

Fri. Mar 19, 2021

Room 19

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

[A19-1pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Nobuyuki Matubayasi, Yasuteru Shigeta

1:00 PM - 3:20 PM Room 19 (Online Meeting)

[A19-1pm-01] Triple point of Ar by constant energy molecular dynamics

○Yosuke Kataoka¹ (1. Hosei University)

1:00 PM - 1:20 PM

[A19-1pm-02] Study on Electron Density Distribution Map and Crystal Structure Factor of Low Pressure Phase and High Pressure Phase of Mg₃BN₃ by Using Modified Discrete Cosine Transform○Hideo Hiraguchi¹ (1. The Institution of Professional Engineers, Japan)

1:20 PM - 1:40 PM

[A19-1pm-03] ISRS-induced terahertz wave generation process in DCMBI crystalline solid by Maxwell + polarizable MD multi-scale simulation

○Atsushi Yamada¹ (1. University of Tsukuba)

1:40 PM - 2:00 PM

[A19-1pm-04] Reaction dynamics of ion-molecule collision beyond reaction-path-based understanding

○Kohei Oda¹, Takuro Tsutsumi¹, Srihari Keshavamurthy^{2,3}, Kenji Furuya⁴, Tetsuya Taketsugu^{3,5} (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Department of Chemistry, Indian Institute of Technology, Kanpur, 3. Department of Chemistry, Faculty of Science, Hokkaido University, 4. Faculty of Arts and Science, Kyushu University, 5. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)

2:00 PM - 2:20 PM

[A19-1pm-05] Theoretical study on isotope fractionation in biotic uranium multistep reduction reaction

○Ataru Sato¹, Minoru Abe¹, Masahiko Hada¹ (1. Graduate School of Science, Tokyo Metropolitan University)

2:20 PM - 2:40 PM

[A19-1pm-06] Water Oxidation at N-Doped Graphene Oxides - Structure-Property Relationships and PCET Dynamics

○Fabian Weber^{1,3}, Jean Christophe Tremblay², Annika Bande³ (1. Chuo University, 2. Université de Lorraine, 3. Helmholtz-Zentrum Berlin)

2:40 PM - 3:00 PM

[A19-1pm-07] Static-field ionization rates of He-like ions by MCTDHF method

○Erik Loetstedt¹, Marcelo F Ciappina², Kaoru Yamanouchi¹ (1. The University of Tokyo, 2. Guangdong Technion - Israel Institute of Technology)

3:00 PM - 3:20 PM

Room 7

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

[A07-1pm] 04. Physical Chemistry -Properties-

Chair: Hiroki Akutsu, Kazuya Kubo

1:00 PM - 3:20 PM Room 7 (Online Meeting)

[A07-1pm-01] Synthesis of TTF derivatives for fabricating conductive one-dimensional structures

○Hirohisa Oishi¹, Yuto Kimura¹, Nishihara Sadahumi², Tomoyuki Akutagawa³, Takayoshi Nakamura⁴, Yoko Tatewaki¹ (1. Tokyo University of Agriculture and Technology, 2. Hiroshima University, 3. Tohoku University, 4. Hokkaido University)

1:00 PM - 1:20 PM

[A07-1pm-02] Electromagnetic properties of molecular nanocoils of TTF derivatives with chiral units.

○Yoko Tatewaki¹, Sadafumi Nishihara², Tomoyuki Akutagawa³, Takayoshi Nakamura⁴ (1. Tokyo University of Agriculture and Technology, 2. Hiroshima University, 3. Tohoku University, 4. Hokkaido University)

1:20 PM - 1:40 PM

[A07-1pm-03] Synthesis of novel single-crystalline ethylenedioxythiophene oligomer charge

transfer salts and the conjugation-length-elongation effects on their physical properties

○Ryohei Kameyama¹, Tomoko Fujino¹, Shun Dekura¹, Mitsuaki Kawamura¹, Taisuke Ozaki¹, Hatsumi Mori¹ (1. ISSP, The University of Tokyo)

1:40 PM - 2:00 PM

[A07-1pm-04] Syntheses of Benzenetriimide-based molecular conductors

○Shohei Koyama¹, Hiroaki Iguchi¹, Shinya Takaishi¹ (1. Tohoku university)

2:00 PM - 2:20 PM

[A07-1pm-05] Electrochemical tuning-induced magnetic properties in geometrically frustrated LiMn_2O_4

○Qi Chen¹, Zhongyue Zhang¹, Kunio Awaga¹ (1. Nagoya University)

2:20 PM - 2:40 PM

[A07-1pm-06] Charge-transfer-induced phase transition materials with electromagnetic wave absorption properties

○Koji Nakabayashi¹, Takaya Yoshida¹, Kenta Imoto¹, Marie Yoshikiyo¹, Kouji Chiba, Hiroko Tokoro², Asuka Namai¹, Shin-ichi Ohkoshi¹ (1. The University of Tokyo, 2. University of Tsukuba)

2:40 PM - 3:00 PM

[A07-1pm-07] Polarity and Chirality in Ferroelectric Triglycine sulfate Crystals

○Yukana Terasawa¹, Toshio Kikuta², Masaaki Ichiki³, Sota Sato⁴, Kazuhiko Ishikawa¹, Toru Asahi¹ (1. Waseda Univ., 2. Univ. of Toyama, 3. AIST, 4. The Univ. of Tokyo)

3:00 PM - 3:20 PM

Room 5

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

[A05-1pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair:Yoshiyuki Kageyama, Hiro Minamimoto
1:00 PM - 3:20 PM Room 5 (Online Meeting)

[A05-1pm-01] Acquisition voltage vibration in sensitized thermal cells

○Sachiko Matsushita¹, Haruki Kohata¹, Hayato

Sekiya¹, Takumi Ikeda¹, Yoshiharu Hida¹, HAOTONG SONG¹, Toshihiro Isobe¹, Akira Nakajima¹ (1. Tokyo Institute of Technology)

1:00 PM - 1:20 PM

[A05-1pm-02] Dynamics of Interfacial Tension Concerning to Self-Propelled Motion of Droplet

○Nobuhiko J. Suematsu^{1,2} (1. IMS, Meiji University, 2. MIMS, Meiji University)

1:20 PM - 1:40 PM

[A05-1pm-03] Formation of Novel Self-organized Periodic Precipitation Pattern by pH-induced Gold Nanoparticles Aggregation

○Masaki Itatani¹, Qing Fang², Hideki Nabika² (1. Grad. Sch. of Sci. and Eng., Yamagata Univ., 2. Fac. of Sci., Yamagata Univ.)

1:40 PM - 2:00 PM

[A05-1pm-04] Electrochemical control of spatio-temporal patterns in the Belousov-Zhabotinsky reaction

○Masakazu Kuze¹, Mari Horisaka¹, Nobuhiko J. Suematsu², Takashi Amemiya³, Oliver Steinbock⁴, Satoshi Nakata¹ (1. Graduate School of Integrated Sciences for Life, Hiroshima Univ., 2. Graduate School of Advanced Mathematical Sciences, Meiji Univ., 3. Graduate School of Environment and Information Sciences, Yokohama National Univ., 4. Department of Chemistry and Biochemistry, Florida State Univ.)

2:00 PM - 2:20 PM

[A05-1pm-05] Model for swimming of micro-sized crystals in water with an oscillating fin under continuous blue-light irradiation

○Kazuma Obara¹, Yoshiyuki Kageyama², Sadamu Takeda² (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

[A05-1pm-06] Elucidation of melting during the initial process of electron-crystal interactions

○Dongxin Liu¹, Takayuki Nakamuro¹, Koji Harano¹, Eiichi Nakamura¹ (1. The University of Tokyo)

2:40 PM - 3:00 PM

[A05-1pm-07] Reformation of thalidomide from its hydrolysis compound via intramolecular

dehydration

○Toru Asahi¹, Toru Aashi¹, Koichi Tsutao¹, Kohei Otagawa¹, Miri Nakamura¹, Yoshiyuki Ogino¹
(1. Waseda University)
3:00 PM - 3:20 PM

Room 4

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

[A04-1 am] 07. Inorganic Chemistry

Chair: Shintaro Ida, Makoto Kobayashi

9:00 AM - 11:20 AM Room 4 (Online Meeting)

[A04-1 am-01] Synthesis and characterisation of the high pressure polymorphs of BaRhO₃

○Sean Dusan Injac¹, Fabio Denis Romero¹,
Yuichi Shimakawa¹ (1. Kyoto University)
9:00 AM - 9:20 AM

[A04-1 am-02] New Alkali Hydride Antiperovskites as Fast Ionic Conductors

○Cedric Tassel¹, Shenghan Gao¹, Thibault Broux¹, Susumu Fujii², Kentaro Yamamoto¹, Yao Xiao¹, Itaru Oikawa⁴, Hitoshi Takamura⁴, Hiroki Ubukata¹, Yuki Watanabe¹, Kotaro Fujii³, Masatomo Yashima³, Akihide Kuwabara², Yoshiharu Uchimoto¹, Hiroshi Kageyama¹ (1. Kyoto University, 2. Japan Fine Ceramics Center, 3. Tokyo Institute of Technology, 4. Tohoku University)
9:20 AM - 9:40 AM

[A04-1 am-03] Large latent heat and barocaloric effects at charge transfer transitions of A-site ordered perovskite oxides

○Yoshihisa Kosugi¹, Masato Goto¹, Asaya Fujita², Takashi Saito³, Takashi Kamiyama³, Yuichi Shimakawa¹ (1. Kyoto University, 2. National Institute of Advanced Industrial Science and Technology, 3. High Energy Accelerator Research Organization)
9:40 AM - 10:00 AM

[A04-1 am-04] A comparative study of A-site ordered quadruple perovskite structures containing divalent manganese, iron, cobalt and nickel square-planar centers

○Midori Estefani Amano Patino¹, Fabio Denis Romero^{1,2}, Sean Injac¹, Masato Goto¹, Yuichi Shimakawa¹ (1. Institute for Chemical

Research, Kyoto University, 2. Hakubi Center for Advanced Research, Kyoto University)

10:00 AM - 10:20 AM

[A04-1 am-05] Two-dimensional Li-ion conduction in a Ruddlesden-Popper phase of lithium-hydroxide-halide antiperovskites

○Anucha Koedtrud¹, Midori Amano Patino¹, Daisuke Kan¹, Yuichi Shimakawa¹ (1. Institute for Chemical Research, Kyoto Univ.)

10:20 AM - 10:40 AM

[A04-1 am-06] Selective fabrication of Ca₂NH epitaxial thin films using magnetron sputtering system

○Seoungmin Chon¹, Shigeru Kobayashi¹, Kazunori Nishio¹, Ryota Shimizu^{1,2}, Taro Hitosugi¹ (1. Department of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo, 152-8552, Japan, 2. PRESTO, Japan Science and Technology Agency, Saitama, 332-0012, Japan)

10:40 AM - 11:00 AM

[A04-1 am-07] Ultra-high concentration hydrogen doping into rutile-TiO₂ with in situ transport measurements

○GyeongCheol Lim¹, Mitsuhiro Maesato¹, Ryo Nakayama², Dae-Woon Lim^{1,3}, Takahiro Ozawa⁴, Markus Wilde⁴, Katsuyuki Fukutani⁴, Hiroshi Kitagawa¹ (1. Kyoto Univ., 2. Tokyo Tech., 3. Yonsei Univ., 4. The Univ. of Tokyo)
11:00 AM - 11:20 AM

Room 6

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

[A06-1 pm] 08. Catalysts and Catalysis

Chair: Hisao Yoshida, Akira Yamakata

1:00 PM - 3:20 PM Room 6 (Online Meeting)

[A06-1 pm-01] Decarboxylative transformation modulated by photocatalyst

○Yota Sakakibara¹, Kei Murakami², Kenichiro Itami¹ (1. Nagoya University, 2. Kwansei Gakuin University)
1:00 PM - 1:20 PM

[A06-1 pm-02] Electron Transfer Kinetics of Aluminum Porphyrin/ Metal Oxide Systems

○Abin Sebastian¹, Fazalurahman Kuttassery²,

Hiroshi Tachibana¹, Haruo Inoue¹ (1. Tokyo Metropolitan Univeristy, 2. Tokyo Institute of Technology)

1:20 PM - 1:40 PM

[A06-1pm-03] Construction of visible-light Z-scheme water splitting system using

nitrogen/fluorine codoped TiO₂

○Akinobu Miyoshi¹, Junie Jhon M. Vequizo², Shunta Nishioka¹, Shunsuke Yamashita³, Shunsuke Nozawa⁴, Akihito Kuwabara⁵, Akira Yamakata², Koji Kimoto³, Kazuhiko Maeda¹ (1. Tokyo Tech., 2. TTI, 3. NIMS, 4. KEK, 5. JFCC)

1:40 PM - 2:00 PM

[A06-1pm-04] Co-catalyst effects on

photoelectrochemistry of bismuth vanadate studied with kinetic analysis of photocarrier and reaction

○Yoshiyasu Matsumoto¹, Akihiko Kudo² (1. Toyota Physical and Chemical Research Institute, 2. Tokyo University of Science)

2:00 PM - 2:20 PM

[A06-1pm-05] Improvement of photoelectrochemical performances of particulate ZnSe:ClGS photocathodes by particle size control and electrochemical evaluation for surface and bulk characteristics

○Fumiaki TAKAGI¹, Yosuke KAGESHIMA^{1,2}, Katsuya TESHIMA^{1,2}, Kazunari DOMEN^{2,3}, Hiromasa Nishikiori^{1,2} (1. Graduate School of Engineering, Shinshu Univ., 2. Research Initiative for Supra-Materials(RISM), 3. The Univ. of Tokyo)

2:20 PM - 2:40 PM

[A06-1pm-06] Effects of composition of Cu₂Sn_xGe_{1-x}S₃ particles on photocatalytic and photoelectrochemical hydrogen evolution activity

○Yosuke Kageshima^{1,2}, Sota Shiga¹, Tatsuki Ode¹, Fumiaki Takagi¹, Katsuya Teshima^{1,2}, Kazunari Domen^{2,3}, Hiromasa Nishikiori^{1,2} (1. Shinshu Univ., 2. Research Initiative for Supra-Materials, Shinshu Univ., 3. The Univ. of Tokyo)

2:40 PM - 3:00 PM

[A06-1pm-07] Extremely small cobalt oxide particle formation on BiVO₄ film electrode by successive ionic layer adsorption and

reaction-calcination cycle method and the property for photoelectrochemical water oxidation

○Furukawa Yuichi¹, Shu Nakashima¹, Musashi Fujishima², Hiroaki Tada¹ (1. Graduate School of Science and Engineering, Kindai University, 2. Faculty of Science and Engineering, Kindai University)

3:00 PM - 3:20 PM

Room 14

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

[A14-1am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Takahiro Sasamori, Hitoshi Miyasaka

9:00 AM - 11:00 AM Room 14 (Online Meeting)

[A14-1am-01] Synthesis of Unsaturated Silicon Clusters Utilizing Asymmetrically Substituted

Disilanes

○Yamato Omatsu¹, Yoshiyuki Mizuhata¹, Norihiro Tokitoh¹ (1. Institute for Chemical Research, Kyoto University)

9:00 AM - 9:20 AM

[A14-1am-02] Synthesis of 2-Heteroazulenes Containing a Silicon or Germanium Atom as a Skeletal Element

○Taku Oshiro¹, Yoshiyuki Mizuhata¹, Norihiro Tokitoh¹ (1. Institute for Chemical Research, Kyoto University)

9:20 AM - 9:40 AM

[A14-1am-03] Syntheses and properties of dinuclear Co complexes containing unique tetra-oxolene bridging ligands with different substituents and bulky ancillary ligands

○Takuto Mibu¹, Yusaku Suenaga¹, Masahiko Maekawa², Takashi Okubo^{1,2}, Takayoshi Kuroda¹ (1. Graduate school of science and engineering of Kindai university, 2. Research and Institute of Science and Technology, Kindai University)

9:40 AM - 10:00 AM

[A14-1am-04] Development of 3d-4f heterometallic polynuclear complexes with a large magnetocaloric effect

○Takuya SHIGA¹, Haruka Miyamoto¹, Honami Ito¹, Hiroki Oshio¹, Masayuki Nihei¹ (1.

University of Tsukuba)

10:00 AM - 10:20 AM

- [A14-1am-05] Selective formation of cyclic Cu(II)-Ni(II) arrangement showing effective antiferromagnetic spin coupling by using a tripeptide ligand

○Eri Suganuma¹, Shun Kimura^{2,4}, Hirotoshi Mori^{3,4}, Jun Okabayashi², Tetsuro Kusamoto⁴, Ryosuke Miyake¹ (1. Ochanomizu Univ., 2. The Univ. of Tokyo, 3. Chuo Univ., 4. IMS)

10:20 AM - 10:40 AM

- [A14-1am-06] Characterization of the Cu(I)-phenoxyl radical complex formed by the valence tautomerization of the Cu(II)-phenolate complex

○Yuto Shima¹, Takashi Suzuki¹, Yuichi Shimazaki¹ (1. Graduate School of Science and Engineering, Ibaraki University)

10:40 AM - 11:00 AM

Room 12

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

[A12-1am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Yuma Morimoto, Shigeyuki Masaoka, Yasuhiro Arikawa
9:00 AM - 11:40 AM Room 12 (Online Meeting)

- [A12-1am-01] Proton transfer in electrochemical CO₂ reduction by iron porphyrin complexes: mechanistic investigation and active control

○Kento Kosugi¹, Mio Kondo¹, Shigeyuki Masaoka¹ (1. Osaka university)

9:00 AM - 9:20 AM

- [A12-1am-02] Catalytic Nitrogen Fixation by Iron Dinitrogen Complexes Bearing Anionic PCP-type Pincer Ligands

○Shogo Kuriyama¹, Takeru Kato¹, Hiromasa Tanaka², Asuka Konomi³, Yoshizawa Kazunari³, Yoshiaki Nishibayashi¹ (1. School of Engineering, The University of Tokyo, 2. School of Liberal Arts and Sciences, Daido University, 3. Institute for Materials Chemistry and Engineering, Kyushu University)

9:20 AM - 9:40 AM

- [A12-1am-03] Rate Determining Factor in C–H Bond

Scission of Inert Alkanes by Fe(IV)(oxide)(porphyrin- π -cation radical)

○Yuma Morimoto¹, Kosuke Fukui¹, Hiroshi Fujii², Shino u Itoh¹ (1. Osaka Univ., 2. Nara Women's Univ.)

9:40 AM - 10:00 AM

- [A12-1am-04] Development of dehydrogenation of ammonia borane or hydrosilanes catalyzed by iron complexes

○Yoshinao Kobayashi¹, Yusuke Sunada^{1,2} (1. School of Engineering, The Univ. of Tokyo, 2. IIS, The Univ. of Tokyo)

10:00 AM - 10:20 AM

- [A12-1am-05] DFT Studies on the Mechanism of CO₂ Reduction Catalyzed by Diazapyridinophane Metal Complexes

○Yuto Sakaguchi¹, Kosei Yamauchi¹, Ken Sakai¹ (1. Dept. Chem. Kyushu Univ.)

10:20 AM - 10:40 AM

- [A12-1am-06] Structures and chemical properties of oxidized forms of ferrocene-substituted dihydroquinazolinone showing self-complementary hydrogen-bond interactions

○Mikihiro Hayashi¹ (1. Nagasaki University)

10:40 AM - 11:00 AM

- [A12-1am-07] Photocatalytic CO₂ reduction to CO using osmium complexes bearing PNNP-type tetradentate ligands

○Kenji Kamada¹, Jieun Jung¹, Susumu Saito^{1,2} (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

11:00 AM - 11:20 AM

- [A12-1am-08] Alkane Oxidation with Peroxide Species Catalyzed by Osmium Tetroxide

○Tomohiro Fujimoto¹, Hideki Sugimoto¹, Shinobu Itoh¹ (1. Grad. Sch. Eng., Osaka Univ.)

11:20 AM - 11:40 AM

Room 13

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

[A13-1am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryo Ohtani, Yoko Sakata, Hiroshi Sato

9:00 AM - 11:40 AM Room 13 (Online Meeting)

- [A13-1am-01] The development of stimuli-responsive metal complex
 ○Yoshihiro Sekine¹, Shinya Hayami¹ (1. Kumamoto University)
 9:00 AM - 9:20 AM
- [A13-1am-02] CO₂-induced spin-state conversion in a porous molecular crystal consisting of a cobalt(II) complex
 ○Manabu Nakaya¹, Shinya Hayami² (1. Josai University, 2. Kumamoto University)
 9:20 AM - 9:40 AM
- [A13-1am-03] [2]Catenane-Based Porous Crystals
 ○Hiroshi Sato^{1,2} (1. The University of Tokyo, 2. JST-PRESTO)
 9:40 AM - 10:00 AM
- [A13-1am-04] Structural conversions of xanthene-based dinuclear macrocyclic cobalt(III) metallohosts by ligand exchange and control of their guest recognition behavior
 ○Okura Kenji¹, Yoko Sakata^{1,2}, Shigehisa Akine^{1,2} (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. WPI Nano Life Science Institute, Kanazawa University)
 10:00 AM - 10:20 AM
- [A13-1am-05] Selective encapsulation of alkali metal ions in a chiral trinickel(II) metallocryptand and its regulation of helicity inversion
 ○Sk Asif Ikbal¹, Yoko Sakata², Shigehisa Akine² (1. Nano Life Science Institute, Kanazawa University, 2. Nano Life Science Institute, Graduate School of Natural Science and Technology, Kanazawa University)
 10:20 AM - 10:40 AM
- [A13-1am-06] Mononuclear and Polynuclear Cobalt(II) or Cobalt(III) Complexes Bearing Multidentate Hydrazonato Ligands with Pyridyl and Imidazolyl Donor Groups: Synthesis, Crystal Structures and Properties.
 ○DANIEL BOATENG ACHEAMPONG¹, YUKINARI SUNATSUKI¹, TAKAYOSHI SUZUKI¹ (1. OKAYAMA UNIVERSITY)
 10:40 AM - 11:00 AM
- [A13-1am-07] Classification of Crystallization Behavior and Chirality Control of M^{II}-Ln^{III}-M^{II} Trinuclear Complexes exhibiting Absolute

Spontaneous Resolution

○Kazuma Takahara¹, Yuuki Horino¹, Yukinari Sunatsuki¹, Takayoshi Suzuki¹ (1. The Univ. of Okayama)

11:00 AM - 11:20 AM

- [A13-1am-08] A Monatomic Silicon Complex Coordinated by Two Different Silylene Ligands and Ligand Exchange Reactions at the Monatomic Silicon Center

○Taichi Koike¹, Takeaki Iwamoto¹ (1. Tohoku Univ.)

11:20 AM - 11:40 AM

Room 15

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

[A15-1pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Naoki Ishida, Kazuhiko Semba

1:00 PM - 3:20 PM Room 15 (Online Meeting)

- [A15-1pm-01] Rh(I)-Catalyzed [2+2+1] Carbonylative Cycloaddition Reaction of Diynes
 Tsumoru Morimoto¹, ○JINGWEN JIA¹, Yoshiko Yamaguchi¹, Hiroko Yamada¹, Kiyomi Kakiuchi¹ (1. NAIST)
 1:00 PM - 1:20 PM
- [A15-1pm-02] Rh(I)- and Rh(II)-catalyzed C-H alkylation of benzylamines with alkenes and its application in flow.
 ○Amrita Das¹, Naoto Chatani¹ (1. Osaka University)
 1:20 PM - 1:40 PM
- [A15-1pm-03] Construction of a Helical Exocyclic Diene Scaffold via Rh-Catalyzed Cycloisomerization of 1,6-Diynes Bearing a Cyclopropanol Moiety
 ○Tomohiro Kikuchi¹, Takeshi Yasui¹, Yoshihiko Yamamoto¹ (1. Grad. Sch. Pharm. Sci., Nagoya Univ.)
 1:40 PM - 2:00 PM
- [A15-1pm-04] Synthesis of Chiral Cyclohexadienylamines by Cationic Rhodium(I)-Catalyzed Highly Selective Intermolecular Cross-Cyclotrimerization
 ○Kohei Fujii¹, Koji Masutomi¹, Yu Shibata¹, Yuki Naagashima¹, Ken Tanaka¹ (1. Tokyo Institute

of Technology)

2:00 PM - 2:20 PM

[A15-1pm-05] Catalytic hydrogenation of carboxylic acids though *in situ* esterification using a sterically confined Ir complex

○Bendik Groemer¹, Shota Yoshioka¹, Susumu Saito^{2,1} (1. Nagoya University, Graduate School of Science, 2. Nagoya University, RCMS)

2:20 PM - 2:40 PM

[A15-1pm-06] Site-Selective Magnesiation of Multi-Fluorinated Arenes Catalyzed by Rhodium-Aluminum Bimetallic Complexes

○Ikuya Fujii¹, Kazuhiko Semba¹, Yoshiaki Nakao¹ (1. Grad. Sch. Eng., Kyoto Univ.)

2:40 PM - 3:00 PM

[A15-1pm-07] Facile synthesis of indeno[1,2-c]isoquinolines by rhodium(III)-catalyzed cyclocondensation of benzamides with diazo compounds *via* catalytic cleavage of C-H bond followed by cyclization

○Dongyoung Kim¹, Risako Miura¹, Yu Kimura¹, Teruyuki Kondo¹ (1. Grad. Sch. Eng., Kyoto Univ.)

3:00 PM - 3:20 PM

Room 17

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

[A17-1am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair:Hiroshi Shinokubo, Masashi Hasegawa
9:00 AM - 11:40 AM Room 17 (Online Meeting)

[A17-1am-01] Synthesis and Properties of Spiro-double Sila[7]helicene: The LUMO Spiro-conjugation

○Nozomi Terada¹, Keisuke Uematsu², Ryota Higuchi², Yuki Tokimaru¹, Yosuke Sato¹, Koji Nakano², Kyoko Nozaki¹ (1. Department of Chemistry and Biotechnology, The University of Tokyo, 2. Department of Applied Chemistry, Tokyo university of Agriculture and Technology)

9:00 AM - 9:20 AM

[A17-1am-02] Modulation of Aromaticity and Properties of Porphyrins by Peripheral Heterole-fused Structures

○Issei Nishimura¹, Tomohiro Higashino¹, Hiroshi

Imahori^{1,2} (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ.)

9:20 AM - 9:40 AM

[A17-1am-03] Development of Heavy Chalcogen-Embedded U-Shaped Heteroacenes Having Bilayer Self-Organization Capability

○Tatsuya Mori^{1,2}, Takuma Yasuda^{1,2} (1. Grad. Sch. Eng., Kyushu Univ., 2. IFRC, Kyushu Univ.)

9:40 AM - 10:00 AM

[A17-1am-04] Development of polycyclic aromatic compounds with a nitrogen-based redox property

○Keisuke Fujimoto¹, Shota Masuda¹, Kentaro Sasaki¹, Satoshi Takimoto¹, Masaki Takahashi¹ (1. Shizuoka University)

10:00 AM - 10:20 AM

[A17-1am-05] Nearly Quantitative Emission from the Crystals of Boron β -Diiminate Complexes

○Shunichiro ITO¹, Miyako HASHIZUME¹, Kazuo TANAKA¹, Yoshiki CHUJO¹ (1. Kyoto University)

10:20 AM - 10:40 AM

[A17-1am-06] Creation of Luminescent Polymorphic Material Based on Chirality of Boron-Fused Azomethine Complex

○Shunsuke Ohtani¹, Masayuki Gon¹, Kazuo Tanaka¹, Yoshiki Chujo¹ (1. Grad. Sch. Eng., Kyoto Univ.)

10:40 AM - 11:00 AM

[A17-1am-07] Synthesis of a hyperconjugative antiaromatic compound and weakened antiaromaticity in its dimeric structure.

○Shotaro Ito¹, Takuya Kuwabara¹, Youichi Ishii¹ (1. Chuo University)

11:00 AM - 11:20 AM

[A17-1am-08] Synthesis and Photophysical Properties of Dipyrrolyldiketone Pt^{II} Complexes as Anion-Responsive π -Electronic Systems Forming Ion-Pairing Assemblies

○Atsuko Kuno¹, Hiromitsu Maeda¹ (1. Ritsumeikan Univ.)

11:20 AM - 11:40 AM

Room 9

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

[A09-1am] 12. Organic Chemistry -Organic Crystals,
Supramolecular Chemistry-

Chair:Katsuaki Konishi, Norimitsu Tohnai

9:00 AM - 11:40 AM Room 9 (Online Meeting)

[A09-1am-01] Dynamic Structural Conversions of
Rotaxanes Having a Cyclic Cobalt(III)
Metallohost by Addition of Amines
○Misato Yamamoto¹, Yoko Sakata^{1,2}, Shigehisa
Akine^{1,2} (1. Graduate School of Natural Science
and Technology, Kanazawa University, 2. WPI
Nano Life Science Institute, Kanazawa
University)

9:00 AM - 9:20 AM

[A09-1am-02] Seeded polymerization of D-A-D-type dyes
and its fluorescence imaging
○Soichiro Ogi¹, Yoshiki Imai¹, Shigehiro
Yamaguchi^{1,2} (1. Graduate School of Science,
Nagoya University, 2. Institute of Transformative
Bio-Molecules, Nagoya University)

9:20 AM - 9:40 AM

[A09-1am-03] The effects of alkyl chain lengths on the
emission of PEG-terminated gold(I)-alkane
thiolate coordination polymer
○Midori Murakami¹, Yukatsu Shichibu¹, Katsuaki
Konishi¹ (1. Grad. Sch. Env. Sci., Hokkaido
Univ.)

9:40 AM - 10:00 AM

[A09-1am-04] Fluorinated Porous Organic Cage
Compounds

○Bernd M. Schmidt¹ (1. Heinrich Heine
University Dusseldorf)

10:00 AM - 10:20 AM

[A09-1am-05] Photo-induced spatial control of out-of-
equilibrium network pattern of peptide
nanofibers in a supramolecular double
network hydrogel

○Wataru Tanaka¹, Ryou Kubota¹, Itaru
Hamachi^{1,2} (1. Graduate School of Engineering,
Kyoto University, 2. JST-ERATO)

10:20 AM - 10:40 AM

[A09-1am-06] Controlled Synthesis of Supramolecular
Concentric Toroid

○Norihiko Sasaki^{1,2}, Masayuki Takeuchi²,
Kazunori Sugiyasu^{1,2} (1. Kyushu university, 2.
National Institute for Materials)

10:40 AM - 11:00 AM

[A09-1am-07] Control of supramolecular self-sorting
network by dynamic covalent chemistry.
○Kazutoshi Nagao¹, Ryou Kubota¹, Wataru
Tanaka¹, Ryotaro Matsumura¹, Takuma Aoyama²,
Kenji Urayama², Itaru Hamachi^{1,3} (1. Kyoto
university Grad. Sch. of Eng., Kyoto Univ., 2. Grad.
Sch. of Sci. and Tech., Kyoto Inst. of Tech., 3.
JST-ERATO)

11:00 AM - 11:20 AM

[A09-1am-08] Multiscale imaging reveals four distinct
hierarchical networks in
supramolecular/polymer hydrogel
composites
○Keisuke Nakamura¹, Ryou Kubota¹, Kei Sada¹,
Takuma Aoyama², Kenji Urayama², Itaru
Hamachi^{1,3} (1. Grad. Sch. of Eng., Kyoto Univ.,
2. Grad. Sch. of Sci. and Eng., Kyoto Inst. of Tech.,
3. JST ERATO)

11:20 AM - 11:40 AM

Room 11

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

[A11-1pm] 14. Organic Chemistry -Aromatic,
Heterocyclic, and Heteroatom
Compounds-

Chair:Yohei Shimizu, Okano Kentaro

1:00 PM - 3:00 PM Room 11 (Online Meeting)

[A11-1pm-01] Defluorophosphinylative Synthesis of Aryl
Phosphorus Compounds

○Zhensheng You¹, Kosuke Higashida^{1,2},
Tomohiro Iwai³, Masaya Sawamura^{1,2} (1.
Department of Chemistry, Faculty of Science,
Hokkaido University, 2. WPI-ICReDD, 3.
Department of Basic Science, Graduate School
of Art and Sciences, The University of Tokyo)

1:00 PM - 1:20 PM

[A11-1pm-02] Sulfonylthiolation of Arenes via Selective
Activation of SS-morpholino
dithiosulfonate

○Kazuya Kanemoto¹, Koudai Furuhashi¹,
Tokiharu Watanabe¹, Hayato Asanuma¹, Shin-
ichi Fukuzawa¹ (1. Chuo University)

1:20 PM - 1:40 PM

[A11-1pm-03] Development of Selective Mono- and
Difluorination of Silyl Enol Ethers using

Novel Electrophilic Fluorinating Reagents

○Akiya Adachi¹, Kohsuke Aikawa¹, Yuichiro Ishibashi², Kyoko Nozaki¹, Takashi Okazoe^{1,2}
(1. Sch. of Eng., The Univ. of Tokyo, 2. AGC Inc.)

1:40 PM - 2:00 PM

- [A11-1pm-04] Alkyltriflones in the Ramberg–Bäcklund Reaction for the synthesis of *gem*-difluoroalkenes
○Yuki Maekawa^{1,3}, Masakazu Nambo¹, Daisuke Yokogawa², Cathleen M Crudden^{1,3} (1. Nagoya University, Institute of Transformative Bio-Molecules, 2. University of Tokyo, 3. Queen's University)

2:00 PM - 2:20 PM

- [A11-1pm-05] Trapping of Transient Thienyllithiums in Halogen Dance Using Zinc Chloride Diamine Complex
○Kengo Inoue¹, Suguru Hirai¹, Yuki Hayashi¹, Kentaro Okano¹, Atsunori Mori^{1,2} (1. Kobe Univ., 2. Research Center for Membrane and Film Technology)

2:20 PM - 2:40 PM

- [A11-1pm-06] Control of Regioselectivity in Hypervalent Iodine-mediated Sulfonyloxylactonization by Noncovalent Interactions in Ion Pairs
○Masaki Fujie¹, Yoshihiro Nishimoto¹, Makoto Yasuda¹ (1. Osaka University)

2:40 PM - 3:00 PM

Room 10

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

[A10-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair:Junichi Ito, Yoshihiro Nishimoto
1:00 PM - 3:00 PM Room 10 (Online Meeting)

- [A10-1pm-01] Model Study on the Catalytic Cycle of GPx1 and GPx4 by Utilizing Cradled Selenopeptides
○Ryosuke Masuda¹, Shohei Sase¹, Satoru Kuwano¹, Kei Goto¹ (1. Tokyo Institute of Technology)
- 1:00 PM - 1:20 PM

- [A10-1pm-02] In-catalyzed C–F bond transformation via

oxymetalation/ β -fluorine elimination to access fluorinated isocoumarins

○Tetsuji Yata¹, Yoshihiro Nishimoto¹, Kouji Chiba², Makoto Yasuda¹ (1. Grad. Sch. Eng., Osaka Univ., 2. MOLSIS Inc.)

1:20 PM - 1:40 PM

- [A10-1pm-03] Reactivity of Alkyl-Substituted Al Anion
○Satoshi Kurumada¹, Kengo Sugita¹, Ryo Nakano¹, Makoto Yamashita¹ (1. The Univ. of Tokyo)
- 1:40 PM - 2:00 PM

- [A10-1pm-04] Metal-free Transient Auxiliary Directed C-H Borylation of Benzaldehyde Derivatives
○Supriya Rej¹, Naoto Chatani¹ (1. Osaka University)
- 2:00 PM - 2:20 PM

- [A10-1pm-06] Synthesis and Properties of Two Boron-containing Electron-deficient Heteroacenes
○Masato Ito¹, Naoki Ando¹, Shigehiro Yamaguchi^{1,2} (1. Grad. Sch. Sci., Nagoya Univ., 2. Institute of Transformative bio-Molecules, Nagoya Univ.)
- 2:40 PM - 3:00 PM

Room 20

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

[A20-1am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair:Ryo Yazaki, Tsuyoshi Mita, Hiroki Takezawa
9:00 AM - 11:20 AM Room 20 (Online Meeting)

- [A20-1am-01] Oxidative Dearomatization of Arenols Using High-performance Hypohalite Catalysis
○Takehiro Kato¹, Muhammet Uyanik¹, Kazuaki Ishihara¹ (1. Nagoya university)
- 9:00 AM - 9:20 AM

- [A20-1am-02] Chemoselective Cleavage of Si–C(sp³) Bonds in Unactivated Tetraalkylsilanes Using Iodine Tris(trifluoroacetate)
○Keitaro Matsuoka¹, Narumi Komami¹, Keito Watanabe¹, Masahiro Kojima¹, Tsuyoshi Mita^{2,3}, Kimichi Suzuki^{2,3,4}, Satoshi Maeda^{2,3,4}, Tatsuhiko Yoshino¹, Shigeki Matsunaga^{1,5} (1. Faculty of Pharmaceutical sciences, Hokkaido University, 2. WPI-ICReDD, 3. JST-ERATO, 4. Faculty of

Science, Hokkaido University, 5. GI-CoRE)

9:20 AM - 9:40 AM

[A20-1am-03] Chemo-, Diastereo- and Enantioselective
Catalytic Aldol Reaction of Carboxylic Acids
by Boron and Silicon Hybrid Activation

○Taiki Fujita¹, Harunobu Mitsunuma¹, Motomu
Kanai¹ (1. Grad. Sch. Pharm. Sciences, The
Univ. of Tokyo)

9:40 AM - 10:00 AM

[A20-1am-04] Chemoselective Transesterification of
Methyl (Meth)acrylates Catalyzed by
Sodium(I) or Magnesium(II) Aryloxides

Jie Qi Ng¹, Hiro Arima¹, Takuya Mochizuki¹,
Kohei Toh¹, Kai Matsui¹, Manussada Ratanasak²,
Junya Hasegawa², Manabu Hatano³, ○Kazuakai
Ishihara¹ (1. Nagoya University, 2. Hokkaido
University, 3. Kobe Pharmaceutical University)

10:00 AM - 10:20 AM

[A20-1am-05] Catalytic α - Oxidation of Carboxylic Acids
via Radical Process

○Tsukushi Tanaka¹, Ryo Yazaki¹, Takashi
Ohshima¹ (1. Kyushu Univ.)

10:20 AM - 10:40 AM

[A20-1am-06] Hydrogenation of Aromatic Compounds
Catalyzed by Cooperative Systems of
Heterogeneous Rh-Pt Nanoparticle
catalysts and Lewis Acids

○Hiroyuki Miyamura¹, Shu Kobayashi¹ (1. The
University of Tokyo)

10:40 AM - 11:00 AM

[A20-1am-07] Diastereoselective pericyclic cascades of
linear terpenoids through conformational
control in a bowl-shaped host

○Tomoya Kanda¹, Hiroki Takezawa¹, Makoto
Fujita¹ (1. The University of Tokyo)

11:00 AM - 11:20 AM

Room 21

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

[A21-1am] 16. Natural Products Chemistry,
Chemical Biology

Chair: Yoshio Ando, Keisuke Nishikawa

9:00 AM - 11:40 AM Room 21 (Online Meeting)

[A21-1am-01] Total Synthesis of Antitumor Antibiotic
Saptomycin H

○Jun Shimura¹, Yoshio Ando¹, Ken Ohmori¹,
Keisuke Suzuki¹ (1. Tokyo Institute of
Technology)

9:00 AM - 9:20 AM

[A21-1am-02] Total Synthesis of Tetrameric Epicatechin
Parameritannin A2 via Cascade Pummerer-
type Reaction.

○Vipul Vithal Betkekar¹, Keisuke Suzuki¹, Ken
Ohmori¹ (1. Tokyo Institute of Technology)

9:20 AM - 9:40 AM

[A21-1am-03] Synthetic Study of a Polyol Unit of
Amphotericin B Using Organocatalysts

○Genki Kawauchi¹, Yujiro Hayashi¹ (1. Univ. of
Tohoku)

9:40 AM - 10:00 AM

[A21-1am-04] Intramolecular Oxidative Nucleophilic
Aromatic Substitution Reaction between
Phenols and Alkenes

○Hiroki Deguchi¹, Hanaya Kengo¹, Sugai
Takeshi¹, Higashibayashi Shuhei¹ (1. Faculty of
Pharmacy, Keio Univ.)

10:00 AM - 10:20 AM

[A21-1am-05] Unified Total Synthesis of Pentacyclic
Stemoamide-type Alkaloids

○Yasuki Soda¹, Yasukazu Sugiyama¹, Makoto
Yoritake¹, Hayato Tajima¹, Kana Shibuya¹,
Yoshito Takahashi¹, Chisato Ogihara¹, Takeshi
Oishi¹, Takaaki Sato¹, Noritaka Chida¹ (1. Keio
University)

10:20 AM - 10:40 AM

[A21-1am-06] Total Synthesis and Structural
Determination of a Marine Natural Product
Callicladol with Potent Antitumor Activity
against Mouse Leukemia Cells

○Kento Nishikibe¹, Keisuke Nishikawa¹, Yoshiki
Morimoto¹ (1. Osaka City University)

10:40 AM - 11:00 AM

[A21-1am-07] Development of New Synthetic Method of
the DFGH-ring of Physalin-Type Natural
Products and SAR Study of the Pseudo-
Natural Products

○Makoto Yoritake¹, Yuki Morita¹, Masaki
Morita^{1,2}, Tomohiro Yamashita¹, Mikiko
Sodeoka², Go Hirai^{1,2} (1. Kyushu University
Graduate School of Pharmaceutical Science, 2.
RIKEN)

11:00 AM - 11:20 AM

[A21-1am-08] Unusual Skeletal Rearrangement Reaction in Brasilane-Type Structure Biosynthesis○Hajime Sato^{1,2,3}, Masanobu Uchiyama^{2,3,4} (1.

Grad. Sch. Pharm. Chiba Univ., 2. Grad. Sch.

Pharm. Univ. Tokyo, 3. RIKEN, 4. Shinshu Univ.

RISM)

11:20 AM - 11:40 AM

Room 26

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

[A26-1am] 17. Biofunctional Chemistry, Biotechnology

Chair:Shinya Hanashima, Kazuhito Tanabe

9:00 AM - 11:40 AM Room 26 (Online Meeting)

[A26-1am-01] Effects of Isovaleraldehyde on Biomimetic MembranesYudai Yamada¹, Yukiyasu Chounan¹, ○TsuyoshiYoda² (1. Department of Natural Science,

Faculty of Education, Hirosaki University, 2.

Aomori Prefectural Industrial Technology

Research Center, Hirosaki Industrial Research Institute)

9:00 AM - 9:20 AM

[A26-1am-02] Thioacid-based strategy for the semi-synthesis of glycoproteins○Kota Nomura¹, Yuta Maki¹, Ryo Okamoto¹,Yasuhiro Kajihara¹ (1. Grad. Sch. Sci., Osaka Univ.)

9:20 AM - 9:40 AM

[A26-1am-03] Development of calreticulin inhibitor based on hybrid binding concept○Taiki Kuribara¹, Taiga Kojima¹, KeitaShibayama¹, Yoichi Takeda², Kiichiro Totani¹

(1. Seikei University, 2. Ritsumeikan University)

9:40 AM - 10:00 AM

[A26-1am-04] Development of Bioluminescent Probes for Visualizing and Quantifying of Endogenous RNAs in Real Time○Masatoshi Eguchi¹, Hideaki Yoshimura¹,Takeaki Ozawa¹ (1. The Univ. of Tokyo)

10:00 AM - 10:20 AM

[A26-1am-05] Development of DNA complex for efficient recognition of target cancer cells○Tatsuya Nishihara¹, Yuto Motohashi¹, ShuheiMoritani¹, Ryota Hidaka¹, Yuka Matsumura¹, RisaYamada¹, Kazuhito Tanabe¹ (1. Aoyama Gakuin University)

10:20 AM - 10:40 AM

[A26-1am-06] Development of waterproof bioelectrode using

polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) nanosheets and electrocardiogram measurements during bathing.

○Sho Mihara¹, Hui-Lin Lee², Shinji Takeoka¹ (1.

Waseda university, 2. Singapore Polytechnic)

10:40 AM - 11:00 AM

[A26-1am-07] Structural analysis of the lipid packing structures inside a single membrane

domain by low-flux scanning electron diffraction

○Masanao Kinoshita¹, Shimpei Yamaguchi¹,Nobuaki Matusmori¹ (1. Kyushu University)

11:00 AM - 11:20 AM

[A26-1am-08] Membrane lipids affect the interplay

between the transmembrane domain of the EGF receptor and ganglioside GM3 – thermodynamic quantification of the lateral interaction using FRET

○Mikito Nakano¹, Shinya Hanashima¹, ToshiakiHara¹, Kazuya Kabayama¹, Naoko Komura²,Hiromune Ando², Thomas K.M. Nyholm³, Peter JSlotte³, Michio Murata¹ (1. Graduate School of

Science, Osaka University, 2. Center for Highly

Advanced Integration of Nano and Life Sciences

(G-CHAIN), 3. Department of Biosciences, Åbo

Akademi University)

11:20 AM - 11:40 AM

Room 23

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

[A23-1am] 17. Biofunctional Chemistry, Biotechnology

Chair:Toshiyuki Kowada, Masayasu Taki

9:00 AM - 11:40 AM Room 23 (Online Meeting)

[A23-1am-01] Exploration of synthetic agents that inhibit intrinsically disordered circadian clock transcription factors

[○]Yusuke Hosoya¹, Wataru Nojo², Isao Kii¹,
Takanori Suzuki², Miki Imanishi³, Junko
Ohkanda¹ (1. Academic Assembly, Institute of
Agriculture, Shinshu University, 2. Department of
Chemistry, Faculty of Science, Hokkaido
University, 3. Institute for Chemical Research,
Kyoto University)

9:00 AM - 9:20 AM

[A23-1am-02] Synthetic Small Molecules for 14-3-3
Isoform-Selective Inhibition and Regulation
of Plant Functions

[○]Kotaro Nishiyama¹, Norio Kudo¹, Minoru
Yoshida^{1,2,3}, Yusuke Aihara⁴, Koji Takahashi^{4,5},
Toshinori Kinoshita^{4,5}, Takehiro Suzuki¹, Naoshi
Dohmae¹, Ayato Sato⁵, Sakuya Nakamura¹,
Shinya Hagihara^{1,5} (1. RIKEN Center for
Sustainable Resource Science, 2. Graduate
School of Agricultural and Life Sciences, The
University of Tokyo, 3. Collaborative Research
Institute for Innovative Microbiology, The
University of Tokyo, 4. Graduate School of
Science, Nagoya University, 5. WPI-ITbM, Nagoya
University)

9:20 AM - 9:40 AM

[A23-1am-03] Simultaneous detection of double-stranded
and G4 DNAs using a tripodal quinone-
cyanine dye

[○]Takashi Sakamoto^{1,2}, Zehui Yu², Yuto Otani¹
(1. Grad. School of Systems Eng., Wakayama
Univ., 2. Faculty of Systems Eng., Wakayama
Univ.)

9:40 AM - 10:00 AM

[A23-1am-04] Development of high-affinity fluorescent
probes for quantification of organellar
labile Zn²⁺

[○]Liu Rong¹, Toshiyuki Kowada^{1,2}, Toshitaka
Matsui^{1,2}, Shin Mizukami^{1,2} (1. Graduate School
of Life Sciences, Tohoku University, 2. Institute of
Multidisciplinary Research for Advanced
Materials, Tohoku University)

10:00 AM - 10:20 AM

[A23-1am-05] Development of multicolor labeling
reagents for Raman imaging using an algal
carotenoid by stable-isotope labelling

[○]Yusuke Yonamine¹, Joshua Mba², Yu Hoshino³,
Hideyuki Mitomo¹, Kuniharu Ijiri¹ (1. Research

Institute for Electronic Science, Hokkaido
University, 2. Graduate School of Life Science,
Hokkaido University, 3. Department of Chemical
Engineering, Faculty of Engineering, Kyushu
University)

10:20 AM - 10:40 AM

[A23-1am-06] Visualization of Lipid Metabolism Using an
Environment-Sensitive Fluorescent Fatty
Acid

[○]Keiji Kajiwara¹, Hiroshi Osaki¹, Keiko Kuwata¹,
Frank Glorius², Masayasu Taki¹, Shigehiro
Yamaguchi¹ (1. Nagoya Univ., 2. Universität
Münster)

10:40 AM - 11:00 AM

[A23-1am-07] Effect of Stereoisomerism in Developing
Highly Photostable and Fluorogenic NIR
Probes for Long-term Imaging

[○]Qian WU¹, Masayasu Taki¹, Shigehiro
Yamaguchi¹ (1. Nagoya University)

11:00 AM - 11:20 AM

[A23-1am-08] Development of Aldehyde Dehydrogenase-
Responsive Turn-on Fluorescent Probe for
Cancer Stem Cell Imaging

[○]Masahiro Oe¹, Koji Miki¹, Yoshifumi Ueda¹,
Yasuo Mori¹, Kouichi Ohe¹ (1. Grad. Sch. Eng.,
Kyoto Univ.)

11:20 AM - 11:40 AM

Room 25

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

[A25-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Kunihiro Morihiro, Yusuke Takezawa

9:00 AM - 11:40 AM Room 25 (Online Meeting)

[A25-1am-01] Development of the artificial triplex-forming
oligonucleotides containing chemically
modified nucleobases or sugar moieties

[○]Shuhei Nishizawa¹, Diasuke Ogata¹, Gaohong
Tu¹, Yu Itoh¹, Akihiro Ohkubo¹ (1. School of Life
Science and Technology, Department of Life
Science and Technology, Tokyo Institute of
Technology)

9:00 AM - 9:20 AM

[A25-1am-02] Synthesis of oligonucleotides containing
2'-O-alkylcarbamoylethyl modifications

and their properties.

○Tomohiro Kishimura¹, Koya Uekusa¹, Takahito Tomori¹, Yoshiaki Masaki¹, Kohji Seio¹ (1. Tokyo Tech.)

9:20 AM - 9:40 AM

[A25-1am-03] Hypoxia-Activated Floxuridine Oligomers via Bio-reduction of Nitro and/or Azo Functionalities

○Kunihiko Morihoro¹, Takuro Ishinabe¹, Masako Takatsu², Tsuyoshi Osawa^{1,2}, Akimitsu Okamoto^{1,2} (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. RCAST, The Univ. of Tokyo)

9:40 AM - 10:00 AM

[A25-1am-04] Development of small molecular efficient photosensitizer and application to sequence-selective photo-oxidation of guanosine

○Takashi Kanamori¹, Yuki Tsuga¹, Kohji Hamamoto¹, Chao Wang¹, Tomohiro Yube¹, Ruoyu Li¹, Hideya Yuasa¹ (1. Tokyo Institute of Technology)

10:00 AM - 10:20 AM

[A25-1am-05] Formation in solutions and crystal structure of a novel short Ag-DNA wire.

○Takahiro Atsugi¹, Jiro Kondo², Akira Ono¹ (1. Kanagawa Univ., 2. Sophia Univ.)

10:20 AM - 10:40 AM

[A25-1am-06] Metal-dependent stabilization of DNA duplexes containing 2-oxo-imidazole-4-carboxylate/carboxamide as nucleobases

○Lingyun Hu¹, Yusuke Takezawa¹, Mitsuhiro Shionoya¹ (1. Dept. of Chemistry, Grad. School of Science, The Univ. of Tokyo)

10:40 AM - 11:00 AM

[A25-1am-07] DNA-based Molecular Switches Driven by Metal Complexation of 5-Hydroxyuracil Nucleobases

○Keita Mori¹, Yusuke Takezawa¹, Mitsuhiro Shionoya¹ (1. Grad. School of Science, The Univ. of Tokyo)

11:00 AM - 11:20 AM

[A25-1am-08] Photocontrolled assembly of DNA origami nanostructures using photoswitching molecules

○Shubham Mishra¹, Soyoung Park¹, Tomoko Emura¹, Kumi Hidaka¹, Hiroshi Sugiyama^{1,2},

Masayuki Endo^{1,2} (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Sciences, Kyoto University)

11:20 AM - 11:40 AM

Room 24

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

[A24-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Satoshi Abe, Osami Shoji

9:00 AM - 11:40 AM Room 24 (Online Meeting)

[A24-1am-01] Features and properties of catalytic antibody, H34, capable of degrading an immune checkpoint PD-1 molecule.

○Emi Hifumi¹, Hiroaki Taguchi², Tamami Nonaka¹, Taizo Uda³ (1. Oita University, 2. Suzuka University of Medical Science, 3. ISIT)

9:00 AM - 9:20 AM

[A24-1am-02] Production and properties of a bifunctional catalytic antibody that simultaneously degrades two types of antigens (Tau & Aβ) (II)

○Taizo Uda¹, Hiroaki Taguchi², Tamami Nonaka³, Emi Hifumi³ (1. ISIT, 2. Suzuka University of Medical Science, 3. Oita University)

9:20 AM - 9:40 AM

[A24-1am-03] The unfolding mechanism of Pseudoazurin determined by Small Angle Neutron Scattering and Molecular Dynamics simulation

○Attila Taborosi¹, Takahide Yamaguchi^{1,2}, Seiji Mori¹, Takamitsu Kohzuma^{1,2} (1. Ibaraki University, 2. Frontier Research Center for Applied Atomic Sciences)

9:40 AM - 10:00 AM

[A24-1am-04] Properties of Prussian blue encapsulated in the cavity of ferritin L134P mutant

○Yuta Ikenoue¹, Takanori Nishioka¹, Hiroshi Nakajima¹ (1. Osaka City Univ.)

10:00 AM - 10:20 AM

[A24-1am-05] Construction of aromatic clusters in protein cages.

○Hiroki Noya¹, Yuki Hishikawa¹, Basudev Maity¹, Satoshi Abe¹, Takafumi Ueno¹ (1. School of Life

Science and Technology, Tokyo Institute of Technology)

10:20 AM - 10:40 AM

[A24-1am-06] Accumulation of aromatic molecules and reaction control in a protein cage

[○]Yuki Hishikawa¹, Hiroki Noya¹, Basudev Maity¹, Satoshi Abe¹, Takafumi Ueno¹ (1. Tokyo Institute of Technology)

10:40 AM - 11:00 AM

[A24-1am-07] Dimerization of Heme Acquisition System Protein A (HasA) with Meso-substituted Porphyrin Dimer

[○]Garyo Ueda¹, Yuma Shisaka¹, Erika Sakakibara¹, Shinya Ariyasu¹, Hiroshi Sugimoto^{2,3}, Osami Shoji^{1,3} (1. The Univ. of Nagoya, 2. Institute of Physical and Chemical Research, SPring8, 3. JST CREST)

11:00 AM - 11:20 AM

[A24-1am-08] Construction of Heme Protein HasA Capturing Artificial Metal Complexes for Novel Biocatalysts

[○]Erika Sakakibara¹, Yuma Shisaka¹, Hiroshi Sugimoto^{2,3}, Osami Shoji^{1,3} (1. Grad. Sch. Sci., Nagoya Univ., 2. RIKEN SPring-8 Center, 3. JST-CREST)

11:20 AM - 11:40 AM

Room 27

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

[A27-1pm] 18. Polymer

Chair: Yasuhiro Kohsaka, Kanbayashi Naoya

1:00 PM - 3:40 PM Room 27 (Online Meeting)

[A27-1pm-02] Synthesis of unsaturated polyesters via ring-opening polymerization induced by conjugate substitution

Keito Hagiwara¹, [○]Yasuhiro Kohsaka^{1,2} (1. Fac. of Textile Sci. & Tech., Shinshu University, 2. RISM, Shinshu University)

1:20 PM - 1:40 PM

[A27-1pm-03] 2D Polymeric Nanomaterials via MOF-Templated Copolymerization

[○]Marta Ximenis Campins¹, Nobuhiko Hosono¹, Takashi Uemura¹ (1. The University of Tokyo)

1:40 PM - 2:00 PM

[A27-1pm-04] Three Dimensionally-Hyperbranched Fe(II)-

based Metallo-Supramolecular Polymer for Electrochromic Application

[○]Narayana Yemineni¹, Masayoshi HIGUCHI¹ (1. National Institute for Materials Science)

2:00 PM - 2:20 PM

[A27-1pm-05] Ligand Induced Low Operation Voltage Ru-based Metallo-supramolecular Polymer as Energy Saving Electrochromic Film with Long Optical Memory

[○]SANTRA Chandra Dines¹, HIGUCHI Masayoshi¹ (1. NIMS)

2:20 PM - 2:40 PM

[A27-1pm-06] Synthesis of Poly(quinolylene-2,3-methylene) Bearing Various Types of Amino Acid Derivatives as the Side Chain: Stability of π -Stacked Helical Architecture

[○]Kanbayashi Naoya¹, Yuki Kataoka¹, Taka-aki Okamura¹, Kiyotaka Onitsuka¹ (1. Department of Macromolecular Science Graduate School of Science Osaka University)

2:40 PM - 3:00 PM

[A27-1pm-07] The mechanochemistry of the cross-linked polymer containing cyclic mechanophores

[○]Jumpei Kida¹, Daisuke Aoki¹, Hideyuki Otsuka¹ (1. Dept. of Chem. Sci. and Eng., Tokyo Tech)

3:00 PM - 3:20 PM

[A27-1pm-08] Visualization of Polymer Crystallization and Neck-initiation in Uniaxial Tensile Deformation by Using Fluorescent Mechanochromophore

[○]Sota Kato¹, Daisuke Aoki¹, Kazusato Oikawa³, Kousuke Tsuchiya³, Naohiko Shimada², Atsushi Maruyama², Keiji Numata³, Hideyuki Otsuka¹ (1. Dept. of Chem. Sci. and Eng., Tokyo Tech., 2. Dept. of Life Sci. and Tech., Tokyo Tech., 3. RIKEN)

3:20 PM - 3:40 PM

Room 7

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

[A07-1am] 19. Colloid and Interface Chemistry

Chair: Yasuhiro Ishida, Masato Ikeda

9:00 AM - 11:40 AM Room 7 (Online Meeting)

[A07-1am-01] Polyester microdroplets, DNA liquid crystal coacervates, and other membraneless LLPS

assemblies as primitive compartments at the origins of life

○Tony Z Jia^{1,2}, Tommaso Fraccia³, Kuhan Chandru^{8,9}, Yayoi Hongo⁴, Rehana Afrin¹, Tomohiro Usui^{1,5}, Kunihiro Myojo⁶, H James Cleaves^{1,2,7}, Niraja Bapat^{1,10}, Ajay Verma¹⁰, Irena Mamajanov¹ (1. Earth-Life Science Institute, Tokyo Institute of Technology, 2. Blue Marble Space Institute of Science, 3. Institut Pierre-Gilles de Gennes, CBI, ESPCI Paris, Université PSL, CNRS, 4. Okinawa Institute of Science and Technology Graduate University, 5. JAXA Institute of Space and Astronautical Science, 6. Tokyo Institute of Technology, 7. Institute of Advanced Study, 8. Space Science Center (ANGKASA), Institute of Climate Change, Level 3, Research Complex, National University of Malaysia, 9. Department of Physical Chemistry, University of Chemistry and Technology, Prague, 10. Indian Institute of Science Education and Research)

9:00 AM - 9:20 AM

[A07-1am-02] Thermo-induced dynamics in cell-sized droplets of the aqueous hydroxypropyl cellulose solution coated with phospholipids

○Kazunari Yoshida¹, Keitaro Horii², Azusa Saito², Akito Takashima², Izumi Nishio² (1. Yamagata University, 2. Aoyama Gakuin University)

9:20 AM - 9:40 AM

[A07-1am-03] Creation of molecular system emerging multi-step phase transition of supramolecular architectures

○Daichi Sawada¹, Kouichi Asakura¹, Taisuke Banno¹ (1. Faculty of Science and Technology, Keio University)

9:40 AM - 10:00 AM

[A07-1am-04] Hydrogel Formed with 3D Continuous Phospholipid Membrane

○Saya Otake¹, Kou Okuro², Takuzo Aida¹ (1. The University of Tokyo, 2. The University of Hong Kong)

10:00 AM - 10:20 AM

[A07-1am-05] Life-like hydrogels of inorganic nanosheets

○Koki Sano^{1,2}, Yasuo Ebina³, Takayoshi Sasaki³, Yasuhiro Ishida¹ (1. RIKEN, 2. JST PRESTO, 3.

NIMS)

10:20 AM - 10:40 AM

[A07-1am-06] In situ Polymerization of a Highly Oriented Molecular Self-Assembly Formed by Acoustic Levitation

○Takashi Kajitani¹, Hiroki Tanaka¹, Koji Ohara², Takanori Fukushima¹ (1. Tokyo Tech, 2. JASRI)

10:40 AM - 11:00 AM

[A07-1am-07] Highly ordered quantum dot arrangements based on molecular assembly

○Mitsuaki Yamauchi¹, Seiya Yamamoto¹, Sadahiro Masuo¹ (1. Kwansei Gakuin University)

11:00 AM - 11:20 AM

[A07-1am-08] Orientational change of liquid crystals in a metal-organic framework

○Shizuka Anan¹, Hirotsugu Kikuchi¹ (1. Kyushu Univ.)

11:20 AM - 11:40 AM

Room 3

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

[A03-1pm] 20. Materials Chemistry -Basic and Application-

Chair: Jiro Abe, Takashi Kitao

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

[A03-1pm-01] Comparison of TD-DFT and semi-empirical methods for description of spectral properties of anthraquinone dyes using X-ray crystal structure.

○JIYONG HWANG¹, Sunghoon Kim¹, Shinya Matsumoto¹ (1. Yokohama National University)

1:00 PM - 1:20 PM

[A03-1pm-02] Chiral photovoltaic effect of liquid-crystalline binary mixtures based on π -conjugated compounds

○Atsushi Seki¹, Masafumi Yoshio², Yuki Mori³, Masahiro Funahashi^{3,4} (1. Tokyo University of Science, 2. National Institute for Materials Science, 3. Kagawa University, 4. National Institute of Advanced Industrial Science and Technology)

1:20 PM - 1:40 PM

[A03-1pm-03] Three-Dimensional Control of Periodic

Nanostructure of Cholesteric-Liquid-Crystals in Monodisperse Microparticles

○Tomoki Shigeyama¹, Kyohei Hisano¹, Osamu Tsutsumi¹ (1. Ritsumeikan Univ.)

1:40 PM - 2:00 PM

Science and Technology)

3:20 PM - 3:40 PM

[A03-1pm-04] A molecular crystal of a gold complex exhibiting reversible shape memory effect with luminescent color changes

○Chi Feng¹, Tomohiro Seki², Shunichi Sakamoto³, Toshiyuki Sasaki³, Satoshi Takamizawa³, Hajime Ito^{1,4} (1. Graduate School of Engineering, Hokkaido University, 2. Faculty of Science, Shizuoka University, 3. Graduate School of Nanobioscience, Yokohama City University, 4. WPI-ICReDD, Hokkaido University)

2:00 PM - 2:20 PM

[A03-1pm-05] Donor-acceptor-type organic semiconductors based on acendichalcogenophenediones

○Kohsuke Kawabata^{1,2}, Kazuo Takimiya^{1,2} (1. Tohoku Univ., 2. RIKEN)

2:20 PM - 2:40 PM

[A03-1pm-06] Scanning wave photopolymerization directs three-dimensional molecular alignment patterns in liquid-crystalline polymer films as an alignment layer

○Yoshiaki Kobayashi¹, Norihisa Akamatsu¹, Shoichi Kubo¹, Atsushi Shishido¹ (1. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

[A03-1pm-07] Angularly Anisotropic Giant Circularly Polarized Luminescence from Chiral Conjugated Polymer Microsphere

○Osamu Oki¹, Chidamber Kulkarni², Hiroshi Yamagishi¹, Stefan C. J. Meskers², Zhan-Hong Lin³, Jer-Shing Huang³, Bert Meijer², Yohei Yamamoto¹ (1. Fac. Pure and Appl. Sci., Univ. Tsukuba, 2. Eindhoven University of Technology, 3. Leibniz-IPHT)

3:00 PM - 3:20 PM

[A03-1pm-08] Bio-based Polymer Derived Anode Material for Fast Charging and Long Cycle Life Li-ion Battery

○Rajashekar Badam¹, Kottisa Sumala Patnaik¹, Yueying Peng¹, Tatsuo Kaneko¹, Noriyoshi. Matsumi¹ (1. Japan Advanced Institute of

[A19-1pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Nobuyuki Matubayasi, Yasuteru Shigeta

Fri. Mar 19, 2021 1:00 PM - 3:20 PM Room 19 (Online Meeting)

[A19-1pm-01] Triple point of Ar by constant energy molecular dynamics

○Yosuke Kataoka¹ (1. Hosei University)

1:00 PM - 1:20 PM

[A19-1pm-02] Study on Electron Density Distribution Map and Crystal Structure Factor of Low Pressure Phase and High Pressure Phase of Mg₃BN₃ by Using Modified Discrete Cosine Transform

○Hideo Hiraguchi¹ (1. The Institution of Professional Engineers, Japan)

1:20 PM - 1:40 PM

[A19-1pm-03] ISRS-induced terahertz wave generation process in DCMBI crystalline solid by Maxwell + polarizable MD multi-scale simulation

○Atsushi Yamada¹ (1. University of Tsukuba)

1:40 PM - 2:00 PM

[A19-1pm-04] Reaction dynamics of ion-molecule collision beyond reaction-path-based understanding

○Kohei Oda¹, Takuro Tsutsumi¹, Srihari Keshavamurthy^{2,3}, Kenji Furuya⁴, Tetsuya

Taketsugu^{3,5} (1. Graduate School of Chemical Sciences and Engineering, Hokkaido

University, 2. Department of Chemistry, Indian Institute of Technology, Kanpur, 3.

Department of Chemistry, Faculty of Science, Hokkaido University, 4. Faculty of Arts and

Science, Kyushu University, 5. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)

2:00 PM - 2:20 PM

[A19-1pm-05] Theoretical study on isotope fractionation in biotic uranium multistep reduction reaction

○Ataru Sato¹, Minoru Abe¹, Masahiko Hada¹ (1. Graduate School of Science, Tokyo Metropolitan University)

2:20 PM - 2:40 PM

[A19-1pm-06] Water Oxidation at N-Doped Graphene Oxides - Structure-Property Relationships and PCET Dynamics

○Fabian Weber^{1,3}, Jean Christophe Tremblay², Annika Bande³ (1. Chuo University, 2. Université de Lorraine, 3. Helmholtz-Zentrum Berlin)

2:40 PM - 3:00 PM

[A19-1pm-07] Static-field ionization rates of He-like ions by MCTDHF method

○Erik Loetstedt¹, Marcelo F Ciappina², Kaoru Yamanouchi¹ (1. The University of Tokyo, 2. Guangdong Technion - Israel Institute of Technology)

3:00 PM - 3:20 PM

定エネルギー分子動力学によるアルゴンの 3 重点

(法政大、生命科学) 片岡洋右

Triple point of Ar by constant energy molecular dynamics

(Faculty of Chemistry, Hosei University) Yosuke Kataoka

The triplet of argon was estimated by constant energy molecular dynamics. The basic cell consisted of 15552 Ar atoms. The initial atomic configuration had FCC, elongated FCC and vacuum part. The calculated triple point was consistent with the experimental and equation of state results.

Keywords : Triple Point; Molecular Dynamics; Ar; Constant Energy

直方体的基本セル内に 15552 個のアルゴン原子を配置し、定エネルギー法(NEV-MD)により 3 重点を定めた。初期配置には結晶部分と液体的密度の部分と空白部分を用意した。X,y,z 方向に周期境界条件を課した。レナードジョーンズ関数を仮定した。ポテンシャルエネルギーの平均値と原子配置の温度変化から 3 重点を定めた。圧力は表面張力の影響を受けない z 軸方向の成分を使用した。得られた 3 重点温度と圧力は実験値と比較して合理的なものである

Fig.1 にポテンシャルエネルギーの平均値 (E_p) の温度変化を示した。83K 付近のオレンジの点は固体液体気体が共存する(S+L+G)3 重点に対応する状態である。固体と気体の共存する系 (S+G) の値よりわずかに高いエネルギーであり液体と気体の共存系(L+G)の値よりは低い値を取っている。83K という値は実験値 83.8K に近い。

Fig.2 の 3 重点に対応する原子配置の例を示した。規則的構造が固体部分であり、それに隣接するランダムな構造が液体であり、低密度の領域が気体部分である。

3 重点における圧力は圧力テンソルの z 成分から求めた。これは Fig.2 に示すように界面が z 軸に垂直であるため、この成分は表面張力の影響を受けないためである。得られた圧力は 1atm である。この値は実験値 0.89atm に近い。

今回は定エネルギー法(NEV-MD)であるが、別に定温定体積分子動力学法(NTV-MD)で 3 重点を求めたところ、ほぼ同様の結果を得ている。

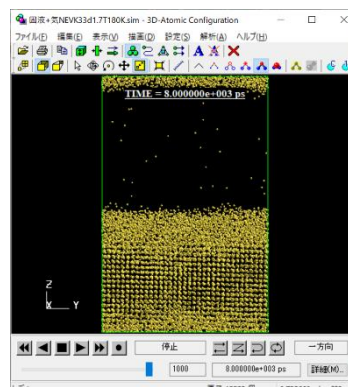
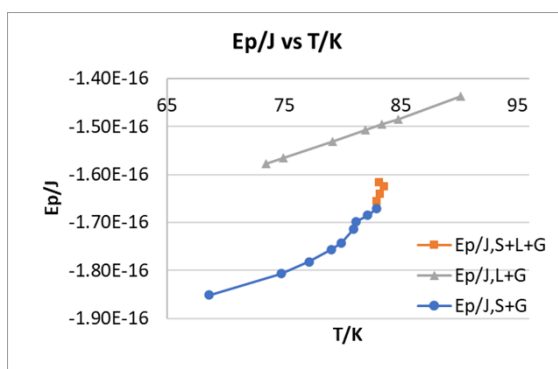


Fig.1 Potential energy vs temperature plot. Fig.2 Example of atomic configuration at triple point

Study on Electron Density Distribution Map and Crystal Structure Factor of Low Pressure Phase and High Pressure Phase of Mg_3BN_3 by Using Modified Discrete Cosine Transform

(¹Professional Engineer, Japan belonging to the Institution of Professional Engineers, Japan)

○Hideo Hiraguchi ¹

Keywords: Modified DCT; Electron Density Distribution Projection Map; Mg_3BN_3

We have found out that the 2D modified discrete cosine transform (DCT)^{1),2),6)} can draw the electron density distribution projection map of $\text{Mg}_3\text{BN}_3(\text{L})$ ^{3)~5)} by using 9×9 2D reflections shown in Fig. 1. Moreover, we have found out that the 3D DCT can draw a mirror symmetric electron density distribution map shown in Fig. 2 and the 3D modified DCT⁶⁾ can draw the electron density map of $\text{Mg}_3\text{BN}_3(\text{L})$ shown in Fig. 3 by using $9 \times 9 \times 9$ 3D reflections $((h,k,l), h:0 \sim 8, k:0 \sim 8, l:0 \sim 8)$. In

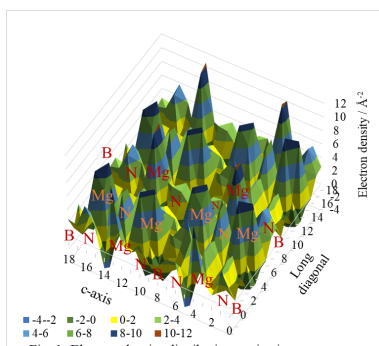


Fig. 1 Electron density distribution projection map of (110) hexagonal plane of $\text{Mg}_3\text{BN}_3(\text{L})$ by DCT

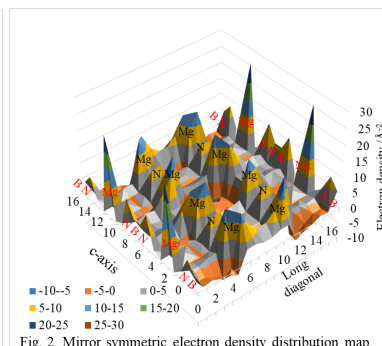


Fig. 2 Mirror symmetric electron density distribution map of (110) hexagonal plane of $\text{Mg}_3\text{BN}_3(\text{L})$ by DCT

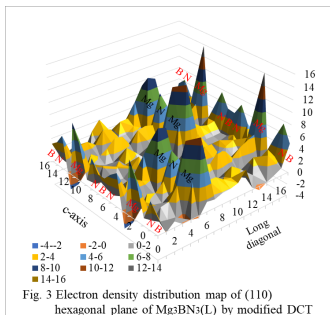


Fig. 3 Electron density distribution map of (110) hexagonal plane of $\text{Mg}_3\text{BN}_3(\text{L})$ by modified DCT

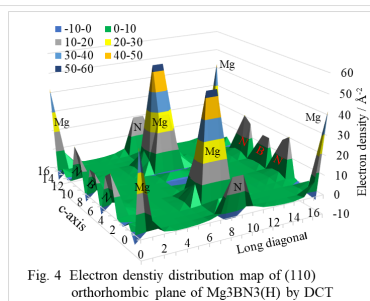


Fig. 4 Electron density distribution map of (110) orthorhombic plane of $\text{Mg}_3\text{BN}_3(\text{H})$ by DCT

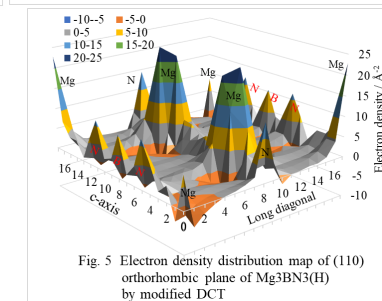


Fig. 5 Electron density distribution map of (110) orthorhombic plane of $\text{Mg}_3\text{BN}_3(\text{H})$ by modified DCT

addition, we have found out that both 3D DCT and modified DCT can draw the electron density distribution map of $\text{Mg}_3\text{BN}_3(\text{H})$ shown in Fig. 4 and Fig. 5. This is because $\text{Mg}_3\text{BN}_3(\text{H})$ doesn't have any glide planes and only have a center of symmetry and mirror planes. The crystal structure factor (F) obtained by the 3D inverse DCT is the same as the original one. However, F obtained by the 3D inverse modified DCT is slightly different from the original one. To find out this reason is our future task for this study. 1) N. AHMED, T. NATARAJAN and K. R. RAO.(1974), IEEE Trans. Comp., C-23, No.1. 2) H. HIRAGUCHI.(2019). Heliyon Vol.5, Issue 10. 3) H.HIRAGUCHI, O.SAKATA, H.HASHIZUME, A.TAKENAKA, O.FUKUNAGA.(1990). J. Cryst. Soc.Jp. OB-11, 32. 4) H. HIRAGUCHI, H. HASHIZUME, O. FUKUNAGA, A. TAKENAKA, M. SAKATA.(1991). J. Appl. Cryst. 24. 5) H. HIRAGUCHI, H. HASHIZUME, S. SASAKI, S. NAKANO, O. FUKUNAGA. (1993). Acta Cryst. B49. 6) H. Hiraguchi, the 100th annual meeting of Chem. Soc. Jp., March, 2020, 1 E2-11.

Maxwell + 分極力場 MD マルチスケールシミュレーションによる DCMBI 結晶の瞬間誘導ラマン散乱誘起テラヘルツ波発生プロセス (筑波大 計算センター) ○山田 篤志

ISRS-induced terahertz wave generation process in DCMBI crystalline solid by Maxwell + polarizable MD multi-scale simulation (*Center for Computational Sciences, University of Tsukuba*) ○Atsushi Yamada

We present a novel computational scheme of classical molecular simulation that is unified with Maxwell's equations based on a multi-scale model to describe the coupled dynamics of light electromagnetic waves and molecules in crystalline solids [1]. The method is applicable to light-matter interaction systems that involve atomic motions in spectroscopy, photonics and optical science. Since the scheme simultaneously traces the light propagation on a macroscopic scale and the microscopic molecular motion under the light, this enables us to treat experimental setup and mimic its measurement process. We performed simulation of vibrational spectroscopy of terahertz wave generation induced by ISRS (impulsive stimulated Raman scattering) in organic molecular crystal [2], DCMBI. The simulation provides the detailed behaviors of the interacting light fields and molecules in the spectroscopic process.

Keywords: Maxwell+Polarizable MD method, Multi-scale simulation, Molecular Vibrational Spectroscopy, ISRS

分光測定で得られる光シグナルは、非線形性を含む光と物質の相互作用と、反射や干渉、増幅のような光の伝搬により引き起こされる変調の結果である。そこには分子の構造や電子状態、振動といった微視的な状態と、波長、時間幅、強度、偏光方向、パルス間隔といったレーザー光の条件、さらに物質の膜厚やマクロ形状など様々な実験系の要因を反映している。このような複雑な物理に対してこれまでの計算化学では、物質の原子・分子レベルの状態に基づく分光解析が発展してきた。本研究では、物質中の光伝搬も取り入れることによる分光系の詳細な記述を可能にする計算化学を目指し、分極力場モデルを用いた分子シミュレーションと Maxwell 方程式とを統合した手法: Maxwell + Polarizable MD 法を開発した[1]。これは、マクロスケール (波長サイズ $\sim\mu\text{m}$) で伝搬する光電磁波とミクロスケール ($\text{\AA}\sim\text{nm}$) の分子運動の大きく異なる両スケールの物理を、多階層 (マルチスケール) モデルに基づき時間領域で統合した手法であり、振動分光やフォトンクスなどの固体系において相互作用する光電磁波と分子の動力学を詳細かつ包括的に記述することができる。本発表では、有機分子結晶 DCMBI に対する瞬間誘導ラマン散乱 (ISRS) 誘起テラヘルツ波発生の分光実験のシミュレーションを行い、パルス光入射からテラヘルツ波発生までの分光過程における光と分子の運動の詳細と解析結果を報告する[2]。

[1] A. Yamada, *J. Chem. Phys.*, **152**, 094110 (2020)

[2] A. Yamada, *J. Chem. Phys.*, **153**, 244506 (2020)

Reaction dynamics of ion-molecule collision beyond reaction-path-based understanding

(¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, ²Department of Chemistry, Indian Institute of Technology, Kanpur, ³Department of Chemistry, Faculty of Science, Hokkaido University, ⁴Faculty of Arts and Science, Kyushu University, ⁵Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University) ○Kohei Oda,¹ Takuro Tsutsumi,¹ Srihari Keshavamurthy,^{2,3} Kenji Furuya,⁴ Tetsuya Taketsugu^{3,5}

Keywords: Chemical Reaction Dynamics; Automated Reaction Path Search; Ion-molecule Collision Reaction; On-the-fly Molecular Dynamics; Potential Energy Surface

The automated reaction path search methods enable us to construct the network of an enormous number of reaction paths over a vast potential energy surface of a molecular system.¹ The guided ion beam experiment can obtain all the relative formation energies of product ions in ion-molecule collision reactions. These two techniques were supposed to give consistent information. However, the experiment on the CF_3^+/CO system showed much higher formation energy for CF^+ ion (7.48 ± 0.15 eV) than the theoretical prediction (2.30 eV), suggesting that the experimental molecular system ignored reaction paths leading to the $\text{CF}^+/\text{F}_2\text{CO}$ channel (**Fig. 1**).² Although this inconsistency necessitated further investigations of reaction dynamics, it was difficult to simulate this reaction due to a small reaction cross section. In this study, we carried out on-the-fly molecular dynamics (MD) simulations with appropriate initial conditions that efficiently cause chemical reactions and revealed the reaction dynamics far different from the reaction-path-based understanding.

In bimolecular reactions with high translational energy, on-the-fly MD studies have demonstrated that reactants directly reach a transition state without forming a pre-reaction complex.³ For such a direct reaction, there seems to be an optimal relative orientation of reactants to cross a transition state efficiently.⁴ We prepared initial conditions for collisional simulations based on the optimal situation and obtained reactive trajectories, which smoothly reached the FCO^+/CF_2 channel. The MD simulations indicate that the molecular systems which cross a transition state have significantly limited relative orientations and atomic-momentum directions, resulting in the ignorance of reaction paths in the experiment.

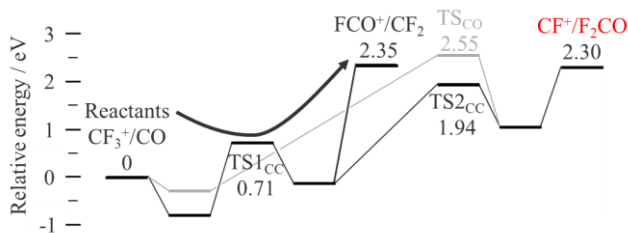


Fig. 1. Two series of reaction paths (black or gray lines) leading to $\text{CF}^+/\text{F}_2\text{CO}$ (red) and schematic reaction dynamics (black arrow) reaching FCO^+/CF_2 .

1) S. Maeda, K. Ohno, and K. Morokuma, *Phys. Chem. Chem. Phys.* **2013**, *15*, 3683. 2) K. Furuya, *The 4th Ann. Meeting of Jpn. Soc. for Mol. Sci.*, **2011**, 4P001. 3) X. Ma, and W. L. Hase, *Phil. Trans. R. Soc. A*, **2017**, 375, 20160204. 4) B. Jiang, and H Guo, *J. Chem. Phys.* **2013**, *138*, 234104.

