Terpolymerization of CO_2, epoxides, and comonomers, such as lactones, lactides, cyclic anhydrides, and heteroallenes, is an effective strategy for the development of new CO_2-based polymers. Heteroallenes used as comonomers have been limited to SO_2 and COS, while iso(thio)cyanates are promising heteroallenes with substituents.

Previously, bifunctional Mg^{II} or Zn^{II} porphyrin catalysts showed high catalytic activities for the synthesis of cyclic carbonates from CO_2 and epoxides,[1] while bifunctional Al^{III} porphyrin catalysts **1** catalyzed the copolymerization of CO_2 and epoxides or oxetanes to give polycarbonates.[2,3] We envisioned that isocyanates or isothiocyanates could be used as comonomers in our catalytic system. Here we report the terpolymerization of CO_2, epoxides, and isocyanates or isothiocyanates for the first time.

The terpolymerization of cyclohexene oxide (CHO), CO_2, and isothiocyanates under solvent-free conditions in an autoclave was catalyzed by **1** to give new poly(carbonate–thioimidocarbonate)s, which showed degradability with light or acid. The kinetic studies and the degradation behaviors indicated that the terpolymers had gradient character, where the ratio of the PTIC unit to the PCHC unit changed gradually along the polymer chain. On the other hand, in the terpolymerization of CHO, CO_2, and isocyanates, the slow dropwise addition of isocyanates to a mixture of CHO and **1** under 1 atom of CO_2 (balloon) in a Schlenk flask was needed to suppress isocyanurates produced by the trimerization of isocyanates, and new poly(carbonate–urethane)s with tertiary carbamate linkages were synthesized. The CO_2 contents of these CO_2-based polymers were changed by the reaction conditions or substituents on the heteroallenes.



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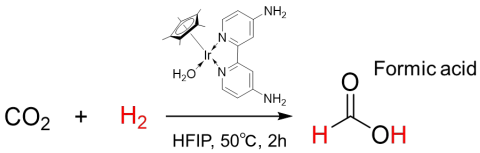
Formic acid formation from supercritical CO_2 catalyzed by Ir complexes

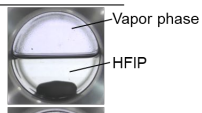
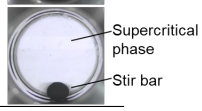
([1]*Doctoral Program in Chemistry, Degree Programs in Pure and Applied Sciences, Graduate School of Science and Technology, University of Tsukuba*, [2]*National Institute of Advanced Industrial Science and Technology*) ○Seo Ono,[1,2] Ryoichi Kanega,[2] Hajime Kawanami[1,2]
Keywords: CO_2 Hydrogenation; Formic acid; Ir complex; Supercritical CO_2; HFIP

Although CO_2 hydrogenation to "free-formic acid" is an attractive topic, it requires efficient catalysts for the reaction and a low-cost process under "non-basic" conditions. Noble metal complexes such as Ir, Ru, and Rh, are highly active in both CO_2 hydrogenation and formic acid dehydrogenation (FADH).[1)] However, formic acid (FA) is hardly obtained in water in the presence of these catalysts under non-basic conditions because of the equilibrium between FA and CO_2/H_2. Recently, we reported that the Ir complex with 4,4'-diamino-2,2'-bipyridine ligand (4DABP) and cyclopentadienyl ligand (Cp*Ir-4DABP) has a very high catalytic activity resulting in the generation of high-pressure gases over 150 MPa from FA aqueous solution.[2)] However, the Ir catalyst is highly active in an aqueous solution, the activity was very low in organic solvents. Especially using HFIP (hexafluoro-2-propanol), the Ir catalyst hardly works and gives only a few MPa of gas pressure. This implies that formic acid is less progress in the dehydrogenation in HFIP.

Following these results, we studied the reverse reaction of FADH, that is CO_2 hydrogenation, under less aqueous and high-pressure conditions in HFIP. CO_2 hydrogenation with Cp*Ir-4DABP was investigated at various pressure (Table 1). As a result, Cp*Ir-4DABP gave "free-formic acid" and the TON of 130 at p_{H_2}/p_{CO_2}= 0.5/0.5 (MPa). When CO_2 pressure was increased to 12 MPa, the TON reached up to 370. Phase behavior during the reaction was observed by view cells, and it was observed to change from the vapor phase and HFIP to the supercritical phase by increasing pressure. These results are attributed to the dissolution of all, HFIP, catalysts, formic acid, CO_2 and H_2 in the supercritical phase thereby improving the reaction efficiency.

