Mon. Mar 22, 2021

Room 5

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

[A05-4pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair:Masakazu Nambo, Sadahiro Masuo
1:00 PM - 2:40 PM Room 5 (Online Meeting)

[A05-4pm-01] Size-dependent halide segregation of single mixed-halide perovskite nanocrystals

○Yoshua Albert Darmawan[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

1:00 PM - 1:20 PM

[A05-4pm-02] Synthesis and Transformation of *N*-Heterocyclic Carbene Functionalized Gold Nanoclusters

○Kimberly Osten[1], Paul Lummis[2], Masakazu Nambo[1], Cathleen Crudden[1,2] (1. Nagoya University, Institute of Transformative Bio-Molecules (WPI-ITbM), 2. Queen's University)

1:20 PM - 1:40 PM

[A05-4pm-03] Fabrication and Electrical Characterization of Naked Superatom Assembled Films based on High Intensity Nanocluster Source and Soft Landing

○Takaho Yokoyama[1], Tatsuya Chiba[1], Naoyuki Hirata[1], Masahiro Shibuta[1], Atsushi Nakajima[1] (1. Keio University)

1:40 PM - 2:00 PM

[A05-4pm-04] Bidentate N-heterocyclic carbenes protected chiral Au_{13} nanoclusters: Synthesis, characterization and application

○Hong Yi[1], Masakazu Nambo[1], Cathleen Crudden[1] (1. Institute of Transformative Bio-Molecules (WPI-ITbM) Nagoya University)

2:00 PM - 2:20 PM

[A05-4pm-05] Development of muon detecting system for revealing muon catalyzed fusion elementary processes

○Kenichi Okutsu[1], Yasushi Kino[1], Ryota Nakashima[1], Konan Miyashita[1], Yasuda Kazuhiro[1], Takuma Yamashita[1], Shinji Okada[2], Motoyasu Sato[2], Toshitaka Oka[3], Naritoshi Kawamura[4], Koichiro Shimomura[4], Patirck Strasser[4], Soshi Takeshita[4], Tampo Motonobu[4], Shogo Doiuchi[4], Yukinori Nagatani[4], Hiroaki Natori[4], Amba Datt Pant[4], Yasuhiro Miyake[4], Katsuhiko Ishida[5] (1. Tohoku Univ., 2. Chubu Univ., 3. JAEA, 4. KEK, 5. Riken)

2:20 PM - 2:40 PM

Room 6

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

[A06-4pm] 06. Analytical Chemistry

Chair:Takeshi Hashimoto, Kosuke Ino
1:00 PM - 3:20 PM Room 6 (Online Meeting)

[A06-4pm-01] Visualization of submicron structures within deeper layers of biological tissues utilizing spatial light modulator

○Kazushi Yamaguchi[1,2,3], Kohei Otomo[1,2,3,4,5], Yuichi Kozawa[6], Motosuke Tsutsumi[2,3,4], Tomoko Inose[1,2], Kenji Hirai[1,2], Shunichi Sato[6], Tomomi Nemoto[1,2,3,4,5], Hiroshi Uji-i[1,2,7] (1. IST, Hokkaido Univ., 2. RIES, Hokkaido Univ., 3. NIPS, 4. ExCELLS, 5. The Graduate School for Advanced Study, 6. IMRAM, Tohoku Univ., 7. KU Leuven)

1:00 PM - 1:20 PM

[A06-4pm-02] Highly sensitive immunoassay with dual signal amplification systems of redox cycling in nanospace and cascade reaction

○Kentaro Ito[1], Kumi Y. Inoue[1,3], Kosuke Ino[2], Tomokazu Matsue[4], Hitoshi Shiku[2] (1. Graduate School of Environmental Studies, Tohoku University, 2. Graduate School of Engineering, Tohoku University, 3. Graduate Faculty of Interdisciplinary Research, University of Yamanashi , 4. Center for Promotion of Innovation Strategy, Tohoku University)

1:20 PM - 1:40 PM

[A06-4pm-03] Quantitative analysis of vasculature-on-a-chip using scanning probe microscopy

○Yuji Nashimoto[1,2,3], Minori Abe[3], Ryota Fujii[3], Noriko Taira[3], Hiroki Ida[1,4,5], Yasufumi Takahashi[6,5], Kosuke Ino[2], Hitoshi Shiku[2,3] (1. Frontier Research Institute for Interdisciplinary Science, 2. Graduate School of Engineering, Tohoku University, 3. Graduate School of Environmental Studies, Tohoku University, 4.

Advanced Institute for Materials Research, Tohoku University, 5. JST PRESTO, 6. Nano Life Science Institute, Kanazawa University)
1:40 PM - 2:00 PM

[A06-4pm-04] Development of chemical measurement descriptors to explore physical properties of biopolymers (hairs)
○Ayari Takamura[1], Kaede Tsukamoto[2], Kenji Sakata[1], Jun Kikuchi[1,2] (1. RIKEN, 2. Yokohama City Univ.)
2:00 PM - 2:20 PM

[A06-4pm-05] Development of sensitive bacterial detection by phenylboronic acid modified dendrimer with fluorescent dansyl group
○Ayame Mikagi[1], Riho Tsuruhusa[1], Yuji Tsuchido[2], Takeshi Hashimoto[1], Takashi Hayashita[1] (1. Sophia Univ., 2. Waseda Univ.)
2:20 PM - 2:40 PM

[A06-4pm-06] Supramolecular Cyclodextrin Complexes for Electrochemical Detection of Metabolites in Water
○Maria Antonietta Casulli[1], Takeshi Hashimoto[1], Takashi Hayashita[1] (1. Sophia University, Department of Materials and Life Sciences, Faculty of Science and Technology)
2:40 PM - 3:00 PM

[A06-4pm-07] Colorimetric detection of bacteria pathogens through aggregation of gold nanoparticles induced by thiolated bacteriophages
○Satoshi Yamashita[1], Yosuke Niko[1], Shingo Hadano[1], Shigeru Watanabe[1], Iyo Uchiyama[2], Jyunpei Uchiyama[2], Shigenobu Matsuzaki[3] (1. Graduate School of Science, kochi university, 2. School of Veterinary Medicine, Azabu University, 3. Faculty of Health Science, Kochi Gakuen University)
3:00 PM - 3:20 PM

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

[A06-4am] 07. Inorganic Chemistry

Chair:Shinya Hayami, Kenji Okada
9:00 AM - 11:20 AM Room 6 (Online Meeting)

[A06-4am-01] Configurational and communal entropies in non-stoichiometric PdH_x
○Yoshihiro Shimizu[1], Manshi Ohyanagi[1] (1. Ryukoku Univ.)
9:00 AM - 9:20 AM

[A06-4am-02] 3D Porous Ni/NiO_x as a bifunctional oxygen electrocatalyst derived from Freeze-dried $Ni(OH)_2$
○Yuta Shudo[1], Shinya Hayami[1] (1. Kumamoto University)
9:20 AM - 9:40 AM

[A06-4am-03] Oriented growth of COF crystals on metal-hydroxides thin film
○Ken Ikigaki[1], Kenji Okada[1], Paolo Falcaro[3], Christian Doonan[2], Masahide Takahashi[1] (1. Osaka Prefecture University, 2. University of Adelaide, 3. Graz University of Technology)
9:40 AM - 10:00 AM

[A06-4am-04] Development of Efficient Triplet-DNP System Using Metal-Organic Frameworks
○Arijit Mallick[1,2], Saiya Fujiwara[2], Nobuhiro Yanai[2,3,4], Nobuo Kimizuka[2,4] (1. JSPS Postdoctoral Fellow, 2. Kyushu University, 3. PRESTO, JST, 4. CMS, Kyushu Univ.)
10:00 AM - 10:20 AM

[A06-4am-05] Polycarboxylates as synthetic tools for small and efficient perovskite quantum dots.
○Olivier Chevalier[1], Takayuki Nakamuro[1], Rui Shang[1], Eiichi Nakamura[1] (1. The University of Tokyo, Graduate School of Science)
10:20 AM - 10:40 AM

[A06-4am-06] Synthesis and structure of porous ionic crystals based on delta-Keggin-type aluminum polyoxocation
○Wei Zhou[1], Sayaka UCHIDA[1], Naoki OGIWARA[1], Wei Zhe Weng[1] (1. Department of Basic Science, School of Arts and Sciences, The University of Tokyo)
10:40 AM - 11:00 AM

[A06-4am-07] Porous ionic crystals composed of Nb/W mixed-addenda polyoxometalates as solid base catalysts
○Zhewei Weng[1], Sayaka Uchida[1] (1. Department of Basic Science, School of Arts and Sciences, The University of Tokyo)
11:00 AM - 11:20 AM

Room 7

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

[A07-4pm] 08. Catalysts and Catalysis

Chair:Hiroyuki Asakura, Kazuya Yamaguchi
1:00 PM - 3:20 PM Room 7 (Online Meeting)

[A07-4pm-01] Direct catalytic arylation of cubane and bicyclo[1.1.1]pentane
○Ryo Okude[1], Genki Mori[1], Akiko Yagi[1], Kenichiro Itami[1] (1. Nagoya University)
1:00 PM - 1:20 PM

[A07-4pm-02] Iron-Catalyzed Regioselective Thienyl C–H/C– H Coupling and Polycondensation
○Takahiro Doba[1], Laurean Ilies[2], Rui Shang[1], Eiichi Nakamura[1] (1. The University of Tokyo, 2. RIKEN)
1:20 PM - 1:40 PM

[A07-4pm-03] Accessing 1*H*-Indenyl and Dihydro-*s*-Indacenyl Magnesium Reagents via Iron-catalyzed C– O Activation/Acetylenic Cyclization with Magnesium Powder
○MENGQING CHEN[1], Rui Shang[1], Eiichi Nakamura[1] (1. The University of Tokyo)
1:40 PM - 2:00 PM

[A07-4pm-04] Oxygen Reduction Reaction Activity and Characterization of Fe/N/C Catalysts Prepared by Pyrolysis of Fe Complexes Containing 1,12-Diazatriphenylene as a Ligand Structure
○Koki Matsumoto[1], Akira Onoda[2], Takashi Hayashi[1] (1. Graduate school of Engineering, Osaka University, 2. Faculty of Environmental Earth Science, Hokkaido University)
2:00 PM - 2:20 PM

[A07-4pm-05] Water electrolysis in saturated phosphate buffer at neutral pH
○Takahiro Naito[1], Tatsuya Shinagawa[1], Kazuhiro Takanabe[1] (1. The University of Tokyo)
2:20 PM - 2:40 PM

[A07-4pm-07] Highly Stable and Active Solid-Solution-Alloy Three-Way Catalysts by Utilizing the Entropy Effect
○Kohei Kusada[1], Dongshuang Wu [1], Yusuke Nanba[2], Michihisa Koyama[2], Tomokazu Yamamoto[3], Takaaki Toriyama[3], Xuan Tran[3], Syo Matstumura[3], Katsutoshi Sato[1], Katsutoshi Nagaoka[4], Hiroshi Kitagawa[1] (1. Kyoto University, 2. Shinshu University, 3. Kyushu University, 4. Nagoya Universtiy)
3:00 PM - 3:20 PM

Room 12

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

[A12-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Kyoko Nozaki, Hajime Ito, Hiroaki Kotani
9:00 AM - 11:40 AM Room 12 (Online Meeting)

[A12-4am-01] Probing Key Reaction Steps in Ce(IV)-driven Water Oxidation Catalyzed by a Mononuclear Ruthenium Complex
○Yutaro Aimoto[1], Alexander Parent[2], Kenton Rodgers[2], Kosei Yamauchi[1], Ken Sakai[1] (1. Dept. Chem. Kyushu Univ., 2. North Dakota State University)
9:00 AM - 9:20 AM

[A12-4am-02] Mechanistic Investigations and Photocatalytic Properties of CO_2-reduction Using Supramolecular Photocatalyst Fixed on Solid Surface
○Daiki Saito[1], Osamu Ishitani[1] (1. Tokyo Institute of Technology)
9:20 AM - 9:40 AM

[A12-4am-03] Control over Catalytic Activity of a Multinuclear Metal Complex Using a Encapsulated Hydrogen Ion
○Misa Tomoda[1,2,3], Yutaka Saga[1], Mio Kondo[1], Shigeyuki Masaoka[1] (1. Osaka University, 2. IMS, 3. SOKENDAI)
9:40 AM - 10:00 AM

[A12-4am-04] Luminescence intensity enhancement for Ir(Ⅲ) complex in dimethyl sulfoxide under photoirradiation
○Shuntaro Hirata[1], Shingo Hattori[1], Kazuteru Shinozaki[1] (1. Yokohama City Univ.)
10:00 AM - 10:20 AM

[A12-4am-05] Regio- and Stereoselective Synthesis of Multi-Alkylated Allylic Boronates through Borylative Coupling of 1,1-Disubstituted Allenes and Alkyl Halides
○Yu Ozawa[1], Kohei Endo[1], Hajime Ito[1,2] (1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-Institute for Chemical Reaction Design and

Discovery (WPI-ICReDD), Hokkaido University)
10:20 AM - 10:40 AM

[A12-4am-06] Aerobic Oxidation Activity of Cu(Phen) Embedded in Hydrophobic Environment
○Shoko Kume[1], Shota Shimizu[2] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. Graduate School of Science, Hiroshima University)
10:40 AM - 11:00 AM

[A12-4am-07] Analysis of Catalytic Performance by Machine Learning for Understanding of Ethylene/Methyl Acrylate Copolymerization Catalyzed by Palladium/Phosphine–Sulfonate Complexes
○Shumpei Akita[1], Jin-Yao Guo[2], Sigman M Sigman[2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. The University of Utah)
11:00 AM - 11:20 AM