Theoretical study on isotope fractionation in multistep biotic uranium reduction reaction

(Graduate School of Science, Tokyo Metropolitan University) ○Ataru Sato, Minori Abe, Masahiko Hada

Keywords: Ab-initio calculation; Uranium; Isotope fractionation; Multistep non-equilibrium reaction; Biotic reduction

Metabolically varied microorganisms can reduce the hexavalent uranium (U(VI)) to the tetravalent uranium (U(IV)). During this biotic reduction, the heavier isotope (^{238}U) is enriched in U(IV) and the apparent isotope fractionation coefficient Δ was obtained as 0.85–0.88‰.¹ However, its mechanism has not been well uncovered. By introducing the steady-state model for multistep reaction,² we could derive the representation of Δ as below.

$$\Delta = (\varepsilon_{ab} + \alpha_{ba}\tilde{X}_b) + (\varepsilon_{bc} + \alpha_{cb}\tilde{X}_c)X_b + (\varepsilon_{cd} + \alpha_{dc}\tilde{X}_d)X_bX_c + (\varepsilon_{de} + \alpha_{ed}\tilde{X}_e)X_bX_cX_d + (\varepsilon_{ef} + \alpha_{fe}\tilde{X}_f)X_bX_cX_dX_e + (\varepsilon_{fg} + \alpha_{gf}\tilde{X}_g)X_bX_cX_dX_eX_f + \alpha_{gh}X_bX_cX_dX_eX_fX_g \quad (1)$$

Here, ε and α are the equilibrium and kinetic isotope fractionation coefficients for each reaction step, respectively. X is the flux ratio and \tilde{X} is defined as $1-X$. The reaction is in equilibrium when X is 1, and it is irreversible when X is 0. In this study, we calculated ε for each reaction step in the biotic uranium reduction pathway³ (Fig. 1). Because the nuclear volume term, the dominant term of ε in uranium,⁴ is highly affected by relativity, we used *ab-initio* methods based on the relativistic quantum chemical theory.⁵

Because ε_{bc} is larger than the experimental Δ value¹ (Fig. 1), the contribution of the second term in Eq. 1 must be decreased. Thus, either X_b is smaller than one, \tilde{X}_c is non-zero with a negative α_{cb} , or both. These conditions mean that the binding of the substrate to an enzyme (A→B) or the reduction of U(VI) to U(V) (B→C) is not in equilibrium.

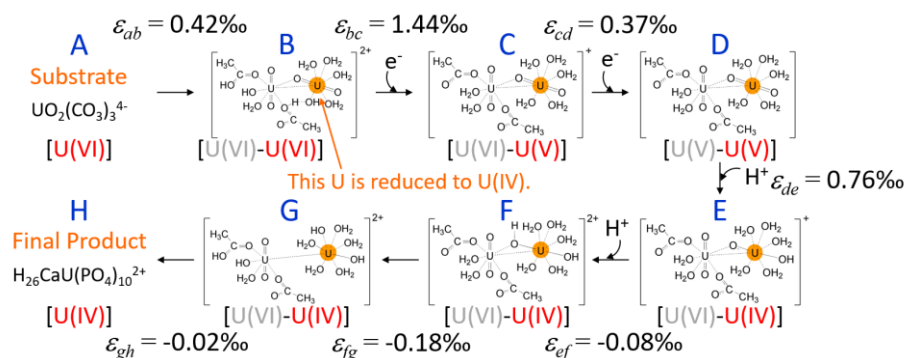


Fig. 1. Model of biotic uranium reduction pathway and obtained ε for each reaction step.

1) M. Stylo *et al.* *PNAS*. **2015**, *112*, 5619. 2) C. E. Rees, *GCA*. **1973**, *37*, 1141. 3) M. Sundararajan *et al.* *JPCA*. **2008**, *112*, 4451. 4) J. Bigeleisen, *JACS*. **1996**, *118*, 3676. 5) a) E. A. Schauble, *GCA*. **2007**, *71*, 2170. b) M. Abe *et al.* *JCP*. **2008**, *129*, 164309.

Water Oxidation at N-Doped Graphene Oxides – Structure Property Relationships and PCET Dynamics

(¹Dept. Appl. Chem., Chuo University, ²Université de Lorraine, ³Helmholtz-Zentrum Berlin)
○Fabian Weber,^{1,3} Jean Christophe Tremblay,² Annika Bande³

Keywords: Molecular Design; Water Oxidation; PCET; Quantum Dynamics

The generation of energy with resource-friendly materials has become one of the central challenges in modern material design and chemistry. One key process of particular interest in this field is the photoinduced proton-coupled electron-transfer (PCET) that concludes the first step of the water-oxidation reaction.¹ By applying theoretical model calculations it was proposed recently that graphitic carbon-nitrides, which are only composed of organic materials, are able to photo-catalyze this process.² Seeing how these graphitic carbon-nitrides have nitrogen as their reactive sites, we present here a similar study on the related fully-organic material family of N-doped graphene oxides (NGO) that has also been shown to catalyze water splitting under irradiation with light.³

Applying time-dependent density functional theory calculations for a large set of differently functionalized NGO model molecules, we find recurring designs that thermodynamically favor a PCET reaction using wavelengths closer and closer to the sunlight spectral maximum. Based on the relaxed reaction pathway for the hydrogen transfer from water towards the NGO model molecule, we estimate the necessary hydrogen transfer time and apply quantum dynamics calculations using the time-dependent configuration interaction scheme in its reduced density operator formulation (ρ -TDCI)⁴ to simulate the PCET dynamics upon laser excitation in the presence of thermal dissipation. By studying the importance of non-adiabatic coupling strengths we may find optimal thermalization life-times that may be helpful to design related devices.

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Static-field ionization rates of He-like ions by MCTDHF method

(¹*School of Science, The University of Tokyo*, ²*Guangdong Technion–Israel Institute of Technology, China*, ³*Technion–Israel Institute of Technology, Israel*)

○Erik Lötstedt,¹ Kaoru Yamanouchi,¹ Marcelo F. Ciappina^{2,3}

Keywords: Ultraintense laser pulses; Field ionization; He-like ions; Time-dependent multiconfiguration theory; Exchange interaction

Ultraintense laser pulses having intensities of 10^{20} W/cm² or above are currently becoming available at facilities such as the ELI Beamlines in the Czech Republic and the Shanghai Super-Intense Ultrafast Laser Facility. In order to use these laser pulses for scientific research, the pulses must be well characterized. Ciappina et al.¹ proposed a method for determining the peak field intensity of ultraintense laser pulses by recording the relative yields of H- and He-like ions generated through the field ionization proceeding in the laser field. In order that this method is to be implemented, a reliable theoretical formula for the intensity-dependent field ionization rates of He-like ions needs to be developed.

We derive a general formula for the static-field ionization rates of He-like ions with nuclear charge numbers $Z \leq 36$, valid in both the tunneling and over-the-barrier regimes of ionization.² The formula is derived by fitting a modified Perelemov-Popov-Terent'ev (PPT) formula^{3,4} to ionization rates calculated by the multiconfiguration time-dependent Hartree-Fock (MCTDHF) method.⁵ The newly proposed formula reproduces well the rate obtained by the MCTDHF method both in the tunneling and over-the-barrier regimes.

We also compare the rates obtained by the MCTDHF method and the rates obtained by a single-active electron (SAE) approximation. We find that the SAE rates are larger than the MCTDHF rates by as much as 30% for He and by about 2% for He-like Kr ($Z = 36$). We ascribe the difference to the omission of the exchange interaction between the bound electron and the electron being ejected in the SAE approximation. We conclude that it is necessary to employ properly antisymmetrized two-electron wave functions to obtain accurate static-field ionization rates of He-like ions.

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

[A07-1pm] 04. Physical Chemistry -Properties-

Chair: Hiroki Akutsu, Kazuya Kubo

Fri. Mar 19, 2021 1:00 PM - 3:20 PM Room 7 (Online Meeting)

[A07-1pm-01] Synthesis of TTF derivatives for fabricating conductive one-dimensional structures

○Hirohisa Oishi¹, Yuto Kimura¹, Nishihara Sadahumi², Tomoyuki Akutagawa³, Takayoshi Nakamura⁴, Yoko Tatewaki¹ (1. Tokyo University of Agriculture and Technology, 2. Hiroshima University, 3. Tohoku University, 4. Hokkaido University)

1:00 PM - 1:20 PM

[A07-1pm-02] Electromagnetic properties of molecular nanocoils of TTF derivatives with chiral units.

○Yoko Tatewaki¹, Sadafumi Nishihara², Tomoyuki Akutagawa³, Takayoshi Nakamura⁴ (1. Tokyo University of Agriculture and Technology, 2. Hiroshima University, 3. Tohoku University, 4. Hokkaido University)

1:20 PM - 1:40 PM

[A07-1pm-03] Synthesis of novel single-crystalline ethylenedioxythiophene oligomer charge transfer salts and the conjugation-length-elongation effects on their physical properties

○Ryohei Kameyama¹, Tomoko Fujino¹, Shun Dekura¹, Mitsuaki Kawamura¹, Taisuke Ozaki¹, Hatsumi Mori¹ (1. ISSP, The University of Tokyo)

1:40 PM - 2:00 PM

[A07-1pm-04] Syntheses of Benzenetriimide-based molecular conductors

○Shohei Koyama¹, Hiroaki Iguchi¹, Shinya Takaishi¹ (1. Tohoku university)

2:00 PM - 2:20 PM

[A07-1pm-05] Electrochemical tuning-induced magnetic properties in geometrically frustrated LiMn_2O_4

○Qi Chen¹, Zhongyue Zhang¹, Kunio Awaga¹ (1. Nagoya University)

2:20 PM - 2:40 PM

[A07-1pm-06] Charge-transfer-induced phase transition materials with electromagnetic wave absorption properties

○Koji Nakabayashi¹, Takaya Yoshida¹, Kenta Imoto¹, Marie Yoshikiyo¹, Kouji Chiba, Hiroko Tokoro², Asuka Namai¹, Shin-ichi Ohkoshi¹ (1. The University of Tokyo, 2. University of Tsukuba)

2:40 PM - 3:00 PM

[A07-1pm-07] Polarity and Chirality in Ferroelectric Triglycine sulfate Crystals

○Yukana Terasawa¹, Toshio Kikuta², Masaaki Ichiki³, Sota Sato⁴, Kazuhiko Ishikawa¹, Toru Asahi¹ (1. Waseda Univ., 2. Univ. of Toyama, 3. AIST, 4. The Univ. of Tokyo)

3:00 PM - 3:20 PM

・導電性を有する 1 次元組織体作成へ向けた新規 TTF 誘導体の合成

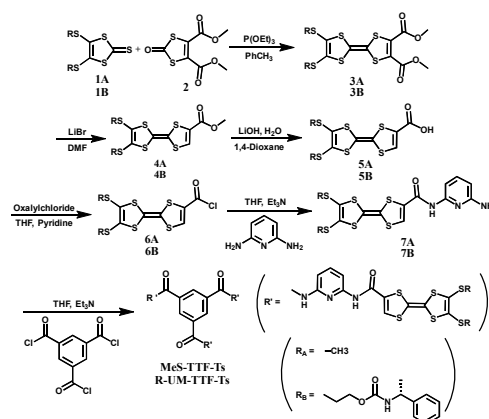
(農工大院工¹・広島大院²・東北大多元研³・北大電子研⁴) 大石 博久¹・木村 雄登¹・西原 禎文²・芥川 智行³・中村 貴義⁴・帯刀 陽子¹

Synthesis of TTF Derivatives for Fabricating Conductive One-dimensional Structures (¹Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, ²Graduate School of Advanced Science and Engineering, Hiroshima University, ³Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, ⁴Research Institute for Electronic Science, Hokkaido University) Hirohisa Oishi¹, Yuto Kimura¹, Sadafumi Nishihara², Tomoyuki Akutagawa³, Takayoshi Nakamura⁴, Yoko Tatewaki¹

Charge-transfer complexes consisting of Tetrathiafulvalene (TTF) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ) are known to form a separated stacked one-dimensional column structure and exhibit high conductivity at room temperature. The application of this property to one-dimensional structures such as nanowires has become important in the field of molecular electronics. In our laboratory, we have fabricated molecular assembly nanowires, but the formation of 1D structures depends on the crystal structure of the substrate. In this study, we synthesized two types of disk-shaped TTF derivatives to create molecular nanowires with stable structures by introducing π - π interactions and hydrogen bonds into the core of the molecule. **MeS-TTF-Ts** and **(MeS-TTF-Ts)(F₄TCNQ)₃** complexes, in which the acceptor molecule F₄TCNQ was introduced, successfully formed a nanowire network structure. The electrical conductivity of the nanowires was measured to be 1.24×10^{-2} S / cm. The structural and electrical properties of **R-UM-TTF-Ts** will be reported on the same day.

Keywords : Self-assembly; Nanowires; Charge-transfer Complexes

Tetrathiafulvalene(TTF)と 7,7,8,8-Tetracyanoquinodimethane(TCNQ)からなる電荷移動錯体は、分離積層型の 1 次元カラム構造を形成し、室温で高い導電性を示すことが知られている。この特性を利用した 1 次元構造体であるナノワイヤなどへの応用が分子エレクトロニクス分野において重要視されている。我々の研究室ではこれまでに分子集合体ナノワイヤを作成してきたが、1 次元構造の形成が基板の結晶構造に依存してしまうという問題点を有していた。そこで本研究では、分子のコア部分に π - π 相互作用と水素結合を導入することで、安定構造を有する分子性ナノワイヤを作成することを目的に 2 種類のディスク状 TTF 誘導体を合成した。**MeS-TTF-Ts** および、アクセプター分子である F₄TCNQ を導入した**(MeS-TTF-Ts)(F₄TCNQ)₃** 錯体では、ナノワイヤネットワーク構造を形成することに成功した。このナノワイヤについて電気伝導度測定を行ったところ、伝導度は 1.24×10^{-2} S / cm であった。R-UM-TTF-Ts の構造・電気物性については当日報告する。



Scheme 1. Synthesis of **MeS-TTF-Ts** and **R-UM-TTF-Ts**

キラル側鎖を有する TTF 誘導体からなる電荷移動錯体を用いた分子ナノコイルの作成と電磁特性評価

(農工大院工¹・広島大院理²・東北大多元研³・北大電子研⁴)

○帯刀 陽子¹、西原 禎文²、芥川智行³、中村貴義⁴

Electromagnetic properties of molecular nanocoils of TTF derivatives with chiral units. (¹Tokyo University of Agriculture and Technology, ²Hiroshima University, ³Tohoku University, ⁴Hokkaido University) ○Yoko Tatewaki¹, Sadafumi Nishihara², Tomoyuki Akutagawa³, Takayoshi Nakamura⁴

The CT complexes of Tetrathiafulvalene (TTF) and 7,7,8,8-Tetracyanoquinodimethane(TCNQ) showed high conductivities at room temperature. The application of these complexes has been studied to create the one-dimensional nanostructure, for example the nanowires and nanocoils. On the other hand, the development of a conductive scaffold materials was interested in this regenerative medicine engineering. The induced current of nanocoil is generated by application of a magnetic field, so the cell activation is expected. In this study, we report that structures and electromagnetic properties of molecular nanocoils composed of TTF derivatives and acceptors. These TTF derivatives had hydrogen bonding units and chiral molecules in alkyl chains. After mixing acceptors, these CT complexes show the conductivity like semiconductor. These formed molecular nanocoils, its electromagnetic property will be reported.

Keywords : Nanocoils; Charge Transfer Complexes; Electromagnetic properties; Conductivity; Scaffold

電荷移動錯体は高い伝導性を示すことから注目されており、これら誘導体を用いた低次元材料の開発が盛んに行われている。一方、再生医工学に関する研究は医歯薬学分野から理工学分野まで広い範囲に渡り報告がなされており、特に再生に必要な細胞を効果的に機能させる新規スキャホールド材料の開発が求められている。スキャホールドが効率的に細胞培養を補助するためには、多孔質性、大表面積といった構造的特徴が求められている。そこで本研究では、TTF 誘導体 (S-TTF-4UM、R-TTF-4UM)(図 1)とアクセプターを混合することで得られた電荷移動錯体を用いて分子性ナノコイルを作製し、その電磁特性を明らかにした。分子性ナノコイルは一方向に傷を付与した固体基板上にキャストすることで、特定方向に配列させることが可能であった。次に、ナノコイルの電気伝導度を測定したところ 10^{-3} S/cm と半導体程度の特徴を示すことが明らかとなった。さらに、本錯体は交流磁場印加下で誘導起電力が得られることも分かった。ナノコイルを用いて作製したスキャホールドを利用した細胞培養の結果についても当日併せて報告する。

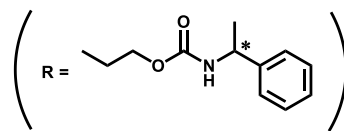
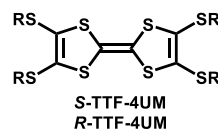


図 1 TTF 誘導体の分子構造。末端にキラル分子を有していることからヘリカルな構造を形成する。

Synthesis of novel single-crystalline ethylenedioxythiophene oligomer charge transfer salts and the conjugation-length-elongation effects on their physical properties

(The Institute for Solid State Physics, The University of Tokyo)

○Ryohei Kameyama, Tomoko Fujino, Shun Dekura, Mitsuaki Kawamura, Taisuke Ozaki, Hatsumi Mori

Keywords: Charge-transfer salts, Thiophene, Molecular crystal, Electrical conductivity, radical cation

Conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) show excellent electronic transport properties, mainly based on the highly ordered structures in their crystalline region.¹ The detailed structures, however, have still been in "black boxes" because their wide-ranged molecular-weight distribution inevitable for polymers severely hampers single-crystal formation, limiting their structure-based elucidation of conduction mechanism. As the structurally well-defined models for doped PEDOT, we have focused on discrete EDOT oligomer models. The shortest models, dimer charge-transfer salts (i.e., **2**•*A* in Figure 1a, *A* = BF₄, ClO₄, PF₆) were suggested to have one-dimensional (1D) metallic band structures with strong intracolumnar orbital interactions (band width *W* ~ 1 eV) indicative of the origin of the doped PEDOT's excellent conductivity by DFT-based band calculations, whereas exhibited a semiconducting behavior due to the large on-site Coulomb repulsion *U*.² Here, we clarified the effect of conjugation length on the electronic properties through comparing the dimer charge-transfer salt **2**•PF₆ and a newly synthesized trimer charge-transfer salt **3**•PF₆. The single-crystalline salt **3**•PF₆ showed a 1D columnar structure in which the donors were dimerized (Figure 1b), while donors were uniformly stacked in **2**•*A*. Band calculations of **3**•PF₆ identified a band gap of 58 meV derived from dimerization of the donor molecule. Like **2**•*A*, **3**•PF₆ exhibited a semiconducting behavior (Figure 1c). Interestingly, the resistivity and the activation energy of **3**•PF₆ was lower ($\rho_{\text{rt}} = 1.0 \times 10^3 \text{ ohm}\cdot\text{cm}$, $E_a = 197 \pm 0.2 \text{ meV}$) than that of **2**•PF₆ ($\rho_{\text{rt}} = 4.3 \times 10^4 \text{ ohm}\cdot\text{cm}$, $E_a = 278 \pm 1.4 \text{ meV}$). Decrease of the resistivity and the activation energy in **3**•PF₆ may originate from the reduction of *U* due to the expansion of conjugated system while maintaining the +1 charge degree as in **2**•PF₆.

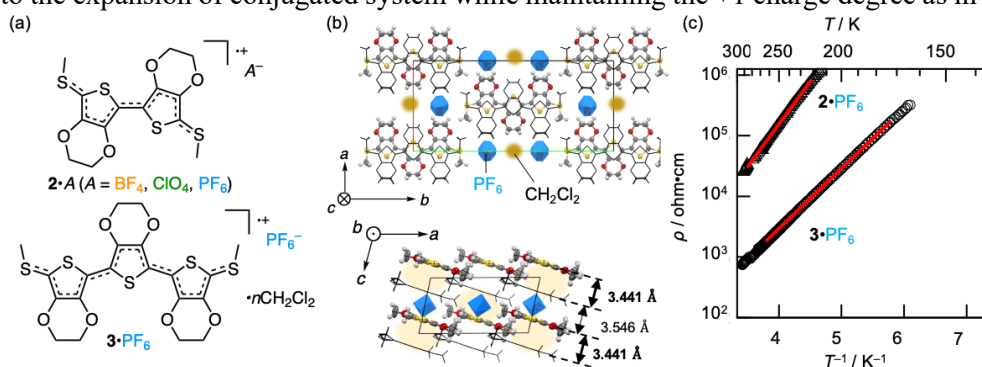


Figure 1. (a) Molecular structures of **2**•*A* and **3**•PF₆. (b) Crystal structures of **3**•PF₆. (c) Resistivity–temperature plots for **2**•*A* and **3**•PF₆. The resistivities were measured along the π -stacking direction of the single crystals.

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ベンゼントリイミド誘導体を原料とした分子性導体の合成

(東北大院理) ○小山 翔平・井口 弘章・高石 慎也

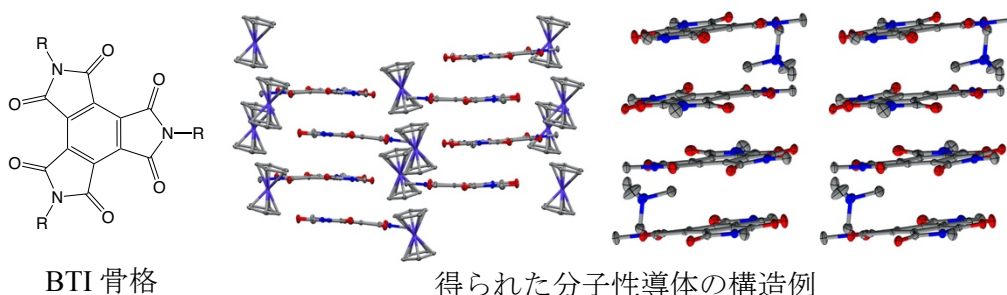
Syntheses of Benzenetriimide-based molecular conductors

(Graduate School of Science, Tohoku University,) Shohei Koyama, Hiroaki Iguchi, Shinya Takaishi

Benzenetriimide derivatives (BTIs) are curious compounds as novel molecules in materials and supramolecular chemistry because they possess a π -acidic skeleton which is stable against three-electron reduction and a characteristic three-way reaction point. In this study, we focused on the redox properties of the BTI skeleton and investigated the structure and electronic properties of the partially reduced form of BTI-Me, where methyl groups are attached to the nitrogen of the imide groups of BTI. Some of the obtained structures have one-dimensional π -stacking structures, those were expected to be electrically conductive. The temperature dependences of the electrical conductivity in these compounds were found to be semiconductive behavior. Detailed discussion will be reported in the day.

Keywords : Benzenetriimide; Molecular conductor

ベンゼントリイミド誘導体(BTIs)は3電子の還元に対して安定である π 酸性骨格を有することや、3方向に対して反応点を有する特徴的な分子であることから、材料化学や超分子化学における新規分子として非常に興味深い。従来は合成収率の低さから十分な研究はなされていなかったが、マレイミド骨格から1 stepで合成するスキームが最近報告され¹⁾、入手の簡便さからもBTIsを利用した研究はますます重要になることが考えられる。本研究ではBTI骨格の酸化還元能に着目し、固体状態におけるこの分子の部分還元状態の構造と電子物性を明らかにすることを目的として研究を行った。具体的にはイミド基の先にメチル基を有するBTI-Meを用いて、BTI-Meが部分還元された構造を得ることに成功し、これらの構造や電子物性の評価を行った。得られた構造の中には1次元 π 積層構造を有するものもあり、電子伝導性が期待された。電気伝導度の温度依存性は半導体的な挙動を示すことが確認された。詳細な伝導物性、磁気物性に関する報告は当日行う。



BTI 骨格

得られた分子性導体の構造例

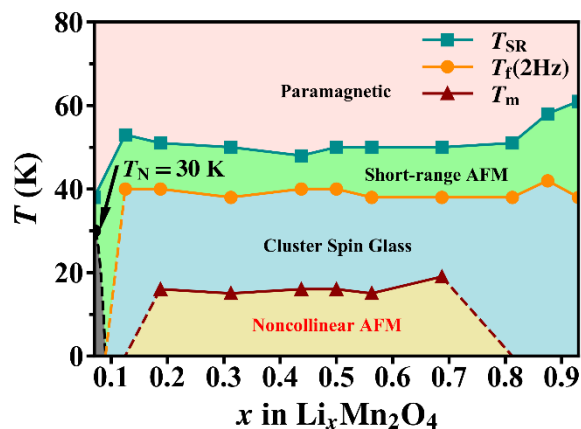
1) D. -H. Tuo.; Q. He.; Q.-Q. Wang.; Y. -F. Ao.; D. -X. Wang. Benzene Triimides: Facile Synthesis and Self-Assembly Study. *Chin. J. Chem.* **2019**, 37, 684–688.

Electrochemical tuning-induced magnetic properties in geometrically frustrated LiMn_2O_4

Qi Chen, Zhongyue Zhang, Kunio Awaga

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Precise tuning of the magnetic states of geometrically frustrated materials remains a critical challenge, as this process will not only promote understanding of fundamental magnetism, but also accelerate the discovery of new materials with unprecedented magnetic behaviors. Among the well-known metal oxide cathode materials¹, LiMn_2O_4 has attracted vast research interest for being a three-dimensional Heisenberg antiferromagnet with well-defined geometrical frustration, making it a worthy subject of magnetic studies². Hence, we present a study of the tuning magnetic properties of spinel LiMn_2O_4 by electrochemical oxidation/reduction in a lithium battery. The ex-situ magnetic susceptibility and specific heat measurements were performed on electrochemically modified $\text{Li}_x\text{Mn}_2\text{O}_4$ with $0.07 \leq x \leq 0.93$ to monitor the evolution of magnetic phase transitions and identify the new magnetic intermediate state. The results showed that the strong frustrated $\text{Li}_{0.93}\text{Mn}_2\text{O}_4$ is in a spin-glass ground state, while the weak frustrated $\text{Li}_{0.07}\text{Mn}_2\text{O}_4$ (or $\lambda\text{-MnO}_2$) exhibits long-range antiferromagnetic order. In addition, a unique magnetic ground state of noncollinear antiferromagnetic order was found in the intermediate phase $\text{Li}_{0.50}\text{Mn}_2\text{O}_4$ below 16 K, which was unveiled for the first time in the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ system. The results of our work suggest that the non-trivial magnetic order may arise from the asymmetric Dzyaloshinskii–Moriya interactions between two spins in a geometrically frustrated lattice³ and could be easily achieved by an electrochemical method but more difficult to prepare via traditional chemical methods.



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Charge-transfer-induced phase transition materials with electromagnetic wave absorption properties

(¹*School of Science, The University of Tokyo*, ²*Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba*, ³*Material Science Div., MOLSI Inc.*) ○ Koji Nakabayashi,¹ Takaya Yoshida,¹ Kenta Imoto,¹ Marie Yoshikiyo,¹ Kouji Chiba,³ Hiroko Tokoro,^{1,2} Asuka Namai,¹ Shin-ichi Ohkoshi¹

Keywords: Charge transfer; THz wave absorption; Photomagnet; Coordination network; Phase transition

Metal complexes showing charge transfer have been studied because of their switching characters on magnetic, optical, and electric properties. We have reported functional charge-transfer materials based on cyanido-bridged metal assemblies.^{1,2} Herein, we introduce two-dimensional layered cyanido-bridged metal assemblies, $A[\text{Co}^{\text{II}}(3\text{-cyanopyridine})_2][\text{W}^{\text{V}}(\text{CN})_8]$ ($A = \text{Rb}, \text{Cs}$), exhibiting an electromagnetic wave absorption in the low-frequency THz region from sub-THz to THz.

The presented compounds have an identical layered coordination network with Rb^+/Cs^+ ions trapped between the layers (Figure 1a). The compound with Rb^+ ions shows a charge-transfer-induced phase transition (CTIST) at 150 K and 190 K in the cooling and warming processes, respectively (Figure 1b). THz time-domain spectroscopy (THz-TDS) and revealed optical phonon modes at 0.58, 0.78, 1.06, 1.22, 1.30, 1.41, 1.51, and 1.89 THz. The low-frequency phonon modes are due to slow vibrations of the Rb^+ ions between the layers, confirmed by first-principles phonon mode calculations. The THz wave absorption property is switched when the CTIST is caused by the temperature change or photoirradiation.³

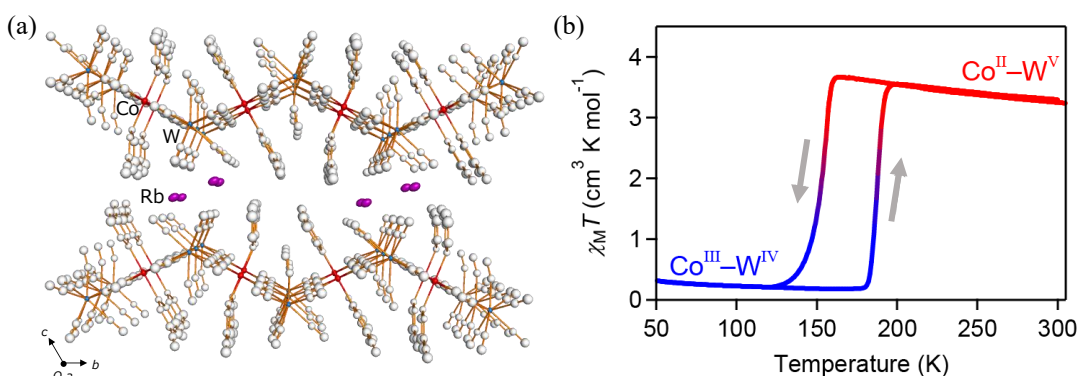


Figure 1. Crystal structure (a) and $\chi_{\text{M}}T$ - T plot (b) of $\text{Rb}[\text{Co}^{\text{II}}(3\text{-cyanopyridine})_2][\text{W}^{\text{V}}(\text{CN})_8]$

- 1) H. Tokoro, A. Namai, M. Yoshikiyo, K. Chiba, R. Fujiwara, S. Ohkoshi, *Scientific Reports*, **2018**, 8, 63.
- 2) M. Reczyński, D. Pinkowicz, K. Nakabayashi, C. Näther, J. Stanek, M. Kozieł, J. Kalinowska-Thüscik, B. Sieklucka, S. Ohkoshi, B. Nowicka, *Angew. Chem. Int. Ed.*, **2020**, 59, 2.
- 3) T. Yoshida, K. Nakabayashi, H. Tokoro, M. Yoshikiyo, A. Namai, K. Imoto, K. Chiba, S. Ohkoshi, *Chem. Sci.*, **2020**, 11, 8989.

強誘電体硫酸トリグリシン結晶における分極とキラリティ

(早大院先理¹・富大工²・産総研³・東大工⁴) ○寺澤 有果菜¹・喜久田 寿郎²・一木正聡³・佐藤 宗太⁴・石川 和彦¹・朝日 透¹

Polarity and Chirality in Ferroelectric Triglycine sulfate Crystals (¹Graduate School of Advanced Science and Engineering, Waseda University, ²School of Engineering, Toyama University, ³Sensing System Research Center, Advanced Industrial Science and Technology, ⁴Department of Applied Chemistry, The University of Tokyo) ○Yukana Terasawa,¹ Toshio Kikuta,² Masaaki Ichiki,³ Sota Sato,⁴ Kazuhiko Ishikawa,¹ Toru Asahi¹

Right- or left-handed crystals derived from molecular chirality are grown from chiral molecules. On the other hand, mix of right- and left-handed crystals are grown from achiral molecules. Therefore, desired chiral crystals composed of achiral molecules are not obtained through crystallization. Triglycine sulfate (TGS) is a ferroelectric chiral crystal composed of achiral molecules, glycine and sulfuric acid ¹⁾. We have found that doping with a tiny amount of alanine prefers chirality of TGS crystals below Curie temperature. TGS crystals, ferroelectric chiral materials, have attracted interest because chirality relates to polarity ²⁾. Therefore, we have discussed the mechanism of preferred chirality in TGS crystals by doping with a tiny amount of alanine.

Keywords : Crystal; Ferroelectricity; Polarity; Chirality

キラル分子からは、分子のキラリティに依存した右結晶もしくは左結晶が育成される。一方、アキラル分子からは、右結晶と左結晶が混在して育成される。そのため、アキラル分子からなるキラル結晶の育成により、所望のキラル結晶を得ることはできない。硫酸トリグリシン(Triglycine sulfate; TGS)は、アキラル分子であるグリシンと硫酸からなる強誘電性キラル結晶である ¹⁾。我々は、微量のアラニンのドーピングにより、キュリー温度以下で TGS 結晶のキラリティが偏ることを見出した。強誘電性キラル材料である TGS 結晶は、キラリティが分極と関連しているため、関心がもたれている ²⁾。そのため、微量のアラニンのドーピングにより TGS 結晶のキラリティを偏らせる機構を考察した。

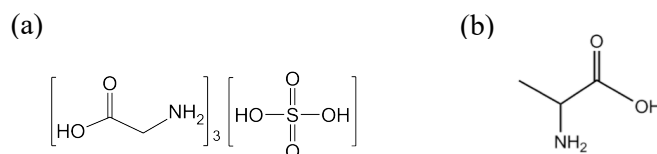


Fig. 1 Molecular structure. (a) TGS, (b) alanine

References

- 1) B. T. Matthias, C. E. Miller, and J. P. Remeika, *Phys. Rev.*, **1956**, 104(3), 849-850.
- 2) J. Kobayashi, K. Uchino, H. Matsuyama, and K. Saito, *J. Appl. Phys.*, **1991**, 69(1), 409-413.

[A05-1pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair:Yoshiyuki Kageyama, Hiro Minamimoto

Fri. Mar 19, 2021 1:00 PM - 3:20 PM Room 5 (Online Meeting)

[A05-1pm-01] Acquisition voltage vibration in sensitized thermal cells[○]Sachiko Matsushita¹, Haruki Kohata¹, Hayato Sekiya¹, Takumi Ikeda¹, Yoshiharu Hida¹, HAOTONG SONG¹, Toshihiro Isobe¹, Akira Nakajima¹ (1. Tokyo Institute of Technology)

1:00 PM - 1:20 PM

[A05-1pm-02] Dynamics of Interfacial Tension Concerning to Self-Propelled Motion of Droplet[○]Nobuhiko J. Suematsu^{1,2} (1. IMS, Meiji University, 2. MIMS, Meiji University)

1:20 PM - 1:40 PM

[A05-1pm-03] Formation of Novel Self-organized Periodic Precipitation Pattern by pH-induced Gold Nanoparticles Aggregation[○]Masaki Itatani¹, Qing Fang², Hideki Nabika² (1. Grad. Sch. of Sci. and Eng., Yamagata Univ., 2. Fac. of Sci., Yamagata Univ.)

1:40 PM - 2:00 PM

[A05-1pm-04] Electrochemical control of spatio-temporal patterns in the Belousov-Zhabotinsky reaction[○]Masakazu Kuze¹, Mari Horisaka¹, Nobuhiko J. Suematsu², Takashi Amemiya³, Oliver Steinbock⁴, Satoshi Nakata¹ (1. Graduate School of Integrated Sciences for Life, Hiroshima Univ., 2. Graduate School of Advanced Mathematical Sciences, Meiji Univ., 3. Graduate School of Environment and Information Sciences, Yokohama National Univ., 4. Department of Chemistry and Biochemistry, Florida State Univ.)

2:00 PM - 2:20 PM

[A05-1pm-05] Model for swimming of micro-sized crystals in water with an oscillating fin under continuous blue-light irradiation[○]Kazuma Obara¹, Yoshiyuki Kageyama², Sadamu Takeda² (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

[A05-1pm-06] Elucidation of melting during the initial process of electron-crystal interactions[○]Dongxin Liu¹, Takayuki Nakamuro¹, Koji Harano¹, Eiichi Nakamura¹ (1. The University of Tokyo)

2:40 PM - 3:00 PM

[A05-1pm-07] Reformation of thalidomide from its hydrolysis compound via intramolecular dehydration[○]Toru Asahi¹, Toru Aashi¹, Koichi Tsutao¹, Kohei Otagawa¹, Miri Nakamura¹, Yoshiyuki Ogino¹ (1. Waseda University)

3:00 PM - 3:20 PM

増感型熱利用発電における取得電圧振動

(東工大物質) ○松下 祥子・木幡 春輝・関谷 颯人・池田 拓未・樋田 圭晴・宋 皓同・磯部 敏宏・中島 章

Acquisition voltage vibration in sensitized thermal cells (*Graduate School of Materials and Chemical Engineering, Tokyo Institute of Technology*) ○Sachiko Matsushita, Haruki Kohata, Hayato Sekiya, Takumi Ikeda, Yoshiharu Hida, Haotong Song, Toshihiro Isobe, Akira Nakajima

A sensitized thermal cell (STC) is a new energy conversion system that obtains electricity directly from heat.¹⁻³⁾ The thermally excited carriers in semiconductors generate redox reactions of electrolyte ions to generate power (Figure). It had been reported that some electric devices such as a liquid display and LED lights worked using the STCs over 40 °C. However, in the STC power generation, sometimes the vibration of the acquired voltage was confirmed during the long-term constant current discharge. In this presentation, we focus on the voltage vibration from the viewpoint of the balance of redox ion concentrations at the electrode/electrolyte interface.

Keywords : Voltage Oscillation; Dye-sensitized Solar Cell; Heat Energy Conversion; Renewable Energy; Low-Carbon Society

増感型熱利用発電は、熱エネルギーから直接電気を得る、新しいエネルギー変換方式である。¹⁻³⁾ 色素増感型太陽電池における光励起を半導体内の熱励起に代替した発電システムであり、熱励起電荷が電解質イオンを酸化還元して発電する。すでに 40°C 以上での発電の確認や、液晶ディスプレイ・LED ライトの作動などが確認されているが、長期一定電流放電において取得電圧の振動が確認されることがある。今回我々は、本振動に対し、電極/電解液界面での酸化還元イオン濃度のバランスに注目し検討したので報告する。

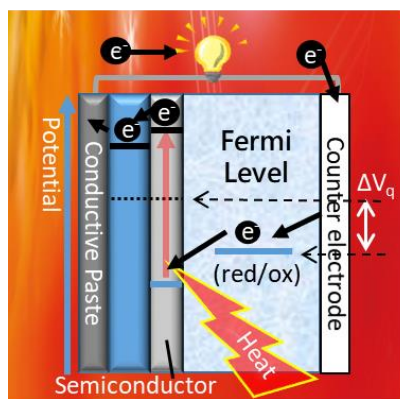


Figure. Schematic image of the sensitized thermal cell. The obtained voltage (ΔV_q) is the difference between the Fermi level of the semiconductor electrode and the redox potential of electrolyte ions.³⁾

増感型熱利用発電の模式図。取得電圧は半導体電極のフェルミ準位と電解質イオンの酸化還元準位の差となる。³⁾

- 1) S. Matsushita, T. Araki, B. Mei, S. Sugawara, Y. Inagawa, J. Nishiyama, T. Isobe, A. Nakajima, *J. Mater. Chem. A* **2019**, 7, 18249-18256.
- 2) S. Matsushita, A. Tsuruoka, E. Kobayashi, T. Isobe, A. Nakajima, *Mater. Horiz.* **2017**, 4, 649-656.
- 3) 松下祥子, *Acc. Mater. Surf. Res.* **2020**, 5, 60-67. (日本語解説 オープンアクセス)

液滴運動を誘発する界面張力ダイナミクス

(明大院先端数理・明大 MIMS) ○末松 J. 信彦

Dynamics of Interfacial Tension Concerning to Self-Propelled Motion of Droplet (*Graduate School of Advanced Mathematical Sciences, Meiji University; MIMS, Meiji University*)

○Nobuhiko J. Suematsu

It is known that a small droplet of bromine aqueous solution spontaneously moves within a squalane solution of monoolein (MO) under appropriate conditions. The droplet motion is driven by brominating reaction of MO on the oil/aqueous interface (Fig. 1a). In order to quantitatively discuss the mechanism of such droplet motion, physicochemical parameters concerning to interfacial dynamics must be estimated. Here, we measured time series of interfacial tension with different chemical conditions of the aqueous phase. The experimental results were analyzed using a mathematical model for the interfacial dynamics (Fig. 1b), and physicochemical parameters such as desorption rate and reaction constant of interfacial chemical reaction were estimated (Fig. 1c,d). Based on those experimental estimations, we will suggest a simple mechanism for the droplet motion.

Keywords : *Interfacial tension, Far from equilibrium condition, Self-propelled droplet*

モノオレイン(MO)を界面活性剤として含むスクアラン油相中に臭素水溶液の微小液滴を浮かべると自発的に運動する。これは油水界面に吸着した MO が水溶液中の臭素と反応して臭素化 MO を生成する化学反応と、それに伴う界面張力変化に起因すると言われている (Fig. 1a, b)。しかし、この機構の定量的な評価はまだ行われていない。そこで、界面張力の時間変化を計測し、その時系列データを解析することで、界面ダイナミクスに関わる種々の物理化学変数を定量的に評価した (Fig. 1c, d)。これらのデータに基づいて、液滴運動の機構を定量的に議論することが可能になった。

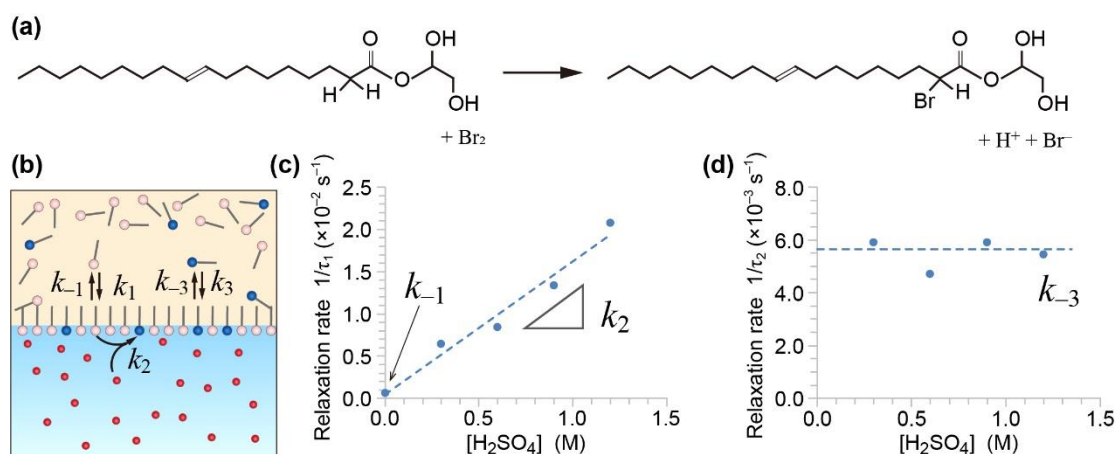


Figure 1. (a) Brominating reaction of MO. (b) Illustration of interfacial dynamics. (c, d) Relaxation rate of interfacial tension depending on $[\text{H}_2\text{SO}_4]$ in (c) short time and (d) long time.

1) N. J. Suematsu, K. Saikusa, T. Nagata, and S. Izumi, *Langmuir* **2019**, 25, 11601-11607.

Formation of Novel Self-organized Periodic Precipitation Pattern by pH-induced Gold Nanoparticles Aggregation

(¹Graduate School of Science and Engineering, Yamagata University, ²Faculty of Science, Yamagata University) ○Masaki Itatani,¹ Qing Fang,² and Hideki Nabika²

Keywords: Far from equilibrium, Self-organization, Pattern formation, Reaction-Diffusion systems, Liesegang pattern

Spontaneous pattern formation under far-from equilibrium condition is driven by self-organization via reaction-diffusion processes. So far, it has attracted many researchers because chemical and mathematical modeling of such phenomena being ubiquitous in nature lead to help understanding the pattern formation mechanism in nature. Liesegang pattern (LP) is one of the chemical models for the self-organized patterns. So far, most of its formation mechanisms are limited to discussion of spatially heterogeneous precipitation driven by a diffusion concentration gradient of material for precipitates. Because of this limitation, the universality of LP as the model for natural pattern formation is limited.^{1,2} In this study, we tried to form the novel LP based on an idea mimicking another condition in nature which is driven by that a gradient inducing instability was imposed to the reaction medium dispersed precipitation precursors uniformly. In detail, the pH gradient was imposed into a hydrogel doped with gold nanoparticles (Au NPs) to trigger their aggregation and pattern formation.

Au NPs were synthesized by chemical reduction with citric acid and modified by 11-mercaptoundecanoic acid (MUA) through a surface ligand exchange in NaOH aq. soln.. Then, 0.5 w/w% agarose gel doped with this deprotonated MUA-Au NPs was prepared in a test tube. Subsequently, HCl aq. soln. was poured on the top of the gel, then the pH gradient was evolved toward the bottom due to the diffusion of H⁺. Figure 1a shows the pattern formation by pH-induced aggregation of MUA-Au NPs, where MUA-Au NPs aggregate at the position showing a slightly deep red color. To make it more clearly, a gray scale of Figure 1a is shown as Figure 1b, in which four darker discrete bands consisting of aggregates of MUA-Au NPs are observed. Between each band, aggregates were almost absent, and an inter-band spacing increased geometrically. This unique feature is good agreement with the characteristic geometrical feature of LP. Finally, its novel mechanism was discussed by simulation considering the phase transition from dispersion to aggregation states, and consistent results were obtained. As a conclusion, we succeeded novel LP formation from the uniform distribution and revealed its detailed mechanism, which could make LP a universal model for various periodic structure with geometric series in nature.

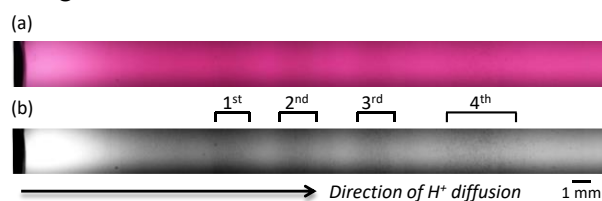


Figure 1. Pattern formation by pH-induced aggregation of MUA-Au NPs: [MUA-Au NPs] = 4.0 nM, [agarose] = 0.20 w/w%, [HCl]₀ = 1.5×10^{-4} M. (a) original and (b) gray scale.

- 1) **M. Itatani** et al., *J. Phys. Chem. C*, **2018**, 122, 3669-3676.
- 2) **M. Itatani** et al., *J. Phys. Chem. B*, **2020**, 124, 8402-8409.

Electrochemical control of spatio-temporal patterns in the Belousov-Zhabotinsky reaction

(¹Graduate School of Integrated Sciences for Life, Hiroshima University, ²Graduate School of Advanced Mathematical Sciences, Meiji University, ³Graduate School of Environment and Information Sciences, Yokohama National University, ⁴Department of Chemistry and Biochemistry, Florida State University) ○Masakazu Kuze¹, Mari Horisaka¹, Nobuhiko J. Suematsu², Takashi Amemiya³, Oliver Steinbock⁴, Satoshi Nakata¹

Keywords: Belousov-Zhabotinsky reaction; Oscillations; Spatio-temporal patterns; Chemical waves; Nonlinear

The Belousov–Zhabotinsky (BZ) reaction, which self-organizes spatio-temporal patterns based on autocatalytic redox reactions, is a widely studied experimental system. The metal catalyst of the BZ reaction was loaded into a cation-exchange resin bead. We call this bead the BZ bead. Global oscillations (GO), which are the uniform oscillations in the entire bead, and traveling waves (TW), which are the propagating chemical waves from one end of the bead, were observed when BZ bead was immersed into a BZ solution without a catalyst (Fig. 1a). Previous study has reported that GO and TW could be selectively and reversibly generated by positive and negative values of the electrical potential, E , respectively.¹⁾ In this study, we found the hysteresis on the switching of the spatio-temporal patterns depending on the scanning direction of E . In addition, we discuss our results in the context of an increased concentrations of the activator, HBrO_2 , or the inhibitor, Br^- , to clarify the mechanism of switching between GO and TW.

The switching from GO to TW occurred near -0.2 V in negative scan, i.e., from $E = +1.0$ V to -1.0 V (Fig. 1b). On the other hand, when E was scanned from -1.0 V to $+1.0$ V (positive scan), the switching from TW to GO occurred near $+0.2$ V. In the negative scan, GO was maintained because oscillations in the bead were strongly affected by sufficient concentration of the inhibitor which accumulated near the positive electrode. On the other hand, TW was maintained at a small value of E due to the electrochemical production of the activator in the positive scan.

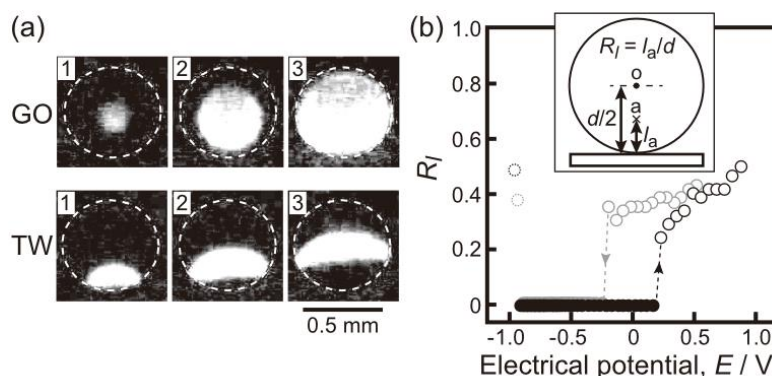


Figure 1. (a) Snapshots of GO and TW for the single bead (Time interval: 2 s). (b) The ratio (R_l) of the minimum length (l_a) between the generation point of the oscillations (a) and the surface of the plate electrode to the diameter of the bead (d) at the scanning of the electrical potential. Gray and black circles represent to the negative and positive scan, respectively.

1) M. Kuze et al., *J. Phys. Chem. A* **2019**, 123, 4853–4857.

青色光照射で自律振動するマイクロサイズの結晶の 水中での遊泳とモデル

(北大院総化¹・北大院理²) ○小原 一馬¹・景山 義之²・武田 定²

Model for swimming of micro-sized crystals in water with an oscillating fin under continuous blue-light irradiation (¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, ²Faculty of Science, Hokkaido University) ○ Kazuma Obara,¹ Yoshiyuki Kageyama,¹ Sadamu Takeda²

Microorganisms and artificial microrobots with connected-rods or helical-filaments can propel in viscous fluid with spatiotemporally asymmetric motion. We found that a micron-sized crystal composed of organic molecules swam in water by autonomous reciprocal motion using like a fin under continuous blue-light irradiation. Here, we report observation and numerical analyses about the swimming crystals.

The crystal propelled unidirectionally although it moved forward-and-backward in each cycle of flipping motion of the crystal. We classified the swimming styles of the crystals into two types. One is “butterfly-stroke style”, the other is “flutter-kicks style”. The fin length of flutter-kicks style was 1.5 times longer in average than that of butterfly-stroke style. The swimming crystal was modeled by three plates connected with two torque spring. Numerical analyses suggested that swimming styles of crystals depended on delay in motions of each plate.

Keywords : Swimming; Self-organized motion; Oscillation; Viscous drag; Mesoscopic science

連結したロッドやらせん型フィラメントなどの人工マイクロロボット¹⁾や微生物は、時空間的の非対称な動きをすることで、粘性支配的な媒体中を推進する。一方で、我々は、有機分子からなるマイクロサイズの板状結晶が、定常青色光照射下で、結晶の一部をヒレのように自律的な反復運動²⁾をさせて水中を一意的方向に遊泳することを発見した。ここでは、この結晶の泳ぎを顕微鏡観察と数理モデルから検討した。

結晶は、変形する度に前進と後退を繰り返しながら、総和として一方向に推進した (Fig. 1)。結晶の振動部分であるヒレの位置と結晶全体の推進方向を指標に、結晶の遊泳形態を分類した。結晶の前方が振動するバタフライ型と後方が振動するバタ足型の2種類である (Fig. 3 左図)。遊泳した結晶の顕微鏡像から、バタ足型のヒレはバタフライ型よりも平均して 1.5 倍長かった (Fig. 2)。次に、結晶の形状と遊泳方向の関係を明らかにすることを目的とし、粗視化モデルを構築した。結晶のヒレ部分を2枚に分割し、それぞれトルクばねで連結した運動体として、この遊泳運動をモデル化した。計算の結果、結晶の遊泳方向はヒレの動きの位相差で決まると示唆され (Fig. 3 右図)、ヒレ間の動きの位相差はヒレ長と関係していると推測された。

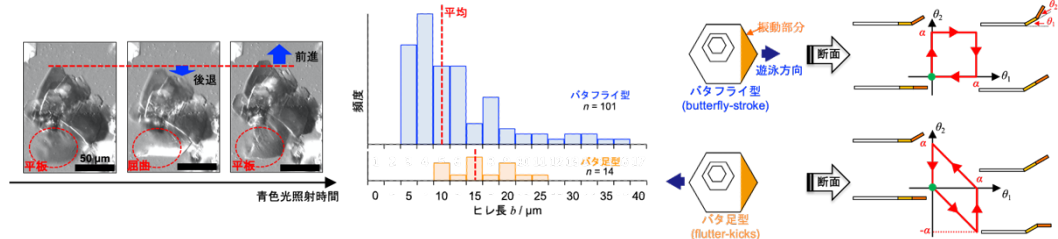


Fig. 1 結晶の顕微鏡像

Fig. 2 ヒレ長の分布

Fig. 3 遊泳形態と結晶のモデル化

- 1) e. g. J. J. Abbott *et al.*, *Annu. Rev. Biomed. Eng.* **2010**, 12, 55-85.
- 2) Y. Kageyama *et al.*, *Angew. Chem. Int. Ed.* **2016**, 55, 8239-8243.

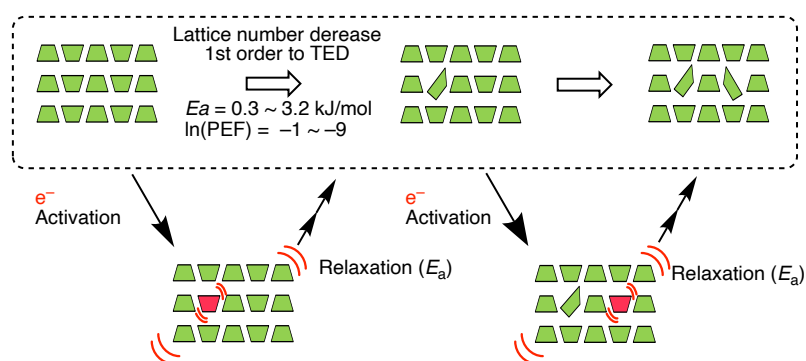
Elucidation of melting during the initial process of electron-crystal interactions

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

Keywords: Electron diffraction; Melting; Phase Transition; Microscopy; Kinetic Study

Electron beam (e-beam) has been indispensable probe in acquiring structural information or dynamic behavior at atomic resolution, however, analytical methods utilize e-beam often suffer from loss of information. Such a loss is unavoidable even within the initial process of e-beam irradiation but the molecular mechanism behind the process remains elusive.^{1, 2} In this study, we conducted kinetic study for the low electron dose process by following the fading of electron diffraction (ED) patterns and found the behavior of molecules in crystals can collectively be understood as melting.

To investigate physical or chemical mechanism during the initial process induced by e-beam, we formulated a model to extract molecular information from ED patterns and conducted a kinetic study for a diverse molecular scope including organic molecules in addition to inorganic matters using the Arrhenius plot. We found the initial process has a small activation energy for a thermal process, which indicates the process proceeds in a non-equilibrium way with the help of e-beam. Furthermore, we found a correlation between the frequencies of the process and bulk melting entropy, which indicates the molecular mechanism behind the fading of ED patterns that occurs within the low dose process can be understood as melting.



1) C. J. Russo, L. A. Passmore *Science* **2014**, 346, 1377. 2) K. Maydenova, P. Jia, C. J. Russo *Science* **2020**, 370, 223.

サリドマイド加水分解物の分子内脱水戻り

(早大院先進理工¹・早大データ科学センター²) ○朝日 透¹・蔦尾 滉一¹・谷口 卓也²・乙川 光平¹・中村 美利¹・荻野 禎之¹

Reformation of thalidomide from its hydrolysis compound via intramolecular dehydration
(¹Graduate School of Advanced Science and Engineering, Waseda University, ²Center for Data Science, Waseda University) ○Toru Asahi,¹ Koichi Tsutao,¹ Takuya Taniguchi,² Kohei Otagawa,¹ Miri Nakamura,¹ Yoshiyuki Ogino¹

Thalidomide is a famous chiral drug, which has both negative and positive effects. While the drug caused severe harmful side effects over a half-century ago, thalidomide has again been commercialized for some intractable diseases. Thalidomide can be metabolized by some processes including hydrolysis, which can afford three different compounds depending on the reaction site. The physicochemical behavior of hydrolysis compounds would be, in part, the origin of the effectiveness of thalidomide, and thus to be investigated. This research reports that one of these hydrolysis compounds returns to thalidomide via intramolecular dehydration reaction in an organic solvent, but that the other two do not. The difference of dehydration behavior was rationalized based on molecular structures: the reformable molecule has the preferable geometric environment for intramolecular dehydration.

Keywords: Thalidomide; Hydrolysis Compounds; Intermolecular Dehydration; Chiral Drug

サリドマイドは薬効及び副作用の両面から有名なキラルな医薬品である。半世紀以上前に重篤な副作用を示したサリドマイドであったが、現在では抗難病薬として再び商品化されている。サリドマイドは加水分解を含むいくつかのプロセスによって代謝され、加水分解の場合、反応部位によって α -(2-

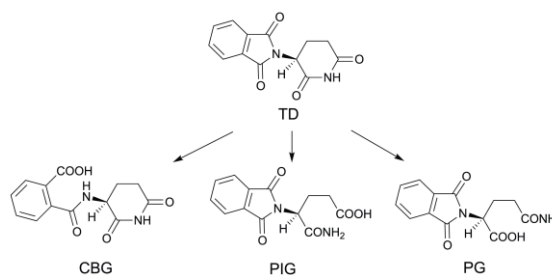


図 1. サリドマイド(TD)の加水分解物

Carboxybenzamido) glutarimide (CBG)、Phthaloylisoglutamine (PIG)、Phthaloylglutamine (PG)の3つの化合物を生成しうる (図 1)。加水分解物はサリドマイドが示す薬効の根源の一部となり得るため、その物理化学的挙動を調べることは重要である。本研究では3つの加水分解物のうち CBG だけが有機溶媒中で分子内脱水反応によってサリドマイドに戻ることを報告する。¹⁾

3つの加水分解物をアセトニトリル中に11日間、60 °Cで放置したところ、PIG、PGでは変化がなかったが、CBGがサリドマイドに変化していることが高速液体クロマトグラフィー分析により分かった。この理由を説明するため、単結晶 X 線構造解析を行い、開環した C-N 間の距離に注目した。その結果、CBG では 3.3-3.6 Å と分子内脱水を起こすに十分近い距離である一方、PIG、PG ではそれぞれ 6.3Å、5.6Å と長く、C-N 間の距離に基づいて加水分解物間での脱水挙動の違いを説明できた。

1) T. Taniguchi, M. Nakamura, K. Tsutao, K. Otagawa, Y. Ogino, T. Asahi, under review.

[A04-1am] 07. Inorganic Chemistry

Chair: Shintaro Ida, Makoto Kobayashi

Fri. Mar 19, 2021 9:00 AM - 11:20 AM Room 4 (Online Meeting)

[A04-1am-01] Synthesis and characterisation of the high pressure polymorphs of BaRhO₃○Sean Dusan Injac¹, Fabio Denis Romero¹, Yuichi Shimakawa¹ (1. Kyoto University)

9:00 AM - 9:20 AM

[A04-1am-02] New Alkali Hydride Antiperovskites as Fast Ionic Conductors○Cedric Tassel¹, Shenghan Gao¹, Thibault Broux¹, Susumu Fujii², Kentaro Yamamoto¹, Yao Xiao¹, Itaru Oikawa⁴, Hitoshi Takamura⁴, Hiroki Ubukata¹, Yuki Watanabe¹, Kotaro Fujii³, Masatomo Yashima³, Akihide Kuwabara², Yoshiharu Uchimoto¹, Hiroshi Kageyama¹ (1. Kyoto University, 2. Japan Fine Ceramics Center, 3. Tokyo Institute of Technology, 4. Tohoku University)

9:20 AM - 9:40 AM

[A04-1am-03] Large latent heat and barocaloric effects at charge transfer transitions of A-site ordered perovskite oxides○Yoshihisa Kosugi¹, Masato Goto¹, Asaya Fujita², Takashi Saito³, Takashi Kamiyama³, Yuichi Shimakawa¹ (1. Kyoto University, 2. National Institute of Advanced Industrial Science and Technology, 3. High Energy Accelerator Research Organization)

9:40 AM - 10:00 AM

[A04-1am-04] A comparative study of A-site ordered quadruple perovskite structures containing divalent manganese, iron, cobalt and nickel square-planar centers○Midori Estefani Amano Patino¹, Fabio Denis Romero^{1,2}, Sean Injac¹, Masato Goto¹, Yuichi Shimakawa¹ (1. Institute for Chemical Research, Kyoto University, 2. Hakubi Center for Advanced Research, Kyoto University)

10:00 AM - 10:20 AM

[A04-1am-05] Two-dimensional Li-ion conduction in a Ruddlesden-Popper phase of lithium-hydroxide-halide antiperovskites○Anucha Koedtrud¹, Midori Amano Patino¹, Daisuke Kan¹, Yuichi Shimakawa¹ (1. Institute for Chemical Research, Kyoto Univ.)

10:20 AM - 10:40 AM

[A04-1am-06] Selective fabrication of Ca₂NH epitaxial thin films using magnetron sputtering system○Seoungmin Chon¹, Shigeru Kobayashi¹, Kazunori Nishio¹, Ryota Shimizu^{1,2}, Taro Hitosugi¹ (1. Department of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo, 152-8552, Japan, 2. PRESTO, Japan Science and Technology Agency, Saitama, 332-0012, Japan)

10:40 AM - 11:00 AM

[A04-1am-07] Ultra-high concentration hydrogen doping into rutile-TiO₂ with in situ transport measurements○GyeongCheol Lim¹, Mitsuhiko Maesato¹, Ryo Nakayama², Dae-Woon Lim^{1,3}, Takahiro Ozawa⁴, Markus Wilde⁴, Katsuyuki Fukutani⁴, Hiroshi Kitagawa¹ (1. Kyoto Univ., 2. Tokyo

Tech., 3. Yonsei Univ., 4. The Univ. of Tokyo)

11:00 AM - 11:20 AM

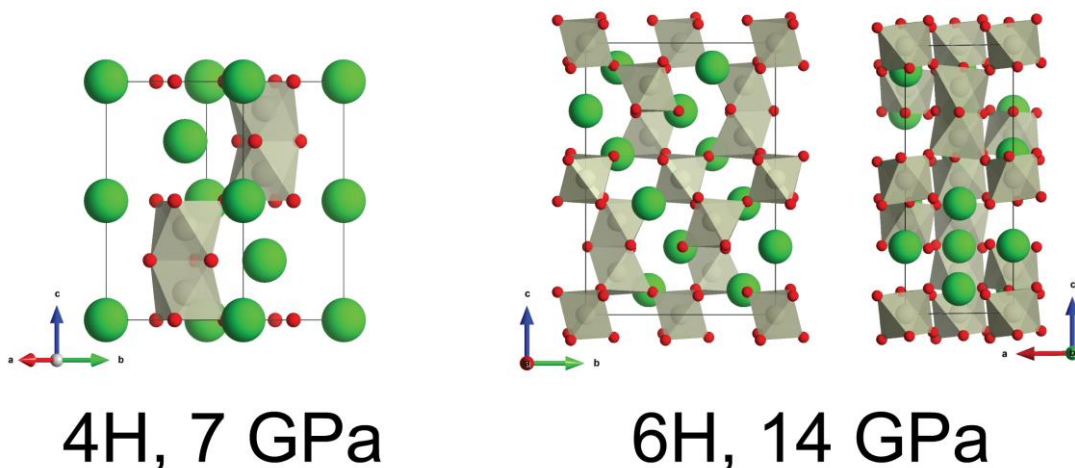
Synthesis and characterisation of the high pressure polymorphs of BaRhO₃

(¹*Institute for Chemical Research, Kyoto University*), ○Injac Sean Dusan,¹ Denis Fabio Romero,¹ Xu Yuanhui,¹ Shimakawa Yuichi,¹

Keywords: High Pressure, High Temperature Synthesis; Metallic Oxides; Hexagonal Perovskites; Strongly Correlated Electrons

We report the synthesis and characterisation of two phases of BaRhO₃ stabilised under high pressure, high temperature (HPHT) synthesis conditions. Synthesis at pressures of 4 to 7 GPa resulted in stabilisation of the 4H perovskite polymorph. Synthesis at higher pressures of 14 to 22 GPa stabilised a novel 6H phase of BaRhO₃. Structure refinement carried out against X-ray diffraction data collected at SPring-8 confirms the hexagonal *P*6₃/*mmc* structure for the 4H polymorph.¹ The 6H polymorph was determined to crystallise in the monoclinic space group *C*2/*c*. X-ray data did not indicate any oxygen or rhodium non-stoichiometry. This confirms the uncommonly high oxidation state of Rh⁴⁺ (*S* = ½) is stabilised through high oxygen pressures achieved via HPHT synthesis.

Magnetisation, heat capacity, and resistivity measurements were carried out for both compounds. The magnetic susceptibilities include large temperature-independent terms. Metallic conductivity is observed for the 4H polymorph, while resistivity measurements indicate the 6H polymorph is a semiconductor due to grain boundary effects. High Wilson ratios of approximately $R_w \approx 2$ indicate both polymorphs are strongly electron correlated systems, consistent with the high spatial diffusivity of the 4*d* orbitals. Magnetic ground state and density of state calculations were carried out for both compounds. These electronic structure calculations give metallic ground states for both structures. All these results indicate Pauli paramagnetic ground states for both polymorphs.



1) B. L. Chamberland and J. B. Anderson, *J. Solid State Chem.* **1981**, 39(1), 114-119.

アルカリイオン伝導体としての新規水素化物アンチペロブスカイト化合物

(京都大学¹・JFCC²・東北大学³・東京工業大学⁴) ○タッセル
セドリック¹・高勝寒¹・ブルーチボー¹・藤井進²・山本健太郎¹・肖
遥¹・及川格³・高村仁³・生方宏樹¹・渡邊雄貴¹・藤井孝太郎⁴・八島
正知⁴・桑原彰秀²・内本喜晴¹・陰山洋¹

New Alkali Hydride Antiperovskites as Fast Ionic Conductors (¹Kyoto University,
²Japan Fine Ceramics Center, ³Tohoku University, ⁴Tokyo Institute of Technology)
○Cédric Tassel¹, Shenghan Gao¹, Thibault Broux¹, Susumu Fujii², Kentaro
Yamamoto¹, Yao Xiao¹, Itaru Oikawa³, Hitoshi Takamura³, Hiroki Ubukata¹, Yuki
Watanabe¹, Kotaro Fujii⁴, Masatomo Yashima⁴, Akihide Kuwabara², Yoshiharu
Uchimoto¹, Hiroshi Kageyama¹

The antiperovskite (AP) structural type is a vast family of materials which can be described as charge inverted perovskites where anions occupy the cuboctahedral and octahedral sites and cations sit at the corner of octahedra. It has been suggested that soft anionic body centered cubic sublattice, as observed in AP, could be interesting towards the development of alkali metal ionic conductors. From this, we explored the use of the highly polarizable hydride H⁻ anion in AP and discovered a new series of alkali rich ion conducting structures (A₃HX, A = Li, Na and X = S, Se, Te) via high pressure synthesis.^[1] In this presentation, the structure, stability and ionic transport properties of the new materials will be discussed.

Keywords : Perovskite; Antiperovskite; Hydrides; Ionic conductivity

アンチペロブスカイト (AP) 構造は、通常のペロブスカイト構造の電荷反転型構造として説明できる。一般式は M₃BA と書かれ、M が陽イオン、A、B は陰イオンである。陰イオン A、B は、それぞれ立方八面体サイトと八面体サイトを占有し、カチオンは B 中心八面体の頂点に位置する。ペロブスカイト型化合物と同様に、単純な構造と組成を併せ持つため、新物質探索に有望な化合物群である。また、AP 構造で見られるような柔軟なアニオン体心立方副格子においては、優れた陽イオン伝導性の発現が期待できる。本研究では、高い分極率を有する水素化物イオン H⁻を含む新規 AP 型化合物 A₃HX (A = Li, Na; X = S, Se, Te) の高圧合成およびイオン伝導性を報告する。^[1]当日は、理論計算の結果も交えて、構造安定性、構造とイオン伝導性の相関について議論する。

[1] Hydride-based antiperovskites with soft anionic sublattices as fast alkali ionic conductors. S. Gao et al. *Nat. Commun.* **2021**, *12*, 201.

Large latent heat and barocaloric effects at charge transfer transitions of A-site ordered perovskite oxides

(¹*Institute for Chemical Research, Kyoto University*, ²*National Institute of Advanced Science and Technology*, ³*High Energy Accelerator Research Organization*) ○Yoshihisa Kosugi¹, Masato Goto¹, Asaya Fujita², Takashi Saito³, Takashi Kamiyama³, Yuichi Shimakawa¹

Keywords: Unusual High Valence Ion; Charge Transfer; Latent Heat; Barocaloric Effect; Magnetic Entropy

An A-site ordered perovskite oxide $\text{NdCu}_3\text{Fe}_4\text{O}_{12}$ containing unusual high valence Fe ions shows an intersite charge transfer transition between Cu at the A' site and Fe at the B site represented by $3\text{Cu}^{2+} + 4\text{Fe}^{3.75+} \rightarrow 3\text{Cu}^{3+} + 4\text{Fe}^{3+}$ near room temperature.^{1,2} The transition is accompanied by a large volume change as well as metal-to-insulator and paramagnetic-to-antiferromagnetic transitions (Figure 1). We found that the present $\text{NdCu}_3\text{Fe}_4\text{O}_{12}$ released large latent heat 25.5 kJ/kg and the corresponding entropy change 84.2 J/K·kg by the intersite charge transfer transition (Figure 2). We also demonstrated that the latent heat could be utilized through a barocaloric effect by applying pressure.³

The observed large entropy change is contributed by the lattice and spin degrees of freedom. The large negative-thermal-expansion-like volume change and the unusual first-order magnetic transition at the charge transition temperature should play important roles in giving rise to the significant entropy change.

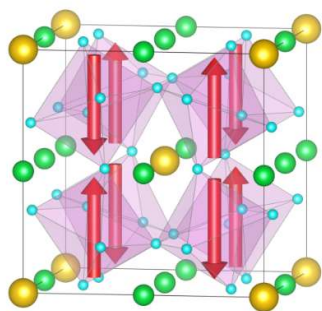


Figure 1 Crystal and magnetic structure of $\text{NdCu}_3\text{Fe}_4\text{O}_{12}$.

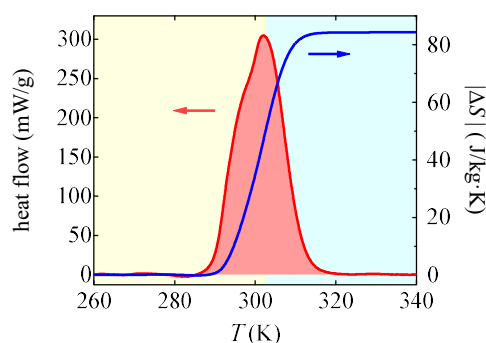


Figure 2 Heat flow and the corresponding entropy change of $\text{NdCu}_3\text{Fe}_4\text{O}_{12}$.

- [1] Y. Long, *et al.*, *Nature* **458**, 60 (2009), [2] Y. Shimakawa, *et al.*, *APL Materials* **6**, 086106 (2018), [3] Y. Kosugi, *et al.*, *submitted* (2020)

A comparative study of *A*-site ordered quadruple perovskite structures containing divalent manganese, iron, cobalt and nickel square-planar centers

(¹*Institute for Chemical Research, Kyoto University*, ²*Hakubi Center for Advanced Research, Kyoto University*) ○ Midori Estefani Amano Patino¹, Fabio Denis Romero^{1,2}, Sean Injac¹, Masato Goto¹, Yuichi Shimakawa¹

Keywords: *A*-site ordered quadruple perovskites, High pressure synthesis, Crystal structure characterization, Magnetic property characterization, Magnetic spin ordering

The *A*-site-ordered quadruple perovskite structure of general formula $AA'_3B_4O_{12}$ (Figure 1) can accommodate transition metal (TM) cations at the square-planar *A'* site. The stabilization of these compounds is often challenging and their preparation requires high pressure and high temperature. When the *B* sites of quadruple perovskite structures are occupied by non-magnetic cations, the complex magnetic interactions between the spins at the orthogonally-oriented *A'*-sites can provide a variety of exotic magnetic orders.¹⁻³

We recently found that the magnetic structure of the *A'*-site Fe^{2+} spin-sublattice in $CaFe_3Ti_4O_{12}$ adopts an unusual multi-*k* antiferromagnetic arrangement which is affected by applied magnetic fields. Building on these results, we have turned our attention to the synthesis of the series $CaA'_3Ti_4O_{12}$ ($A' = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}$) for a comparative study towards further understanding the non-trivial behaviour of the *A'*-site magnetic sublattices in this structural class. Here we present some insights on the challenging synthesis and the results from characterization of these materials.

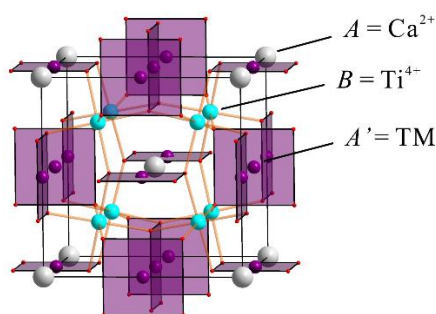


Figure 1. Representation of the structure of the quadruple perovskites where small TM cations (*e.g.* Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+}) can be accommodated at the *A'* square-planar site.

1) Y. Shimakawa and T. Saito, *Phys. Status Solidi Basic Res.* **2012**, 249, 423. 2) T. Saito, M. Toyoda, C. Ritter, S. Zhang, T. Oguchi, J. P. Attfield, and Y. Shimakawa, *Phys. Rev. B.* **2014**, 90, 214405. 3) M. Toyoda, T. Saito, K. Yamauchi, Y. Shimakawa, and T. Oguchi, *Phys. Rev. B.* **2015**, 92, 014420.

Two dimensional Li-ion conduction in a Ruddlesden-Popper phase of lithium-hydroxide-halide antiperovskites

(Institute for Chemical Research, Kyoto University) ○Anucha Koedtruad, Midori Amano Patino, Daisuke Kan, Yuichi Shimakawa

Keywords: Li-batteries; Antiperovskites; ionic conductivity; crystal structure

Lithium-oxide-halide and lithium-hydroxide-halide antiperovskites were intensively studied for potential electrolytes in all-solid Li-ion batteries. In this work, Ruddlesden Popper (RP) phases of $\text{LiX}(\text{Li}_{3-p}\text{OH}_p\text{X})_n$ antiperovskites with $\text{X} = \text{Br}$ and Cl , $n = 1, 2$, and 3 , and $p = 0, 0.5$, and 1 , were explored. The $n = 2$ RP phase $\text{LiBr}(\text{Li}_2\text{OHBr})_2$ was successfully obtained. The compound crystallizes in a tetragonal structure with space group $I4/mmm$. The crystal structure consists of double antiperovskite Li_2OHBr layers intercalated with rock-salt type LiBr layers. Li-ion vacancies are introduced selectively to the antiperovskite layers, and the rock-salt type LiBr layers are rigid. The RP $\text{LiBr}(\text{Li}_2\text{OHBr})_2$ exhibits ionic conductivity of $1.27 \times 10^{-7} \text{ S/cm}$ at 30°C with an activation energy of 0.57 eV . The rigid rock-salt type LiBr layers contribute less in Li-ion hopping and thus the Li-ion conduction occurs through the Li-ion vacancies within the antiperovskite layers, resulting in the two-dimensional ion conduction. Cl-containing compounds, in contrast, cannot be crystallized with the RP phases due to the structural mismatch between the antiperovskite layers and the rock-salt type LiCl layers.

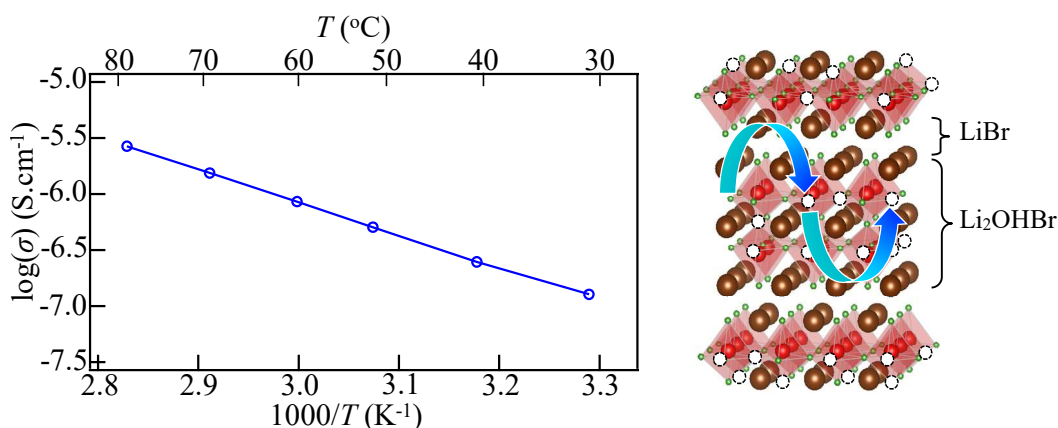


Figure 1 Temperature-dependent ionic conductivity (left) and two-dimensional Li-ion conduction (right) in the $n = 2$ RP phase $\text{LiBr}(\text{Li}_2\text{OHBr})_2$.

Selective fabrication of Ca_2NH epitaxial thin films using magnetron sputtering system

(¹Department of Materials and Chemical Technology, Tokyo Institute of Technology, ²PRESTO, Japan Science and Technology Agency) ○ Seoungmin Chon,¹ Ryota Shimizu,^{1,2} Shigeru Kobayashi,¹ Kazunori Nishio,¹ Taro Hitosugi¹

Keywords: Epitaxial thin films; Metal nitride hydride; Reactive sputtering;

Ca_2NH is a promising catalyst for the production of NH_3 , which is an important chemical such as fertilizers and hydrogen storage [1]. To quantitatively understand the mechanism of the catalytic reactions, epitaxial thin film surfaces can provide an ideal platform due to well-defined size and crystal orientation. However, Ca_2NH thin film has not been reported to date. In addition, due to the structural similarity between Ca_2NH and CaNH , it is difficult to selectively stabilize the Ca_2NH phase using epitaxial effects. In this study, under various gas conditions, we study a route to selectively fabricate Ca_2NH epitaxial thin films using reactive magnetron sputtering.

Ca-N-H thin films were deposited on $\text{MgO}(110)$ (a) substrates using reactive magnetron sputtering. A Ca metal plate (diameter of 1 inch) was used as a target material. The substrate temperature was set to 400 °C, and RF power of 30 W was supplied. The total pressure was set to 1.0 Pa, and the partial pressures of Ar, N_2 , and H_2 gases (P_{Ar} , P_{N_2} , and P_{H_2} , respectively) were varied to explore the growth conditions for Ca_2NH phase. The structural properties were characterized by X-ray diffraction (XRD) and Raman spectroscopy. Due to the air-instability of the thin films, air-tight cells were used for the characterizations.

Figure 1a shows out-of-plane XRD patterns of thin films fabricated at different $P_{\text{H}_2}/P_{\text{N}_2}$ (0.033 - 1.00). A peak appeared at $2\theta \sim 50.9^\circ$ for $P_{\text{H}_2}/P_{\text{N}_2} = 0.033$, suggesting Ca_2NH 440. As $P_{\text{H}_2}/P_{\text{N}_2}$ increased to 0.13, the peak position was shifted to a lower angle ($\sim 49.9^\circ$), suggesting the phase transition from Ca_2NH to CaNH . Note that there is almost no peak in higher $P_{\text{H}_2}/P_{\text{N}_2}$.

This phase transition scenario is also confirmed by Raman spectroscopy. In Figure 1b, a sharp peak appears at 321 cm^{-1} for $P_{\text{H}_2}/P_{\text{N}_2} = 0.033$, corresponding to Ca_2NH [1], whereas the peak is diminished as $P_{\text{H}_2}/P_{\text{N}_2}$ increased. Namely, Ca_2NH thin film is selectively fabricated in $P_{\text{H}_2}/P_{\text{N}_2} = 0.033$. To the best of our knowledge, this study is the first report of metal-nitrogen-hydrogen epitaxial thin films.

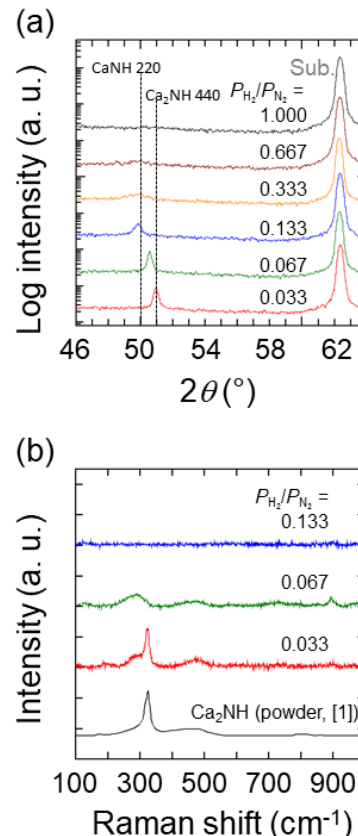


Fig. 1 $P_{\text{H}_2}/P_{\text{N}_2}$ dependence of (a) Out-of-plane XRD patterns and (b) Raman spectra

1) M. Kitano *et al.*, *Chem. Sci.* **2016**, 7.