Table 1 Effect of pressure on CO_2 hydrogenation to formic acid in HFIP solution at 50°C using Cp*Ir-4DABP.



Entry	p_{H_2}/p_{CO_2} (MPa)	TON	Phase
1	0.5/0.5	130	
2	0.5/12	370	

1) a) S. Chatterjee *et al.*, *Energy Environ. Sci.*, **2021**, *14*, 1194-1246. b) N. Onishi *et al.*, *Adv. Energy Mater.*, **2019**, *9*, 1801275. 2) H. Kawanami *et al.*, *Inrg. Chem.*, **2020**, *59*, 7, 4191-4199.

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ルテニウム錯体触媒を用いたグリコールアルデヒドの酸化反応によるグリオキサール合成

（東理大工）○佐川 拓矢・近藤 淳史・橋詰 峰雄

Synthesis of Glyoxal by Oxidation of Glycolaldehyde Using Ruthenium Complex Catalysts

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Cellulose is the most abundant biomass on the earth and it is a polymer of glucose. Thus, it can be used for the carbon resources. Glucose is converted to glycolaldehyde (GA) by retro-aldol reaction. Furthermore, the oxidation of GA gives glyoxal (Gox), which is utilized as a modifier in fibers and paper. However, the selective oxidation of GA to Gox has not been achieved. In this study, the selective synthesis of Gox from GA using a ruthenium complex catalyst (**Ru Cat.**) was investigated. Optimizing reaction conditions, the conversion of GA was 68%, and Gox was obtained with a reaction yield of 32%.

Keywords: Glucose; Glycol Aldehyde; Glyoxal; Ruthenium Catalyst; Oxidation Reaction

地球上最大のバイオマスであるセルロースを加水分解することで得られるグルコースは、安価で大量供給可能な糖であり、その炭素源としての利用が期待されている。グルコースから誘導される有機化合物の一つにグリコールアルデヒド（GA）がある。さらに GA を酸化することで、繊維や紙の改質剤として利用されるグリオキサール（Gox）が得られる。しかしながら GA の選択的酸化反応による Gox への変換は達成されていない。そこで本研究では、ルテニウム錯体触媒（**Ru Cat.**）を用いた GA から Gox への選択合成を検討した。

Ru Cat.は既報 [1]を参考に合成し、各種 NMR、MS により同定した。酸化反応は、10 mL テフロンチューブを備えた耐圧容器に GA 0.5 mmol，**Ru Cat.** 0.01 mmol（基質触媒比 S/C = 50），DMF 1.5 mL を加え、O_2 ガスを 0.25 MPa で加圧して行った（Figure 1）。反応の進行は HPLC により確認した。反応条件を最適化したところ、反応温度 100 ℃で 3 時間反応させることで GA の変換率が 68%となり、反応収率 32%で Gox が得られた。さらなる変換率、収率の向上を目指して反応時間を延ばしたところ、Gox 収率は減少した。反応終了後に CO_2 の生成が確認されたことから、Gox の一部がシュウ酸，ギ酸を経由し CO_2 に変換されたことが考えられる。講演では生成した Gox を DMF 溶媒から分離する方法についても報告する。

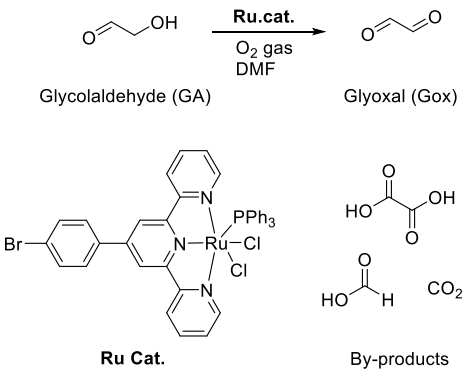

Figure 1. Oxidation of GA to form Gox using Ru Cat.

1) E. W. Dahl, T. L. Goff, N. K. Szymczak, *Chem. Commun.* **2017**, *53*, 2287.