[A12-4am-08] Cleavage of C– H Bonds by Cyclopentadienone Iridium Complex
○Takuya Higashi[1], Shuhei Kusumoto[1,2], Kyoko Nozaki[1] (1. Graduate School of Engineering, the University of Tokyo, 2. JST PRESTO)
11:20 AM - 11:40 AM

Room 13

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

[A13-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Shouhei Tashiro, Takane Imaoka, Yukatsu Shichibu, Takashi Fukushima
9:00 AM - 11:40 AM Room 13 (Online Meeting)

[A13-4am-01] Concentration dependence of absorption and emission spectra of Pt(II) and Au(I) complexes oligomers in aqueous solutions
○Munetaka Iwamura[1], Koichi Nozaki[1], Rina Urayama[1], Airi Fukui[1] (1. Univ. of Toyama)
9:00 AM - 9:20 AM

[A13-4am-02] Spectroscopic properties of aggregates composed of square-planar platinum(II) complexes
○Shingo Hattori[1], Rina Owada[1], Kazuteru Shinozaki[1] (1. Yokohama City Univerisity)
9:20 AM - 9:40 AM

[A13-4am-03] Synthesis of a chiral-at-Pt(II)-Cu(I) complex with a bisphenanthroline macrocycle
○Shun Shimizu[1], Shohei Tashiro[1], Mitsuhiko Shionoya[1] (1. The University of Tokyo)
9:40 AM - 10:00 AM

[A13-4am-04] Syntheses, Crystal Structures, and Properties of Paramagnetic Multinuclear Assembles with Trans Pt-M-Pt Trinuclear Complexes
○Atsushi Takamori[1], Kazuhiro UemuraUemura[2] (1. Graduate School of Engineering, Gifu University, 2. Faculty of Engineering, Gifu University)
10:00 AM - 10:20 AM

[A13-4am-05] Synthesis and Catalytic Properties of Platinum and Platinum Alloy Sub-nanoparticles with Single-Digit Atomicity
○Yuki Akanuma[1], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-ERATO)
10:20 AM - 10:40 AM

[A13-4am-06] Thin film formation of thiolate-protected Au_{25} cluster through inter-cluster covalent linking
○Yuki Saito[1], Yukatsu Shichibu[1,2], Katsuaki Konishi[2,1] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)
10:40 AM - 11:00 AM

[A13-4am-07] Heteropolymetallic Pd/Cu and Pt/Cu for metal-metal cooperative bond activation
○Shubham Deolka Deolka[1], Orestes Rivada wheelaghan[1], Govindarajan ramadoss[1], Eugene Khaskin[1], Julia Khusnutdinova[1] (1. OIST ,JAPAN)
11:00 AM - 11:20 AM

[A13-4am-08] Preparation and Reactivity of Molybdenum Complexes Bearing Pyrrole-Based PNP-Type Pincer Ligand
○Yoshiaki Tanabe[1], Yoshiya Sekiguchi[1], Shogo Kuriyama[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo)
11:20 AM - 11:40 AM

Room 16

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

[A16-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair:Yoichi Hoshimoto, Kohei Takahashi
9:00 AM - 11:40 AM Room 16 (Online Meeting)

[A16-4am-01] Ni-Catalyzed Aryl Transfer Reaction Between Two Different Aromatic Compounds
○Ryota Isshiki[1], Miki Kurosawa[1], Naomi Inayama[1], Kei Muto[1], Junichiro Yamaguchi[1] (1. Waseda University)
9:00 AM - 9:20 AM

[A16-4am-02] Solar-Driven Hydrogenation Using Ethanol as Hydrogen Source
○Naoki Ishida[1], Yoshiki Kamae[1], Keigo Ishizu[1], Yuka Kamino[1], Hiroshi Naruse[1], Masahiro Murakami[1] (1. Kyoto University)
9:20 AM - 9:40 AM

[A16-4am-03] Nickel-Catalyzed C-O/N-H, C-S/N-H and C-CN/N-H Annulation of Aromatic Amides with Alkynes
○Yasuaki Iyori[1], Rina Ueno[1], Aoi Morishige[1], Naoto Chatani[1] (1. Faculty of Engineering, Osaka University)
9:40 AM - 10:00 AM

[A16-4am-04] Nickel-Catalyzed Cross-Coupling Reaction of Acyl Fluorides with Terminal alkynes
○Qiang Chen[1], Liyan Fu[1], Jingwen You[1], Yasushi Nishihara[2] (1. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayama Univ.)
10:00 AM - 10:20 AM

[A16-4am-05] Asymmetric Coupling of 1,3-Dienes and C-Nucleophiles by Ni/Cu Cooperative Catalysts Bearing Planer Chiral Diphosphine Ligand
○Takahiro Hirai[1], Jingzhao Xia[1,2], Shoichiro Katayama[1], Haruki Nagae[1], Wanbin Zhang[2], Kazushi Mashima[1] (1. Department of Chemistry, Graduate School of Engineering Science, Osaka University, 2. Shanghai Jiao Tong University)
10:20 AM - 10:40 AM

[A16-4am-06] Synthesis of (hydrosilyl)boranes via Si– H monoborylation of dihydrosilanes
○Takumi Takeuchi[1,2], Ryosuke Shishido[1,2], Koji Kubota[1,2], Hajime Ito[1,2] (1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)
10:40 AM - 11:00 AM

[A16-4am-07] Mechanism of Asymmetric Coupling of 1,3-Dienes and C-Nucleophiles by Ni/Cu Cooperative Catalysts by DFT Calculations
○Haruki Nagae[1], Jingzhao Xia[1,2], Shoichiro Katayama[1], Takahiro Hirai[1], Wanbin Zhang[2], Kazushi Mashima[1] (1. Osaka University, 2. Shanghai Jiao Tong University)
11:00 AM - 11:20 AM

[A16-4am-08] Catalytic Cycloaddition Reactions between Propargylic Alcohols Derivatives and Hydrazones
○Shiyao Liu[1], Yoshiaki Tanabe[1], Shogo Kuriyama[1], Ken Sakata[2], Yoshiaki Nishibayashi[1] (1. The University of Tokyo, 2. Toho University)
11:20 AM - 11:40 AM

Room 15

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

[A15-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair:Yoshihiro Nishimoto, Sobi Asako
9:00 AM - 11:20 AM Room 15 (Online Meeting)

[A15-4am-01] Synthesis of Alkynylsilanes by Catalytic Decarboxylation of Silyl Alkynoates
○Takahiro Kawatsu[1], Keiya Aoyagi[1], Sho Kataoka[2], Yumiko Nakajima[1], Norihisa Fukaya[1], Jun-Chul Choi[1], Kazuhiko Sato[1], Kazuhiro Matsumoto[1] (1. AIST, IRC3, 2. AIST, CPT)
9:00 AM - 9:20 AM

[A15-4am-02] Development of Silylsilanolates as New Silylating Reagents
○Hiroki Yamagishi[1], Jun Shimokawa[1], Hideki Yorimitsu[1] (1. Kyoto University)
9:20 AM - 9:40 AM

[A15-4am-03] Development of 7-Membered Dialkoxysilyl Group and Its Application to Organic Synthesis
○Hayate Saito[1], Jun Shimokawa[1], Hideki Yorimitsu[1] (1. Kyoto Univ.)
9:40 AM - 10:00 AM

[A15-4am-04] Borylation Reactions with Novel

Borylstannanes via Radical Mechanism

○Kensuke Suzuki[1], Yoshihiro Nishimoto[1], Makoto Yasuda[1] （1. Osaka University）

10:00 AM - 10:20 AM

[A15-4am-05] Solvent-less mechanochemical synthesis of magnesium-based carbon nucleophiles and their application to organic synthesis

○Rina Takahashi[1], Anqi Hu[2], Yadong Pang[2], Tamae Seo[1], Koji Kubota[1,2], Hajime Ito[1,2] （1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University）

10:20 AM - 10:40 AM

[A15-4am-06] Organic Synthesis Using Sodium Dispersion

○Ikko Takahashi[1], Hirotaka Nakajima[2], Laurean Ilies[1], Yoshiaki Murakami[3], Sobi Asako[1,2], Kazuhiko Takai[2] （1. RIKEN Center for Sustainable Resource Science, 2. Graduate School of Natural Science and Technology, Okayama University, 3. KOBELCO ECO-Solutions Co., Ltd.）

10:40 AM - 11:00 AM

[A15-4am-07] Sodium-Metal-Promoted 1,2-Dimagnesiation and 1,2-Dialumination of Alkynes

○Fumiya Takahashi[1], Hideki Yorimitsu[1] （1. Kyoto University）

11:00 AM - 11:20 AM

Room 17

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

[A17-4pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair:Soji Shimizu, Yohei Haketa

1:00 PM - 3:20 PM Room 17 (Online Meeting)

[A17-4pm-01] Metalation-Induced Formation of Novel Fused Porphyrinoid Dimers from Tetrabromo-[36]octaphyrin *via* Transannular Bond Formation

○Akito Nakai[1], Takayuki Tanaka[1], Atsuhiro Osuka[1,2] （1. Kyoto University, 2. Ritsumeikan University）

1:00 PM - 1:20 PM

[A17-4pm-02] Modulation of Physicochemical Properties for Thiophene-fused Naphthodiphospholes by Precise Fusion of Heterole Rings

○Keiichi Ishida[1], Tomohiro Higashino[1], Hiroshi Imahori[1,2] （1. Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ.）

1:20 PM - 1:40 PM

[A17-4pm-03] Synthesis of novel peripherally fused corannulenes based on quintuple amination reactions and their structural and electronic perturbations

○Koki Kise[1], Shota Ooi[1], Takayuki Tanaka[1], Atsuhiro Osuka[1] （1. Kyoto University）

1:40 PM - 2:00 PM

[A17-4pm-04] Synthesis of Covalently Linked Norcorrole Dimers and Their Association Behavior

○Siyu Liu[1], Norihito Fukui[1], Hiroshi Shinokubo[1] （1. Nagoya Univ.）

2:00 PM - 2:20 PM

[A17-4pm-05] Synthesis of xanthene derivative exhibiting twisted intramolecular charge transfer emission

○Taro Koide[1], Shohei Iwamori[1], Satoshi Koga[2], Yasutaka Suzuki[2], Jun Kawamata[2], Yoshio Hisaeda[1] （1. Kyushu University, 2. Yamaguchi University）

2:20 PM - 2:40 PM

[A17-4pm-06] Synthesis and Properties of Pyrrole-Bridged Quinones

○Shinya Sugiura[1], Hiromitsu MAEDA[1] （1. Ritsumeikan Univ.）

2:40 PM - 3:00 PM

[A17-4pm-07] Borole-Embedded Polycyclic π-Electron Systems and Photoresponsive Behavior of their B– P Lewis Adducts

○Naoki Ando[1], Takuya Yamada[1], Hiroki Narita[1], Niels Oehlmann[2], Matthias Wagner[2], Shigehiro Yamaguchi[1,3] （1. Grad. Sch. Sci., Nagoya Univ. , 2. Goethe-Universität Frankfurt, 3. ITbM, Nagoya Univ.）

3:00 PM - 3:20 PM

Room 8

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

[A08-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair:Takashi Hirano, Kenta Kokado

9:00 AM - 11:40 AM Room 8 (Online Meeting)

[A08-4am-01] A novel platform for crystalline molecular rotor based on NHC metal complexes
○Mingoo Jin Jin[1,2], Rempei Ando[4], Marcus J. Jellen[3], Miguel A. Garcia-Garibay[3], Hajime Ito[1,2] (1. Hokkaido Univ. Dep. Eng., 2. Hokkaido Univ. WPI-ICReDD, 3. University of California Los Angeles, 4. Hokkaido Univ. Sch. Chem.)
9:00 AM - 9:20 AM

[A08-4am-02] Organofullerene Nano- and Microspheres Containing Inorganic and Biological Nanoparticles: Self-Assembly and Electron Tomography
○Ryosuke Sekine[1], Prince Ravat[1], Haruaki Yanagisawa[2], Chao Liu[1], Masahide Kikkawa[2], Koji Harano[1], Eiichi Nakamura[1] (1. Grad. School of Sci., The Univ. of Tokyo, 2. Grad. School of Med., The Univ. of Tokyo)
9:20 AM - 9:40 AM

[A08-4am-03] Identification and thermodynamics of rim binding modes of cyclodextrins by atomic-resolution electron microscopy
○Hiroki Hanayama[1], Junya Yamada[1], Koji Harano[1], Eiichi Nakamura[1] (1. The University of Tokyo)
9:40 AM - 10:00 AM

[A08-4am-04] Quantitative Evaluation of Noncovalent Interactions at the C_{60} Surface
○Michio Yamada[1], Haruna Narita[1], Yutaka Maeda[1] (1. Tokyo Gakugei University)
10:00 AM - 10:20 AM

[A08-4am-05] Linear momentum of a microfluid realizes an anisotropic reaction at the ends of a supramolecular nanofiber
○Chisako Kanzaki[1], Arinori Inagawa[2], Gaku Fukuhara[3,4], Tetsuo Okada[3], Tetsuya Narushima[5], Hiromi Okamoto[5], Munenori Numata[1] (1. Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, 2. Graduate School of Regional Development and Creativity, Utsunomiya University, 3. Department of Chemistry, Tokyo Institute of Technology, 4. JST, PRESTO, 5. Institute for Molecular Science)
10:20 AM - 10:40 AM

[A08-4am-06] Asymmetric benzoin condensation reaction involving dynamic crystallization
Aoi Washio[1], Yasushi Yoshida[1], ○Takashi Mino[1], Masami Sakamoto[1] (1. Graduated school of engineering, chiba University)
10:40 AM - 11:00 AM