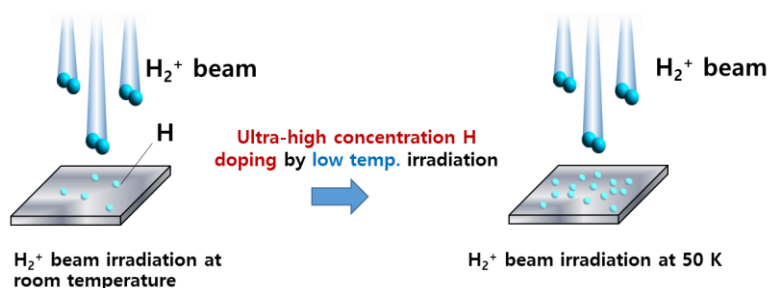
Ultra-high concentration hydrogen doping into rutile-TiO₂ with in situ transport measurements

(¹Graduate School of Science, Kyoto University, ²Department of Chemical Science and Engineering, Tokyo Institute of Technology, ³College of Science and Technology, Yonsei University, ⁴Institute of Industrial Science, The University of Tokyo) ○GyeongCheol Lim,¹ Mitsuhiro Maesato,¹ Ryo Nakayama,² Dae-Woon Lim,^{1,3} Takahiro Ozawa,⁴ Markus Wilde,⁴ Katsuyuki Fukutani,⁴ Hiroshi Kitagawa¹

Keywords: H doping; H ion beam; NRA; Transport measurement

Hydrogen doping can be a powerful method for controlling the properties of materials since hydrogen shows various charge states from -1 to +1 when it interacts with materials. However, high-concentration hydrogen doping and investigation of its effects are still challenging due to a limitation of the doping amount with conventional methods such as hydrogen gas exposure. It is also difficult to investigate the effect of hydrogen doping since doped hydrogens could be easily desorbed. To overcome these difficulties, we have developed a low-temperature hydrogen ion beam irradiation system with in situ transport measurements.¹ Using this system, we have investigated the effect of ultra-high-concentration hydrogen doping into rutile-TiO₂ which is one of the most widely studied metal oxide for potential applications such as transparent conductor, photocatalysis, hydrogen sensor and so on.

Herein, we report the achievement of ultra-high-concentration hydrogen doping into rutile-TiO₂ by a low-temperature (50 K) irradiation with its unforeseen charge transport properties, such as reversible resistance switching. Remarkably, the polycrystalline thin film shows a reversible resistance switching between 3D-Mott and Efros-Shklovskii variable range hopping conductions.² The heavily doped hydrogen with a certain distribution along the depth direction in rutile-TiO₂ was confirmed by in situ nuclear reaction analysis (NRA). We discuss the effects of hydrogen doping on the basis of the various in situ or ex-situ measurements such as transport, Hall effects, and crystal structure analysis.



1) R. Nakayama, N. Suzuki, M. Maesato, T. Nagaoka, M. Arita, H. Kitagawa, *Rev. Sci. Instrum.*, 2017, 88, 123904.

2) G. Lim, M. Maesato, R. Nakayama, D. Lim, H. Kitagawa, *Appl. Phys. Express*, 2020, 13, 105502.

[A06-1pm] 08. Catalysts and Catalysis

Chair: Hisao Yoshida, Akira Yamakata

Fri. Mar 19, 2021 1:00 PM - 3:20 PM Room 6 (Online Meeting)

[A06-1pm-01] Decarboxylative transformation modulated by photocatalyst○Yota Sakakibara¹, Kei Murakami², Kenichiro Itami¹ (1. Nagoya University, 2. Kwansei Gakuin University)

1:00 PM - 1:20 PM

[A06-1pm-02] Electron Transfer Kinetics of Aluminum Porphyrin/ Metal Oxide Systems○Abin Sebastian¹, Fazalurahman Kuttassery², Hiroshi Tachibana¹, Haruo Inoue¹ (1. Tokyo Metropolitan University, 2. Tokyo Institute of Technology)

1:20 PM - 1:40 PM

[A06-1pm-03] Construction of visible-light Z-scheme water splitting system using nitrogen/fluorine codoped TiO₂○Akinobu Miyoshi¹, Junie Jhon M. Vequizo², Shunta Nishioka¹, Shunsuke Yamashita³, Shunsuke Nozawa⁴, Akihide Kuwabara⁵, Akira Yamakata², Koji Kimoto³, Kazuhiko Maeda¹ (1. Tokyo Tech., 2. TTI, 3. NIMS, 4. KEK, 5. JFCC)

1:40 PM - 2:00 PM

[A06-1pm-04] Co-catalyst effects on photoelectrochemistry of bismuth vanadate studied with kinetic analysis of photocarrier and reaction○Yoshiyasu Matsumoto¹, Akihiko Kudo² (1. Toyota Physical and Chemical Research Institute, 2. Tokyo University of Science)

2:00 PM - 2:20 PM

[A06-1pm-05] Improvement of photoelectrochemical performances of particulate ZnSe:ClGS photocathodes by particle size control and electrochemical evaluation for surface and bulk characteristics○Fumiaki TAKAGI¹, Yosuke KAGESHIMA^{1,2}, Katsuya TESHIMA^{1,2}, Kazunari DOMEN^{2,3}, Hiromasa Nishikiori^{1,2} (1. Graduate School of Engineering, Shinshu Univ., 2. Research Initiative for Supra-Materials(RISM), 3. The Univ. of Tokyo)

2:20 PM - 2:40 PM

[A06-1pm-06] Effects of composition of Cu₂Sn_xGe_{1-x}S₃ particles on photocatalytic and photoelectrochemical hydrogen evolution activity○Yosuke Kageshima^{1,2}, Sota Shiga¹, Tatsuki Ode¹, Fumiaki Takagi¹, Katsuya Teshima^{1,2}, Kazunari Domen^{2,3}, Hiromasa Nishikiori^{1,2} (1. Shinshu Univ., 2. Research Initiative for Supra-Materials, Shinshu Univ., 3. The Univ. of Tokyo)

2:40 PM - 3:00 PM

[A06-1pm-07] Extremely small cobalt oxide particle formation on BiVO₄ film electrode by successive ionic layer adsorption and reaction-calcination cycle method and the property for photoelectrochemical water oxidation○Furukawa Yuichi¹, Shu Nakashima¹, Musashi Fujishima², Hiroaki Tada¹ (1. Graduate School of Science and Engineering, Kindai University, 2. Faculty of Science and Engineering, Kindai University)

3:00 PM - 3:20 PM

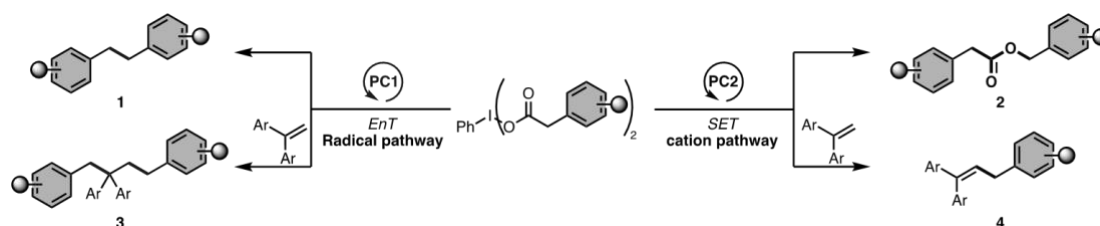
Decarboxylative transformation modulated by photocatalyst

(¹Graduate School of Science, Nagoya University, ²Graduate School of Science and Engineering, Kwansei Gakuin University, ³Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University) ○Yota Sakakibara,¹ Kei Murakami,² Kenichiro Itami^{1,3}

Keywords: Photoredox catalyst; Radical; Cation; Visible light; Hypervalent iodine

Carboxylic acids are abundant and readily available starting material. The recent development of photoredox catalysts, which can induce single-electron transfer (SET) under visible light irradiation, has enhanced the utility of carboxylic acids as an alkyl radical precursor.¹ Because of the inherent nucleophilic nature of alkyl radicals, various electrophilic substrates can react with carboxylic acid under photoredox-conditions. Recently, reactions between carboxylic acid and nucleophilic substrates were attained.² In these reactions, carbocations are utilized as key intermediates, which generate via photoredox-catalyzed radical-polar crossover mechanism from carboxylic acid. During the course of our study^{2a}, we envisioned that the control of these distinct reactive intermediates by the choice of photocatalyst (PC) would offer an opportunity to develop divergent decarboxylative reactions that give different products from the same starting materials.

Herein, we report a photocatalyzed divergent decarboxylative transformation of arylacetic acids activated by hypervalent iodine. Our reaction enables the divergent synthesis of 1,2-diarylethane **1** and arylmethyl arylacetate **2** from arylacetic acids. The divergency of our decarboxylation is derived from two distinctive reaction pathways of photocatalytic triplet excited state: energy transfer (EnT) and SET. With a catalyst that favors EnT, C–C bond formation proceeds via the radical-radical coupling. Under SET conditions, on the other hand, benzyl cation is a reactive intermediate that generates through the radical-polar crossover mechanism, and C–O bond formed product is obtained. Additionally, by adding 1,1-diaryl ethylene as a reactant into our optimal conditions, dibenzylated product **3** or monobenzylated product **4** were obtained with good selectivity by changing the photocatalyst, respectively.



- 1) Jin, Y.; Fu, H. *Asian J. Org. Chem.* **2017**, *6*, 368.
 2) a) Sakakibara, Y.; Ito, E.; Fukushima, T.; Murakami, K.; Itami, K. *Chem.–Eur. J.* **2018**, *24*, 9254. b) Shibutani, S.; Kodo, T.; Takeda, M.; Nagao, K.; Tokunaga, N.; Sasaki, Y. Ohmiya, H. *J. Am. Chem. Soc.* **2020**, *142*, 1211. c) Webb, E. W.; Park, J. B.; Cole, E. L.; Donnelly, D. J.; Bonacorsi, S. J.; Ewing, W. R.; Doyle, A. G. *J. Am. Chem. Soc.* **2020**, *142*, 9493.

Electron Transfer Kinetics of Aluminum Porphyrin/ Metal Oxide Systems

(Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University) ○Abin Sebastian, Fazalurahman Kuttassery, Hiroshi Tachibana, and Haruo Inoue

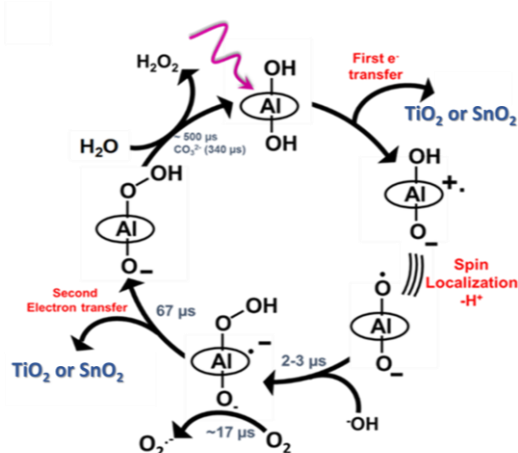
Keywords: Molecular Catalyst, Water Splitting, Metalloporphyrin, Electron transfer, Hydrogen peroxide

Molecular catalyst sensitized system (MCSS) for the simultaneous photocatalytic generation of hydrogen and hydrogen peroxide solely from water is a coveted, yet less explored route for sustainable energy systems. In Recent years, we probed into various earth-abundant metalloporphyrins for their potential application as two-electron water oxidation catalyst. Substantial progresses have been made from electrochemical one-electron initiated two-electron water oxidation to visible light-induced one-photon initiated water splitting.¹ These metalloporphyrin incorporated MCSS systems would be an ideal candidate for photocatalytic water splitting to hydrogen and hydrogen peroxide. Such systems have potential to solve photon flux density hurdle of artificial photosynthesis through one photon-initiated process.

Anionic 5,10,15,20-tetra(4-carboxy)phenylporphyrinatealuminum (AITCPP) and Cationic 5,10,15,20-tetrakis(1-methylpyridin-1-ium-4-yl)porphyrinatealuminum (AITMPyP) both show electrochemical one-electron initiated two electron water oxidation. Photocatalytic water-splitting of AITCPP incorporated on TiO₂

served as the first exemplum to get through the above-mentioned bottle neck of artificial photosynthesis.¹ The disparity in electrochemical and photochemical activity of AITMPyP and AITCPP lead us to further investigate the electron transfer in one photon-initiated water splitting process by these MCSS systems. The first and second electron transfer from metalloporphyrin to the semiconductor plays a crucial role in designing an efficient photocatalytic MCSS system. How

can we improve the electron transfer from molecular catalyst to semiconductor system? Here we focused our attention to the electron transfer processes in ionically adsorbed AITCPP and AITMPyP in titanium(IV) oxide and tin (IV) oxide. Through fluorescence lifetime and photoelectrochemical studies we compare the electron transfer of aluminum porphyrins in these two metal oxides.



1)F. Kuttassery, S. Sagawa, S. Mathew, Y. Nabetani, A. Iwase, A. Kudo, H. Tachibana, H. Inoue, *ACS Appl. Energy Mater.* **2019**, 2, 11, 8045-8051.

Construction of visible-light Z-scheme water splitting system using nitrogen/fluorine codoped TiO₂

(¹Tokyo Institute of Technology, ²Toyota Technological Institute, ³National Institute for Material Science, ⁴High Energy Accelerator Research Organization, ⁵Japan Fine Ceramics Center) ○Akinobu Miyoshi,¹ Junie Jhon M. Vequizo,² Shunta Nishioka,¹ Shunsuke Yamashita,³ Shunsuke Nozawa,⁴ Akihide Kuwabara,⁵ Akira Yamakata,² Koji Kimoto,³ Kazuhiko Maeda¹

Keywords: Codoping; Visible-Light Response; Photocatalyst; Mixed-Anion Compounds

Significant efforts have been devoted to develop visible-light responsive photocatalysts from the viewpoint of solar energy conversion. Nitrogen doping into TiO₂ has been studied intensively as a way to obtain a visible-light-responsive photocatalyst.¹ In this study, nitrogen/fluorine codoping² into rutile TiO₂ was conducted in the aim of increasing the nitrogen incorporation and to obtain enhanced visible-light absorption. Nitrogen/fluorine codoped rutile TiO₂ (TiO₂:N,F) was synthesized by nitriding a mixture of rutile TiO₂ and (NH₄)₂TiF₆ at 773 K for 1 h under an NH₃ flow. By increasing the (NH₄)₂TiF₆ concentration in the precursor mixture, visible-light absorption became more pronounced. The pronounced visible light absorption in TiO₂:N,F was attributed to increased nitrogen content along with fluorine incorporation, which was confirmed by elemental analysis. It should be noted that no nitrogen and visible light absorption was observed without addition of (NH₄)₂TiF₆. By using first-principle calculation, copresence of fluorine during nitridation enhances incorporation of nitrogen and fluorine into rutile TiO₂ lattice. Furthermore, the addition of fluorine along with nitrogen was revealed to suppress formation of defect states caused by titanium reduced species and/or oxygen vacancies, which usually lower photocatalytic activity.³

TiO₂:N,F loaded with RuO_x was applied in Z-scheme water splitting system as an O₂ evolution photocatalyst in combination with Ru loaded Rh doped SrTiO₃ (Ru/SrTiO₃:Rh; H₂ evolution photocatalyst), in the presence of [Co(bpy)₃]^{3+/2+} (bpy = 2,2'-bipyridine) as a redox mediator. This system evolved H₂ and O₂ at a ratio close to 2:1 under visible light as well as simulated sunlight irradiation. The solar to hydrogen energy conversion efficiency of the system reached 0.027%. Also we succeeded in decreasing the particle size of the TiO₂:N,F by optimizing synthesis conditions and increased visible-light photocatalytic activity by a factor of 6.

1) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, 293, 269. 2) a) K. Nukumizu, J. Nunoshige, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *Chem. Lett.* **2003**, 32, 196. b) K. Maeda, Y. Shimodaira, B. Lee, K. Teramura, D. Lu, H. Kobayashi, K. Domen, *J. Phys. Chem. C* **2007**, 111, 18264. 3) A. Nakada, S. Nishioka, J. J. M. Vequizo, K. Muraoka, T. Kanazawa, A. Yamakata, S. Nozawa, H. Kumagai, S.-i. Adachi, O. Ishitani, K. Maeda, *J. Mater. Chem. A* **2017**, 5, 11710.

光キャリアと反応についての速度論的解析：バナジン酸ビスマスの光電気化学反応における助触媒担持効果

(豊田理研¹・東京理科大²) ○松本 吉泰¹・工藤 昭彦²

Co-catalyst effects on photoelectrochemistry of bismuth vanadate studied with kinetic analysis of photocarrier and reaction (¹Toyota Physical and Chemical Research Institute, ²Faculty of Science, Tokyo University of Science) ○Yoshiyasu Matsumoto,¹ Akihiko Kudo²

In the heterogeneous photocatalysis, the dynamics of photo-generated charge and the electrochemical reactions at catalyst surfaces are involved in a complex manner, thus it is not easy to elucidate the overall reaction mechanism. Because oxygen evolution reaction (OER) is a rate determining step of total water splitting, it is important to understand how co-catalyst enhances the reaction rate. Here, we conducted simultaneous measurements of transient absorption of photohole and anodic photocurrent density at a working electrode of bismuth vanadate (BiVO₄) thin film during the irradiation of a 405 nm light pulse (time duration 2 s). These measurements provide the hole concentration accumulated in the working electrode and the reaction rate (charge transfer rate) at the interface with electrolyte. Our choice of co-catalyst is cobalt oxide (CoO_x). First, we confirm that the reaction rate is approximately doubled by loading the co-catalyst. Second, the simultaneous measurements provide invaluable information for an understanding of OER kinetics: the relation between reaction rate and hole density. In the case of oxidation of hole scavenger, Na₂SO₃, the photocurrent increases with photohole density linearly. In contrast, the photocurrent of OER depends on photohole density nonlinearly particularly for BiVO₄ with the co-catalyst. This indicates that OER has a rate determining step that proceeds when multiple photoholes are accumulated at a reaction site.

Keywords : Photocatalysis; Transient Absorption ; Bismuth Vanadate; Photocurrent;

不均一光触媒反応には、光励起により生成された電荷のダイナミクスと触媒表面反応が複雑に関与しているため、全体の反応機構の解明は容易ではない。また、酸素発生過程は水の完全分解における律速段階となっており、助触媒担持による反応加速の反応機構解明が重要である。本研究では、バナジン酸ビスマス (BiVO₄) 薄膜を陽極とした光電気化学的水の酸化反応について、光誘起正孔による過渡吸収と光電流を同時測定することにより反応機構の理解を促進することを試みた。助触媒としてはコバルト酸化物 (CoO_x) を用いた。この同時測定から 405 nm 励起光照射中の BiVO₄ 薄膜に蓄積された正孔密度と電極界面での反応速度 (電荷移動速度) を見積ることができる。まず、助触媒担持により反応速度には約 2 倍の増強がみられた。さらに反応速度論を展開する上で重要な反応速度の正孔密度依存性を明らかにできた。興味深いことに、正孔スカベンジャーである Na₂SO₃ の速い酸化反応においては反応速度が正孔密度にほぼ線形に増加するのに対して、反応速度がはるかに遅い水の酸化においては反応速度が正孔密度に大きく非線形に依存する。酸素発生反応ではいくつかの素過程が関与しているが、この実験結果は複数個の正孔が活性サイトに集結してから酸素発生に至るといった律速過程が存在することを示唆している。

ZnSe:CIGS 粉末光カソードの粒径制御による性能向上と電気化学的手法を用いた表面・バルク特性評価

(信州大院総合工¹・信州大先鋭材料研²・東大³) ○高木 文彰¹・影島 洋介^{1,2}・手嶋 勝弥^{1,2}・堂免 一成^{2,3}・錦織 広昌^{1,2}

Improvement of Photoelectrochemical Performances of Particulate ZnSe:CIGS Photocathodes by Particle Size Control and Electrochemical Evaluation for Surface and Bulk Characteristics (¹Graduate School of Engineering, Shinshu University, ²Research Initiative for Supra-Materials, ³The University of Tokyo) ○Fumiaki Takagi¹, Yosuke Kageshima^{1,2}, Katsuya Teshima^{1,2}, Kazunari Domen^{2,3}, Hiromasa Nishikiori^{1,2}

Particulate ZnSe:CIGS (a solid solution of ZnSe and $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$) photocathodes have the absorption edge at 800–900 nm and are active for photoelectrochemical (PEC) reduction of water under simulated sunlight¹⁾. Since the as-synthesized ZnSe:CIGS powder possess wide size distribution ranging from submicron to several tens of micron, inadequate size of particles with low photocatalytic activities should possibly coexist. Therefore, there are still room for improvement of PEC performances of the particulate photocathodes *via* the particle size control.

In this study, we classified the as-synthesized ZnSe:CIGS powder into three categories of particle sizes with average sizes of 14.2 μm (Large), 4.46 μm (Middle) and 1.09 μm (Small), and evaluated the PEC performances of the classified ZnSe:CIGS photocathodes. The photocathode made from “Middle” exhibited larger photocurrent than unclassified one in all potential range (Fig.1). The origin of the particle size dependence of the PEC performances were evaluated by various electrochemical measurements in detail. We revealed that the PEC performances of particulate photocathodes were determined by the trade-off between “the number of active sites (Pt)”, “the carrier density” and “the resistance of the bulk particles”²⁾.

Keywords : Hydrogen evolution; Photocathode; Photocatalyst, Photoelectrochemistry

ZnSe:CIGS(ZnSe と $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ の固溶体)粉末光カソードは、800–900 nm 付近に吸収端を有し、疑似太陽光照射下で水の光電気化学的還元反応に活性な材料である¹⁾。合成直後の ZnSe:CIGS 粉末はサブミクロン～数十ミクロンの広い粒度分布を有するため、光触媒活性の低い不適切な粒径の粉末が混在している可能性がある。そのため、粒径制御による粉末光カソードの活性改善の余地があると考えられる。

本研究では、合成した ZnSe:CIGS 粉末を、平均粒径が 14.2 μm (Large)、4.46 μm (Middle)、1.09 μm (Small)の粉末に分級し、各粒径から成る粉末光カソードの光電気化学(PEC)特性を評価した。粒径が Middle の粉末から成る光カソードが、すべての電位領域で分級前より活性が向上した(Fig.1)。粉末光カソードの PEC 特性の粒径依存性について、ストリッピングボルタンメトリーや電気化学インピーダンス測定等の各種電気化学測定を用いて詳細な解析を実施した。「粉末光カソードの活性点(Pt)の数」・「キャリア密度」・「バルクの抵抗値」のトレードオフが、粉末光カソードの PEC 特性に影響していることを明らかにした²⁾。

1) Y. Kageshima et al., *Sustainable Energy Fuels*, **2018**, 2, 1957–1965.

2) F. Takagi, et. al., *Sustainable Energy Fuels*, in press, DOI:10.1039/D0SE00998A.

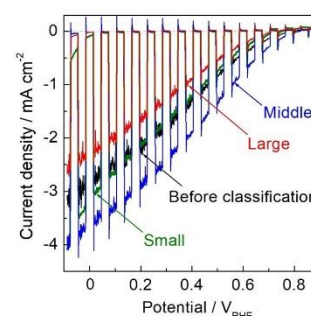


Fig.1 Current-potential curves for the photocathodes composed of different particle size of ZnSe:CIGS.

Effects of composition of $\text{Cu}_2\text{Sn}_x\text{Ge}_{1-x}\text{S}_3$ particles on photocatalytic and photoelectrochemical hydrogen evolution activity

(¹ Faculty of Engineering, Shinshu University, ² Research Initiative for Supra-Materials, Shinshu University, ³ Office of University Professors, The University of Tokyo) ○Yosuke Kageshima,^{1,2} Sota Shiga,¹ Tatsuki Ode,¹ Fumiaki Takagi,¹ Katsuya Teshima,^{1,2} Kazunari Domen,^{2,3} Hiromasa Nishikiori^{1,2}

Keywords: Photocatalysts; Photocathodes; Hydrogen evolution; Sulfide; Composition

Photocatalytic and photoelectrochemical (PEC) water splitting has been regarded as a potential means of solar energy harvesting in the form of hydrogen. Recently, $\text{Cu}_2\text{Sn}_x\text{Ge}_{1-x}\text{S}_3$ (CTGS) polycrystalline thin films have attracted significant attention as light-absorbing materials responsive up to near-infrared (IR) light with applications to efficient solid-state solar cells.¹ CTGS shows tunable band gap energies according to the Sn/Ge ratio. The chemical stability and lack of toxicity of CTGS are also advantageous points compared with the other photovoltaic materials such as $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CdTe . However, photocatalytic or PEC water reduction at the surface of CTGS have been rarely reported to date. In the present study, we demonstrated the photocatalytic and PEC hydrogen evolution using CTGS particles for the first time.

The current-potential curves for the particulate CTGS photocathodes with various Sn/Ge ratio prepared by the particle transfer method² are presented in Figure 1. The cathodic photocurrent at negative potential gradually enhanced according to the increased Sn contents and reached approximately 5 mA cm^{-2} at 0 V_{RHE} for $\text{Sn}/(\text{Sn}+\text{Ge}) = 0.62$. Meanwhile, the relatively Ge-rich specimens ($\text{Sn}/(\text{Sn}+\text{Ge}) = 0$ and 0.38) showed relatively high photocurrent at positive potential around the onset potential. The positive shift of the conduction band according to the increased Sn contents, as well as the Cu-deficient secondary phase, can affect the PEC performances. In the presentation, the photocatalytic hydrogen evolution and the effect of the Cu-deficiency will be also discussed.

1) M. Umehara, *et. al.*, Appl. Phys. Express **2016**, 9, 072301. 2) T. Minegishi, *et. al.*, Chem. Sci. **2013**, 4, 1120–1124.

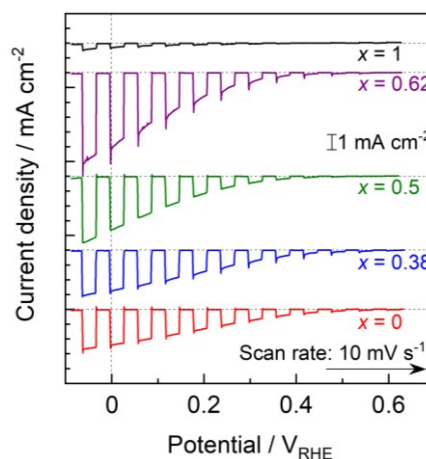


Figure 1. Current-potential curves for the particulate CTGS photocathodes in 1 M potassium phosphate buffer electrolyte (pH = 7) under simulated sunlight.

逐次イオン層吸着反応-熱処理サイクル法によるバナジン酸ビスマス薄膜電極上への酸化コバルトナノ粒子形成と水の光酸化特性

(近大院理工¹・近大理工²) ○古川 雄一¹・中島 脩¹・藤島 武蔵²・多田 弘明^{1,2}

Extremely small cobalt oxide particle formation on bismuth vanadate film electrode by successive ionic layer adsorption and reaction-calcination cycle method and the property for photoelectrochemical water oxidation (¹ Graduate School of Science and Engineering, Kindai University, ² Faculty of Science and Engineering, Kindai University) ○Yuichi Furukawa,¹ Shu Nakashima,¹ Musashi Fujishima,² Hiroaki Tada¹

BiVO₄ is one of the promising materials as a semiconductor photocatalyst for water oxidation under visible-light irradiation. Loading cobalt oxide (CoO_x) nanoparticles on BiVO₄ as an electrocatalyst is known to be effective in improving the activity. Although the particle size of CoO_x prepared by the conventional impregnation method is ~10 nm, further minimization can be expected to enhance the activity. In this study, we have developed a successive ionic layer adsorption and reaction-calcination cycle technique for depositing ~5 nm CoO_x particles on BiVO₄ film (CoO_x/BiVO₄) in a highly dispersed state, further studying its activity for photoelectrochemical water oxidation was studied.

Keywords: Photocatalyst; Cobalt oxide nanoparticle; SILAR; Bismuth Vanadate; Water Oxidation

バナジン酸ビスマス(BiVO₄)は、代表的な水の酸化用可視光応答型光触媒であり、酸化コバルト(CoO_x)を担持することで活性が向上することが知られている。従来の含浸法を用いると、BiVO₄上に10 nm以上の平均サイズをもつCoO_x粒子が担持される。この場合に、CoO_x粒子内部のCo²⁺イオンが電子正孔対の再結合中心になるほか、表面に担持されたCoO_x粒子によりBiVO₄の光吸収が阻害されるという問題がある。従って、高活性化の点から、さらなる粒子の微小化と精密な担持量制御が可能な担持法の開発が強く望まれる。本研究では、新規に開発した逐次イオン層吸着反応-熱処理サイクル(SILAR-CC)法を用いることにより、BiVO₄薄膜上に担持量を精密に制御しながら平均サイズ約5 nmのCoO_x粒子を高分散状態で形成させることに成功した(CoO_x/BiVO₄/FTO)。さらに、CoO_x/BiVO₄/FTO電極の水の光電気化学酸化特性について検討を行った。

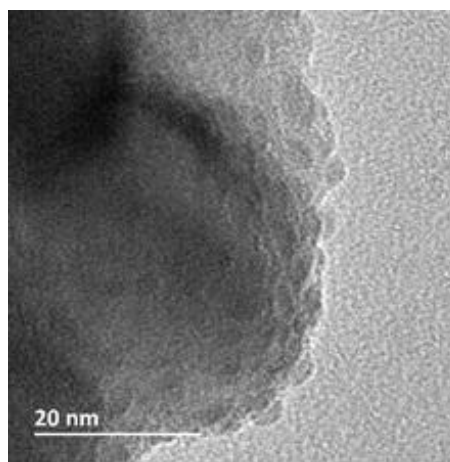


Fig. 1. TEM image CoO_x/BiVO₄/FTO

1) A. Kudo, K. Ueda, H. Kato, I. Mikami, *Catal. Lett.* **1998**, 53, 229.

2) J. Ran, J. Zhang, J. Yu, M. Jaroniec S. Z. Qiao, *Chem. Soc. Rev.* **2014**, 43, 7787.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[A14-1am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Takahiro Sasamori, Hitoshi Miyasaka

Fri. Mar 19, 2021 9:00 AM - 11:00 AM Room 14 (Online Meeting)

[A14-1am-01] Synthesis of Unsaturated Silicon Clusters Utilizing Asymmetrically Substituted Disilanes○Yamato Omatsu¹, Yoshiyuki Mizuhata¹, Norihiro Tokitoh¹ (1. Institute for Chemical Research, Kyoto University)

9:00 AM - 9:20 AM

[A14-1am-02] Synthesis of 2-Heteraazulenes Containing a Silicon or Germanium Atom as a Skeletal Element○Taku Oshiro¹, Yoshiyuki Mizuhata¹, Norihiro Tokitoh¹ (1. Institute for Chemical Research, Kyoto University)

9:20 AM - 9:40 AM

[A14-1am-03] Syntheses and properties of dinuclear Co complexes containing unique tetra-oxolene bridging ligands with different substituents and bulky ancillary ligands○Takuto Mibu¹, Yusaku Suenaga¹, Masahiko Maekawa², Takashi Okubo^{1,2}, Takayoshi Kuroda¹ (1. Graduate school of science and engineering of Kindai university, 2. Research and Institute of Science and Technology, Kindai University)

9:40 AM - 10:00 AM

[A14-1am-04] Development of 3d-4f heterometallic polynuclear complexes with a large magnetocaloric effect○Takuya SHIGA¹, Haruka Miyamoto¹, Honami Ito¹, Hiroki Oshio¹, Masayuki Nihei¹ (1. University of Tsukuba)

10:00 AM - 10:20 AM

[A14-1am-05] Selective formation of cyclic Cu(II)-Ni(II) arrangement showing effective antiferromagnetic spin coupling by using a tripeptide ligand○Eri Suganuma¹, Shun Kimura^{2,4}, Hiroto Mori^{3,4}, Jun Okabayashi², Tetsuro Kusamoto⁴, Ryosuke Miyake¹ (1. Ochanomizu Univ., 2. The Univ. of Tokyo, 3. Chuo Univ., 4. IMS)

10:20 AM - 10:40 AM

[A14-1am-06] Characterization of the Cu(I)-phenoxyl radical complex formed by the valence tautomerization of the Cu(II)-phenolate complex○Yuto Shima¹, Takashi Suzuki¹, Yuichi Shimazaki¹ (1. Graduate School of Science and Engineering, Ibaraki University)

10:40 AM - 11:00 AM

Synthesis of Unsaturated Silicon Clusters Utilizing Asymmetrically Substituted Disilanes

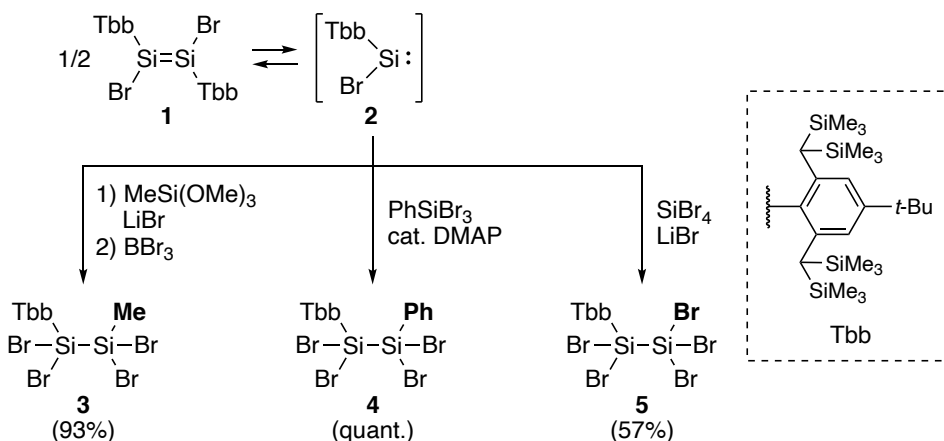
(¹*Institute for Chemical Research, Kyoto University*)

○Yamato Omatsu,¹ Yoshiyuki Mizuhata,¹ Norihiro Tokitoh¹

Keywords: Disilane; Oligosilane; Silicon Cluster

Reductive dehalogenation of disilanes is an effective synthetic method for disilenes, disilynes, or silicon clusters. Commonly, such disilanes have same bulky substituent on each silicon center. On the other hand, it has been clarified in recent studies that reductive condensation of asymmetrically substituted disilanes shows different reactivity and affords unsaturated silicon clusters.¹ Herein, we report the synthesis of novel disilanes with different substituents on each silicon center.

The reaction of MeSi(OMe)₃ with LiBr and silylene **2** generated from the dissociation of dibromodisilene **1** afforded the corresponding methoxydisilane, and the further bromination gave disilane **3** in high yield. On the other hand, when silylene **2** was treated with PhSiBr₃ and a catalytic amount of DMAP, disilane **4** was obtained quantitatively. Moreover, pentabromodisilane **5** was prepared by the reaction of **2** with SiBr₄ and LiBr. Such disilanes were characterized by NMR spectroscopy and X-ray crystallographic analysis. In this presentation, their reductive debromination with several reductants will also be discussed.



1) a) S. Ishida, T. Iwamoto, C. Kabuto, M. Kira, *Nature* **2003**, 421, 725–727; b) K. Uchiyama, S. Nagendran, S. Ishida, T. Iwamoto, M. Kira, *J. Am. Chem. Soc.* **2007**, 129, 10638–10639.

ケイ素およびゲルマニウムを骨格原子として含む 2-ヘテラアズレンの合成

(京大化研) ○大城 卓・水畑 吉行・時任 宣博

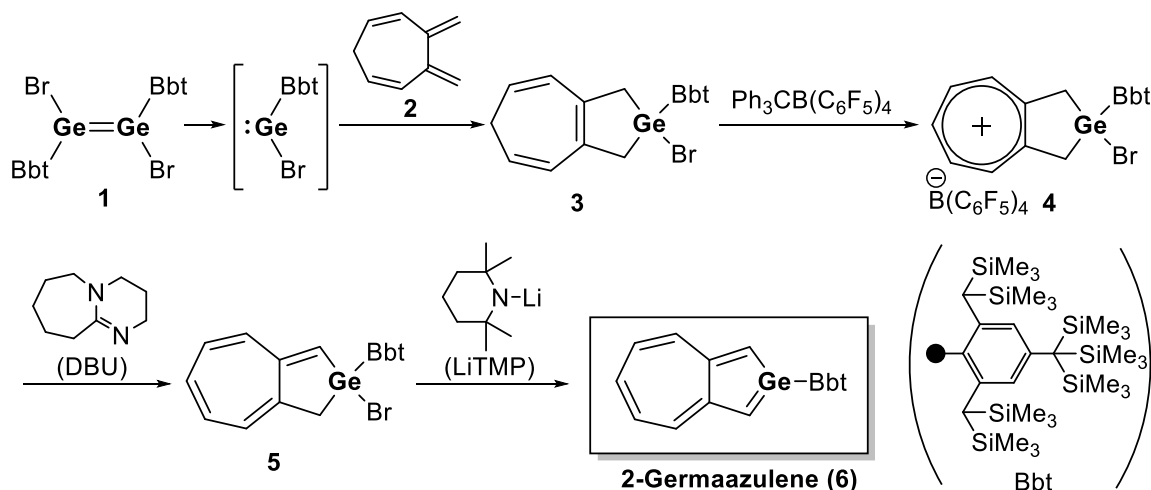
Synthesis of 2-Heteraazulenes Containing a Silicon or Germanium Atom as a Skeletal Element
(Institute for Chemical Research, Kyoto University) ○Taku Oshiro, Yoshiyuki Mizuhata, Norihiro Tokitoh

While a number of aromatic compounds containing (a) heavy group 14 element(s) as (a) skeletal element(s) have already been synthesized and isolated, there is no example of a heavier congener of azulene, which is the representative for neutral non-benzenoid aromatic compounds. In this presentation, we will report the synthesis of silicon and germanium analogues of azulene, *i.e.*, 2-sila- and 2-germaazulenes.

Keywords : azulene; germanium; silicon; aromatic compound

芳香族化合物の骨格構成元素を高周期14族元素に置換した化合物群が多数報告されている中で¹⁾、中性非ベンゼン系芳香族化合物であるアズレン骨格に高周期14族元素を組み込んだ化学種の合成は未だ報告されていない。今回我々は、アズレンの2位に高周期14族元素であるケイ素およびゲルマニウムを組み込んだ2-シラ-および2-ゲルマアズレンの合成を検討したので報告する。

Bbt 基を有するジプロモジゲルメン **1** とテトラエン **2** を反応させると、アズレンの基本骨格をもつ **3** が得られた。これをトロピリウムカチオン **4** へと誘導し、さらに DBU を作用させることで 2-ゲルマアズレンの前駆体となる **5** を合成した。最終的に、**5** と強塩基である LiTMP を反応させることで 2-ゲルマアズレン **6** の合成に成功した。本発表では芳香族性など **6** の性質、およびケイ素で核置換された 2-シラアズレンの合成も検討したので併せて発表する。



1) N, Tokitoh. *Acc. Chem. Res.* **2004**, 37, 86-94.

特異なテトラオキソレン架橋配位子を用いたコバルト二核錯体の合成と磁氣的性質—架橋配位子の置換基効果—

(近畿大院総理工¹・近畿大理工総研²) ○壬生 託人¹・末永 勇作¹・前川 雅彦²・大久保 貴志^{1,2}・黒田 孝義¹

Syntheses and properties of dinuclear cobalt complexes containing unique tetra-oxolene bridging ligands with different substituents and bulky ancillary ligands (¹*Graduate School of Science and Engineering, Kindai University*, ²*Research and Institute of Science and Technology, Kindai University*) ○Takuto Mibu,¹ Yusaku Suenaga,¹ Masahiko Maekawa,² Takashi Okubo^{1,2}, Takayoshi Kuroda-Sowa¹

Cobalt complexes containing redox active catechol ligand show drastic several properties changes involving valence change of cobalt center. This phenomena is called valence Tautomerism (VT), VT complexes involve reversible change of magnetic and spectroscopic properties induced by external stimuli such as light and heat. We focused on the synthesis of cobalt di-nuclear complexes containing three different substituents tetra-oxolene bridging ligands H_4L^R ($R = t\text{-Bu, H, F}$) and steric bulky tetradentate ancillary ligands. ¹⁾ Three complexes are expected significant electron communication between both di-oxolene units (Fig.1).

Electronic spectra in MeCN solution of complex 1, 2 exhibited MLCT bands in visible region corresponding with $hs\text{-Co}^{II}\text{-[Sq-Sq]}-hs\text{-Co}^{II}$ electron state, whereas complex 3, 4 exhibited IVCT bands in near infrared region corresponding with $hs\text{-Co}^{II}\text{-[Cat-Sq]}-hs\text{-Co}^{II}$ electron state (Fig. 2).

Keywords : *Electrochemistry; Magnetic property; Dinuclear complex, Redox active ligand*

カテコールなどに代表される、酸化還元活性な配位子を有するコバルト錯体は、熱、光などの外部刺激により、配位子—コバルト間で分子内電子移動が誘起され、コバルトの価数変化に伴い、各種物性に顕著な変化が生じる。これを原子価互変異性 (Valence Tautomerism: VT) と呼び、分光学的及び磁氣的性質の可逆的変化から、磁気メモリや分子センサーなどの応用に期待されている。本研究では置換基の異なる 3 種の特異的なテトラオキソレン架橋配位子及び、かさ高い窒素四座補助配位子¹⁾を用いた、コバルト二核錯体の合成に着目した(Fig. 1)。用いる架橋配位子 H_4L^R ($R = t\text{-Bu, H, F}$) は互いのダイオキソレンユニットが単結合で連結されていることから、今までに無い、非常に強い電子的相互作用が期待される。実際に、アセトニトリル溶液における、4 種類の錯体の電子スペクトルの比較から、錯体 1, 2 に関して、 $hs\text{-Co}^{II}\text{-[Sq-Sq]}-hs\text{-Co}^{II}$ に対応する MLCT が可視領域に観測されるのに対し、錯体 3, 4 は $hs\text{-Co}^{II}\text{-[Cat-Sq]}-hs\text{-Co}^{II}$ に対応する、IVCT が近赤外領域に観測された(Fig. 2)。当日は、これらの電子状態を踏まえ、磁氣的性質を中心に詳細を報告予定である。

1) T. Mibu, Y. Suenaga, T. Okubo, M. Maekawa, T. Kuroda-Sowa, *Inorg. Chem. Commun.*, **114** (2020) 107826

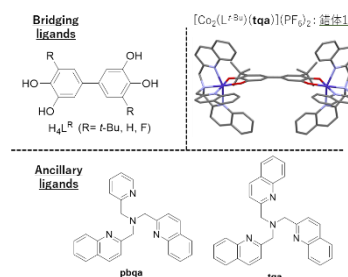


Fig.1 Synthesized ligands and complex

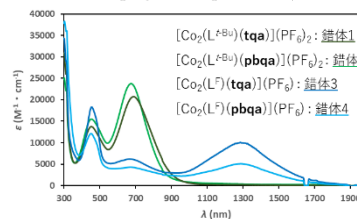


Fig.2 Electronic spectra of four complexes

Development of 3d-4f heterometallic polynuclear complexes with a large magnetocaloric effect

(¹ Graduate School of Pure and Applied Sciences, University of Tsukuba) ○Takuya Shiga,¹ Haruka Miyamoto,¹ Honami Ito,¹ Hiroki Oshio,¹ Masayuki Nihei¹

Keywords: Polynuclear Complexes; Molecular Magnetism; Heterometal Complexes

Heterometallic polynuclear complexes exhibit interesting physical properties and functions derived from their unique electronic and magnetic interactions. Control of the molecular structures, electronic states, and magnetic properties is important for the construction of functional molecular materials.

In this work, a series of planar 3d-4f mixed-metal tetranuclear complexes, $[\text{M}^{\text{II}}_3\text{Ln}^{\text{III}}(\text{L})_3(\text{X})_m](\text{Y})_n$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Co}, \text{Mn}, \text{Zn}$; $\text{Ln} = \text{La}, \text{Gd}, \text{Dy}, \text{Tb}$; X and $\text{Y} = \text{NO}_3^-$, solv.), were synthesized by using a tetraketone ligand H_2L ((3*z*,5*z*)-4,5-dihydroxy-3,5-octadiene-2,7-dione) (Fig. 1a). X-ray structural analyses of all complexes reveal the complexes have planar triangular structures comprised of three deprotonated ligand L^{2-} , three 3d metal ions, and one 4f metal ion (Fig. 1b).

The cryomagnetic study revealed that ferromagnetic interactions between M and Ln ions except for the case of diamagnetic $\text{M} = \text{Zn}$ and $\text{Ln} = \text{La}$ were operative. In the case of $[\text{Cu}_3\text{Tb}]$, $[\text{Cu}_3\text{Dy}]$, and $[\text{Co}_3\text{Tb}]$ complexes, single-molecule magnet behavior was observed. $[\text{Mn}_3\text{La}]$ complex shows very weak antiferromagnetic interactions between terminal $\text{Mn}(\text{II})$ ions, which has $S = 5/2 + 5/2 + 5/2$ spin ground state. On the other hand, $[\text{Mn}_3\text{Gd}]$ complex shows relatively strong ferromagnetic interactions between $\text{Mn}(\text{II})$ and $\text{Gd}(\text{III})$ ions, which has $S = 11$ spin ground state (Fig. 1c). The magnetic entropy change of $[\text{Mn}_3\text{Gd}]$ complex was measured, and the large $\Delta S = 66.3 \text{ J kg}^{-1} \text{ K}^{-1}$ was observed at 4.5 K under 5 T. We believe that the developments of discrete polynuclear complexes with giant magnetocaloric effect will have an impact on material designs for low-temperature magnetic refrigeration.

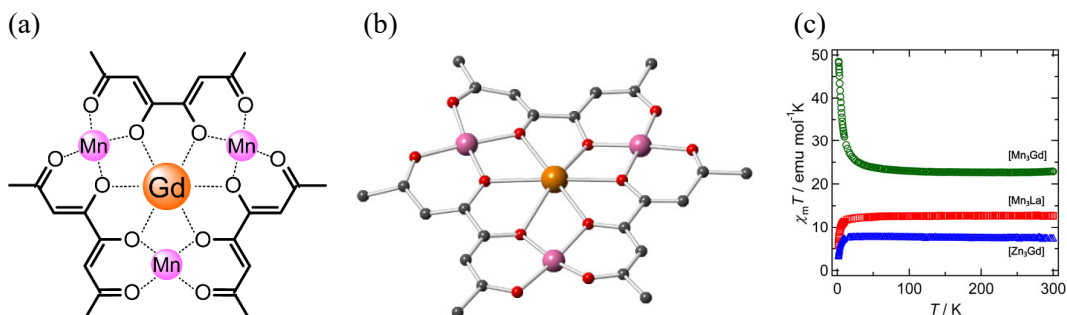


Fig. 1 (a) Schematic drawing of $[\text{Mn}_3\text{Gd}]$ complex, (b) Crystallographic structure of $[\text{Mn}_3\text{Gd}]$ complex, (c) Magnetic properties of $[\text{Mn}_3\text{Gd}]$, $[\text{Mn}_3\text{La}]$, and $[\text{Zn}_3\text{Gd}]$ complex.

トリペプチド配位子を用いた Cu(II)-Ni(II)環状配列の選択的形成とその反強磁性的相互作用

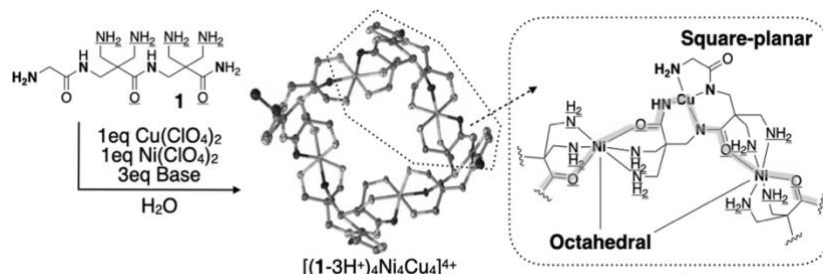
(お茶大院¹・東大院²・中大³・分子研⁴) ○菅沼 瑛里¹・木村 舜^{2,4}・森 寛敏^{3,4}・岡林 潤²・草本 哲郎⁴・三宅 亮介¹

Selective formation of cyclic Cu(II)-Ni(II) arrangement showing effective antiferromagnetic spin coupling by using a tripeptide ligand (¹*Ochanomizu University*, ²*The University of Tokyo*, ³*Chuo University*, ⁴*Institute for Molecular Science*) ○Eri Suganuma,¹ Shun Kimura,^{2,4} Mori Hirotohi,^{3,4} Jun Okabayashi,² Tetsuro Kusamoto,⁴ Ryosuke Miyake¹

Herein, we report a selective formation of a complex possessing cyclic Cu(II)-Ni(II) arrangement by using a flexible tripeptide **1**¹⁾ (Fig.). ²⁾ The cyclic heterometallic complex was obtained as a purple crystal from equiv mixture of **1**, Cu (II), and Ni (II) ions in basic water solution. Single crystal X-ray structural analysis and XAFS measurement revealed that the cyclic complex is formed with 4 square planar Cu (II) centers and 4 octahedral Ni (II) centers, which is connected through the amide groups in cyclic manner. This cyclic complex was obtained even if the ratio of Cu(II) and Ni(II) ions in the solution is different from 1. The SQUID measurement indicated an efficient antiferromagnetic interaction between the metal centers. **Keywords** : heterometallic complex; peptide; metal-metal interaction; cyclic array

ペプチドはデザイン性が高く、異種金属イオンを配列しその相互作用を制御するための鋳型として適している。最近我々は、アミノ酸側鎖と主鎖に異なる金属配位部位を持つトリペプチド配位子 **1** を用いることでアミド基を介して連結し、4 配位と 6 配位の金属中心に環状の相互作用を創出できることを報告した¹⁾。今回、**1** を用いて 4 配位 Cu(II) 中心と 6 配位 Ni(II) 中心の環状配列を持つヘテロ金属錯体 ($[(1-3H^+)_4Ni_4Cu_4]^{4+}$) の選択的合成に成功したので報告する²⁾ (図)。

塩基存在下、**1** と Cu(II), Ni(II) イオンを 1:1:1 の比率で混合することで紫色針状結晶を得た。単結晶 X 線結晶構造解析と X 線吸収分光測定から、4 配位の Cu(II) と 6 配位の Ni(II) を持つ環状錯体であることがわかった。この結晶は Cu(II) と Ni(II) イオンの混合比がずれていても選択的に合成できた。また、SQUID 測定から Cu(II) と Ni(II) の間に効率的な反強磁性相互作用が働くことも明らかにした。



図：今回合成した Cu(II)-Ni(II)環状配列を持つ金属錯体

1) R. Miyake, A. Ando, M. Ueno, T. Muraoka, *J. Am. Chem. Soc.* **2019**, *141*, 8675.

2) R. Miyake, E. Suganuma, S. Kimura, H. Mori, J. Okabayashi, T. Kusamoto, *Angew. Chem. Int. Ed. in press*.

Cu(II)-フェノラート錯体の原子価互変異性により生成する Cu(I)-フェノキシラジカル錯体の同定

(茨大院) ○島 悠人・鈴木 崇・島崎 優一

Characterization of the Cu(I)-phenoxyl radical complex formed by the valence tautomerization of the Cu(II)-phenolate complex (*Graduate School of Science and Engineering, Ibaraki University*) ○Yuto Shima, Takashi Suzuki, Yuichi Shimazaki

A Cu-containing enzyme, copper amine oxidase (CAO) catalyzes oxidation of a primary amine to the corresponding aldehyde by O₂. A 2,4,5-trihydroxyphenylalaninequinone (TPQ) cofactor plays important role for the catalytic reaction in the active site. In the biogenesis of the TPQ cofactor, The Cu(I)-phenoxyl radical intermediate has been proposed to be formed by the valence tautomerization of Cu(II)-phenolate species. We have previously reported formation of the Cu(I)-phenoxyl radical species by the valence tautomerization. However, the detail properties of Cu(I)-phenoxyl radical species have not been reported yet. In this study, we have characterized the Cu(I)-phenoxyl radical complex in detail.

Reaction of a Cu(II) salt with a ligand having a *p*-(dimethylamino)phenol moiety in CH₂Cl₂/MeOH (1:1 v/v) under inert gas atmosphere gave a purple solution, which showed the phenoxyl radical EPR signal at *g* = 2. This solution caused the color change to reddish purple by addition of O₂ to form Cu(II)-phenoxyl radical species. On the other hand, the solution was kept stand at room temperature under inert gas atmosphere to give a Cu(I) complex having an *p*-iminoquinone moiety. From the results, the purple solution was assigned to the Cu(I)-phenoxyl radical species.

Keywords : *Cu(I)-phenoxyl radical; valence tautomerization; Copper amine oxidase*

銅アミンオキシダーゼ(CAO)は酸素分子を用いて一級アミンをアルデヒドへと酸化する銅酵素であり、活性中心に補酵素として 2,4,5-トリヒドロキシフェニルアラニンキノン(TPQ)を有することが報告されている¹⁾。TPQ 生成過程で Cu(II)-フェノラート種の原子価互変異性により Cu(I)-フェノキシラジカル種が生成する。当研究室では Cu(I)-フェノキシラジカル種を観測しているが、詳細は明らかになっていない²⁾。そこで本研究では、Cu(I)-フェノキシラジカル錯体の詳細な同定を目的とした。

p-ジメチルアミノフェノール部位を有する三脚型配位子と Cu(II)塩を不活性ガス雰囲気下で反応させると青紫色の溶液が得られた。この溶液は、*g* = 2 にフェノキシラジカル由来の EPR シグナルを観測した。この溶液に酸素分子を加えると赤紫色の溶液へと変色し、Cu(II)-フェノキシラジカル種が生成した。一方、青紫色の溶液を室温で放置すると *p*-イミノキノン部位を有する Cu(I)錯体を得られた。これらのことから、青紫色の溶液は Cu(I)-フェノキシラジカル種であると考えられる。

(1) M. C. Wilce, D. M. Dooley, H. C. Freeman, J. M. Guss, H. Matsunami, W. S. MvIntie, C. E. Ruggiero, K. Tanizawa, H. Yamaguchi, *Biochemistry*, **1997**, 36, 16116-16133.

(2) T. Suzuki, H. Oshita, T. Yajima, F. Tani, H. Abe, and Y. Shimazaki, *Chem. Eur. J.* **2019**, 25, 15805-15814.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[A12-1am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Yuma Morimoto, Shigeyuki Masaoka, Yasuhiro Arikawa

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 12 (Online Meeting)

[A12-1am-01] Proton transfer in electrochemical CO₂ reduction by iron porphyrin complexes: mechanistic investigation and active control○Kento Kosugi¹, Mio Kondo¹, Shigeyuki Masaoka¹ (1. Osaka university)

9:00 AM - 9:20 AM

[A12-1am-02] Catalytic Nitrogen Fixation by Iron Dinitrogen Complexes Bearing Anionic PCP-type Pincer Ligands○Shogo Kuriyama¹, Takeru Kato¹, Hiromasa Tanaka², Asuka Konomi³, Yoshizawa Kazunari³, Yoshiaki Nishibayashi¹ (1. School of Engineering, The University of Tokyo, 2. School of Liberal Arts and Sciences, Daido University, 3. Institute for Materials Chemistry and Engineering, Kyushu University)

9:20 AM - 9:40 AM

[A12-1am-03] Rate Determining Factor in C–H Bond Scission of Inert Alkanes by Fe(IV)(oxide)(porphyrin- π -cation radical)○Yuma Morimoto¹, Kosuke Fukui¹, Hiroshi Fujii², Shino u Itoh¹ (1. Osaka Univ., 2. Nara Women's Univ.)

9:40 AM - 10:00 AM

[A12-1am-04] Development of dehydrogenation of ammonia borane or hydrosilanes catalyzed by iron complexes○Yoshinao Kobayashi¹, Yusuke Sunada^{1,2} (1. School of Engineering, The Univ. of Tokyo, 2. IIS, The Univ. of Tokyo)

10:00 AM - 10:20 AM

[A12-1am-05] DFT Studies on the Mechanism of CO₂ Reduction Catalyzed by Diazapyridinophane Metal Complexes○Yuto Sakaguchi¹, Kosei Yamauchi¹, Ken Sakai¹ (1. Dept. Chem. Kyushu Univ.)

10:20 AM - 10:40 AM

[A12-1am-06] Structures and chemical properties of oxidized forms of ferrocene-substituted dihydroquinazolinone showing self-complementary hydrogen-bond interactions○Mikihiro Hayashi¹ (1. Nagasaki University)

10:40 AM - 11:00 AM

[A12-1am-07] Photocatalytic CO₂ reduction to CO using osmium complexes bearing PNNP-type tetradentate ligands○Kenji Kamada¹, Jieun Jung¹, Susumu Saito^{1,2} (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

11:00 AM - 11:20 AM

[A12-1am-08] Alkane Oxidation with Peroxide Species Catalyzed by Osmium Tetroxide○Tomohiro Fujimoto¹, Hideki Sugimoto¹, Shinobu Itoh¹ (1. Grad. Sch. Eng., Osaka Univ.)

11:20 AM - 11:40 AM

Proton Transfer in Electrochemical CO₂ Reduction by Iron Porphyrin Complexes: Mechanistic Investigation and Active Control

(¹Graduate School of Engineering, Osaka University, ²JST PRESTO) ○Kento KOSUGI,¹ Mio KONDO,^{1,2} Shigeyuki MASAOKA¹

Keywords: Proton Coupled Electron Transfer Reaction; CO₂ Reduction; Porphyrin; Electrochemistry; Solvation Effect

Electron and proton transfer processes play key roles in many schemes of artificial photosynthetic reactions as well as natural photosynthesis. In this context, the deep understanding of these processes should lead to the development of catalysts for artificial photosynthetic reactions with excellent performance. Based on this consideration, in this work, we aimed to develop catalyst molecules with multi-electron/proton transfer ability. A novel iron porphyrin complex with proton responsive sites (**1**) was newly designed and synthesized (Figure 1).

In order to investigate the electrochemical catalytic ability of **1**, cyclic voltammetry measurement of **1** were conducted in various solvents under CO₂ atmosphere in the presence of proton source (Figure 2a). In acetonitrile (MeCN), the catalytic current increases dramatically compared with those in other solvents. This result indicates that solvation effect is also an important factor which affect the catalytic activity.

To clarify whether this solvation effect is unique to **1** or universal to iron porphyrin complex, we synthesized one of the simplest iron porphyrin complexes (**2**), and investigated its catalytic ability in *N,N*-dimethylformamide (DMF) and MeCN (Figure 2b). We found that the catalytic current increases dramatically and the onset potential shifts to positive potential side in MeCN compared with that in DMF. This result suggests that the solvation effect which enhances the catalytic ability is common to iron porphyrin complexes.

The details of catalytic mechanisms in conjunction with proton and electron transfer behaviors and the solvation effects will be discussed in the presentation.

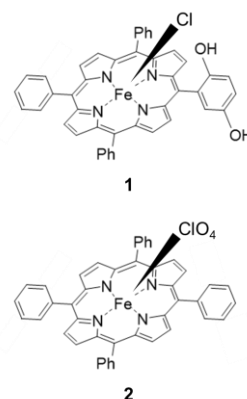


Figure 1. Chemical structures of **1** and **2**.

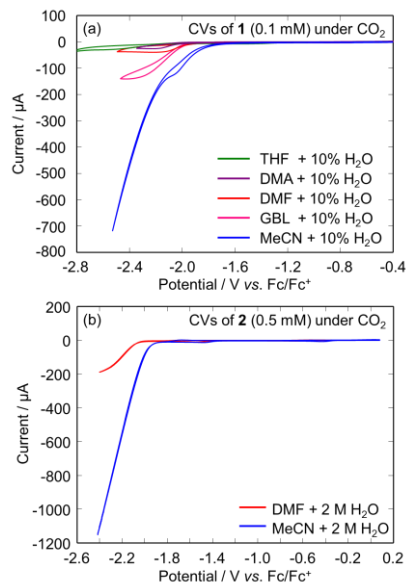


Figure 2. Cyclic voltammograms of the (a) **1** (b) **2** in 0.1 M TBAP/solvent systems under CO₂ atmosphere in the presence of water (WE: GC; CE: Pt wire; RE: Ag/Ag⁺; scan rate: 100 mV/s)

アニオン性 PCP 型ピンサー配位子を有する鉄窒素錯体を用いた触媒的窒素固定反応

(東大院工¹・大同大²・九大先導研³) ○栗山 翔吾¹・加藤 孟¹・田中 宏昌²・許斐 明日香³・吉澤 一成³・西林 仁昭¹

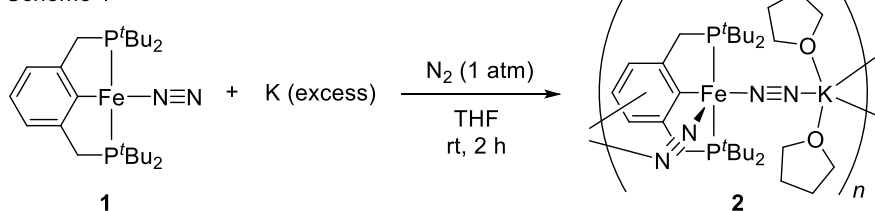
Catalytic Nitrogen Fixation by Iron Dinitrogen Complexes Bearing Anionic PCP-type Pincer Ligands (¹*Graduate School of Engineering, The University of Tokyo*, ²*School of Liberal Arts and Sciences, Daido University*, ³*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Shogo Kuriyama,¹ Takeru Kato,¹ Hiromasa Tanaka,² Asuka Konomi,³ Kazunari Yoshizawa,³ Yoshiaki Nishibayashi¹

To develop efficient nitrogen fixation system, transformation of dinitrogen into ammonia and hydrazine catalyzed by homogeneous transition-metal complexes under mild reaction conditions has been actively studied. Previously we reported the synthesis of iron(I) dinitrogen complexes bearing anionic PCP-type pincer ligands. Here, we have found that reduction of the iron(I) complex afforded the corresponding anionic Fe(0) dinitrogen complex. These iron(I) and iron(0) complexes have been found to work as efficient catalysts toward the formation of ammonia and hydrazine from dinitrogen under ambient reaction conditions.

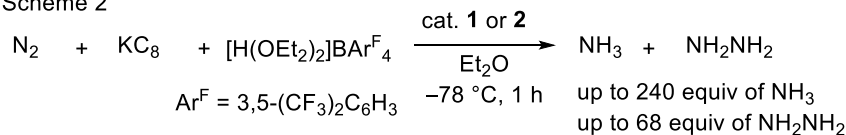
Keywords : Iron Complex; Nitrogen Fixation; Pincer Ligand; Ammonia; Hydrazine

近年、効率的な窒素固定法の開発を志向して、遷移金属錯体を用いた温和な反応条件下での窒素分子からの触媒的アンモニア・ヒドラジン合成反応の開発が大きな注目を集めている¹⁾。以前に我々はアニオン性 PCP 型ピンサー配位子を有する鉄(I)窒素錯体 **1** の合成を報告している。今回、鉄窒素錯体 **1** の量論反応および窒素分子の触媒的還元反応への触媒能の詳細な検討を行った。錯体 **1** を常圧の窒素雰囲気下、カリウムで還元することによりアニオン性鉄(0)窒素錯体 **2** 合成に成功した (Scheme 1)。錯体 **2** は2つの末端窒素配位子を有する5配位構造を有することを単結晶 X 線構造解析により確認した。合成した一連の鉄窒素錯体が窒素分子からのアンモニア・ヒドラジンへの触媒的還元反応に対して優れた触媒となることを見出した (Scheme 2)。

Scheme 1



Scheme 2



1) Chalkley, M. J.; Drover, M. W.; Peters, J. C. *Chem. Rev.* **2020**, *120*, 5582.

2) Kato, T.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. 99th CSJ Annual Meeting, 3D1-06 (2019).

Rate Determining Factor in C–H Bond Scission of Inert Alkanes by Fe(IV)(oxide)(porphyrin- π -cation radical)

(¹Graduate School of Engineering Osaka University, ²Graduate School of Humanity and Science, Nara Women's University) ○ Yuma Morimoto,¹ Kosuke Fukui,¹ Hiroshi Fujii,² Shinobu Itoh¹

Keywords: Oxido-iron(IV) Porphyrin π -Cation Radical Complexes, Alkane Hydroxylation, Reaction Mechanism, Fluorocarbon Solvent, Ozone,

Hydrogen atom transfer (HAT) is a fundamental reaction process determining the overall reaction rate in the oxidation of alkanes. A deep understanding of this elementary step is essential for developing useful chemical tools to convert inert alkanes to valuable materials. Generally, the activation energy of HAT can be predicted from the bond dissociation energy of C–H bonds (BDE_{C-H}) of substrates. However, BDE_{C-H} is not the sole parameter to determine the activation energies of HAT. For instance, C–H bonds existing near electron-withdrawing groups such as chloride and nitrile are hard to be oxidized regardless of their relatively weaker BDE_{C-H} compared to those of simple alkanes. Polarity matching between substrates and oxidants have been invoked as the critical factor, although systematic experiments have not been performed to scrutinize this concept yet.

Fe(IV)-oxido porphyrin- π -cation radical species, so-called compound I, is one of the most well-known class of oxidant showing high reactivity toward inert C–H bond, including the primary one. In our previous study, the HAT activation energy from simple alkane substrate to compound I did not show a simple linear dependence on the BDE_{C-H} of alkane substrates. We herein attempted to employ the vibration frequency of C–H as the secondary factor in the determination of activation energy of HAT.

First, we optimized the solvent conditions for the kinetic studies of highly reactive compound I, Fe^{IV}(O)(TDCPP^{•+})(Cl) (**2**^{TDCPP}) (TDCPP = 5,10,15,20-tetrakis-[2,6-dichlorophenyl]-porphyrinato dianion) to find that 3:7 mixed solvent system consisting of α,α,α -trifluorotoluene and 1,3- $\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexafluoro-*m*-xylene is the most suitable. Then, the reaction of **2**^{TDCPP} with substrates was followed by UV-vis spectroscopy, which affords the normalized second-order reaction-rate constants k' (M⁻¹ s⁻¹). The logarithm of k' ($\log k'$) did not show a linear dependence on BDE_{C-H} , where the coefficient of determination (R^2) was 0.38 (Figure 1A). However, $\log k'$ was nicely explained by BDE_{C-H} and vibration frequency of the C–H bonds of substrates with R^2 of 0.82 (Figure 1B, C).

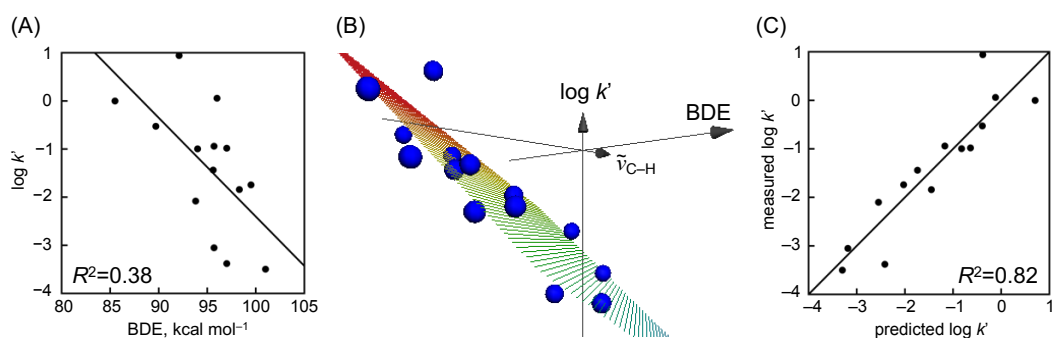


Figure 1. (A) Plot of $\log k'$ vs BDE_{C-H} with a regression line, (B) $\log k'$ for BDE_{C-H} and $\tilde{\nu}_{C-H}$ with a regression plane, and (C) measured $\log k'$ vs predicted $\log k'$ from the regression plane.

Development of dehydrogenation of ammonia borane or hydrosilanes catalyzed by iron complexes

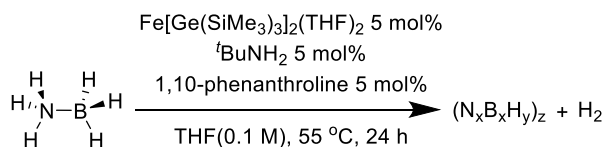
(¹*School of Engineering and* ²*Institute of Industrial Science, The University of Tokyo*) ○ Yoshinao Kobayashi¹, Yusuke Sunada^{1,2}

Keywords: Base Metal Catalysts; Dehydrogenation; Ammonia Borane; Germanium Ligand; Silyl Compounds; Hydrosilanes

Dehydrogenative reactions are the important reaction from the point of view of not only organic synthesis but also efficient hydrogen production. Precious metal compounds are often used as dehydrogenation catalysts due to their high catalytic performance. However, development of base metal catalysts that can replace the conventional precious metal catalysts is highly desired from the viewpoint of cost and availability. Because group 14 can contribute to stabilize the highly reactive coordinatively unsaturated metal species due to their high *trans* influence and strong electron donating property, we focused on the synthesis of base metal complexes bearing group 14 ligands to develop the novel catalysts¹. In this presentation, we wish to report the synthesis of 14 electron coordinatively unsaturated iron(II) complexes having germanium ligands, and application of the obtained complex as the catalyst toward dehydrogenation of ammonia borane. Catalytic dehydrogenation of hydrosilanes catalyzed by iron complexes will also be demonstrated.

First, iron digermyl complex $\text{Fe}[\text{Ge}(\text{SiMe}_3)_2](\text{THF})_2$ (**1**) was obtained by the reaction of commercially available FeBr_2 and 2 eq. of $\text{KGe}(\text{SiMe}_3)_3$ in 74% isolated yield². The molecular structure of this complex was determined by X-ray diffraction analysis. The iron center adopts the distorted tetrahedral coordination geometry. Then we checked the catalytic performance of **1** in the dehydrogenation of ammonia borane (AB), because AB is identified as an appropriate solid hydrogen storage material due to its high hydrogen content. We found that combination of complex **1** (5 mol%) and *tert*-butylamine (5 mol%) in the presence of 1,10-phenanthroline (5 mol%) resulted in efficient dehydrogenation of AB in THF at 55°C (Scheme 1).

Catalytic dehydrogenation of hydrosilanes mediated by iron complexes to form organosilicon compounds such as disilanes will also be demonstrated in this presentation.



Scheme 1 Dehydrogenation of ammonia borane catalyzed by combination of **1**, *t*BuOH, and 1,10-phenanthroline.

This work was supported by a project of Kanagawa Institute of Industrial Science and Technology (KISTEC).

1) Arata, S.; Sunada, Y. *Dalton. Trans.* **2019**, 48, 2891. 2) Kobayashi, Y.; Sunada, Y. *Catalysts* **2020**, 10, 29.

DFT Studies on the Mechanism of CO₂ Reduction Catalyzed by Diazapyridinophane Metal Complexes

(Dept. Chem., Kyushu Univ.) ○Yuto Sakaguchi, Kosei Yamauchi, Ken Sakai

Keywords: CO₂ reduction, First-row transition metal complexes, Photochemistry, Mechanistic study, DFT calculation

There is an increasing demand to reduce atmospheric CO₂ because of the recent threat of global warming and climate changes. To solve these problems, there has been a growing interest in light-driven reduction of CO₂ by molecular catalysts. Recently, an increasing number of studies focusing on the precious-metal-free systems for photocatalytic CO₂ reduction have been reported.¹ In this context, we previously demonstrated that the visible light-driven CO₂ reduction catalyzed by diazapyridinophane (dapp) derivatives of Fe and Co (Fig. 1) can be effectively promoted by combining them with a heteroleptic Cu(I) photosensitizer.²

In this study, the density functional theory (DFT) calculations were carried out in order to clarify the mechanisms of CO₂ reduction by these metal complexes. All the intermediates were fully optimized by the B3P86/6-31G* level of DFT with the effect of solvation in DMF taken into consideration using C-PCM. We also succeeded to optimize the transition states for the CO₂ binding processes, leading to determine the activation free energy of each catalysis. In addition, it has been shown that the SOMO together with the HOMO of M(I) center cooperatively provides the electron density at the less sterically hindered reactive metal center, offering the CO₂ binding site. This is the first example of a catalyst demonstrating the CO₂ binding with the high spin metal center. Moreover, we have found that an unusual side-on-(CO₂²⁻) M(II) intermediate can be given in these systems (Fig. 1).³

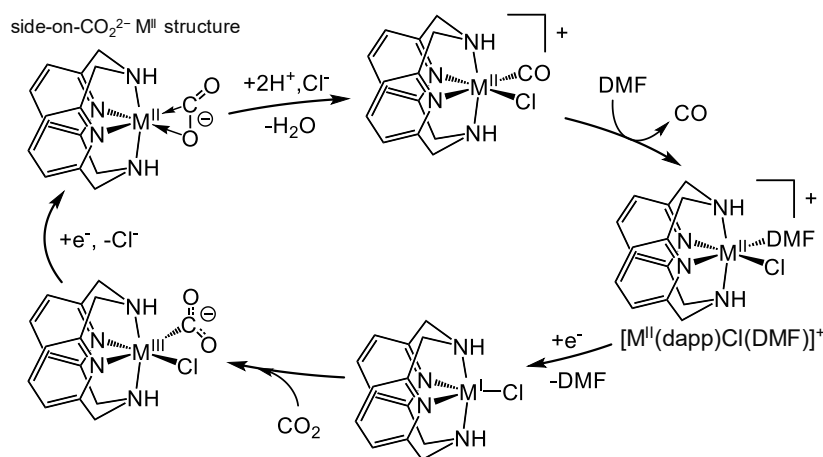


Fig. 1 Proposed mechanism of CO₂ reduction catalyzed by the M(dapp) complexes (M = Fe, Co).

- 1) K. E. Dalle, J. Warnan, J. J. Leung, B. Reuillard, I. S. Karmel and E. Reisner, *Chem. Rev.*, **2019**, *119*, 2752.
- 2) Y. Sakaguchi, A. Call, M. Cibian, K. Yamauchi and K. Sakai, *Chem. Commun.*, **2019**, *55*, 8552.
- 3) Y. Sakaguchi, A. Call, K. Yamauchi and K. Sakai, *submitted*.

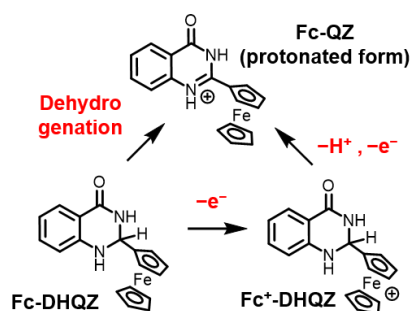
Structures and chemical properties of oxidized forms of ferrocene-substituted dihydroquinazolinone showing self-complementary hydrogen-bond interactions

(Faculty of Education, Nagasaki University) ○Mikihiro Hayashi

Keywords: Radical molecule; Hydrogen bond; Disproportionation reaction; Heterocycles

[Introduction] Hydrogen-bond (H-bond) pairs comprising electron donor and acceptor molecules have attracted attention because of correlated phenomena of electron transfer with proton transfer or H-bond vibration, which play important roles in biological activities or unique properties of materials.¹⁾ Among such pairs, self-complement H-bond dimers have been studied in terms of the mixed valency influenced by H-bond states.²⁾ However, a small number of examples of such H-bond dimers prevents further understanding of relationship between electron self-exchange reactions and proton displacements. Herein, I report that ferrocene-substituted dihydroquinazolinone (**Fc-DHQZ**) is a candidate for mixed valence H-bond dimers, where the charge distribution has an influence on the proton coordination.

[Results and discussion] **Fc-DHQZ** undergoes sequential oxidation reactions to afford its mono-oxidized (**Fc⁺-DHQZ**) and dehydrogenated (**Fc-QZ**) states (Scheme 1). These molecules form lactam-type H-bond dimers in their crystal structures, that of **Fc⁺-DHQZ** are shown in Figure 1. Contribution of *d*-orbitals to a spin distribution of **Fc⁺-DHQZ** was confirmed by magnetic susceptibility measurements and calculations. Electrochemical and optical studies indicate a base-catalyzed disproportionation of **Fc⁺-DHQZ** to **Fc-DHQZ** and **Fc-QZ** in its acetonitrile solution. In an acetonitrile–dichloromethane solvent system, the formation of a H-bond dimer comprising **Fc-DHQZ** and **Fc⁺-DHQZ** was investigated by measuring infrared and NMR spectroscopies. A spontaneous production of **Fc-QZ** in the mixed solution would stem from a deprotonation step of **Fc⁺-DHQZ**, which is a proton transfer from **Fc⁺-DHQZ** to **Fc-DHQZ** within the dimer.



Scheme 1. Sequential oxidation of **Fc-DHQZ**

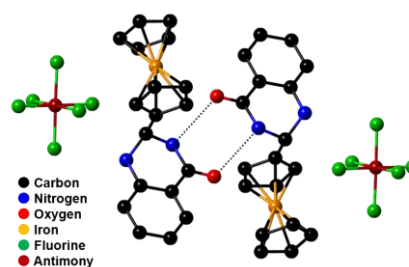


Figure 1. Ortep drawing of **Fc⁺-DHQZ**. Hydrogen atoms were omitted for clarity.

- 1) a) A. Migliore, *et al. Chem. Rev.* **2014**, *114*, 3381. b) K. Nakasuji, *et al. J. Am. Chem. Soc.* **1991**, *113*, 1862.
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Photocatalytic CO₂ reduction to CO using osmium complexes bearing PNNP-type tetradentate ligands

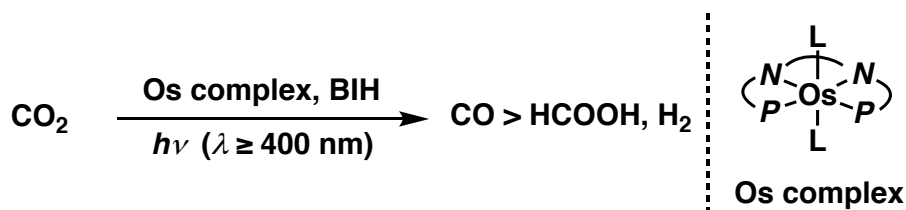
(¹Graduate School of Science, Nagoya University, ²Research Center for Materials Science, Nagoya University) ○Kenji Kamada,¹ Jieun Jung,¹ Susumu Saito,^{1,2}

Keywords: carbon dioxide; photoreduction; photocatalyst; osmium complex; carbon monoxide

Photocatalytic reduction of carbon dioxide (CO₂) is recognized as an important research area owing to problems related to the depletion of fossil fuels and environmental issues. Two electron reduction of CO₂ gives carbon monoxide (CO) and formic acid (HCOOH), which are useful and more energy-rich compounds than CO₂. CO₂ photoreduction by transition metal complexes in many cases has been achieved with the combination of photosensitizer (PS) and reduction catalyst (Cat). On the other hand, photocatalysts which act as both PS and Cat enable the mononuclear photocatalytic systems.

In our previous work, an iridium complex bearing a PNNP-type tetradentate ligand was developed as an efficient photocatalyst to reduce CO₂ to formic acid selectively with a turnover number (TON) of 2560.¹ We report here that osmium (Os) photocatalysts bearing PNNP-type tetradentate ligands reduce CO₂ to CO instead of the formic acid in the presence of a sacrificial reagent, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) under visible light irradiation (Scheme 1). The Os photocatalysts can utilize a wider wavelength range of the solar radiation as a photosensitizer of Os(II) tris-diimine complex.² A high TON and long photocatalyst lifespan were achieved owing to the structural robustness of PNNP-type tetradentate ligands. Mechanistic insights were provided by cyclic voltammetry, UV-Vis absorption spectroscopy, EPR measurements and laser flash photolysis measurements.

Scheme 1. Photocatalytic reduction of CO₂ with an Os complex as a photocatalyst under visible light irradiation



1) K. Kamada, J. Jung, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *J. Am. Chem. Soc.* **2020**, *142*, 10261. 2) Y. Tamaki, K. Koike, T. Morimoto, Y. Yamazaki, O. Ishitani, *Inorg. Chem.* **2013**, *52*, 11902.

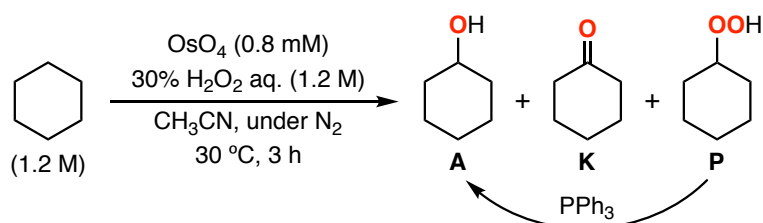
Alkane Oxidation with Peroxide Species Catalyzed by Osmium Tetroxide

(Graduate School of Engineering, Osaka University) ○ Tomohiro Fujimoto, Hideki Sugimoto, Shinobu Itoh

Keywords: Osmium Tetroxide; Hydrogen Peroxide; Alkyl Hydroperoxide; Alkane Oxidation; Reaction Mechanism

Osmium tetroxide (OsO_4) is known to catalyze oxidation of alkanes. Recently, alkane hydroxylation with NaIO_4 as a re-oxidant was reported, where the overoxidation proceeded exclusively to yield the corresponding carboxylic acids.¹ Since OsO_4 is easily re-produced after a reaction of the reduced Os^{VI} species with an appropriate oxidant, a simple catalytic reaction system can be developed by the use of OsO_4 . In this study, we examined alkane oxidation catalyzed by OsO_4 with peroxide species such as hydrogen peroxide (H_2O_2) as an environmentally benign oxidant.