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イノシトールの酸化物を利用した羊毛布の黒色着色

（大阪技術研）○大江 猛・吉村 由利香

Black coloration of wool fibers using inositol oxides (*Osaka Research Institute of Industrial Science and Technology*) ○Takeru Ohe, Yurika Yoshimura

We have experienced in our daily living well that foods including both reducing sugars and proteins, become yellow or brown after the heating process or long storage. These coloration reactions are called the Maillard reaction. In our laboratory, new textile coloration using Maillard reactions has been investigated as alternative dyeing technology using toxic synthetic dyes. Our recent works also afforded an important result that coloration reactions of wool fibers with oxides of reducing sugar or sugar alcohol gave them deeper coloration, such as dark brown, than the original sugars. Here we investigated coloration reactions of wool fibers with oxides of inositol, which is one of cyclic polyols. Interestingly, these reactions became them darker, almost black, than oxides of reducing sugars.

Keywords : Black Coloration; Maillard Reaction; Wool Fiber; Inositol Oxide; Cyclic Polyol

当研究室では、食品のメイラード反応を利用して、有害性が問題視されている合成染料の代替技術の開発に取り組んでいる。しかしながら、着色原料に還元糖を用いた場合、羊毛などのアミノ基を持つ繊維材料を濃色に着色するには 48 時間以上の長時間の反応時間が必要となった。最近の研究で、還元糖や糖アルコールなどの酸化物を利用することによって 2 時間程度の着色時間で深みのある茶褐色に着色することできた。本研究では、環状構造を有する糖アルコールであるイノシトールの酸化物を利用した羊毛の着色について検討を行った。

はじめに、着色原料として還元糖であるグルコースと環状構造のイノシトールの酸化物を利用して羊毛布の着色実験を行った。今回の実験では、着色後の羊毛布は黒色に近いため、$L^*a^*b^*$表色系で羊毛布の着色について評価を行った。図 1 には明度に相当する L^*値を用いて羊毛布の色の濃淡を調べた結果を示す。興味深いことに、イノシトールの酸化物による濃色化の効果は極めて高く、着色時間が 8 分の 1 以下まで短縮された。おそらく、イノシトールの酸化物は環状構造を維持しており、鎖状構造が水溶液中で存在するグルコースの酸化物とは異なり、色素の生成に関与しない副生物の生成が抑制されたと予測される。さらに、イノシトールの酸化条件や得られた酸化物による反応条件を調べることによって羊毛布のさらなる濃色化についても検討した。

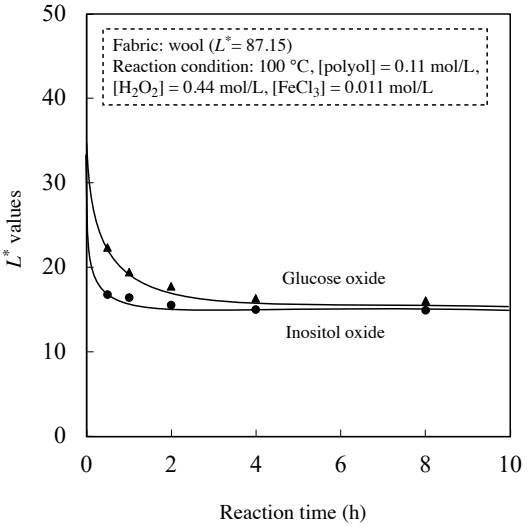

図 1 イノシトールおよびグルコースの酸化物との反応による羊毛布の明度（L^*値）の変化

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低濃度 CO_2 回収を志向した高密度アミン修飾シリカの合成

（都立大院理 [1]・JST-さきがけ [2]）○吉川聡一 [1], 片岡実織 [1], 山添誠司 [1,2] Fabrication of Amine Immobilized Silica with High Density for Capturing Low-Concentration CO_2
([1]*Graduate School of Science, Tokyo Metropolitan University*, [2]*JST PRESTO*) ○ Soichi Kikkawa,[1] Miori Kataoka,[1] Seiji Yamazoe[1,2]