[A08-4am-07] Rotaxane-based supramolecular mechanophores exhibiting reversible/irreversible change in their fluorescence property
○Tatsuya Muramatsu[1], Yoshimitsu Sagara[1,2] (1. School of Materials and Chemical Technology, Tokyo Institute of Technology, 2. JST PRESTO)
11:00 AM - 11:20 AM

[A08-4am-08] Relationship between Cooperative Photodimerization Reaction Process and Size Change of 9-Methylanthracene Single Crystal
○Kohei Morimoto[1], Daichi Kitagawa[1], Fei Tong[2], Christopher J. Bardeen[2], Seiya Kobatake[1] (1. Grad. Sch. Eng., Osaka City Univ., 2. Department of Chemistry, University of California, Riverside)
11:20 AM - 11:40 AM

Room 9

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

[A09-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair:Seiya Kobatake, Hiroshi Katagiri
9:00 AM - 11:40 AM Room 9 (Online Meeting)

[A09-4am-01] Accuracy of intermolecular interaction energies of molecules including hetero atoms using Grimme’ s dispersion corrections
○Seiji Tsuzuki[1], Tadafumi Uchimaru[1] (1. National Institute of Advanced Industrial Science and Technology)
9:00 AM - 9:20 AM

[A09-4am-02] Control of stacking patterns of two-dimensional molecular layers in hydrogen-bonded cocrystals composed of 2-pyrrolidone and anilic acids
○Masaki Donoshita[1], Yukihiro Yoshida[1], Mikihiro Hayashi[1], Ryuichi Ikeda[1], Kunihisa Sugimoto[2], Shogo Kawaguchi[2], Yasuhisa Yamamura[3], Kazuya Saito[3], Hiroshi Kitagawa[1] (1. Kyoto University,

2. JASRI/SPring-8, 3. University of Tsukuba)
9:20 AM - 9:40 AM

[A09-4am-03] Crystalline-state chemiluminescence property of 1,2-dioxetanes conjugated with a strongly fluorescent chromophore
○Chihiro Matsuhashi[1], Hironaga Ohyama[2], Hidehiro Uekusa[2], Ayana Sato-Tomita[3], Kouhei Ichiyanagi[4], Shojiro Maki[1], Takashi Hirano[1] (1. The Univ. of Electro-Communications, 2. Tokyo Tech, 3. Jichi Medical Univ., 4. KEK)
9:40 AM - 10:00 AM

[A09-4am-04] Control of Molecular Orientation in Organic Semiconductors Using Weak Iodine-Iodine Interactions
○Amane Matsunaga[1], Yuta Ogawa[1], Daisuke Kumaki[2], Shizuo Tokito[2], Hiroshi Katagiri[1] (1. Graduate School of Science and Engineering, Yamagata University, 2. Graduate School of Organic Materials Science, Yamagata University)
10:00 AM - 10:20 AM

[A09-4am-05] Design of photo-functional soft crystals based on degree of protonation in the acid-base complexes
○Yoshio Yano[1], Ono Toshikazu[1,2], Hisaeda Yoshio[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. Center for Molecular Systems, Kyushu Univ.)
10:20 AM - 10:40 AM

[A09-4am-06] Development of Thermo-responsive Solid-State Luminescent Materials Utilizing Intermolecular Interactions between Carboranes and Nitrogen Atoms
○Junki Ochi[1], Kazuo Tanaka[1] (1. Kyoto University)
10:40 AM - 11:00 AM

[A09-4am-07] Thermo- and Mechanoresponsive Turn-On Phosphorescence of Thienyl Diketone Crystal
○Yosuke Tani[1], Takuji Ogawa[1] (1. Osaka University)
11:00 AM - 11:20 AM

[A09-4am-08] Synthesis and Photophysical Properties of Extended Pyrazinacenes
○Gary James Richards[1,2], Jonathan Hill[2], Shinji Yamada[3], Katsuhiko Ariga[2], Akiko Hori[1] (1. Shibaura Institute of Technology, 2. National Institute of Materials Science, 3. Ochanomizu University)
11:20 AM - 11:40 AM

Room 18

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

[A18-4pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair:Takashi Koike, Shinji Yamada
1:00 PM - 3:40 PM Room 18 (Online Meeting)

[A18-4pm-01] Mechanoredox C-H functionalization reactions
○YADONG PANG[2], JOO WON LEE[1], KOJI KUBOTA[1,2], HAJIME ITO[1,2] (1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)
1:00 PM - 1:20 PM

[A18-4pm-02] Substituent effects on gas-phase stabilities of 2-phenyl-1,3-dehydroadamantane-5,7-diyliums
○Kazuhide Nakata[1], Mizue Fujio[2] (1. Hosei University, 2. Kyushu University)
1:20 PM - 1:40 PM

[A18-4pm-05] Photocatalytic reductive cleavage C-O bond of ether using carbazole catalyst
○Tatsushi Yabuta[1], Masahiko Hayashi[1], Ryosuke Matsubara[1] (1. Graduate school of science, Kobe university)
2:20 PM - 2:40 PM

[A18-4pm-06] Photocarboxylation of aromatic amine derivatives by fixing CO_2 driven via excited-state hydrogen detachment
○Akinobu Nakada[1,2], Kanae Abe[1], Ho-Chol Chang[1] (1. Chuo University, 2. PRESTO/JST)
2:40 PM - 3:00 PM

[A18-4pm-07] Synthesis of Propargyl Silanes from Propargyl Pivalates via C-O Bond Cleavage by Ca-Promoted Reductive Silylation
○Tianyuan Zhang[1], Hirofumi Maekawa[1] (1. Nagaoka Univ. of Tech.)
3:00 PM - 3:20 PM

[A18-4pm-08] Electrolyte-coordination-induced electrochemical multiple electron oxidation

of 2,5-diarylthiophenes and following unprecedented dimerization reaction to give sulfonium salt

○Naoki Shida[1,2], Takuma Maekawa[2], Ikuyoshi Tomita[2], Shinsuke Inagi[2] (1. Yokohama National University, 2. Tokyo Institute of Technology)

3:20 PM - 3:40 PM

Room 11

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

[A11-4pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair:Koji Hirano, Akihiro Orita
1:00 PM - 3:20 PM Room 11 (Online Meeting)

[A11-4pm-01] Study of the mechanism of selective recognition of p-*tert*-butylcalix[4]thiacrown-5 for organic mercury(II) compounds

○Tatsuya Takimoto[1], Yuu Hashimoto[1], Gen Inoue[1], kazuhito Hioki[1], Hideaki Sasaki[1] (1. Kobegakuin University)

1:00 PM - 1:20 PM

[A11-4pm-02] One-pot enantiodivergent synthesis of axially chiral biaryls using organocatalyst

○Seitaro Koshino[1], Tohru Taniguchi[2], Kenji Monde[2], Eunsang Kwon[1], Yujiro Hayashi[1] (1. Tohoku University,Graduate School of Science , 2. Hokkaido University, FrontierResearch Center of Advanced Material andLife Science Faculty of Advanced Life Science)

1:20 PM - 1:40 PM

[A11-4pm-04] Synthesis of Benzophosphole Derivatives via Phosphenium Dication Mediated Sequential Bond Forming Reaction

○Kazutoshi Nishimura[1], Koji Hirano[1], Masahiro Miura[1] (1. Graduate School of Engineering, Osaka University)

2:00 PM - 2:20 PM

[A11-4pm-05] Dearomative Activation of Fused Aromatic Compounds toward Achieving Regioselective Annulative π-Extension (APEX)

○Wataru Matsuoka[1], Hideto Ito[1], David Sarlah[3], Kenichiro Itami[1,2] (1. Nagoya Univ., 2. Institute of Transformative Bio-Molecules, 3. University of Illinois)

2:20 PM - 2:40 PM

[A11-4pm-06] Synthesis and Properties of a New Element-Substituted Pentalene Derivative

○Junki Kashida[1], Yoshiaki Shoji[1], Yasuhiro Ikabata[2], Hideo Taka[3], Hayato Sakai[4], Taku Hasobe[4], Hiromi Nakai[2], Takanori Fukushima[1] (1. CLS, Tokyo Tech, 2. Facul. Sci. and Eng., Waseda Univ., 3. Konica Minolta, 4. Facul. Sci. and Technol., Keio Univ.)

2:40 PM - 3:00 PM

[A11-4pm-07] Base- and Process-Controlled Regiodivergent [4+2] Benzannulation of Phosphoryl Ynamine

○Yasuhiro Okuda[1], Kazunori Masuda[1], Nobuyuki Akagi[1], Akihiro Orita[1] (1. Fac. of Eng., Okayama Univ. of Sci.)

3:00 PM - 3:20 PM

Room 19

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

[A19-4pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair:Takuya Kodama, Muhammet Uyanik
1:00 PM - 2:40 PM Room 19 (Online Meeting)

[A19-4pm-01] Phosphine-Catalyzed Carbofluorination of Alkynes via a P(V) Intermediate

○Hayato Fujimoto[1], Takuya Kodama[1], Masahiro Yamanaka[2], Mamoru Tobisu[1] (1. Osaka University, 2. Rikkyo University)

1:00 PM - 1:20 PM

[A19-4pm-02] Reductive Cyclization of α-Iminocarbonyl Compounds Catalyzed by Organosuperbase

○Azusa Kondoh[1], Masahiro Terada[1] (1. Tohoku University)

1:20 PM - 1:40 PM

[A19-4pm-03] Amine-catalyzed asymmetric Mannich reaction or conjugate addition using alkynyl *Z*-ketimines

○Chihiro Homma[1], Taichi Kano[1], Keiji Maruoka[2] (1. Graduate School of Science, Kyoto

University, 2. Graduate School of Pharmaceutical Sciences, Kyoto University)
1:40 PM - 2:00 PM

[A19-4pm-04] Helix Inversion of Chiral Poly(quinoxaline-2,3-diyl)s through Nonbonding Interaction with Specific Haloalkanes
○Takaya Fujie[1], Takeshi Yamamoto[1], Michinori Suginome[1] (1. Kyoto University)
2:00 PM - 2:20 PM

[A19-4pm-05] Hypoiodite-catalyzed Chemoselective Oxidative Cyclization of Indole Derivatives
○Hiroki Tanaka[1], Muhammet Uyanik[1], Kazuaki Ishihara[1] (1. Nagoya University)
2:20 PM - 2:40 PM

Room 22

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

[A22-4am] 16. Natural Products Chemistry, Chemical Biology

Chair:Kaname Sasaki, Akihiro Ishiwata
9:00 AM - 11:40 AM Room 22 (Online Meeting)

[A22-4am-01] Synthetic Studies on Ikoamide, a highly *N*-methylated linear lipopeptide
○YUNG-HAN LO[1] (1. Keio University)
9:00 AM - 9:20 AM

[A22-4am-02] Discovery of a cyclotide-based coagulation Factor XIIa inhibitor by mRNA display
○Wenyu LIU[1], Simon J. de Veer[2], Yen-Hua Huang[2], Toby Passioura[1], Hiroaki Suga[1], David Craik[2] (1. Department of Chemistry, Graduate School of Science, the University of Tokyo, 2. Institute for Molecular Bioscience, The University of Queensland)
9:20 AM - 9:40 AM

[A22-4am-03] One Pot-Chemical Synthesis of Glycoproteins and Their Glycan-Hydration Effect
○Hiroyuki Shibata[1], Yuya Tanaka[1], Donglin Zhao[1], Yuta Maki[1], Yasuhiro Kajihara[1], Ryo Okamoto[1] (1. Grad. Sch. Sci., Osaka Univ.)
9:40 AM - 10:00 AM

[A22-4am-04] Semisynthetic Study of Interleukin-6 (IL-6)
○Yanbo Liu[1], Ryo Okamoto[1], Yuta Maki[1], Yasuhiro Kajihara[1] (1. Grad. Sch. Sci., Osaka Univ.)
10:00 AM - 10:20 AM

[A22-4am-05] Development of High-mannose Glycan Library Synthesized by Dendritic Glycosylation
○Ruchio Usui[1], Megumi Kabasawa[1], Taiki Kuribara[1], Kiichiro Totani[1] (1. Seikei University)
10:20 AM - 10:40 AM

[A22-4am-06] Synthesis of Oligoglucosamine Analogues Equipped with Trimethylammonium Glycoside
○Md Azadur Rahman[1], Shuji Takahashi[1], Toshiki Nokami[1] (1. Tottori University)
10:40 AM - 11:00 AM

[A22-4am-07] Systematic Synthesis of Squaryl Group Modified Glycolipid Analogues as Potential Ligands of GPR55
○Junpei Abe[1], Adam Tsuda Guy[2], Feiqing Ding[3], Peter Greimel[2], Yoshio Hirabayashi[4], Hiroyuki Kamiguchi[2], Yukishige Ito[1,4] (1. Grad. Sch. Sci. Osaka Univ. , 2. RIKEN CBS, 3. Sch. Pharm. Sci. SunYat-sen Univ., 4. RIKEN CPR)
11:00 AM - 11:20 AM

[A22-4am-08] Diosgenin-induced physicochemical effects on phospholipid bilayers in comparison with cholesterol
○Joan Candice Ondevilla[1] (1. Osaka University)
11:20 AM - 11:40 AM

Room 25

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

[A25-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair:Ryosuke Ueki, Kou Okuro
1:00 PM - 3:00 PM Room 25 (Online Meeting)

[A25-4pm-01] A DNA aptamer that inhibits aberrant receptor signaling in cancer cells
○Akihiro Eguchi[1], Ayaka Ueki[1], Keiko Kuwata[2], Yoko Chikaoka[3], Takeshi Kawamura[3], Satoru Nagatoishi[4], Kouhei Tsumoto[1,4], Ryosuke Ueki[1], Shinsuke Sando[1] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. WPI-ITbM, Nagoya University,, 3. ISC, The University of Tokyo, 4. IMS, The University of Tokyo,)