Oxidation of cyclohexane with H_2O_2 was carried out in the presence of a catalytic amount of OsO_4 in CH_3CN at 30 °C under N_2 atmosphere. GC-FID analysis of the products after 3 hours indicated that cyclohexanol (**A**) and cyclohexanone (**K**) were produced with turn over numbers (TONs) of OsO_4 as 16 and 20, respectively. On the other hand, upon a workup treatment of the reaction solution with triphenylphosphine (PPh_3), **A** was obtained selectively ($\text{A/K} = 29$) with TON of OsO_4 as 61, suggesting the generation of cyclohexyl hydroperoxide (**P**) *in situ* prior to formation of **A** (**Scheme 1**). The generation of **P** was suppressed under N_2 bubbling conditions, indicating that O_2 participated in the formation of **P**. Furthermore, the radical trap experiment with CCl_3Br obtained the corresponding brominated product. These results suggested that this oxidation reaction involves a cyclohexyl radical intermediate. The oxidation reaction of other substrates besides cyclohexane with H_2O_2 was also investigated. We, further, examined the catalytic oxidation reaction with other alkyl hydroperoxide species to compare the results in terms of product distribution and turnover number. The reaction mechanism was discussed on the basis of kinetic analysis on the catalytic alkane oxidation reactions.



Scheme 1. Reaction scheme on the oxidation of cyclohexane catalyzed by OsO_4

1) B. C. Bales, P. Brown, A. Dehestani and J. M. Mayer, *J. Am. Chem. Soc.* **2005**, 127, 2832-7433

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[A13-1am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Ryo Ohtani, Yoko Sakata, Hiroshi Sato

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 13 (Online Meeting)

[A13-1am-01] The development of stimuli-responsive metal complex○Yoshihiro Sekine¹, Shinya Hayami¹ (1. Kumamoto University)

9:00 AM - 9:20 AM

[A13-1am-02] CO₂-induced spin-state conversion in a porous molecular crystal consisting of a cobalt(II) complex○Manabu Nakaya¹, Shinya Hayami² (1. Josai University, 2. Kumamoto University)

9:20 AM - 9:40 AM

[A13-1am-03] [2]Catenane-Based Porous Crystals○Hiroshi Sato^{1,2} (1. The University of Tokyo, 2. JST-PRESTO)

9:40 AM - 10:00 AM

[A13-1am-04] Structural conversions of xanthene-based dinuclear macrocyclic cobalt(III) metallohosts by ligand exchange and control of their guest recognition behavior○Okura Kenji¹, Yoko Sakata^{1,2}, Shigehisa Akine^{1,2} (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. WPI Nano Life Science Institute, Kanazawa University)

10:00 AM - 10:20 AM

[A13-1am-05] Selective encapsulation of alkali metal ions in a chiral trinickel(II) metallocryptand and its regulation of helicity inversion○Sk Asif Iqbal¹, Yoko Sakata², Shigehisa Akine² (1. Nano Life Science Institute, Kanazawa University, 2. Nano Life Science Institute, Graduate School of Natural Science and Technology, Kanazawa University)

10:20 AM - 10:40 AM

[A13-1am-06] Mononuclear and Polynuclear Cobalt(II) or Cobalt(III) Complexes Bearing Multidentate Hydrazonato Ligands with Pyridyl and Imidazolyl Donor Groups: Synthesis, Crystal Structures and Properties.○DANIEL BOATENG ACHEAMPONG¹, YUKINARI SUNATSUKI¹, TAKAYOSHI SUZUKI¹ (1. OKAYAMA UNIVERSITY)

10:40 AM - 11:00 AM

[A13-1am-07] Classification of Crystallization Behavior and Chirality Control of M^{II}-Ln^{III}-M^{II} Trinuclear Complexes exhibiting Absolute Spontaneous Resolution○Kazuma Takahara¹, Yuuki Horino¹, Yukinari Sunatsuki¹, Takayoshi Suzuki¹ (1. The Univ. of Okayama)

11:00 AM - 11:20 AM

[A13-1am-08] A Monatomic Silicon Complex Coordinated by Two Different Silylene Ligands and Ligand Exchange Reactions at the Monatomic Silicon Center○Taichi Koike¹, Takeaki Iwamoto¹ (1. Tohoku Univ.)

11:20 AM - 11:40 AM

The development of stimuli-responsive metal complex

(¹ Graduate School of Science and Technology, Kumamoto University, ² Priority Organization for Innovation and Excellence, Kumamoto University, ³ Institute of Industrial Nanomaterials (IINa), Kumamoto University)

○Yoshihiro Sekine,^{1,2} Shinya Hayami^{1,3}

Keywords: Switching, stimuli-responsiveness

The development of switchable metal complexes, such as spin crossover, valence tautomerism, and metal-to metal electron transfers, is an attractive theme in the field of materials science. Numerous metal complexes showing various switching behavior in their electronic, magnetic, optical properties has been reported. Of these, we have recently demonstrated novel tetraoxolene-bridged Fe-based 2-D honeycomb layered systems exhibiting electron transfers between metal ions and bridging ligands.^[1-3] The electron transfer behavior in this system is influenced through temperature variation, solvation/desolvation treatment, chemical doping of ligands and pressure application. Especially, the desolvated sample showed stepwise thermally driven electron transfers. As the examples of another switchable metal complexes, our group have comprehensively investigated on the synthesis, structural features and physical properties of a series of Co(II) or Fe(III)-based spin crossover complexes.^[4] Among such materials with flexible spin-state switching, multi-step spin-transition systems could be a good candidate for molecular-based high order data storage. However, such multi-stable systems are still relatively rare because of less development of suitable molecular designs.

Systems incorporating multiple switchable building units is expected to show more than two stable phases when stimulated by external perturbation. To development of new materials for observation of multi-step spin state conversion, the co-crystallization of cationic and anionic stimuli-responsive building blocks as the simple molecular design, has been utilized in this study. We report on the synthesis, structural and magnetic properties data for new metal complexes based on this strategy.

[1] J. Chen, Y. Sekine, Y. Komatsumaru, S. Hayami, H. Miyasaka, *Angew. Chem. Int. Ed.* **2018**, 57, 12043-12047. [2] J. Chen, Y. Sekine, A. Okazawa, H. Sato, W. Kosaka, H. Miyasaka, *Chem. Sci.*, **2020**, 11, 3610-3618. [3] Y. Sekine, J. Chen, N. Eguchi, H. Miyasaka, *Chem. Commun.*, **2020**, 56, 10867-10870. [4] M. Nakaya, R. Ohtani, L. F. Lindoy, S. Hayami, *Inorg. Chem. Front.*, *in press*.

CO₂-induced spin-state conversion in a porous molecular crystal consisting of a cobalt(II) complex

(¹Department of Chemistry, Josai University, ²Faculty of Advanced Science and Technology, Kumamoto University) ○Manabu Nakaya,¹ Shinya Hayami²

Keywords: Porous molecular crystal; Cobalt(II) complex; Spin state conversion; Spin crossover

Porous molecular crystals (PMCs) that are composed by molecular assembly of discrete metal complexes have attracted much attention due to the potential to be a new type of guest adsorbable materials through the flexible pseudo-framework structure. Spin-crossover (SCO) phenomenon represents a stimulus-driven spin-state change between the low-spin (LS) and high-spin (HS) states of a metal center and is quite sensitive to structural changes. Thus, SCO behaviors in PMCs are expected to be controlled by structural changes through guest adsorption.¹

In this research, we designed a neutral mononuclear cobalt(II) complex of type [Co(COO-terpy)₂] (**1**). **1** was found to form cavities generated via π - π stacking motifs and hydrogen bond networks in the molecular assemblies (**Figure (a)**), initially resulted in crystals with four water molecules in the cavity (**1**·4H₂O). Desolvated **1** maintained the cavity and it was found to show selective CO₂ gas adsorption. Unlike **1** showing gradual SCO behavior and was in the HS state at 290 K (near room temperature), the CO₂-accommodated form **1**·CO₂ varied the SCO behavior based on the CO₂ pressure, and was stabilized in the LS state under 110 kPa CO₂ pressure at 290 K (**Figure (b)**). This provided a reversible spin-state conversion by introducing/evacuating CO₂ gas into/from **1** at 290 K.²

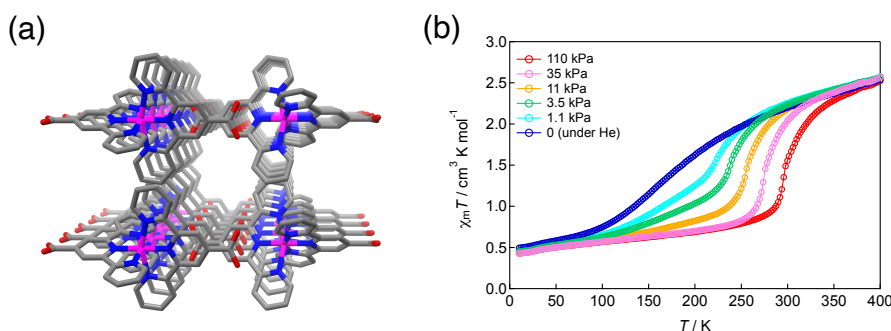


Figure (a) The porous assembly structure in the crystal packing of **1**. **(b)** Magnetic behaviors of **1**·CO₂ at various pressures (0–110 kPa) of CO₂ for the cooling process.

(1) M. Nakaya, R. Ohtani, S. Hayami, *Eur. J. Inorg. Chem.*, **2020**, 3709-3719. (2) M. Nakaya, W. Kosaka, H. Miyasaka, Y. Komatsumaru, S. Kawaguchi, K. Sugimoto, Y. Zhang, M. Nakamura, L. F. Lindoy, S. Hayami, *Angew. Chem. Int. Ed.*, **2020**, 59, 10658-10665.

[2]Catenane-Based Porous Crystal

(¹*School of Engineering, The University of Tokyo*, ²*JST-PRESTO*, ³*RIKEN Center for Emergent Matter Science*) ○Hiroshi Sato,^{1,2} Wenjing Meng,¹ Takuzo Aida^{1,3}

Keywords: Porous Materials; Metal–Organic Frameworks; Catenane; Mechanical Properties; Nanoindentation

Topological bonds in mechanically interlocked molecules (MIMs) such as catenanes have received great research attention as a new type of chemical bonds due to their intriguing topology and potentials in a wide range of applications such as molecular machines, switches, sensors, catalysis, computing, *etc.* While the dynamic nature of mechanical bonds has been extensively studied for MIMs in solution or on substrates where they are allowed to independently function, harvesting materials with intriguing mechanical properties derived from collective motions of MIMs is also considered to be a promising strategy to create bulk materials^{1,2}. Although MIMs have been introduced into a variety of amorphous polymer materials such as polymer glasses and gels, the MIMs were randomly arranged in the materials and collective motions of the MIMs were allowed only in a local space. Here we report a new strategy to incorporate topological bonds in a crystalline framework to develop unique mechanical properties.

We designed a [2]catenane-based organic ligand, H₄^{CTN}L (Fig. 1a), which is conformationally flexible. A three-dimensional (3D) metal–organic framework (Fig. 1b, ^{CTN}MOF) with topological bonds involved in the backbone was synthesized by the reaction of H₄^{CTN}L with metal ions. The macrocycles of [2]catenanes are joined together by paddlewheel units to form 1D metal–organic chains. The topological bonds of catenanes connects two sets of such 1D chain orthogonally, resulting in a 3D porous crystalline network. The incorporation of the topological bonds within the backbone of ^{CTN}MOF imparts elasticity to the overall crystalline material, as revealed through by far the smallest empirical Young's modulus for MOFs measured *via* nanoindentation³.

References

1) S. Choi *et al.* *Science*, **2017**, 357, 279. 2) K. Ito, *Polym. J.* **2012**, 44, 38. 3) W. Meng *et al.* *to be submitted*.

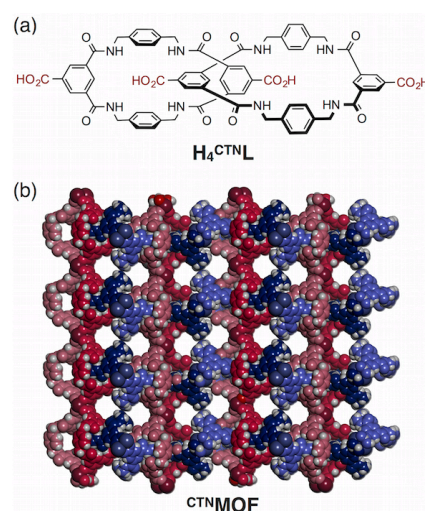


Figure 1. (a) Chemical structure of a [2]catenane-based ligand (H₄^{CTN}L) with four carboxylic acid moieties. (b) Single crystal X-ray structure of a MOF (^{CTN}MOF) composed of ^{CTN}L.

キサンテン型環状二核コバルト(III)メタロホストの配位子交換による構造変換とゲスト認識挙動の制御

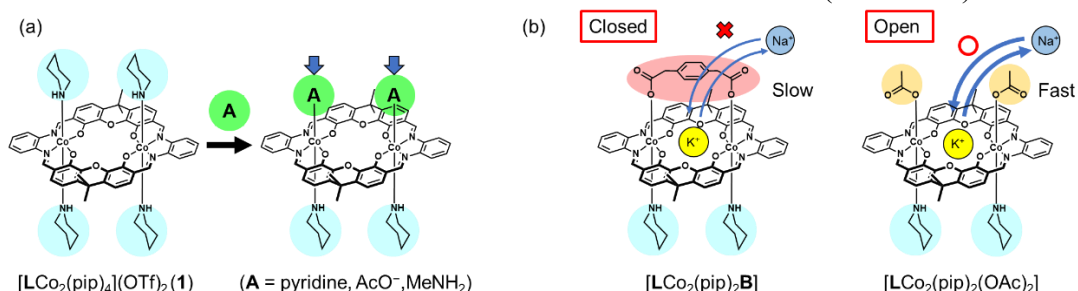
(金沢大院自然¹・金沢大 NanoLSI²) ○大藏 健史¹・酒田 陽子^{1,2}・秋根 茂久^{1,2}
 Structural Conversions of Xanthene-based Dinuclear Macrocyclic Cobalt(III) Metallohosts by Ligand Exchange and Control of Their Guest Recognition Behavior (¹Graduate School of Natural Science and Technology, Kanazawa University, ²WPI Nano Life Science Institute, Kanazawa University) ○Kenji Okura,¹ Yoko Sakata,^{1,2} Shigehisa Akine^{1,2}

We synthesized a new cobalt metallohost [$\text{LCo}_2(\text{pip})_4(\text{OTf})_2$ (**1**) (pip = piperidine) in which two saloph moieties are connected by xanthene scaffolds. Two pip ligands in **1** on the same side were selectively replaced by the ligand **A** (= pyridine, acetate, MeNH_2). We also synthesized singly-bridged complex [$\text{LCo}_2(\text{pip})_2\text{B}$] using site-selective ligand exchange with H_2B (= 1,4-phenylenediacetic acid). The guest uptake/release rates of the singly-bridged complex were much slower than those of the corresponding non-bridged complex.

Keywords : Metallohost; Ion recognition; Ligand exchange; Guest exchange

超分子ホスト化合物において、主骨格を保持したまま化学修飾を行うことができれば、ホストの認識能が制御可能になると期待される。本研究では、キサンテン骨格を有する新規コバルトメタロホスト [$\text{LCo}_2(\text{pip})_4(\text{OTf})_2$ (**1**) (pip = ピペリジン)]を用いて、様々な配位子との配位子交換を検討した(Scheme 1a)。その結果、位置選択的な配位子交換が起こることを見出した。また、この配位子交換を利用して単架橋錯体を合成し、架橋構造の有無によるゲスト認識挙動の比較を行った。

錯体 **1** を合成し、これに対して軸配位子 **A** (= ピリジン、酢酸イオン、メチルアミン)を加えると、四つのピペリジン配位子のうち環平面に対して同じ側に位置する二つのピペリジンが **A** に位置選択的に交換されることが各種スペクトル測定および X 線結晶構造解析から明らかとなった。また、この軸配位子交換の位置選択性に基づいて、錯体 **1** と 1,4-フェニレン二酢酸(H_2B)の反応により単架橋錯体 [$\text{LCo}_2(\text{pip})_2\text{B}$] を合成した。上部の開口部が閉じている単架橋錯体は開いた構造である無架橋錯体よりも K^+ から Na^+ へのゲスト交換速度が遅くなることが明らかとなった(Scheme 1b)。



Scheme 1. (a) Ligand exchange behavior of [$\text{LCo}_2(\text{pip})_4$]²⁺. (b) Structures and guest recognition behavior of [$\text{LCo}_2(\text{pip})_2\text{B}$] and [$\text{LCo}_2(\text{pip})_2(\text{OAc})_2$].

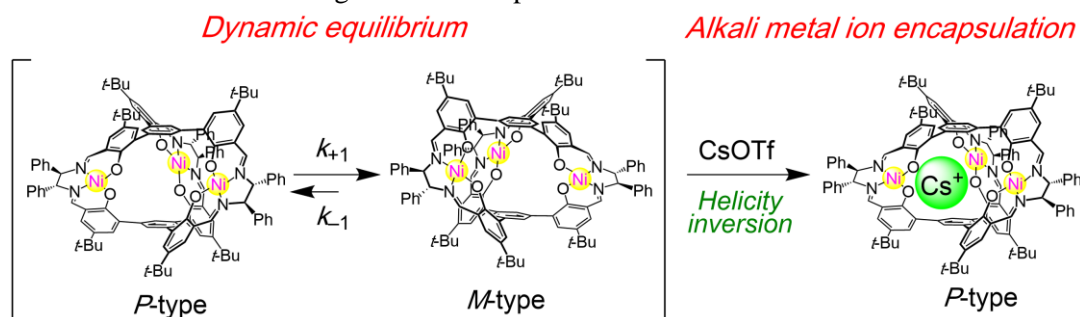
Selective encapsulation of alkali metal ions in a chiral trinickel(II) metallocryptand and its regulation of helicity inversion

(¹WPI-Nano Life Science Institute, Kanazawa University, ²Graduate School of Natural Science and Technology, Kanazawa University) ○ Sk Asif Iqbal,¹ Yoko Sakata,^{1,2} Shigehisa Akine^{1,2}

Keywords: Selective encapsulation; Chirality; Helix inversion; Alkali metal ions; Nickel complex

Dynamic helical molecules, which are capable of undergoing reversible helicity inversion, are useful as a basic framework for chiral switching systems.¹ There have been several examples of dynamic helical molecules whose helix inversion rates can be tuned by changing solvent polarity, constituent metal ions of helicates, etc.^{2,3} However, in order to efficiently control the helix inversion rate, combination of such a dynamic helix inversion with host-guest complexation would be effective.

We have synthesized a novel tris(salen)-type trinickel(II) metallocryptand having six chiral carbon centers (Scheme 1). This complex was characterized by various spectroscopic techniques such as ¹H NMR, ESI-MS, UV-vis, CD spectroscopy, X-ray crystallography, etc. The nickel(II) metallocryptand underwent a dynamic conversion between the *P* and *M* isomers in solution, preferring one isomer in a ratio of up to 10:90. In contrast, the single crystals showed the presence of both *P* and *M* isomers exactly in a 1:1 ratio in the unit cell. Guest encapsulation studies on a series of alkali metal ions were performed with this metallocryptand. Whereas it showed first negative Cotton effect (tentatively assigned to the *M*-type helicity) in the absence of guests, the complexation with CsOTf caused the CD signal inversion (*P*-type helicity major). We will present such helicity inversion and helicity control behaviour associating with the encapsulation of a series of alkali metal ions.



Scheme 1. Helical metallocryptand for recognition of alkali metal ions and helicity inversion.

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- 2) S. Akine, T. Taniguchi, T. Matsumoto, T. Nabeshima, *Chem. Commun.*, **2006**, 4961-4963.
- 3) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front.*, **2014**, 1, 53-57.

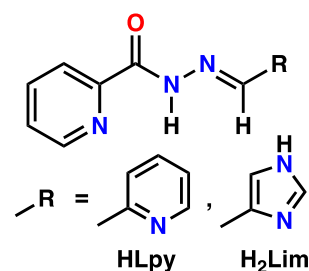
Mononuclear and Polynuclear Cobalt(II) or Cobalt(III) Complexes Bearing Multidentate Hydrazonato Ligands with Pyridyl and Imidazolyl Donor Groups: Synthesis, Crystal Structures and Properties.

(¹Grad. Sch. Nat. Sci. Technol., Okayama University, Okayama 700-8530, ²RIIS, Okayama University, Okayama 700-8530) ○Acheampong, Daniel K.B.;¹ Sunatsuki, Yukinari;¹ Suzuki, Takayoshi^{1,2}

Keywords: 2-picolinoylhydrazone; mixed-valent complex; coordination modes.

2-Picolinoylhydrazones having a *N*-heterocyclic (2-pyridyl or 4-imidazolyl) substituents (**Scheme 1**: HLpy or H₂Lim) are promising multidentate ligands, because their neutral and deprotonated forms (Lpy[−], HLim[−] and Lim^{2−}) have a variety of donor atoms and are possible to act as both multidentate chelating and bridging ligands. In this study, we have prepared a series of cobalt(II or III) complexes bearing such monoanionic ligands (Lpy[−] or HLim[−]), and their molecular and crystal structures were investigated.

Two types of mononuclear cobalt(III) complexes with Lpy[−], [Co(Lpy)₂]BF₄ and *mer*-[Co(Lpy)₃], were obtained by reactions of HLpy with Co(BF₄)₂•6H₂O and [Co(acac)₃], respectively, in an appropriate molar ratio. In these complexes, the ligand Lpy[−] coordinated to a Co^{III} center in a tridentate κ³N,N',N'' or a bidentate κ²N,N' mode. In addition, a trinuclear Co^{III}–Co^{II}–Co^{III} complex bridged by Lpy[−], [{Co(Lpy)₂}₂Co(H₂O)₂](BF₄)₄ (**Fig. 1a**) was prepared. In the case of the imidazole-based ligand, HLim[−], both mononuclear and dinuclear Co^{III} complexes, [Co(HLim)₂]BF₄ and [Co₂(μ-HLim)₃](BF₄)₃ (**Fig. 1b**), respectively, were isolated and characterized.



Scheme 1 Hydrazones used in this research.

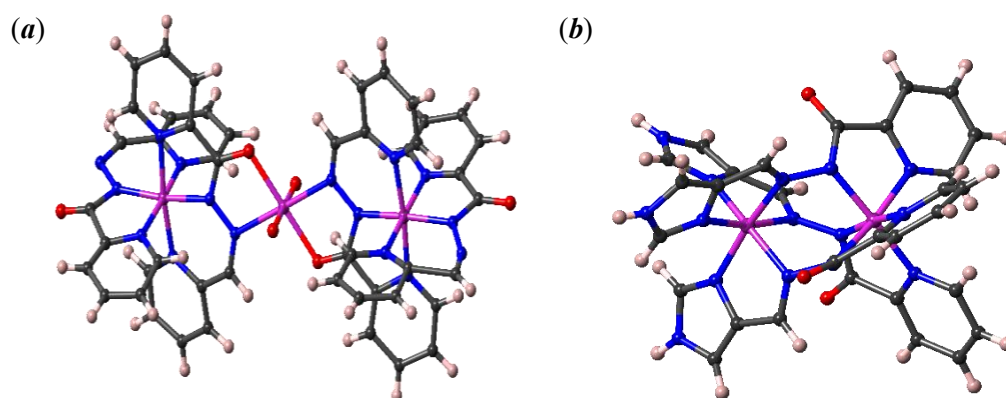


Fig. 1 Perspective views of (a) [{Co(Lpy)}₂Co(H₂O)₂]⁴⁺ and (b) [Co₂(μ-HLim)₃]³⁺ (color codes: Co, purple; O, red; N, blue; C, black; H, pale pink).

Classification of Crystallization Behavior and Chirality Control of M^{II} - Ln^{III} - M^{II} Trinuclear Complexes exhibiting Absolute Spontaneous Resolution

(¹Graduate School of Natural Science and Technology, Okayama University, ²Research Institute for Interdisciplinary Science, Okayama University) ○Kazuma Takahara,¹ Yuuki Horino,¹ Yukinari Sunatsuki,¹ Takayoshi Suzuki^{1,2}

Keywords: Chiral; Spontaneous Resolution

A series of trinuclear complexes, $[(M^{II}L)_2Ln^{III}]\text{NO}_3$ (M - Ln - M), which were synthesized from achiral tripodal Schiff base ligand H_3L (Fig. 1), 3d-metal acetate $M(\text{OAc})_2$, and lanthanoid nitrate $Ln(\text{NO}_3)_3$ in a 2:2:1 molar ratio, have two asymmetric centers at M^{II} sites derived from twist of the tripodal arms of the ligand. In the most cases, the absolute configuration of the resulting molecule was homochiral, i.e., Δ,Δ and Λ,Λ enantiomers.

Among these complexes, a specific combination of the metal ions, such as Zn-Tb-Zn (Fig. 2), resulted exclusively in a particular enantiomeric crystals (Δ,Δ conglomerates). This novel phenomenon is named as “Absolute Spontaneous Resolution.”

In this study, we have classified the crystallization behaviors of these complexes dependent on the kind of lanthanoid ion. In the case of the Mn^{II} complexes, it was revealed that all lanthanoids exhibited at least total spontaneous resolution (i.e., only left-handed Δ,Δ enantiomeric crystals were deposited in a crystallization experiment). On the other hand, crystallization behaviors of the Zn^{II} complexes were obviously affected by the lanthanoids. For instance, Zn-Y-Zn provided both Δ,Δ and Λ,Λ conglomerates in an experiment (i.e., a normal spontaneous resolution) and Zn-La-Zn was crystallized as a racemic compound which contains both enantiomers in a crystal.

Also, the control of chiral crystallization by addition of seed crystals was attempted. For instance, when Δ,Δ -crystals of Zn-Y-Zn were crushed and seeded into a saturated Zn-Tb-Zn solution, all of the resulting crystals were Δ,Δ -conglomerates of Zn-Tb-Zn, which have never been obtained by synthesis and recrystallization in a normal condition.

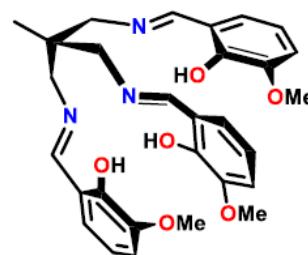


Fig. 1 The structure of H_3L

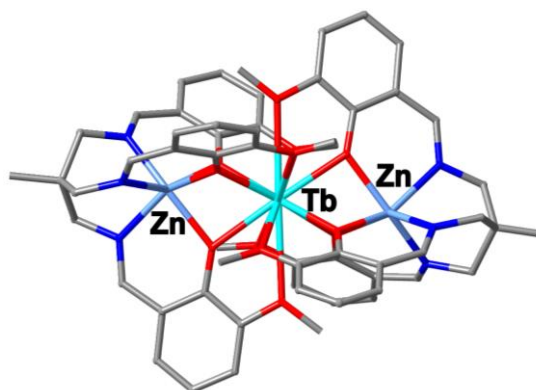


Fig. 2 Crystal structure of Δ,Δ -Zn-Tb-Zn

A Monatomic Silicon Complex Coordinated by Two Different Silylene Ligands and Ligand Exchange Reactions at the Monatomic Silicon Center

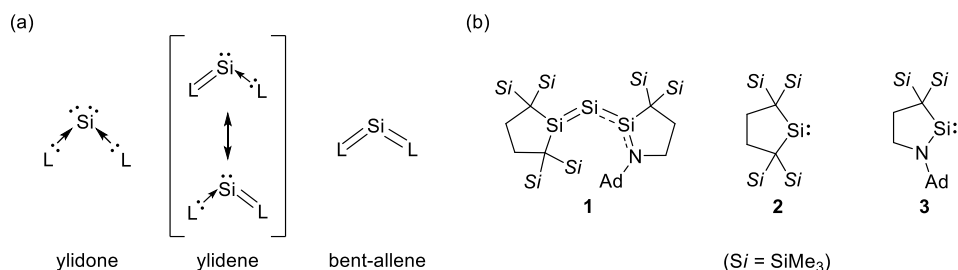
(Graduate School of Science, Tohoku University) ○Taichi Koike, Takeaki Iwamoto

Keywords: Monatomic Silicon Transfer, Ligand Exchange, Silylone, Silylene

Ligand exchange reaction is one of the basic reactions of transition metal complexes alongside oxidative addition and reductive elimination. While such reactions have long been understood to occur only at transition metal centers, recently, low-valent main-group element species have also been demonstrated to show similar reactivities.¹ Nevertheless, reports of ligand exchange reactions at low-valent main-group element centers are yet scarce.

Silylones, compounds with a monatomic silicon coordinated by two-electron donor ligands, have emerged as one of the new classes of low-valent silicon species (Chart a).² Although several silylones have been synthesized and their electronic properties and reactivities were investigated, ligand exchange at the monatomic silicon center remained elusive. Herein, we report that incorporating two different silylene ligands, cyclic dialkylsilylene **2**³ and cyclic (alkyl)(amino)silylene **3**⁴ to a silicon atom (silylone **1**) enables the labilization of silylene **3** leading to ligand exchange reactions.

Chart.



1) T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608–3680. 2) P. K. Majhi, T. Sasamori, *Chem. Eur. J.* **2018**, *24*, 9441–9455; S. Yao, Y. Xiong, M. Driess, *Acc. Chem. Res.* **2017**, *50*, 2026–2037. 3) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723. 4) T. Kosai, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2016**, *55*, 15554–15558.

Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- | Oral B**[A15-1pm] 10. Organic Chemistry -Organometallic Compounds-**

Chair: Naoki Ishida, Kazuhiko Semba

Fri. Mar 19, 2021 1:00 PM - 3:20 PM Room 15 (Online Meeting)

[A15-1pm-01] Rh(I)-Catalyzed [2+2+1] Carbonylative Cycloaddition Reaction of DiynesTsumoru Morimoto¹, [○]JINGWEN JIA¹, Yoshiko Yamaguchi¹, Hiroko Yamada¹, Kiyomi Kakiuchi¹ (1. NAIST)

1:00 PM - 1:20 PM

[A15-1pm-02] Rh(I)- and Rh(II)-catalyzed C-H alkylation of benzylamines with alkenes and its application in flow.[○]Amrita Das¹, Naoto Chatani¹ (1. Osaka University)

1:20 PM - 1:40 PM

[A15-1pm-03] Construction of a Helical Exocyclic Diene Scaffold via Rh-Catalyzed Cycloisomerization of 1,6-Diynes Bearing a Cyclopropanol Moiety[○]Tomohiro Kikuchi¹, Takeshi Yasui¹, Yoshihiko Yamamoto¹ (1. Grad. Sch. Pharm. Sci., Nagoya Univ.)

1:40 PM - 2:00 PM

[A15-1pm-04] Synthesis of Chiral Cyclohexadienylamines by Cationic Rhodium(I)-Catalyzed Highly Selective Intermolecular Cross-Cyclotrimerization[○]Kohei Fujii¹, Koji Masutomi¹, Yu Shibata¹, Yuki Naagashima¹, Ken Tanaka¹ (1. Tokyo Institute of Technology)

2:00 PM - 2:20 PM

[A15-1pm-05] Catalytic hydrogenation of carboxylic acids though *in situ* esterification using a sterically confined Ir complex[○]Bendik Groemer¹, Shota Yoshioka¹, Susumu Saito^{2,1} (1. Nagoya University, Graduate School of Science, 2. Nagoya University, RCMS)

2:20 PM - 2:40 PM

[A15-1pm-06] Site-Selective Magnesiation of Multi-Fluorinated Arenes Catalyzed by Rhodium–Aluminum Bimetallic Complexes[○]Ikuya Fujii¹, Kazuhiko Semba¹, Yoshiaki Nakao¹ (1. Grad. Sch. Eng., Kyoto Univ.)

2:40 PM - 3:00 PM

[A15-1pm-07] Facile synthesis of indeno[1,2-*c*]isoquinolines by rhodium(III)-catalyzed cyclocondensation of benzamides with diazo compounds *via* catalytic cleavage of C-H bond followed by cyclization[○]Dongyoung Kim¹, Risako Miura¹, Yu Kimura¹, Teruyuki Kondo¹ (1. Grad. Sch. Eng., Kyoto Univ.)

3:00 PM - 3:20 PM

Rh(I)-Catalyzed [2+2+1] Carbonylative Cycloaddition Reaction of Diynes

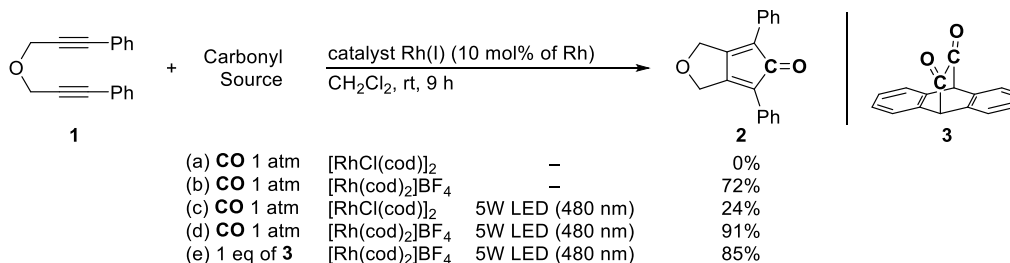
(Division of Materials Science, Nara Institute of Science and Technology)

Tsumoru Morimoto, ○JingWen Jia, Yoshiko Yamaguchi, Hiroko Yamada, Kiyomi Kakiuchi

Keywords: Rhodium; [2+2+1]; Diyne; Visible light; Acene α -diketone

Cyclopentadienones (CPDs) are a diverse class of fascinating molecules with broader potential in synthetic organic chemistry, biology, materials science, and nanotechnology. [2+2+1] Carbonylative cycloaddition of two alkynes, especially diynes, with carbon monoxide (CO) represents one of the accessible synthetic strategies to CPDs. Although there have been some reports using, such as cobalt,¹ iridium,^{2,3} and palladium complexes,⁴ rhodium complexes have not shown high catalytic activity on this transformation.^{3,5} Herein we will present a highly catalytic [2+2+1] carbonylative cycloaddition of diynes with Rh(I) complexes.

First, the reaction of diyne **1** with atmospheric CO in the presence of a catalytic amount of a neutral rhodium(I) complex at room temperature, $[\text{RhCl}(\text{cod})]_2$, resulted in no formation of CDP **2** as the previous report (Scheme (a)).⁵ When a cationic rhodium complex, $[\text{Rh}(\text{cod})_2]\text{BF}_4$, was used instead of $[\text{RhCl}(\text{cod})]_2$ as a catalyst, the [2+2+1] carbonylative cycloaddition proceeded efficiently to afford CDP **2** in 72% yield (b).⁶ Photoirradiation made the $[\text{RhCl}(\text{cod})]_2$ -mediated reaction catalytic. The irradiation of visible light (5W LED (480 nm)) in the presence of $[\text{RhCl}(\text{cod})]_2$ complex promoted catalytically the reaction of **1** with CO to give CPD **2** in 24% yield (c). The combined utilization of the irradiation of visible light with a cationic rhodium(I) catalyst, $[\text{Rh}(\text{cod})_2]\text{BF}_4$, also led to more highly efficient catalysis to give **2** in 91% yield (d). Both the cationic character of rhodium catalyst and the irradiation of visible light would contribute to provide the essential vacant site on the rhodium center to which diyne coordinates in the catalysis. Furthermore, the reaction of **1** with anthracene α -diketone (**3**), which is easily decarbonylated under photoirradiation to release two molecules of CO,⁷ in the presence of $[\text{Rh}(\text{cod})_2]\text{BF}_4$ catalyst under the irradiation of visible light resulted in the transformation without the direct use of CO to yield **2** in high yield (e). This is the first demonstration of the use of acene α -diketone as a substitute for CO.



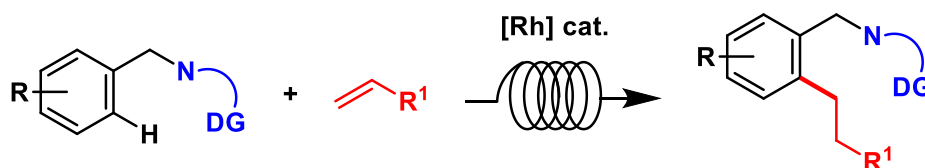
- 1) T. Sugihara *et al.* *Chem. Commun.* **2001**, 37, 2456. 2) T. Shibata *et al.* *Org. Lett.* **2001**, 3, 1217. 3) T. Shibata *et al.* *Tetrahedron* **2002**, 58, 8661. 4) H. Jiang *et al.* *Chem. Commun.* **2014**, 50, 2488. 5) N. Chatani *et al.* *Chem. Commun.* **2010**, 46, 3345. 6) T. Morimoto *et al.* *Asian J. Org. Chem.* **2020**, 9, 1778. 7) A. C. Udding *et al.* *Tetrahedron Lett.* **1969**, 3, 125.

Rh(I)- and Rh(II)-Catalyzed C-H Alkylation of Benzylamines with Alkenes and its Application in Flow

(Faculty of Engineering, Osaka University) ○Amrita Das, Naoto Chatani

Keywords: Rhodium Catalyst; Carbon-Hydrogen Bond Cleavage; Benzylamine; Alkylation; Flow Chemistry

The Rh-catalyzed C-H alkylation of benzylamines with alkenes using a picolinamide derivative as a directing group is reported. Having significant utility of benzylamine derivatives in various biologically active compounds and natural products,¹ the functionalization of benzylamine derivatives via C-H bond activation strategies is one of the more important areas in organic chemistry.² Given our continuous interest in C-H alkylation reactions,³ we were strongly motivated to investigate the *ortho*-alkylation of benzylamines with alkenes as an alkyl source. In recent years flow transformation reactions have found their way into academic research laboratories.⁴ To this context, a flow set up was designed to successfully mimic this process under flow. Several examples are presented under flow conditions and its advantage over a batch process was confirmed.



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2) (a) Orito, K.; Horibata, A.; Nakamura, T.; Ushito, H.; Nagasaki, H.; Yuguchi, M.; Yamashita, S.; Tokuda, M. *J. Am. Chem. Soc.*, **2004**, 126, 14342. (b) Cai, G.; Fu, Y.; Li, Y.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.*, **2007**, 129, 7666. (c) Zhao, Y.; Chen, G. *Org. Lett.* **2011**, 13, 4850.

3) (a) Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.*, **2013**, 135, 5308. (b) Rouquet G.; Chatani, N. *Chem. Sci.*, **2013**, 4, 2201. (c) Shibata, K.; Chatani, N. *Org. Lett.*, **2014**, 16, 5148. (d) Shibata, K.; Yamaguchi, T.; Chatani, N. *Org. Lett.*, **2015**, 17, 3584. (e) Chatani, N. *Bull. Chem. Soc. Jpn.*, **2018**, 91, 211.

4) (a) Webb, D.; Jamison, T. F. *Chem. Sci.*, **2010**, 1, 675. (b) Porta, R.; Benaglia, M.; Puglisi, A. *Org. Process Res. Dev.*, **2016**, 20, 2. (c) Plutschack, M. B.; Gilmore, K.; Seeberger, P. H. *Chem. Rev.*, **2017**, 117, 11796. (d) Santoro, S.; Ferlin, F.; Ackermann, L.; Vaccaro, L. *Chem. Soc. Rev.*, **2019**, 48, 2767.

Construction of a Helical Exocyclic Diene Scaffold via Rh-Catalyzed Cycloisomerization of 1,6-Diynes Bearing a Cyclopropanol Moiety

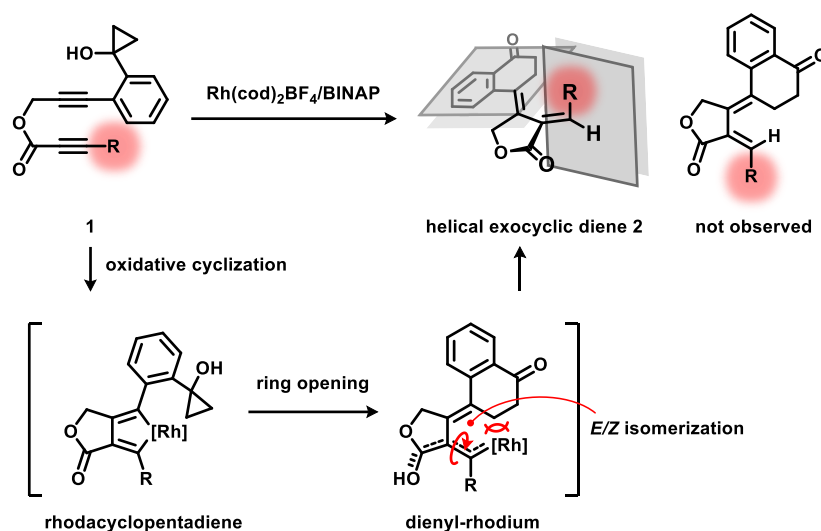
(¹Graduate School of Pharmaceutical Sciences, Nagoya University)

○Tomohiro Kikuchi,¹ Takeshi Yasui,¹ Yoshihiko Yamamoto¹

Keywords: Rh Catalysis; Cycloisomerization; Exocyclic Dienes; Helical Scaffold; Cyclopropanol

Exocyclic dienes possessing terminal substituents oriented inside the diene moiety can create a helical motif.¹ Such helical exocyclic dienes have been used as photochromic molecules, ligands, organocatalysts.² However, the synthetic method for them has been limited due to the steric hindrance between the substituents inside the diene moiety.

Herein, we report the rhodium-catalyzed cycloisomerization of ester-tethered 1,6-diynes **1** bearing a cyclopropanol moiety.³ This reaction gave helical exocyclic dienes **2** with excellent stereoselectivity. Control experiments and density functional theory calculations indicated that oxidative cyclization of the diyne afforded a rhodacyclopentadiene species, followed by the ring-opening of the cyclopropanol moiety. We also found that the construction of thermodynamically unfavorable geometry of the diene moiety is enabled by *E/Z* isomerization in a dienyl-rhodium intermediate.



1) T. V. RajanBabu *et al.*, *J. Am. Chem. Soc.* **2010**, 132, 13078. 2) a) Y. Yokoyama, *Chem. Rev.* **2000**, 100, 1717. b) M. Ogasawara *et al.*, *Angew. Chem., Int. Ed.* **2013**, 52, 13798. c) M. Ogasawara *et al.*, *Org. Lett.* **2017**, 19, 4102. 3) Y. Yamamoto *et al.*, *Chem. Commun.* **2020**, 56, 12865.

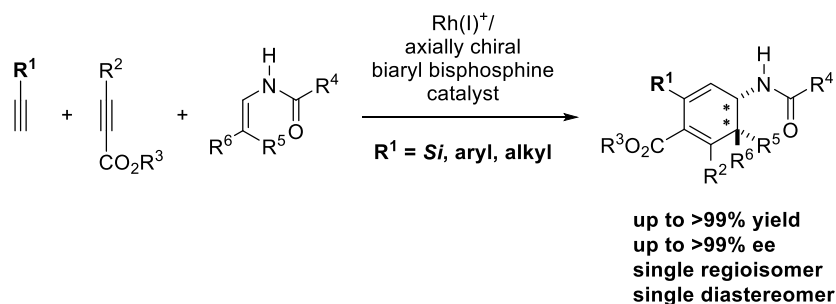
カチオン性ロジウム(I)触媒を用いた高選択的分子間三量化反応による光学活性シクロヘキサジエニルアミンの合成

(東工大物質理工¹) ○藤井 航平¹・益富 光児¹・柴田 祐¹・永島 佑貴¹・田中 健¹
 Synthesis of Chiral Cyclohexadienylamines by Cationic Rhodium(I)-Catalyzed Highly Selective Intermolecular Cross-Cyclotrimerization (¹*Graduate School of Science and Engineering, Tokyo Institute of Technology*) ○Kohei Fujii,¹ Koji Masutomi,¹ Yu Shibata,¹ Yuki Nagashima,¹ Ken Tanaka¹

Chiral 2,4-cyclohexadienyl-1-amines are attractive synthetic targets since they are core structural motifs in biologically active natural products and are also applied as synthetic intermediates in pharmaceuticals.¹ Most of the synthetic approaches to them are multi-step and/or diastereoselective synthesis, although the straightforward enantioselective synthesis is highly desired. Herein, we report a synthetic method of polysubstituted cyclohexadienylamines by the chemo-, regio-, diastereo-, and enantioselective intermolecular cross-cyclotrimerization of terminal alkynes, acetylenecarboxylates, and enamides in the presence of cationic rhodium catalysts.

Keywords: *Asymmetric Catalysis; Cross-Cyclotrimerization; Cyclohexadienylamine; Enamides; Rhodium*

キラル 2,4-シクロヘキサジエニル-1-アミン骨格は天然物や生理活性物質に含まれ、医薬品の合成中間体として応用される有用な化合物群である¹。しかし、その合成法のほとんどが多段階を要するものや、ジアステレオ選択的なものであり、短工程かつエナンチオ選択的合成法が求められている。本研究では、カチオン性ロジウム触媒存在下、末端アルキン、アセチレンカルボン酸エステル、エナミドによる化学/位置/ジアステレオ/エナンチオ選択的分子間交差環化三量化反応による、多置換シクロヘキサジエニルアミン合成法を見出した。



- (1) a) Bunnage, M. E.; Ganesh, T.; Masesane, I. B.; Orton, D.; Steel, P. G. *Org. Lett.* **2003**, *5*, 239–242.
 b) Fukuyama, T.; Nakatsuka, S.; Kishi, Y. *Tetrahedron* **1981**, *37*, 2045–2078. c) Yeung, Hong, S.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 6310–6311.

Catalytic hydrogenation of mono-carboxylic acid using iridium complexes and its application to di-carboxylic acids

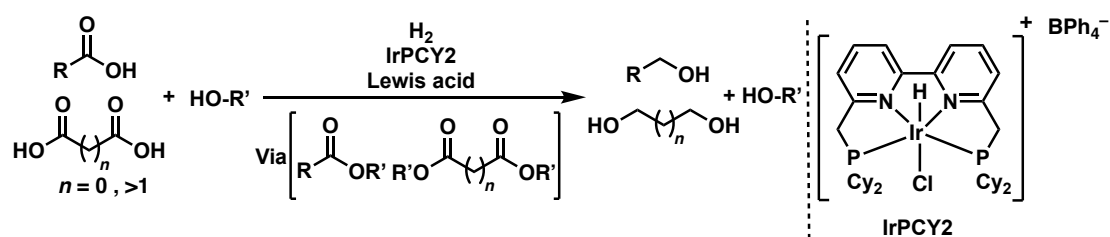
(¹Grad. Sch. Sci. Nagoya Univ., ²RCMS, Nagoya Univ.)

○Bendik Grømer,¹ Shota Yoshioka¹ and Susumu Saito^{1,2}

Keywords: Iridium complex; Hydrogenation; Carboxylic acids; Esterification

Catalytic hydrogenation of carboxylic acids to alcohols by hydrogen gas represents a green method to cheaply obtain platform chemicals from biomass. In recent years, several systems have been reported for this transformation, but the selectivity and substrate scope of the current systems have been unsatisfactory¹. In particular, hydrogenation of di-carboxylic acids is scarcely reported, due to the amount of side reactions that can occur. The selective transformation of dicarboxylic acids to diols represents a green method to obtain important polymer precursors and platform chemicals and thus warrants further research. In particular, the hydrogenation of oxalic- and glycolic acid to yield ethylene glycol is highly sought after.

Our group has in the past years been developing a novel structurally robust PNNP-Ir catalyst, IrPCY2, for hydrogenation of lactones and esters that maintains its functionality in the presence of a wide range of functional groups and additives². Herein, we show that IrPCY2 in the presence of a simple Lewis acid additive can catalyze the one-pot esterification and hydrogenation of a wide range of mono- and di-carboxylic acids, giving desired alcohols in high to quantitative selectivity at low catalyst loadings. The developed system is highly effective for a plethora of industrial relevant substrates, including long-chained dicarboxylic acids, oxalic acid and glycolic acid, all of which has never before been reported using a homogeneous system. Kinetic studies in conjunction with electron spray ionization measurements elucidates a plausible reaction mechanism, and clarifies why the interplay between IrPCY2 and Lewis acid additive was found to be essential for obtaining high reactivity.



1) Selected examples: a) T. J. Korstanje, J. I. van der Vlugt, C. J. Elsevier, B. de Bruin, *Science* **2015**, 350, 298. b) J. Ullrich, B. Breit, *ACS Catal.* **2018**, 8, 785. c) M. Naruto, S. Saito, *Nat. Commun.* **2015**, 6, 8140. d) M. Naruto, S. Agrawal, K. Toda, S. Saito, *Sci. Rep.* **2017**, 7, 3425. e) S. Yoshioka, S. Saito, *Chem. Commun.* **2018**, 54, 13319. f) A. Saito, S. Yoshioka, M. Naruto, S. Saito, *Adv. Synth. Catal.* **2019**, 362, 424. 2) S. Yoshioka, S. Nimura, M. Naruto, S. Saito, *Science Advances* **2020**, 6, 43

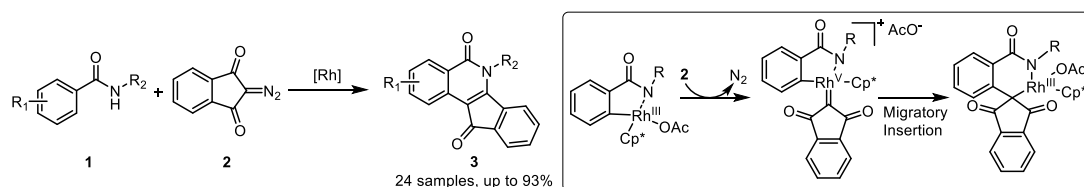
Facile Synthesis of Indeno[1,2-*c*]isoquinolines by Rhodium(III)-catalyzed Cyclocondensation of Benzamides with Diazo compounds via Catalytic Cleavage of C-H Bond followed by Cyclization

(¹Graduate School of Engineering, Kyoto University) ○Dongyoung Kim,¹ Risako Miura,¹ Yu Kimura,¹ Teruyuki Kondo¹

Keywords: Rhodium; C-H activation; Heterocyclization; Indenoisoquinoline

Recently, considerable interest has been focused on transition-metal complex-catalyzed direct activation of a C(sp²)-H bond, and various methods for the construction of diverse bioactive heterocyclic compounds have been developed through catalytic cleavage of a C(sp²)-H.¹ For example, Yu and coworkers succeeded in developing electrophilic rhodium(III) complex-catalyzed coupling reaction of arenes with α -diazomalonate, in which diazo compounds played an important role for generation of a carbenoid intermediates, under mild reaction conditions to give the desired α -aryl malonate together with an evolution of N₂.² After this report, a variety of diazo compounds have been employed for transition metal-catalyzed formation of a carbenoid intermediate which inserted directly into a C(sp²)-H bond, leading to synthesis of various biologically active heterocyclic compounds. Several catalytic methods for synthesis of biologically active indeno[1,2-*c*]isoquinolines have also been reported in the past few decades. However, almost all methods reported so far have serious drawbacks including the severe reaction conditions, limitation of the substrates, and multistep synthesis.³ Thus, the development of novel, facile, and practical methods for catalytic synthesis of indeno[1,2-*c*]isoquinolines are still desired.

In a continuation of our study on rhodium-catalyzed synthesis of heterocyclic compounds, we succeeded in developing novel rhodium(III)-catalyzed synthesis of indeno[1,2-*c*]isoquinolines (**3**), in which a (carbene)rhodium intermediate was formed by the reaction of an active rhodium species with 2-diazo-1*H*-indene-1,3(2*H*)-dione (**2**), and subsequent insertion of a (carbene)rhodium intermediate into a C(sp²)-H bond of benzamides (**1**) may occur, followed by new C-C/C-N bond forming cyclocondensation to give the corresponding indeno[1,2-*c*]isoquinolines in high yield with high selectivity.



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Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[A17-1am] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair:Hiroshi Shinokubo, Masashi Hasegawa

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 17 (Online Meeting)

[A17-1am-01] Synthesis and Properties of Spiro-double Sila[7]helicene: The LUMO Spiro-conjugation

○Nozomi Terada¹, Keisuke Uematsu², Ryota Higuchi², Yuki Tokimaru¹, Yosuke Sato¹, Koji Nakano², Kyoko Nozaki¹ (1. Department of Chemistry and Biotechnology, The University of Tokyo, 2. Department of Applied Chemistry, Tokyo university of Agriculture and Technology)

9:00 AM - 9:20 AM

[A17-1am-02] Modulation of Aromaticity and Properties of Porphyrins by Peripheral Heterole-fused Structures

○Issei Nishimura¹, Tomohiro Higashino¹, Hiroshi Imahori^{1,2} (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ.)

9:20 AM - 9:40 AM

[A17-1am-03] Development of Heavy Chalcogen-Embedded U-Shaped Heteroacenes Having Bilayer Self-Organization Capability

○Tatsuya Mori^{1,2}, Takuma Yasuda^{1,2} (1. Grad. Sch. Eng., Kyushu Univ., 2. IFRC, Kyushu Univ.)

9:40 AM - 10:00 AM

[A17-1am-04] Development of polycyclic aromatic compounds with a nitrogen-based redox property

○Keisuke Fujimoto¹, Shota Masuda¹, Kentaro Sasaki¹, Satoshi Takimoto¹, Masaki Takahashi¹ (1. Shizuoka University)

10:00 AM - 10:20 AM

[A17-1am-05] Nearly Quantitative Emission from the Crystals of Boron β -Diiminate Complexes

○Shunichiro ITO¹, Miyako HASHIZUME¹, Kazuo TANAKA¹, Yoshiki CHUJO¹ (1. Kyoto University)

10:20 AM - 10:40 AM

[A17-1am-06] Creation of Luminescent Polymorphic Material Based on Chirality of Boron-Fused Azomethine Complex

○Shunsuke Ohtani¹, Masayuki Gon¹, Kazuo Tanaka¹, Yoshiki Chujo¹ (1. Grad. Sch. Eng., Kyoto Univ.)

10:40 AM - 11:00 AM

[A17-1am-07] Synthesis of a hyperconjugative antiaromatic compound and weakened antiaromaticity in its dimeric structure.

○Shotaro Ito¹, Takuya Kuwabara¹, Youichi Ishii¹ (1. Chuo University)

11:00 AM - 11:20 AM

[A17-1am-08] Synthesis and Photophysical Properties of Dipyrrolyldiketone Pt^{II} Complexes as Anion-Responsive π -Electronic Systems Forming Ion-Pairing Assemblies

○Atsuko Kuno¹, Hiromitsu Maeda¹ (1. Ritsumeikan Univ.)

11:20 AM - 11:40 AM

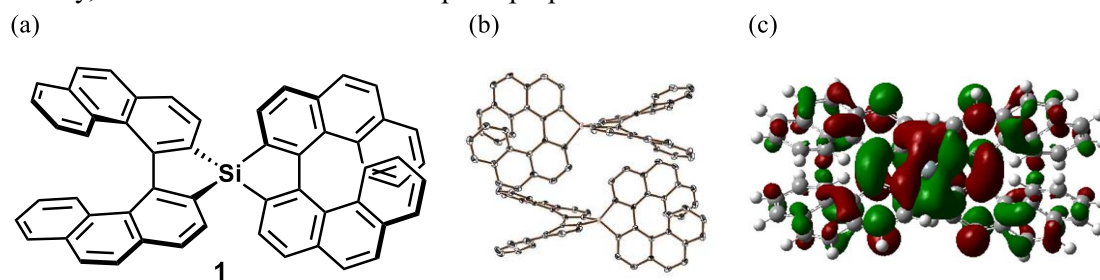
Synthesis and Properties of Spiro-double Sila[7]helicene: The LUMO Spiro-conjugation

(¹Graduate School of Engineering, The University of Tokyo, ²Graduate School of Engineering, Tokyo University of Agriculture and Technology) ○ Nozomi Terada,¹ Keisuke Uematsu,² Ryota Higuchi,² Yuki Tokimaru,¹ Yosuke Sato,¹ Koji Nakano,² Kyoko Nozaki¹

Keywords: Doublehelicene; Silole; Spiro compound; Helicene; Chirality

Helicenes, π -conjugated molecules with helical chirality have attracted attention from various research fields due to their unique helical structures and concomitant chiroptical properties. A class of them, doublehelicenes often have higher curved π -surface than mono-helicenes leading to unique three-dimensional structures and/or intermolecular interactions of the helicene units. Doublehelicenes and doublehelicene-like compounds synthesized until now have conjugated linkers between the two helicene units and thus the π -conjugation spreads to the entire molecule. In such fully conjugated doublehelicenes, the two helical axes corresponding to each helicene unit are approximately parallel, rendering them planar.

Here, we report the synthesis and properties of spiro-double sila[7]helicene (Figure (a), **1**) consisting of two sila[7]helicenes linked by a shared spiroisilabi[fluorene] moiety. The structure was determined by single crystal X-ray analysis (Figure (b)). The enantiomers of **1** were successfully separated by HPLC. The two helicene units were symmetrically and nearly perpendicularly arranged in one molecule. The structural characteristics, optical properties, and DFT calculations were investigated for evaluating the effect of the spiro linkage of two helicene units. Notably, LUMO distribution of **1** (Figure (c)), which delocalized through the σ^* orbitals of the C–Si bonds and the π^* orbitals of the butadiene structure in the spiroisilabi[fluorene] moiety, was found to affect the absorption properties.



Figure

(a) The structures of (*P,P*)-spiro-double sila[7]helicene (**1**).

(b) An ORTEP drawing of *rac*-**1**. triclinic $P\bar{1}$; $a = 10.5082(2)$ Å, $b = 12.1417(3)$ Å, $c = 17.2598(5)$ Å, $\alpha = 91.337(2)^\circ$, $\beta = 98.018(2)^\circ$, $\gamma = 96.874(2)^\circ$; $R_1 = 0.0979$, $wR_2 = 0.2187$, GoF = 1.130.

(c) LUMO distribution of **1**.

Acknowledgement: We are grateful to Dr. Shuhei Kusumoto for single crystal X-ray analysis.

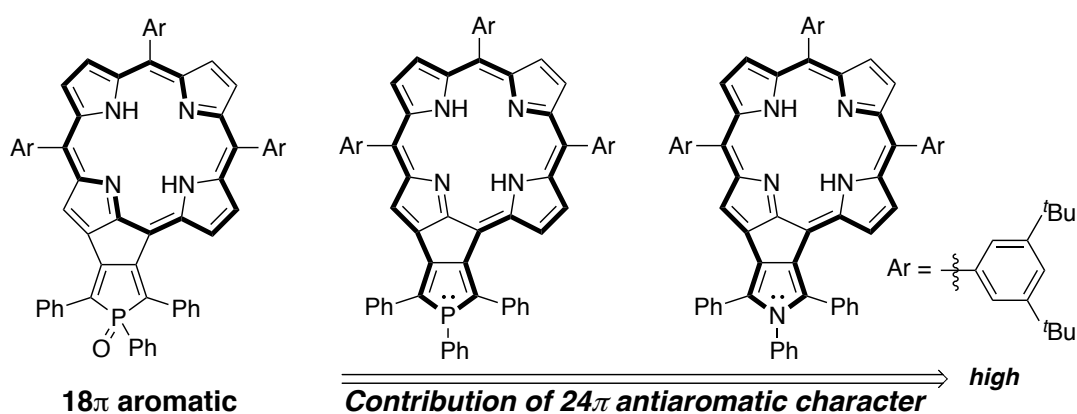
Modulation of Aromaticity and Properties of Porphyrins by Peripheral Heterole-fused Structures

(¹Graduate School of Engineering, Kyoto University, ²WPI-iCeMS, Kyoto University) ○ Issei Nishimura,¹ Tomohiro Higashino,¹ Hiroshi Imahori^{1,2}

Keywords: Porphyrin, Aromaticity, Phosphorus, Nitrogen

Porphyrins are macrocyclic 18π aromatic molecules that have been actively studied in various fields owing to their intriguing properties for diverse applications. Introducing peripheral fused structures is quite effective for electronic perturbations (i.e., red-shift in absorption) because of their expanded π -conjugated networks. Among various fused porphyrins, heteroatom-embedded fused-porphyrins have attracted much attention because of their unique optical and electrochemical properties derived from effective interaction between porphyrins and main group elements. However, the introduction of fused heterole structures into peripheral regions is still a challenge. Considering the properties of heterole derivatives can be modulated by main group elements and their oxidation states, we envisioned that the properties of fused porphyrins would also be tuned by peripheral heterole-fused structures.

Herein, we established a new synthetic strategy for heterole-fused porphyrins using [2+2+1] cyclization of bis(alkynyl)porphyrin and succeeded in the synthesis of phosphole-fused^[1] and pyrrole-fused^[2] porphyrins. The difference of main group elements (i.e., nitrogen or phosphorus) as well as oxidation states of the phosphorus atom have a clear influence on the whole aromatic character and the resultant electronic properties of porphyrins. Therefore, we demonstrated the modulation of aromaticity and properties of heterole-fused porphyrins by control of main group elements and their oxidation states.



[1] I. Nishimura, T. Higashino, H. Imahori, *Chem. Eur. J.* **2019**, *25*, 13816.

[2] I. Nishimura, T. Higashino, H. Imahori, *Chem. Eur. J.* **2020**, *26*, 12043.

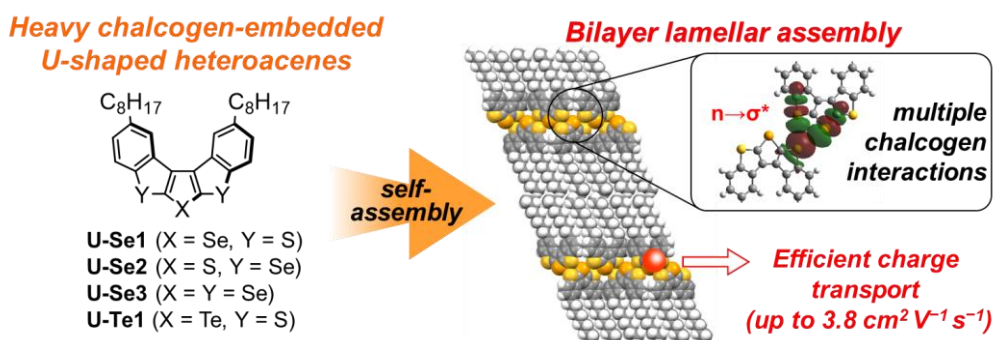
Development of Heavy Chalcogen-Embedded U-Shaped Heteroacenes Having Bilayer Self-Organization Capability

(¹Grad. Sch. Eng., Kyushu Univ. ²IFRC, Kyushu Univ.) ○ Tatsuya Mori,^{1,2} Takuma Yasuda^{1,2}

Keywords: Heteroacenes; Heavy chalcogens; Organic transistors; Self-organization; Organic semiconductors

Controlling the supramolecular assemblies of π -conjugated molecules is essential to achieve excellent functions such as charge carrier transport. One needs to carefully consider both π -cores and heteroatoms to fully exploit the material properties. Heteroatom-containing fused aromatic π -scaffold, referred to as heteroacenes, have been actively studied for high-performance organic semiconductors because their highly ordered molecular packing in the solid states maximizes the intermolecular electronic couplings to facilitate the charge transport. So far, most of the heteroacene-based materials showing excellent semiconducting properties adopted the linear-shaped π -cores with sulfur atoms. However, there are countless combinations of available π -cores and heteroatoms, offering opportunities to develop novel materials endowed with attractive properties.

In this work, we developed a new series of U-shaped heteroacenes featuring unconventional “U” geometric configuration embedded with chalcogen atoms (sulfur, selenium, and tellurium).^{1,2} The incorporation of heavier chalcogen atoms instead of sulfur effectively altered not only the basic optoelectronic properties but also the self-organization behaviors. Notably, U-shaped heteroacenes were found to form bilayer lamellar assemblies with a head-to-head arrangement, which is stabilized by the multiple intermolecular chalcogen interactions. High solvent solubility and crystallinity of U-shaped heteroacenes allowed us to apply them for a facile solution-based thin-film fabrication. Consequently, thin-film organic transistors based on selenium-embedded heteroacene exhibited high hole mobilities of up to $3.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This work provided the advanced molecular design based on the U-shaped molecular configuration and strategic chalcogen substitution.^{1,2}



1) T. Mori, T. Yasuda, *Adv. Electron. Mater.* **2021**, in press.

2) T. Mori, T. Oyama, H. Komiyama, T. Yasuda, *J. Mater. Chem. C* **2017**, 5, 5872.

窒素原子のレドックスに着目した新規多環芳香族化合物の開発

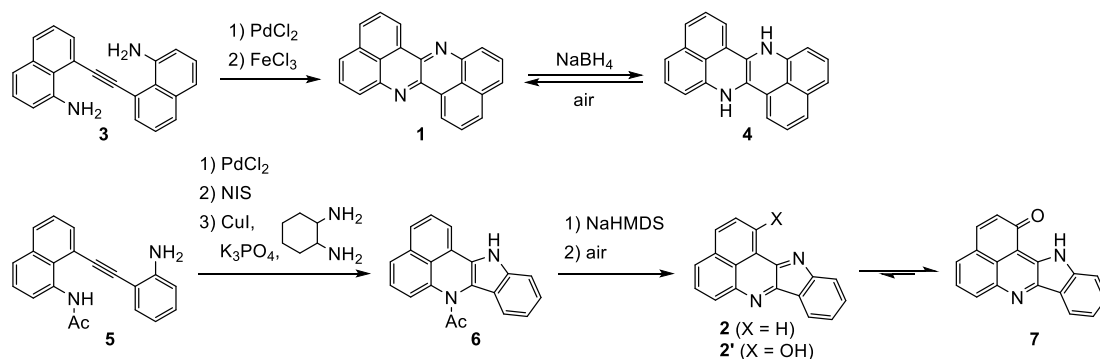
(静岡大工) ○藤本 圭佑・増田 翔太・佐々木 健太郎・滝本 哲・高橋 雅樹
 Development of polycyclic aromatic compounds with a nitrogen-based redox property (*Faculty of Engineering, Shizuoka University*) ○Keisuke Fujimoto, Shota Masuda, Kentaro Sasaki, Satoshi Takimoto, Masaki Takahashi

5,11-Diazadibenzo[*hi,qr*]tetracene (**1**) and benzo[*de*]indolo[3,2-*b*]quinoline (**2**) were synthesized as a series of nitrogen-substituted polycyclic heteroaromatic compounds (PHAs) that included a nitrogen-based redox-active moiety by two-fold cyclization of diarylacetylene precursors possessing two amino groups adjacent to the alkyne moiety. We investigated photophysical properties, electrochemical properties, and redox interconversion between pyridine-type and pyrrole-type structures of the nitrogen atoms of **1** and **2**.

Keywords : Polycyclic Heteroaromatic Compound; Tetracene; Cyclization; Redox Activity

多環ヘテロ芳香族化合物 (PHA) は、ヘテロ原子に特有の電子状態や分子間相互作用を示すことから、機能性色素や有機電子材料として魅力的な化合物である。なかでも、窒素原子は電子求引性のピリジン型構造と電子供与性のピロール型構造に分類され、対照的な性質を示す。本研究では、酸化還元による両構造の相互変換に基づいた機能を示す PHA 創出を目指して、5,11-ジアザジベンゾ[*hi,qr*]テトラセン (**1**) およびベンゾ[*de*]インドロ[3,2-*b*]キノリン (**2**) の開発を行った。

化合物 **1** は二つのナフタレン環を有するアルキン前駆体 **3** に対する PdCl₂ を用いた環化異性化反応と、それに続く FeCl₃ を用いた酸化反応により合成された。化合物 **1** は、定量的な酸化還元反応による相互変換が可能であり、空气中速やかに **1** へと酸化される還元生成物 **4** を与えることが示唆された。また、化合物 **2** の合成を検討したところ、アルキン前駆体 **5** に対する一連の環化反応により、アセチル基を有する還元型構造 **6** として合成することができた。化合物の **6** の脱アセチル化を行ったところ、空気酸化によりヒドロキシ基が導入された **2'** を与え、さらに互変異性化によりケト-エナミン体 **7** へと変換されることが明らかとなった。当日は、得られた一連の化合物の光学特性および電気化学特性と合わせて報告する。



Nearly Quantitative Emission from the Crystals of Boron β -Diiminate Complexes

(Graduate School of Engineering, Kyoto University) ○Shunichiro Ito, Miyako Hashizume, Kazuo Tanaka, Yoshiki Chujo

Keywords: Aggregation-Induced Emission; Group 13 Elements; β -Diimine; Boron

Abstract

Solid-state luminescent molecules are essential for the development of advanced optical materials and devices, such as organic light-emitting diodes, chemical sensors, and organic lasers. Luminescent boron complexes have attracted attention because of their electron-accepting character and stimuli-responsive properties. However, there are still limited examples of efficient solid-state emission from boron complexes. We have developed solid-state emissive materials based on group 13 elements β -diiminate complexes with crystallization-induced emission.¹ Herein, we synthesized boron complexes with highly efficient luminescence both in the solutions and solids. We will describe their molecular design, synthesis and properties.

Results and Discussion

We synthesized boron complexes with aromatic groups at different positions as shown in Figure 1. **3Ph** and **3Tol** exhibited efficient luminescence in solution at the room temperature, although

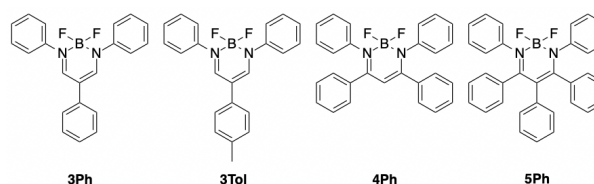


Figure 1. Chemical structures of synthesized complexes.

4Ph and **5Ph** showed only negligible emission under the same condition (Table 1). Furthermore, **3Ph** and **3Tol** strongly emitted with nearly quantitative quantum yields in the crystalline states at the room temperature.

Table 1. Photophysical properties of β -diiminate complexes

	λ_{abs}^a	$\lambda_{\text{PL}}^{\text{solution}, b}$	$\Phi_{\text{PL}}^{\text{solution}, c}$	$\lambda_{\text{em}}^{\text{crystal}, d}$	$\Phi_{\text{PL}}^{\text{crystal}, e}$
3Ph	398	495	0.48	501	0.99
3Tol	402	503	0.75	496	0.96
4Ph	376	n.d. ^f	<0.01	473	0.23
5Ph	370	464	<0.01	443 ^g	0.66 ^g

^aAbsorption maxima in solutions. ^bPhotoluminescence maxima in the solution determined with excitations at λ_{abs} . ^cAbsolute quantum yield in the solution determined with excitations at λ_{abs} .

^dPhotoluminescence maxima in crystalline states determined with excitations at λ_{abs} . ^eAbsolute photoluminescence quantum yield in crystalline states determined with excitations at λ_{abs} . ^fNot determined. ^gThe crystals of **5Ph** contain 1 equiv. of dichloromethane molecule.

Reference

[1] Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2014**, *136*, 18131.

Creation of Luminescent Polymorphic Material Based on Chirality of Boron-Fused Azomethine Complex

(Graduate School of Engineering, Kyoto University)

○ Shunsuke Ohtani, Masayuki Gon, Kazuo Tanaka, Yoshiki Chujo

Keywords: Boron; Azomethine; Luminescence; Fused structure; Polymorph

Polymorphism alteration is currently recognized as a promising strategy to tune a crystalline-state emissive property and various types of optically-functional materials have been developed. However, precise controls of polymorphism are extensively challenging because it is difficult to predict whether a newly synthesized compound is polymorphic or not. To propose one solve for this problem, we focused on the stereogenic boron center of boron-fused azomethine (**BAm**) complex. In our previous research, we obtained the two polymorphs as racemic crystals consisting of (*R*)- and (*S*)-enantiomers of **BAm** with intense solid-state emission.¹⁾ From these results, we assumed that another luminescent homochiral crystal would be available by the chiral resolution. In this work, we synthesized a new **BAm** derivative with the chlorine substitution (**BAmCl**) and separated its enantiomers (Figure 1).²⁾ As a result, we succeeded in obtaining the homochiral crystals of (*R*)- and (*S*)-**BAmCl** as well as the racemic crystal *rac*-**BAmCl**.

From the result of a single crystal X-ray diffraction (SCXRD) analysis, it was proposed that a variety of the intermolecular interactions and the intrinsic flexibility of **BAm** framework contributed to the stabilization of the homochiral crystal (Figure 2). Moreover, these two crystals showed different emission colors dependent on the molecular arrangements. Additionally, in the homochiral crystal, the homogeneous racemization was observed through the molten state in the absence of any solvents and catalysts. To the best of our knowledge, this is the first example of homogeneous racemization in the boron-centered chiral compounds.

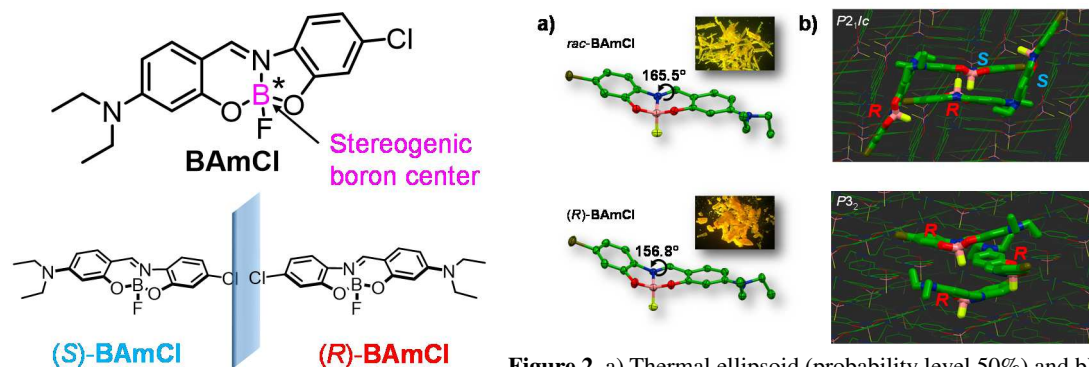


Figure 1. Chemical structure of **BAmCl** and its stereogenic boron center.

Figure 2. a) Thermal ellipsoid (probability level 50%) and b) packing structures of *rac*-**BAmCl** and (*R*)-**BAmCl** (green carbon atoms; blue nitrogen atoms; red oxygen atoms; pink boron atoms; yellow fluorine atoms; gold chlorine atoms; hydrogen atoms are omitted for clarity).

1) Ohtani, S.; Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2017**, *23*, 11827.

2) Ohtani, S.; Takeda, Y.; Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Commun.* **2020**, *56*, 15305.

Synthesis of a Hyperconjugative Antiaromatic Compound and Weakened Antiaromaticity in Its Dimeric Structure

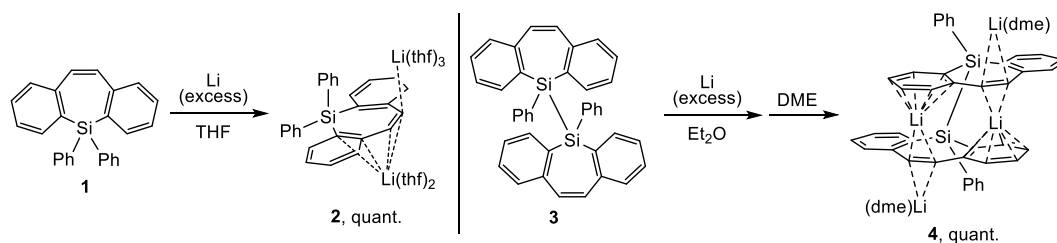
(Graduate School of Science and Engineering, Chuo University) ○Shotaro Ito, Takuya Kuwabara, Youichi Ishii

Keywords: Silicon; Antiaromaticity; Hyperconjugation; Anionic Species

In contrast to well-established chemistry of conventional antiaromatic compounds with $4n\pi$ electron systems, studies of hyperconjugative antiaromatic compounds, in which an sp^3 hybridized atom is doped into a cyclic π conjugated system, are very limited.¹ Herein, we report a novel anionic hyperconjugative antiaromatic compound that shows weakened antiaromatic character in a dimeric structure.

Reaction of diphenyldibenzosilepin **1** and excess lithium in THF yielded dilithium diphenyldibenzosilepinide **2**. The ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR signals of the dibenzosilepin skeleton of **2** in THF- d_8 were found in a characteristic high-field region ($\delta(^1\text{H})$: 5.63–2.88 ppm), suggesting the anionic charges are delocalized over the dibenzosilepin scaffold. The Si–Ph and the endocyclic Si–C bonds of **2** are slightly elongated and shortened compared to those of **1**, respectively. These structural changes suggest the anionic charges are delocalized through the σ^* orbitals of the Si–Ph bonds. The NICS(0) values were calculated to be 13.6 and 12.8 ppm for the annulated benzene rings and 5.1 ppm for the silepin ring, which indicates the antiaromatic character of **2** originating from the 16π -electron system.

Treatment of a Et_2O solution of bis(phenyldibenzosilepin) **3** with excess lithium afforded lithium salt of bissilepinyl tetraanion **4**. The NICS(0) values of **4** were calculated to be nearly zero (2.8 and -0.3 ppm for the annulated benzene rings and -3.3 ppm for the silepin ring), which is in sharp contrast to the positive NICS(0) values in **2**. Importantly, the ^1H NMR signals of the dibenzosilepin skeleton of **4** in THF- d_8 were low-field shifted compared to those of **2** ($\Delta\delta = +0.12$ – 0.90 ppm), suggesting the antiaromatic character of the dibenzosilepin skeletons is weakened in **4**. This phenomenon seems to be closely related to three-dimensional aromaticity.²



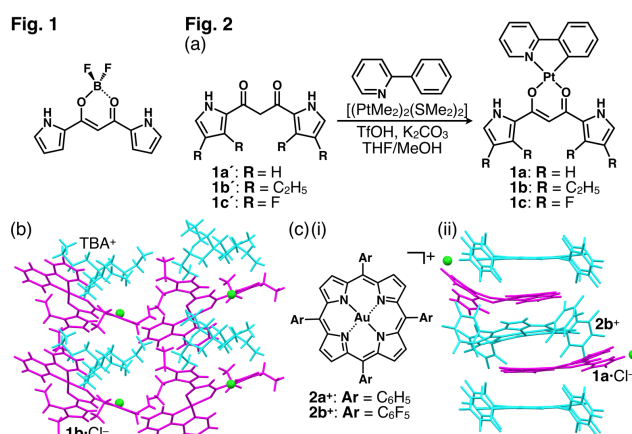
1) a) Nyulászai, L.; Réau, R. *et al. Org. Biomol. Chem.* **2006**, *4*, 996–998. b) Fernández, I.; Wu, J. I.; Schleyer, P. von R. *Org. Lett.* **2013**, *15*, 2990–2993. 2) a) Schleyer, P. von R.; Warner, P. *et al. Org. Lett.* **2007**, *9*, 3263–3266. b) Shinokubo, H. *et al. Nat. Commun.* **2019**, *10*, 3576.

Synthesis and Photophysical Properties of Dipyrrolyldiketone Pt^{II} Complexes as Anion-Responsive π -Electronic Systems Forming Ion-Pairing Assemblies

(College of Life Sciences, Ritsumeikan University) ○Atsuko Kuno, Hiromitsu Maeda

Keywords: π -electronic anion receptors; pyrrole derivatives; Pt^{II} complexes; phosphorescence; ion-pairing assemblies

Well-controlled assemblies composed of appropriately designed charged π -electronic systems would provide functional materials. Dipyrrolyldiketone BF₂ complexes as anion-responsive π -electronic molecules (Fig. 1) are highly emissive and available as fluorescence sensors. Various dipyrrolyldiketone BF₂ complexes have been synthesized by the modifications at the pyrrole and boron units, and their anion complexes have provided ion-pairing assemblies in combination with various counteranions.¹ In this study, Pt^{II} complexes were focused on as building units of assemblies based on their planar tetracoordinated geometries and modulating electronic properties.² Pt^{II} complexes **1a–c**, synthesized under the appropriate conditions (Fig. 2a), displayed anion-binding behavior with the binding constants of 1,300, 520, and 10,000 M^{−1}, respectively, for Cl[−] in CH₂Cl₂. In the solid state, the ion pair of **1b**·Cl[−] with a tetrabutylammonium (TBA) cation exhibited the formation of charge-by-charge assembly (Fig. 2b), while **1a**·Cl[−] and **1c**·Cl[−] showed the ion-pairing assemblies with porphyrin-Au^{III} cations **2b**⁺ and **2a**⁺,² respectively, forming the charge-by-charge assemblies (Fig. 2c). In addition, **1a** exhibited the emission at 520 nm with a quantum yield of 0.42 upon excitation at the absorption maximum (410 nm) in CH₂Cl₂. The large Stokes shift and emission lifetime (3.65 μ s) suggested the phosphorescent property. Furthermore, the component of the excited triplet state was observed in the transient absorption spectra.³



- Recent reports: (a) Watanabe, Y.; Haketa, Y.; Nakamura, K.; Kaname, S.; Yasuda, N.; Maeda, H. *Chem. Eur. J.* **2020**, *26*, 6767; (b) Sugiura, S.; Maeda, H. *Org. Biomol. Chem.* **2020**, *18*, 4433.
- (a) Haketa, Y.; Bando, Y.; Sasano, Y.; Tanaka, H.; Yasuda, N.; Hisaki, I.; Maeda, H. *iScience* **2019**, *14*, 241; (b) Tanaka, H.; Haketa, Y.; Yasuda, N.; Maeda, H. *Chem. Asian J.* **2019**, *14*, 2129.
- Kuno, A.; Hirata, G.; Kobayashi, Y.; Yasuda, N.; Maeda, H. to be submitted.