Carbon Capture and Storage (CCS) have recently been attracting much attention and the capturing existing low-concentration CO_2 form air, so-called direct air capture (DAC), is an essential technology for carbon neutral society. Chemical CO_2 absorption method using amines is one of the effective techniques for CCS, and a solid CO_2 sorbent that an amine was immobilized on the surface of solid support such as silica is suitable for the CO_2 sorbent for DAC due to easy collection and regeneration, selective CO_2 adsorption, and tolerance to moisture. The sorbent with high amine loadings has been developed by a surface modification of silica with silane coupling reagent having amino group or an impregnation of amines. In this study, we developed a solid CO_2 sorbent with high-dense surface amino groups by surface modification of silica having organic functional group with diamine. The fabricated amine-immobilized silica possessed thermal stability up to 240°C due to chemically immobilization. The CO_2 absorption property was evaluated in a fixed bed flow reactor and the fabricated amine-immobilized silica adsorbed 400ppm CO_2 with >99% removal efficiency for 6 h. The total adsorbed CO_2 was 4.3wt% with the terminal amine utilization efficiency of 41%. The captured CO_2 desorbed at 80°C, and the capacity was not degraded by repeated use. Thus, developed amine-immobilized silica for highly efficient adsorption of low-concentration CO_2.
Keywords : Carbon Dioxide, Direct Air Capture, Solid Sorbent, Amine-Immobilized Silica

近年，CO_2 を回収し貯留する Carbon Capture and Storage（CCS）が注目されている．特に，これまでに排出された大気中の低濃度 CO_2 を直接回収する Direct Air Capture（DAC）は脱炭素社会の実現に必須の技術である．アミンを用いた化学吸収法は CCS に広く用いられている技術の一つであり，中でもシリカなどの表面にアミンを修飾した固体 CO_2 吸収剤は回収・再生が容易であり，CO_2 吸着への選択性や耐湿性があるため DAC に向けた CO_2 吸収剤として有効である [1)]．アミノ基を有するシラン化剤による表面修飾やアミンを含浸担持する手法など，単位重量あたりのアミン担持量を高める設計がなされている．本研究では，有機修飾シリカへのジアミンの修飾により，高密度にアミンを修飾したシリカを合成した．熱重量分析から 240°C までの熱安定性を示し，アミンがシリカ表面に化学的に固定化されたことがわかる．固定床流通式の反応容器に試料を充填し，400ppm の CO_2 を 10 sccm で流通すると，>99%の除去効率で約 6 時間にわたり CO_2 を吸収した．CO_2 吸収量は 4.3wt%に相当し，修飾した末端アミノ基のうち 41%を CO_2 吸収に利用した．また，吸収した CO_2 を N_2 流通下 80°C ですべて脱離し，吸収と脱離を繰り返しても顕著な劣化は認められなかった．以上のように，低濃度 CO_2 を高効率で吸収可能なアミン修飾シリカを開発した．

1) E. S. Sanz-Perez, C. R. Murdock, S.A. Didas, C.W. Jones, *Chem. Rev.* , **2016**, *116*, 11840.

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液ー固相分離を利用した Direct Air Capture システムの開発

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Development of Direct Air Capture system using liquid-Solid Phase Separation ([1]*Graduate School of Science, Tokyo Metropolitan University*, [2]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University*, [3] *Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency*, [4]*Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*) ○Seiji Yamazoe[1,2,3]・Soichi Kikkawa[1,2]・Kazushi Amamoto[1]・Yu Fujiki[1]・Jun Hirayama[1,2]・Gen Kato[4]・Hiroki Miura[2,4]・Tetsuya Shishido[2,4]

Liquid-solid phase separation between a liquid amine and the solid carbamic acid exhibited >99% CO_2 removal efficiency under a 400 ppm CO_2 flow system using diamines bearing an aminocyclohexyl group. Among them, isophorone diamine (IPDA) exhibited the highest CO_2 removal efficiency. IPDA reacted with CO_2 in a CO_2/ IPDA molar ratio of ≥1 even in H_2O as a solvent. The captured CO_2 was completely desorbed at 333 K because the dissolved carbamate ion releases CO_2 at low temperatures. The reusability of IPDA under CO_2 adsorption and desorption cycles without degradation, the >95% efficiency for 100 h under direct air capture conditions, and the high CO_2 capture rate suggest that the phase separation system using IPDA is robust and durable for practical use.