1:00 PM - 1:20 PM

[A25-4pm-02] Photoreactive molecular glue for immobilizing DNA aptamer onto targeted proteins

○Ai Kohata[1], Kou Okuro[2], Takuzo Aida[1] (1. The University of Tokyo, 2. University of Hong Kong)

1:20 PM - 1:40 PM

[A25-4pm-03] Studies on Synthesis and Property of Chimeric Artificial Nucleic Acid Conjugated with DNA for Catalytic Target RNA Cleavage

○Akira Yano[1], Masahito Inagaki[1], Tsuyoshi Yamamoto[2], Masaki Nishijima[1], Yasuyuki Araki[1], Asako Yamayoshi[2], Satoru Ishibashi[3], Takanori Yokota[3], Takehiko Wada[1] (1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Department of Chemistry of Biofunctional Molecules, School of Pharmaceutical Sciences, Nagasaki University, 3. Department of Neurology and Neurological Science, Tokyo Medical and Dental University)

1:40 PM - 2:00 PM

[A25-4pm-04] X-ray crystal structure analysis of a reverse binding orientation cyclic-PIP and DNA complex and structural comparison with forward binding orientation complex

○Katsuhiko Abe[1], Yuki Hirose[1], Haruhiko Eki[1], Kazuki Takeda[1], Endo Masayuki[1], Bando Toshikazu[1], Hiroshi Sugiyama[1] (1. Kyoto University)

2:00 PM - 2:20 PM

[A25-4pm-05] Elucidation of mechanism and function of TERRA aggregates

○Tatsuki Masuzawa[1], Kentaro Takahama[1], Ayako Okushima[1], Riki Kurokawa[2], Takanori Oyoshi[1] (1. Shizuoka University, 2. Saitama Medical University)

2:20 PM - 2:40 PM

[A25-4pm-06] Development of large-scale analytical system for RNA alkylation reactions

○Kazumitsu Onizuka[1], Kaoru Richard Komatsu[2], Shunya Ishikawa[1], Yutong Chen[1], Kanna Ojima[1], Hirotaka Murase[1], Ryosuke Nagasawa[1], Mamiko Ozawa[1], Emi Miyashita[2], Hirohide Saito[2], Fumi Nagatsugi[1] (1. Tohoku Univ., 2. Kyoto Univ.)

2:40 PM - 3:00 PM

Room 24

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

[A24-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair:Yuki Goto, Rie Wakabayashi
1:00 PM - 3:20 PM Room 24 (Online Meeting)

[A24-4pm-01] Total Chemical Synthesis and Investigation of Modified Linker Histone H1.2 and HP1α Utilizing Ru catalyst

○Naoki Kamo[1], Tomoya Kujirai[2], Hitoshi Kurumizaka[2], Hiroshi Murakami[3], Gosuke Hayashi[3], Akimitsu Okamoto[1,4] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. IQB, The Univ. of Tokyo, 3. Grad. Sch. Eng., Nogoya Univ., 4. RCAST, The Univ. of Tokyo)

1:00 PM - 1:20 PM

[A24-4pm-02] Ribosomal synthesis of helical peptide libraries containing cyclic β-amino acids and its application to drug screening

○Marina Kawai[1], Takayuki Katoh[1], Hiroaki Suga[1] (1. The University of Tokyo)

1:20 PM - 1:40 PM

[A24-4pm-03] *In vitro* selection of a library of pseudo-natural prenylated peptides

○Sumika Inoue[1], RIka Okuma[1], Yuki Goto[1], Hiroaki Suga[1] (1. The Univ. of Tokyo)

1:40 PM - 2:00 PM

[A24-4pm-04] Rebuilding ring-type decameric assembly of peroxiredoxin by chemical modification

○Tomoki Himiyama[1], Tsutomu Nakamura[1] (1. National Institute of Advanced Industrial Science and Technology)

2:00 PM - 2:20 PM

[A24-4pm-05] Entropy-driven ring-opening polymerization of the cyclic hemoglobin monomer containing a high molecular weight PEG

○Takashi Matsuhira[1], Hiromi Sakai[1] (1. Nara Medical University)

2:20 PM - 2:40 PM

[A24-4pm-06] Controlled co-assembly of peptide amphiphiles and its cell adhesion

○Rie Wakabayashi[1], Rino Imatani[1], Noriho Kamiya[1], Masahiro Goto[1] (1. Kyushu University)

2:40 PM - 3:00 PM

[A24-4pm-07] Development of protein nanoparticles displaying IgG binding domain and luciferase

○Gaoyang Wang[1], Yasumasa Mashimo[1], Masayasu Mie[1], Eiry Kobatake[1] （1. Tokyo Institute of Technology）

3:00 PM - 3:20 PM

Room 23

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

[A23-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair:Shinichi Sato, Tomonori Tamura
1:00 PM - 3:00 PM Room 23 (Online Meeting)

[A23-4pm-01] A new reactive peptide tag-probe pair for the site-specific incorporation of designer chemical probes into proteins

○Vikram Thimaradka[1], Jae Hoon Oh[2], Christina Heroven[3,4], Radu Aricescu[3,4], Michisuke Yuzaki[5], Tomonori Tamura[1], Itaru Hamachi[1,2] （1. Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, JAPAN., 2. ERATO (Exploratory Research for Advanced Technology, JST), Sanbancho, Chiyodaku, Tokyo, 102-0075, JAPAN., 3. Division of Structural Biology, University of Oxford, Oxford OX3 7BN, UK., 4. Neurobiology Division, MRC Laboratory of Molecular Biology, Cambridge CB2 0QH, UK., 5. Department of Physiology, Keio University School of Medicine, Tokyo 160-8582, JAPAN.）

1:00 PM - 1:20 PM

[A23-4pm-02] Ligand-directed two-step labeling to quantify AMPA-type glutamate receptor trafficking

○Kento Ojima[1], Kyohei Soga[2], Itaru Hamachi[1,3], Shigeki Kiyonaka[2] （1. Kyoto Univ., 2. Nagoya Univ., 3. ERATO JST）

1:20 PM - 1:40 PM

[A23-4pm-03] Extra-cellular loop (ECL) engineering for GPCR-chemogenetics (3): Allosteric control of metabotropic glutamate receptor signaling

○Tomohiro Doura[1], Kanta Hasegawa[1], Shigeki Kiyonaka[1] （1. Graduate school of engineering, Nagoya University）

1:40 PM - 2:00 PM

[A23-4pm-04] Investigation on the local structural effects on chemical modification of cysteine residues on protein surface

Ryosei Tamaki[1], Teruyuki Miyake[1], Shun Hirota[1], ○Takashi Matsuo[1] （1. Nara Institute of Science and Technology）

2:00 PM - 2:20 PM

[A23-4pm-05] Development of photocatalyst-proximity protein labeling for profiling protein-protein interaction in intracellular microenvironment

○Michihiko Tsushima[1,2], Shinichi Sato[3], Hiroyuki Nakamura[1] （1. Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 2. School of Life Science and Engineering, Tokyo Institute of Technology,, 3. Frontier Research Institute for Interdisciplinary Sciences, Tohoku University）

2:20 PM - 2:40 PM

[A23-4pm-06] *De novo* design of transmembrane coiled-coil peptide channels

○Ai Niitsu[1], Andrew R Thomson[2], Alistair J Scott[2], Jason T Sengel[3], Yuji Sugita[1], Mark I Wallace[3], Hagan Bayley[4], Derek N Woolfson[2] （1. Riken, 2. Univ. of Bristol, 3. KCL, 4. Univ. of Oxford）

2:40 PM - 3:00 PM

Room 2

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

[A02-4am] 19. Colloid and Interface Chemistry

Chair:Kensuke Akamatsu, Masafumi Harada
9:00 AM - 11:40 AM Room 2 (Online Meeting)

[A02-4am-01] Threading Ultra-long Polymer into MOF: Synthesis and Physical Properties

○Tomoya Iizuka[1], Etsuhiro Miwa[2], Nobuhiko Hosono[1], Takashi Uemura[1,2] （1. Grad. Sch. of Front. Sci., Univ. of Tokyo, 2. Grad. Sch. of Eng., Univ. of Tokyo）

9:00 AM - 9:20 AM

[A02-4am-02] Novel redox and optical properties of thiolate-protected gold superatom

$Au_{25}(SR)_{18}$ induced by bulky ligands

○Tsubasa Omoda[1], Shinjiro Takano[1], Tatsuya Tsukuda[1,2] (1. Grad. Sch. Sci., The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)

9:20 AM - 9:40 AM

[A02-4am-03] Shape memory behaviour of Cu1.8S nanoparticles during cation exchange reaction

○ZHANZHAO LI[1], Masaki Saruyama[2], Toshiharu Teranishi[2] (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Chemical Research, Kyoto University)

9:40 AM - 10:00 AM

[A02-4am-04] Fabirication of aqueous nanoparticle colloids of metal porphyrins and photosensitized singlet oxygen generation by visible light irradiation.

○Tsuyoshi Asahi[1], Eiji Yukihiro[1], Taisei Himeda[1], Tamotsu Zako[1] (1. Ehime University)

10:00 AM - 10:20 AM

[A02-4am-05] Synthesis of Mo and Ru solid-solution alloy NPs and their hydrogen evolution reaction activity

○Shinya Okazoe[1], Kohei Kusada[1], Dongshuang Wu[1], Tomokazu Yamamoto[2], Takaaki Toriyama[2], Syo Matsumura[2], Shogo Kawaguchi[3], Yoshiki Kubota[4], Hiroshi Kitagawa[1] (1. Kyoto Univ., 2. Kyushu Univ., 3. JASRI/SPring-8, 4. Osaka Pref. Univ.)

10:20 AM - 10:40 AM

[A02-4am-06] Crystal-structure-controlled solid-solution alloy nanoparticles and their hydrogen evolution reaction performance

○QUAN ZHANG[1], Kohei Kusada[1], Dongshuang Wu[1], Tomokazu Yamamoto[2], Syo Matsumura[2], Yoshiki Kubota[3], Susan Meñez Aspera[4], Hiroshi Nakanishi[4], Hiroshi Kitagawa[1] (1. Kyoto University, 2. Kyushu University, 3. Osaka Prefecture University, 4. Akashi College)

10:40 AM - 11:00 AM

[A02-4am-07] Synthesis and Structural Transformation of Ternary Alloy Nanoparticles Containing Boron: Pd–*TM*– B

○Keigo KOBAYASHI[1], Kohei KUSADA[1], Dongshuang WU[1], Naoki OGIWARA[1], Hirokazu KOBAYASHI[1,2], Mitsutaka HARUTA[3], Hiroki KURATA[3], Tomokazu YAMAMOTO[4], Takaaki TORIYAMA[4], Syo MATSUMURA[4,5], Satoshi HIROI[6,7], Okkyun SEO[6,8], Chulho SONG[8], Yanna CHEN[6,8], Jaemyung KIM[8], Akhil TAYAL[8], Osami SAKATA[6,7,8,9], Koji OHARA[7], Tetsuo HONMA[7], Hiroshi KITAGAWA[1] (1. Graduate School of Science, Kyoto University, 2. JST PRESTO, 3. Institute of Chemical Research, Kyoto University, 4. Ultramicroscopy Research Center, Kyushu University, 5. Graduate School of Engineering, Kyushu University, 6. Research Center for Advanced Measurement and Characterization, NIMS, 7. JASRI, 8. Synchrotron X-ray Station at SPring-8, NIMS, 9. School of Materials and Chemical Technology, Tokyo Institute of Technology)

11:00 AM - 11:20 AM

[A02-4am-08] Vapor phase synthesis of bimetal nanoparticles with different nanostructures

○Naomi Sakono[1], Kazuki Omori, Koki Yamamoto, Naru Ishikuro (1. National Institute of Technology, Toyama College)

11:20 AM - 11:40 AM

Room 21

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

[A21-4am] 20. Materials Chemistry -Basic and Application-

Chair:Kazunori Matsuura, Shoichi Kubo
9:00 AM - 11:40 AM Room 21 (Online Meeting)

[A21-4am-01] Development of Self-healing hydrogels designed based on the Intercalation of Polymeric Ions into Mica.

○Shingo Tamesue[1], Yushin Saito[1] (1. Utsunomiya Uniersity)

9:00 AM - 9:20 AM

[A21-4am-02] Effect of Positional Isomerism of Picenodithiophene Derivatives on Semiconducting Properties

○Zhenfei Ji[1], Hiroki Mori[2], Yasushi Nishihara[2] (1. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayama Univ.)