[A09-1am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Katsuaki Konishi, Norimitsu Tohnai

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 9 (Online Meeting)

[A09-1am-01] Dynamic Structural Conversions of Rotaxanes Having a Cyclic Cobalt(III) Metallohost by Addition of Amines

○Misato Yamamoto¹, Yoko Sakata^{1,2}, Shigehisa Akine^{1,2} (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. WPI Nano Life Science Institute, Kanazawa University)

9:00 AM - 9:20 AM

[A09-1am-02] Seeded polymerization of D-A-D-type dyes and its fluorescence imaging

○Soichiro Ogi¹, Yoshiki Imai¹, Shigehiro Yamaguchi^{1,2} (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University)

9:20 AM - 9:40 AM

[A09-1am-03] The effects of alkyl chain lengths on the emission of PEG-terminated gold(I)-alkane thiolate coordination polymer

○Midori Murakami¹, Yukatsu Shichibu¹, Katsuaki Konishi¹ (1. Grad. Sch. Env. Sci., Hokkaido Univ.)

9:40 AM - 10:00 AM

[A09-1am-04] Fluorinated Porous Organic Cage Compounds

○Bernd M. Schmidt¹ (1. Heinrich Heine University Dusseldorf)

10:00 AM - 10:20 AM

[A09-1am-05] Photo-induced spatial control of out-of-equilibrium network pattern of peptide nanofibers in a supramolecular double network hydrogel

○Wataru Tanaka¹, Ryou Kubota¹, Itaru Hamachi^{1,2} (1. Graduate School of Engineering, Kyoto University, 2. JST-ERATO)

10:20 AM - 10:40 AM

[A09-1am-06] Controlled Synthesis of Supramolecular Concentric Toroid

○Norihiko Sasaki^{1,2}, Masayuki Takeuchi², Kazunori Sugiyasu^{1,2} (1. Kyushu university, 2. National Institute for Materials)

10:40 AM - 11:00 AM

[A09-1am-07] Control of supramolecular self-sorting network by dynamic covalent chemistry.

○Kazutoshi Nagao¹, Ryou Kubota¹, Wataru Tanaka¹, Ryotaro Matsumura¹, Takuma Aoyama², Kenji Urayama², Itaru Hamachi^{1,3} (1. Kyoto university Grad. Sch. of Eng., Kyoto Univ., 2. Grad. Sch. of Sci. and Tech., Kyoto Inst. of Tech., 3. JST-ERATO)

11:00 AM - 11:20 AM

[A09-1am-08] Multiscale imaging reveals four distinct hierarchical networks in supramolecular/polymer hydrogel composites

○Keisuke Nakamura¹, Ryou Kubota¹, Kei Sada¹, Takuma Aoyama², Kenji Urayama², Itaru Hamachi^{1,3} (1. Grad. Sch. of Eng., Kyoto Univ., 2. Grad. Sch. of Sci. and Eng., Kyoto Inst. of Tech., 3. JST ERATO)

11:20 AM - 11:40 AM

環状コバルト(III)メタロホストを有するロタキサンのアミン添加による動的構造変換

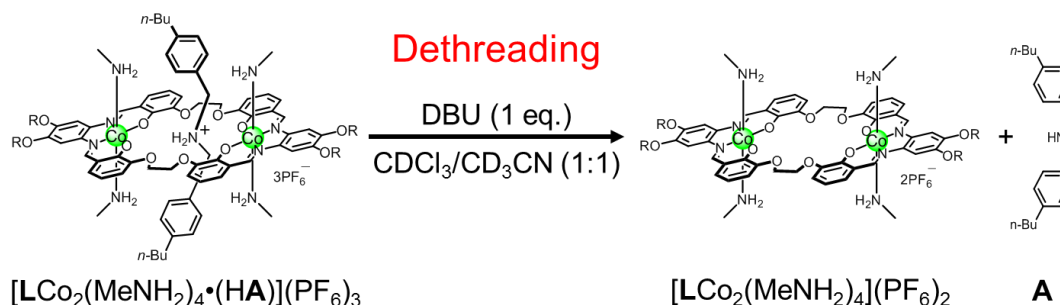
(金沢大院自然¹・金沢大 WPI-NanoLSI²) ○山本 美里¹・酒田 陽子^{1,2}・秋根 茂久^{1,2}
 Dynamic Structural Conversions of Rotaxanes Having a Cyclic Cobalt(III) Metallohost by Addition of Amines (¹Graduate School of Natural Science and Technology, Kanazawa University・²WPI Nano Life Science Institute, Kanazawa University) ○Misato Yamamoto,¹ Yoko Sakata,^{1,2} Shigehisa Akine^{1,2}

We synthesized a new metallorotaxane ([LCo₂(MeNH₂)₄•(HA)](PF₆)₃) composed of a secondary ammonium cation and a macrocyclic cobalt(III) metallohost in which two methylamine ligands axially coordinate to each cobalt(III) ion. Upon the addition of DBU, the axle molecule was dethreaded from the metallohost. This dethreading reaction efficiency depends on the kinds of the metal ions in the metallohost and bulkiness of the stopper units in the axle molecule. We also investigated the efficiency of the ligand exchange and the structural conversion of this rotaxane upon the addition of various amines.

Keywords : Rotaxane; Structural Conversion; Dethreading; Ligand Exchange

インターロック分子の絡み合い構造を状況に応じて制御することは重要である。例えばロタキサンにおいて、外部刺激により輪分子に貫通していた軸分子を抜くことができれば、任意のタイミングで輪分子などを放出する機能性分子として有用となる。本研究では、輪分子骨格にコバルト(III)を導入したメタロロタキサンに対して塩基である DBU を添加することで、輪分子が開環せずに軸分子が抜けるという興味深い現象を見出した。

二核コバルト(III)ロタキサン[LCo₂(MeNH₂)₄•(HA)](PF₆)₃ に DBU を 1 当量添加したところ、輪分子に貫通していた軸分子がデスレッディングし、フリーの輪分子[LCo₂(MeNH₂)₄](PF₆)₂ と軸分子 **A** が生成したことが確認された。この構造変換は軸分子の-NH₂-基の脱プロトン化に起因しており、導入している金属の違いや、軸分子のストッパー部位の嵩高さの違いによってその効率が変わることが示唆された。また、このコバルト(III)ロタキサンに対して様々な二級アミンを添加し、コバルト(III)上のメチルアミン配位子の交換による構造変換を試みた結果についても報告する。



D-A-D 型色素の種重合と蛍光イメージング

(名大院理¹・名大 ITbM²) ○大城宗一郎¹・今井芳樹¹・山口茂弘^{1,2}

Seeded polymerization of D-A-D-type dyes and its fluorescence imaging (¹*Graduate School of Science, Nagoya University*, ²*Institute of Transformative Bio-Molecules, Nagoya University*) ○Soichiro Ogi,¹ Yoshiki Imai,¹ Shigehiro Yamaguchi^{1,2}

Fluorescence imaging is an effective way for understanding dynamics of molecular assembly. In this study, we designed and synthesized a diamide-functionalized D-A-D-type fluorescent dye for imaging of seeded supramolecular polymerization. We confirmed that spontaneous self-assembly in 1,2-dichloroethane was proceeded with a lag time, during which supramolecular polymers with controlled length could be produced using a seeding method. Fluorescence imaging allowed us to directly observe the growth of the supramolecular polymers from the termini of the seeds on a glass substrate.

Keywords : *Supramolecular chemistry, Supramolecular polymer, Metastable state, Seeded supramolecular polymerization, Fluorescence imaging*

超分子ポリマーの構造を精密に制御する上で、重合過程を速度論的に制御する種重合が有用である。種重合の詳細な機構の解明により、均質な機能性材料の創出につながると期待される。そこで本研究では、分子集合体のダイナミクス研究において有効な蛍光イメージングに着目し、基板上における種重合過程のライブイメージングに取り組んだ。

自己集合を促すアミノ酸ジアミド基を導入した D-A-D 型色素 **1** を設計、合成し、種々のスペクトル測定により集合特性を評価した (Figure 1a). 1,2-ジクロロエタン中、**1** の超分子重合過程において、自発的な集合が一時的に抑制された誘導期が観測された。本挙動は、ジアミド部位の分子内水素結合により、速度論的に準安定な折りたたみ構造が形成されたことを示唆する¹⁾。得られた準安定状態の溶液を、集合体の断片(種)を散布した基板上に添加し、顕微鏡観察を行なったところ、時間の経過とともに種の両末端から超分子ポリマーが伸長する様子が観察された (Figure 1b)。本発表では、D-A-D 型色素 **1** の光物性と集合特性、種重合の蛍光イメージングから得られた知見について発表する。

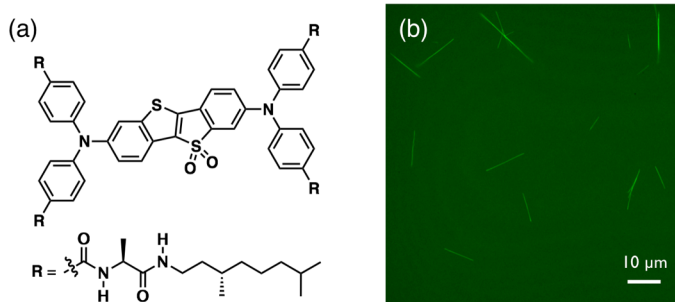


Figure 1. (a) Chemical structure of **1** and (b) fluorescence imaging of seeded polymerization.

1) S. Ogi, K. Matsumoto, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2018**, 57, 2339–2343.

The effects of alkyl chain lengths on the emission of PEG-terminated gold(I)-alkane thiolate coordination polymer

(Graduate School of Environmental Science, Hokkaido University) oMidori Murakami, Yukatsu Shichibu, Katsuaki Konishi

Keywords: gold; alkyl chain; PEG; Even-odd effect; photoluminescence

During our recent efforts to synthesize novel soluble gold(I)-thiolate (AuSR) coordination polymers by using PEG-modified thiols, we have found that highly luminescent products are obtained specifically when the thiols with a sufficiently long alkyl spacer were used under certain conditions¹). The critical role of the long alkyl segment is demonstrated by the absence of such photoluminescence (PL) emissions when analogous thiols with a short alkyl spacer were employed. In this work, we synthesized a series of AuSR coordination polymers derived from PEGylated alkanethiols with different alkyl-chain lengths (**C6-C11**), and discuss the relationship between the PL properties and the alkyl spacer.

The synthesis of AuSR from **C6-C11** was performed by the reaction with H₂AuCl₄ in water at 70 °C for 24 h, and the products were purified by ultrafiltration. Except AuSR derived from **C6** (AuS-C6), the AuSR products were PL active. As shown in Fig.1, upon the increase of the alkyl-chain spacer length, the PL bands were enhanced in intensity. For example, the intensity of AuS-C11 was more than ten times larger than that of AuS-C7, and negligible emission was found for AuS-C6. Interestingly, the emission peak position depended on the even/odd character of the carbon number of the alkyl spacers. AuS-C7, AuS-C9, and AuS-C11 showed the emission bands at ~600 nm, whereas the corresponding bands of AuS-C8 and AuS-C10 were observed at red-shifted positions (~610 nm). On the other hands, the UV-Vis absorption and PL excitation spectra of these AuSR were similar to each other, suggesting that the slight difference in the interligand packing of the alkyl segments causes perturbation on the excited state energy.

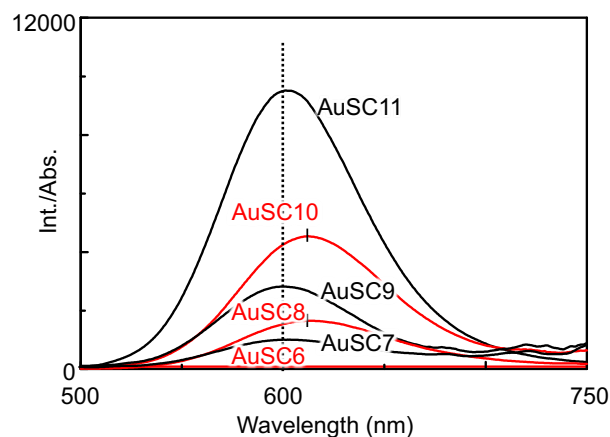
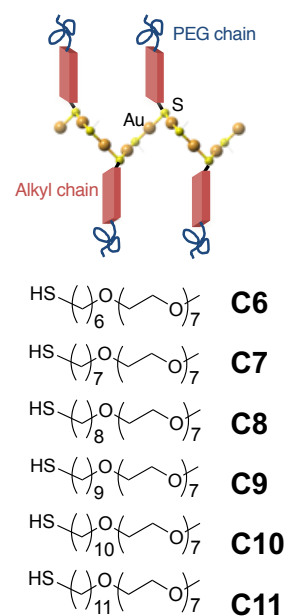


Fig. 1. Photoluminescence spectra ($\lambda_{\text{ex}} = 320 \text{ nm}$) in water at 20°C of the purified coordination polymers prepared by the reactions of H₂AuCl₄ with **C6-C11** thiols.

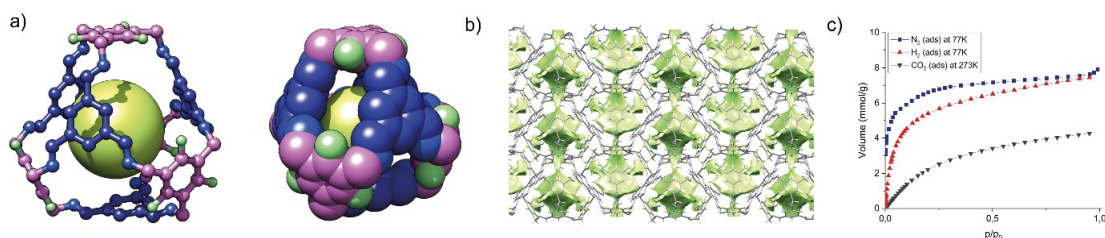
1) M. Murakami, R. Matsumine, T. Ono, K. Konishi, *Chem. Lett.* **2020**, 49, 1228.

Fluorinated Porous Organic Cage Compounds

(¹*Organic Chemistry and Macromolecular Chemistry, Heinrich-Heine-University Düsseldorf, Düsseldorf, Germany*) ○ Bernd M. Schmidt¹

Keywords: supramolecular chemistry; porous organic cages; fluorine chemistry; organic cages; dynamic covalent chemistry

Supramolecular chemistry continued to evolve in the last decades and successfully found its way into nanotechnology and materials. In addition to the properties of metal-organic frameworks (MOFs) and metal-organic cages, covalent-organic frameworks (COFs) and porous dynamic-covalent cage compounds (POCs) attracted tremendous attention in the past years.¹ We focus on the synthesis and characterization of novel POCs by inverting the electron density of the aromatic panels used for the self-assembly by fluorination. This not only creates highly reactive building blocks for dynamic covalent imine chemistry, but also hydrophobic nanospaces within the formed cage compounds. These cages show distinct gas adsorption properties and significantly increased thermal stabilities, exemplarily shown by the synthesis of the first highly fluorinated, porous, organic [4+4] imine cage, **FC1**, containing perfluorinated aromatic panels und hydrogenated panels.²



Gas adsorption experiments show an uptake of 19.0 wt% CO₂ (4.2 mmol g⁻¹, 273 K and at 1 bar) and 1.5 wt% H₂ (7.5 mmol g⁻¹, 77 K and at 1 bar) for the specific surface area of 536 m² g⁻¹ of the crystalline **FC1** material obtained directly from the reaction mixture. Combined with an outstanding thermal stability, a very interesting porous material for further research regarding exciting properties of this new class of organic cages is presented. Additionally, the unique reactivity of the employed building blocks will be showcased by studies regarding organic [4+6] imine cage formation.

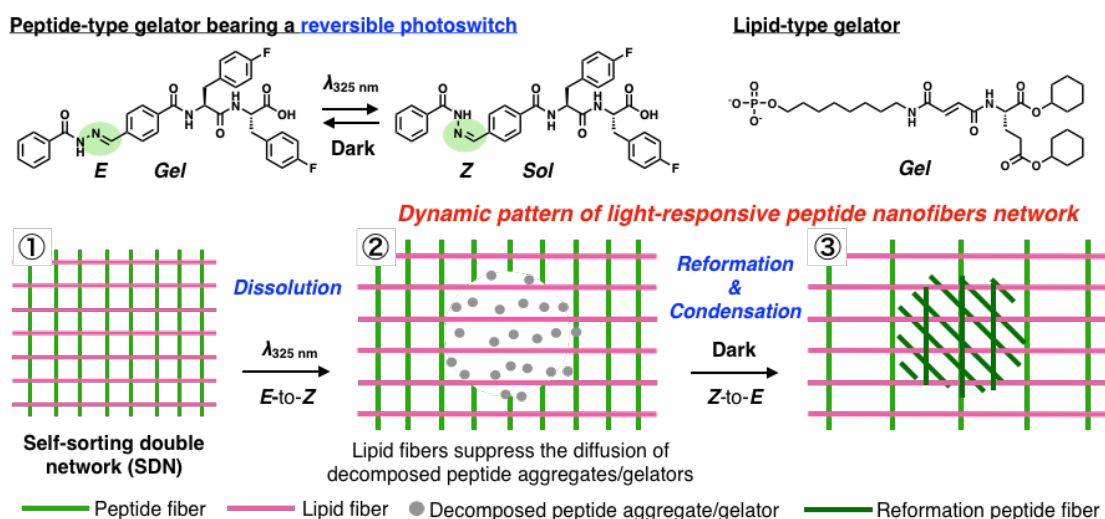
1) T. Hasell, A. I. Cooper, *Nat. Rev. Mater.* **2016**, *1*, 16053. 2) T. Kunde, E. Nieland, H. V. Schröder, C. A. Schalley, B. M. Schmidt, *Chem. Commun.* **2020**, *56*, 4761.

Photo-induced spatial control of out-of-equilibrium network pattern of peptide nanofibers in a supramolecular double network hydrogel

(¹Graduate School of Engineering, Kyoto University, ²JST ERATO) ○Wataru Tanaka,¹ Ryou Kubota,¹ Itaru Hamachi^{1,2}

Keywords: supramolecular hydrogel; self-sorting; patterning; light-responsive

In living cells, cytoskeletal proteins orthogonally self-assemble to form self-sorted nanofibers, which in some cases cooperatively work to control the spatial organizations and the collective motions. Such precise control of interactions between self-sorted nanofibers would be invaluable to design artificial intelligent soft materials. However, there have been limited varieties of such synthetic materials. Herein, we developed a self-sorting double network (SDN) hydrogel composed of a lipid-type gelator and a light-responsive peptide-type gelator bearing an acylhydrazone moiety. Upon photo-irradiation with a photomask, the peptide nanofibers in a photo-irradiation area were selectively decomposed through the light-induced *E*-to-*Z* isomerization of the acylhydrazone moiety, as confirmed by *in situ* confocal laser scanning microscopy imaging. During incubation under dark after the photo-decomposition, the gradual reformation of the peptide nanofibers in the photo-irradiation area took place through the *Z*-to-*E* isomerization of the acylhydrazone moiety. In sharp contrast, such reformation was never observed in the single component peptide hydrogel. These suggested that interactions between the lipid fibers and the collapsed peptide aggregates/monomers would be important to suppress the diffusion of the peptide aggregates/monomers. Surprisingly, subsequent incubation of the photo-irradiated SDN hydrogel under dark caused formation of the denser network of the peptide nanofibers in the photo-irradiation area. In this presentation, I'll also discuss the mechanisms in detail.



Controlled Synthesis of Supramolecular Concentric Toroid

(¹Graduate School of Engineering, Kyushu University, ²National Institute for Materials Science) ○Norihiko Sasaki,^{1,2} Masayuki Takeuchi,² Kazunori Sugiyasu^{1,2}

Keywords: Self-assembly; Porphyrin; Supramolecular polymer; Concentric toroid

Supramolecular polymers have found a variety of application in materials science, nanotechnology, and biotechnology¹. Control of shapes and sizes of supramolecular polymers is therefore of great importance²; although it remains a significant challenge.

Previously, we have reported pathway complexity in supramolecular polymerization of porphyrin derivative **6** (Fig. a). **6** has the capacity to form nanofiber and nanosheet structures, and we achieved the selective formation of one of these structures by mechanical stimuli³. Based on the mechanistic insight into this unique molecular assembly, we designed porphyrin **6FFZn** which has fluorinated side chains (Fig. a). Interestingly, **6FFZn** was found to self-assemble into concentric toroid (Fig. b). AFM observation unveiled the growth mechanism of concentric toroid (Fig. c-g). Based on this understanding, we succeeded in controlling the size of concentric toroid through seeded supramolecular polymerization (Fig. h)⁴.

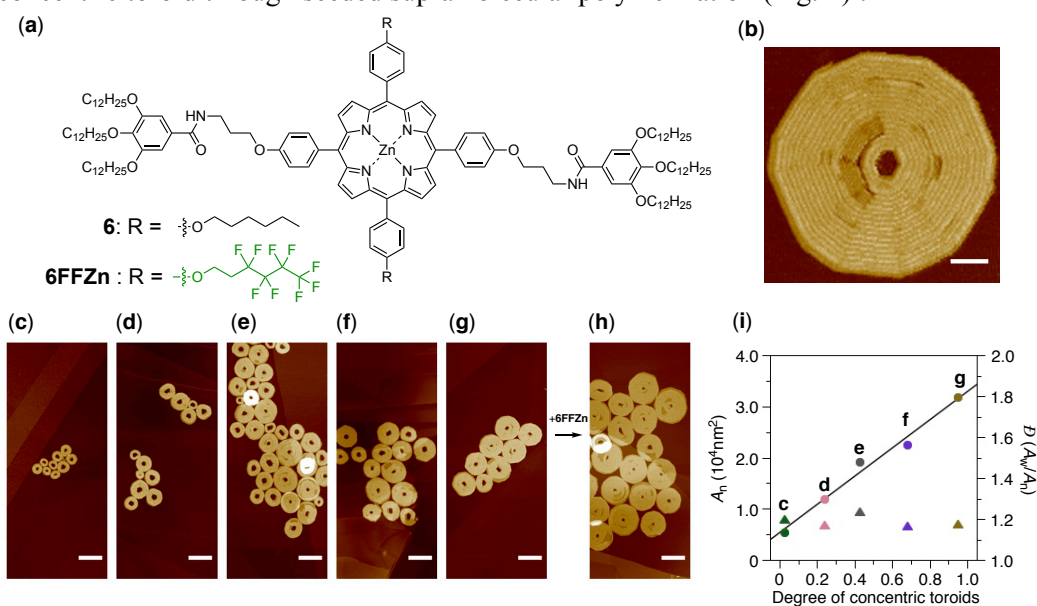


Figure (a) Structures of porphyrin derivatives (b) AFM image of concentric toroid of **6FFZn**. Scale bar, 50 nm. AFM images of concentric toroids obtained during the time-dependent evolution at (c) 60 s, (d) 180 s, (e) 300 s, (f) 480 s, (g) 1200 s, (h) 1800 s (i.e., after the incremental addition of a **6FFZn** solution). Scale bar, 200 nm. (i) Plot of number-average area (A_n) and polydispersity (D) of the concentric toroids as a function of the degree of the concentric toroids c-h.

- (1) T. Aida, E. W. Meijer, S. I. Stupp. *Science* **2012**, 335, 813-817. (2) A. K. Pearce, T. R. Wilks, M. C. Arno, R. K. O'Reilly. *Nat. Rev. Chem.* **2020**, 5, 21-45. (3) T. Fukui *et al.* *Nat. Chem.* **2017**, 9, 493-499. (4) N. Sasaki *et al.* *Nat. Commun.* **2020**, 11, 3578.

動的共有結合を用いた超分子 Self-sorting ネットワークの構造制御

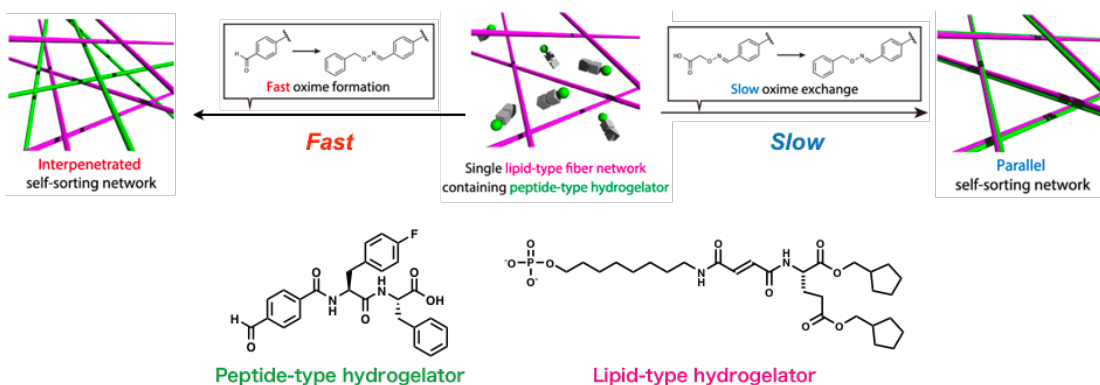
(京大院工¹・京都工芸繊維大学²・JST-ERATO³) ○長尾 和俊¹・窪田 亮¹・田中 航¹・松村 亮太郎¹・青山 拓磨²・浦山 健治²・浜地 格^{1,3}

Control of supramolecular self-sorting networks by dynamic covalent chemistry. (¹ Grad. Sch. of Eng., Kyoto Univ., ² Grad. Sch. of Sci. and Tech., Kyoto Inst. of Tech., ³ JST-ERATO) ○Kazutoshi Nagao¹, Ryou Kubota¹, Wataru Tanaka¹, Ryotaro Matsumura¹, Takuma Aoyama², Kenji Urayama², Itaru Hamachi^{1,3}

Supramolecular double network hydrogels comprising self-sorted nanofibers have attracted considerable attentions due to their rational integration of multiple stimulus-responses. Here, we describe the construction of two distinct self-sorting network patterns by controlling the kinetics of seeds formation through dynamic covalent oxime chemistry. Confocal imaging revealed the formation of interpenetrated self-sorting network upon treatment of *O*-benzylhydroxylamine to an aldehyde-tethered peptide-type hydrogelator in the presence of lipid-type nanofibers. In addition, deceleration of the kinetics of seeds formation by oxime exchange allowed for construction of the parallel self-sorting network through preferential nucleation of the peptide-type nanofibers on the lipid-type nanofibers.

Keywords : Supramolecular; Self-sorting; Dynamic covalent chemistry; confocal laser scanning microscopy; Hydrogel

Self-sortingは、複数の超分子ナノファイバーの機能を干渉させずに統合化する優れた戦略である。これまでに我々は独自に開発したペプチド型および脂質型ゲル化剤がSelf-sorting現象を示すことを発見している¹⁾。近年、モノマーレベルでのSelf-sorting現象の制御は達成されつつある一方で、Self-sortingファイバーのネットワーク構造を制御することは未だ困難である。本研究では、動的共有結合によりペプチド型ナノファイバーの形成速度を制御することで、2種類のSelf-sortingネットワークパターン(Interpenetrated or Parallel)の作り分けに成功した(Figure)²⁾。ベンズアルデヒド基を有するペプチド型ゲル化剤と脂質型ファイバーを含む溶液に*O*-benzylhydroxylamineを添加すると、オキシム形成反応を介してペプチド型ファイバーと脂質型ファイバーが相互貫入したInterpenetrated Self-sortingネットワークを構築することが、共焦点顕微鏡観察によって確かめられた。一方オキシム交換反応を利用してペプチド型ファイバーの形成速度を遅くすると、ペプチド型ファイバーの核形成が脂質型ファイバー上で進行することで、Parallel Self-sortingネットワークが構築されることを見出した。これらの知見は、多成分系超分子マテリアルの物性・機能をより高次に制御するために有用であると期待される。



1) Shoji Onogi *et al*, *Nature Chem.* **8**, 743-752 (2016).

2) Ryou Kubota *et al*, *Nature Commun.* **11**, 1, 4100 (2020).

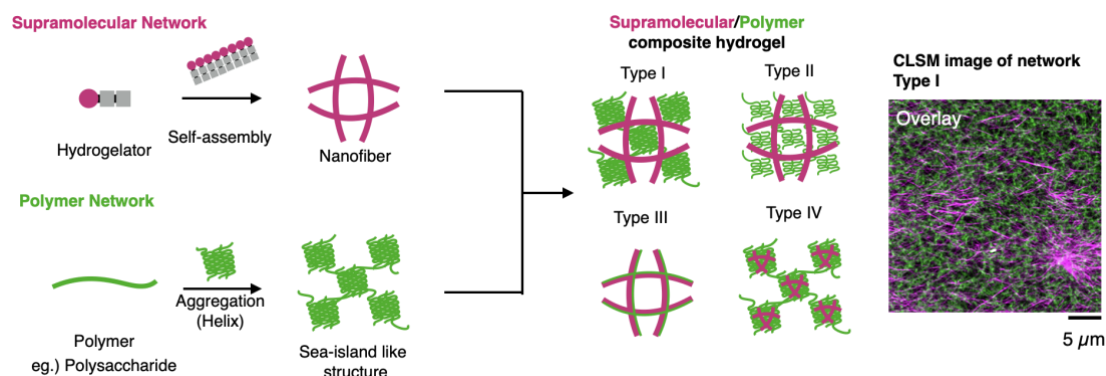
Multiscale imaging reveals four distinct hierarchical networks in supramolecular/polymer hydrogel composites

(¹Graduate School of Engineering, Kyoto University, ²Graduate School of Science and Technology, Kyoto Institute of Technology, ³JST ERATO) ○ Keisuke Nakamura,¹ Ryou Kubota,¹ Kei Sada,¹ Takuma Aoyama,² Kenji Urayama,² Itaru Hamachi^{1,3}

Keywords: *Supramolecular/polymer Composite Hydrogel; Stimuli Responsive Material; Confocal Laser Scanning Microscopy; Hierarchical Structure*

Supramolecular hydrogels formed by self-assembly of small molecules (hydrogelators) via noncovalent interactions have been developed as unique and promising stimuli-responsive soft materials. Composite materials consisting of supramolecular and polymer hydrogels were recently proposed to overcome the mechanical weakness of supramolecular hydrogels¹. However, the relationships between the network structure and mechanical properties of the composite hydrogels are still unclear due to lack of reliable imaging methods. To date, structural analysis of the composite hydrogels has been mainly conducted by electron microscopy (EM), which can visualize the nanoscale structure of the network. However, EM is not suitable for analyzing the composite network due to a poor capability to discriminate the distinct networks. Recently, confocal laser scanning microscopy (CLSM) has emerged as a powerful tool for structural analysis of multicomponent supramolecular hydrogel systems². CLSM not only allows imaging of supramolecular nanofibers and hydrogels without the need for a drying process, but can distinguish between chemical species through the use of appropriately designed fluorescent probes.

In this work, we sought to evaluate the network structure of various kinds of composite hydrogels by both SEM and CLSM imaging. Multiscale imaging reveals that these are classified into four distinct hierarchical structures based on the morphology and spatial distribution of each network. To investigate structure-mechanical properties relationships of the composite hydrogels, rheological experiments are also conducted.



1) H. Shigemitsu *et al.*, *Nat. Commun.* **2020**, *11*, 3859. 2) R. Kubota *et al.*, *Chemistry Open*, **2020**, *9*, 67.

[A11-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Yohei Shimizu, Okano Kentaro

Fri. Mar 19, 2021 1:00 PM - 3:00 PM Room 11 (Online Meeting)

[A11-1pm-01] Defluorophosphinylation Synthesis of Aryl Phosphorus Compounds

○Zhensheng You¹, Kosuke Higashida^{1,2}, Tomohiro Iwai³, Masaya Sawamura^{1,2} (1.

Department of Chemistry, Faculty of Science, Hokkaido University, 2. WPI-ICReDD, 3.

Department of Basic Science, Graduate School of Art and Sciences, The University of Tokyo)

1:00 PM - 1:20 PM

[A11-1pm-02] Sulfonylthiolation of Arenes via Selective Activation of SS-morpholino dithiosulfonate

○Kazuya Kanemoto¹, Koudai Furuhashi¹, Tokiharu Watanabe¹, Hayato Asanuma¹, Shin-ichi Fukuzawa¹ (1. Chuo University)

1:20 PM - 1:40 PM

[A11-1pm-03] Development of Selective Mono- and Difluorination of Silyl Enol Ethers using Novel Electrophilic Fluorinating Reagents

○Akiya Adachi¹, Kohsuke Aikawa¹, Yuichiro Ishibashi², Kyoko Nozaki¹, Takashi Okazoe^{1,2} (1. Sch. of Eng., The Univ. of Tokyo, 2. AGC Inc.)

1:40 PM - 2:00 PM

[A11-1pm-04] Alkyltriflones in the Ramberg-Bäcklund Reaction for the synthesis of *gem*-difluoroalkenes

○Yuki Maekawa^{1,3}, Masakazu Nambo¹, Daisuke Yokogawa², Cathleen M Crudden^{1,3} (1. Nagoya University, Institute of Transformative Bio-Molecules, 2. University of Tokyo, 3. Queen's University)

2:00 PM - 2:20 PM

[A11-1pm-05] Trapping of Transient Thienyllithiums in Halogen Dance Using Zinc Chloride Diamine Complex

○Kengo Inoue¹, Suguru Hirai¹, Yuki Hayashi¹, Kentaro Okano¹, Atsunori Mori^{1,2} (1. Kobe Univ., 2. Research Center for Membrane and Film Technology)

2:20 PM - 2:40 PM

[A11-1pm-06] Control of Regioselectivity in Hypervalent Iodine-mediated Sulfonyloxylactonization by Noncovalent Interactions in Ion Pairs

○Masaki Fujie¹, Yoshihiro Nishimoto¹, Makoto Yasuda¹ (1. Osaka University)

2:40 PM - 3:00 PM

Defluorophosphinylation of Aryl Phosphorus Compounds

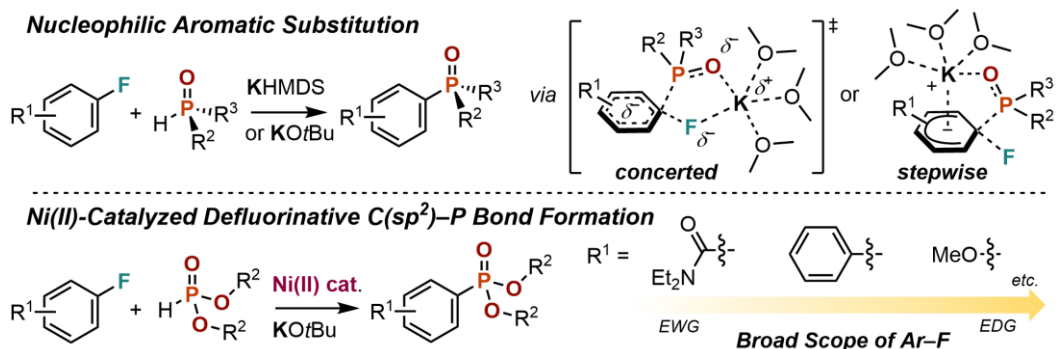
(¹Department of Chemistry, Faculty of Science, Hokkaido University, ²WPI-ICReDD, ³Department of Basic Science, Graduate School of Art and Sciences, The University of Tokyo)
 ○Zhensheng You,¹ Kosuke Higashida,^{1,2} Tomohiro Iwai,³ Masaya Sawamura^{1,2}

Keywords: Defluorophosphinylation; Aryl Fluorides; Aryl Phosphorus Compounds; Nucleophilic Aromatic Substitution; Quantum Chemical Calculation

Nucleophilic aromatic substitution (S_NAr) is a classical and fundamental chemical reaction. The S_NAr reactions occur most commonly between strong nucleophilic reagents and aryl halides with strongly electron-withdrawing substituents, proceeding through a widely-accepted stepwise manner intermediated by Meisenheimer complexes. Meanwhile, a series of reports have revealed that electron-neutral and electron-deficient aryl electrophiles prefer a concerted manner without the presence of an intermediate (CS_NAr). Generally, mechanisms in S_NAr are dominated by electronic properties of electrophiles rather than nucleophiles.¹

Herein, we report a new S_NAr reaction. Non-activated aryl fluorides reacted with potassium diorganophosphinites ($KOPR^1R^2$) prepared *in-situ* from secondary phosphine oxide [$H(O)PR^1R^2$] and potassium bases such as KHMDS and $KOtBu$.² A variety of aryl fluorides, including strongly electron-rich *p*-fluoroaniline derivatives, participated in the reaction with the substantially stabilized anionic P-nucleophiles, forming the corresponding tertiary phosphine oxides. Quantum chemical calculations revealed a nucleophile-dependent mechanism, which involves both stepwise and concerted S_NAr reaction pathways. This is due to non-covalent interactions and ambiphilic nature of the potassium diorganophosphinite nucleophiles.

Moreover, the addition of a catalytic amount of a Ni(II) complex enables the defluorinative $C(sp^2)-P$ bond formation reaction of aryl fluorides with diorganophosphites [$H(O)P(OR)_2$] using $KOtBu$ as a base. A wide range of electron-rich and electron-deficient aryl fluorides participated in this Ni catalysis without an exogenous ligand.



- 1) Rohrbach, S.; Murphy, J. A.; Tuttle, T. *J. Am. Chem. Soc.* **2020**, *142*, 14871–14876
- 2) You, Z.; Higashida, K.; Iwai, T.; Sawamura, M. *Angew. Chem., Int. Ed.* in press (DOI: 10.1002/anie.202013544).

SS-morpholino dithiosulfonate のアミノ基選択的な活性化を経由する，芳香族化合物のスルホニルチオ化反応

(中大理工¹・中大院理工²) ○金本 和也¹・古橋 昂大²・渡邊 時春²・浅沼 隼人¹・福澤 信一¹

Sulfonylthiolation of Arenes via Selective Activation of SS-morpholino dithiosulfonate

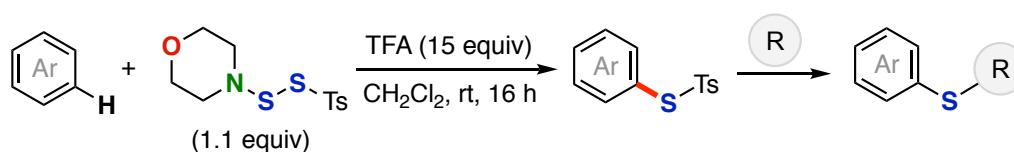
(¹Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University,

²Department of Applied Chemistry, Graduate School of Science and Engineering, Chuo University) ○ Kazuya Kanemoto,¹ Koudai Furuhashi,² Tokiharu Watanabe,¹ Hayato Asanuma,¹ Shin-ichi Fukuzawa¹

A trifluoroacetic acid-mediated desulfurilative sulfonylthiolation of arenes using SS-morpholino dithiosulfonate was achieved. This system is based on the selective activation of the morpholino group over the tosyl group of SS-morpholino dithiosulfonate. Control experiments and theoretical calculations suggested that the reaction proceeds via the electrophilic aromatic substitution mechanism and subsequent sulfur extrusion. The wide substrate scope of this reaction and the transformability of the resulting thiosulfonates enable expeditious access to divergent multi-functionalized sulfides via the assembly of various combinations of modules.

Keywords : thiosulfonate; electrophilic thiolation; thiosulfonylation; sulfide; trifluoroacetic acid

スルフィド類は医薬品などにおいて重要な化合物群であり，これらを簡便かつ迅速に合成できる手法の開発が求められている．今回我々はモルホリノ基とスルホニル基の二種の脱離基を有する SS-morpholino dithiosulfonate に対して TFA を作用させると，モルホリノ基が選択的に活性化され，硫黄の脱離を伴いながら芳香族化合物をスルホニルチオ化できることを明らかにした．さらに残存したスルホニル基を変換することで，^{1,4} 二度の C-S 結合形成を経て様々な組み合わせのスルフィド類が迅速に得られた．



- 1 S. Yoshida, Y. Sugimura, Y. Hazama, Y. Nishiyama, T. Yano, S. Shimizu, T. Hosoya, *Chem. Commun.* **2015**, 51, 16613.
- 2 K. Kanemoto, Y. Sugimura, S. Shimizu, S. Yoshida, T. Hosoya, *Chem. Commun.* **2017**, 53, 10640.
- 3 K. Kanemoto, S. Yoshida, T. Hosoya, *Org. Lett.* **2019**, 21, 3172.
- 4 K. Kanemoto, Y. Sakata, T. Hosoya, S. Yoshida, *Chem. Lett.* **2020**, 49, 593.

Development of Selective Mono- and Difluorination of Silyl Enol Ethers using Novel Electrophilic Fluorinating Reagents

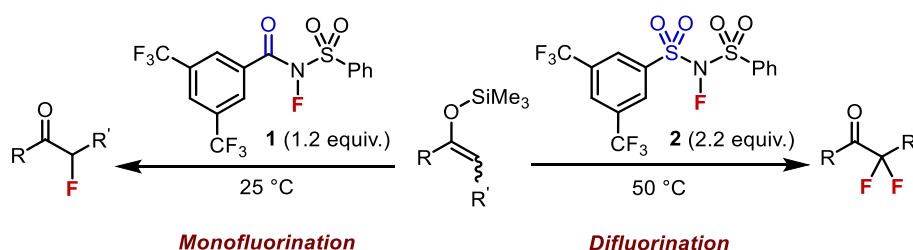
(¹Graduate School of Engineering, the University of Tokyo, ²AGC Inc.)

○Akiya Adachi,¹ Kohsuke Aikawa,¹ Yuichiro Ishibashi,² Kyoko Nozaki,¹ Takashi Okazoe^{1,2}

Keywords: Organofluorine Compound; Selective Fluorination; Electrophilic Fluorinating Reagent; NFSI; Silyl Enol Ether

Organofluorine compounds constitute a valuable class in the fields of pharmaceuticals and agrochemicals, because biological activity and physicochemical properties, such as bioavailability, lipophilicity, and metabolic stability, can be improved by the introduction of fluorine atom(s).^[1] Therefore, efficient methods for the synthesis of fluorinated compounds have been intensively studied, recently.^[2] Development of practical electrophilic fluorinating reagents is indispensable for this purpose.^[3] Herein, we report the synthesis of novel and bench-stable electrophilic fluorinating reagents **1** and **2** as substitutes for NFSI (*N*-fluorobenzenesulfonimide). With these in hand, the highly selective mono- and difluorination of silyl enol ethers were accomplished.

Reagent **1**, obtained by replacing one of the sulfonyl groups of NFSI with an acyl group, led to the highly selective monofluorination of silyl enol ethers derived from ketones with suppression of the undesired overreaction, that is difluorination. In sharp contrast, reagent **2**, bearing electron-withdrawing substituents on one of the benzenesulfonyl groups of NFSI, efficiently facilitated the difluorination of silyl enol ethers derived from ketones without any bases. These results indicate that both mono- and difluorinated target materials can be selectively synthesized from the same substrates through the molecular design of NFSI-derivatives.



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Alkyltriflones in the Ramberg–Bäcklund Reaction: Synthesis of *gem*-difluoroalkenes

(¹*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*, ²*Department of Chemistry, Queen's University*, ³*Department of Basic Science, The University of Tokyo*)

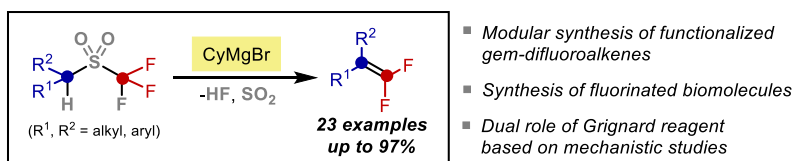
○Yuuki Maekawa,^{1,2} Masakazu Nambo,¹ Daisuke Yokogawa,³ Cathleen, M. Crudden^{1,2}

Keywords: Ramberg–Bäcklund Reaction, Alkyltriflone, Grignard Reagent, Organofluorine Compounds,

The Ramberg–Bäcklund reaction is a textbook method for the preparation of functionalized alkenes from readily available α -halogenated alkylsulfones. However, fluorinated alkylsulfones have not been employed, likely due to the low leaving ability of fluoride.

gem-Difluoroalkenes, which represent an interesting class of fluorinated compounds, are bioisosteres of vinyl and carbonyl compounds. *gem*-Difluoroalkenes and their derivatives have been employed in pharmaceutical chemistry due to their ability to enhance and change molecular properties.¹ Hu and co-workers have reported the versatile synthesis of fully substituted *gem*-difluoroalkenes from diazo compounds,² but there is still lack of straightforward and modular approach for dialkyl *gem*-difluoroalkenes.

Herein we report the first example of the use of alkyltriflones in the Ramberg–Bäcklund reaction, providing ready access to *gem*-difluoroalkenes.³ Structurally diverse, fully-substituted *gem*-difluoroalkenes that are difficult to prepare by other methods can be easily prepared from readily available triflones by treatment with specific Grignard reagents. Experimental and computational studies provide insight into the unique and critical role of Grignard reagent, which serves both as a base to remove the α -proton, and as a Lewis acid to assist C–F bond activation.



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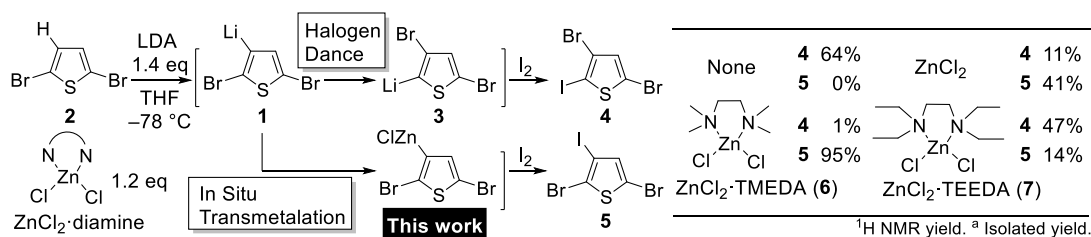
Trapping of Transient Thienyllithiums in Halogen Dance Using Zinc Chloride Diamine Complex

(¹Graduate School of Engineering, Kobe University, ²Research Center for Membrane and Film Technology, Kobe University) ○ Kengo Inoue,¹ Suguru Hirai,¹ Yuki Hayashi,¹ Kentaro Okano,¹ Atsunori Mori^{1,2}

Keywords: Halogen Dance; Zinc Chloride Diamine Complex; In Situ Transmetalation; Thienyllithium; In Situ IR Spectroscopy

Thienyllithiums bearing a bromo group often undergo halogen dance, the exchange of the lithium atom and the bromo group.¹ The halogen dance of thienyllithium **1** generated from 2,5-dibromothiophene (**2**) proceeded smoothly even at $-78\text{ }^{\circ}\text{C}$ to furnish thienyllithium **3**, which then reacts with iodine to afford thiophene **4**. Although the reaction of the first generated thienyllithium **1** provides another constitutional isomer **5**, suppression of the halogen dance has been reported to be difficult.² Recently, we also attempted to trap the transient thienyllithium **1** using a flow microreactor; however, selective trapping of thienyllithium **1** could not be realized under the optimized reaction conditions.³

We began with the trapping of thienyllithium **1** by in situ transmetalation.⁴ Based on the report by Knochel,⁵ we treated a mixture of 2,5-dibromothiophene (**2**) and ZnCl_2 with LDA at $-78\text{ }^{\circ}\text{C}$, and subsequent addition of iodine provided thiophene **4** and the desired thiophene **5** in 11% and 41% yields, respectively, with a 23% recovery of substrate **2**. These results indicated that ZnCl_2 reacted with LDA to provide less basic zinc amide species. Switching to $\text{ZnCl}_2 \cdot \text{TMEDA}$ (**6**) exclusively provided the desired thiophene **5** in 95% yield. The product ratio was affected by the alkyl group on the nitrogen atom in the diamine ligand. Thus, $\text{ZnCl}_2 \cdot \text{TEEDA}$ (**7**) resulted in the formation of a mixture of thiophene **4** and thiophene **5**. The effects of the diamines on in situ transmetalation, which was observed by in situ IR spectroscopy, and its synthetic application will be also presented.



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Control of Regioselectivity in Hypervalent Iodine-mediated Sulfonyloxylactonization by Noncovalent Interactions in Ion Pairs

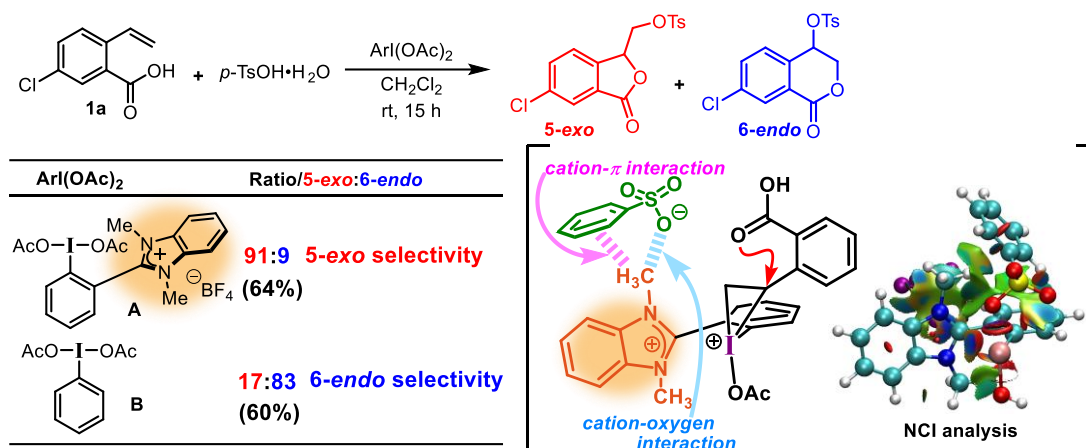
(Graduate School of Engineering, Osaka University) ○Masaki Fujie, Yoshihiro Nishimoto, Makoto Yasuda

Keywords: Hypervalent Iodine; Cationic Substituent; Cyclization; Regioselectivity; Noncovalent Interaction

Hypervalent iodines are important non-metal oxidants in organic chemistry and their reactivities are controlled by organic ligands sterically and/or electronically. The sophisticated hypervalent iodines are available for asymmetric reactions, efficient group transfer reactions, and so on.¹ Therefore, an efficient strategy based on a new concept is highly promising even now. In this study, we developed a new methodology using noncovalent interactions derived by cationic heterocyclic substituents on organic framework of hypervalent iodine.

We synthesized hypervalent iodine **A** bearing a benzimidazolium moiety at the ortho position of the iodine atom. For the evaluation of **A**, we chose a model reaction as oxidative tosyloxylactonization of 2-vinylbenzoic acid **1a**.² Hypervalent iodine **A** showed 5-*exo* selectivity, while conventional iodobenzene diacetate **B** gave 6-*endo* selectivity. Furthermore, the investigation of various types of substituents revealed that cationic nitrogen-containing heterocyclic moieties close to iodine center was essential to high 5-*exo* selectivity.

Monitoring intermediates and DFT calculation revealed that the regioselectivity was controlled by noncovalent interactions composed of cation- π interaction and cation-oxygen interaction between sulfonate anions and cationic substituents. The trapping of a sulfonate ion retards the intermolecular nucleophilic attack and favors an intramolecular attack leading to the 5-*exo* product.



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

[A10-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair:Junichi Ito, Yoshihiro Nishimoto

Fri. Mar 19, 2021 1:00 PM - 3:00 PM Room 10 (Online Meeting)

[A10-1pm-01] Model Study on the Catalytic Cycle of GPx1 and GPx4 by Utilizing Cradled Selenopeptides

[○]Ryosuke Masuda¹, Shohei Sase¹, Satoru Kuwano¹, Kei Goto¹ (1. Tokyo Institute of Technology)

1:00 PM - 1:20 PM

[A10-1pm-02] In-catalyzed C– F bond transformation via oxymetalation/ β -fluorine elimination to access fluorinated isocoumarins

[○]Tetsuji Yata¹, Yoshihiro Nishimoto¹, Kouji Chiba², Makoto Yasuda¹ (1. Grad. Sch. Eng., Osaka Univ., 2. MOLSIS Inc.)

1:20 PM - 1:40 PM

[A10-1pm-03] Reactivity of Alkyl-Substituted Al Anion

[○]Satoshi Kurumada¹, Kengo Sugita¹, Ryo Nakano¹, Makoto Yamashita¹ (1. The Univ. of Tokyo)

1:40 PM - 2:00 PM

[A10-1pm-04] Metal-free Transient Auxiliary Directed C-H Borylation of Benzaldehyde Derivatives

[○]Supriya Rej¹, Naoto Chatani¹ (1. Osaka University)

2:00 PM - 2:20 PM

[A10-1pm-06] Synthesis and Properties of Two Boron-containing Electron-deficient Heteroacenes

[○]Masato Ito¹, Naoki Ando¹, Shigehiro Yamaguchi^{1,2} (1. Grad. Sch. Sci., Nagoya Univ., 2. Institute of Transformative bio-Molecules, Nagoya Univ.)

2:40 PM - 3:00 PM

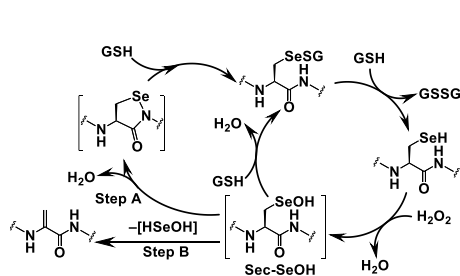
Model Study on the Catalytic Cycle of GPx1 and GPx4 by Utilizing Cradled Selenopeptides

(School of Science, Tokyo Institute of Technology) ○Ryosuke Masuda, Shohei Sase, Satoru Kuwano, Kei Goto

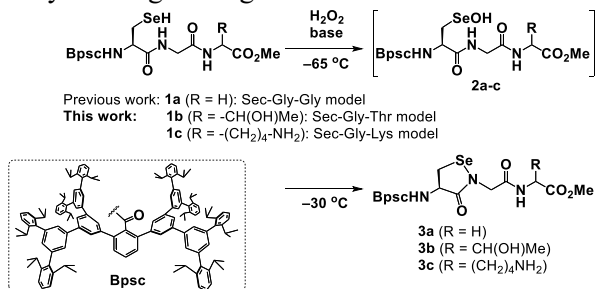
Keywords: Glutathione Peroxidase; Selenocystiene; Selenenic Acids; Molecular Cradles; Redox Regulation

Glutathione peroxidase (GPx) plays crucial roles in redox regulation. GPx1 is a typical isozyme of GPx and catalyzes the reduction of H_2O_2 . In contrast, GPx4 is known as a membrane protein that catalyzes the reduction of lipid peroxidase. Selenocysteine selenenic acids (Sec-SeOH) have been accepted as important but elusive intermediates in their catalytic cycle. Recently, we reported the model study on the chemical processes composing the catalytic cycle of GPx (Scheme 1) by the observable Sec-SeOH **2a** of a Sec-Gly-Gly model system, and demonstrated that a Sec-SeOH undergoes the intramolecular cyclization (Step A)¹ more rapidly than the thermal deselenation (Step B).² Sec-SeOH **2a** is stabilized by a nano-sized molecular cradle (Bpsc group). Herein, we report the development of tripeptide model systems that mimic the catalytic centers of GPx1 and GPx4. Elucidation of reactivities of Sec-SeOH including the intramolecular cyclization have been examined.

We synthesized selenol **1b** of the Sec-Gly-Thr model for modeling GPx1 and the Sec-Gly-Lys model **1c** for modeling GPx4. Generation of the corresponding Sec-SeOH **2b** and **2c** by oxidation of **1a** and **1b**, respectively, and their conversion to the cyclic *N*-selenoamides **3a** and **3b** were observed (Scheme 2). The intramolecular cyclization of Sec-SeOH was found to proceed more rapidly in the Sec-Gly-Thr and Sec-Gly-Lys models than in the Sec-Gly-Gly model. These results provide chemical corroboration to the proposed protective bypass process of the catalytic cycle of GPx. It is also suggested that the reactivities of Sec-SeOH are modulated by the neighboring amino acid residues.



Scheme 1. Proposed mechanism for GPx function.



Scheme 2. Generation and elucidation of the reactivities of Sec-SeOH.

1) L. Orian, L. Flohé *et al.* *Free Radic. Biol. Med.* **2015**, 87, 1.

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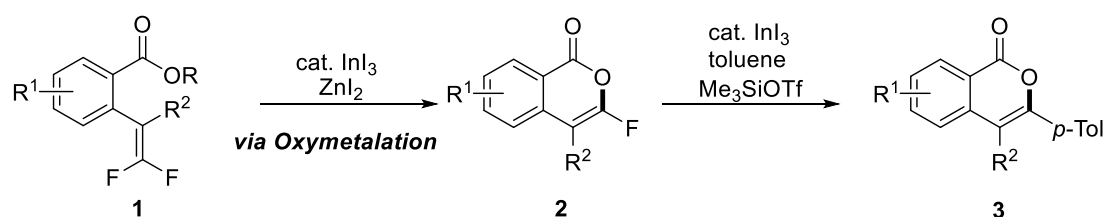
In-catalyzed C-F bond transformation via oxymetalation/ β -fluorine elimination to access fluorinated isocoumarins

(¹Graduate School of Engineering, Osaka University, ²Material Science Division, MOLSYS Inc.) ○Tetsuji Yata,¹ Yoshihiro Nishimoto,¹ Kouji Chiba,² Makoto Yasuda¹

Keywords: Indium; Heterocycles; C-F bond functionalization; β -fluorine elimination; gem-difluoroalkene

The introduction of fluorine group or fluorine-containing structural motifs into small molecules often brings about desirable properties in their bioactivity and provides unique chemical and physical properties. Fluorinated heterocycles have found widespread use in numerous bioactive compounds and drugs. Thus, the assembly of fluorinated heterocycles has been a topic of ongoing interest.¹ Despite the fact that isocoumarine derivatives are an important class of oxygen-containing heterocycles that possess a variety of biological properties, a synthetic strategy for fluorinated isocoumarins has not been established yet. Therefore, the exploration of new synthetic methods for the synthesis of fluorine-containing isocoumarin derivatives is highly desirable. Our group reported the intramolecular oxymetalation of alkynes using indium salts as a π -electrophilic Lewis acid.² Herein, we report indium-catalyzed C-F bond transformation of β,β -difluorostyrene derivatives bearing ester groups to give various fluorinated isocoumarins.

When difluorostyrene derivative **1** was treated with a catalytic amount of InI₃ and ZnI₂ under the optimized conditions, fluorinated isocoumarin **2** was efficiently obtained. This novel synthetic strategy allows access to a wide variety of fluorinated isocoumarins. DFT calculation clarified that the path through oxymetalation/ β -fluorine elimination is adapted for C-F bond transformation of a gem-difluoroalkene moiety. Furthermore, by using toluene as a solvent in the presence of InI₃ and Me₃SiOTf, further transformation at the C-F bond of fluorinated isocoumarins **2** occurred to give aryl isocoumarin derivatives **3**.



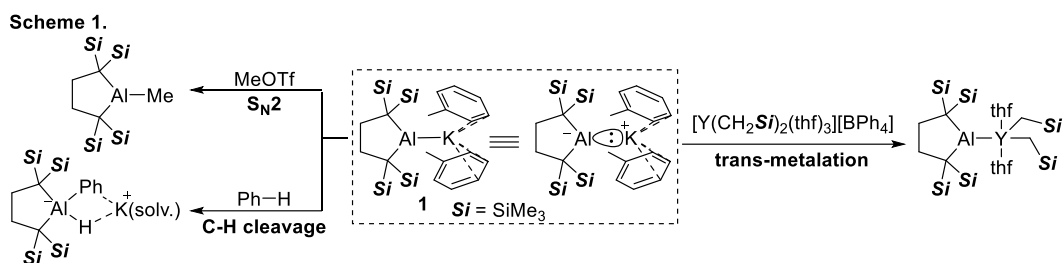
1) Petrov, V. A. In *Fluorinated Heterocyclic Compounds: Synthesis, Chemistry, and Applications*; John Wiley & Sons: Hoboken, 2009. 2) a) Y. Kita, T. Yata, Y. Nishimoto, K. Chiba, M. Yasuda, *Chem. Sci.* **2018**, 9, 6041. b) T. Yata, Y. Kita, Y. Nishimoto, M. Yasuda, *J. Org. Chem.* **2019**, 84, 14330.

Reactivity of Alkyl-Substituted Al Anion

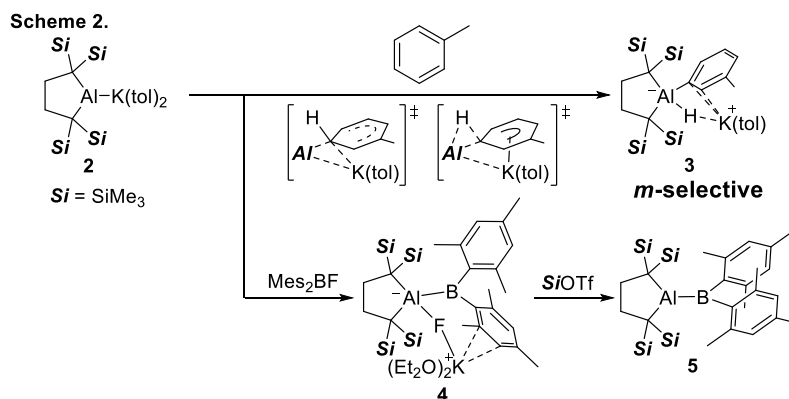
(Graduate School of Engineering, Nagoya University) ○Satoshi Kurumada, Kengo Sugita, Ryo Nakano, Makoto Yamashita

Keywords: aluminium; boron; nucleophile; nucleophilic aromatic substitution

Neutral three-coordinate Al compounds possess a Lewis acidity due to its vacant 3p-orbital. Recently, several anionic Al compounds possessing a Lewis basicity have been reported.¹ These compounds have strong basicity due to the lone-pair on the most electropositive Al element in the p-block. We recently reported dialkyl-Al anion **1** without stabilization by heteroatoms and its high basicity and nucleophilicity (Scheme 1).²⁻³



In this study, we report two characteristic reactions of **2**. One is meta-selective C-H bond cleavage of toluene through a H-eliminating S_NAr reaction.⁴ The detailed reaction mechanism for the present S_NAr reaction toward toluene, which was investigated with kinetic-isotope-effect and DFT calculations, will be presented. The other one is synthesis of the first example of non-stabilized alumaborane **5** via nucleophilic alumination of fluoroborane and defluorination. The photophysical properties of **5** and its reactivity toward small molecules will be presented.



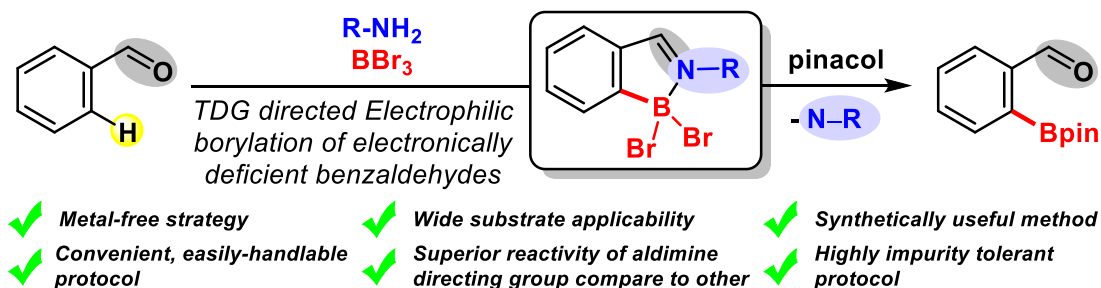
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- 3) Sugita, K.; Yamashita, M. *Chem. Eur. J.* **2020**, 26, 4520-4523.
- 4) Kurumada, S.; Sugita, K.; Nakano, R.; Yamashita, M. *Angew. Chem. Int. Ed.* **2020**, 59, 20381-20384.

Metal-free Transient Auxiliary Directed C-H Borylation of Benzaldehyde Derivatives

(Faculty of Engineering, Osaka University) ○Supriya Rej, Naoto Chatani

Keywords: Metal-free; Carbon-Hydrogen Bond Cleavage; Borylation; Transient Imine Directing Group; Benzaldehyde

Organoboron reagents are important synthetic intermediates and have wide applications in synthetic organic chemistry.¹ The selective C-H borylation strategies that are currently in use largely rely on the use of transition metal catalysts.² Although these transition metal-catalyzed directed-C-H borylation is reliable in terms of regioselectivity,³ the major concern involves the requirement of a precious metal and the production of metal-containing residues in the final product, which limit the application of this process in a large-scale organic synthesis. Hence, identifying much milder conditions for transition-metal-free borylation would be highly desirable.⁴ We herein present a unified strategy for the selective C-H borylation of electron-deficient benzaldehyde derivatives using a simple metal-free approach, utilizing an imine transient directing group. The strategy covers a wide spectrum of reactions and (i) even highly sterically hindered C-H bonds can be borylated smoothly, (ii) despite the presence of other potential directing groups, the reaction selectively occurs at the *ortho*-C-H bond of the benzaldehyde moiety, and (iii) natural products appended to benzaldehyde derivatives can also give the appropriate borylated products. Moreover, the efficacy of the protocol was confirmed by the fact that the reaction proceeds, even in the presence of a series of external impurities.



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Synthesis and Properties of Two Boron-containing Electron-deficient Heteroacenes

(¹Graduate School of Science, Nagoya University, ²Institute of Transformative Bio-Molecules, Nagoya University) ○Masato Ito,¹ Naoki Ando,¹ Shigehiro Yamaguchi^{1,2}

Keywords: Boron; π -conjugated skeleton; Near infrared absorption; Heteroacenes; Fluorescence

Xanthene is one of the most widely used π -conjugated scaffolds for organic dyes, as exemplified by fluorescein and rhodamine. To produce attractive π -electron materials using this scaffold, various chemical modifications have been conducted, such as the extension of the π -skeleton and the replacement of an oxygen atom at the 10-position with other main-group elements. Among them, the incorporation of boron atoms is effective to furnish significantly red-shifted absorption and emission through lowering the LUMO level due to the electron-accepting effect of the boron atom. As such example, we previously succeeded in the synthesis of borafluorescein,¹ which exhibited absorption and emission in the near-infrared (NIR) region.

Herein, we report the synthesis of diboron-containing heteroacene **1** in which two xanthene skeletons are fused. This molecule exhibited intense absorption and emission in the NIR region due to the electronic effects of the boron and oxygen atoms as well as the effective π -extension. Replacement of the central benzene ring with a thienothiophene scaffold in **2** resulted in further bathochromic shifts of the absorption bands. Furthermore, these molecules showed multi-step reversible redox processes. In this presentation, we will discuss about their synthesis, crystal structures, electronic properties, and photophysical properties.

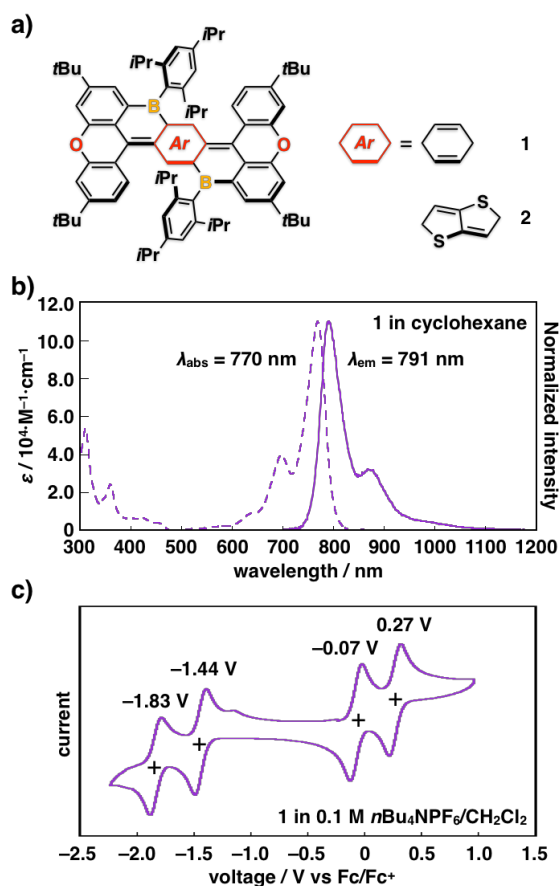


Figure 1. a) Molecular structures. b) Absorption and emission spectrum of compound **1** in cyclohexane. c) Cyclic voltammogram of compound **1** in CH_2Cl_2 ; scan rate: 0.05 V s^{-1} ; supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M); all potentials referenced vs. Fc/Fc^+ .

1) N. Ando, H. Soutome, S. Yamaguchi, *Chem. Sci.* **2019**, *10*, 7816.

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

[A20-1am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Ryo Yazaki, Tsuyoshi Mita, Hiroki Takezawa

Fri. Mar 19, 2021 9:00 AM - 11:20 AM Room 20 (Online Meeting)

[A20-1am-01] Oxidative Dearomatization of Arenols Using High-performance Hypohalite Catalysis

○Takehiro Kato¹, Muhammet Uyanik¹, Kazuaki Ishihara¹ (1. Nagoya university)

9:00 AM - 9:20 AM

[A20-1am-02] Chemoselective Cleavage of Si– C(sp³) Bonds in Unactivated Tetraalkylsilanes Using Iodine Tris(trifluoroacetate)

○Keitaro Matsuoka¹, Narumi Komami¹, Keito Watanabe¹, Masahiro Kojima¹, Tsuyoshi Mita^{2,3}, Kimichi Suzuki^{2,3,4}, Satoshi Maeda^{2,3,4}, Tatsuhiko Yoshino¹, Shigeki Matsunaga^{1,5} (1. Faculty of Pharmaceutical sciences, Hokkaido University, 2. WPI-ICReDD, 3. JST-ERATO, 4. Faculty of Science, Hokkaido University, 5. GI-CoRE)

9:20 AM - 9:40 AM

[A20-1am-03] Chemo-, Diastereo- and Enantioselective Catalytic Aldol Reaction of Carboxylic Acids by Boron and Silicon Hybrid Activation

○Taiki Fujita¹, Harunobu Mitsunuma¹, Motomu Kanai¹ (1. Grad. Sch. Pharm. Sciences, The Univ. of Tokyo)

9:40 AM - 10:00 AM

[A20-1am-04] Chemoselective Transesterification of Methyl (Meth)acrylates Catalyzed by Sodium(I) or Magnesium(II) Aryloxides

Jie Qi Ng¹, Hiro Arima¹, Takuya Mochizuki¹, Kohei Toh¹, Kai Matsui¹, Manussada Ratanasak², Junya Hasegawa², Manabu Hatano³, ○Kazuakai Ishihara¹ (1. Nagoya University, 2. Hokkaido University, 3. Kobe Pharmaceutical University)

10:00 AM - 10:20 AM

[A20-1am-05] Catalytic α – Oxidation of Carboxylic Acids via Radical Process

○Tsukushi Tanaka¹, Ryo Yazaki¹, Takashi Ohshima¹ (1. Kyushu Univ.)

10:20 AM - 10:40 AM

[A20-1am-06] Hydrogenation of Aromatic Compounds Catalyzed by Cooperative Systems of Heterogeneous Rh-Pt Nanoparticle catalysts and Lewis Acids

○Hiroyuki Miyamura¹, Shu Kobayashi¹ (1. The University of Tokyo)

10:40 AM - 11:00 AM

[A20-1am-07] Diastereoselective pericyclic cascades of linear terpenoids through conformational control in a bowl-shaped host

○Tomoya Kanda¹, Hiroki Takezawa¹, Makoto Fujita¹ (1. The University of Tokyo)

11:00 AM - 11:20 AM

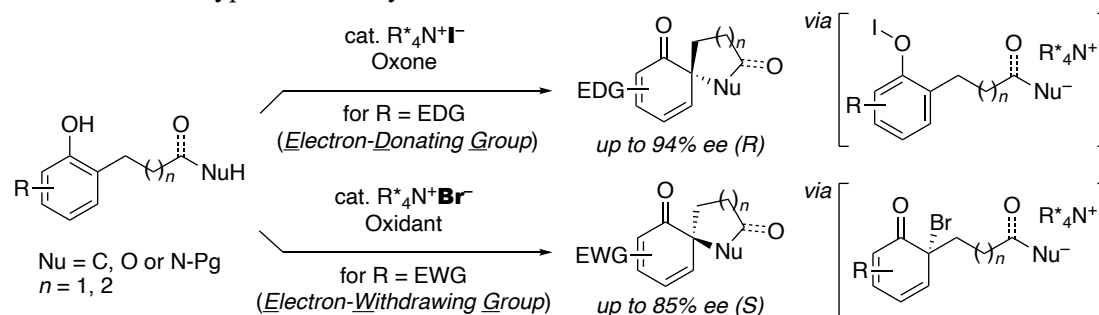
Oxidative Dearomatization of Arenols Using High-performance Hypohalite Catalysis

(Graduate School of Engineering, Nagoya University) ○Takehiro Kato, Muhammet Uyanik, Kazuaki Ishihara

Keywords: Chiral hypohalite catalysts; Oxidative dearomatization; Phenol; Enantioselective; Oxone

Enantioselective oxidative dearomatization of arenols is an important tool for the synthesis of several biologically important compounds. To date, many elegant strategies have been developed using transition metal or hypervalent iodine catalysts or reagents.¹ On the other hand, we have developed chiral quaternary ammonium hypoiodite-catalyzed enantioselective oxidative dearomatization of 1-naphthols.² In this catalytic system, hypoiodite active species were generated *in situ* from the corresponding quaternary ammonium iodides in the presence of hydrogen peroxide as an environmentally benign oxidant. However, the substrate scope was limited to 1-naphthols, and, in most cases, long times were required to complete the reactions even for these highly reactive substrates.

Here, we developed a high-performance ammonium hypohalite catalysis for the enantioselective oxidative dearomatization reactions. Hypohalite catalytic active species could be generated *in situ* from the corresponding chiral quaternary ammonium halides with oxone as an environmentally benign oxidant, and only inorganic wastes were generated from the oxidant used. By using hypoiodite catalysis, the oxidation of a wide range of naphthols and electron-rich phenols could proceed under mild conditions to afford the corresponding spirolactones with high enantioselectivity.^{3,4} On the other hand, by using hypobromite catalysis, oxidative dearomatization of electron-deficient phenols, which were hardly reactive using the hypoiodite catalysis, readily proceeded to give the corresponding adducts. Control experiments revealed that the reaction mechanism of hypobromite catalysis might be different from that of the hypoiodite catalysis.



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- (2) M. Uyanik, N. Sasakura, E. Kaneko, K. Otori, K. Ishihara, *Chem. Lett.* **2015**, 44, 179.
- (3) M. Uyanik, T. Kato, N. Sahara, O. Katade, K. Ishihara, *ACS Catal.* **2019**, 9, 11619.
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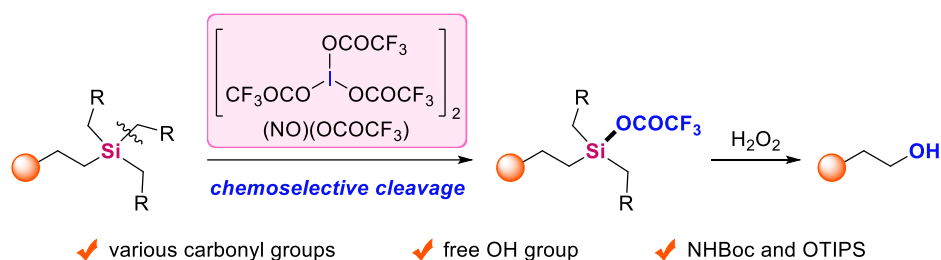
Chemoselective Cleavage of Si–C(sp³) Bonds in Unactivated Tetraalkylsilanes Using Iodine Tris(trifluoroacetate)

(¹Faculty of Pharmaceutical sciences, Hokkaido University, ²WPI-ICReDD, ³JST-ERATO, ⁴Faculty of Science, Hokkaido University, ⁵GI-CoRE) ○ Keitaro Matsuoka,¹ Narumi Komami,¹ Keito Watanabe,¹ Masahiro Kojima,¹ Tsuyoshi Mita,^{2,3} Kimichi Suzuki,^{2,3,4} Satoshi Maeda,^{2,3,4} Tatsuhiko Yoshino,¹ Shigeki Matsunaga^{1,5}

Keywords: Hypervalent iodine; Organosilane; Cleavage of unactivated bonds; Chemoselectivity; Tamao-Fleming oxidation

Tamao–Fleming oxidation, which converts alkylsilanes into the corresponding alcohols, is a powerful synthetic tool in organic chemistry. This protocol permits silyl groups that are substituted with heteroatomic functional groups or aryl/allyl groups to serve as a masked hydroxy group. However, unactivated tetraalkylsilanes are intact under Tamao–Fleming oxidation conditions. Excessive stability of simple Si–C(sp³) bonds impedes the application of trialkylsilyl groups as synthetic linchpins. Although some methods to convert a trimethylsilyl group into a hydroxy group have been reported, the scope of those methods are limited to non-functionalized substrates or a few oxygen-containing substrates,¹ and the functional group compatibility has not yet been investigated.

Herein we present the chemoselective cleavage of Si–C(sp³) bonds in unactivated tetraalkylsilanes using iodine tris(trifluoroacetate) (ITT). The reaction proceeds smoothly under mild conditions (–50 °C to room temperature), and the resulting intermediates can be converted into the corresponding alcohols via Tamao–Fleming oxidation. The reaction tolerates a broad range of carbonyl groups, an oxidizable free hydroxy group, acid-sensitive Boc and TIPS moieties, and others. In addition, we applied our protocol to the multistep synthesis of functionalized molecules, wherein trimethylsilyl groups served as highly stable masked hydroxy groups. Mechanistic studies on the cleavage of Si–C(sp³) bonds with ITT indicate that the reaction would afford an alkyl-λ³-iodane and silyl trifluoroacetate through a concerted exchange of the alkyl group and trifluoroacetate moiety between the Si and the I(III) center.²



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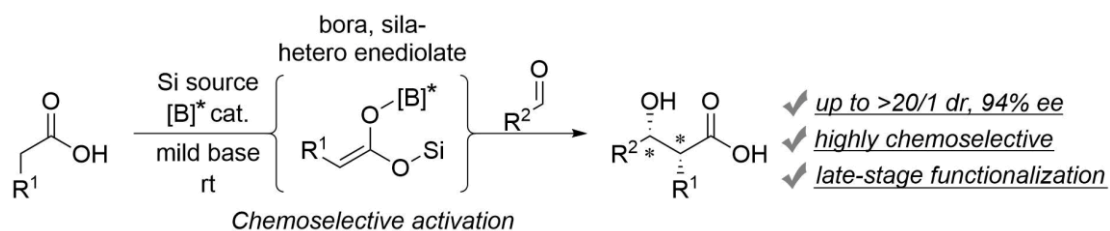
Chemo-, Diastereo-, and Enantioselective Catalytic Aldol Reaction of Carboxylic Acids by Boron and Silicon Hybrid Activation

(Graduate School of Pharmaceutical Sciences, The University of Tokyo,) ○ Taiki Fujita, Harunobu Mitsunuma, Motomu Kanai

Keywords: Boron Catalyst; Carboxylic Acids; Chemoselectivity; Asymmetric Aldol Reaction

Carboxylic acids are ubiquitous in biologically active natural products and pharmaceuticals. Chemoselective functionalization of carboxylic acid in the presence of other functional groups is useful for streamlining synthetic processes and late-stage functionalization of complex molecules. Our group developed a strategy of carboxylic acid-selective enolate formation by boron catalysis.¹ However, this method was not applicable to substrates bearing hydroxy groups that frequently appear in organic synthesis. This is because a boron catalyst is irreversibly bound to hydroxy groups and deactivated. In particular, application to a catalytic aldol reaction of carboxylic acid is difficult.² To overcome this problem, we started to develop chemoselective catalytic asymmetric aldol reaction of carboxylic acids with high functional group tolerance.

We considered that in-situ conversion of carboxylic acids to the corresponding silyl esters could realize chemoselective asymmetric aldol reaction with the boron catalyst. This method would realize a practical one-pot synthesis of carboxylic acid derivatives with a tolerance of a broad range of functional groups by traceless silicon protection. After screening reaction conditions, we found that the reaction proceeded with high diastereoselectivity only in the presence of a silicon source and the boron catalyst. Furthermore, introduction of a chiral amino acid ligand induced high enantioselectivity. The reaction proceeded in the presence of the inherently more reactive α -position of ketones and esters. In addition, easily enolizable aliphatic aldehydes can be used as electrophiles. Utilizing the high chemoselectivity and functional group tolerance of this method, we also succeeded in late-stage functionalization of highly functionalized pharmaceuticals.³



1) Morita, Y.; Yamamoto, T.; Nagai, H.; Shimizu, Y.; Kanai, M.; *J. Am. Chem. Soc.* **2015**, *137*, 7075.