Keywords : Direct Air Capture, DAC, CO_2, Phase Separation, Amine

現在、気候変動問題を解決するため、CO_2 の回収、利用技術の確立が急務となっている。KOH/$Ca(OH)_2$ や固体吸着材を用いた低濃度 CO_2（400ppm）を回収する技術（Direct air capture, DAC）による実証実験が行われているが、効率・コストの面で改善の余地があり、新しい DAC 技術の開発が望まれている。近年、相分離を利用した CO_2 回収技術が注目を集めており、液ー液相分離 [1)]や液ー固相分離 [2)]による DAC 技術が報告されている。本研究では、アミンと CO_2 が反応して生成するカルバミン酸の低い溶解度を利用した液ー固相分離による大気中の低濃度 CO_2 を吸収・回収できる DAC 技術の開発を行った。

種々のアミンを用いて CO_2 の吸収・脱離実験を行った結果、シクロヘキシル環にアミノ基をもつジアミン、特にイソホロンジアミン（IPDA）が本技術に高い性能を示すことを見出した。IPDA を溶かした吸収液を用いたところ、400ppm の CO_2 を 95%以上の効率で吸収し、白色沈殿が生成した。また、N_2 流通下、60℃に加熱したところ、吸収した CO_2 が全て脱離し、元の状態に戻った。IPDA は CO_2 の吸収・脱離を５回繰り返し行っても性能は劣化しなかった。また、100 h の連続吸収実験でも性能が落ちなかったこと、水溶媒でも高い CO_2 吸収特性を示したことから、液ー固相分離を利用した高効率な DAC システムの開発に成功した [3)]。

1) A.I. Papadopoulos, F. Tzirakis, I. Tsivintzelis, P. Seferlis, *Ind. Eng. Chem. Res*. **2019**, *58*, 5088− 5111.
2) F. Inagaki, C. Matsumoto, T. Iwata, T.; Mukai, *J. Am. Chem. Soc*. **2017**, *139*, 4639−4642.
3) S. Kikkawa, K. Amamoto, Y. Fujiki, J. Hirayama, G. Kato, H. Miura, T. Shishido, S. Yamazoe, *ACS Environ. Au*, **2022**, *2*, 354-362.

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リグノセルロースの有機酸可溶化とバイオマスフィルムの構造特性解析

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Solubilization of lignocelluloses in organic acid and structural characterization of biomass film

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We are converting lignocellulosic biomass into new functional materials via solubilization in organic acids[1,2)]. Biomass film was produced by treatments of wood chips, sawdust and agricultural wastes under ultra-mild conditions. The physical and morphological properties of the biomass film were characterized and the mechanism of solubilization was analyzed. Multi-dimensional NMR revealed that cellulose, xylan and lignin were esterified with formic acid. The formylation breaks the intermolecular and intramolecular hydrogen bonds of cellulose, hemicellulose and lignin, resulting in the disintegration and solubilization of wood cell walls.

Keywords : Wood; Biorefinery; Bioplastics; Lignin; Cellulose

木材チップやおが屑からプラスチックと紙の性質をもつバイオマスフィルムを温和な条件のギ酸溶解により作製した。ユーカリ（*Eucalyptus globulus*）由来のプラスチック様フィルムではガラス転移点 177°C、応力 61 MPa、弾性率 3096 MPa とアクリル樹脂に匹敵する強度を示したが、スギ由来のフィルムではガラス転移点が検出されず、ペーパーボードの物性に類似していた。2D ^{13}C-^{1}H HSQC 及び HMBC NMR 解析によりリグニンのβ-*O*-4 やβ-5 構造のαとγ位や、グルコース残基 6 位とキシロース残基 3 位のホルミル化が示された。ホルミル化によりセルロース、ヘミセルロース、リグニンの分子間及び分子内水素結合が切断され、植物細胞壁を固めるこれらの高分子ネットワークが弛緩すると考察した。

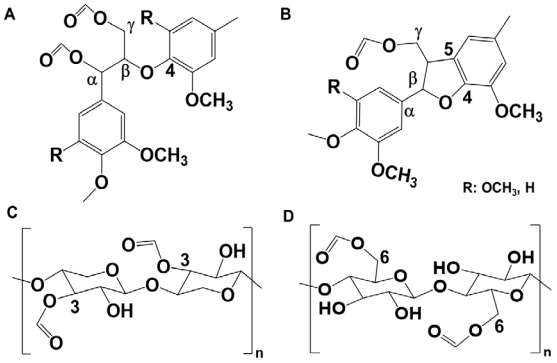

Fig. 1 Formylation at a and γ positions of β-*O*-4 (A) and γ position of β-5 linkages in lignin (B), 3 position of xylose residues in xylan (C) and 6 position of glucose residues in cellulose (D).

1) 渡辺隆司、他: セルロース学会第 29 回年次大会講演要旨集、44-45 (2022).
2) Nishiwaki-Akine, Y., Watanabe, T., Green Chem., 16, 3569-3579 (2014)

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