9:20 AM - 9:40 AM

[A21-4am-03] Photochromism of Imidazole Dimer Bridged

by Helical Aromatic Molecule

○Katsuya Mutoh[1], Jiro Abe[1] （1. Aoyama Gakuin University）

9:40 AM - 10:00 AM

[A21-4am-04] Propulsion of DNA microspheres driven by light-induced peptide nanofiber growth

○Hiroshi Inaba[1], Kenji Hatta[1], Kazunori Matsuura[1] （1. Grad. Sch. of Eng., Tottori Univ.）

10:00 AM - 10:20 AM

[A21-4am-05] "Bio-Adhesive" Covalent Organic Framework for Bioapplications

○Hyuna Jo[1], Kou Okuro[1,2], Takuzo Aida[1,3] （1. The Univ. of Tokyo, 2. The Univ. of Hong Kong, 3. Riken Center for Emergent Matter Science）

10:20 AM - 10:40 AM

[A21-4am-06] Investigation of SN-38 Anticancer Nano-prodrugs Intracellular Dynamics

○Farsai Taemaitree[1], Beatrice Fortuni[2], Yoshitaka Koseki[1], Eduard Fron[2], Susana Rocha[2], Johan Hofkens[2,3], Hiroshi Uji-i[2,4], Anh Thi Ngoc Dao[1], Ryuju Suzuki[1], Tomoko Inose[5], Hitoshi Kasai[1] （1. Tohoku University, 2. KU Leuven, 3. Max Planck Institute for Polymer Research, 4. Hokkaido University, 5. Kyoto University）

10:40 AM - 11:00 AM

[A21-4am-07] Fabrication of nano-prodrugs composed of hinokitiol-modified podophyllotoxin

○Keita Tanita[1], Yoshitaka Koseki[1], Takaaki Kamishima[1], Hitoshi Kasai[1] （1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University）

11:00 AM - 11:20 AM

[A21-4am-08] Fabrication of guaiazulene derivatives nano-prodrugs and their structure-activity evaluation

○Kiyotaka Maruoka[1], Keita Tanita[1], Ryuju Suzuki[1], Yoshitaka Koseki[1], Toshihiro Murafuji[2], Hitoshi Kasai[1] （1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Graduate School of Sciences and Technology for Innovation, Yamaguchi University）

11:20 AM - 11:40 AM

Room 4

[A04-4am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair:Qing Shen, Masashi Ikegami

9:00 AM - 10:40 AM Room 4 (Online Meeting)

[A04-4am-01] Inhibition of Dendrite Growth on Lithium-Metal Negative Electrode for All-Solid-State Rechargeable Batteries Using Porous Current Collector with High Aperture Ratio

○Shota Shinzo[1], Masanobu Chiku[1], Eiji Higuchi[1], Akitoshi Hayashi[1], Hiroshi Inoue[1] （1. Osaka Prefecture University）

9:00 AM - 9:20 AM

[A04-4am-03] Control of ZnO nanowire quality by annealing atmosphere and its influence on $AgBiS_2$ nanocrystal-based solar cells

○Yun Xiao[1], Haibin Wang[1], Takaya Kubo[1], Hiroshi Segawa[1,2] （1. RCAST, The Univ. of Tokyo, 2. Grad. Sch. Arts and Sci. The Univ. of Tokyo）

9:40 AM - 10:00 AM

[A04-4am-04] Dye Molecules Assisted $CsPbIBr_2$ Based All Inorganic Perovskite Solar Cells for Excellent Performance

○Yang Shuzhang[1], Liang Wang[1], Tingli Ma[1] （1. kyushu institute of technology）

10:00 AM - 10:20 AM

[A04-4am-05] Carbon-Free Connected Nanoparticle Catalysts for Oxygen Reduction Reaction in PEFCs

○Hidenori Kuroki[1,2], Takanori Tamaki[1,2], Takeo Yamaguchi[1,2] （1. Tokyo Institute of Technology, 2. Kanagawa Institute of Industrial Science and Technology）

10:20 AM - 10:40 AM

[A05-4pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair:Masakazu Nambo, Sadahiro Masuo

Mon. Mar 22, 2021 1:00 PM - 2:40 PM Room 5 (Online Meeting)

[A05-4pm-01] Size-dependent halide segregation of single mixed-halide perovskite nanocrystals

○Yoshua Albert Darmawan[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University）

1:00 PM - 1:20 PM

[A05-4pm-02] Synthesis and Transformation of *N*-Heterocyclic Carbene Functionalized Gold Nanoclusters

○Kimberly Osten[1], Paul Lummis[2], Masakazu Nambo[1], Cathleen Crudden[1,2] （1. Nagoya University, Institute of Transformative Bio-Molecules (WPI-ITbM), 2. Queen's University）

1:20 PM - 1:40 PM

[A05-4pm-03] Fabrication and Electrical Characterization of Naked Superatom Assembled Films based on High Intensity Nanocluster Source and Soft Landing

○Takaho Yokoyama[1], Tatsuya Chiba[1], Naoyuki Hirata[1], Masahiro Shibuta[1], Atsushi Nakajima[1] （1. Keio University）

1:40 PM - 2:00 PM

[A05-4pm-04] Bidentate N-heterocyclic carbenes protected chiral Au_{13} nanoclusters: Synthesis, characterization and application

○Hong Yi[1], Masakazu Nambo[1], Cathleen Crudden[1] （1. Institute of Transformative Bio-Molecules (WPI-ITbM) Nagoya University）

2:00 PM - 2:20 PM

[A05-4pm-05] Development of muon detecting system for revealing muon catalyzed fusion elementary processes

○Kenichi Okutsu[1], Yasushi Kino[1], Ryota Nakashima[1], Konan Miyashita[1], Yasuda Kazuhiro[1], Takuma Yamashita[1], Shinji Okada[2], Motoyasu Sato[2], Toshitaka Oka[3], Naritoshi Kawamura[4], Koichiro Shimomura[4], Patirck Strasser[4], Soshi Takeshita[4], Tampo Motonobu[4], Shogo Doiuchi[4], Yukinori Nagatani[4], Hiroaki Natori[4], Amba Datt Pant[4], Yasuhiro Miyake[4], Katsuhiko Ishida[5] （1. Tohoku Univ., 2. Chubu Univ., 3. JAEA, 4. KEK, 5. Riken）

2:20 PM - 2:40 PM

Size-dependent halide segregation of single mixed-halide perovskite nanocrystals

Department of Applied Chemistry for Environment, Kwansei Gakuin University
○Yoshua Albert Darmawan, Mitsuaki Yamauchi, Sadahiro Masuo
Keywords: Perovskite, Nanocrystal, Quantum Dot, Single-Particle Spectroscopy, Photon Antibunching

It is well known that $CsPbX_3$ (X= Cl, Br, I) perovskite nanocrystal (PNC) is unstable under ambient atmosphere owing to its ionic properties. In the earlier research, single PNC exhibited photoluminescence (PL) spectrum blue-shift upon continuous photoirradiation which attributed to decreasing PNC size. [1] Moreover, halide segregation was observed in mixed halide ($CsPbBr_{1.2}I_{1.8}$) PNC due to halide migration during continuous photoirradiation.[2] However, size dependent halide segregation process in single PNCs has not been investigated, particularly in a PNCs with size beyond the quantum confinement regime. PNC size larger than the quantum confinement of approximately 11 nm allow the formation of multiple emission sites in a single PNC.

Herein, we successfully observed the photodegradation and size dependent halide segregation process at the single $CsPbBr_xI_x$ PNCs using a simultaneous atomic force microscope (AFM) and single-particle spectroscopy measurement. We obtained size dependent behavior of PL spectra, photon correlation histogram, and PL lifetime. Fig. 1 shows the blueshift of PL peaks upon continuous photoirradiation. The blueshift is attributed to the halide loss and decreasing size during photodegradation process obtained from AFM measurements. Our results show that small sized (11 nm) single PNCs exhibited single PL peak and photon antibunching behavior which attributed to quantum confinement effect. On the other hand, large (25 nm) PNCs showed multiple PL peak which attributed to the nucleation of Br^- and I^- rich region after photoirradiation induced halide segregation process. The Large PNC also exhibited multiphoton emission as shown by high $g^{(2)}(0)$ value (> 0.25) obtained from photon correlation histogram, which indicates the formation of multiple emission sites in a single large PNCs. This work shows the size dependent emission behavior and halide segregation of single PNC at the single PNC level.

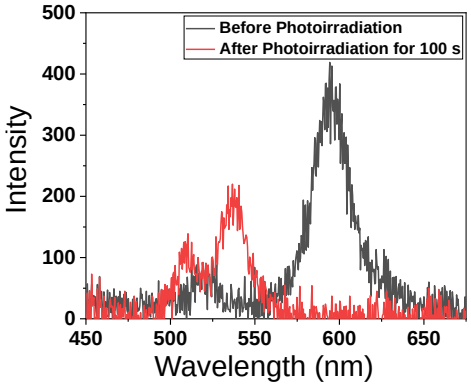


Fig. 1. PL peaks of a single PNC (25 nm) before (black) and after continuous photoirradiation for 100 s (red).

1) Y. A. Darmawan, M. Yamauchi, S. Masuo, *J. Phys. Chem. C* **2020**, *124*, 18770-18776.
2) H. Zhang, X. Fu, Y. Tang, H. Wang, C. Zhang, W. W. Yu, X. Wang, Y. Zhang, M. Xiao, *Nat. Commun.* **2019**, *10*, 1088.

Synthesis and Transformation of *N*-Heterocyclic Carbene Functionalized Gold Nanoclusters

([1] *Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Japan;* [2] *Department of Chemistry, Queen's University, Canada*) ○ Kimberly M. Osten,[1] Paul A. Lummis,[2] Masakazu Nambo,[1] Cathleen M. Crudden[1,2]

Keywords: *N*-Heterocyclic carbene; gold; nanocluster; catalysis

Our group has previously reported the isolation of various gold nanoclusters with *N*-Heterocyclic carbenes (NHCs) as robust protecting ligands.[1-3] Here we will report our ongoing efforts in the synthesis, characterization and purification of novel carbene-functionalized gold nanoclusters, as well our studies on the interconversion of clusters with different core architectures.

1) Narouz, M.R. *et al. Nat. Chem.* **2019**, *11,* 419; 2) Narouz, M.R. *et. al. J. Am. Chem. Soc.* **2019**, *141*, 14997; 3) Salorinne, K. *et. al. Chem. Commun.* **2020**, *56*, 6102.

気相精密大量合成とソフトランディング法による超原子ナノクラスター集積膜の作製とその電気特性評価

（慶大理工）○横山 高穂・千葉 竜弥・平田 直之・渋田 昌弘・中嶋 敦
Fabrication and Electrical Characterization of Naked Superatom Assembled Films based on High Intensity Nanocluster Source and Soft Landing (*Fac. Sci. Tech., Keio Univ*) ○Takaho Yokoyama, Tatsuya Chiba, Naoyuki Hirata, Masahiro Shibuta, Atsushi Nakajima

Temperature dependent electrical characteristics of group 5 metal encapsulating silicon cage superatom ($M@Si_{16}$) films were evaluated, revealing that conduction mechanism can be described by Efros-Shklovskii variable range hopping. The mechanism suggests small transfer integral between $M@Si_{16}$ superatoms, which is consistent with multiple-node structure of the singly occupied molecular orbital (SOMO) of isolated $M@Si_{16}$.

Keywords : Superatom; Nanocluster; Soft landing; Sputtering; Silicon

新奇な電子材料の創製に向けて、数個から数百個の原子集合体であるナノクラスターから構成される集積機能物質の創出が期待されている。中でも、金属原子 1 個を 16 個のケイ素原子から成るカゴで内包させた金属内包シリコンケージクラスター($M@Si_{16}$)は金属原子の種類を変えることで電子物性を制御できることからボトムアップ的アプローチによる機能設計が可能となる [1]。しかしながら、レーザー蒸発に代表される従来の合成法では収量が少ないことと基板上に非破壊で蒸着する難しさから、集積薄膜を作製することに課題があった。本研究では高強度なナノクラスターイオン源とソフトランディング法を用いることで高効率に $M@Si_{16}^+$を合成し、基板上へと非破壊的に蒸着することで集積薄膜を作製した。さらに、嫌気一貫システムにより真空低温プローバーへと搬送することで、電気伝導度の温度変化を観測した。

マグネトロンスパッタリングナノクラスター合成装置 [2] (nanojima®-NAP01, ayabo Corp.)により 5 族金属である V, Nb, Ta のいずれかを内包させた $M@Si_{16}^+$を合成し、くし型電極(Au)パターンを表面に有する Si 基板上に質量選択的にソフトランディングさせた。作製した集積薄膜において電流-電圧測定を 90～300 K の範囲で行い、電気電導度の温度依存性を評価した。

$V@Si_{16}$ 薄膜の電気伝導度(G)の温度依存性は図に示すように、$\ln G$ と $T^{-1/2}$ が良い直線関係にあることから、$V@Si_{16}$ 薄膜の電気伝導メカニズムは Efros-Shklovskii の広域ホッピング伝導(ES-VRH)であることがわかった。また、Nb, Ta を内包した $M@Si_{16}$ でも伝導機構は同様の解析から ES-VRH であることがわかった。ES-VRH はキャリアが局在した電子準位を移動し、キャリア間のクーロン相互作用が大きい場合の伝導機構である。DFT 計算を用いて $M@Si_{16}$ (M = V, Nb, Ta) の構造として提案されている 2 つの異性体 [3,4]の正イオンにおいて構造最適化を行ったところ、電気伝導に関与する軌道はいずれも節が多い。この節の多い電子準位間の伝導では、隣接する $M@Si_{16}$ 間の軌道の重なりが小さいと考えられ、電子状態が局在しているという電気伝導機構と対応していると考えられる。

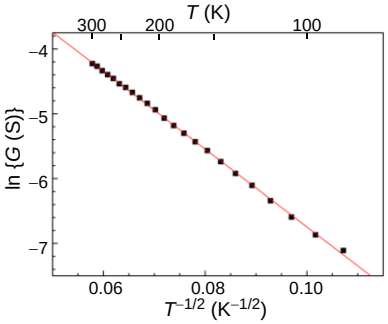


図 ES-VRH モデルに基づく $V@Si_{16}$ 薄膜の電気伝導度 G の温度($T^{-1/2}$)依存性

1) K. Koyasu *et al., J. Am. Chem. Soc.* **2005**, *127*, 4998. 2) H. Tsunoyama *et al., Chem. Lett.* **2013**, *42*, 857. 3) H. Tsunoyama *et al. J. Phys. Chem. C* **2017**, *121*, 20507. 4) J. Liu *et al. J. Phys. Chem. C* **2020**, *124*, 6861.