2)(a) Nagai, H.; Morita, Y.; Shimizu, Y.; Kanai, M. *Org. Lett.* **2016**, *18*, 2276. (b) Ishizawa, K.; Nagai, H.; Shimizu, Y.; Kanai, M. *Chem. Pharm. Bull.* **2018**, *66*, 231. 3) Fujita, T.; Mitsunuma, H.; Kanai, M. *Manuscript in Preparation*.

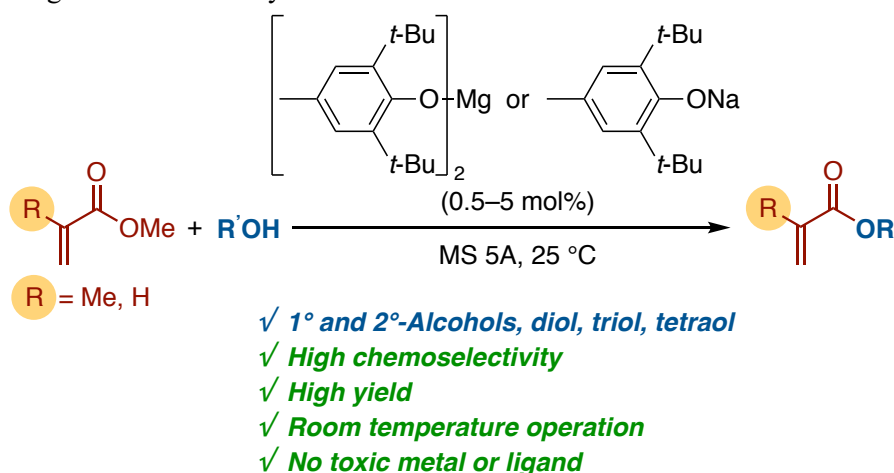
Chemoselective Transesterification of Methyl (Meth)acrylates Catalyzed by Sodium(I) or Magnesium(II) Aryloxides

(¹Graduate School of Engineering, Nagoya University, ²Institute for Catalysis, Hokkaido University, ³Graduate School of Pharmaceutical Sciences, Kobe Pharmaceutical University)
Jie Qi Ng,¹ Hiro Arima,¹ Takuya Mochizuki,¹ Kohei Toh,¹ Kai Matsui,¹ Manussada Ratanasak,² Jun-ya Hasegawa,² Manabu Hatano,³ ○Kazuaki Ishihara¹

Keywords: Transesterification; Sodium(I) Aryloxide; Magnesium(II) Aryloxide; Acrylate; Methacrylate

With industrial applications involving heat-resistant adhesives, varnishes, UV-coatings, photoresists, polymeric plastics, and so forth, (meth)acrylates are produced on a million-ton scale per year as some of the most important manufactured chemicals. The desirable physical properties of (meth)acrylate polymers, such as flexibility, transparency, and weatherability, can be controlled and fine-tuned by functionalization of the ester group. Therefore, the chemoselective synthesis of various (meth)acrylates is important in this field.

Here we developed a highly chemoselective transesterification of methyl (meth)acrylates catalyzed by sterically demanding 2,6-di-*tert*-butyl-4-methylphenol-derived NaOAr or Mg(OAr)₂.¹ The desired transesterification proceeded without the undesired Michael additions under mild reaction conditions at 25 °C, and various primary and secondary alcohols, diols, triol, and tetraol on a scale of up to 10 mmol could provide the corresponding functionalized acrylates in high yields. Transition states were proposed based on monomeric and dimeric active species, and computational density functional theory calculations strongly supported high chemoselectivity to minimize undesired Michael additions.



1) J. Q. Ng, H. Arima, T. Mochizuki, K. Toh, K. Matsui, M. Ratanasak, J. Hasegawa, M. Hatano, K. Ishihara, *ACS Catal.* **2021**, *11*, ASAP.

Catalytic α -Oxidation of Carboxylic Acids via Radical Process

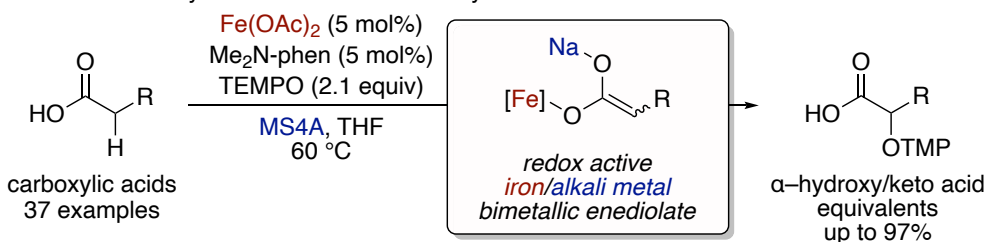
(Graduate School of Pharmaceutical Sciences, Kyushu University) ○Tsukushi Tanaka, Ryo Yazaki, Takashi Ohshima

Keywords: Carboxylic Acids; Iron; Sodium; Bimetallic Catalysis; Radical

Ubiquitous carboxylic acids are ideal carbonyl donors for the synthesis of functionalized carboxylic acid derivatives. Also, carboxylic acids get attention as a radical precursor in redox active catalysis recently. The innate Brønsted acidic carboxylic acid functionality disrupts the deprotonation of α -protons. Therefore, stoichiometric amount of base is required for conventional enolization methods.¹ Furthermore, recent enolization methods were only applied to redox neutral coupling using $2e^-$ electrophiles and catalytic α -functionalization of carboxylic acids through a $1e^-$ radical process, which could complement the chemoselectivity, and functional group tolerance restricted in the classical $2e^-$ ion reaction, has never been achieved.

Herein, we developed direct α -oxidation of carboxylic acids via radical process through redox active Lewis acid activation strategy (Scheme 1).² The present catalysis required no external Brønsted base and exhibited wide functional group tolerance. In this reaction, the addition of molecular sieves dramatically improved the product yield. Extensive mechanistic studies revealed that alkali metal in molecular sieves substantially increased the catalytic activity. It was clarified that this catalytic system is an iron and alkali metal bimetallic cooperative catalytic system in which the efficient enolization of carboxylic acids. This mechanism enables the chemoselective functionalization of carboxylic acids in the presence of carbonyl compounds such as ketones, esters, and amides.

Scheme 1. Catalytic α -Oxidation of Carboxylic Acids via Radical Process



- Direct α -Functionalization of Carboxylic Acids via Radical Process
- Enolization without Stoichiometric Brønsted Base Reagent
- Heterobimetallic Catalysis with Alkali Metal in Molecular Sieves

(1) (a) Hauser, C. R.; Chambers, W. J. *J. Am. Chem. Soc.* **1956**, 78, 4942. (b) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, 103, 3099. (c) Morita, Y.; Yamamoto, T.; Nagai, H.; Shimizu, Y.; Kanai, M. *J. Am. Chem. Soc.* **2015**, 137, 7075. (d) Kotani, S.; Yoshiwara, Y.; Ogasawara, M.; Sugiura, M.; Nakajima, M. *Angew. Chem. Int. Ed.* **2018**, 57, 15877.

(2) Tanaka, T.; Yazaki, R.; Ohshima, T. *J. Am. Chem. Soc.* **2020**, 142, 4517.

不均一系ロジウム-白金二元金属ナノ粒子と Lewis 酸の協調触媒系による芳香族化合物の水素化反応

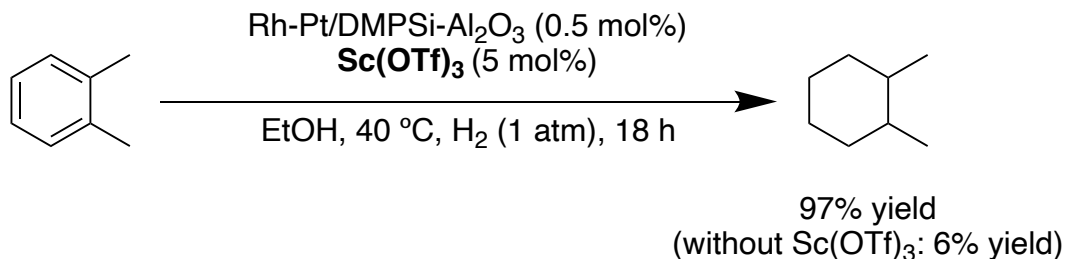
(東大院理) ○宮村浩之・小林 修

Hydrogenation of Aromatic Compounds Catalyzed by Cooperative Systems of Heterogeneous Rh-Pt Nanoparticle catalysts and Lewis Acids (School of Science, The Univ. of Tokyo) ○ Hiroyuki Miyamura, Shū KOBAYASHI,

We have developed Rh-Pt bimetallic nanoparticles immobilized on composite support of polydimethylsilane and alumina (Rh-Pt/DMPSi-Al₂O₃) as highly active catalysts for arene hydrogenation.¹⁾ However, hydrogenation of sterically hindered substrates like *o*-xylene required relatively harsh conditions; higher temperature and pressure. In this study, we found a significant rate acceleration of cooperative catalytic systems of Rh-Pt/DMPSi-Al₂O₃ and Lewis acids compared to the case without use of Lewis acids, and sterically hindered substrates could be hydrogenated under mild conditions. Mechanistic studies about the cooperative catalytic systems will be included in the presentation.

Keywords: Arene hydrogenation; Metal nanoparticle; Lewis acid; Cooperative catalysis; Heterogeneous catalyst

我々は、Rh-Pt 二元金属ナノ粒子をポリジメチルシランとアルミナの複合担体に固定化した触媒(Rh-Pt/DMPSi-Al₂O₃)を開発し、本触媒が芳香環の水素化反応において高い活性を示すことを見出した¹⁾。しかしながら、*o*-xylene のような立体的に混んだ基質の場合においては、高温、高圧といった比較的過酷な反応条件を必要としていた。今回、我々は、Lewis 酸と Rh-Pt/DMPSi-Al₂O₃ の協調触媒系において、Lewis 酸を用いない場合と比較して、反応が大幅に加速され、立体的に混んだ基質においても、温和な条件下、円滑に反応が進行することを見出した。本講演では、本協調触媒系についての反応機構研究の結果についても報告予定である。



1) Miyamura, H. Kobayashi, S. *et al. J. Am. Chem. Soc.* **2018**, *140*, 11325.

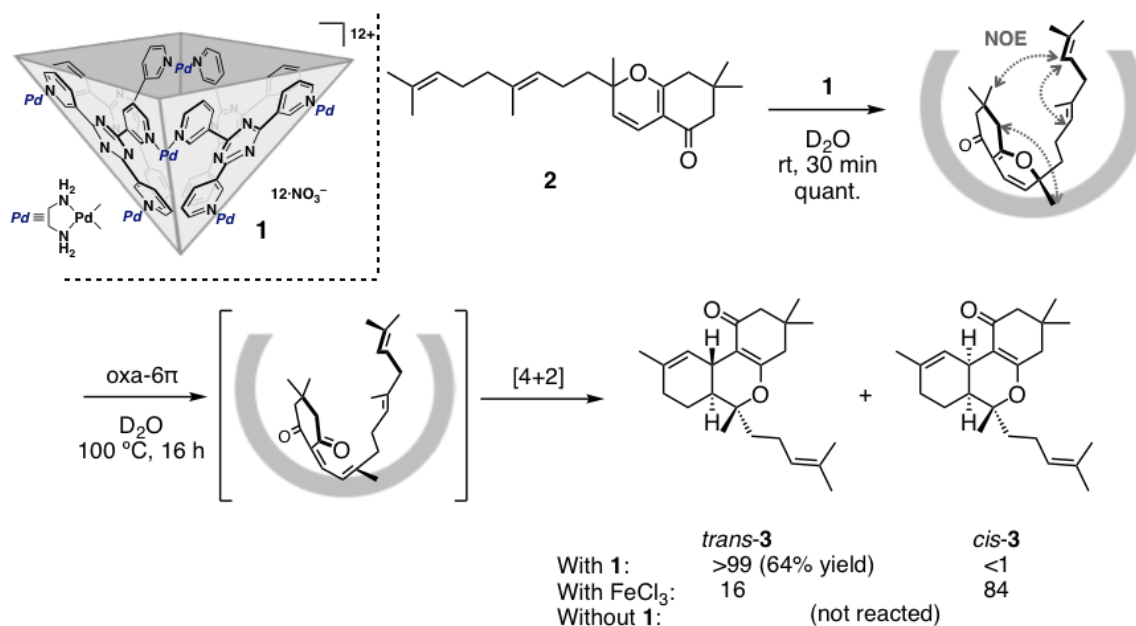
Diastereoselective pericyclic cascades of linear terpenoids through conformational control in a bowl-shaped host

(Graduate School of Engineering, The University of Tokyo) ○ Tomoya Kanda, Hiroki Takezawa, Makoto Fujita.

Keywords: Coordination cage; Terpenoid; Cascade reaction; Conformational control; Polycyclic scaffold

Enzymes construct a wide variety of polycyclic structures from flexible linear precursors via conformational control in a hydrophobic cavity. Here, we succeeded in the stereoselective construction of polycyclic isochromene scaffold through conformational control of linear terpenoid in bowl-shaped host **1**.

Terpenoid **2** was suspended in an aqueous solution of the bowl **1** at room temperature for 30 min to afford inclusion complex **1•2** quantitatively. The conformation of the included guest was analyzed by ^1H - ^1H NOESY measurement. NOESY analysis of inclusion complex showed NOE correlations indicating U-shaped conformation inside the cavity. When the aqueous solution of **1•2** was heated at 100 °C, *trans*-**3** was selectively obtained in 64% yield. The reaction involves oxa-6 π electrocyclicization and hetero-Diels-Alder reactions. The hetero-Diels-Alder reaction proceeds through *exo* transition state which gives *trans* diastereomer. The control experiments in the absence of the bowl-shaped complex did not produce **3**. Furthermore, when iron(III) chloride was used, *cis*-**3** was selectively obtained. These results indicate that the confinement in the bowl-shaped complex is essential for not only acceleration of the reaction but also the stereoselectivity switching.



Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B**[A21-1am] 16. Natural Products Chemistry, Chemical Biology**

Chair: Yoshio Ando, Keisuke Nishikawa

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 21 (Online Meeting)

[A21-1am-01] Total Synthesis of Antitumor Antibiotic Saptomycin H○Jun Shimura¹, Yoshio Ando¹, Ken Ohmori¹, Keisuke Suzuki¹ (1. Tokyo Institute of Technology)

9:00 AM - 9:20 AM

[A21-1am-02] Total Synthesis of Tetrameric Epicatchin Parameritannin A2 via Cascade Pummerer-type Reaction.○Vipul Vithal Betkekar¹, Keisuke Suzuki¹, Ken Ohmori¹ (1. Tokyo Institute of Technology)

9:20 AM - 9:40 AM

[A21-1am-03] Synthetic Study of a Polyol Unit of Amphotericin B Using Organocatalysts○Genki Kawauchi¹, Yujiro Hayashi¹ (1. Univ. of Tohoku)

9:40 AM - 10:00 AM

[A21-1am-04] Intramolecular Oxidative Nucleophilic Aromatic Substitution Reaction between Phenols and Alkenes○Hiroki Deguchi¹, Hanaya Kengo¹, Sugai Takeshi¹, Higashibayashi Shuhei¹ (1. Faculty of Pharmacy, Keio Univ.)

10:00 AM - 10:20 AM

[A21-1am-05] Unified Total Synthesis of Pentacyclic Stemoamide-type Alkaloids○Yasuki Soda¹, Yasukazu Sugiyama¹, Makoto Yoritake¹, Hayato Tajima¹, Kana Shibuya¹, Yoshito Takahashi¹, Chisato Ogihara¹, Takeshi Oishi¹, Takaaki Sato¹, Noritaka Chida¹ (1. Keio University)

10:20 AM - 10:40 AM

[A21-1am-06] Total Synthesis and Structural Determination of a Marine Natural Product Callicladol with Potent Antitumor Activity against Mouse Leukemia Cells○Kento Nishikibe¹, Keisuke Nishikawa¹, Yoshiki Morimoto¹ (1. Osaka City University)

10:40 AM - 11:00 AM

[A21-1am-07] Development of New Synthetic Method of the DFGH-ring of Physalin-Type Natural Products and SAR Study of the Pseudo-Natural Products○Makoto Yoritake¹, Yuki Morita¹, Masaki Morita^{1,2}, Tomohiro Yamashita¹, Mikiko Sodeoka², Go Hirai^{1,2} (1. Kyushu University Graduate School of Pharmaceutical Science, 2. RIKEN)

11:00 AM - 11:20 AM

[A21-1am-08] Unusual Skeletal Rearrangement Reaction in Brasilane-Type Structure Biosynthesis○Hajime Sato^{1,2,3}, Masanobu Uchiyama^{2,3,4} (1. Grad. Sch. Pharm. Chiba Univ., 2. Grad. Sch. Pharm. Univ. Tokyo, 3. RIKEN, 4. Shinshu Univ. RISM)

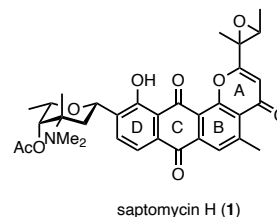
11:20 AM - 11:40 AM

Total Synthesis of Antibiotic Saptomycin H

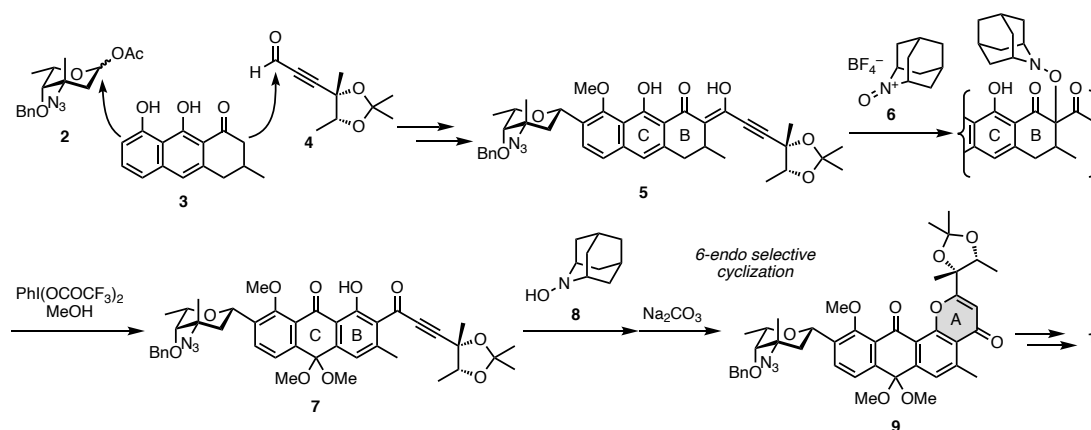
(Department of Chemistry, Tokyo Institute of Technology) ○Jun Shimura, Yoshio Ando, Ken Ohmori, Keisuke Suzuki

Keywords: saptomycin H; pluramycins; hydroxylamine; natural product synthesis

Saptomycin H (**1**) is a member of the pluramycin-class antitumor antibiotics,¹ featuring the anthrapyranone skeleton with one C-glycoside and the oxirane ring at the side chain. Although the oxirane is important for the bioactivity, total synthesis of the pluramycins bearing the oxirane ring has not been achieved.



Herein, we will disclose a successful synthetic route to **1** by exploiting efficient assembly of three building blocks, vancosamine **2**, anthrone **3**, and aldehyde **4**, which enables an access to diketone **5** with the full carbon skeleton. After the stepwise oxidation of the B and C rings by using oxoammonium salt **6** and $\text{PhI}(\text{OCOCF}_3)_2$, the A-ring formation from anthraquinone acetal **7** was carried out by the 6-*endo* selective cyclization exploiting a peculiar reactivity of hydroxylamine **8** to give anthrapyranone **9**.² Further transformations including deprotection on the sugar moiety and construction of the oxirane ring allowed the first total synthesis of saptomycin H (**1**).



1) N. Abe, N. Enoki, Y. Nakakita, H. Uchida, T. Nakamura, M. Munekata, *J. Antibiot.* **1993**, 46, 1530.

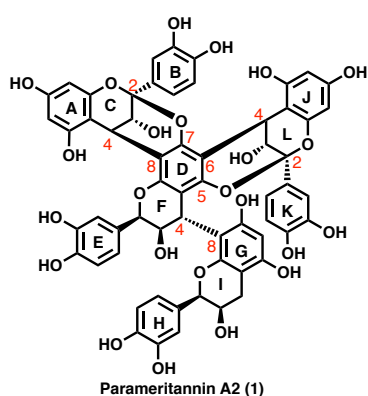
2) J. Shimura, Y. Ando, K. Suzuki, *Org. Lett.* **2020**, 22, 175.

Total Synthesis of Tetrameric Epicatechin Parameritannin A2 via Cascade Pummerer-type Reaction.

(Department of Chemistry, Tokyo Institute of Technology)

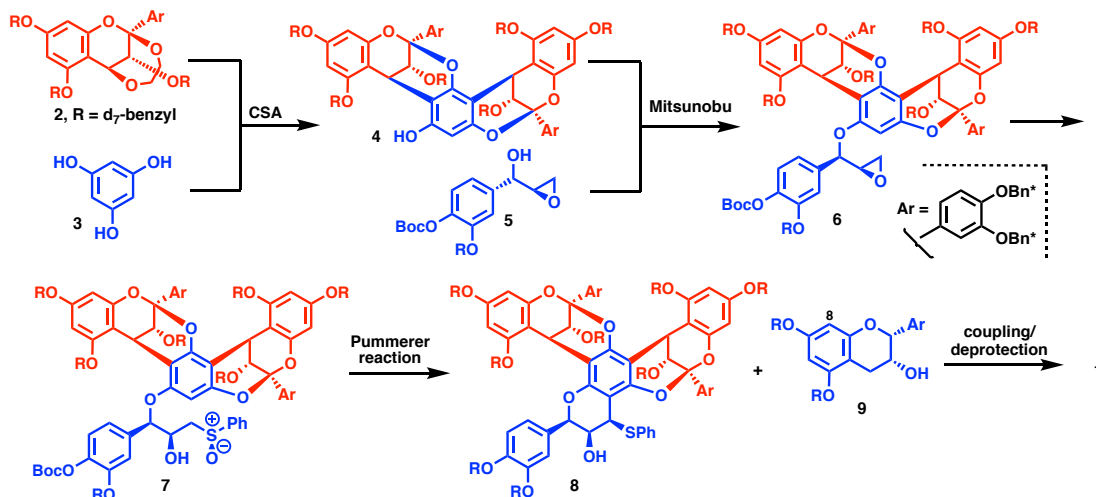
○Betkekar Vipul, Ohmori Ken, Suzuki Keisuke

Keywords: Total synthesis; Pummerer; Cascade reactions; Regioselective reactions



Parameritannin A2 (**1**), isolated from Indonesian folk medicinal plant *Parameria laevigata*,¹ is a tetrameric epicatechin derivative possessing two-fold double connection in the middle epicatechin unit, which is additionally connected to bottom epicatechin unit through single linkage. Biological study of **1** has been restricted by the scarcity, thus calling for the availability by organic synthesis.

Two molecules of dioxy compound **2** upon annulation with phloroglucinol **3** gave dioxabicyclo compound **4** as the sole product. Alcohol **5**, derived from (*S*)-glycidol, was then reacted with phenol **4** under the modified Mitsunobu conditions, and the resultant coupled product **6** was transformed to sulfoxide **7**.



The key pyran-ring cyclisation of sulfoxide **7** involving Pummerer reaction and intramolecular Friedel-Crafts reaction promoted by TMSOTf successfully delivered cyclized product **8**. Activation of sulfide **8** under soft Lewis acidic conditions followed by union with the flavan **9** attached the bottom epicatechin unit. Finally, removal of all protecting groups gave **1**.

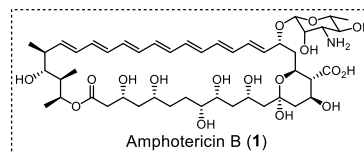
1) Kamiya, K.; Watanabe, C.; Endang, H.; Umar, M.; Satake, T. *Chem. Pharm. Bull.* **2001**, *49*, 551-557.

Synthetic Study of a Polyol Unit of Amphotericin B Using Organocatalysts

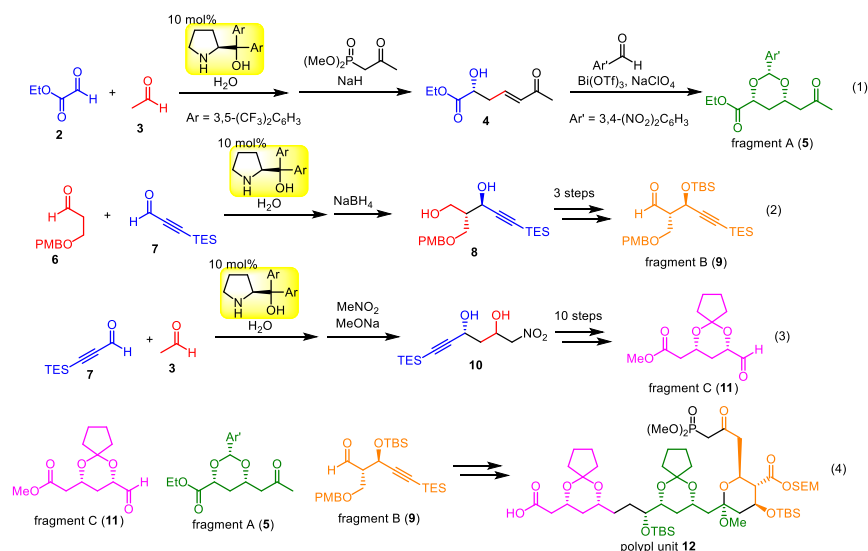
(Graduate School of Science, Tohoku University) ○Genki Kawauchi, Yujiro Hayashi

Keywords: Total Synthesis; Organocatalyst; Asymmetric Aldol Reaction; 1,3-Asymmetric Induction; Polyol Compound

Amphotericin B (**1**) is a natural product isolated from *Streptomyces nodosus* and containing polyene and polyol units in 38-membered macrolide. In this presentation, authors established the method for the synthesis of polyol unit of Amphotericin B through the synthesis of three fragments using organocatalyst-mediated asymmetric aldol reaction and 1,3-asymmetric induction developed by our group as key steps.



Asymmetric aldol reaction of ethyl glyoxylate (**2**) and acetaldehyde (**3**) catalyzed by diarylprolinol^{1a} followed by Horner-Wadsworth-Emmons reaction afforded compound **4**. Bi(OTf)₃ and NaClO₄ mediated 1,3-asymmetric induction with 3,4-dinitrobenzaldehyde² gave 1,3-*syn*-diol fragment A (**5**) (eq. 1). Diarylprolinol mediated asymmetric aldol reaction of alkoxyaldehyde **6** and alkynylaldehyde **7**^{1b} followed by reduction gave diol **8**. After 3 steps transformations, fragment B (**9**) was obtained (eq. 2). Asymmetric aldol reaction of alkynylaldehyde **7** and acetaldehyde **3**^{1b} followed by Henry reaction afforded nitrodiol **10**. After several transformations, 1,3-*syn*-diol fragment C (**11**) was synthesized³ (eq. 3). After coupling reactions of these three fragments and several transformations, we synthesized polyol unit of Amphotericin B **12** (eq. 4).



- 1) a) T. Urushima, Y. Yasui, H. Ishikawa, Y. Hayashi, *Org. Lett.* **2010**, *12*, 2966. b) Y. Hayashi, M. Kojima, Y. Yasui, Y. Kanda, T. Mukaiyama, H. Shomura, D. Nakamura, L. Ritmaleni, I. Sato, *ChemCatChem* **2013**, *5*, 2887.
- 2) Y. Hayashi, T. Saito, H. Arase, G. Kawauchi, N. Takeda, Y. Shimasaki, I. Sato, *Chem. Eur. J.* **2018**, *24*, 8409.
- 3) Y. Hayashi, X. Wang, G. Kawauchi, *Chem. Lett.* **2020**, *49*, 940.

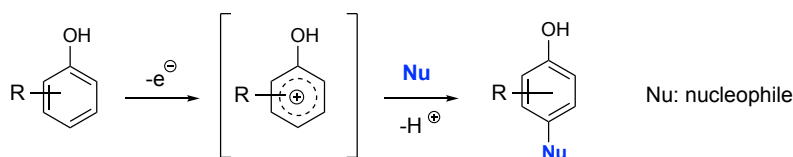
Intramolecular Oxidative Nucleophilic Aromatic Substitution Reaction between Phenols and Alkenes

(¹Faculty of Pharmacy, Keio University)

○Hiroki Deguchi,¹ Kengo Hanaya,¹ Takeshi Sugai,¹ Shuhei Higashibayashi¹

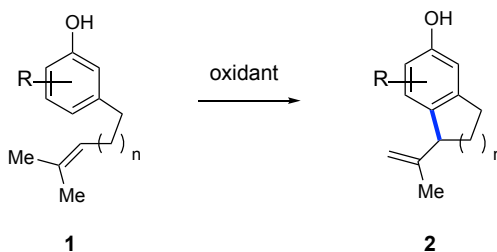
Keywords: Phenol; Alkene; Oxidative Nucleophilic Aromatic Substitution; Intramolecular cyclization

Oxidative phenol coupling reaction is a versatile transformation for the syntheses of various bioactive substances, pharmaceuticals, and functional molecules. Electron-rich phenols express nucleophilic reactivity. However, oxidative activation can convert these phenols into cations or electron-deficient species, which would react with appropriate nucleophiles to perform nucleophilic aromatic substitution (Scheme 1). Under this concept, various oxygen or nitrogen nucleophiles have been reported for the formation of C-O or C-N bond. However, reported carbon nucleophiles were limited in such as aromatics or 1,3-dicarbonyl compounds. Exploration of new carbon nucleophiles along this methodology would allow us to synthesize a more variety of molecular skeletons of useful compounds. Herein, we succeeded to develop novel intramolecular oxidative nucleophilic aromatic substitution of phenol derivatives with alkenes as carbon nucleophiles.



Scheme 1

Cyclization of phenol derivatives **1** bearing alkenyl side chains through intramolecular oxidative nucleophilic aromatic substitution was investigated (Scheme 2). By applying organic oxidants, the phenol substrates **1** underwent the desired cyclization, giving expected bicycles **2**. In this presentation, we report the elaboration of the reaction conditions and the scope of the aromatic rings and alkenyl side chains.



Scheme 2

Unified Total Synthesis of Pentacyclic Stemoamide-type Alkaloids

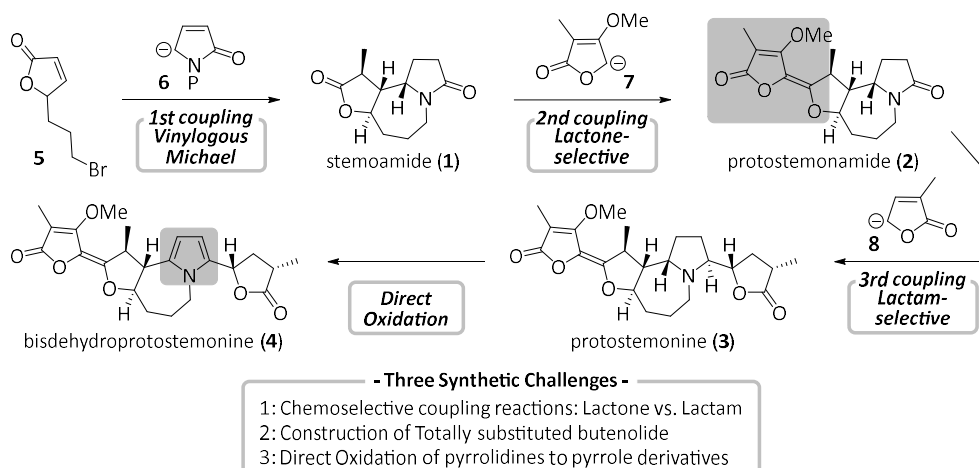
(Faculty of Science and Technology, Keio University)

○Yasuki Soda, Yasukazu Sugiyama, Makoto Yoritake, Hayato Tajima, Kana Shibuya, Yoshito Takahashi, Chisato Ogihara, Takeshi Oishi, Takaaki Sato, Noritaka Chida

Keywords : amide; alkaloids; nucleophilic addition; stemoamide; total synthesis

Stemoamide-type alkaloids comprise one of the largest groups in *stemon* family. While tricyclic stemoamide (**1**) does not exhibit any pivotal biological activity, protostemonine (**3**) is known to show diverse biological activities such as anti-inflammatory effect. These facts suggest that complex pentacyclic derivatives might possess better biological profiles than tricyclic and tetracyclic stemoamide-type alkaloids. However, comprehensive biological studies have been prohibited owing to the structural complexity of pentacyclic alkaloids. Here, we disclose a unified total synthesis of pentacyclic stemoamide-type alkaloids.

The unified total synthesis must overcome three synthetic challenges. The first challenge was development of three chemoselective coupling reactions using five-membered heterocyclic rings (**5**→**1**, **1**→**2**, **2**→**3**). The lactam-selective coupling was challenging because a lactone is more electrophilic than a lactam (**2**→**3**). We solved this issue by an iridium-catalyzed reductive nucleophilic addition.¹ The second challenge was construction of a totally substituted butenolide embedded in **2**, **3** and **4**. This structure is highly oxygenated and contains two tetrasubstituted olefins, one of which requires stereocontrol. The third challenge was direct oxidation of pyrrolidines to pyrroles (**3**→**4**). Establishment of mild oxidation was required without affecting tertiary amine and the ene-diol structure. The developed strategy was highly effective, resulting in the total syntheses of eight pentacyclic alkaloids within 13 steps.^{2,3}



1) T. Sato, N. Chida, *Chem. Lett.* **2019**, 48, 1138. 2) T. Sato, N. Chida, *J. Am. Chem. Soc.* **2017**, 139, 18386. 3) T. Sato, N. Chida, *Org. Lett.* **2020**, 22, 7502. *Current position of Makoto Yoritake: Graduate School of Pharmaceutical Sciences, Kyushu University

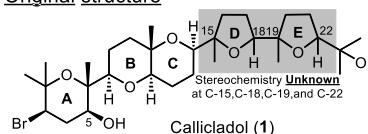
Total Synthesis and Structural Determination of a Marine Natural Product Callicladol with Potent Antitumor Activity against Mouse Leukemia Cells

(Graduate School of Science, Osaka City University) ○ Kento Nishikibe, Keisuke Nishikawa, and Yoshiki Morimoto

Keywords: Total Synthesis; Marine Natural Products; Cyclic Polyether; Red Algae; Cytotoxicity

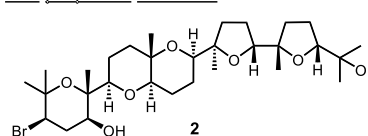
Callicladol (**1**), a marine triterpene polyether isolated from the red alga *Laurencia calliclada* by Suzuki *et al.* in 1993, exhibits potent cytotoxicity against P388 murine leukemia cell.¹⁾ The structural features of **1** are a bromine-containing THP ring (A ring), a dioxabicyclo[4.4.0]decane ring (BC rings), and two THF rings (DE rings). It is also rare for **1** to possess a hydroxy group at the C5 position in A ring, which is unprecedented in other thysiferol congeners. However, due to limitations of analytical techniques, the relative configuration around DE rings in **1** remains undetermined.

Original structure

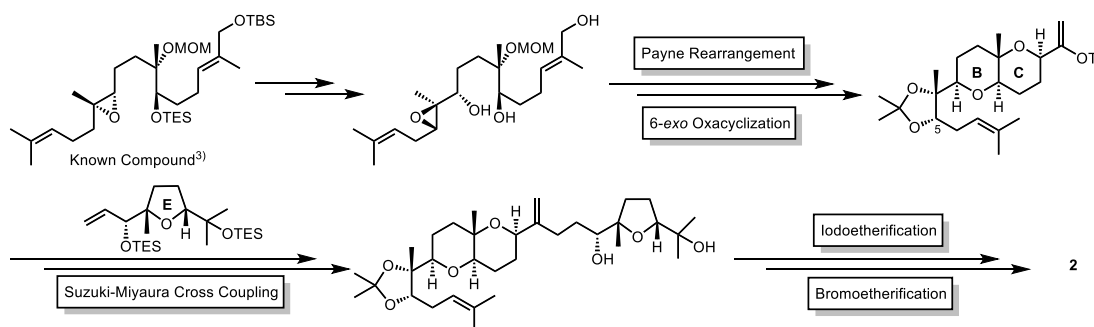


Suggestion based on the Model Synthesis

Our proposed structure



Previously, we suggested the relative configuration of callicladol as shown in **2** based on the model synthesis.²⁾ In this work, we succeeded in the efficient construction of B ring with introduction of the C5-hydroxy group utilizing a tandem reaction *via* a Payne rearrangement followed by a 6-*exo* oxacyclization as a key step. As a result, we have achieved the first total synthesis and structural determination of callicladol.



1) M. Suzuki *et al.* *Chem. Lett.* **1995**, 24, 1045.

2) The 100th CSJ Annual Meeting, Noda City, Chiba, Japan, Mar. **2020**.

3) K. Nishikibe, K. Nishikawa and Y. Morimoto *et al.* *Angew. Chem., Int. Ed.* **2017**, 56, 3064.

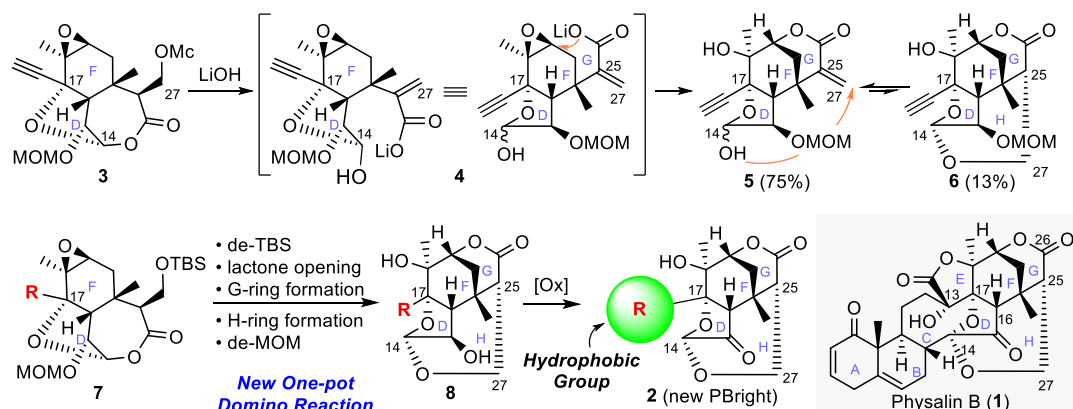
Development of New Synthetic Method of the DFGH-ring of Physalin-Type Natural Products and SAR Study of the Pseudo-Natural Products

(¹Graduate School of Pharmaceutical Science, Kyushu University, ²RIKEN) ○ Makoto Yoritate,¹ Yuki Morita,¹ Manuel Gemander,² Masaki Morita,^{1,2} Tomohiro Yamashita,¹ Mikiko Sodeoka,² and Go Hirai^{1,2}

Keywords: Physalin; Steroid; Domino Reaction; Cascade Reaction; Structure-Activity Relationship

Physalins are steroidal constituents of *Physalis* plants and contain a complex, highly oxygenated fused-ring system. More than 30 physalin-type natural products have been isolated so far, and most of them possesses a highly fused and oxygenated DEFGH-ring structure like that of physalin B (**1**). The significance of the left-side (AB-ring) structure of **1** for biological activity is well established, but the importance of the right-side (D(E)FGH-ring) structure has long been unclear. Based on our previous study,¹⁾ we designed the simplified DFGH-ring structure **2** with the hydrophobic substituent (**R**) at C17, which may exhibit high inhibitory activity of NF-κB activation.

Since the right-side structure of physalin B (PBright) possesses a highly functionalized and fused ring structure, we required a robust synthetic route to **5** involving mild reaction conditions. In particular, the key GH-ring construction previously achieved via the base-mediated domino ring-opening/closure sequence (**3**→**4**→**5**→**6**)²⁾, was problematic due to a bias of the equilibrium towards the more stable **5** rather than the desired **6**. During the synthetic study, we found an alternative synthetic route toward **2** via newly found domino sequence of **7** to directly give DFGH-ring compound **8**. Here we present the synthesis and SAR study of **2**.³⁾



1) Ozawa, M.; Morita, M.; Hirai, G.; Tamura, S.; Kawai, M.; Tsuchiya, A.; Oonuma, K.; Maruoka, K.; Sodeoka, M., *ACS Med. Chem. Lett.* **2013**, 4, 730–735. 2) Ohkubo, M.; Hirai, G.; Sodeoka, M., *Angew. Chem. Int. Ed.* **2009**, 48, 3862–3866. 3) Yoritate, M.; Morita, Y.; Gemander, M.; Morita, M.; Yamashita, T.; Sodeoka, M.; Hirai, G., *Org. Lett.* **2020**, 22, 8877–8881.

ブラシラン型骨格生合成反応機構の理論解析

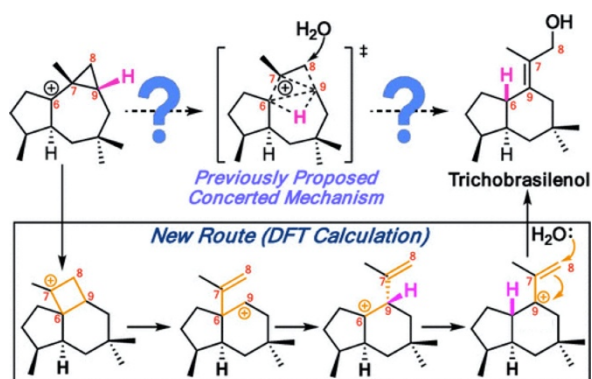
(¹千葉院薬,²東大院薬,³理研,⁴信州大) 佐藤 玄^{1,2,3}、内山 真伸^{2,3,4}

Unusual Skeletal Rearrangement Reaction in Brasilane-Type Structure Biosynthesis
(¹Graduate School of Pharmaceutical Sciences, Chiba University, ²Graduate School of Pharmaceutical Sciences, University of Tokyo, ³RIKEN, ⁴RISM, Shinshu University)
○Hajime Sato,^{1,2,3} Masanobu Uchiyama^{2,3,4}

Brasilane-type sesquiterpenes have been known for a long time, but their biosynthetic pathways and mechanisms remain elusive. Recently, Kuzuyama et al. performed labeling experiment and proposed a biosynthetic pathway of trichobrasilenol. In this study, we intended to reveal the biosynthetic mechanism using both experimental and computational approaches. On the basis of DFT calculations, we propose a new pathway for brasilane-type structure biosynthesis, involving a multistep carbocation cascade in which cyclopropylcarbinyl cations in equilibrium with homoallyl cations play a pivotal role. The details of mechanistic investigation including the other related terpene biosynthetic pathways will be discussed herein.
Keywords : terpene; DFT calculation; Brasilane Type; rearrangement; carbocation

ブラシラン型骨格は、bicyclo[4.3.0]nonane 骨格、ジメチル基、イソプロピル基を特徴とし、セスキテルペノイドに広く見られる構造であるが、その生合成メカニズムは長い間謎とされてきた。最近、葛山らにより trichobrasilenol 生合成の標識実験が行われ、反応機構が提唱された¹。本研究では、実験化学と計算化学の両面からブラシラン型骨格の生合成メカニズムの全容解明を目的とした。

DFT 計算の結果、ブラシラン型骨格形成には、予想されていた協奏的な反応機構とは異なり、4員環形成、C-C 結合開裂によるホモアリルカチオンの生成、イソプロペニル基の 1,2-転位、アリルカチオンへの水和反応を経て trichobrasilenol が生成することが明らかとなった。この大胆な骨格転位には、安定な 3° カチオンやアリルカチオンに加えて、シクロプロピルカルビニルカチオンとの平衡にあるホモアリルカチオンが重要であることも明らかとなった。本発表では、これまで我々が明らかにしてきたカルボカチオンを駆動力とする種々のテルペン環化反応についても議論する。



- 1) Murai, K.; Lauterbach, L.; Teramoto, K.; Quan, Z.; Barra, L.; Yamamoto, T.; Nonaka, K.; Shiomi, K.; Nishiyama, M.; Kuzuyama, T.; Dickschat, J. S. An Unusual Skeletal Rearrangement in the Biosynthesis of the Sesquiterpene Trichobrasilenol from Trichoderma. *Angew. Chem., Int. Ed.* **2019**, 58, 15046–15050.
- 2) Sato, H.;* Hashishin, T.; Kanazawa, J.; Miyamoto, K.; Uchiyama M.* *J. Am. Chem. Soc.*, **2020**, 142, 19830-19834.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[A26-1am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Shinya Hanashima, Kazuhito Tanabe

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 26 (Online Meeting)

[A26-1am-01] Effects of Isovaleraldehyde on Biomimetic MembranesYudai Yamada¹, Yukiyasu Chounan¹, [○]Tsuyoshi Yoda² (1. Department of Natural Science, Faculty of Education, Hirosaki University, 2. Aomori Prefectural Industrial Technology Research Center, Hirosaki Industrial Research Institute)

9:00 AM - 9:20 AM

[A26-1am-02] Thioacid-based strategy for the semi-synthesis of glycoproteins[○]Kota Nomura¹, Yuta Maki¹, Ryo Okamoto¹, Yasuhiro Kajihara¹ (1. Grad. Sch. Sci., Osaka Univ.)

9:20 AM - 9:40 AM

[A26-1am-03] Development of calreticulin inhibitor based on hybrid binding concept[○]Taiki Kuribara¹, Taiga Kojima¹, Keita Shibayama¹, Yoichi Takeda², Kiichiro Totani¹ (1. Seikei University, 2. Ritsumeikan University)

9:40 AM - 10:00 AM

[A26-1am-04] Development of Bioluminescent Probes for Visualizing and Quantifying of Endogenous RNAs in Real Time[○]Masatoshi Eguchi¹, Hideaki Yoshimura¹, Takeaki Ozawa¹ (1. The Univ. of Tokyo)

10:00 AM - 10:20 AM

[A26-1am-05] Development of DNA complex for efficient recognition of target cancer cells[○]Tatsuya Nishihara¹, Yuto Motohashi¹, Shuhei Moritani¹, Ryota Hidaka¹, Yuka Matsumura¹, Risa Yamada¹, Kazuhito Tanabe¹ (1. Aoyama Gakuin University)

10:20 AM - 10:40 AM

[A26-1am-06] Development of waterproof bioelectrode using polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) nanosheets and electrocardiogram measurements during bathing.[○]Sho Mihara¹, Hui-Lin Lee², Shinji Takeoka¹ (1. Waseda university, 2. Singapore Polytechnic)

10:40 AM - 11:00 AM

[A26-1am-07] Structural analysis of the lipid packing structures inside a single membrane domain by low-flux scanning electron diffraction[○]Masanao Kinoshita¹, Shimpei Yamaguchi¹, Nobuaki Matusmori¹ (1. Kyushu University)

11:00 AM - 11:20 AM

[A26-1am-08] Membrane lipids affect the interplay between the transmembrane domain of the EGF receptor and ganglioside GM3 – thermodynamic quantification of the lateral interaction using FRET[○]Mikito Nakano¹, Shinya Hanashima¹, Toshiaki Hara¹, Kazuya Kabayama¹, Naoko Komura², Hiromune Ando², Thomas K.M. Nyholm³, Peter J Slotte³, Michio Murata¹ (1. Graduate School of Science, Osaka University, 2. Center for Highly Advanced Integration of Nano and Life Sciences (G-CHAIN), 3. Department of Biosciences, Åbo Akademi University)

11:20 AM - 11:40 AM

イソバレルアルデヒドの生体模倣膜小胞への影響

(弘前大教育¹・青森産技弘工研²) 山田 祐大¹・長南 幸安¹・○依田 毅²

Influence of Isovaleraldehyde on Biomimetic Membranes (¹*Department of Natural Science, Faculty of Education, Hirosaki University,* ²*Aomori Prefectural Industrial Technology Research Center, Hirosaki Industrial Research Institute*) Yudai Yamada,¹ Yukiyasu Chounan¹ ○Tsuyoshi Yoda²

Flavor is important and some flavors are found several foods. The flavors have been studied with interaction between cell wall. Recently our group has reported that flavor compounds such as Ethyl caproate and its precursor caproic acid should influence yeast cell membranes.^{1,2)} One of an important flavor, isovalaldehyde (IVA) is known as cocoa flavors and used to improve the foods quality though the function is not researched enough in especial against membranes and its dynamics.

Then we prepared lipid vesicles containing IVA and observed. It was found that IVA-containing lipid vesicles were large and the size of lipid vesicles correspond the concentration of IVA. To be clear the mechanism, we investigated the membrane dynamics of lipid vesicles containing IVA on temperature increasing. This present study will be useful to understand not only cell organization such as signal transduction but also physical subjects in especial soft matter physics.

Keywords : *Isovalaldehyde; Lipid vesicles; biomimetic membranes; Temperature increasing*

【背景・方法】

飲料の香りは商品価値の重要な構成要素である。とくに清酒の香りは、品質評価をする上で重要な評価基準である。我々は、これまで代表的な吟醸香の影響を調べるために、不飽和リン脂質からなる細胞サイズの生体模倣膜小胞を用いた研究を行ってきた^{1,2)}。本研究では清酒の特徴的な香り成分であるイソバレルアルデヒド(IVA)を含む細胞サイズの生体模倣膜小胞を作製して観察した。

【結果・考察】

我々は、IVA 含有脂質小胞は含まないものよりも大きく、IVA 濃度に依存してサイズが大きくなることを発見した。

さらに膜に対する IVA の影響を明らかにするために、温度上昇時の IVA を含む生体模倣膜小胞の膜ダイナミクスを調べた。結果、含まないものと比べ温度に対する揺動する生体模倣膜小胞の割合の増加のプロファイルが異なることが分かった。

本研究は、香り成分がもたらす機能を推測するだけでなく、膜脂質と香り成分の分子間相互作用の理解へ役立つ。

1) Influence of Ethyl Caproate on the Size of Lipid Vesicles and Yeast Cells, T. Yoda, A. Ogura and T. Saito, *Biomimetics*, **2020**, 5, 16

2) Size of Cells and Physicochemical Properties of Membranes are Related to Flavor Production during Sake Brewing in the Yeast *Saccharomyces cerevisiae* T. Yoda and T. Saito, *Membranes*, **2020**, 10, 440

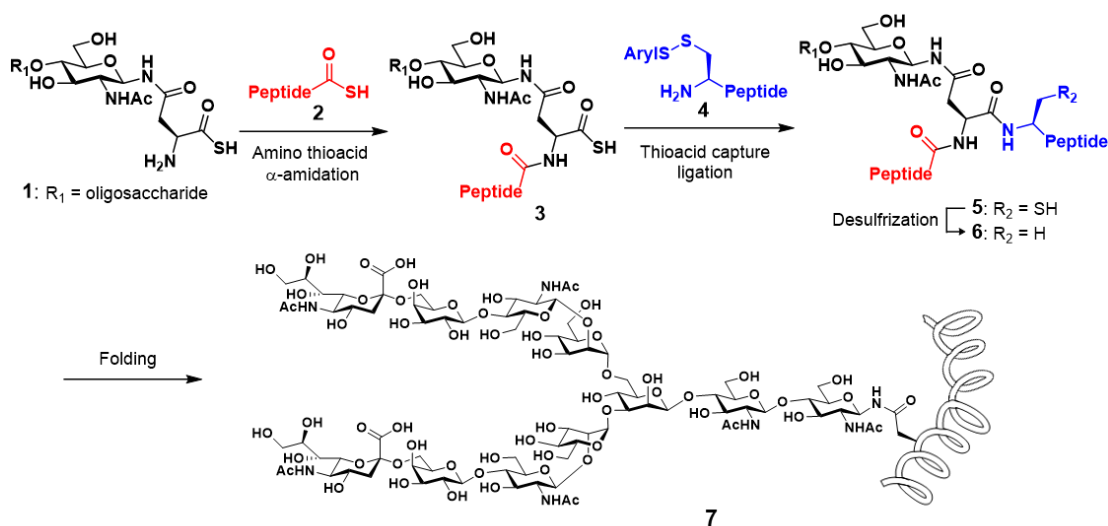
Thioacid-based strategy for the semi-synthesis of glycoproteins

(¹Graduate School of Science and ²Project Research Center for Fundamental Science², Osaka University) ○ Kota Nomura¹, Yuta Maki^{1,2}, Ryo Okamoto^{1,2}, Yasuhiro Kajihara^{1,2}

Keywords: Thioacid; Oligosaccharide; Glycoprotein; Amide; Peptide

Protein semisynthesis is a powerful approach for the synthesis of homogeneous glycoproteins, employing the coupling of recombinant peptides and glycopeptides prepared by chemical synthesis.

Herein we have developed a new semisynthetic strategy for glycoproteins using glycosyl asparagine thioacid. This strategy can selectively couple two peptides with both of N and C termini of glycosyl asparagine thioacid. As shown in figure, we employed glycosyl asparagine thioacid as the junction point for the coupling of N and C terminal peptides. The first coupling is designed to perform between peptide thioacid **2** and glycosyl asparagine thioacid **1** applying our chemoselective amide formation.¹ This amidation occurs through mild oxidation without drastic condensation reagents. Because the resultant glycopeptide **3** has thioacid form at its C-terminal, we could apply the thioacid capture ligation (TCL)² for the coupling of the resultant glycopeptide thioacid **3** and another peptide **4** having disulfide functional group at its N-terminal to afford glycopeptide **5**. The glycoprotein **7** can be efficiently obtained by the subsequent desulfurization and folding of **6**. In this presentation, we will discuss chemical characteristic nature of glycosyl asparagine thioacid. The approach for the semisynthesis of glycoproteins will also be discussed.



1) a) Okamoto, R. et al. *Biochemistry*, **2019**, 52, 1672. B) Okamoto, R. et al. *Chem. Lett.* **2019**, 48, 1391.

2) a) Liu, C. F. et al. *Tetrahedron*, **1996**, 37, 933. b) Zhang, X. et al. *Chem. Commun.* **2011**, 47, 1746. c) How, W. et al. *R. Soc. Open Sci.* **2018**, 5, 172455

ハイブリッド結合概念に基づくカルレティキュリン阻害剤の開発

(成蹊大理工¹・立命館大生命科学²) ○栗原 大輝¹・児島 大河¹・柴山 佳大¹・武田 陽一²・戸谷 希一郎¹

Development of calreticulin inhibitor based on hybrid binding concept (¹*Faculty of Science and Technology, Seikei University*, ²*College of Life Science, Ritsumeikan University*) ○Taiki Kuribara,¹ Taiga Kojima,¹ Keita Shibayama,¹ Yoichi Takeda,² Kiichiro Totani¹

Calreticulin is a lectin-like molecular chaperone in the endoplasmic reticulum (ER), and assists folding of glycoproteins. It is believed that misfolded glycoproteins induce ER stress. In this respect, the utility of ER-chaperones inhibitor on ER stress regulation has been suggested, while CRT inhibitor had not been reported. Thus, CRT inhibitor might contribute to ER stress study. Regarding to development of CRT inhibitor, we have reported CRT is a bifunctional chaperone that the binding ability is altered depends on aglycone hydrophobicity.

In this study, we synthesized a novel CRT-binding compound (G1M2-EG₈-Fmoc) that glycan (G1M2) and aglycone (Fmoc) are connected with octaethylene glycol (EG₈) linker. The G1M2-EG₈-Fmoc showed 1000-fold higher binding ability compared to G1M2 alone by hybrid binding concept. Furthermore, the G1M2-EG₈-Fmoc inhibited chaperone activity of CRT. These results indicate G1M2-EG₈-Fmoc is a novel hybrid binding type CRT inhibitor.

Keywords : Endoplasmic reticulum; Calreticulin; Hybrid binding type inhibitor

小胞体内レクチン様分子シャペロンであるカルレティキュリン (CRT) は、糖鎖結合ドメインおよびタンパク質相互作用ドメインを有し、糖タンパク質のフォールディング促進を担う。フォールディング不全糖タンパク質の蓄積は、小胞体ストレスを誘発する。この観点から、小胞体シャペロン阻害剤の小胞体ストレスの調節に有用性が示唆されているが、CRT 阻害剤の報告はない。すなわち、CRT 阻害剤は小胞体ストレス研究に役立つ可能性がある。CRT 阻害剤の開発に対する先行知見として、我々は種々のアグリコンを有する合成糖鎖群を用いて、CRT がアグリコンの疎水性度に応じてその結合力を変化させる多機能性タンパク質であると明らかにしている¹⁾。

本研究では、この多機能性に着目し、糖鎖認識部位および疎水性アグリコンをオクタエチレングリコールリンカーで連結した G1M2-EG₈-Fmoc (図 1) を合成した。CRT と G1M2-EG₈-Fmoc との結合はハイブリッド結合により、G1M2-OH との結合より 1000 倍向上すると判明した。さらに、本化合物は CRT のシャペロン活性を阻害した。これらの結果は、G1M2-EG₈-Fmoc がハイブリッド結合型 CRT 阻害剤であることを示唆している。

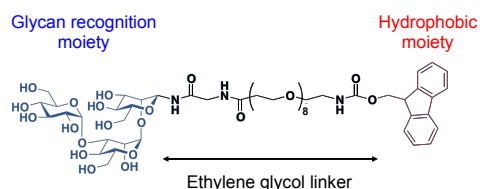


図 1. ハイブリッド結合型 CRT 阻害剤

1) M. Hirano *et al.*, *Biochem. Biophys. Res. Commun.* **2015**, 466, 350-355.

Development of Bioluminescent Probes for Visualizing and Quantifying of Endogenous RNAs in real time

(Department of Chemistry, School of Science, The University of Tokyo)

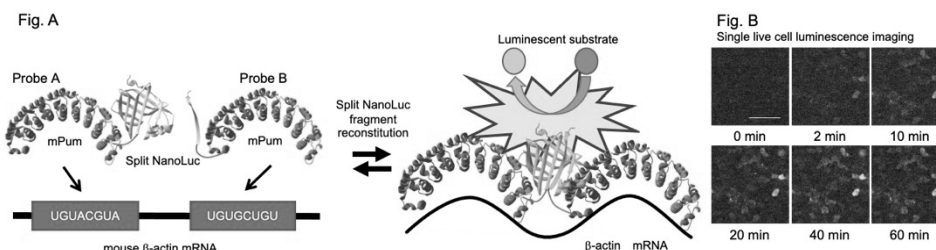
○Eguchi, Masatoshi; Yoshimura, Hideaki; Ozawa, Takeaki

Keywords: Luminescent imaging, Single cell analysis, Protein engineering

Gene expression plays important roles in physiological and pathophysiological phenotypic changes such as tumorigenesis, differentiation, and reprogramming. Temporal gene expression alteration includes important clues for comprehension of the mechanisms in the phenotypic changes. However, quantification of temporal changes in specific gene expression has not achieved in living samples at single cell resolution. In this study, we aim to develop probes for temporal monitoring of a specific RNA as the target gene expression product in single living cells by luminescence observation. We designed a luminescence-based RNA probe which consists of two fusion proteins with each different domain; One is an RNA recognition domain that binds to a specific RNA sequence, and the other is a split luciferase domain. The probe emits a luminescence signal through luciferase reconstitution by responding to the presence of target RNAs. (Fig. A).

Firstly, luminescence measurement was performed on living cells expressing the probes. The cells harboring the target RNA showed stronger luminescence in comparison to those without the RNA, indicative the target RNA-specific response of the probe. To assess the reversible reaction of the probe to target RNAs, we monitored luminescence of purified probe solution. The luminescence of the probe was weak in the absence of the target RNA. Upon addition of the RNA, the luminescence intensity increased, and following RNase treatment of the sample decreased the luminescence. Thus, the probe worked reversibly upon addition and digestion of target RNA. The time lapse luminescence images of living cells expressing the probes and target RNA were acquired under a luminescence microscope. The luminescence images were observed over several minutes at single cell resolution (Fig. B). We also prepared plasmid DNAs the coding region of which includes the gene of fluorescent protein mCherry fused with the target RNA sequence, and therefore the cells expressing the target RNA can be identified by mCherry fluorescence. We introduce the plasmid into cultured cells together with the probe plasmid. The images of single-cell time-lapse observation showed that a substantial positive correlation between the mCherry fluorescence and the luminescence intensities. The time-lapse images suggest the potential of the probe to detect and quantify the target RNAs in single living cells.

These results totally suggest that the probes have potential to monitor target RNA abundance in single living cells over time. The RNA probes would provide a tool to monitor gene expression alteration for comprehension of the mechanisms of the phenotypic changes.



標的がん細胞の高効率な認識を指向した DNA 複合材料の開発、及び応用

(青山学院大理工) ○西原 達哉・本橋 優人・盛谷 周平・日高 綾太・松村 有花・山田 梨紗・田邊 一仁

Development of DNA complex for efficient recognition of target cancer cells (*Department of Science and Engineering, Aoyama Gakuin University*) ○Tatsuya Nishihara, Yuto Motohashi, Shuhei Moritani, Ryota Hidaka, Yuka Matsumura, Risa Yamada, Kazuhito Tanabe

In recent years, antibody drugs receive attentions as promising drug via the recognition of antigen on cancer cell surface. Although the antibody drug is one of powerful tool for cancer treatment, the affinity to the target antigen depends on the property of the antibody. In this study, we attempt to construct a molecular system that shows selective recognition properties for target cancer cells by adjustment of types of ligands, and their spatial configuration. We focused on EpCAM and integrin as model of cell surface antigen and evaluate the affinity to the target cell using confocal laser scanning microscope. In fact, we succeeded in improving the recognition ability by recognizing multiple antigens and forming higher order structure under acidic environment. In this presentation, we report on the design, synthesis, recognition ability, and application of DNA complex.

Keywords : *Antigen recognition; Anti-tumor drug*

抗体医薬をはじめとして、様々な分子標的薬が現在開発されている。そのため、がん細胞特異的な分子の高効率な認識を実現する材料開発は、がん治療において極めて重要であると言える。

本研究では、プログラム性に優れ、化学修飾を容易に行える DNA に着目し、新たな認識材料開発を進めた。具体的には、がん細胞膜表層における抗原の発現パターンに応じて、リガンドの種類、空間配向を制御した DNA 複合材料を設計し、標的細胞の選択的な認識を目指した。本コンセプトの実証にあたり、がん細胞表層に高発現している細胞接着分子 (インテグリン)、及び上皮細胞接着分子 (EpCAM) に着目した。RGD ペプチドを配した合成 DNA、及び EpCAM を特異的に認識する DNA アプタマーを活用し、本方法論に基づく細胞認識能の向上が実現可能か検証した。

実際に、これまでに前述した 2 つの抗原を発現している MCF-7 に対して DNA 複合材料を用い、細胞認識能を評価した。1 成分のリガンドを担持した場合と比較し、2 成分のリガンドを担持した場合において、認識能の向上が確認された。さらに、足場として用いた DNA に対して i-motif 配列を組み込むことにより、酸性環境下での高次構造形成に伴い、親和性が向上することを新たに明らかとなった。そのため、本材料を用いることで、がん微小環境 (弱酸性環境) での高効率な細胞認識が可能になると期待される。本発表では、DNA 複合材料の設計、合成、細胞認識能評価、及び、応用展開について報告する。

ポリエチレンジオキシチオフエン：ポリスチレンスルホン酸 (PEDOT:PSS) ナノシートを用いた防水生体電極の開発と入浴中の心電図測定

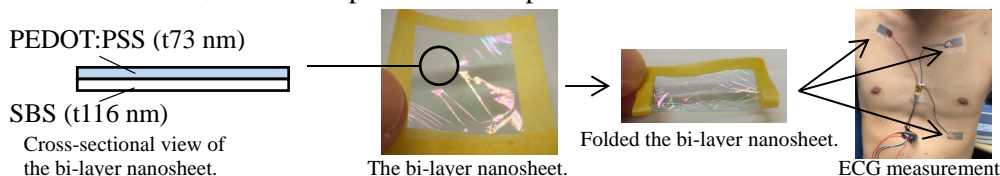
(早大先進研生医¹・早大理工総研²・シンガポールポリテクニック CLS³・早大理工学術院⁴) ○三原将^{1,2}・Hui-Lin Lee³・武岡真司^{2,4}

Development of waterproof bioelectrode using polyethylenedioxythiophene : polystyrenesulfonate (PEDOT:PSS) nanosheets and electrocardiogram measurements during bathing. (¹*Grad. Sch. Adv. Sci. Eng., Waseda Univ.*, ²*WISE, Waseda Univ.*, ³*CLS, Singapore Polytechnic*, ⁴*Fac. Sci. Eng., Waseda Univ.*) ○Sho Mihara,^{1,2} Hui-Lin Lee,³ Shinji Takeoka^{2,4}

Accurate and long-term electrocardiogram (ECG) measurement is effective method for the early detection of cardiovascular diseases. Particularly in the current situation where COVID-19 spreading over the world, daily biosensing is desirable because neglected chronic conditions may lead to fatal consequences.¹ Conductive hydrogels have been used for ECG measurement, However they swell upon contact with water and lose their adhesiveness and electrical properties. In this study, we developed a comfortable and waterproof bioelectrode using a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS)/poly(styrene-butadiene-styrene) (SBS) bi-layer nanosheet and a waterproof film. PEDOT:PSS/SBS nanosheet was completely folded with a conductivity loss of only 5%, providing a reliable electrical connection between the skin and the wires. This electrode can measure ECG in water with a signal-to-noise ratio similar to that in air, and revealed an increase in heart rate from 79 bpm to 131 bpm with changes in body temperature during bathing.

Keywords : Biomedical engineering, Sensor, Thin film, Polymer, Electronics

正確かつ長期的な心電図測定は心血管疾患の早期発見のために有効である。特に COVID-19 が世界的に蔓延している現況では、無自覚の慢性疾患が致命的な結果に繋がること可能性があり、日常的な生体信号の監視が望まれている¹。これまで心電図測定には導電性ハイドロゲルが使用されていたが、水との接触によってゲルが膨潤して接着性と電気特性を失うために日常的な使用が難しかった。本研究では、ポリ(3,4-エチレンジオキシチオフエン):ポリ(スチレンスルホン酸) (PEDOT:PSS)/ポリ(スチレン-ブタジエン-スチレン) (SBS) の 2 層ナノシートと防水フィルムを用いた快適かつ防水性に優れた生体電極を開発した。PEDOT:PSS/SBS は、わずか 5% の導電率損失で完全に折りたたまれ、皮膚と配線間の信頼性の高い電氣的接続を実現した。この電極は水中においても大気中と変わらないシグナルノイズ比で心電図計測が行え、入浴時に心拍数が体温変化に伴って 79 bpm から 131 bpm まで増加することを明らかにした²。



1) S. Keesara, A. Jonas and K. Schulman, *N. Engl. J. Med.*, **382**, 1–2 (2020).

2) S. Mihara, H. Lee and S. Takeoka, *MRS Communications*, **10**, 628–635 (2020).

低流量走査電子線散乱法による人工脂質膜ドメイン内部での炭素鎖充填構造の解析

(九大院理) ○木下 祥尚・山口 晋平・松森 信明

Analysis of the lipid packing structures inside a single membrane domain by low-flux scanning electron diffraction. (*Graduate School of Science, Kyushu University*)

○Masanao Kinoshita, Shimpei Yamaguchi, Nobuaki Matsumori

Ordered membrane domains, called lipid rafts, form a platform for important signal transductions. So far, the structure of lipid rafts has been examined using raft-like ordered/non-raft like disordered phase separated membranes. However, lipid packing structure inside the ordered membrane domains remains unknown. Previously, we reported that lipid compositions change gradually from the center to the outer regions of the ordered domain¹⁾. In that case, lipid packing structures should be inhomogeneous inside the domain. In the present study, we examined lipid packing structure inside an ordered domain using newly developed low-flux scanning-electron-diffraction (LFSED). LFSED revealed that an ordered domain consists of several sub-domains with different orientation of the lipid chain packing. Moreover, size of the sub-domain is larger in the center than in the outer regions of the domain²⁾.

Keywords : Lipid Membrane; Electron Diffraction; Lipid Raft; Nano-structures

細胞膜に存在する秩序的膜領域「脂質ラフト」は様々な生体機能発現の発端となることが知られ注目されている。これまでラフトの構造情報はラフト様秩序領域と無秩序領域が相分離した脂質膜を用いて取得されてきた。しかし、多くの研究ではラフト様秩序領域を均質な「相」とみなしており、その領域内部で生じる構造の不均一性については議論されていない。近年、我々は単一の秩序領域内でも脂質の分布は不均一であり、その中心部から周辺部に向かって脂質の組成が変化することを報告した¹⁾。その場合、脂質充填構造も領域内で不均一が生じるはずである。本研究では低流量走査電子線散乱法(LFSED)を開発し、単一の秩序領域内部での脂質炭素鎖の充填構造を精査した(Fig. 1a)。その結果、秩序領域内部には炭素鎖の充填方向が異なる複数のサブドメインが存在することが明らかになった(Fig. 1bとc)。さらに、領域の中央部では大きなサブドメインが形成されるのに対し、周辺部では比較的小さいサブドメインが形成することが分かった²⁾。

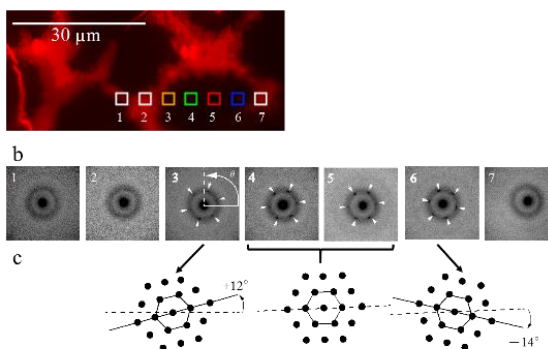


Fig. 1. (a) DSPC/DOPC 単分子膜の蛍光顕微鏡写真。暗い領域が DSPC-rich 秩序領域を示す。(b) 領域 1 から 7 で得られる電子線散乱パターン。(c) 領域 3-6 における炭素鎖充填構造の模式図。

1) Ando and Kinoshita *et al.*, 2015. *Proc. Natl. Acad. U.S.A.* 112 (15), 4558–4563.

2) Kinoshita *et al.*, 2020. *Sci. Rep.* 10, 22188.

Membrane Lipids Affect the Interplay between the Transmembrane Domain of the EGF Receptor and Ganglioside GM3 – Thermodynamic Quantification of the Lateral Interaction using FRET

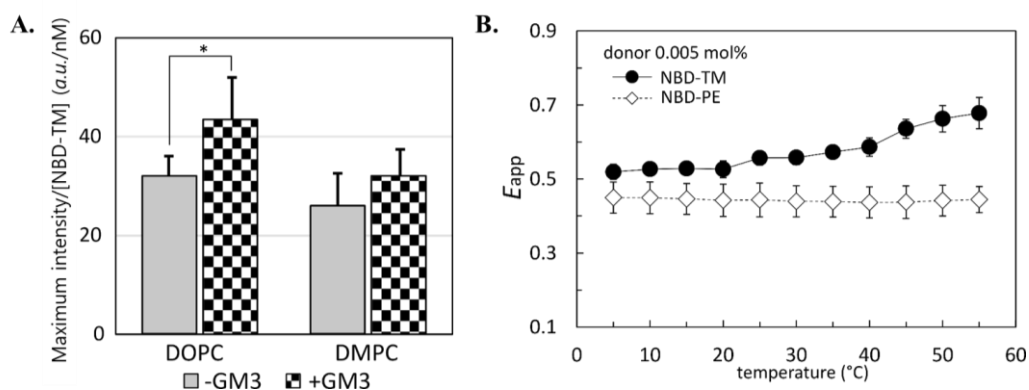
(¹ Graduate School of Science, Osaka University, ² Center for Highly Advanced Integration of Nano and Life Sciences (G-CHAIN), ³ Department of Biosciences, Åbo Akademi University)

○Mikito Nakano,¹ Shinya Hanashima,¹ Toshiaki Hara,¹ Kazuya Kabayama,¹ Naoko Komura,² Hiromune Ando,² Thomas K. M. Nyholm,³ Peter J. Slotte,³ Michio Murata¹

Keywords: GM3, EGFR, FRET, Protein-Lipid Interaction, Model Membrane

Ganglioside GM3 in the plasma membranes has been reported to suppress cell growth by preventing the autophosphorylation of the epidermal growth factor (EGF) receptor.¹ In previous studies, it was supposed that dimerization of the transmembrane (TM) domain of the receptor is one of the most crucial steps of the activation.² Thus, surrounding lipids such as GM3 possibly regulate the topology of the TM domain. However, the direct interaction between GM3 and the TM domain of the EGF receptor has not been proven yet.

To elucidate the mechanism by which ganglioside GM3 regulates the dimerization states of the EGF receptor, we performed fluorescence analysis using fluorescently labeled probes of GM3 and the receptor transmembrane peptide (NBD-TM). NBD-TM was prone to form dimer in DOPC bilayer by observing NBD self-quenching, while the addition of GM3 increased the NBD fluorescence intensity due to recovery from self-quenching. The data indicated that GM3 promotes peptide disassociation depending on lipid bilayer thickness. The apparent FRET efficiency (E_{app}) between NBD-TM and ATTO594-GM3 in DOPC bilayer was significantly higher than that of using NBD-PE as a control, indicating a specific TM-GM3 interaction. Furthermore, E_{app} between NBD-TM and labeled GM3 increased significantly in response to temperature increases, suggesting that the quantitative analysis was achieved with the lipid bilayers conditions where the monomer peptide was stable.



- 1) E. Bremer, *et al. J. Biol. Chem.*, **1984**, 259, 6818–6825.
- 2) N. Endres, *et al. Cell*, **2013**, 152, 543–556.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[A23-1am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Toshiyuki Kowada, Masayasu Taki

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 23 (Online Meeting)

[A23-1am-01] Exploration of synthetic agents that inhibit intrinsically disordered circadian clock transcription factors

○Yusuke Hosoya¹, Wataru Nojo², Isao Kii¹, Takanori Suzuki², Miki Imanishi³, Junko Ohkanda¹ (1. Academic Assembly, Institute of Agriculture, Shinshu University, 2. Department of Chemistry, Faculty of Science, Hokkaido University, 3. Institute for Chemical Research, Kyoto University)

9:00 AM - 9:20 AM

[A23-1am-02] Synthetic Small Molecules for 14-3-3 Isoform-Selective Inhibition and Regulation of Plant Functions

○Kotaro Nishiyama¹, Norio Kudo¹, Minoru Yoshida^{1,2,3}, Yusuke Aihara⁴, Koji Takahashi^{4,5}, Toshinori Kinoshita^{4,5}, Takehiro Suzuki¹, Naoshi Dohmae¹, Ayato Sato⁵, Sakuya Nakamura¹, Shinya Hagihara^{1,5} (1. RIKEN Center for Sustainable Resource Science, 2. Graduate School of Agricultural and Life Sciences, The University of Tokyo, 3. Collaborative Research Institute for Innovative Microbiology, The University of Tokyo, 4. Graduate School of Science, Nagoya University, 5. WPI-ITbM, Nagoya University)

9:20 AM - 9:40 AM

[A23-1am-03] Simultaneous detection of double-stranded and G4 DNAs using a tripodal quinone-cyanine dye

○Takashi Sakamoto^{1,2}, Zehui Yu², Yuto Otani¹ (1. Grad. School of Systems Eng., Wakayama Univ., 2. Faculty of Systems Eng., Wakayama Univ.)

9:40 AM - 10:00 AM

[A23-1am-04] Development of high-affinity fluorescent probes for quantification of organellar labile Zn²⁺

○Liu Rong¹, Toshiyuki Kowada^{1,2}, Toshitaka Matsui^{1,2}, Shin Mizukami^{1,2} (1. Graduate School of Life Sciences, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

10:00 AM - 10:20 AM

[A23-1am-05] Development of multicolor labeling reagents for Raman imaging using an algal carotenoid by stable-isotope labelling

○Yusuke Yonamine¹, Joshua Mba², Yu Hoshino³, Hideyuki Mitomo¹, Kuniharu Ijima¹ (1. Research Institute for Electronic Science, Hokkaido University, 2. Graduate School of Life Science, Hokkaido University, 3. Department of Chemical Engineering, Faculty of Engineering, Kyushu University)

10:20 AM - 10:40 AM

[A23-1am-06] Visualization of Lipid Metabolism Using an Environment-Sensitive Fluorescent Fatty Acid

○Keiji Kajiwara¹, Hiroshi Osaki¹, Keiko Kuwata¹, Frank Glorius², Masayasu Taki¹, Shigehiro Yamaguchi¹ (1. Nagoya Univ., 2. Universität Münster)

10:40 AM - 11:00 AM

[A23-1am-07] Effect of Stereoisomerism in Developing Highly Photostable and
Fluorogenic NIR
Probes for Long-term Imaging

○Qian WU¹, Masayasu Taki¹, Shigehiro Yamaguchi¹ (1. Nagoya University)

11:00 AM - 11:20 AM

[A23-1am-08] Development of Aldehyde Dehydrogenase-Responsive Turn-on
Fluorescent Probe for Cancer Stem Cell Imaging

○Masahiro Oe¹, Koji Miki¹, Yoshifumi Ueda¹, Yasuo Mori¹, Kouichi Ohe¹ (1. Grad. Sch.
Eng., Kyoto Univ.)

11:20 AM - 11:40 AM

天然変性概日時計転写因子を標的とする阻害剤の開発

(信州大農¹・北大院理²・京大化研³) ○細谷 侑佑¹・能條 航²・喜井 勲¹・鈴木 孝紀²・今西 未来³・大神田 淳子¹

Exploration of synthetic agents that inhibit intrinsically disordered circadian clock transcription factors (¹*Academic Assembly, Institute of Agriculture, Shinshu University*, ²*Department of Chemistry, Faculty of Science, Hokkaido University*, ³*Institute for Chemical Research, Kyoto University*) ○Yusuke Hosoya,¹ Wataru Nojo,² Isao Kii,¹ Takanori Suzuki,² Miki Imanishi,³ Junko Ohkanda¹

Circadian transcription factors, BMAL1 and CLOCK, are intrinsically disordered proteins and agents capable of specific inhibition their function would serve as potential therapeutic for insomnia and cancer. In this study, we developed a DNA-binding assay based on fluorescence polarization using recombinant proteins of BMAL1 and CLOCK. Screening of a chemical library of 1,785 compounds identified quinone derivative **1** that significantly inhibits the DNA-binding of the heterodimer of BMAL1 and CLOCK. The result of structure-activity relationship and Cys-capping experiment suggest that **1** covalently reacts with nucleophilic residues in PAS region of BMAL1¹. These results suggest that covalent agents may provide a promising chemical basis for controlling disordered proteins.

Keywords : *intrinsically disordered proteins; inhibitors; BMAL1; CLOCK; circadian clock*

天然変性たんぱく質 (intrinsically disordered proteins; IDPs) BMAL1 と CLOCK は概日リズム形成の核となる転写因子である。概日リズムの乱れが不眠症や腫瘍形成の要因となることから両者の2量体形成もしくはDNA結合機能を阻害する化合物は治療薬となることが期待される。本研究ではBMAL1およびCLOCKの組み換えたんぱく質を用いて、蛍光偏光変化を指標とするHigh-throughput DNA結合試験系を確立した。

1,785個の小分子化合物ライブラリのスクリーニングを実施しBMAL1/CLOCKヘテロダイマーとDNA間の相互作用を顕著に阻害するキノキサリンジオン**1**を見出した。**1**の構造活性相関研究、MALDI-TOFによる質量分析、BMAL1/CLOCKシステイン残基マスキング実験によって**1**は共有結合的にBMAL1のPAS領域に作用していることが示唆された¹。以上よりBMAL1/CLOCKのDNA結合を阻害する小分子**1**を新規に見出すと共にIDPの機能調節において共有結合性の化合物が有効である可能性を示した。

1) Hosoya, Y.; Nojo, W.; Kii, I.; Suzuki, T.; Imanishi, M.; Ohkanda, J. *Chem. Commun.* **2020**, 56, 11203.

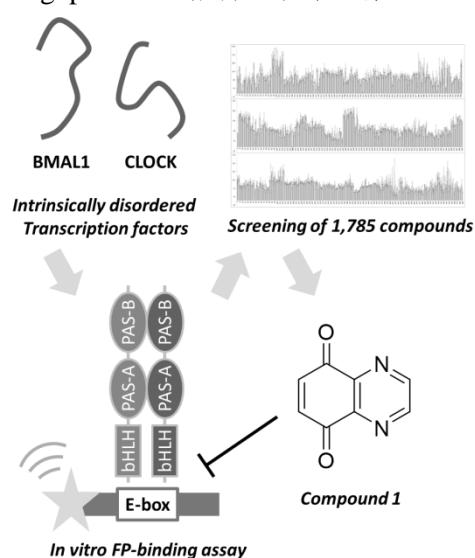


Fig 1. 蛍光偏光変化を指標とする天然変性概日時計転写因子に対する阻害剤探索

合成小分子による 14-3-3 アイソフォーム選択的阻害と植物機能制御

(理研 CSRS¹・東大農²・東大 CRIIM³・名大理⁴・名大 WPI-ITbM⁵)

○西山 康太郎¹・工藤 紀雄¹・吉田 稔^{1,2,3}・相原 悠介⁴・高橋 宏二^{4,5}・

木下 俊則^{4,5}・鈴木 健裕¹・堂前 直¹・佐藤 綾人⁵・中村 咲耶¹・萩原 伸也^{1,5}

Synthetic Small Molecules for 14-3-3 Isoform-Selective Inhibition and Regulation of Plant Functions (¹RIKEN Center for Sustainable Resource Science, ²Graduate School of Agricultural and Life Sciences, The University of Tokyo, ³Collaborative Research Institute for Innovative Microbiology, The University of Tokyo, ⁴Graduate School of Science, Nagoya University, ⁵WPI-ITbM, Nagoya University) ○Kotaro Nishiyama,¹ Norio Kudo,¹ Minoru Yoshida,^{1,2,3} Yusuke Aihara,⁴ Koji Takahashi,^{4,5} Toshinori Kinoshita,^{4,5} Takehiro Suzuki,¹ Naoshi Dohmae,¹ Ayato Sato,⁵ Sakuya Nakamura,¹ Shinya Hagihara^{1,5}

14-3-3 is a "hub" possessing multifunctionality due to interaction with various client proteins and a prospective target for human drugs and plant growth regulators. Because the 14-3-3 family is composed by many isoforms which show individual functions, 14-3-3 isoform-selective inhibitors are required in the field of drug discovery to reduce side effects. However, development of the isoform-selective inhibitors has been challenging because the reported inhibitory site is highly conserved among all 14-3-3s.

In this study, we discovered an isoform-selective inhibitor named **KN002**. As a result of estimation of each inhibitory activity against 7 isoforms in *Arabidopsis thaliana* 14-3-3 family, **KN002** clearly showed the inhibitory selectivity. Investigation of the inhibitory mechanism suggested that **KN002** covalently and allosterically inhibited 14-3-3 proteins. In conclusion, we successfully demonstrated the 14-3-3 isoform-selective inhibition based on the covalent and allosteric manner. In presentation, in planta activity of **KN002** was further discussed.

Keywords: 14-3-3 family, Protein-protein interactions, Chemical screening, X-ray crystal structure, Stomata

すべての真核生物がもつ 14-3-3 タンパク質は、様々なタンパク質と相互作用することで多様な機能を示す「ハブ」であり、ヒトでは治療薬の、植物では成長調節剤の標的となる。また、14-3-3 は複数のアイソフォームから構成され、それぞれが固有の役割を担う。そのため、14-3-3 を標的とした薬剤の副作用を抑えるためには、各アイソフォームに対する選択性を高める必要がある。しかし、14-3-3 の阻害部位として知られるタンパク質認識ポケットは、アミノ酸残基の保存性が非常に高く、低分子化合物によって各アイソフォームの機能を選択的に制御することは困難であった。

本研究では、シロイヌナズナ 14-3-3 ファミリーに対してアイソフォーム選択性を示す阻害剤として、**KN002** を開発した。7 種類のシロイヌナズナ 14-3-3 に対する阻害活性を評価すると、最大 10 倍程度の選択性が確認された。そこで、**KN002** の阻害機構を調べた結果、14-3-3 のタンパク質認識ポケットから離れたシステイン残基と共有結合することで、アロステリックな阻害作用を示すことが示唆された。以上のように、新規な阻害機構を示す低分子化合物によって、14-3-3 アイソフォーム選択的な阻害に成功した。本発表では、**KN002** の植物に対する生物活性についても議論する。

三脚型キノン-シアニン蛍光プローブによる2重鎖及び4重鎖DNAの同時検出

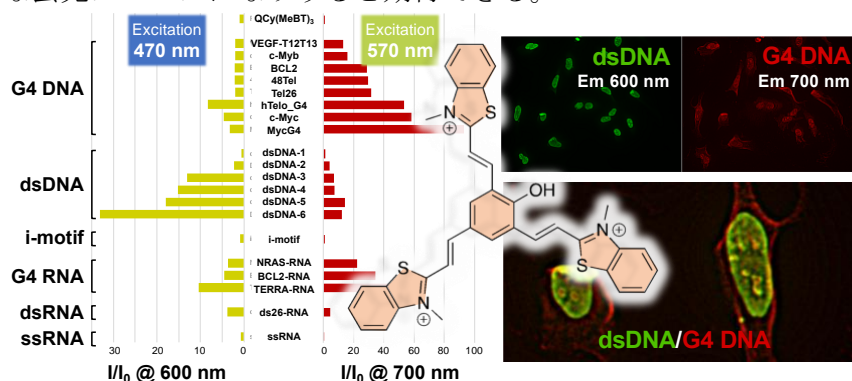
(和大院シス工¹・和大シス工²) ○坂本 隆^{1,2}・于 ゾウ慧²・大谷 悠人¹

Simultaneous detection of double-stranded and G4 DNAs using a tripodal quinone-cyanine dye
(¹Graduate School of Systems Engineering, Wakayama University, ²Faculty of Systems Engineering, Wakayama University,) ○Takashi Sakamoto,^{1,2} Zehui Yu,² Yuto Otani¹

Donor-two-acceptor (D2A) typed quinone-cyanine dyes are good fluorescent skeleton for developing target-selective NIR-fluorescence turn-on probes. There have been a lot of reports about D2A typed quinone-cyanine molecular probe, however, the application study of donor-three-acceptor (D3A) typed quinone-cyanine (tripodal QCy) dyes have been scarcely reported. In this study, we synthesized tripodal QCy dye having three *N*-methylbenzothiazolium cation as the electron acceptor (QCy(MeBT)₃), and the fluorescence property of QCy(MeBT)₃ was investigated. Results indicated that the fluorescence intensity of QCy(MeBT)₃ at 600 nm (ex: 470 nm) and 700 nm (ex: 570 nm) was enhanced individually by the addition of double-stranded DNA and G-quadruplex DNA, respectively. This suggests that QCy(MeBT)₃ might be useful probe for analyzing structural dynamics of non-canonical G4 DNA in cells.

Keywords : Quinone-Cyanine Dye; Fluorescent Probe; G-quadruplex; Double-stranded DNA; Simultaneous Detection

1 ドナー・2 アクセプター (D2A) 型のキノン-シアニン蛍光色素は、近赤外領域の蛍光を示すこと、また、適切な保護基の導入により蛍光シグナルに刺激応答性を付与できることから、種々の標的選択的な蛍光 OFF/ON 型の分子プローブとして応用されている。一方で、1 ドナー・3 アクセプター (D3A (or 三脚)) 型のキノン-シアニン蛍光色素の分子プローブとしての報告例は少なく、その応用可能性は十分に検討されていない。本研究では、アクセプター部位として3つの *N*-メチルベンゾチアゾリウムカチオンをもつキノン-シアニン蛍光色素 (QCy(MeBT)₃) を合成し、その蛍光特性を調べた。結果、QCy(MeBT)₃ の 600 nm 蛍光 (ex: 470nm) 及び 700 nm 蛍光 (ex: 570 nm) は、それぞれ2重鎖DNA及び4重鎖DNAを添加した場合に個別に増加することが示された。以上から、QCy(MeBT)₃ が4重鎖DNA構造の細胞内ダイナミクス解析に有用な蛍光プローブになりうると期待できる。



(¹Graduate School of Life Sciences, ²IMRAM, Tohoku University)

Keywords: Fluorescent probe; Protein-labeling technology; Organellar $[Zn^{2+}]$; Quantification

CCCCCCCCCOCCOCCNC(=O)CCN1CCc2c3c(c1)oc(=O)c(NCc4cccnc4)c3cc2

Figure 1. Structure of ZnDA-1H.

1) T. Kambe, T. Tsuji, A. Hashimoto, N. Itsumura, *Physiol. Rev.* **2015**, 95, 749; 2) W. Maret, *Adv. Nutr.* **2013**, 4, 82; 3) T. Kowada, T. Watanabe, Y. Amagai, R. Liu, M. Yamada, H. Takahashi, T. Matsui, K. Inaba, S. Mizukami, *Cell Chem. Biol.*, **2020**, 9, 1521.

藻類由来ラマンイメージング色素の安定同位体標識による多色化

(北大電子研¹・北大 GI-CoRE²・北大院生命³・九大院工⁴) ○与那嶺雄介^{1,2}・ンバジヨシユア³・星野友⁴・三友秀之^{1,2}・居城邦治^{1,2}

Development of multicolor labeling reagents for Raman imaging using an algal carotenoid by stable-isotope labelling (¹Research Institute for Electronic Science, Hokkaido University, ²GI-CoRE, Hokkaido University, ³Graduate School of Life Science, Hokkaido University, ⁴Department of Chemical Engineering, Faculty of Engineering, Kyushu University) ○Yusuke Yonamine,^{1,2} Joshua C. Mba,³ Yu Hoshino,⁴ Hideyuki Mitomo,^{1,2} Kuniharu Ijro^{1,2}

Fluorescence microscopy can detect multiple proteins and organelles in a cell simultaneously when combined with fluorescent dyes that have different emission wavelengths. However, fluorescence spectra are intrinsically broad and need to be avoided overlapping, limiting the number of the color channels. On the other hand, Raman spectroscopy provides much narrower spectra and the peaks can be resolved, which is suitable for multi-color Raman imaging. In particular, a Raman spectrum can be shifted to varying degrees by replacing elements of a Raman imaging reagent with stable isotopes at various ratios. In this research, we develop multicolor Raman imaging reagents using a carotenoid produced by a photosynthetic algal cell. Specifically, we induce astaxanthin of a *Haematococcus pluvialis* cell with culture media including stable isotopes (D₂O, ¹³CO₂) at various ratios. The produced pigments show various resonance Raman shifts caused by stable isotope replacement.

Keywords : Raman imaging; microalgae; stable isotope

蛍光顕微鏡観察では、異なる波長の蛍光検出剤を用いて、細胞内の複数の生体分子を同時に検出可能である。しかし、蛍光スペクトルの波長はブロードであり、重なりを避けるため使用可能な色数が制限される。一方、ラマン分光法ではスペクトル形状がシャープでありピーク分離も可能なため、ラマンイメージング試薬は多色化できる余地がある。特に、ラマン検出分子の元素を安定同位体 (SI) 置換すると、分子振動の変化に伴いラマンスペクトルが低波数シフトする。このシフト度合いは SI 置換率に応じて異なるため、SI の割合を様々に変化させることで、多色のラマンイメージング試薬を容易に調製できる。本研究では、光合成を行う微細藻類 (ヘマトコッカス) が生産するカロテノイド色素 (アスタキサンチン: AXT) を SI 置換して¹⁾、ラマン分光法用の多色イメージング試薬を開発する。具体的には、SI 標識した光合成基質(²H₂O、¹³CO₂) を様々な割合でヘマトコッカス細胞に取り込ませ (Fig.)、生成した SI-AXT を多色化しラマンイメージング試薬として利用した。AXT は共鳴ラマン分光法によりシグナルを著しく増強できる

ため、高感度多色ラマン検出剤としての応用が期待できる。

1) Y. Yonamine, K. Hiramatsu, T. Ideguchi, T. Ito, T. Fujiwara, Y. Miura, K. Goda, Y. Hoshino, *RSC Adv.* **2020**, *10*, 16679–16686.

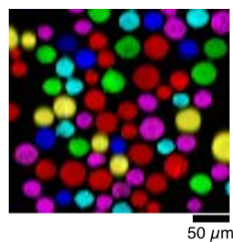


Fig. Resonance Raman imaging of *H. lacustris* cells accumulating SI-AXTs. Yellow, AXT; Blue, 30% ²H-AXT; Cyan, 50% ²H-AXT; Red, 100% ¹³C-AXT, Green, [30% ²H+100% ¹³C]-AXT, Magenta, [50% ²H+100% ¹³C]-AXT. Scale bar: 50 μm.

Visualization of Lipid Metabolism Using an Environment-Sensitive Fluorescent Fatty Acid

(¹Graduate School of Science, Nagoya University, ²Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, ³Westfälische-Wilhelms Universität Münster) ○Keiji Kajiwar, ¹Hiroshi Osaki, ¹Keiko Kuwata, ²Frank Glorius, ³Masayasu Taki, ²Shigehiro Yamaguchi^{1,2}

Keywords: Environment-sensitive dye; Fluorescent fatty acid; Lipid metabolism; Fluorescence imaging; Autophagy

Lipid metabolism plays a key role in various biological systems such as energy homeostasis and cell proliferations. Because the metabolic pathways of fatty acids (FAs) are strongly related to cell functions, understanding how FAs are metabolized in cells has been an important research objective. Although fluorescent fatty acids are useful tools for monitoring intracellular FA dynamics in real time, they have several drawbacks such as low metabolic efficiency and different cellular distribution from those of natural FAs. Herein, we report a novel fluorescent fatty acid **AP-C12** based on 3a-azapyrene-4-on (AP) and demonstrate its practical utilities for visualizing FA metabolism in living cells.

The AP dye is an environment-responsive compound that shows a hypsochromic shift of absorption and emission maxima as the solvent polarity increases, while the fluorescence quantum yields are almost constant. Therefore, when **AP-C12** metabolites are transported to various organelles including mitochondria, lipid droplets (LDs), and endoplasmic reticulum (ER), differences in the polarity of the organelles can be detected as the differences in fluorescence properties, leading to the visualization of their subcellular distributions.

Upon incubation of oleate-treated HepG2 cells with **AP-C12**, we successfully visualized the cytosol, ER and mitochondrial membranes, and LDs, where **AP-C12** metabolites were located, in green, yellow, and red, respectively (Figure 1). We then analyzed the fatty acid metabolic pathways by using known inhibitors of the related enzymes. For example, when the cells were treated with a DGAT1 inhibitor T863, fluorescence signal of ER in yellow increased, indicating that diacylglycerol was highly accumulated in the ER membrane. Finally, we monitored the distribution of the metabolites in autophagic cells and found that autophagy-supplied FAs were re-metabolized and stored in LDs. These results demonstrated that **AP-C12** is a powerful tool for evaluating the fatty acid metabolism.

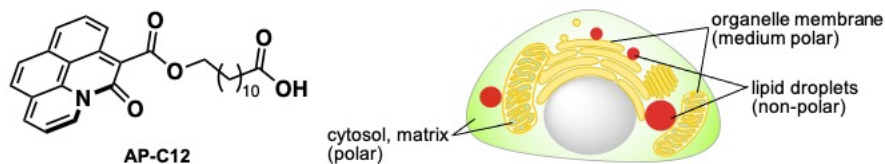


Figure 1. Schematic representation of the visualization of the distribution of fatty acid metabolites in cells stained with **AP-C12**.

Effect of Molecular Stereoisomerism in Developing Highly Photostable and Fluorogenic NIR Probes for Long-term Imaging

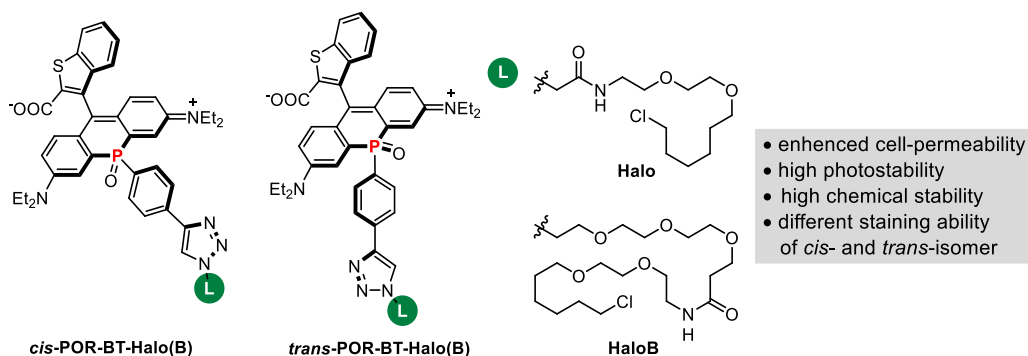
(¹*Institute of Transformative Bio-Molecules (ITbM), Nagoya University,* ²*Department of Chemistry, Graduate School of Science, Nagoya University*)

Qian Wu,¹ Masayasu Taki,¹ Shigehiro Yamaguchi,^{1,2}

Keywords: P-Rhodamine; stereoisomers; fluorogenic; NIR probe; long-term imaging

Prominent progress of fluorescence microscopy rising in recent years, such as multi-photon, super-resolution, and single-molecule microscopies, opens a new door to visualize the cellular morphology and dynamics for an extended period of time with high spatiotemporal details. However, these advances put forward higher demands of fluorescent labelling reagents, including high photostability and brightness, good cell-membrane permeability, target specificity, and suitable excitation and emission wavelengths. These demands, it should be noted, are usually difficult to meet at the same time.

Recent studies on rhodamine-based probes have shown their advantages to overcome these obstacles. The dynamic equilibrium between a fluorescent zwitterion and a non-fluorescent spirolactone enables the tunability of cell-membrane permeability. Inspired by our previous works on PREX (photoresistant xanthene) dyes,^{1,2} we developed new phosphorhodamine dyes with improved performance for protein labeling by introducing a benzo-thiophene-2-carboxylic acid at the 9-position of the xanthene motif. The resulting *cis*- and *trans*-isomers, namely *cis*- and *trans*-POR-BT, were successfully separated, and structurally identified by X-ray diffraction. The corresponding dyes with a HaloTag ligand showed different staining ability in living cell imaging. *Cis*-POR-BT-Halo non-specifically stained membrane structures of cellular organelle, such as endoplasmic reticulum, mitochondria, lysosome *etc.*, while the *trans*-isomer selectively labeled to HaloTag-fused proteins, which allowed long-term imaging of cell division and four-color imaging in the vis-NIR region.



1) M. Grzybowski, M. Taki, K. Kajiwar, S. Yamaguchi, *Chem. Eur. J.* **2020**, 26, 7912. 2) M. Grzybowski, M. Taki, K. Senda, Y. Sato, T. Ariyoshi, Y. Okada, R. Kawakami, T. Imamura, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2020**, 57, 10137.

Development of Aldehyde Dehydrogenase-Responsive Turn-on Fluorescent Probe for Cancer Stem Cell Imaging

(Graduate School of Engineering, Kyoto University) ○Masahiro Oe, Koji Miki, Yoshifumi Ueda, Yasuo Mori, and Kouichi Ohe

Keywords: enzyme-responsive; fluorescence; pH-responsive; Cy5 dye; aldehyde dehydrogenase, cancer stem cell

Aldehyde dehydrogenase 1A1 (ALDH1A1) is a crucial biomarker for identifying cancer stem cells (CSCs), which are responsible for the proliferation, metastasis, and chemoresistance displayed by cancer.¹ Development of ALDH1A1-responsive turn-on fluorescence probes that can be used to visualize CSCs is highly desirable. However, it remains a challenge because the enzymatic transformation of a formyl group into a carboxylate has little effect on the electronic property of fluorescence dyes. This research focused on anionic property of carboxylate and we have developed ALDH1A1-activatable probe **C5SA** for CSC imaging. To our knowledge, **C5SA** is the first example of an ALDH-responsive near-infrared (NIR) probe.

We previously found that enzyme-mediated generation of carboxylate promoted the detachment of the quenching mercapto group from cyanine-type fluorophore (Cy5), which leads to the fluorescence activation.² Based on this discovery, we have designed and prepared an ALDH-responsive turn-on probe **C5SA** (Figure 1a). In a buffered solution (pH 7.4), ALDH1A1 transformed the formyl group of **C5SA** to carboxylate, leading to the NIR fluorescence increment, which is probably caused by thermodynamic stabilization of cationic Cy5 by anionic carboxylate. Confocal images of SUIT-2 cells indicate that **C5SA** successfully visualized CSCs among normal cancer cells more clearly than ALDEFLUOR,³ one of the best reagents available for identifying CSCs¹ (Figure 1b-c). In addition, these brightly emitting cells were isolated by fluorescence-activated cell sorting using a 640 nm red laser, indicating that **C5SA** can be used to isolate CSCs for analytical and clinical purposes.

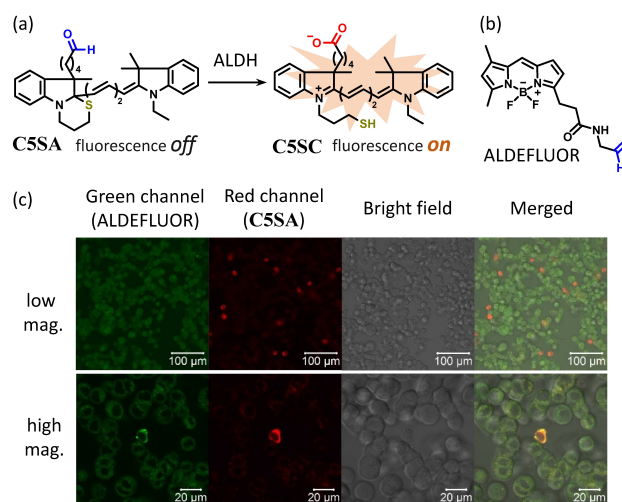


Figure 1. (a) ALDH-responsive turn-on probe **C5SA**. (b) The structure of ALDEFLUOR ($\lambda_{\text{em}} = 500\text{--}550\text{ nm}$). (c) Confocal images of SUIT-2 cells incubated with ALDEFLUOR and **C5SA**.

1) a) Ma, I.; Allan, A. L. *Stem Cell Rev. Rep.* **2011**, 7, 292–306. b) Rodriguez-Torres, M.; Allan, A. L. *Clin. Exp. Metastasis* **2016**, 33, 97–113. 2) Oe, M.; Miki, K.; Ohe, K. *Org. Biomol. Chem.* **2020**, 18, 8620–8624. 3) Storms, R. W. et al. *Proc. Natl. Acad. Sci. U. S. A.* **1999**, 96, 9118–9123.

[A25-1am] 17. Biofunctional Chemistry, Biotechnology

Chair:Kunihiko Morihiko, Yusuke Takezawa

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 25 (Online Meeting)

- [A25-1am-01] Development of the artificial triplex-forming oligonucleotides containing chemically modified nucleobases or sugar moieties**
○Shuhei Nishizawa¹, Diasuke Ogata¹, Gaohong Tu¹, Yu Itoh¹, Akihiro Ohkubo¹ (1. School of Life Science and Technology, Department of Life Science and Technology, Tokyo Institute of Technology)
9:00 AM - 9:20 AM
- [A25-1am-02] Synthesis of oligonucleotides containing 2'-O-alkylcarbamoyl ethyl modifications and their properties.**
○Tomohiro Kishimura¹, Koya Uekusa¹, Takahito Tomori¹, Yoshiaki Masaki¹, Kohji Seio¹ (1. Tokyo Tech.)
9:20 AM - 9:40 AM
- [A25-1am-03] Hypoxia-Activated Floxuridine Oligomers via Bio-reduction of Nitro and/or Azo Functionalities**
○Kunihiko Morihiko¹, Takuro Ishinabe¹, Masako Takatsu², Tsuyoshi Osawa^{1,2}, Akimitsu Okamoto^{1,2} (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. RCAST, The Univ. of Tokyo)
9:40 AM - 10:00 AM
- [A25-1am-04] Development of small molecular efficient photosensitizer and application to sequence-selective photo-oxidation of guanosine**
○Takashi Kanamori¹, Yuki Tsuga¹, Kohji Hamamoto¹, Chao Wang¹, Tomohiro Yube¹, Ruoyu Li¹, Hideya Yuasa¹ (1. Tokyo Institute of Technology)
10:00 AM - 10:20 AM
- [A25-1am-05] Formation in solutions and crystal structure of a novel short Ag-DNA wire.**
○Takahiro Atsugi¹, Jiro Kondo², Akira Ono¹ (1. Kanagawa Univ., 2. Sophia Univ.)
10:20 AM - 10:40 AM
- [A25-1am-06] Metal-dependent stabilization of DNA duplexes containing 2-oxoimidazole-4-carboxylate/carboxamide as nucleobases**
○Lingyun Hu¹, Yusuke Takezawa¹, Mitsuhiko Shionoya¹ (1. Dept. of Chemistry, Grad. School of Science, The Univ. of Tokyo)
10:40 AM - 11:00 AM
- [A25-1am-07] DNA-based Molecular Switches Driven by Metal Complexation of 5-Hydroxyuracil Nucleobases**
○Keita Mori¹, Yusuke Takezawa¹, Mitsuhiko Shionoya¹ (1. Grad. School of Science, The Univ. of Tokyo)
11:00 AM - 11:20 AM
- [A25-1am-08] Photocontrolled assembly of DNA origami nanostructures using photoswitching molecules**
○Shubham Mishra¹, Soyoung Park¹, Tomoko Emura¹, Kumi Hidaka¹, Hiroshi Sugiyama^{1,2}, Masayuki Endo^{1,2} (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Sciences, Kyoto University)

11:20 AM - 11:40 AM

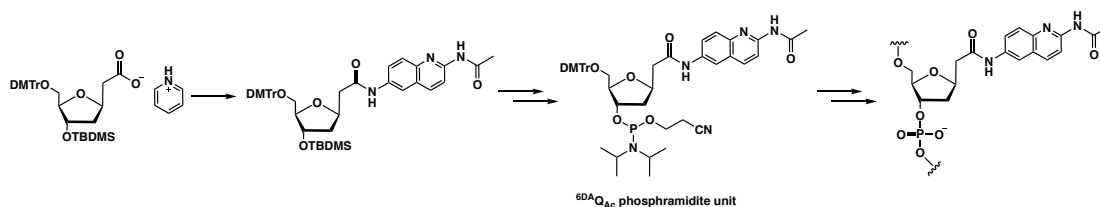
Development of the artificial triplex-forming oligonucleotides containing chemically modified nucleobases or sugar moieties

(School of Life Science and Technology, Department of Life Science and Technology, Tokyo Institute of Technology) ○Shuhei Nishizawa, Daisuke Ogata, Gaohong Tu, Yu Itoh, Akihiro Ohkubo

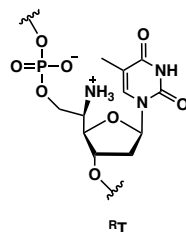
Keywords: Nucleic acid drug, DNA triplex, DNA synthesis, Chemical modification

Triplex-forming oligonucleotides (TFOs), which can bind to the major groove of DNA duplex, are expected to be available for inhibition of the targeted gene expression in gene therapy. However, unmodified TFOs have three serious drawbacks: low binding ability to targeted DNA duplex, high dependency to homopurine sequence, and low nuclease resistance. To overcome these problems, many artificial nucleobases and sugar moieties have been reported. In our previous study we found that introduction of 4-thiotymidine ($_sT$) and 2'-deoxy 6-thioguanosine ($_sG$) into antiparallel-type TFOs remarkably increased their binding abilities by the stacking effects of thiocarbonyl groups.

In this study, we synthesized antiparallel TFOs containing *N*-acetyl-2,6-diamino-1,8-quinoline ($^{6DA}Q_{Ac}$) residues as modified nucleobases to improve sequence-dependencies. As a result, it was revealed that $^{6DA}Q_{Ac}$ incorporated into a TFO can selectively bind to T-A base. Moreover, we evaluated their binding abilities and base recognition abilities of TFOs containing $^{6DA}Q_{Ac}$, $_sT$ and $_sG$.



Furthermore, we carried out introduction of the sugar moieties with the cationic groups into TFOs in order to improve their nuclease resistance. In this paper, we will report the synthesis and the properties of antiparallel TFOs containing 5'-amino-5'-deoxy-5'-hydroxymethylthymidine (RT), as shown below.



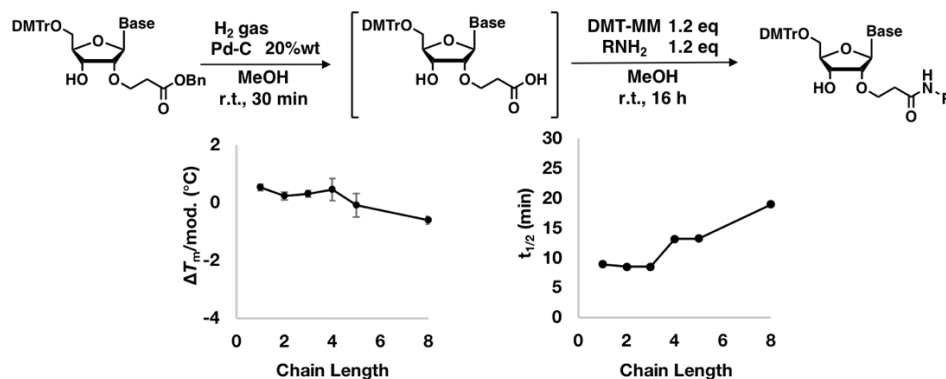
2'-O-アルキルカルバモイルエチル型修飾を持つ人工核酸の合成および性質

○岸村 智太¹、植草 宏哉¹、友利 貴人¹、正木 慶昭¹、清尾 康志¹ (1. 国立大学法人 東京工業大学) Synthesis of oligonucleotides containing 2'-O-alkylcarbamoyl ethyl modifications and their properties. ○Tomohiro Kishimura¹, Koya Uekusa¹, Takahito Tomori¹, Yoshiaki Masaki¹, Kohji Seio¹ (1. *Tokyo Tech.*)

To expand the variety of 2'-O-modified oligonucleotides, we developed efficient synthetic pathway of oligonucleotides containing 2'-O-carbamoylethyl type modification. We established such a synthetic pathway with using 2'-O-benzyloxycarbonylethyl nucleosides. It was able to convert into its carboxylic acid form easily, and then condensation with the appropriate amine gave the desired nucleoside. We synthesized oligonucleotides containing 2'-O-alkylcarbamoylethyl modification with this method. Interestingly, it was revealed that these 2'-O-alkylcarbamoylethyl modifications have a little influence on duplex stability. Also, as the bulkiness of 2'-O-alkylcarbamoylethyl modification increased, the nuclease stability for 3'-exonuclease (SVPDE-1) increased. In addition, we performed MD simulation of duplex. It is suggested that these modification is located into minor groove and the alkyl chain was projecting the outside of duplex.

Keywords : Aziridine; Chemically modified RNA, 2'-O-modification, Hybridization properties, Nuclease resistance, Hydrophobic substituents

核酸に導入可能な修飾の幅を拡充するため、2'-O-カルバモイルエチル型修飾核酸の効率的合成法を開発した。2'-O-ベンジルオキシカルボニルエチルを持つヌクレオシドに対し、接触水素化反応によるカルボキシル基への変換とアミド結合形成反応をワンポットで行なうことにより、2'-O-カルバモイルエチル型修飾を持つ核酸を迅速に合成可能であることを見出した。本手法を用いて直鎖アルキルカルバモイルエチル修飾を持つ核酸を合成し、その性質を評価した。興味深いことに、これらの修飾は、二重鎖の安定性にほとんど影響を与えないことがわかった。また、核酸分解酵素耐性はかさ高さに応じて向上した。さらに、MD シミュレーションを用いて二重鎖の構造を算出したところ、これらの修飾はマイナーグループに位置し、導入したアルキル基は二重鎖の外側に突き出していることがわかった。



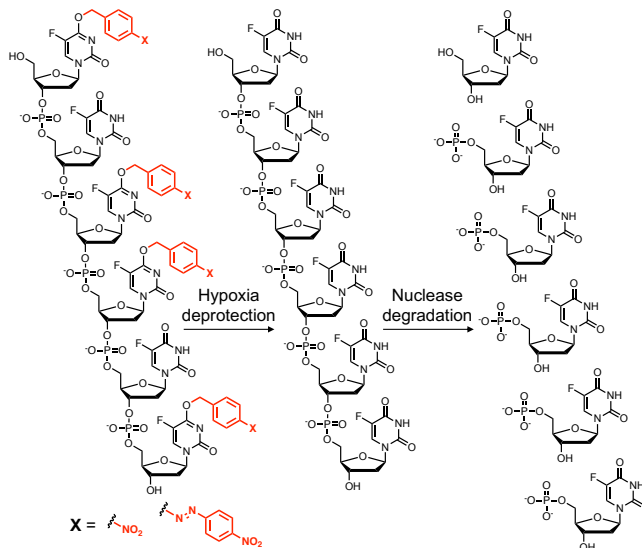
Hypoxia-Activated Floxuridine Oligomers via Bio-reduction of Nitro and/or Azo Functionalities

(¹Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, ²Research Center for Advanced Science and Technology (RCAST), The University of Tokyo) ○Kunihiko Morihoro,¹ Takuro Ishinabe,¹ Masako Takatsu,² Tsuyoshi Osawa,² Akimitsu Okamoto^{1,2}

Keywords: Anticancer Drug; Hypoxia; Nucleic Acids; Bio-reduction; Prodrugs

Chemotherapy is one of the most frequently used methodology for cancer treatment. Although many types of anticancer drugs have been developed and used, their side effects still decrease the therapeutic utility. To overcome this problem, prodrug strategy has been applied. Prodrugs are masked derivatives of drug molecules that undergo enzymatic or chemical transformations to release the active parent drugs, which can exert the therapeutic activity. The cancer specific microenvironment can be used as a trigger of selective prodrug activation and hypoxia is a distinctive feature of various diseased cells including cancer.¹⁾

We designed and synthesized three types of floxuridine prodrug monomers **FdU^{NO2}**, **FdU^{Azo}**, and **FdU^{NA}** bearing a nitrobenzyl group, 4-(dimethylamino)azobenzyl group, and 4-nitroazobenzyl group, respectively. **FdU^{NO2}** and **FdU^{Azo}** are directly reduced to the aniline intermediate and subsequent 1,6-elimination gives floxuridine. On the other hand, **FdU^{NA}** requires a two-phased reduction; the nitro group should be reduced at first because 4-nitroazobenzyl moiety is not a substrate of azoreductases. Only after the reduction of nitro group to amino group, the azo moiety of **FdU^{NA}** is reduced to give the aniline intermediate. As we expected, all three floxuridine prodrug monomers showed cytotoxicity only under hypoxia conditions ($O_2 = 1\%$). We also synthesized and evaluated floxuridine prodrug oligomers and will discuss in vitro and in vivo results (Figure).



1) J. Liu, W. Bu, J. Shi, *Chem. Rev.* **2017**, *117*, 6160.

小型高効率光増感剤の開発とグアノシンの配列選択的光酸化への応用

(東工大・生命理工) ○金森 功吏・津賀 雄輝・浜本 航治・汪 潮・遊部 智大・李 若瑜・金子 翔大・湯浅 英哉

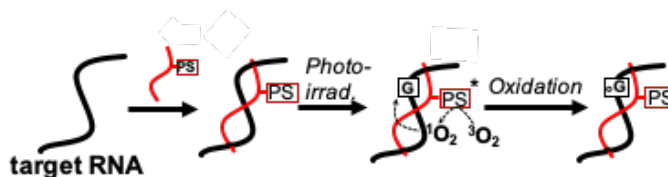
Development of a small, efficient photosensitizer and application to sequence-selective photo-oxidation of guanosine (*School of Life Science and Technology, Tokyo Institute of Technology*)

○Takashi Kanamori, Yuki Tsuga, Koji Hamamoto, Chao Wang, Tomohiro Yube, Ruoyu Li, Shota Kaneko, Hideya Yuasa

Aiming for a spatiotemporal gene control method by photoirradiation, we developed photosensitizer (PS)-oligonucleotide conjugates. Upon photoirradiation, guanosine (G) in the target strand is photooxidized to give 8-oxoG with further oxidized derivatives. The so-far developed PS-oligonucleotide conjugates have a disadvantage of low target selectivity possibly due to the large size of the PSs. We have tried to overcome these problems by using our own small, efficient PS. We will present our recent study on the photooxidation of model oligo duplexes incorporating the small PS.

Keywords : Photosensitizer; 8-oxo-guanosine; optical gene regulation; photodynamic therapy

DNA や RNA 中のグアニン塩基 (G) は、活性酸素種等によって 8-oxo-G へと酸化され、さらに酸化されると鎖切断を引き起こす。この 8-oxo-G は、光増感剤 (PS) を介する光酸化によっても生じ、DNA 中では一部チミン塩基として認識され変異を引き起こし、RNA 中では翻訳を阻害することが知られている。つまり、PS を導入したオリゴ核酸 (ON) を用いれば、特定の G を光酸化し、時空間分解能を有する変異導入や翻訳阻害によって、光遺伝子編集、光遺伝子ノックダウンが可能となる。PS-ON 複合体による光酸化の先行研究では、複数の G を酸化してしまう選択性の低さ等の課題があった。これは、PS が ON の末端にリンカーを介して結合されていることと、PS 自体の大きさに由来すると考えられる。一方、我々は独自の分子設計に基づく小型 PS の開発を行ってきた。^{1,2} なかでもビフェニル型 PS² は、重原子を含まない低分子 (MW 約 230) ながら、スピン軌道相互作用に基づく項間交差によって高い ¹O₂ 生成量子収率 (Φ 0.93, λ_{ex} 405 nm) を有し、二光子励起 (800 nm) によっても光増感可能で生体応用も期待される。そこで本研究では、この小型 PS を二重らせんの主溝に配置し、近接効果によって特定の G の選択的光酸化を目指した。発表では、これらの PS の合成ならびに光増感能と増感機構、PS-ON 複合体を用いた G の光酸化の詳細について発表する。



1) T. Kanamori; A. Matsuyama; H. Naito; Y. Tsuga; Y. Ozako; S. Ogura; S. Okazaki; H. Yuasa, *J. Org. Chem.* **2018**, 83, 13765-13775.; 2) Y. Tsuga; M. Katou; S. Kuwabara; T. Kanamori; S. Ogura; S. Okazaki; H. Ohtani; H. Yuasa, *Chem. Asian J.* **2019**, 14, 2067-2071.

短鎖 Ag-DNA ワイヤーの溶液中での形成と結晶構造

(神奈川大学) ○厚木 隆裕¹、近藤 次郎²、小野 晶¹

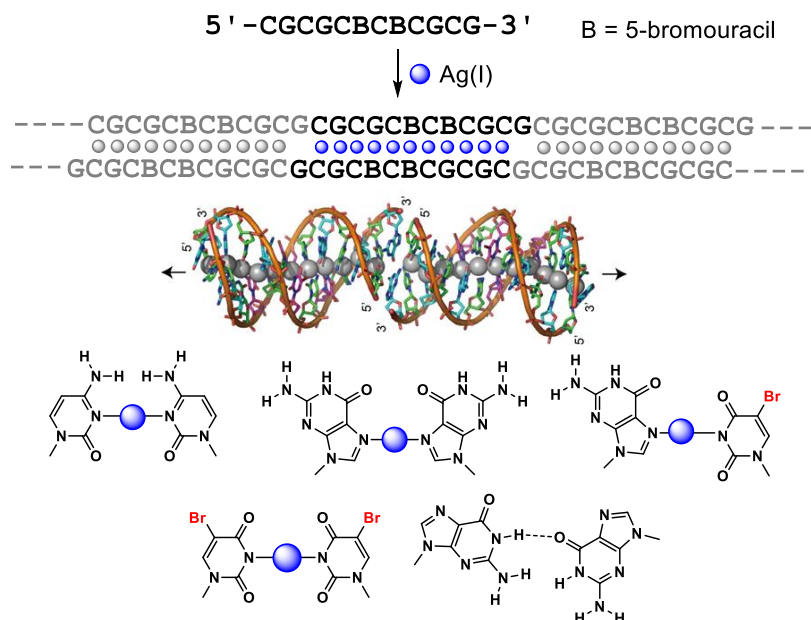
Formation in solutions and crystal structure of a novel short Ag-DNA wire (¹*Department of Materials & Life Chemistry, Faculty of Engineering, Kanagawa University*, ²*Department of Materials and Life Sciences Faculty of Science and Technology, Sophia University*)

○Takahiro Atsugi¹, Jiro Kondo², Akira Ono¹

Recently, the crystal structure of Ag-DNA wire consisting metallo-base pairs has been reported. Ag-DNA wires have been observed in crystals. However, formations of metal-DNA wires in solution state have not been confirmed. In this report, we describe a crystal structure of a short Ag-DNA wires containing 11 Ag(I) ions. Also, Ag(I) – oligonucleotide interactions in solutions were studied by NMR.

Keyword: metallo-base pairs; Ag DNA wire; DNA nanowire; crystal structure; NMR;

ワトソン-クリック塩基対を金属塩基配位錯体で置換した金属媒介塩基対（メタロ塩基対）を含む二重体が発見されており、金属イオンを媒介させた天然、人工塩基対の広範囲な研究は、機能性 DNA 分子の設計の可能性を大きく広げている¹⁾。最近、金属-DNA ワイヤー（DNA 二重鎖中に金属イオンが連続するワイヤー構造）が報告された²⁾。これらの金属-DNA ワイヤーは結晶中で確認されたが、溶液中で形成される実験的証拠が十分ではなかった。本発表では、11 個の Ag(I)イオンを含む短鎖の Ag-DNA ワイヤーの結晶構造を報告する。また、溶液中での挙動を観察した。



- 1) Y. Tanaka, *et al.*, *Chem. Comm.*, **2015**, 51, 17343; Y. Takezawa, *et al.*, *Chem. Lett.*, **2017**, 46, 622.
- 2) J. Kondo, *et al.*, *Nature Chemistry*, **2017**, 9(10), 956-960; A. Ono, *et al.*, *Angew. Chem. Int. Ed.*, **2019**, 58, 16835-16838.

Metal-dependent Stabilization of DNA Duplexes Containing 2-Oxo-imidazole-4-carboxylate/carboxamide as Nucleobases

(Graduate School of Science, The University of Tokyo) ○Lingyun Hu, Yusuke Takezawa, Mitsuhiko Shionoya

Keywords: Metal-mediated base pair; Cu(II) ion; 2-Oxo-imidazole-4-carboxylate; 2-Oxo-imidazole-4-carboxamide; Artificial DNA.

The versatility and programmability of DNA structures have intrigued researchers to design and incorporate novel unnatural base pairs into DNA in a bid to enrich its structural diversity. Among several categories, metal-mediated base pairs, consisting of two ligand-type artificial nucleobases and a bridging metal ion, have gained increasing attention due to its unique coordination binding mode.¹ In addition to thermal stabilization of the duplexes, metal-mediated base pairing also allows for metal-dependent control of functional DNAs such as DNAzymes.^{2,3} Finding suitable ligand-type nucleobases that can specifically and strongly bind to a certain metal ion within a DNA structure is thus important for achieving such functions.

In this study, we synthesized DNA duplexes containing a pair of 2-oxo-imidazole-4-carboxylate (**X**) nucleobases (Fig. 1a) and its carboxamide derivatives (**Y**).⁴ Melting analysis in the presence of various transition metal ions revealed that the duplex containing an **X–X** pair was very unstable on its own, but was stabilized by the addition of 1 equiv of Cu^{II} ($\Delta T_m = +20$ °C) (Fig. 1b). This result indicates the formation of a Cu^{II}-mediated **X–Cu^{II}–X** base pair in the duplex, which was also confirmed by ESI-TOF mass spectrometry. It is likely that the **X** nucleobases coordinated to the Cu^{II} ion via the carboxylate O[−] and the endocyclic N atoms to form a neutral complex.

In contrast, the duplex containing a **Y–Y** pair showed no significant stabilization upon metal addition ($\Delta T_m = -1$ °C), showing that the replacement of the O[−] with NH₂ loses such coordination affinity. Furthermore, the **X** base was found to form a Hg^{II}-mediated base pair in a Cl[−]-free buffer ($\Delta T_m = +11$ °C). The highly stable **X–Cu^{II}–X** base pair is promising for applications in the development of metal-responsive DNA materials.

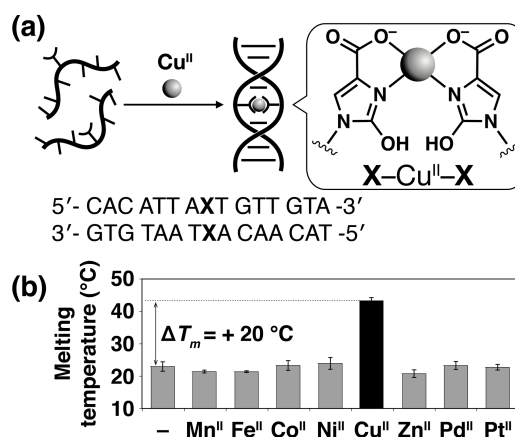


Figure 1. (a) Scheme of metal-mediated base pairing. (b) Duplex melting temperatures (T_m) in the presence of various metal ions. [DNA duplex] = 2 μ M, [metal ion] = 2 μ M, in 10 mM HEPES buffer (pH 7.0), 100 mM NaCl. $N = 3$. Error bars: S. D.

[1] Y. Takezawa *et al.*, *Chem. Lett.* **2017**, 46, 622. [2] Y. Takezawa *et al.*, *J. Am. Chem. Soc.* **2019**, 141, 19342. [3] Y. Takezawa, L. Hu, *et al.*, *Angew. Chem. Int. Ed.* **2020**, 59, 21488. [4] C. Cadena-Amaro *et al.*, *Tetrahedron* **2005**, 61, 5081.

DNA-based Molecular Switches Driven by Metal Complexation of 5-Hydroxyuracil Nucleobases

(¹Grad. School of Science, The Univ. of Tokyo) ○Keita Mori,¹ Yusuke Takezawa,¹ Mitsuhiro Shionoya¹

Keywords: Metal-mediated base pair; 5-Hydroxyuracil; Molecular switch; DNA nanotechnology; Artificial DNA

Switching DNA structures and functions in response to external stimuli is attracting increasing attention as a means of developing dynamic supramolecules for various applications. Metal complexation is a useful trigger for manipulating such DNA-based molecular switches due to its reversible and ligand-specific properties. Previously we found that 5-hydroxyuracil (U^{OH}) bases form metal-mediated $\text{U}^{\text{OH}}\text{-Gd}^{\text{III}}\text{-U}^{\text{OH}}$ base pairs as well as hydrogen-bonded $\text{U}^{\text{OH}}\text{-A}$ pairs (Fig. 1a).¹ Herein, we report metal-responsive DNA molecular switches based on the Gd^{III} -dependent base pairing of U^{OH} .

We first designed a U^{OH} -containing DNA tweezer with four DNA strands, based on the previous work using natural strands (Fig. 1b).² Without Gd^{III} ions, strand **d** is bound to the tweezers through $\text{U}^{\text{OH}}\text{-A}$ pairing to make the tweezers closed. When Gd^{III} ions are added, strand **d** is released via intramolecular $\text{U}^{\text{OH}}\text{-Gd}^{\text{III}}\text{-U}^{\text{OH}}$ complexation, thus resulting in opening of the tweezers. FRET and native PAGE analyses showed that the percentage of the open tweezers was increased from *ca.* 30% to 90% by the addition of Gd^{III} ions. Reversible actuation of the tweezers was also demonstrated under isothermal conditions.

Next, $\text{U}^{\text{OH}}\text{-Gd}^{\text{III}}\text{-U}^{\text{OH}}$ complexation was utilized to trigger a hybridization chain reaction (HCR) which is a signal amplification method well-known in the field of DNA nanotechnology (Fig. 1c).³ The DNA sequence was designed so that the toehold region in strand **e** is exposed after Gd^{III} -triggered switching from $\text{U}^{\text{OH}}\text{-A}$ to $\text{U}^{\text{OH}}\text{-Gd}^{\text{III}}\text{-U}^{\text{OH}}$, initiating strand displacement reactions with hairpins **f** and **g** to yield long DNA duplexes. Native PAGE and fluorescence-based analyses showed that the Gd^{III} addition accelerated the HCR as expected. The detailed mechanism and kinetics will be discussed in the presentation.

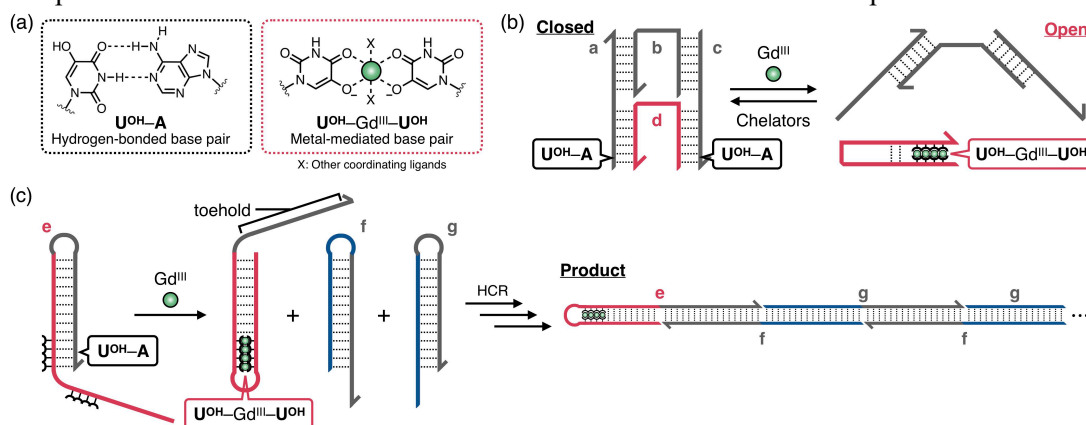


Fig. 1 (a) Gd^{III} -dependent base pairing of 5-hydroxyuracil (U^{OH}) nucleobases. (b) Design of Gd^{III} -responsive DNA tweezers containing U^{OH} bases. (c) Design of Gd^{III} -triggered hybridization chain reaction (HCR) driven by intramolecular switching from $\text{U}^{\text{OH}}\text{-A}$ pairs to $\text{U}^{\text{OH}}\text{-Gd}^{\text{III}}\text{-U}^{\text{OH}}$ pairs.

1) Y. Takezawa *et al.*, *Chem. Eur. J.* **2015**, *21*, 14713. 2) B. Yurke *et al.*, *Nature* **2000**, *406*, 605. 3) R. M. Dirks *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 15275.

Photocontrolled assembly of DNA origami nanostructures using photoswitching molecules

(¹Department of Chemistry, Graduate School of Science, Kyoto University, ²Institute for Integrated Cell-Material Sciences, Kyoto University)

Shubham Mishra¹, Soyoung Park¹, Tomoko Emura¹, Kumi Hidaka¹, Hiroshi Sugiyama^{1,2}, Masayuki Endo^{1,2}

Keywords : DNA origami, photoswitch, programmed assembly, single-molecule observation

There has been significant research on stimuli-responsive molecules for the purpose of mechanical of biomolecules.¹ A class of molecules called Arylazopyrazole (AAP) was recently developed and shows photoisomerization activity, displaying a faster response to light-induced conformational changes and unique absorption spectral properties compared with those of conventionally used azobenzene.² Herein, it is shown how AAP can be used as a photoswitching molecule to control photoinduced assembly and disassembly of DNA origami nanostructures. An AAP-modified DNA origami was designed and constructed and it was observed that the repeated assembly and disassembly of AAP-modified X-shaped DNA origami and hexagonal origami with complementary strands can be achieved by alternating UV and visible-light irradiation. Closed and linear assemblies of AAP-modified X-shaped origami were successfully made to form by photoirradiation, and more than 1 μm linear assemblies were formed. Finally, it is shown that the two photoswitches, AAP and azobenzene,³ can be used together to independently control different assembly configurations by using different irradiation wavelengths (Figure 1). AAP can extend the repertoire of available wavelengths for photoswitches and stably result in the assembly and disassembly of various DNA origami nanostructures.⁴

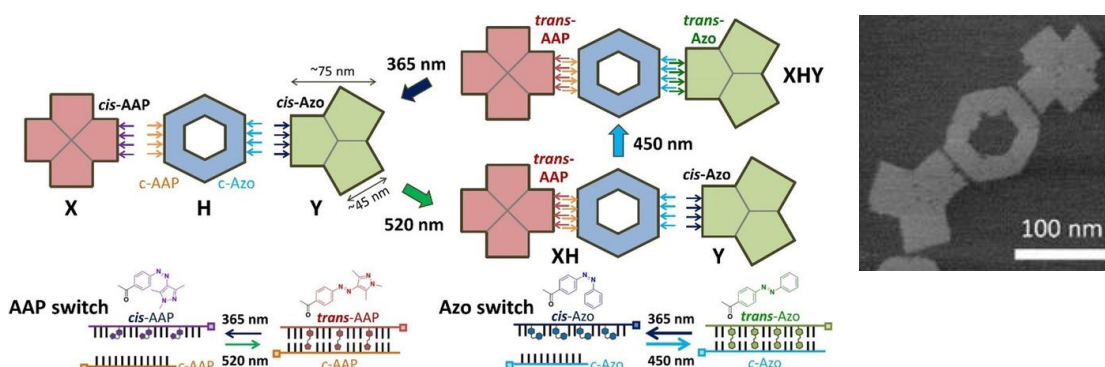


Figure 1. Photo-induced selective DNA origami assembly using AAP and azobenzene photoswitches with photoirradiation at corresponding wavelengths. AFM image of hetero timer assembly.

1. F. Wang, X. Liu, I. Willner, *Angew. Chem. Int. Ed.* **2015**, 54, 1098–1129.
2. V. Adam, D. K. Prusty, M. Centola, M. Skugor, J. S. Hannam, J. Valero, B. Klockner, M. Famulok, *Chem. Eur. J.* **2018**, 24, 1062–1066.
3. X. Liang, T. Mochizuki, H. Asanuma, *Small* **2009**, 5, 1761–1768.
4. S. Mishra, S. Park, T. Emura, H. Kumi, H. Sugiyama, M. Endo, *Chem. Eur. J.* **2021**, 27, 778–784.

[A24-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Satoshi Abe, Osami Shoji

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 24 (Online Meeting)

[A24-1am-01] Features and properties of catalytic antibody, H34, capable of degrading an immune checkpoint PD-1 molecule.○Emi Hifumi¹, Hiroaki Taguchi², Tamami Nonaka¹, Taizo Uda³ (1. Oita University, 2. Suzuka University of Medical Science, 3. ISIT)

9:00 AM - 9:20 AM

[A24-1am-02] Production and properties of a bifunctional catalytic antibody that simultaneously degrades two types of antigens (Tau & A β) (II)○Taizo Uda¹, Hiroaki Taguchi², Tamami Nonaka³, Emi Hifumi³ (1. ISIT, 2. Suzuka University of Medical Science,, 3. Oita University)

9:20 AM - 9:40 AM

[A24-1am-03] The unfolding mechanism of Pseudoazurin determined by Small Angle Neutron Scattering and Molecular Dynamics simulation○Attila Taborosi¹, Takahide Yamaguchi^{1,2}, Seiji Mori¹, Takamitsu Kohzuma^{1,2} (1. Ibaraki University, 2. Frontier Research Center for Applied Atomic Sciences)

9:40 AM - 10:00 AM

[A24-1am-04] Properties of Prussian blue encapsulated in the cavity of ferritin L134P mutant○Yuta Ikenoue¹, Takanori Nishioka¹, Hiroshi Nakajima¹ (1. Osaka City Univ.)

10:00 AM - 10:20 AM

[A24-1am-05] Construction of aromatic clusters in protein cages.○Hiroki Noya¹, Yuki Hishikawa¹, Basudev Maity¹, Satoshi Abe¹, Takafumi Ueno¹ (1. School of Life Science and Technology, Tokyo Institute of Technology)

10:20 AM - 10:40 AM

[A24-1am-06] Accumulation of aromatic molecules and reaction control in a protein cage○Yuki Hishikawa¹, Hiroki Noya¹, Basudev Maity¹, Satoshi Abe¹, Takafumi Ueno¹ (1. Tokyo Institute of Technology)

10:40 AM - 11:00 AM

[A24-1am-07] Dimerization of Heme Acquisition System Protein A (HasA) with Meso-substituted Porphyrin Dimer○Garyo Ueda¹, Yuma Shisaka¹, Erika Sakakibara¹, Shinya Ariyasu¹, Hiroshi Sugimoto^{2,3}, Osami Shoji^{1,3} (1. The Univ. of Nagoya, 2. Institute of Physical and Chemical Research, SPring8, 3. JST CREST)

11:00 AM - 11:20 AM

[A24-1am-08] Construction of Heme Protein HasA Capturing Artificial Metal Complexes for Novel Biocatalysts○Erika Sakakibara¹, Yuma Shisaka¹, Hiroshi Sugimoto^{2,3}, Osami Shoji^{1,3} (1. Grad. Sch. Sci., Nagoya Univ., 2. RIKEN SPring-8 Center, 3. JST-CREST)

11:20 AM - 11:40 AM

免疫チェックポイント PD-1 分子を分解する抗体酵素 H34 クローンの特徴と性質

(大分大¹・鈴鹿医療大²・九州先端研³) ○一二三恵美¹・田口博明²・野中玲実¹・宇田泰三³

Features and properties of catalytic antibody, H34, capable of degrading an immune checkpoint PD-1 molecule (¹Research Promotion Institute, Oita University, ²Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science, ³Nanotechnology Laboratory, ISIT,) ○Emi Hifumi,¹ Hiroaki Taguchi,² Tamami Nonaka,¹ Taizo Uda³

Programmed cell death 1 (PD-1), which was discovered by Honjo *et al.* in 1992, is an immune checkpoint molecule regulating T-cell function. Preventing PD-1 binding to its ligand PD-L1 has emerged as an important tool in immunotherapy. The antibody to PD-1 induces the inhibition of binding of PD-1 with the ligand PD-L1 expressed on cancer cells. The antibody is working as an effective anticancer agent. Here, we report the development of a catalytic antibody H34 clone which could degrade PD-1 molecule and showed a novel function to block PD-1/PD-L1 interaction.

Keywords : Catalytic antibody; Immune checkpoint; PD-1; PD-L1

【目的】免疫チェックポイント PD-1 分子は、T 細胞上に発現し、本席らが 1992 年に発見して世界的に注目を集めている。PD-1 に対する抗体は、がん細胞上に発現している PD-L1 による PD-1 への結合阻害を惹起し、有効な抗癌剤として使用されている。我々は抗体酵素研究を続ける過程で、PD-1/PD-L1 の相互作用を阻止する機能を有する抗体酵素 H34 クローンを開発したので報告する。

【実験手法】ヒト型抗体酵素バンクはボランティアから抗体遺伝子を取得し、クローニング後、大腸菌 BL21(DE3)pLysS に形質転換し IPTG で発現誘導後、培養上清の可溶性画分を回収し、Ni-NTA (QIAGEN) カラムクロマトにより精製した。酵素活性は、合成基質 FRET-PD-1 が抗体酵素により分解される際の蛍光強度を測定する事と、recombinant PD-1 の分解実験から評価した。

【結果と考察】45 種類のヒト型抗体酵素を screening したところ、Pro95 を欠失している H34 が FRET-PD-1 を分解する特徴的な性質を示した。H34 は FRET-PD-1 を $K_m=3.32 \times 10^{-6} \text{ M}$, $k_{cat}=1.3 \times 10^{-2} \text{ min}^{-1}$ 、触媒効率 (k_{cat}/K_m) = $1.96 \times 10^3 / \text{M}^{-1}\text{min}^{-1}$ で切断した。切断サイトは Gln¹³² - Ile¹³³ であった。また、recombinant PD-1 に対しても反応時間 24 時間で 2 つの明確な分解断片を与える事を確認した。PD-1 分解活性を有する H34 が PD-1/PD-L1 相互作用を阻害することは ELISA でも確認した。加えて、H34 は 6 時間の反応で PD-1 分子を半分以上分解する事が判明した。この H34 は Pro95 を欠失しているクローンであるが、Pro95 を付与した変異体を作製し、同様な実験を試みたところ、この変異体は全く酵素活性を示さなかった。この事実は Pro95 が抗体の酵素活性の發揮に大きく寄与する事を指摘した先の報告と一致した¹⁾。

1) E. Hifumi et al., *Science Advances*, **6**(13), eaay6441(2020).

2 種類の抗原 (Tau & A β) を同時分解する 2 機能型抗体酵素の作製と性質 (II)

(九州先端研¹・鈴鹿医療大²・大分大³) ○宇田泰三¹・田口博明²・野中玲実³・
一二三恵美³

Production and properties of a bi-functional catalytic antibody that simultaneously degrades two types of antigens (Tau & A β) (II) (¹*Nanotechnology Laboratory, ISIT*, ²*Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science*, ³*Research Promotion Institute, Oita University*) ○Taizo Uda,¹ Hiroaki Taguchi,² Tamami Nonaka,³ Emi Hifumi³

Alzheimer's disease (AD) is a major cause of dementia, and the latest research attributed it to the formation of extracellular Amyloid-beta (A β) aggregates and intracellular neurofibrillary tangles caused by Tau protein. Therefore, we attempted to produce a bi-functional catalytic antibody capable of simultaneously degrading both of these antigenic molecules by genetically combining two kinds of catalytic antibodies. The bi-functional catalytic antibody could decompose two antigenic molecules. In addition, an amino acid mutation that can increase the activity of catalytic antibody was performed. As some interesting results were obtained, we will report them in detail.

Keywords : *Catalytic antibody; Tau protein; Beta-amyloid; Bi-functional*

【目的】アルツハイマー病 (AD) は認知症の主な原因であり、最新の研究では細胞外 Amyloid-beta(A β)凝集体の生成と Tau 蛋白質による細胞内過リン酸化神経原線維変化がその要因とされている。そこで、これらの両分子を同時に分解できる 2 機能型抗体酵素の作製を試みると同時に、これら 2 種類の酵素活性がより向上するアミノ酸変異を加えたところ、興味あるいくつかの結果を得たので詳しく報告する。

【実験手法】A β ペプチドおよび Tau 蛋白質をそれぞれ分解可能なヒト型抗体酵素遺伝子をリンカーで繋ぎ、pET20b (+)に組み込んだ。次いで大腸菌 BL21(DE3)pLysS に形質転換し IPTG で発現誘導し、培養上清の可溶性画分を回収後、Ni-NTA (QIAGEN) カラムクロマトにより精製した。酵素活性は、FRET-A β および FRET-Tau を化学合成し、これらが抗体酵素により分解されときの蛍光強度を測定する事により評価した。

【結果と考察】#7TR クローンは A β の Gly20-Ala21 間を¹⁾、また、S5 クローンは Tau の Gly21-Asp22 間等のペプチド結合を切断する抗体酵素である。本研究では両クローンの可変領域部分を Linker ((Gly₄Ser)₃)で繋ぎ scFv 型分子とした。次いで、この scFv 型分子を発現・精製後、FRET-A β および FRET-Tau と反応させたところ、同 scFv 型分子は A β および Tau ペプチドをそれぞれ分解した。さらに申請者らが最近見出した抗体の酵素活性向上法²⁾を用いて上記 scFv 型のそれぞれの軽鎖可変領域の Pro95 を欠失させたところ、より高い FRET-A β および FRET-Tau 分解活性を示した。本手法で 2 つの抗原を同時に分解する高活性な 2 機能型抗体酵素の作製が可能となった。

1) E. Hifumi, et al., *FASEB Bioadvances*, 1(2), 93-104(2018). 2) E. Hifumi et al., *Science Advances*, 6(13), eaay6441(2020).

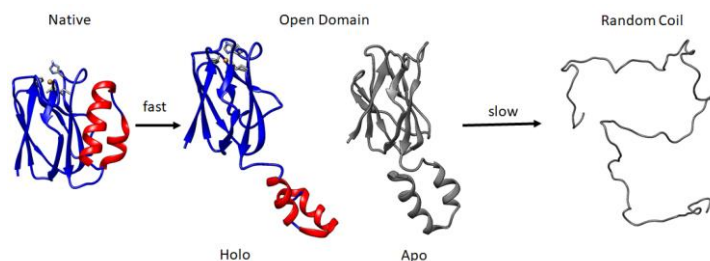
The unfolding mechanism of Pseudoazurin determined by Small Angle Neutron Scattering and Molecular Dynamics simulation

(¹Graduate School of Science and Engineering, Ibaraki University, ²Frontier Research Center for Applied Atomic Sciences, Ibaraki University, ³Australian Neutron Scattering Center, ANSTO) ○Attila Taborosi,¹ Takahide Yamaguchi,^{1,2} Kathleen Wood,³ Andrew Whitten,³ Seiji Mori,¹ Takamitsu Kohzuma,^{1,2}

Keywords: Blue Copper Protein; Pseudoazurin; Unfolding Mechanism; Small Angle Neutron Scattering, Molecular Dynamics

Pseudoazurin (PAz) is a blue copper protein, which function as an electron donor in denitrification process of certain bacteria. The native fold of PAz is composed by the β -barrel structure with two α -helices at the C-terminal, while the Cu ion exist at the surface of protein fold. It has been demonstrated through several of our studies¹⁻⁴ that the stability of PAz depends on the noncovalent weak interactions in the second coordination sphere at the active site. Furthermore, the CD and ESI-MS experiments identified the “folded-holo”, “folded-apo” and “unfolded-apo” forms of PAz under the acidic pH condition. It was also found that the structure around at pH 3 seemed to be an intermediate state between folded and fully unfolded state.

Therefore, further investigation had been done on the unfolding mechanism of PAz WT and two Met16 variants (Phe16 and Ile16) with Small Angle Neutron Scattering (SANS) at ANSTO and Constant pH Molecular Dynamics (CpHMD) methods. The structure of each states were analyzed by SANS, especially the determination of the partially unfolded state at pD 3.0. The structure at pD 3.0 was “Open-Domain” form, where the α -helices is detached from β -barrel domain. The CpHMD simulation, verified by the experimental and theoretical R_g comparison, confirmed this Open-Domain form as the intermediate state of protein unfolding. Also, the CpHMD simulation revealed the reason of the dissociation of α -helices from the β -barrel as the starting step of the unfolding. The kinetic SANS experiment of unfolding process for WT, Met16Phe and Met16Ile verified the existence of Open Domain, and the difference in the rate constants approved the stability variation between WT and Met16 variants.



1) R. F. Abdelhamid, *J. Inorg. Biochem.* **2008**, 102 (5-6), 1373. 2) M. B. Fitzpatrick, *J. Inorg. Biochem.* **2010**, 104 (3), 250 3) T. Yamaguchi, *Protein Sci.* **2017**, 26 (10), 1921 4) T. Yamaguchi, *Chem. Lett.* **2020**, 49 (12) 1456

Properties of Prussian blue encapsulated in the cavity of ferritin L134P mutant

(Graduate School of Science, Osaka City University) ○Yuta Ikenoue, Takanori Nishioka, Hitoshi Nakajima

Keywords: Ferritin; Prussian blue; Redox reaction

Ferritin¹ is a ubiquitous iron storage protein in mammals bodies. It consists of 24 monomer subunits to form a spherical hollow structure. We have succeeded in synthesizing Prussian blue (PB) incorporated in the cavity of ferritin L134P mutant (FrL134P). The composite of PB with the ferritin mutant (PB@FrL134P, Figure 1) showed high solubility to aqueous media. In addition, the inherent instability of PB in alkaline solution was effectively improved for PB@FrL134P; the degradation rates were 10^3 times slower at pH 9 and pH 10 than that of colloidal PB prepared conventionally. The result suggested that the ferritin cavity imparts the tolerance under alkaline conditions to PB by the enclosure with the protein shell. In analogy with the colloidal PB, PB@FrL134P showed catalytic activity in the oxidation reaction of 3,3',5,5'-Tetramethylbenzidine (TMB) in the presence of H_2O_2 . The lower pH of the solution was preferable to the higher catalytic performance of PB@FrL134P.

The UV-Vis spectra of PB@FrL134P showed reversible peak shifts in the IVCT band of PB@FrL134P depending on the solution pH. The treatment of PB@FrL134P with KCN suppressed the catalytic activity. These observations suggested that PB in PB@FrL134P was enriched at vacant coordination sites on iron ions occupied by water molecules, and these vacant sites were associated with the enhanced catalytic activity of PB@FrL134P.

The complete digestion of PB@FrL134P with proteinase K resulted in the recovery of PB species accompanied by a residual peptide. Despite the exposure to bulk solution, the recovered PB species maintained the high stability to alkaline solutions and the catalytic activity. This result suggested that the interior PB was protected by the protein shell in addition to the isolation from bulk solution, possibly through the interaction with amino acid residues located in the inner surface. The peptide interacted with interior PB will be identified by the study in progress.

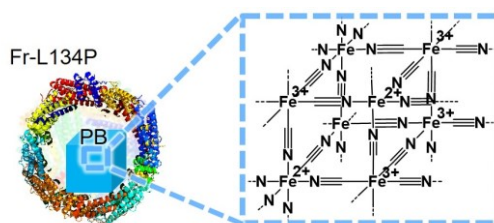


Figure 1. PB@Fr-L134P

1) P. M. Harrison, P. Arosio, *Biochim. Biophys. Acta. Bioenerg.*, **1996**, 1275, 161–203.

タンパク質ケージを利用した芳香族クラスターの構築

(東工大院生命理工¹) ○野谷大樹¹・菱川湧輝¹・Basudev Maity¹・安部聡¹・上野隆史¹
 Construction of aromatic clusters in protein cages. (¹*School of Life Science and Technology, Tokyo Institute of Technology*) ○Hiroki Noya,¹ Yuki Hishikawa,¹ Basudev Maity,¹ Satoshi Abe,¹ Takafumi Ueno¹

Aromatic interactions, such as π - π interactions, have been studied extensively in chemistry and molecular biology, and their applications in biomaterials have attracted much attention. Aromatic clusters consisting of multiple aromatic amino acids within proteins stabilize their structures and bind to foreign molecules. However, the understanding of the structures, physical properties, and chemical reactivities of the aromatic rings by precise control of the number and orientation has not been achieved at the atomic level. In this study, we designed aromatic clusters in the internal space of a protein cage by amino acid substitution. We determined the detailed structures of clusters and elucidated the physicochemical properties of the protein cage.

We used ferritin, which is composed of 24-mer and has internal space with an inner diameter of 8 nm. We introduced phenylalanine into the 2-fold symmetrical interface of ferritin and determined the orientation of the aromatic rings by X-ray crystallography. As a result, it was found that the aromatic rings had different orientation by changing the number and position of phenylalanine.

Keywords : Aromatic clusters; Protein cage; X-ray crystallographic analysis

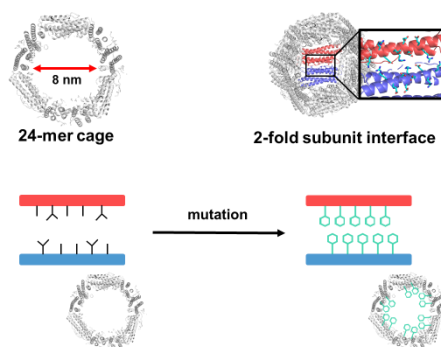


Figure 1. Schematic view of construction of aromatic clusters in protein cage.

π - π 相互作用などの芳香環相互作用は、化学や分子生物学などの分野で広く研究されており、中でも生体材料への応用が大きな注目を集めている¹⁾。タンパク質内部に存在する芳香族アミノ酸が複数密集して形成される芳香族クラスターは、立体構造の安定化や外来分子との結合に関わっていることが知られている²⁾。しかし、タンパク質内での芳香環の数や配向の精密な制御による芳香環クラスターの詳細な構造と物性、反応性の理解は十分に得られていない。そこで本研究では、対称的な構造を持つタンパク質ケージの内部空間にアミノ酸置換による芳香族アミノ酸の導入により芳香族クラスターを構築し、その詳細な構造決定とタンパク質ケージに与える物理化学的性質の解明を目的とした。

タンパク質ケージには 24 量体として内径 8 nm の内部空間を有するフェリチンを用いた。まず、フェリチンの 2 個のサブユニットから成る対称界面にフェニルアラニンを導入し、X 線結晶構造解析により芳香環の配向を決定した (Figure 1)。その結果、導入するフェニルアラニンの個数と位置を変化させることによって、芳香環が異なる配向を示すことが分かった。現在は、様々な変異体の結晶構造決定と、芳香族アミノ酸残基の違いによって生じる芳香族クラスターへの影響について比較検討を進めている。

1) Tao Chen *et al.*, *Cryst Growth Des.* **2018**, 18, 2765–2783.

2) Bryan T. Martin *et al.*, *Structure.* **2016**, 24, 158-164.

タンパク質ケージ内における芳香族分子集積と反応制御

(東工大生命理工¹) ○菱川 湧輝¹・野谷 大樹¹・Basudev Maity¹・安部 聡¹・上野 隆史¹

Accumulation of aromatic molecules and reaction control in a protein cage (¹*School of Life Science & Technology, Tokyo Institute of Technology*) ○Yuki Hishikawa,¹ Hiroki Noya,¹ Basudev Maity,¹ Satoshi Abe,¹ Takafumi Ueno¹

Aromatic residues are important in controlling protein function such as molecular recognition since they can form aromatic interactions with ligands and nucleic acids and exhibit characteristic orientation and dynamic behaviors. Aromatic clusters constructed using peptides and polycyclic aromatic compounds have unique physical properties and molecular encapsulation. However, the methods for obtaining physical properties and controlling function of aromatic clusters in proteins have not been established. In this study, we report the accumulation and dynamic control of aromatic molecules in proteins by substituting the interior surface of the ferritin cage with aromatic amino acids (Phe). We constructed aromatic clusters and controlled accumulation and reaction of foreign aromatic molecules (Figure 1). The results suggest that the hydrophobic environment within the Phe mutant cage promotes the complexation of foreign molecules.

Keywords : Protein cage; Aromatic amino acid; X-ray crystallography; Molecular dynamics simulation; Fluorescent dye

芳香族アミノ酸は、リガンドや核酸との芳香環相互作用や、特徴的な配向と動的挙動を示し、タンパク質の分子認識などの機能制御において重要である¹⁾。ペプチドや多環式芳香族化合物では、複数の芳香環が密集した芳香族クラスターの構築が試みられており、その特異な物性や分子内包が注目されている²⁾。一方、タンパク質内部の芳香族クラスターの物性や機能制御について、分子レベルの詳細な情報を得る手法は確立されていない。そこで、本研究では、タンパク質中での芳香族分子の集積・運動制御を目指し、フェリチンケージの内部表面を芳香族アミノ酸(Phe)で置換することにより、芳香族クラスターの構築、外来芳香族分子集積、反応制御を行った(Figure 1)。フェリチン野生型との比較から、Phe 変異体ケージ内の疎水的な環境が、外来分子の複合化を促進することが示唆された。

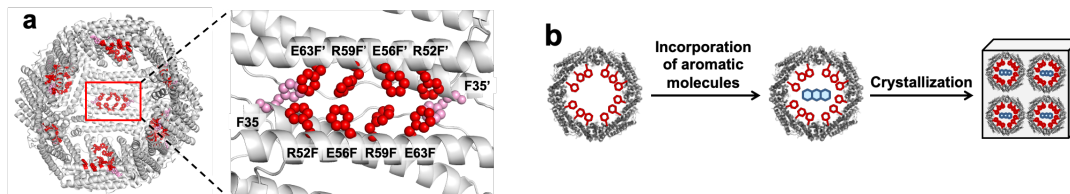


Figure 1. (a) Construction of aromatic clusters in a ferritin cage. (b) Scheme of incorporation of aromatic molecules and crystallization.

1) K. M. Makwana & R. Mahalakshmi, *Protein Sci.* **2015**, 24, 1920.

2) M. Yoshizawa & L. Catti., *Acc. Chem. Res.* **2019**, 52, 2392.

メソ位置換ポルフィリン誘導体によるヘム獲得タンパク質 HasA の二量化

○上田 我竜¹、四坂 勇磨¹、榊原 えりか¹、有安 真也¹、杉本 宏^{2,3}、荘司 長三^{1,3} (名大院理¹・理研 SPring-8²・JST CREST³)

Dimerization of Heme Acquisition Protein HasA with Meso-substituted Porphyrin Derivatives (¹*Grad. Sch. Sci., Nagoya Univ.*, ²*RIKEN SPring-8*, ³*JST CREST*) ○Garyo Ueda,¹ Yuma Shisaka,¹ Erika Sakakibara,¹ Shinya Ariyasu,¹ Hiroshi Sugimoto,^{2,3} Osami Shoji,^{1,3}

Heme proteins are known to have a wide variety of functions such as catalytic properties and sensors, and the research of polymerization of heme proteins have been conducted to improve its functions and stability. Our group previously reported that heme acquisition protein, HasA, which is secreted by some bacteria such as *S. marcescens* and *P. aeruginosa*, can capture meso-substituted porphyrin derivatives. In this study, we attempted to construct HasA dimer with porphyrin dimer so that the chiral interface between two HasA can be used for catalytic reaction and molecular recognition. We designed two types of porphyrin dimers having different linker structures (Fig. 1) and conjugated with HasA. The porphyrin dimer with a hydrophobic linker caused the aggregation of HasA. The average particle size of the HasA aggregates is over 10 times larger than that of HasA monomer. On the other hand, the porphyrin dimer with a flexible and hydrophilic linker successfully constructed the desired HasA dimer (Fig. 2), which is confirmed it with ESI-TOF MS. We plan to synthesize porphyrin dimer bearing hydrophilic rigid linker to construct rigid HasA dimer for the application to catalysts and molecular recognitions.

Keywords : Porphyrin; Protein; Protein Assembly; Heme; HasA

ヘムを補因子とするヘムタンパク質は触媒やセンサーなどの 多種多様な機能を持っており、その機能や安定性の向上などを志向し、多量化させる研究が行われてきた。一方、当研究室では、セラチア菌、緑膿菌などが分泌するヘム獲得タンパク質 HasA がヘム以外にメソ位置換ポルフィリン誘導体を捕捉可能であることを報告した¹⁾。本研究では HasA 間のキラル界面を用いた触媒反応や分子認識を目指し、ポルフィリンダイマーを用いた HasA の二量化を行った。リンカー構造の異なる 2 種類のポルフィリンダイマー (Fig. 1) の設計・合成を行い、HasA との複合化を行ったところ、剛直で疎水的なリンカーを持つポルフィリンダイマーでは単量体の HasA に比べて 10 倍以上の粒径を持つ HasA 凝集体を形成したが、柔軟で親水的なリンカーでは目的の HasA 二量体の構築を ESI-TOF MS により確認した (Fig. 2)。今後は親水的で剛直なリンカーを用いることで、触媒や分子認識への応用を行う予定である。

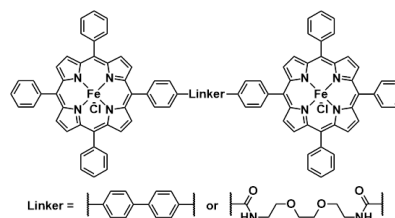


Fig. 1 Synthesized porphyrin dimers

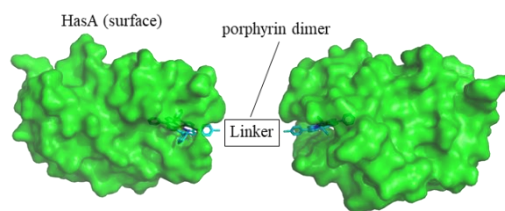


Fig. 2 Molecular modeling of HasA dimers

Blue : Porphyrin Dimer, Green : Protein

1) H. Uehara, *et al.*, *Angew. Chem. Int. Ed.* **2017**, 56, 15279

Construction of Heme Protein HasA Capturing Artificial Metal Complexes for Novel Biocatalysts

(¹Graduate School of Science, Nagoya University, ³RIKEN SPring-8 Center, ⁴JST CREST)

○ Erika Sakakibara¹, Yuma Shisaka¹, Hiroshi Sugimoto^{3,4}, Shinya Ariyasu¹, Osami Shoji^{1,4}

Keywords: Heme protein; Tetraphenylporphyrin; Crystal structure; Biocatalysts

meso-Tetraphenylporphyrin (TPP) is a simple porphyrin that can be synthesized by acid-catalyzed condensation of pyrrole with benzaldehyde in good yield, and its derivatives can be easily prepared by using the corresponding aldehydes. Therefore, TPP and its derivatives have been widely used as multiporphyrin architectures, photosensitizers and catalysts based on their photochemical and redox properties. However, even simple TPP has never been incorporated into native proteins because of the four bulky and hydrophobic phenyl groups on its *meso* positions. It was necessary to find a protein with a space that could accommodate bulky TPP for using unique properties of TPP as prosthetic groups of proteins. Our group focused on heme acquisition protein HasA secreted by *Pseudomonas aeruginosa*. The heme-binding site of HasA is highly exposed to solvent, thereby the moiety of the captured heme can be seen from outside of HasA in the crystal structure of HasA with heme. This notable heme-binding feature allows the accommodation of various artificial metal complexes which are totally different structures from heme.¹⁻⁴

In this study, we constructed the artificial metalloproteins capturing FeTPP by using a HasA. We also succeeded in the X-ray crystal structure analysis of HasA capturing FeTPP (Fig. 1) and evaluated the structural changes induced by FeTPP. To the best of our knowledge, this is the first example of a natural protein that stably binds FeTPP. Furthermore, we found that HasAs containing FeTPP can be used as biocatalysts by tailoring the active site through mutagenesis for the accommodation of substrates.

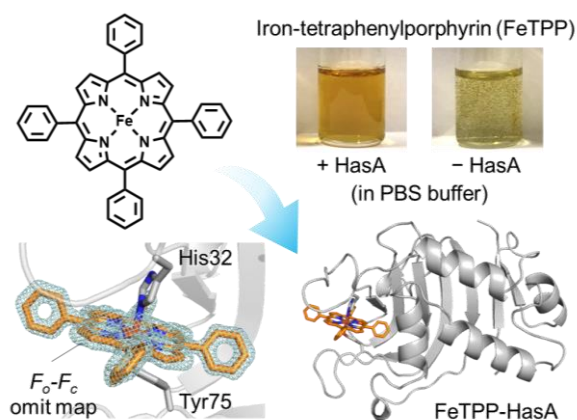


Fig. 1 Crystal structure of FeTPP-HasA

1) C. Shirataki, O. Shoji, M. Terada, S. Ozaki, H. Sugimoto, Y. Shiro, Y. Watanabe, *Angew. Chem. Int. Ed.* **2014**, *53*, 2862. 2) H. Uehara, Y. Shisaka, T. Nishimura, H. Sugimoto, Y. Shiro, Y. Miyake, H. Shinokubo, Y. Watanabe, O. Shoji, *Angew. Chem. Int. Ed.* **2017**, *56*, 15279. 3) E. Sakakibara, Y. Shisaka, H. Onoda, D. Koga, N. Xu, T. Ono, Y. Hisaeda, H. Sugimoto, Y. Shiro, Y. Watanabe, O. Shoji, *RSC Adv.* **2019**, *6*, 18697. 4) Y. Shisaka, Y. Iwai, S. Yamada, H. Uehara, T. Tosha, H. Sugimoto, Y. Shiro, J. K. Stanfield, K. Ogawa, Y. Watanabe, O. Shoji, *ACS Chem. Biol.* **2019**, *14*, 1637.