ABSTRACT: A series of racemic chiral Au_{13} nanoclusters were synthesized via the direct reduction of achiral dinuclear Au(I) halide complexes ligated by *ortho*-xylyl linked bis- N-heterocyclic carbene (NHC)ligands. A broad range of functional groups are tolerated as wingtip substituents, allowing for the synthesis of a variety of functionalized chiral Au_{13} nanoclusters. Single crystal X-ray crystallography confirmed the molecular formula to be $[Au_{13}(bisNHC)_5Cl_2]Cl_3$, with a chiral helical arrangement of the five bidentate NHC ligands around the icosahedral Au_{13} core. The two enantiomers of the Au_{13} clusters can be separated by chiral HPLC, and the isolated enantiomers characterized by circular dichroism spectroscopy. The clusters show remarkable stability, with the chiral structure displaying thermal stability considerably greater than $[Au_{13}(dppe)_5Cl_2]Cl_3$.

ミュオン触媒核融合反応素過程の解明に向けたミュオン検出系の開発

(東北大理[1]、中部大工[2]、原研[3]、高エネ研[4]、理研[5]) ○奥津 賢一[1]、木野 康志[1]、中島 良太[1]、宮下 湖南[1]、安田 和弘[1]、山下 琢磨[1]、岡田 信二[2]、佐藤 元泰[2]、岡 壽崇[3]、河村 成肇[4]、神田 聡太郎[4]、下村 浩一郎[4]、Patrick Strasser[4]、竹下 聡史[4]、反保 元伸[4]、土居内 翔伍[4]、永谷 幸則[4]、名取 寛顕[4]、西村 昇一郎[4]、Amba Datt Pant[4]、三宅 康博[4]、石田 勝彦[5]

Development of muon detecting system for revealing elementary processes in muon catalyzed fusion ([1]*Tohoku University*, [2]*Chubu University*, [3]*JAEA*, [4]*KEK*, [5]*RIKEN*) ○K. Okutsu[1], Y. Kino[1], R. Nakashima[1], K. Miyashita[1], K. Yasuda[1], T. Yamashita[1], S. Okada[2], M. Sato[2], T. Oka[3], N. Kawamura[4], S. Kanda[4], K. Shimomura[4], P. Strasser[4], S. Takeshita[4], M. Tampo[4], S. Doiuchi[4], Y. Nagatani[4], H. Natori[4], S. Nishimura[4], A. D. Pant[4], Y. Miyake[4], K. Ishida[5]

A muon (μ^-) is one of elementary particles which is known to weight 207 times more than an electron. A nuclear fusion reaction occurs in a muonic molecule which consists of two hydrogen isotope nuclei and a muon because the muon binds more tightly than electron. Since the muon does not directly participate in the fusion reaction, the reaction is called muon catalyzed fusion (μCF). The muon released after the reaction is called a “recycling muon”, and maintains the molecular orbital information when the muonic molecule formed. Therefore, information of the muon wavefunction can be investigated by observing the energy distribution of the recycling muon. We will report the experimental setup for measuring the energy distribution of the recycling muons after the nuclear reaction.

Keywords : Muon catalyzed fusion; Solid hydrogen isotope target; Kinetic energy distribution measurement; Muonic molecule; Apparatus development

ミュオン(μ^-)は素粒子の一種で、電子の 207 倍の質量を持ち、2.2 μs の寿命で崩壊する。ミュオンは電子より強く原子核同士を結びつけることができるため、 2 つの水素同位体核とミュオンが形成するミュオン分子内では核反応が起こり、この反応はミュオン触媒核融合とよばれる。分子状態の核同士が互いに接触する状態への変化は瞬時に起こるが、この際ミュオンの分子軌道がどのように変化するかは、量子化学的に大変興味深い。ミュオン触媒核融合反応後にミュオンは、自由になり放出される(再生ミュオン)。この再生ミュオンの運動エネルギー分布を測定することで核反応の際のミュオン分子軌道の変化を調べることができる。実験では固体水素膜表面にミュオンを局在化させ核反応を起こすことで表面から放出される再生ミュオンを真空中に取り出し、電場により輸送し、その後にミュオン特性 X 線を利用して検出を行う。講演では、現在開発しているミュオン触媒核融合のための水素固体標的系と負ミュオン運動エネルギー分布の測定装置の概要[1,2]と粒子輸送シミュレーションの結果などを合わせて報告する。

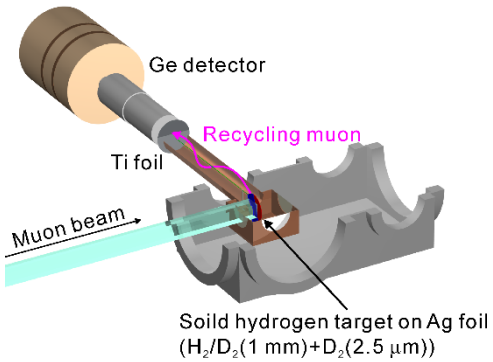


図. 再生ミュオン検出のための実験装置のセットアップ

[1] K. Okutsu, T. Yamashita et al., *Fusion Eng. Des.* submitted.
[2] P. Strasser, T. Matsuzaki et al., *Nucl. Instr. Meth. Phys. Res. A*, **460**, 451 (2000).

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

[A06-4pm] 06. Analytical Chemistry

Chair:Takeshi Hashimoto, Kosuke Ino

Mon. Mar 22, 2021 1:00 PM - 3:20 PM Room 6 (Online Meeting)

[A06-4pm-01] Visualization of submicron structures within deeper layers of biological tissues utilizing spatial light modulator

○Kazushi Yamaguchi[1,2,3], Kohei Otomo[1,2,3,4,5], Yuichi Kozawa[6], Motosuke Tsutsumi[2,3,4], Tomoko Inose[1,2], Kenji Hirai[1,2], Shunichi Sato[6], Tomomi Nemoto[1,2,3,4,5], Hiroshi Uji-i[1,2,7] （1. IST, Hokkaido Univ., 2. RIES, Hokkaido Univ., 3. NIPS, 4. ExCELLS, 5. The Graduate School for Advanced Study, 6. IMRAM, Tohoku Univ., 7. KU Leuven）

1:00 PM - 1:20 PM

[A06-4pm-02] Highly sensitive immunoassay with dual signal amplification systems of redox cycling in nanospace and cascade reaction

○Kentaro Ito[1], Kumi Y. Inoue[1,3], Kosuke Ino[2], Tomokazu Matsue[4], Hitoshi Shiku[2] （1. Graduate School of Environmental Studies, Tohoku University, 2. Graduate School of Engineering, Tohoku University, 3. Graduate Faculty of Interdisciplinary Research, University of Yamanashi , 4. Center for Promotion of Innovation Strategy, Tohoku University）

1:20 PM - 1:40 PM

[A06-4pm-03] Quantitative analysis of vasculature-on-a-chip using scanning probe microscopy

○Yuji Nashimoto[1,2,3], Minori Abe[3], Ryota Fujii[3], Noriko Taira[3], Hiroki Ida[1,4,5], Yasufumi Takahashi[6,5], Kosuke Ino[2], Hitoshi Shiku[2,3] （1. Frontier Research Institute for Interdisciplinary Science, 2. Graduate School of Engineering, Tohoku University, 3. Graduate School of Environmental Studies, Tohoku University, 4. Advanced Institute for Materials Research, Tohoku University, 5. JST PRESTO, 6. Nano Life Science Institute, Kanazawa University）

1:40 PM - 2:00 PM

[A06-4pm-04] Development of chemical measurement descriptors to explore physical properties of biopolymers (hairs)

○Ayari Takamura[1], Kaede Tsukamoto[2], Kenji Sakata[1], Jun Kikuchi[1,2] （1. RIKEN, 2. Yokohama City Univ.）

2:00 PM - 2:20 PM

[A06-4pm-05] Development of sensitive bacterial detection by phenylboronic acid modified dendrimer with fluorescent dansyl group

○Ayame Mikagi[1], Riho Tsuruhusa[1], Yuji Tsuchido[2], Takeshi Hashimoto[1], Takashi Hayashita[1] （1. Sophia Univ., 2. Waseda Univ.）

2:20 PM - 2:40 PM

[A06-4pm-06] Supramolecular Cyclodextrin Complexes for Electrochemical Detection of Metabolites in Water

○Maria Antonietta Casulli[1], Takeshi Hashimoto[1], Takashi Hayashita[1] （1. Sophia University, Department of Materials and Life Sciences, Faculty of Science and Technology）

2:40 PM - 3:00 PM

[A06-4pm-07] Colorimetric detection of bacteria pathogens through aggregation of gold nanoparticles induced by thiolated bacteriophages

○Satoshi Yamashita[1], Yosuke Niko[1], Shingo Hadano[1], Shigeru Watanabe[1], Iyo Uchiyama[2], Jyunpei Uchiyama[2], Shigenobu Matsuzaki[3] （1. Graduate School of Science, kochi university, 2. School of Veterinary Medicine, Azabu University, 3. Faculty of Health Science, Kochi Gakuen University）

3:00 PM - 3:20 PM

空間光位相変調器を用いた収差補正による生体組織深部の微細構造の可視化

(北大院情報[1]・北大電子研[2]・生理研[3]・生命創成探究センター[4]・総研大生理科学[5]・東北大多元研[6]・ルーヴァン大[7]) ○山口 和志[1,2,3]・大友 康平[1,2,3,4,5]・小澤 祐市[6]・堤 元佐[2,3,4]・猪瀬 朋子[1,2]・平井 健二[1,2]・佐藤 俊一[6]・根本 知己[1,2,3,4,5]・雲林院 宏[1,2,7]

Visualization of submicron structures within deeper layers of biological tissues utilizing spatial light modulator ([1]*Graduate School of Information Science and Technology*, *Hokkaido University*, [2]*Research Institute for Electronic Science*, *Hokkaido University*, [3]*National Institute for Physiological Sciences*, *National Institutes of Natural Sciences*, [4]*Exploratory Research Center on Life and Living Systems*, *National Institutes of Natural Sciences*, [5]*Department of Physiological Sciences*, *The Graduate School for Advanced Study*, [6]*Institute of Multidisciplinary Research for Advanced Materials*, *Tohoku University*, [7]*KU Leuven*, *Department of Chemistry*) ○Kazushi Yamaguchi[1,2,3], Kohei Otomo[1,2,3,4,5], Yuichi Kozawa[6], Motosuke Tsutsumi[2,3,4], Tomoko Inose[1,2], Kenji Hirai[1,2], Shunichi Sato[6], Tomomi Nemoto[1,2,3,4,5], Hiroshi Uji-i[1,2,7]

We developed an adaptive optical two-photon microscopy (AO-TPM) utilizing a spatial light modulator (SLM). For correcting optical aberrations caused by refractive index interfaces at specimen's surfaces, spatial phase distributions of the incident excitation light were calculated using 3D-coordination of refractive index interfaces. We applied a calculated 2D phase-shift distribution to a SLM and improved the fluorescence image contrast, resulting in successful visualization of synaptic structures in deep regions of living mouse brains with a curved surface. The AO approach is useful for observing dynamic physiological activities in deep regions of various living specimens with curved surfaces.

Keywords : Adaptive Optics; Two-photon microscopy; in vivo imaging; Live cell imaging

組織機能の理解には、三次元的に分布する細胞の形態と生理活性の非侵襲的な計測が必須だが、組織の複雑な表面形状に起因した収差の影響で光学的な計測は困難だった。本研究では、組織深部の高解像蛍光観察のために、励起光学系に空間光位相変調器 SLM を導入した 2 光子顕微鏡を開発した。細胞形態観察を妨げる収差を補償するために、生体組織の 3 次元表面形状を実測し、組織で生じる励起光の集光時の位相乱れを算出した。これに基づいた位相補償分布を SLM で励起光に与えることで、マウス生体脳深部の微細な樹状突起棘構造を可視化した（図 1）。本手法は、複雑な表面形状を持つ生物組織の深部における細胞形態や生理活性の解析に貢献することが期待される。

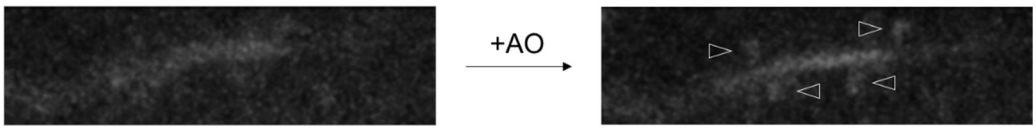


図 1　補償光学技術の適用によるマウス生体脳深部の樹状突起スパインの可視化

1) K. Yamaguchi, K. Otomo, Y. Kozawa, M. Tsutsumi, T. Inose, K. Hirai, S. Sato, T. Nemoto, H. Uji-I, *ACS Omega*, Vol. 6 (1), pp. 438-447, **2021**

Highly sensitive immunoassay with dual signal amplification systems of redox cycling in nanospace and cascade reaction

([1]*Tohoku University*, [2]*Yamanashi University*)
○Kentaro Ito,[1] Kumi Y. Inoue,[1, 2] Kosuke Ino,[1] Tomokazu Matsue,[1] Hitoshi Shiku[1]

Keywords: Electrochemistry; Immunoassay; Redox cycling; Cascade reaction; Nanogap electrode

Sensitivity improvement for immunoassay is desired to detect early stage of infection. In this study, according to our previous report[1], we improved the sensitivity for immunoassay using dual signal amplification systems of redox cycling in nanospace[2] and *Limulus* amebocyte lysate (LAL) reaction[3] which is one of cascade reaction induced by endotoxin. Immunoassay for goat IgG as a model analyte was performed with endotoxin-labeled antibody. After immunoassay, LAL reaction was performed, and *p*-aminophenol (pAP) liberated from peptide-conjugated *p*-aminophenol (LGR-pAP) at the last step of LAL reaction was detected using redox cycling in nanospace (Fig. 1).