Academic Program [Oral B] | 18. Polymer | Oral B**[A27-1pm] 18. Polymer**

Chair: Yasuhiro Kohsaka, Kanbayashi Naoya

Fri. Mar 19, 2021 1:00 PM - 3:40 PM Room 27 (Online Meeting)

[A27-1pm-02] Synthesis of unsaturated polyesters via ring-opening polymerization induced by conjugate substitutionKeito Hagiwara¹, [○]Yasuhiro Kohsaka^{1,2} (1. Fac. of Textile Sci. &Tech., Shinshu University, 2. RISM, Shinshu University)

1:20 PM - 1:40 PM

[A27-1pm-03] 2D Polymeric Nanomaterials via MOF-Templated Copolymerization[○]Marta Ximenis Campins¹, Nobuhiko Hosono¹, Takashi Uemura¹ (1. The University of Tokyo)

1:40 PM - 2:00 PM

[A27-1pm-04] Three Dimensionally-Hyperbranched Fe(II)-based Metallo-Supramolecular Polymer for Electrochromic Application[○]Narayana Yemineni¹, Masayoshi HIGUCHI¹ (1. National Institute for Materials Science)

2:00 PM - 2:20 PM

[A27-1pm-05] Ligand Induced Low Operation Voltage Ru-based Metallo-supramolecular Polymer as Energy Saving Electrochromic Film with Long Optical Memory[○]SANTRA Chandra Dines¹, HIGUCHI Masayoshi¹ (1. NIMS)

2:20 PM - 2:40 PM

[A27-1pm-06] Synthesis of Poly(quinolylene-2,3-methylene) Bearing Various Types of Amino Acid Derivatives as the Side Chain: Stability of π -Stacked Helical Architecture[○]Kanbayashi Naoya¹, Yuki Kataoka¹, Taka-aki Okamura¹, Kiyotaka Onitsuka¹ (1.

Department of Macromolecular Science Graduate School of Science Osaka University)

2:40 PM - 3:00 PM

[A27-1pm-07] The mechanochemistry of the cross-linked polymer containing cyclic mechanophores[○]Jumpei Kida¹, Daisuke Aoki¹, Hideyuki Otsuka¹ (1. Dept. of Chem. Sci. and Eng., Tokyo Tech)

3:00 PM - 3:20 PM

[A27-1pm-08] Visualization of Polymer Crystallization and Neck-initiation in Uniaxial Tensile Deformation by Using Fluorescent Mechanochromophore[○]Sota Kato¹, Daisuke Aoki¹, Kazusato Oikawa³, Kousuke Tsuchiya³, Naohiko Shimada², Atsushi Maruyama², Keiji Numata³, Hideyuki Otsuka¹ (1. Dept. of Chem. Sci. and Eng., Tokyo Tech., 2. Dept. of Life Sci. and Tech., Tokyo Tech., 3. RIKEN)

3:20 PM - 3:40 PM

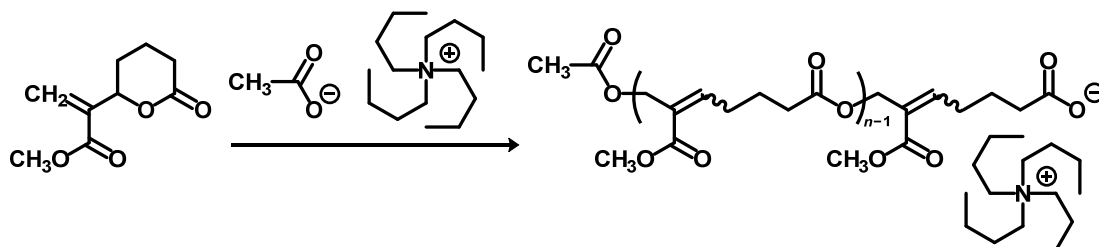
共役置換反応を利用した開環重合による不飽和ポリエステル合成

(信州大繊維¹・信州大先端材料研²) 萩原 敬人¹・○高坂 泰弘^{1,2}Synthesis of unsaturated polyesters via ring-opening polymerization induced by conjugate substitution (¹*Faculty of Textile Science and Technology, Shinshu University*, ²*Research Initiative for Supra-Materials, Shinshu University*) Keito Hagiwara,¹ ○Yasuhiro Kohsaka^{1,2}

Methacrylates, substituted at their allylic position with leaving groups such as halogen atoms and acyloxy groups, undergo nucleophilic conjugate substitution reaction via addition-elimination (S_N2') mechanism. Since the conjugate substitution is applicable with various nucleophiles including carboxylic acids under ambient condition, we have applied it to polymer synthesis and degradation¹. Herein, the ring-opening polymerization (ROP) of lactones by conjugate substitution reaction is reported. Lactone **1** was prepared from δ -valerolactone via four steps. As **1** has a methacrylate skeleton and acyloxy group at the allylic position, ROP by conjugate substitution was expected. In fact, the ROP initiated with $Bu_4N^+OAc^-$ in the presence of K_2CO_3 at 25 °C afforded an unsaturated polyester ($M_n = 3800$, $D = 1.31$). Polymerization in toluene resulted in a similar polymer. As M_n s exhibited a linear increase with conversions, the ROP was living polymerization.

Keywords : conjugate substitution, δ -valerolactone, unsaturated polyester, living polymerization; immortal polymerization

アリル位をハロゲン原子やアシロキシ基で置換したメタクリル酸エステルは、求核剤と付加-脱離 (S_N2') 機構に基づく共役置換反応を起こす。この反応は室温、大気下で実施でき、カルボン酸をはじめ様々な求核種が適用できる点が魅力である。著者らは、共役置換反応を用いた高分子の合成と分解を研究してきた¹。本発表では、共役置換反応に基づくラクTONの開環重合を報告する。ラクTON **1** はメタクリル骨格を持ち、そのアリル位にアシロキシ基を配置した設計で、 δ -バレロラクTONから4段階で合成した。テトラブチルアンモニウムアセテート ($Bu_4N^+OAc^-$) を開始剤に、炭酸カリウム存在下、**1**の開環重合を室温、大気下で実施したところ、不飽和ポリエステルが得られた ($M_n = 3800$, $D = 1.31$)。トルエン中の重合でも類似の結果が得られた。これらの重合では、数平均分子量 M_n がモノマー転化率に応じて直線的に増加したことから、リビング重合であることが明らかになった。一般にラクTONの開環重合は不活性ガス中の禁水条件を要求するが、この重合は通常条件下でもリビング重合が成立する。



1) Y. Kohsaka, *Polym. J.* **52**, 1175–1183(2020).

2D Polymeric Nanomaterials via MOF-Templated Copolymerization

(¹Graduate School of Frontier Sciences, The University of Tokyo, ²Graduate School of Engineering, The University of Tokyo) ○Marta Ximenis,¹ Nobuhiko Hosono,^{1,2} Takashi Uemura^{1,2}

Keywords: Metal-Organic Frameworks; RAFT Polymerization; Block Copolymers.

In recent years, 2D materials have gained importance due to their unique properties derived from their high degree of anisotropy. However, current synthetic procedures are limited to topochemical polymerizations which reduce the monomer scope and consequent polymer growth.¹ Recently, our group developed a synthetic strategy to access unimolecularly thick polymeric networks using two-dimensional pillared-layer type MOFs as template nanoreactors for the free radical polymerization of vinyl monomers.²

In this work, we expand the scope of this novel methodology by using reversible addition-fragmentation chain-transfer (RAFT) polymerization.³ Two consecutive RAFT polymerizations of different monomers in the presence of crosslinker were carried out in identical MOF particles, which provided block-type 2D copolymer networks (Figure 1).

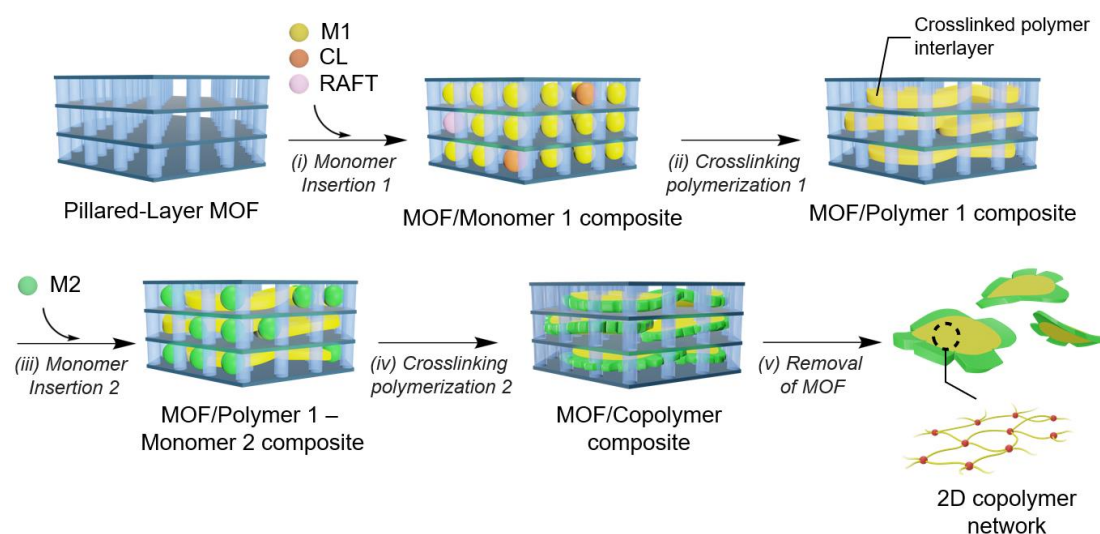


Figure 1. Synthesis of 2D copolymer networks. M1, M2, CL, and RAFT denote the first and second monomers, crosslinker, and raft agent, respectively.

1) a) P. Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, A. D. Schlüter, J. Sakamoto, *Nat. Chem.* **2012**, 4, 287. b) X. Feng, A. D. Schlüter, *Angew. Chem., Int. Ed.* **2018**, 57, 13748 2) N. Hosono, S. Mochizuki, Y. Hayashi, T. Uemura, *Nat. Commun.* **2020**, 11, 3573. 3) J. Hwang, H-C. Lee, M. Antonietti, B. V. K. J. Schmidt, *Polym. Chem.* **2017**, 8, 6204.

Three Dimensionally-Hyperbranched Fe(II)-based Metallo-Supramolecular Polymer for Electrochromic Application

(NIMS) ○Yemini S. L. V. Narayana, Masayoshi Higuchi

Keywords: Metallo-Supramolecular Polymer; Fe(II); Three dimensionally-hyperbranched structure; Electrochromic material

Electrochromic (EC) devices have attracted much attention due to the smart display technology application. The main advantages of metallo-supramolecular polymers (MSPs)-based EC materials to the other EC materials are wide color variation due to the MLCT absorption is adjustable by the combination of the metal and the ligand in the polymers and also show better EC properties.¹ The introduction of a 3D structure to the linear MSP backbone is anticipated to influence the properties like electrochemical, morphology, and thermal stability.² The real sun-shading smart window needs a broad range of the visible region absorption.

In this report, three-dimensionally hyperbranched Fe(II)-based metallo-supramolecular polymer(**polyFe-3D**) was one-step synthesized *via* 5:6 complexation of Fe(II) salt, and an asymmetrical ditopic ligand. The coordination ability of Fe(II) ion to the two different binding sites of **L** was confirmed by the ultraviolet-visible (UV/Vis) titration. The molecular weight of the polymer ($M = 3.96 \times 10^5$ Da) was confirmed by a size-exclusion chromatography-viscometry experiment. The absorption spectrum of **polyFe-3D** has covered a wide visible region from 430 nm to 640 nm. Cyclic voltammogram of **polyFe-3D** showed a single reversible redox wave of the Fe(II)/Fe(III) couple ($E = 0.74$ V). **PolyFe-3D** showed magenta color-to-pale green color electrochromic behavior with good coloration and bleaching times, high coloration efficiency, and switching stabilities and we also fabricated a solid-state electrochromic device (Figure 1).

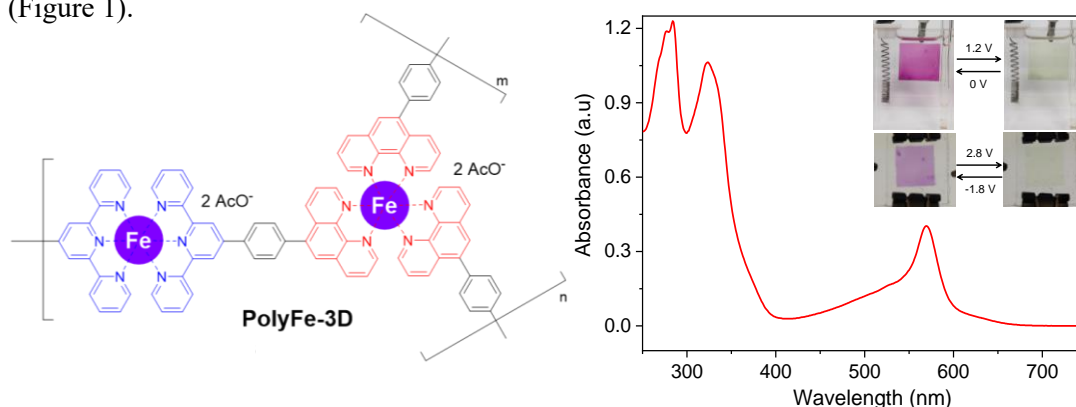


Figure 1. The chemical structure, absorption spectrum, and EC properties of **PolyFe-3D**.

- 1) M. Higuchi, *J. Mater. Chem. C*, **2014**, 2, 9331.
- 2) C.-W. Hu et al. *ACS Appl. Mater. Interfaces*, **2014**, 6, 9118.

Ligand Induced Low Operation Voltage Ru-based Metallo-supramolecular Polymer as Energy Saving Electrochromic Film with Long Optical Memory

(National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. Tel & Fax: 029-860-4721, E-mail: HIGUCHI.Masayoshi@nims.go.jp) ○ Dines Chandra Santra and Masayoshi Higuchi.

Keywords: Low voltage, Metallo-supramolecular polymer, Electrochromism, Devices durability, Optical Memory.

In recent years, considerable interest has been addressed towards smart window in building applications. The effective utilization of electrochromic device (ECD) as “smart window” they must have acceptable levels in performance. Especially, with energy saving and highly stable ECD has received much attention on the development of active smart windows. To realize specific use in buildings large area EC smart windows must shows low power operation, highly stable, fast response, high coloration efficiency and a distinct optical memory effect etc. are important parameters from an industrial perspective. For these purpose metallo-supramolecular polymers have attracted attention and shown benefits as a new type of electrochromic (EC) materials.^{1,2} In a metallo-supramolecular polymer system terpyridine ligands are usually used because of high metallophilic effect with there is a strong metal–ligand chelating effect.

Herein, we report ligand induced low voltage operated Ru²⁺ based metallo-supramolecular polymer(**polyRu-Bip**) for efficient and durable electrochromic (EC) applications. The polymer coated conductive substrate exhibited low-voltage (0 → +0.6 V) operation for coloration/bleaching. The color change polymer film associated with appearance/disappearance of metal-to-ligand charge transfer (**MLCT**) band upon redox transformation of Ru²⁺ → Ru³⁺. The ECD of **polyRu-Bip** exhibited EC response was very fast ($t_b = 1.37$ s and $t_c = 0.67$ s), high color contrast ($\Delta T = 54\%$) and high coloration efficiency (~ 571 cm²/C). The presence of four electron rich N-methylbenzimidazole moieties in each monomeric unit of the polymer, induced the redox transformation of metal center (Ru^{2+/3+}) at low voltage which influence cyclic stability (20,000 cycles). Moreover, the bridging ligand was also involved for stabilization the high oxidation state of Ru³⁺, which restrict the self-bleaching of polymer film implies enhancement of optical memory effect until 1 hour. Therefore, continuous electrical power source is not necessary to maintain a bleached state, which increases the power consumption for ECD operation.

Acknowledgement: this research was supported by JST-CREST (Grant Number JPMJCR1533).

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- 1) M. Higuchi, *J. Mater. Chem. C*, **2013**, 1, 3408.
- 2) R. Reynolds, *Chem. Rev.*, **2010**, 110, 1, 268.

様々なアミノ酸誘導体を側鎖に持つポリ(キノリレン-2,3-メチレン)の合成と π スタック型らせん構造の安定化

(阪大院理) ○神林 直哉・片岡 裕貴・岡村 高明・鬼塚 清孝

Synthesis of poly(quinolylene-2,3-methylene) bearing various types of amino acid derivatives as the side chain: Stability of π -Stacked Helical Structure (*Graduate School of Science, Osaka University*) ○Naoya Kanbayashi, Yuki Kataoka, Taka-aki Okamura, Kiyotaka Onitsuka

π -Stacked polymers, which consist of layered π -electron systems in a polymer, can be expected to be used in molecular electronic devices. We have reported a novel π -stacked helical architecture based on poly(quinolylene-2,3-methylene) bearing alanine derivatives as the side chain, obtained through the living cyclocopolymerization of an *o*-allenylaryl isocyanide. In the resulting polymer, the neighboring quinoline rings of the main chain form a layered structure with π - π interactions stabilized by intramolecular hydrogen bonds. In this study, the synthesis of the poly(quinolylene-2,3-methylene) bearing various types of amino acid derivatives as the side chain was presented. We found that the stability of the resulting π -stacked helical structure was depended on the substituents on α position of amino acid moiety. When the cyclohexyl alanine derivatives is a side chain, the π -stacked helical structure is maintained stably even with dimethyl sulfoxide as a hydrogen bonding inhibitor.

Keywords; Isocyanide, π -Stack; Helix; Hydrogen Bonds; Amino Acid

分子内に π スタック構造を有する π スタック高分子は、特徴的なエネルギー移動特性や吸収・発光特性を示すことが知られており、新たな分子エレクトロニクス of 基盤材料としての応用が期待される。我々は、*o*-allenylaryl isocyanide をモノマーとしたリビング環化共重合反応¹により得られるポリ(キノリレン-2,3-メチレン)の側鎖置換基にアラニン誘導体導入した場合(**poly-1-Ala**)、側鎖同士の水素結合により主鎖キノリン環がらせん状に π スタックした二次構造を形成することを報告している(Figure 1a)²。今回、アラニン以外の様々なアミノ酸誘導体を側鎖置換基とした高分子を合成したところ、置換基 R の形状に応じてらせん構造由来のコットン効果(275 nm)が増大した(Figure 1b)。特に、シクロヘキシルアラニン誘導体を用いた場合(**poly-1-Cha**)、水素結合阻害剤であるジメチルスルホキシドを加えてもらせん構造を維持しており、 π スタックらせん高分子の安定性が大きく向上していることが明らかとなった(Figure 1c)。

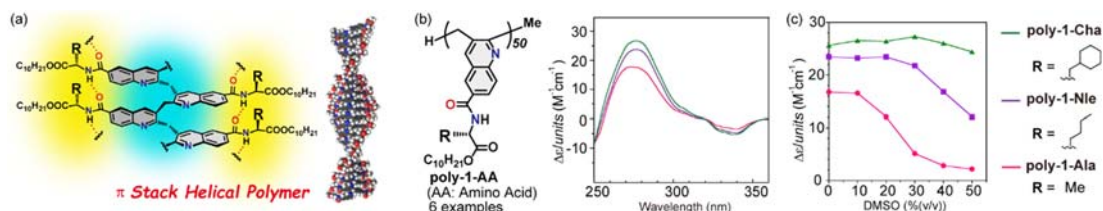


Figure 1. (a) The structure of **poly-1**, (b) CD spectra of **poly-1-AA** at 25 °C in CHCl₃, and (c) the plots of CD intensity at 275 nm against the ratio of DMSO in CHCl₃.

1) N. Kanbayashi, T. Okamura, K. Onitsuka, *J. Am. Chem. Sci.* **2019**, *141*, 15307, 2) Y. Kataoka, N. Kanbayashi, N. Fujii, T. Okamura, T. Haino, K. Onitsuka, *Angew. Chem. Int. Ed.* **2020**, *59*, 10286.

The Mechanochemistry of the Cross-linked Polymer Containing Cyclic Mechanophores

(Department of Chemical Science and Engineering, Tokyo Institute of Technology)

○Jumpei Kida, Daisuke Aoki, and Hideyuki Otsuka

Keywords: Mechanochemistry, Mechanophore, Macrocycles, Mechanical property, Network polymer

Force-responsive molecules, called mechanophores, enable the functionalization of the polymeric materials induced by mechanical stimulus. In this work, we developed a novel cyclic mechanophore which can be cleaved homolytically without chain scission and generate the corresponding stable sulfur radicals, upon the mechanical stimuli. We chose bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) (**Figure 1a**), which is known as dynamic covalent disulfide bond having low bond dissociation energy (26.2 kcal/mol),¹ as a mechanophore. A macrocyclic mechanophore containing BiTEMPS unit (BCM) was newly designed and synthesized (**Figure 1b**). Cross-linked poly(hexyl methacrylate)s (CPHMA) possessing BCM at the cross-linking points (BCM-CPHMA) were synthesized by free radical polymerization. The stress relaxation test and the tensile test revealed the unique mechanical properties of BCM-CPHMA based on the cleavage reaction of BCM at the cross-linked points upon mechanical stimulus (**Figure 1c**). Moreover, we found out the mechanical self-strengthening of BCM-CPHMA. The tensile tests and swelling tests showed the successful strengthening of BCM-CPHMA after compression without any additives such as monomer and modifier, and any other stimulus (**Figure 1d**).

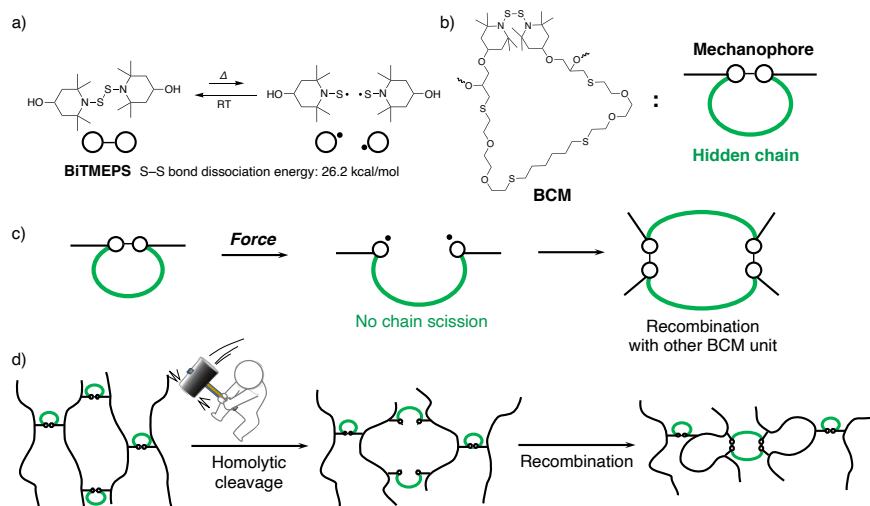


Figure 1. a) Dynamic behavior of BiTEMPS. b) Chemical structure of BCM. c) Cleavage and recombination of BCM. d) Mechanism of mechanical self-strengthening of cross-linked polymer possessing BCM (BCM-CPHMA).

1) H. Otsuka et al., *Angew. Chem. Int. Ed.* **2017**, 56, 2016.

Visualization of Polymer Crystallization and Neck-initiation in Uniaxial Tensile Deformation by Using Fluorescent Mechanochromophore

(¹Department of Chemical Science and Engineering, Tokyo Institute of Technology, ²Department of Life Science and Technology, Tokyo Institute of Technology, ³RIKEN)

○Sota Kato,¹ Daisuke Aoki,¹ Kazusato Oikawa,² Kousuke Tsuchiya,² Naohiko Shimada,³ Atsushi Maruyama,³ Keiji Numata,² and Hideyuki Otsuka¹

Keywords: Spherulites, Confocal laser scanning microscopy, Electron paramagnetic resonance measurement, Necking, Tie molecule

The growth process of lamellar crystals and the effects of the crystallization process on the mechanical properties have been studied. Herein, we propose the strategy for visualizing the polymer crystallization or neck-initiation in uniaxial tensile deformation with quantitative evaluation of mechanical stress by using a mechanochromic probe, called tetraarylsuccinonitrile (TASN, **Fig. 1a**),^[1-4] generating radicals with yellow fluorescence triggered by homolytic cleavage at the central C–C bond in response to mechanical stress. In this work, poly(ϵ -caprolactone)s (PCLs) with TASN in the center of the structure are synthesized by ring-opening polymerization initiated by TASN derivatives. Their primary structures are selected as linear or star, named as **L-PCL** or **S-PCL** (**Fig. 1a**).

The visualization of the polymer crystallization or neck-initiation in uniaxial tensile deformation was studied by confocal fluorescence microscope observations. As shown in **Fig. 1b**, spherulites of **L-PCL** grew from the amorphous part from the beginning of isothermal crystallization. As shown in **Fig. 1c**, spherulites of **S-PCL** were oriented to stretched direction and emit yellow fluorescence in uniaxial tensile tests. Through electron paramagnetic resonance (EPR) measurements in isothermal crystallization or uniaxial tensile deformation, the dissociation ratio of TASN moiety was increased as the molecular weight or the number of arm-PCLs increased. It could indicate (1) an increase of TASN moiety as the tie molecule with increasing molecular weight and (2) a large difference in the number of ‘active’ TASN moiety due to the difference in the formation of lamellar layers.

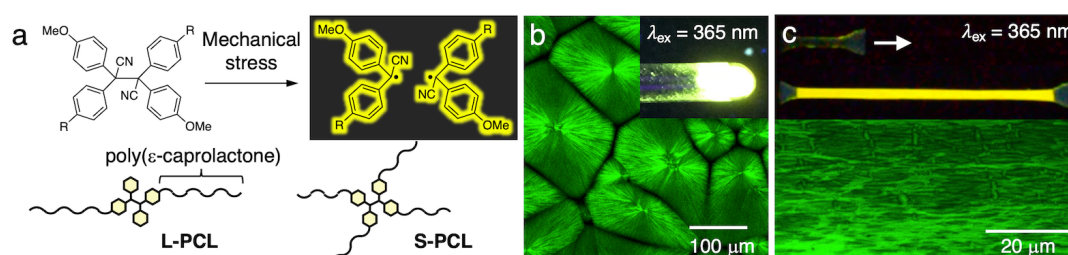


Fig 1. a) Chemical structure of tetraarylsuccinonitrile (TASN) derivative and schematic image of TASN-containing linear polycaprolactone (**L-PCL**) and star polycaprolactone (**S-PCL**). b) Microscopic image of **L-PCL** after isothermal crystallization.^[5] c) Microscopic image of **S-PCL** after uniaxial tensile test.

[1] H. Otsuka *et al.*, *Chem. Commun.* **2017**, 53, 11885. [2] S. Kato, K. Ishizuki, D. Aoki, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2018**, 7, 1087. [3] S. Kato, D. Aoki, H. Otsuka, *Polym. Chem.* **2019**, 10, 2636. [4] S. Kato, D. Aoki, H. Otsuka, *ACS Appl. Polym. Mater.*, **2021**, 3, in press. [5] S. Kato, S. Furukawa, D. Aoki, R. Goseki, K. Oikawa, K. Tsuchiya, N. Shimada, A. Maruyama, K. Numata, H. Otsuka, *Nat. Commun.*, **2021**, 12, 126.

[A07-1am] 19. Colloid and Interface Chemistry

Chair: Yasuhiro Ishida, Masato Ikeda

Fri. Mar 19, 2021 9:00 AM - 11:40 AM Room 7 (Online Meeting)

[A07-1am-01] Polyester microdroplets, DNA liquid crystal coacervates, and other membraneless LLPS assemblies as primitive compartments at the origins of life

○Tony Z Jia^{1,2}, Tommaso Fraccia³, Kuhan Chandru^{8,9}, Yayoi Hongo⁴, Rehana Afrin¹, Tomohiro Usui^{1,5}, Kunihiro Myojo⁶, H James Cleaves^{1,2,7}, Niraja Bapat^{1,10}, Ajay Verma¹⁰, Irena Mamajanov¹ (1. Earth-Life Science Institute, Tokyo Institute of Technology, 2. Blue Marble Space Institute of Science, 3. Institut Pierre-Gilles de Gennes, CBI, ESPCI Paris, Université PSL, CNRS, 4. Okinawa Institute of Science and Technology Graduate University, 5. JAXA Institute of Space and Astronautical Science, 6. Tokyo Institute of Technology, 7. Institute of Advanced Study, 8. Space Science Center (ANGKASA), Institute of Climate Change, Level 3, Research Complex, National University of Malaysia, 9. Department of Physical Chemistry, University of Chemistry and Technology, Prague, 10. Indian Institute of Science Education and Research)

9:00 AM - 9:20 AM

[A07-1am-02] Thermo-induced dynamics in cell-sized droplets of the aqueous hydroxypropyl cellulose solution coated with phospholipids

○Kazunari Yoshida¹, Keitaro Horii², Azusa Saito², Akito Takashima², Izumi Nishio² (1. Yamagata University, 2. Aoyama Gakuin University)

9:20 AM - 9:40 AM

[A07-1am-03] Creation of molecular system emerging multi-step phase transition of supramolecular architectures

○Daichi Sawada¹, Kouichi Asakura¹, Taisuke Banno¹ (1. Faculty of Science and Technology, Keio University)

9:40 AM - 10:00 AM

[A07-1am-04] Hydrogel Formed with 3D Continuous Phospholipid Membrane

○Saya Otake¹, Kou Okuro², Takuzo Aida¹ (1. The University of Tokyo, 2. The University of Hong Kong)

10:00 AM - 10:20 AM

[A07-1am-05] Life-like hydrogels of inorganic nanosheets

○Koki Sano^{1,2}, Yasuo Ebina³, Takayoshi Sasaki³, Yasuhiro Ishida¹ (1. RIKEN, 2. JST PRESTO, 3. NIMS)

10:20 AM - 10:40 AM

[A07-1am-06] In situ Polymerization of a Highly Oriented Molecular Self-Assembly Formed by Acoustic Levitation

○Takashi Kajitani¹, Hiroki Tanaka¹, Koji Ohara², Takanori Fukushima¹ (1. Tokyo Tech, 2. JASRI)

10:40 AM - 11:00 AM

[A07-1am-07] Highly ordered quantum dot arrangements based on molecular assembly

○Mitsuaki Yamauchi¹, Seiya Yamamoto¹, Sadahiro Masuo¹ (1. Kwansei Gakuin)

University)

11:00 AM - 11:20 AM

[A07-1am-08] Orientational change of liquid crystals in a metal-organic framework

○Shizuka Anan¹, Hirotsugu Kikuchi¹ (1. Kyushu Univ.)

11:20 AM - 11:40 AM

Polyester microdroplets, DNA liquid crystal coacervates, and other membraneless LLPS assemblies as primitive compartments at the origins of life

(¹Earth-Life Science Institute, Tokyo Institute of Technology, ²Blue Marble Space Institute of Science, ³Institut Pierre-Gilles de Gennes, CBI, ESPCI Paris, Université PSL, CNRS, ⁴Okinawa Institute of Science and Technology Graduate University, ⁵JAXA Institute of Space and Astronautical Science, ⁶Tokyo Institute of Technology, ⁷Institute of Advanced Study, ⁸Space Science Center (ANGKASA), Institute of Climate Change, Level 3, Research Complex, National University of Malaysia, ⁹Department of Physical Chemistry, University of Chemistry and Technology, Prague, ¹⁰Indian Institute of Science Education and Research)

○Tony Z Jia^{1,2}, Tommaso Fraccia³, Yayoi Hongo⁴, Rehana Afrin¹, Tomohiro Usui^{1,5}, Kunihiro Myojo⁶, H James Cleaves^{1,2,7}, Kuhan Chandru^{8,9}, Niraja Bapat^{1,10}, Ajay Verma¹⁰, Irena Mamajanov¹

Keywords: Origins of Life, Prebiotic Chemistry, Chemical Evolution, Protocells, Liquid-Liquid Phase Separation

Liquid-liquid phase separation (LLPS) phenomena are ubiquitous in biological systems, as various cellular LLPS structures control important biological processes. Due to their ease of in vitro assembly into membraneless compartments and their presence within modern cells, LLPS systems have been postulated to be one potential form that the first cells on Earth took on. Here, we present recent work regarding the structure, assembly, and function of various in vitro LLPS systems, including DNA liquid crystal coacervates and non-biological polyester microdroplets, that produce membraneless compartments which may have been relevant to the emergence of primitive compartments and the first cells.

We first demonstrated compartments based on membraneless microdroplets generated from homo- and heteropolyesters synthesized from drying solutions of α -hydroxy acids α HAs (an abundant primitive molecule) endowed with various side chains. These compartments can preferentially and differentially segregate and compartmentalize fluorescent dyes and fluorescently tagged RNA, providing readily available compartments that could have facilitated chemical evolution by protecting, exchanging, and encapsulating primitive components. Protein function within and RNA function in the presence of certain droplets is also preserved, suggesting the potential relevance of such droplets to various origins of life models.

We next reported liquid crystal (LC)-coacervate droplets assembled from aqueous solutions of short double-stranded DNA (s-dsDNA) and poly-L-lysine (PLL). Such LC-coacervates conjugate the advantages of an associative LLPS with the relevant long-range ordering and fluidity properties typical of LC, which reflect and propagate the physico-chemical properties of their molecular constituents. We investigated the structure, assembly, and function of DNA LC-coacervates in the context of prebiotic molecular evolution and the emergence of functional protocells on early Earth and observed through polarization microscopy that LC-coacervate systems can be dynamically assembled and disassembled based on prebiotically available environmental factors including temperature, salinity, and dehydration/rehydration cycles. Based on these observations, we discuss how LC-coacervates can in principle provide selective pressures effecting and sustaining chemical evolution within partially ordered compartments. Finally, we speculate about the potential for LC-coacervates to perform various biologically relevant properties, such as segregation and concentration of biomolecules, catalysis, and scaffolding, potentially providing additional structural complexity, such as linearization of nucleic acids and peptides within the LC ordered matrix, that could have promoted more efficient polymerization.

While there are still a number of remaining open questions regarding LLPS systems as models for primitive membraneless cells, including how modern biologies acquired such membraneless organelles, understanding the exact connection between LLPS systems and primitive cells will shed light into how primitive cells transitioned to modern cells.

リン脂質でコーティングされたヒドロキシプロピルセルロース水溶液の細胞サイズ液滴における温度変化応答ダイナミクス

(山形大院理工¹・青学大理工²) ○吉田 一也¹・堀井 啓太郎²・齊藤 梓²・高嶋 明人²・西尾 泉²

Thermo-induced dynamics in cell-sized droplets of the aqueous hydroxypropyl cellulose solution coated with phospholipids (¹*Graduate School of Science and Engineering, Yamagata University*, ²*College of Science and Engineering, Aoyama Gakuin University*) ○Kazunari Yoshida,¹ Keitaro Horii,² Azusa Saito,² Akito Takashima,² Izumi Nishio²

Water-in-Oil (W/O) droplets are widely used as simple model systems of cell membranes. In particular, since we can easily encapsulate molecules in W/O droplets, W/O droplets are utilized for the researches on dynamic behaviors of molecules encapsulated by cell-sized regions. Here we report the cell-sized confinement effects and effects of interfacial lipid headgroups of the cell-sized droplets on dynamic behaviors of hydroxypropyl cellulose (HPC) solution with the increase in temperature^{1,2}. The phase separation into HPC-rich and water-rich regions is induced with the increase in temperature. We show the appearing the phase separation patterns of aqueous HPC solution with the increase in temperature. Our findings lead us to the next step of the physicochemical understandings of living cells.

Keywords : *W/O Droplet, Phase Separation, Direct Observation*

油中水滴(W/O 型液滴)は細胞膜の単純なモデル系として広く用いられている。特に W/O 型液滴には簡単に分子を封入できることから、W/O 型液滴は細胞サイズに閉じ込められた分子の動的挙動に関する研究に活用されている。そこで、我々は、ヒドロキシプロピルセルロース(HPC)水溶液の動的挙動に対する、温度を上昇させたときの細胞サイズ閉じ込め効果やリン脂質の親水基のヘッドグループの影響を報告する^{1,2}。HPC を多く含む部分と水を多く含む部分への相分離は温度上昇によって引き起こされる。我々は温度上昇に伴う相分離パターンの出現を示す。我々の研究成果は生細胞の物理化学的理解の次のステップにつながるものである。

1) K. Yoshida, K. Horii, A. Saito, A. Takashima, and I. Nishio, *Poymers*. **2017**, 9, 680.

2) K. Yoshida, K. Horii, A. Saito, A. Takashima, and I. Nishio, submitted.

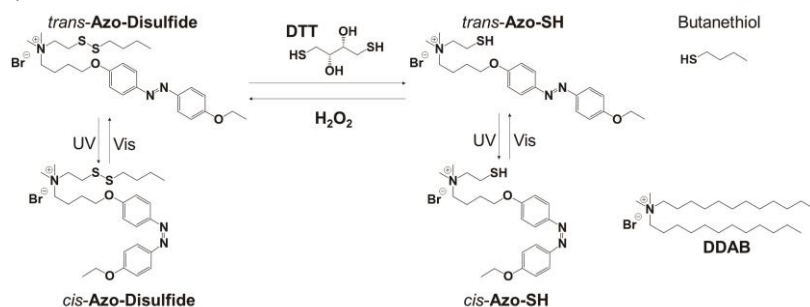
Creation of molecular system emerging multi-step phase transition of supramolecular architectures

(Faculty of Science and Technology, Keio University) ○Daichi Sawada, Kouichi Asakura, Taisuke Banno

Keywords: Cationic Amphiphiles; Vesicles; Supramolecular Chemistry; Multi-step Transition

In viewpoints of dynamic and reversible nature of non-covalent interactions, supramolecular architectures possess stimuli responsiveness accompanied with structural phase transition, making them candidates for adaptive or smart materials. So far, single-responsive soft materials have been designed and achieved. However, there are only a few reports on supramolecular system integrated by multiple responsiveness due to the requirements of consummate molecular design. Here, to induce multi-step phase transition of supramolecular architectures, the cationic lipid, **Azo-Disulfide**, which has an azobenzene skeleton and a disulfide bond, was designed and synthesized. The effect of application order for reducing agent addition and UV irradiation on phase transition of supramolecular assemblies composed of **Azo-Disulfide** and non-reactive lipid **DDAB** was evaluated.

In the dispersion containing 1 mM lipids of which the molar ratio was 4/1, crystals were observed. When dithiothreitol (DTT) was applied to the dispersion, the phase transition from crystals to micrometer-sized vesicles occurred. From the ^1H NMR analysis, it was found that the disulfide group was 60% reduced, and the corresponding **Azo-SH** and butanethiol generated. Under the subsequent UV irradiation, two nearby vesicles gradually fused with no contact each other. The following Vis irradiation also provided the similar dynamics. From fluorescence anisotropy measurements using environment-responsive compounds, the fluidity of membrane became lower after UV irradiation. It was therefore considered that instability at the local area in the membrane occurred due to photoisomerization, inducing the contactless fusion of vesicles. On the other hand, when the UV irradiation was applied to the dispersion composed of **Azo-Disulfide** and **DDAB**, the transformation from crystals to worm-like aggregates were observed. They gradually grew by the subsequent addition of DTT. Though the multiple phase transition of supramolecular architectures was observed in both paths, behavior was significantly affected by applying order of stimuli, suggesting that the current system had hysteresis.



Hydrogel Formed with 3D Continuous Phospholipid Membrane

(¹Graduate School of Engineering, The University of Tokyo, ²Faculty of Science, The University of Hong Kong) ○Saya Otake,¹ Kou Okuro,² Takuzo Aida¹

Keywords: Lipid Membrane, Phospholipid, Hydrogel, Guanidinium

Hydrogel is composed of three-dimensional networks that retain a large amount of water. The network structure is known to be a decisive factor of the hydrogel property including mechanical strength and guest entrapment/release capability. In general, hydrogel network is fibrously formed by covalently and/or noncovalently crosslinked molecules.¹

In the present research, we unprecedentedly developed hydrogel having Voronoi-like crosslink structure (Figure 1), which consists of three-dimensionally continuous phospholipid membranes. The phospholipid is DOPEGu⁺ (Figure 2) bearing a guanidinium ion head, which can strongly bind to oxyanion via salt-bridge formation.² When DOPEGu⁺ was subjected to reverse-phase centrifugation³ for preparing discrete liposomes, it unexpectedly formed the continuous membrane network. This characteristic structure provides the system with viscoelasticity, yielding hydrogel even at low concentration of the phospholipid (~0.1 wt%). In the presentation, the preparation and properties of the hydrogel will be discussed in detail.

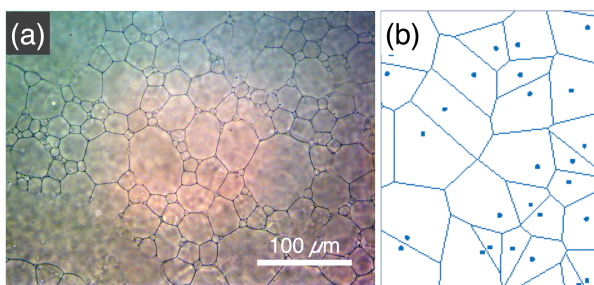


Figure 1. (a) Phase contrast microscopy image of DOPEGu⁺ hydrogel. (b) Voronoi diagram.

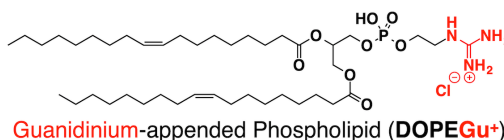


Figure 2. Molecular structure of DOPEGu⁺.

1) a) S. J. Buwalda *et al.*, *J. Controlled Release* **2014**, 190, 254. b) X. Du *et al.*, *Chem. Rev.* **2015**, 115, 13165. 2) R. Mogaki *et al.*, *Chem. Soc. Rev.* **2017**, 46, 6480. 3) K. Tsumoto *et al.*, *Colloids Surf., A* **2018**, 546, 74.

無機ナノシートからなる生き物のようなハイドロゲル

(理研¹・JST さきがけ²・物材機構³)

○佐野 航季^{1,2}・海老名 保男³・佐々木 高義³・石田 康博¹

Life-like Hydrogels of Inorganic Nanosheets (¹RIKEN, ²JST PRESTO, ³NIMS)

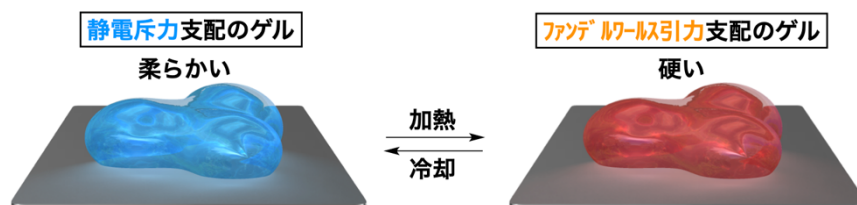
○Koki Sano,^{1,2} Yasuo Ebina,³ Takayoshi Sasaki,³ Yasuhiro Ishida¹

Various biomimetic soft materials that display structural hierarchies and stimuli responsiveness have been developed from organic materials. However, the creation of their counterparts consisting entirely of inorganic materials remains a challenge. Here, we have developed a hydrogel consisting of inorganic nanosheets and water that undergoes thermally induced reversible and abrupt changes in its internal structure and mechanical property.

Keywords : Nanosheet; Hydrogel; Liquid Crystal; Stimuli-responsive Soft Material; Mechanical Property

サイエンスフィクション (SF) や神話には、無機生命体がしばしば登場する。これらのストーリーは、科学者に「無機物質のみを用いて、生体のような動的機能を実現できるのか」といった挑戦的テーマを投げかける。改めて生体に着目すると、水を豊富に含んだ階層構造を持ち、柔軟性や刺激応答性を示す固体である¹。一方、無機物質は基本的に硬く、刺激応答性に乏しいため、生体のような動的機能を実現することは極めて困難である。もし、刺激応答性ハイドロゲルを無機物質のみで作製できれば、無機物質に由来する優れた機械的特性や耐久性などを兼ね備えることが期待され、次世代スマートマテリアルの設計戦略を大きく拡大すると考えられる。

今回我々は、酸化チタンナノシート^{2,4}と水のみからなるハイドロゲルが、温度に応答して内部のネットワーク構造を動的に組み換えることで、生き物のように力学物性を可逆的かつ高速に変化させることを見いだした (図参照)⁵。このゲル-ゲル相転移は、水中にてナノシート間に働くファンデルワールス引力と静電斥力のバランスを精密に制御することで駆動される。さらに、微量の光熱変換ナノ粒子を添加することで、このハイドロゲルの物性を光刺激によって時空間的に制御することにも成功した。



(1) K. Sano *et al.* *Angew. Chem. Int. Ed.* **57**, 2532–2543 (2018).

(2) T. Sasaki *et al.* *J. Am. Chem. Soc.* **118**, 8329–8335 (1996).

(3) K. Sano *et al.* *Nat. Commun.* **7**, 12559 (2016).

(4) K. Sano *et al.* *Angew. Chem. Int. Ed.* **57**, 12508–12513 (2018).

(5) K. Sano *et al.* *Nat. Commun.* **11**, 6026 (2020).

音波浮遊溶融により形成する高配向分子自己集合体の *in situ* 重合

(東工大 OFC¹・東工大化生研²・JASRI³) ○梶谷 孝¹・田中 大喜²・尾原 幸治³・福島 孝典²

In situ Polymerization of a Highly Oriented Molecular Self-Assembly Formed by Acoustic Levitation (¹*Open Facility Center, Tokyo Institute of Technology*; ²*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*; ³*JASRI*) ○Takashi Kajitani,¹ Hiroki Tanaka,² Koji Ohara,³ Takanori Fukushima²

In general, the formation of a single-domain structure by self-assembly of organic materials is difficult, mainly due to random nucleation that occurs at the substrate surface. Recently, we found that highly oriented liquid-crystalline molecular assemblies featuring a single-domain structure can be obtained using a dedicated acoustic levitation system. Herein, we investigated *in situ* thermal- and photo-polymerization reactions of a liquid-crystalline material under acoustic levitation conditions. Here we report the structure and properties of the resultant polymers obtained by the specific conditions.

Keywords : *Molecular Self-assembly; Acoustic Levitation; Single Domain; Polymerization; Liquid Crystal*

一般に物質の構造形成は器壁界面からランダムに起こる多数の核形成を経て進行するため、単一ドメインからなる材料を得ることは困難である。そこで、容器を使わず物質の構造化を実現する手法として、いくつかの無容器浮遊法^[1]が提案されているが、これらの手法が有機・高分子材料に適用された例はあまりない。最近我々は、有機材料を安定に浮遊させる音波浮遊溶融装置を新たに開発し、音波浮遊溶融法が単一ドメインからなる分子集合体の形成に有効であることを見出した^[2]。本研究では、音波浮遊溶融装置に光照射装置とガス吹付装置を組み込んだシステムを構築し (Fig. 1)、不活性ガス雰囲気下で浮遊した液晶モノマーのその場重合を検討した。その結果、液晶の配向秩序を保ったまま重合が進行し、ポリマー鎖同士が複雑に絡み合ったゲルを形成することを明らかにした。発表では、この新手法により得られた液晶ポリマーの構造や性質について述べる。

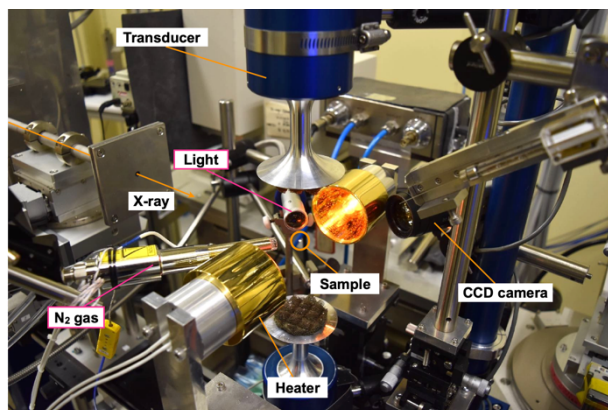


Fig. 1. Experimental setup for *in situ* thermal- and photo-polymerization reactions of a liquid-crystalline material under acoustic levitation conditions.

[1] J. K. R. Weber, C. A. Rey, J. Neuefeind, C. J. Benmore, *Sci. Instrum.* **2009**, 80, 083904.

[2] 田中大喜, 梶谷孝, 尾原幸治, 大隅寛幸, 高田昌樹, 福島孝典 日本化学会第 99 春季年会, 3I1-20.

分子集合を鍵とした量子ドットの高次配列

(関西学院大理工) ○山内 光陽・山本 聖也・増尾 貞弘

Highly ordered quantum dot arrangements based on molecular assembly (Kwansei Gakuin University) ○Mitsuaki Yamauchi, Seiya Yamamoto, Sadahiro Masuo

Semiconductor nanocrystals, quantum dots (QDs), exhibit outstanding emission and optoelectronic properties under single conditions such as dispersed QDs in solution. Moreover, the aggregation of QDs can create novel photophysical properties and functions that are not obtained from single QDs. However, the control over aggregation of QDs is still challenging because the rational method for the aggregation of QDs has not been constructed. Recently, our group demonstrated a new strategy to form assembled QDs using the self-assembly of organic dyes.^{1,2)} In this work, we report the hierarchical coaggregation into highly ordered CdSe QD arrangement structures based on the self-assembly of an azobenzene derivative (Azo).³⁾ The transmission electron microscopic observation revealed that the QDs are uniformly arranged along the two-dimensional aggregates of Azo. In addition, we considered a mechanism of the QD arrangement by in-depth analysis of emission lifetimes.

Keywords : *Self-assembly; Quantum Dot; Organic-inorganic Hybrid; Supramolecular Structure; Azobenzene*

半導体ナノ結晶である量子ドット (QD) は、分散した溶液中などの単独状態において卓越した発光・光電子特性を示す。さらに、QD の集合化により、単一 QD から得られない新たな光物性や機能の創出が期待される。しかしながら、QD の合理的な集合手法は確立されていないため、QD の集合制御は未だに困難である。最近、我々の研究グループは、有機色素の自己集合を利用した新たな QD の配列手法を打ち出した^{1,2)}。本研究では、アゾベンゼン誘導体 (Azo) の自己集合に基づいて、CdSe QD が高次に配列した構造体への階層的共集合に関して報告する³⁾。透過型電子顕微鏡により、Azo の 2 次元集合体に沿って QD が均一に配列していることが明らかになった。さらに、発光寿命の詳細な解析により、QD の配列メカニズムを考察した。

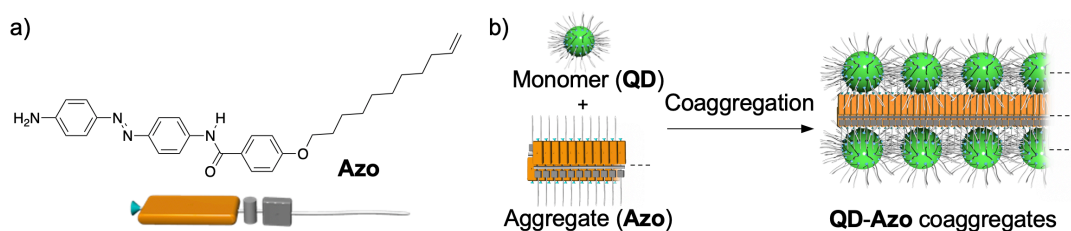


Fig. 1 a) Structure of Azo. b) Schematic representation of coaggregation of QD and Azo.

- 1) M. Yamauchi, S. Masuo, *Chem. Eur. J.* **2019**, 25, 167–172.
- 2) M. Yamauchi, S. Masuo, *Chem. Eur. J.* **2020**, 26, 7176–7184.
- 3) M. Yamauchi, S. Yamamoto, S. Masuo, *Angew. Chem. Int. Ed.* **2021**, in press.

金属-有機構造体中に包接した液晶の配向変化

(九大先導研) ○阿南静佳・菊池裕嗣

Orientation change of liquid crystals in metal-organic framework (*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Shizuka Anan, Hirotsugu Kikuchi

The orientational direction of liquid crystals can be controlled by the molecular alignment at the interface in contact with the liquid crystal. In the present work, the liquid crystal included in metal-organic framework (MOF) was found to show orientational order. FT-IR microscopy revealed the inclusion of liquid crystal inside the MOF, and the polarized microscopic observation showed that the orientational direction of liquid crystal was rotated with change in temperature. Furthermore, the orientational order was kept even at 130 °C which is 97 °C higher than the nematic-isotropic phase transition temperature of the liquid crystal in bulk.

Keywords : Liquid Crystal, Molecular Orientation, Nematic Phase, Metal-Organic Framework, Porous Crystal

液晶の配向方向は液晶との界面の分子の配向方向に依存して決定される。本研究では、ナノサイズの規則的な連続孔を有する金属-有機構造体 (MOF) に着目し、MOF の細孔中に包接した液晶の配向秩序の発現を試みた。MOF 界面との相互作用によりバルクとは異なる配向秩序が発現すると期待される。

硝酸亜鉛六水和物とビフェニルジカルボン酸をジエチルホルムアミド (DEF) に溶解し、100 °C に 24 時間静置することで、**IRMOF9**¹ と同型の結晶を得た。続いて、サーモトロピック液晶の一つである 4-シアノ-4'-ペンチルビフェニル (**5CB**) 中に MOF を浸漬することで MOF

の細孔中に **5CB** を内包した (**5CB/MOF**)。5CB へ浸漬前後の顕微 IR 測定より、浸漬前に観測された DEF 由来の CO 伸縮振動が浸漬後には消失し、5CB 由来の CN 伸縮振動に由来するピークが出現したことから溶媒である DEF が 5CB に置換されたことが示唆された。さらに、偏光顕微鏡観察より、5CB の等方相転移点 (35.3 °C) よりも高温である 50 °C において、MOF 中で一様なリタレーションが観測され、さらに 130 °C まで昇温したところリタレーションが 5CB/MOF 中で一様に連続的に変化した (図 1b,c)。さらに鋭敏色板を導入した観察より、100 °C を境に光学的進相軸と遅相軸が 90 °回転する様子が観測された。以上の結果より、MOF の細孔中で 5CB は配向秩序を示し、温度変化に伴ってその配向秩序が協同的に変化することが示唆された。

1) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, 295, 469.

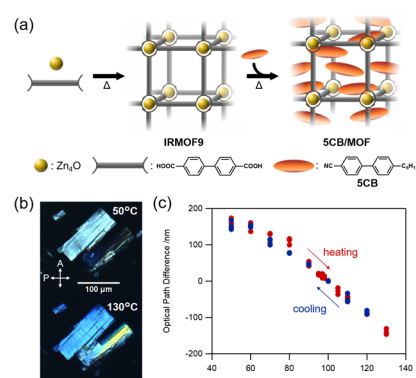


図 1. (a) 5CB/MOF 合成スキーム. (b) 5CB/MOF の偏光顕微鏡像. (c) リタレーションの温度変化.

[A03-1pm] 20. Materials Chemistry -Basic and Application-

Chair: Jiro Abe, Takashi Kitao

Fri. Mar 19, 2021 1:00 PM - 3:40 PM Room 3 (Online Meeting)

[A03-1pm-01] Comparison of TD-DFT and semi-empirical methods for description of spectral properties of anthraquinone dyes using X-ray crystal structure.

○JIYONG HWANG¹, Sunghoon Kim¹, Shinya Matsumoto¹ (1. Yokohama National University)

1:00 PM - 1:20 PM

[A03-1pm-02] Chiral photovoltaic effect of liquid-crystalline binary mixtures based on π -conjugated compounds

○Atsushi Seki¹, Masafumi Yoshio², Yuki Mori³, Masahiro Funahashi^{3,4} (1. Tokyo University of Science, 2. National Institute for Materials Science, 3. Kagawa University, 4. National Institute of Advanced Industrial Science and Technology)

1:20 PM - 1:40 PM

[A03-1pm-03] Three-Dimensional Control of Periodic Nanostructure of Cholesteric-Liquid-Crystals in Monodisperse Microparticles

○Tomoki Shigeyama¹, Kyohei Hisano¹, Osamu Tsutsumi¹ (1. Ritsumeikan Univ.)

1:40 PM - 2:00 PM

[A03-1pm-04] A molecular crystal of a gold complex exhibiting reversible shape memory effect with luminescent color changes

○Chi Feng¹, Tomohiro Seki², Shunichi Sakamoto³, Toshiyuki Sasaki³, Satoshi Takamizawa³, Hajime Ito^{1,4} (1. Graduate School of Engineering, Hokkaido University, 2. Faculty of Science, Shizuoka University, 3. Graduate School of Nanobioscience, Yokohama City University, 4. WPI-ICReDD, Hokkaido University)

2:00 PM - 2:20 PM

[A03-1pm-05] Donor-acceptor-type organic semiconductors based on acendichalcogenophenediones

○Kohsuke Kawabata^{1,2}, Kazuo Takimiya^{1,2} (1. Tohoku Univ., 2. RIKEN)

2:20 PM - 2:40 PM

[A03-1pm-06] Scanning wave photopolymerization directs three-dimensional molecular alignment patterns in liquid-crystalline polymer films as an alignment layer

○Yoshiaki Kobayashi¹, Norihisa Akamatsu¹, Shoichi Kubo¹, Atsushi Shishido¹ (1. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

[A03-1pm-07] Angularly Anisotropic Giant Circularly Polarized Luminescence from Chiral Conjugated Polymer Microsphere

○Osamu Oki¹, Chidamber Kulkarni², Hiroshi Yamagishi¹, Stefan C. J. Meskers², Zhan-Hong Lin³, Jer-Shing Huang³, Bert Meijer², Yohei Yamamoto¹ (1. Fac. Pure and Appl. Sci., Univ. Tsukuba, 2. Eindhoven University of Technology, 3. Leibniz-IPHT)

3:00 PM - 3:20 PM

[A03-1pm-08] Bio-based Polymer Derived Anode Material for Fast Charging and Long Cycle Life Li- ion Battery

○Rajashekar Badam¹, Kottisa Sumala Patnaik¹, Yueying Peng¹, Tatsuo Kaneko¹, Noriyoshi. Matsumi¹ (1. Japan Advanced Institute of Science and Technology)

3:20 PM - 3:40 PM

Comparison of TD-DFT and semi-empirical methods for description of spectral properties of anthraquinone dyes using X-ray crystal structure

(¹Graduate School of Environment and Information Sciences, Yokohama National University)
○Ji-Yong Hwang,¹ Sunghoon Kim,¹ Shinya Matsumoto¹

Keywords: Anthraquinone dyes; Electronic state; Molecular orbital calculation; Organic dyes

Various molecular orbital calculation methods are used in the study of the electronic states of organic dyes. Although the time-dependent density functional theory (TD-DFT) is also often used for the calculation of absorption spectrum, the cases which consider not only the quantitative properties of the absorption wavelength, but also the molecular orbitals related to the transition state and etc., are extremely limited.¹ In this research, we made an attempt to evaluate the applicability of several MO calculation methods to characterize absorption properties of anthraquinone dyes (AQ) by using the X-ray structure analysis.

Among many organic dyes, AQ chromophore was selected in this research considering the industrial importance of organic dyes. From the Cambridge Structural Database (CSD), 12 AQ dyes having donor substituent such as OH and NH₂ were selected. The calculations of absorption properties of the AQ dyes were performed with semi-empirical methods (PM5/RPA and ZINDO/CI) and TD-DFT/B3LYP/6-31G (d, p) method.

Among three methods, there are slight differences in the calculated λ_{max} for AQ dyes depending on the position or torsion angle of the substituent. From the calculation results, it is confirmed that PM5/RPA method is the most suitable to reproduce the experimental λ_{max} .

Furthermore, through the calculation of gross populations of p_z orbital of all atoms in the AQ molecule, the TD-DFT method was found to be overvalued compared to the two semi-empirical methods. These results are also known to be attributed to the states of Rydberg character in TD-DFT method.² The change in the value of the gross populations of N_{pz} due to the rotation angle between the AQ moiety and amino substituents was confirmed in PM5/RPA method. In addition, it was shown that the values of N_{pz} and oscillator strength (f) in HOMO and LUMO states decreased as rotation angles increased.

1) a) A. Matsuura *et. al.*, *J. Mol. Struct: THEOCHEM*, **2008**, 860, 119. b) D. Jacquemin, *et. al.*, *Acc. Chem. Res.*, **2009**, 42, 326. c) J. Fabian, *Dyes Pigm.*, **2010**, 84, 36.

2) a) C.-L. Cheng *et. al.*, *J. Chem. Phys.*, **2008**, 129, 124112. b) M. Schreiber *et. al.*, *Phys. Chem. Chem. Phys.*, **2001**, 3, 3906.

二成分系 π 共役液晶におけるキラル光起電力効果

(東理大 理¹・物材機構 RCFM²・香川大学 材料創造工³・産総研 四国センター⁴)
 ○関 淳志^{1,2}・吉尾 正史²・森 悠喜³・舟橋 正浩^{3,4}

Chiral Photovoltaic Effect of Liquid-Crystalline Binary Mixtures Based on π -Conjugated Compounds (¹*Faculty of Science Division II, Tokyo University of Science*, ²*Research Center for Functional Materials, National Institute for Materials Science*, ³*Faculty of Engineering and Design, Kagawa University*, ⁴*Health Research Institute, National Institute of Advanced Industrial Science and Technology*) ○Atsushi Seki,^{1,2} Masafumi Yoshio,² Yuki Mori,³ Masahiro Funahashi^{3,4}

We have previously reported the chiral photovoltaic (CPV) effect in the liquid-crystalline phases of chiral oligothiophene derivatives.^{1,2} The CPV effect as a type of ferroelectric photovoltaic effect is triggered by the internal electric field derived from the symmetry breaking by a molecular chirality, because the internal electric field originated from spontaneous polarization promotes photocarrier generation and transport. Herein, we report liquid-crystalline binary mixtures constituted by achiral and chiral phenylterthiophene derivatives as a new family of π -conjugated ferroelectric liquid-crystalline materials. Ferroelectric and carrier transport properties as well as CPV effect were examined in smectic liquid-crystalline phases of the binary mixtures.³

Keywords : *Ferroelectric Liquid Crystals; π -Conjugated Compounds; Binary Mixtures; Molecular Chirality; Photovoltaic Effects*

強誘電体の自発分極に由来する内部電界が寄与して生じる光起電力効果は、強誘電性光起電力 (FePV) 効果と呼ばれ、強誘電性セラミクスにおいて盛んに検討されてきた。我々は、種々の強誘電性オリゴチオフェン液晶を合成し、FePV 効果の一種として位置付けられるキラル光起電力 (CPV) 効果に関する構造物性相関について検証し、分子不斉に由来する対称性の破れが CPV 効果の発現に寄与していることを明らかにした。^{1,2} 本研究では、オリゴチオフェン系液晶 **1** とキラル液晶 (*S*)-**2** (Figure 1) を任意組成比で混合した二成分系強誘電性液晶を調製し、強誘電性、電荷輸送特性、CPV 特性と組成の相関について検討した。一定温度において、自発分極はキラル成分含有率に対応して非線形に変化したが、電荷移動度については組成依存性が認められなかった。極性構造を安定に形成するのに十分な量のキラル成分を含む系では CPV 効果が誘起されることが確かめられ、従来系よりも低温での CPV 効果の発現に成功した。³

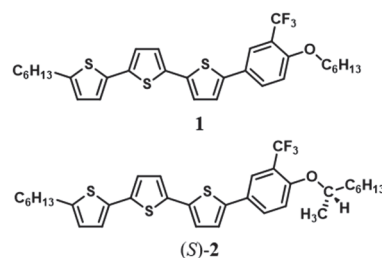


Figure 1. Chemical structures of achiral and chiral liquid crystals **1** and (*S*)-**2**.

1) M. Funatsu, A. Sonoda, M. Funahashi, *J. Mater. Chem. C* **2015**, 3, 1982.

2) A. Seki, M. Funahashi, *Phys. Chem. Chem. Phys.* **2017**, 19, 16446.

3) A. Seki, M. Yoshio, Y. Mori, M. Funahashi, *ACS Appl. Mater. Interfaces* **2020**, 12, 53029.

単分散高分子微粒子におけるコレステリック液晶の3次元ナノ周期構造の制御

(立命館大) ○茂山 友樹・久野 恭平・堤 治

Three-Dimensional Control of Periodic Nanostructure of Cholesteric-Liquid-Crystals in Monodisperse Microparticles (*Ritsumeikan University*) ○Tomoki Shigeyama, Kyohei Hisano, Osamu Tsutsumi

Control of periodic nanostructure is important to modulate optical properties. In this study, we prepared monodisperse polymeric microparticles with cholesteric liquid crystals, which form one-dimensional periodic nanostructure. By dispersion polymerization of cholesteric-liquid-crystal monomers, three-dimensional control of periodic nanostructure in monodisperse microparticles was succeeded (Figure 1). Based on the controlled periodic nanostructure, each single particle showed angular-independent reflection (Figure 2). We discuss the mechanism of periodic nanostructure formation and their optical properties.

Keywords : *Cholesteric Liquid Crystals; Structural Color; Microparticles; Dispersion Polymerization*

屈折率が周期的に変化するナノ周期構造材料は、光の反射や回折など様々な光機能を有する。ナノ周期構造材料で高度な光機能を発現するためには、構造の多次元的制御技術が重要である。コレステリック液晶 (CLCs) は自発的にらせん状分子配向 (屈折率の1次元ナノ周期構造) を形成する。本研究では、分散重合によって単分散 CLC 高分子微粒子を合成し (Figure 1a), 微粒子内部で3次元的にナノ周期構造を制御することに成功した。透過型電子顕微鏡観察により微粒子内の分子配向を観察した結果、らせん軸が放射状に配向していることが明らかとなった (Figure 1b)。また、得られた CLC 微粒子は、ナノ周期構造に起因した全方位反射特性を有するため、微粒子を塗布したサンプルは、どの方向から見ても一定の反射色を示した (Figure 2)。本 CLC 微粒子は、様々な材料へ分散・塗布が可能のため反射コーティング等への応用が期待できる。ナノ周期構造の形成メカニズムと、詳しい光機能について発表する。

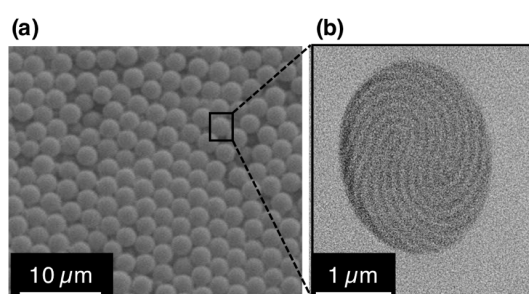


Figure 1. (a), SEM image of CLC particles; (b), TEM image of cross section.

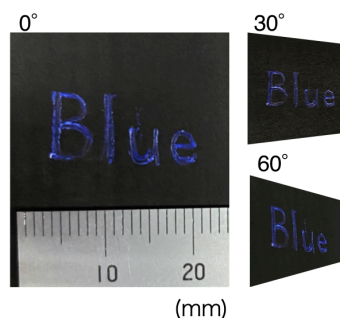


Figure 2. Viewing-angle independent reflection from the CLC particles. The viewing angles are indicated in the figure.

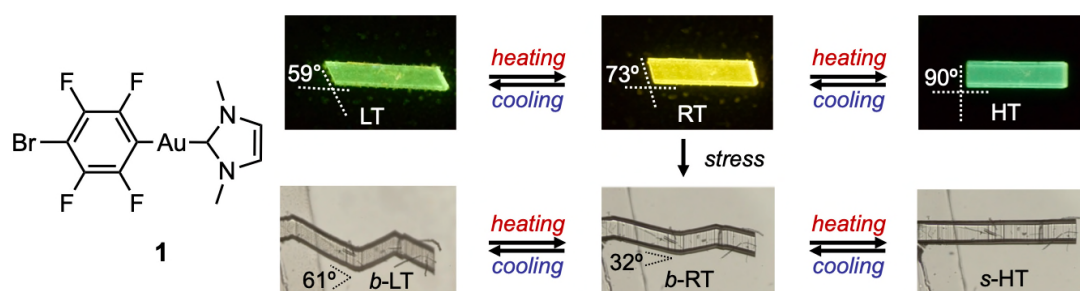
A molecular crystal of a gold complex exhibiting reversible shape memory effects with luminescent color changes

(¹Graduate School of Engineering, Hokkaido University, ²Faculty of Science, Shizuoka University, ³Graduate School of Nanobioscience, Yokohama City University, ⁴WPI-ICReDD, Hokkaido University) ○Chi Feng,¹ Tomohiro Seki,² Shunichi Sakamoto,³ Toshiyuki Sasaki,³ Satoshi Takamizawa,³ Hajime Ito^{1,4}

Keywords: Shape Memory Effect; Luminescent Color Change; Gold Complex; Thermal Phase Transition

Shape memory effect is referred to as the phenomena that mechanically deformed materials (i.e., alloys or polymers) can recover their original shape upon temperature change. Shape memory alloys or polymers attracted attention because of their scientific and technological significance. Recently, the first example of the shape memory effect in the organic molecular crystal was reported.¹⁾ However, such a molecular crystal does not exhibit luminescent properties. If intrinsically luminescent molecules show shape memory effect in their crystalline states, intriguing chromic behaviors can be observed upon deformation/recovery process of the morphologies.²⁾ Here, we report that molecular crystals of a gold complex **1** exhibit reversible shape memory effect with luminescent color changes.

Crystal samples of a gold(I) complex **1** (denoted as an RT phase at room temperature) shows a reversible phase transition to LT or HT phases upon cooling or heating, respectively. These thermal phase transitions lead to the alterations of the luminescence colors and macroscopic morphologies. The RT crystal shows plastic bending upon applying mechanical force. Intriguingly, these mechanically bent crystals showed a reversible shape memory effect with luminescent color changes upon heating or cooling. We performed differential scanning calorimetry (DSC) analyses, single-crystal X-ray structural analyses, and a series of spectroscopic measurements to evaluate the reversible shape memory effects of **1** with luminescent color changes. Thus, we will discuss the origin of the intriguing stimuli-response behavior of **1**.



1) S. Takamizawa and Y. Takasaki, *Chem. Sci.* **2016**, 7, 1527. 2) H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.* **2008**, 130, 10044.

Donor-acceptor-type organic semiconductors based on acenedichalcogenophenediones

(¹Graduate School of Science, Tohoku University, ²Center for Emergent Matter Science, RIKEN) ○Kohsuke Kawabata,^{1,2} Kazuo Takimiya,^{1,2}

Keywords: donor-acceptor; organic semiconductor; quinoid; near-infrared absorption

Organic semiconductors having a small optical energy gap are of great interest for the application for near-infrared-active organic photovoltaics and photodetectors. For designing such materials, lowering LUMO energy levels is a key not only for reducing the energy gaps but also keeping low-lying frontier orbital energy levels for air stable carrier transport. We have recently developed a series of benzo- and naphtho-dithiophenediones as highly electron-deficient acceptor building units for D-A type conjugated oligomers¹ as well as polymers,² some of which exhibited very small optical energy gaps and low-lying frontier orbital energy levels. In this study, we have systematically synthesized thiophene-based D-A-D triads incorporating acenedithiophenedione acceptors and the corresponding oxygen- and selenium-containing analogues, namely, acenedifurandiones and acenediselenophenediones, respectively, to investigate the effect of the chalcogen atoms in the acceptors on the physicochemical properties (Fig. 1).

The D-A-D triads show intense absorption bands in visible to near-infrared region and low-lying frontier orbital energy levels, which enables ambient-stable hole and electron transport in the OFET devices. The electronic structures mostly depend on the size of acene cores and donors, but not on the chalcogen atoms, though some minor differences are observed between the oxygen-containing acceptors and the sulfur- and selenium-containing counterpart. In the presentation, we report the synthesis, structure, optical and electrochemical properties, and carrier transport properties of the series of D-A-D triad molecules, and discuss the structure-property relationships regarding the effect of the chalcogen atoms.

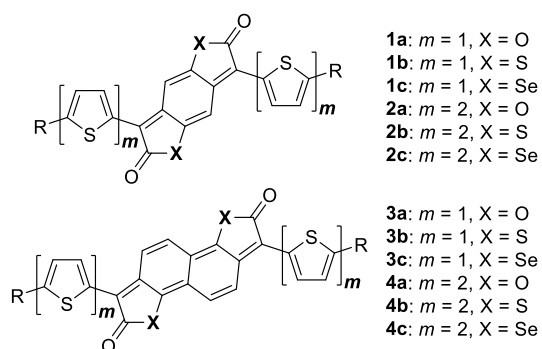


Fig. 1 Benzo- (top) and naphtho- (bottom) dichalcogenophenedione-based D-A-D triads.

1) K. Kawabata, I. Osaka, M. Sawamoto, J. Zafra, P. Burrezo, J. Casado, K. Takimiya, *Chem. Eur. J.* **2017**, *11*, 4579. 2) K. Kawabata, M. Saito, I. Osaka, K. Takimiya, *J. Am. Chem. Soc.* **2016**, *138*, 7725.

Scanning Wave Photopolymerization Directs Three-dimensional Molecular Alignment Patterns in Liquid-crystalline Polymer Films as an Alignment Layer

(Laboratory for Chemistry and Life Science, Tokyo Institute of Technology) ○Yoshiaki Kobayashi, Norihisa Akamatsu, Shoichi Kubo, Atsushi Shishido

Keywords: Liquid Crystal; Photopolymerization; Molecular Alignment; Polymer Film

The control of molecular alignment, which enhances nanoscale molecular functions to macroscale material ones, is crucial for developing high-performance materials and devices.¹ The simple and practical method for the alignment control using mechanical stress enables the fabrication of one-dimensional alignment over large areas. On the other hand, a photoalignment method has drawn much attention due to its clean and non-contact process.² With conventional photoalignment methods, a liquid-crystalline (LC) film containing photoresponsive dyes is irradiated with spatiotemporally uniform linearly polarized light, and the molecular alignment is controlled via the interaction between the dipole of dyes and the polarization axis of the incident light. However, the fine control of microscopic three-dimensional molecular alignment remains a challenge in this method. Recently, we have reported a new photoalignment method based on a concept of scanning wave photopolymerization (SWaP).³ In this study, we fabricated the LC polymer films with three-dimensional alignment patterns by optimizing the photopolymerization conditions and explored the functionality of the polymer films as an alignment layer for LCs.

A sample mixture composed of an anisotropic monomer, an anisotropic crosslinker and a photoinitiator was spin-coated on an ozone-treated glass substrate. Subsequently, SWaP process was conducted to the sample by scanning a slit UV light for fabricating molecularly aligned polymer films. As a result, SWaP successfully induced the homeotropic and pretilt alignment with control of photopolymerization temperature and incident light intensity. Next, a glass cell was prepared by adhering two glass plates with the aligned polymer films. Low-molecular-weight LC molecules doped with a small amount of a dichroic dye were injected into the glass cell. Polarized optical microscopy and polarized UV-visible absorption spectroscopy revealed that both LC molecules and dyes were aligned in the same direction along the alignment direction of the LC polymers. These results indicate that the three-dimensionally aligned polymer films fabricated by SWaP enable the control of homeotropic, tilted and homogeneous alignment of LC molecules, acting as a three-dimensional alignment layer.

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Angularly Anisotropic Giant Circularly Polarized Luminescence from Chiral Conjugated Polymer Microsphere

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Keywords: Conjugated Polymer; Self-Assembly; Microsphere; Circularly Polarized Luminescence; Cholesteric Structure

Pixeled circularly polarized luminescence (CPL) emitter of supramolecular assemblies with large dissymmetry (g_{lum}) and angular anisotropy are valuable for integrated organic optoelectronics devices. However, such CPL emitter has not yet been achieved.¹ The reason for this limitation mainly comes from the difficulty in incorporating ordered nano-helical architectures into a mechanically stiff minute object. Here, we present novel angularly anisotropic CPL emitters from self-assembled polymeric microspheres.

π -conjugated polymers bearing enantiopure chiral side chains ((*S,S*)-PFBT)² (**Fig. 1a**) self-assembly into well-defined solid microspheres upon a sluggish diffusion of poor solvent vapor. Despite its spherical morphology, the resultant microspheres exhibit anisotropic birefringence (**Fig. 1b**) and feature twisted-bipolar topology, where the polymer chains helically stack with one another to form cholesteric helicoids in a structurally anisotropic manner (**Fig. 1c**). The twisted bipolar interior is formed via liquid-liquid phase separation and subsequent condensation into cholesteric lyotropic liquid crystalline mesophase. The methanol suspension of the chiral microspheres displays marked CPL with the average $|g_{lum}|$ value as high as 0.23. Furthermore, single-particle CPL measurements reveal that the twisted-bipolar microspheres show distinct anisotropic CPL emission, where $|g_{lum}|$ toward the equatorial direction reaches ~ 0.5 , which is 2.5-fold greater than that along the bipolar axis (**Fig. 1c, d**).

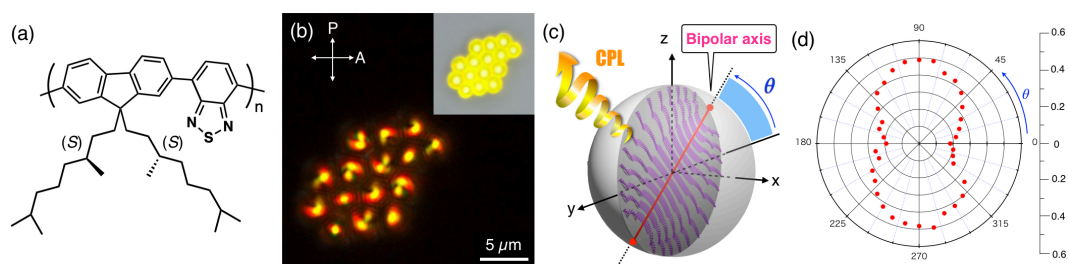


Figure 1. (a) Molecular structure of (*S,S*)-PFBT. (b) Polarized optical and optical (inset) micrographs of the self-assembled microspheres. (c) A schematic representation of twisted bipolar configuration in the microsphere. The cylinders (purple) represent the mainchain of the polymer. (d) Plots of altitudinal (θ) polar coordinate of $|g_{lum}|$ at 546 nm values of the single microsphere.

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Bio-based Polymer Derived Anode Material for Fast Charging and Long-cycle Life Lithium-ion Battery

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Keywords: *Polybenzimidazole, Nitrogen Doped Carbon, Anode Material*

Currently graphite is the most commercially used anode material for lithium-ion batteries (LIB), however its limited theoretical capacity of 372 mAhg^{-1} and slow kinetics cannot satisfy the requirements for EVs. Hence, alternative high energy density anode materials with fast kinetics are need of the hour. Extreme fast charging, with a goal of 15 minutes fast charging, is poised to accelerate mass market production of electric vehicles. Key strategies for improving the rate capability of carbonaceous materials are (a) heteroatom doping, especially nitrogen doping and (b) increasing the d-spacing for accessing more active sites. So, our objective is to use nitrogen rich Bio-based polymer as a single source of nitrogen and carbon to prepare heavily nitrogen doped carbon with nearly 20 at% of nitrogen with increased d-spacing and understand its effect on Li ion storage.

Poly (2, 5-benzimidazole) (PBI) was synthesized by homo-polycondensation method using a bio derivable starting material 3, 4-diaminobenzoic acid¹. The as prepared PBI was pyrolyzed at 800°C in nitrogen atmosphere. The obtained material was systematically characterized before preparation of anodes for Li ion battery application. The SEM-EDX data revealed the content of nitrogen was as high as 18 at%. Further, long cycling studies were performed for >1000 cycles at 0.4, 0.8 and 1.8 Ag^{-1} rates. Results indicated that PY PBI 800 can deliver highest de-lithiation capacity of $\sim 260 \text{ mAhg}^{-1}$ at specific capacity of 0.4 Ag^{-1} rate with nearly 88% capacity retention after 1000 cycles (Figure 1). At higher current rate of 0.8 Ag^{-1} , and 1.8 Ag^{-1} , it showed highest discharge capacity of 165 mAhg^{-1} and 135 mAhg^{-1} with 90% and 75% capacity retention after 1000 cycles respectively. Further, full cell was studied with LiCoO_2 as cathode and PY PBI 800 as anode. Full cell studies also revealed the promising nature of PY PBI 800.

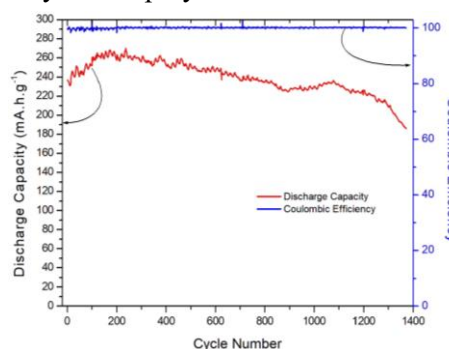


Figure 1: Long cycling studies for 1000 cycles at 0.4 Ag^{-1} .

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