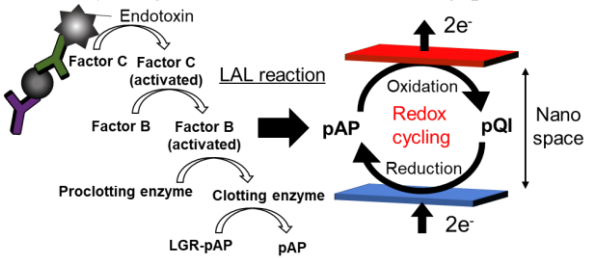


Fig. 1 Schematic illustration of this research

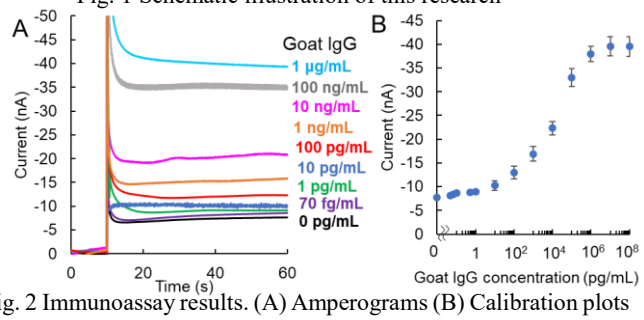


Fig. 2 Immunoassay results. (A) Amperograms (B) Calibration plots

A nanogap device with a pair of ring electrodes facing each other across a 190 nm gap was fabricated with photolithography and sputtering according to our previous report[1]. Immunoassay for goat IgG was performed on carboxylated magnetic beads (d=1.0 μm). First, beads were conjugated with 60 μg/mL anti-goat IgG antibody using carbodiimide cross-linker. Secondly, beads were incubated with 2 mg/mL bovine serum albumin to block non-specific reaction. Then, beads were reacted with goat IgG. After that, beads were reacted with endotoxin-labeled anti-goat IgG antibody. Finally, LAL reaction with 0.5 mM LGR-pAP was performed for 1 h at 37°C. The pAP liberated from LGR-pAP was detected using the nanogap device with the potential of the bottom electrode biased at -0.2 V, while the top electrode stepped from -0.2 to 0.5 V.

Fig. 2 shows amperograms obtained from the bottom electrode (A) and calibration plot obtained by subtracting the current at 9.96 s from the current at 60 s (B). The reduction current increased with the increase of goat IgG concentration. From the result of IgG assay, the limit of detection was calculated to be 70 fg/mL (467 aM) as concentration corresponding to three times the standard deviation of 0 pg/mL. Our strategy can provide highly sensitive immunoassay platform for clinical diagnosis.

1) K. Ito et al., Analyst, 2019, 144, 3659-3667. 2) M. A. G. Zevenbergen et al., Nano Lett., 2007, 11, 2881-2886.
3) K. Y. Inoue et al., Innate Immun., 2012, 18. 343-349.

走査型プローブ顕微鏡を用いた vasculature-on-a-chip の定量的な機能評価法の検討

（東北大学際研[1]・東北大院工[2]・東北大院環境[3]・東北大材料科学[4]・さきがけ[5]・金沢大ナノ生命[6]）○梨本 裕司[1,2,3]・阿部 充里[3]・藤井 遼太[3]・平 典子[3]・井田大貴[1,4,3,5]・高橋 康史[5,6]・伊野 浩介[2]・珠玖 仁[2,3]

Quantitative analysis of vasculature-on-a-chip using scanning probe microscopy ([1]*FRIS, Tohoku Univer.*, [2]*Grad. Sch. Eng., Tohoku Univer.*, [3]*Grad. Sch. Environ., Tohoku Univer.,* [4]*AIMR, Tohoku Univer.,* [5]*PRESTO,* [6] *Nano LSI, Kanazawa Univer.*) ○Yuji Nashimoto,[1,2,3] Minori Abe,[3] Ryota Fujii,[3] Noriko Taira,[3] Hiroki Ida,[1,4,3,5] Yasufumi Takahashi,[5,6] Kosuke Ino,[2] Hitoshi Shiku [2,3]

Microfluidic technologies allow precise control of flow and biochemical cues for studying vascular functions *in vitro* (vasculature-on-a-chip). Electrical and electrochemical sensors are well-suited for integration into vasculature-on-a-chip due to the miniature footprint and the rapid response time: however, an electrochemical sensor with a high spatial resolution is not fully developed for vasculature-on-a-chip. Here, we integrated a scanning probe microscopy with vasculature-on-a-chip for the evaluation of vascular functions at single-cell levels. In a newly designed microfluidic device with an access port for a scanning probe, mechanical stimuli were imposed on the endothelial cells by applying flow. The topographical changes of endothelial cells with and without the flow stimuli were monitored using scanning ion conductance microscopy (SICM). In addition, scanning electrochemical microscopy (SECM) allowed us to quantify the permeability changes of the electrochemical tracers (ferrocyanide ion), depending on the culture conditions. Now, we are evaluating the interface of intestinal epithelium-vasculature in a microfluidic device.

Keywords : organ-on-a-chip; vasculature; microphysiological system; scanning electrochemical microscopy; scanning ion conductance microscopy

マイクロ流体デバイス内に血管内皮細胞を播種し、力学負荷を付与することで、生体内を模した血管界面が再現できる（vasculature-on-a-chip）．血管機能の評価法として，集積性に優れ，リアルタイムモニタリングが可能な電気化学センサが検討されているが，空間分解能に優れたセンシングシステムは報告されていない．本研究では，イメージング機能を有する走査型プローブ顕微鏡（SPM）と vasculature-on-a-chip を統合したシステムを検討した．SPM 観察孔を設けたマイクロ流体デバイスにおいて，細胞への流れ負荷が付与可能であった．また，流れ負荷付与後の細胞を，走査型イオンコンダクタンス顕微鏡で高解像度に観察でき，細胞の配向度，表面粗さが評価可能であった．一方，走査型電気化学顕微鏡により，デバイス内の血管内皮細胞の状態に応じた電気化学活性種（フェリシアン化物イオン）の透過性が評価可能であった．現在，本デバイスで，腸-血管界面を模したモデルを構築し，流れ付与後の形態変化や透過性を評価中である．

生体高分子（被毛）の物性探究に向けた化学計測記述子開発

（理研 CSRS[1]・横市大院生命医[2]・名大院生命農[3]）○髙村 彩里[1]・塚本 楓[2]・坂田 研二[1]・菊地 淳[1,2,3]

Development of chemical measurement descriptors to explore physical properties of biopolymers (hairs) ([1]*RIKEN CSRS*, [2]*Grad. Sch. of Med. Life Sci., Yokohama City Univ.*, [3]*Grad. Sch. Bioagri. Sci., Nagoya Univ.*) ○Ayari Takamura,[1] Kaede Tsukamoto,[2] Kenji Sakata,[1] Jun Kikuchi[1,2,3]

Polymers exhibit various physical properties depending on the higher-order structures as well as the monomers. Chemical measurement data can involve the structural information of polymers. However, the information extraction and association with the physical properties has been difficult. Herein, we collected biopolymer samples, hairs, from several species. The measurements of physical properties and chemical data (i.e., Autograph, solid-state NMR, TD-NMR, FT-IR, TG-DTA) were performed. The chemical measurement data were processed into the descriptors, then applied to machine-learning modeling to predict the physical properties (Figure 1). Consequently, some contributive factors such as α-helix structure of proteins were selected from over 900 descriptors.

Keywords: *Measurement informatics; Polymers; Spectral analysis; Machine learning; Physical properties*

高分子は、単量体種だけでなく高次構造の違いにより多様な物性を発現し得る。各種化学計測データは分子の構造情報を含むと期待されるが、その抽出や物性との関連付けは容易でない。本研究では、化学計測データに様々な情報分離・抽出処理を施すことで「化学計測記述子」を生成し、機械学習の回帰モデリングを用いて記述子と物性値間の関連性探索を試みた（図 1）。試料は、生体由来の高分子である被毛を多動物種から収集した。引張試験により物性値（伸び率・切断強度・降伏点・弾性率）を評価し、化学計測として核磁気共鳴分光・時間領域核磁気共鳴分析・赤外分光・熱重量示差熱分析を行った。各化学計測データから生成した記述子を用いて、物性値予測モデルを構築したところ、タンパク質α-ヘリックス構造等との関連性が示唆された。

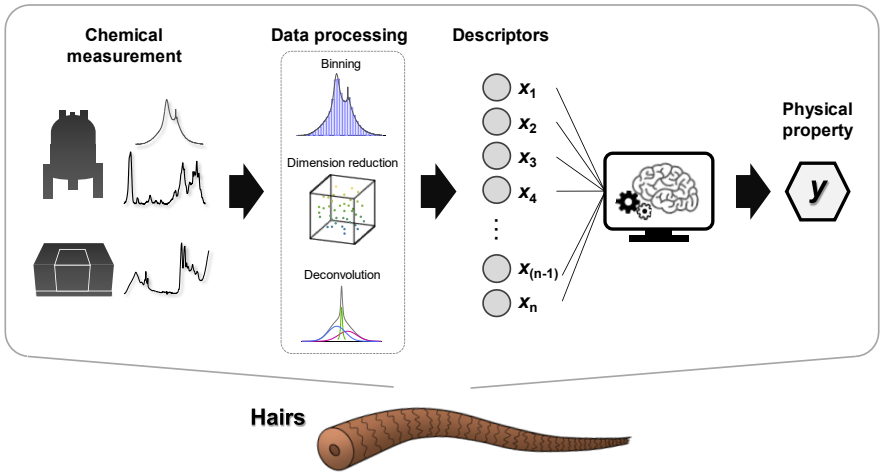


Figure 1. A schematic of generation of chemical measurement descriptors to predict physical properties of biopolymers (hairs).

ダンシル蛍光団を有するフェニルボロン酸デンドリマーを用いた高感度細菌認識法の開発

（上智大理工[1]・早大先進理工[2]）○三ヶ木 彩芽[1]・鶴房 莉帆[1]・土戸 優志[2]・橋本 剛[1]・早下 隆士[1]

Development of sensitive bacterial detection by phenylboronic acid modified dendrimer with fluorescent dansyl group ([1]*Faculty of Science and Technology, Sophia University*, [2]*School of Advanced Science and Engineering, Waseda University*) ○Ayame Mikagi,[1] Riho Tsurufusa,[1] Yuji Tsuchido,[2] Takeshi Hashimoto,[1] Takashi Hayashita[1]

This study reported a convenient and sensitive bacterial detection using fluorescent phenylboronic acid modified PAMAM dendrimer (Dan-B-PAMAM, Figure), which could recognize bacterial surface and formed aggregation. Dan-B-PAMAM was newly synthesized from B-PAMAM and fluorescent dansyl group. When Dan-B-PAMAM was mixed with bacteria, the microscopy images showed aggregation as expected. Following the experiment, the aggregates were removed by filtration and fluorescence decreasing of filtrate solution was measured. Fortunately, changing was obtained even in 10^4 CFU/mL solution and Dan-B-PAMAM gave higher sensitivity than B-PAMAM. It was also worth mentioning that MTT assay showed that about half of gram-negative bacteria existed as dead bacteria. The result described that Dan-B-PAMAM give antibacterial activity for gram-negative bacteria.

Keywords : Bacterial Detection; Phenylboronic Acid; Dendrimer; Fluorescence; Antibacterial Activity

本研究では、細菌を認識し凝集する蛍光型フェニルボロン酸デンドリマーDan-B-PAMAM を用いることで、簡便かつ高感度な細菌認識法の開発を試みた(Figure)。Dan-B-PAMAM は、蛍光を有するダンシル基を B-PAMAM に修飾することで新規に合成した。合成した Dan-B-PAMAM を細菌と懸濁し顕微鏡で観察すると、凝集体の形成が確認できた。さらにろ過で凝集体を除去し、ろ液中に残ったプローブの蛍光強度を測定すると、10^4 CFU/mL でも蛍光強度の減少が見られ、B-PAMAM よりも感度が向上した。また、MTT アッセイで菌の生死判定を行うと、グラム陰性菌は約半数が死細菌として存在することが確認できた。したがって、Dan-B-PAMAM はグラム陰性菌に選択的な抗菌作用を持つことが明らかとなった。

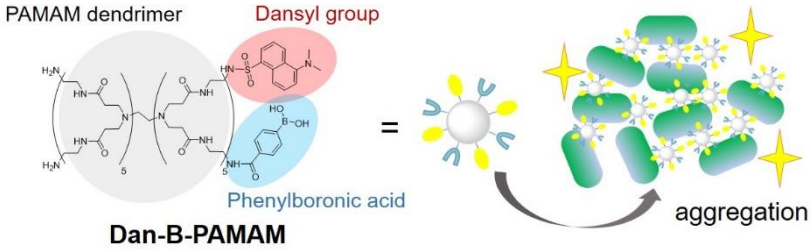


Figure. Bacterial recognition by **Dan-B-PAMAM**.

[1] Y. Tsuchido, R. Horiuchi, T. Hashimoto, K. Ishihara, N. Kanzawa, T. Hayashita, *Anal. Chem.*, **91**, 3929-3935 (2019).

Supramolecular Cyclodextrin Complexes for Electrochemical Detection of Metabolites in Water

"Personalized Health Care" is a new conscience spreading in medicine, where the prediction of a great number of metabolites is necessary. In this work, we showed a new role of cyclodextrins that for the first time are employed in electrochemistry with a unique detection mechanism based on specific chemical interactions with the target molecule by the introduction of proper binding groups. We demonstrated that just by chemically modifying the β-cyclodextrins with different chemical groups, it is possible to detect a series of metabolites (fructose, glucose, ATP) by the formation of supramolecular complex with ferrocene modified with a boronic group.

バクテリオファージを利用した細菌の金ナノ粒子凝集比色検出

（高知大学総合[1]・麻布大獣医[2]・高知学園大健康[3]）○山下 智史[1]・仁子 陽輔[1]・波多野 慎悟[1]・渡辺 茂[1]・内山 伊代[2]・内山 淳平[2]・松崎 茂展[3]
Colorimetric detection of bacteria pathogens through aggregation of gold nanoparticles induced by thiolated bacteriophages (*Graduate School of Science*, *Kochi university*[1], *School of Veterinary Medicine*, *Azabu University*[2], *Faculty of Health Science*, *Kochi Gakuen University*[3])
○Satoshi Yamashita[1], Yosuke Niko[1], Shingo Hadano[1], Shigeru Watanabe[1], Iyo Uchiyama[2], Jyunpei Uchiyama[2], Shigenobu Matsuzaki[3]

Bacterial infections are serious worldwide threat to public health, and so the accurate and rapid detection and identification of pathogenic bacteria are of particular importance. To replace molecular biological and immunological methods, biosensors have recently been developed for the rapid and sensitive detection of bacteria. Among a wide variety of biological materials, bacteriophages have received increasing attention as promising alternatives to antibodies in biosensor applications. Thus, we herein present a rapid and highly selective colorimetric detection method for pathogenic bacteria through aggregation of gold nanoparticles on thiolated bacteriophages.

E.coli, *S.pseudintermedius*, and *S.aureus* were incubated with thiolated *Staphylococcus* virus S13'. The cells were centrifuged and resuspended in a solution of AuNPs. A dramatic color change from red to blue was observed only in *S.aureus* which is the host bacterial strain for Staphylococcus virus S13'. The present method therefore exhibits potential for expanding its application to the selective, sensitive, and rapid detection of any bacterium by changing the phages employed.

Keywords : Gold nanoparticles; Bacteriophages; Bacterium, Colorimetric detection

細菌性感染症の早期診断・早期治療には，原因菌の迅速な検出が必要である．遺伝子検出法や免疫学的検出法とは異なる検出法としてバイオセンサーが注目されており，抗体に代わる細菌認識素子としてバクテリオファージに高い関心が寄せられている．本研究では，チオール化バクテリオファージを利用した細菌の金ナノ粒子凝集比色検出法について報告する．

Figure 1に示す通り，チオール化したファージ（Staphylococcus virus S13'）を大腸菌（*E.coli*）やブドウ球菌（*S.aureus*, *S.pseudintermedius*）と混合・遠心分離後，金ナノ粒子を添加したとき，S13'の宿主細菌*S.aureus*のみ劇的な色調変化を示すことがわかった．細菌の科から属，さらには菌種の違いも識別し，高い選択性を保ちながら標的細菌を迅速に検出できることがわかった．本手法は，バクテリオファージを変えることによって，特定菌種への選択性を自在に制御することが可能であり，選択的かつ簡便な細菌検出が期待できる．

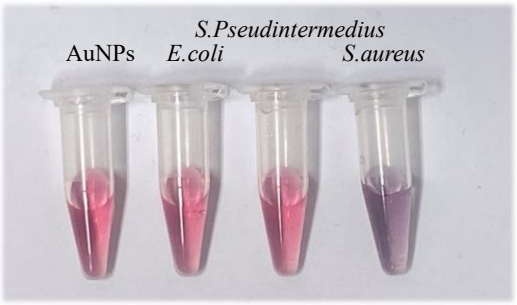


Figure 1. Detection of *S.aureus* with thiolated *Staphylococcus* virus S13' and AuNPs.

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

[A06-4am] 07. Inorganic Chemistry

Chair:Shinya Hayami, Kenji Okada

Mon. Mar 22, 2021 9:00 AM - 11:20 AM Room 6 (Online Meeting)

[A06-4am-01] Configurational and communal entropies in non-stoichiometric PdH_x

○Yoshihiro Shimizu[1], Manshi Ohyanagi[1] （1. Ryukoku Univ.）

9:00 AM - 9:20 AM

[A06-4am-02] 3D Porous Ni/NiO_x as a bifunctional oxygen electrocatalyst derived from Freeze-dried $Ni(OH)_2$

○Yuta Shudo[1], Shinya Hayami[1] （1. Kumamoto University）

9:20 AM - 9:40 AM

[A06-4am-03] Oriented growth of COF crystals on metal-hydroxides thin film

○Ken Ikigaki[1], Kenji Okada[1], Paolo Falcaro[3], Christian Doonan[2], Masahide Takahashi[1] （1. Osaka Prefecture University, 2. University of Adelaide, 3. Graz University of Technology）

9:40 AM - 10:00 AM

[A06-4am-04] Development of Efficient Triplet-DNP System Using Metal-Organic Frameworks

○Arijit Mallick[1,2], Saiya Fujiwara[2], Nobuhiro Yanai[2,3,4], Nobuo Kimizuka[2,4] （1. JSPS Postdoctoral Fellow, 2. Kyushu University, 3. PRESTO, JST, 4. CMS, Kyushu Univ.）

10:00 AM - 10:20 AM

[A06-4am-05] Polycarboxylates as synthetic tools for small and efficient perovskite quantum dots.

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

10:20 AM - 10:40 AM

[A06-4am-06] Synthesis and structure of porous ionic crystals based on delta-Keggin-type aluminum polyoxocation

○Wei Zhou[1], Sayaka UCHIDA[1], Naoki OGIWARA[1], Wei Zhe Weng[1] （1. Department of Basic Science, School of Arts and Sciences, The University of Tokyo）

10:40 AM - 11:00 AM

[A06-4am-07] Porous ionic crystals composed of Nb/W mixed-addenda polyoxometalates as solid base catalysts

○Zhewei Weng[1], Sayaka Uchida[1] （1. Department of Basic Science, School of Arts and Sciences, The University of Tokyo）

11:00 AM - 11:20 AM

Configurational and Communal Entropies in Non-stoichiometric PdH_x

([1] *Graduate School of Science and Technology, Ryukoku University*, [2] *Faculty of Advanced Science and Technology, Ryukoku University*) ○Yoshihiro Shimizu,[1] Manshi Ohyanagi[2]

Keywords: Thermodynamics; Entropy; Configurational entropy; Communal entropy; Palladium Hydride

Non-stoichiometric palladium hydride (PdH_x) with vacancies for hydrogen exhibits a glass transition temperature (T_g), resulting in generation of both configurational and communal entropies. The communal entropy was evaluated under a given configurational entropy with a suitable hydrogen occupation of tetrahedral and octahedral sites of Pd using the standard molar entropy of formation ($\Delta_f S^\circ_{m(exp.)}$) calculated from the equilibrium pressures in pressure–composition–temperature (PCT) curves and the spectroscopic entropies of molecular hydrogen and PdH_x.

PCT curves with little hysteresis between hydrogenation and dehydrogenation processes were obtained just below the critical temperature T_c, at which the lattice volume mismatch between α and β phases of PdH_x is almost negligible. The $\Delta_f S^\circ_{m(exp.)}$ value calculated from the PCT curves was −83.4±1.3 J/(K·mol$_{H_2}$) in the hydrogenation process and −87.3±1.7 J/(K·mol$_{H_2}$) in the dehydrogenation process, showing only a relatively small discrepancy between the two.

Based on data from the literature, we assumed that the α phase, with its lower hydrogen concentration, was $PdH_{0.006}$, and that the β phase, with its higher hydrogen concentration, was $PdH_{0.6}$ in the equilibrium hydrogenation reaction between α and β phases. We then estimated the difference in communal entropy ($\Delta S^\circ_{com.}$) between $PdH_{0.006}$ and $PdH_{0.6}$ in terms of the $\Delta_f S^\circ_{m(exp.)}$ value, the hydrogen molar entropy (S°_{m,H_2}), the vibrational entropy ($\Delta S^\circ_{vib.}$), the electronic entropy ($\Delta S^\circ_{ele.}$), and given configurational entropy ($\Delta S^\circ_{conf.}$). We found that near T_c, H atoms occupied both the octahedral and tetrahedral sites in $PdH_{0.6}$, with $\Delta S^\circ_{com.}$ approaching the value of the gas constant R (Fig.1). On the other hand, $\Delta S^\circ_{com.}$ approached 0 J/(K·mol$_H$) near the glass transition temperature T_g, with H atoms occupying only all the octahedral sites in $PdH_{0.6}$ (Fig.2).

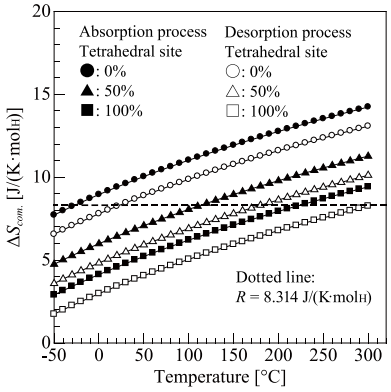


Fig. 1 Estimated communal entropy $\Delta S^\circ_{com.}$ for hydrogen absorption and desorption processes above -50 °C.

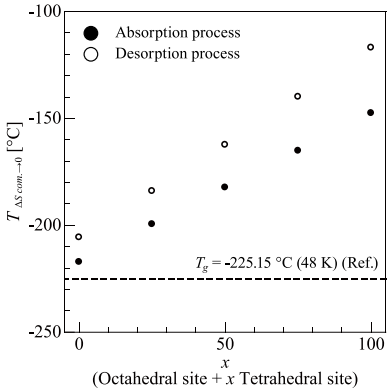


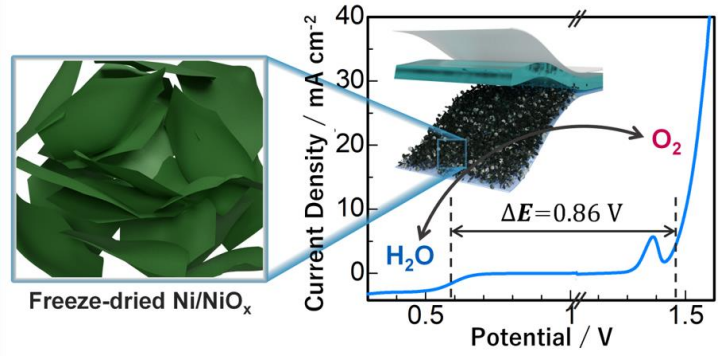
Fig.2 Relationship between temperature and the fraction of tetrahedral sites occupied (during full occupation of octahedral sites as communal entropy $\Delta S^\circ_{com.}$ approaches 0 J/(K·mol$_H$)).

3D Porous Ni/NiO_x as a bifunctional oxygen electrocatalyst derived from Freeze-dried $Ni(OH)_2$

([1] *Graduate School of Science and Technology, Kumamoto University*, [2] *Institute of Industrial Nanomaterials (IINa), Kumamoto University*) ○Yuta shudo,[1] Shinya Hayami[1, 2]
Keywords: Nickel; Electrocatalyst; Oxygen evolution reaction; Oxygen reduction reaction; Nickel hydroxide

The concomitant energy crisis has influenced the global research realm to develop some clean and alternative energy devices including Metal-air battery. However, the Metal-air batteries require further development for improving their efficiency and reducing the fabrication cost by using non-precious electrocatalyst.[1)] The non-precious transition metals including Mn, Co, Ni have well-reported oxygen bifunctional electrocatalyst.[2)] For single metal oxides, oxygen electrocatalyst activities following the order of NiO_x >CoO_x > MnO_x., suggest that NiO_x is an excellent electro catalyst alternative to the precious metals.[3)]

Herein, Bifunctional electrocatalytic property of freeze-dried Ni/NiO_x, freeze-dried NiO, freeze-dried $Ni(OH)_2$ is reported. freeze-dried Ni/NiO_x, freeze-dried Ni was obtained from thermal annealing of the material. Both the $Ni(OH)_2$ and Ni/NiO_x could sustain with freestanding freeze-dried 3D structures without any carbon support. **Freeze-dried Ni/NiO_x exhibited excellent bifunctional electrocatalytic property with the ORR performance at 0.62 V (half-wave potential) and OER at 1.47 V (η= 10 mA cm^{-2}).** Using freeze-dried metal hydroxide can be considered a wide range of carbon-free applications and improved electrocatalyst performance. The bifunctional catalytic activities were calculated to be 0.86, 0.98 and 1.14 V, respectively for freeze-dried Ni/NiO_x, freeze-dried NiO and freeze-dried $Ni(OH)_2$. The stacking of 2D sheets into 3D mass seems to play a vital role behind this excellent bifunctionality of freeze-dried Ni/NiO_x. The strategy that is developed, herein can be justified to obtain other transition metal-oriented bifunctional electrocatalyst as the alternative Pt and Ir/Ru based expensive benchmark catalysts.



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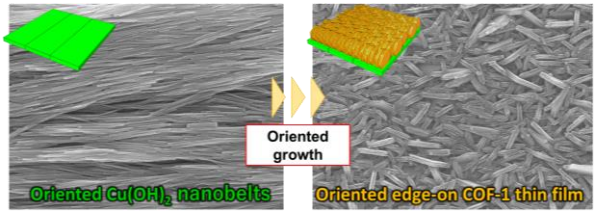
金属水酸化物ナノ結晶表面の水酸基を利用した Covalent Organic Framework (COF)配向性薄膜

(阪府大院工[1]・広島大院工[2]・滋賀大教育[3]・アデレード大学[4]) ○生垣 賢[1]・岡田 健司[1]・樽谷 直紀[2]・徳田 陽明[3]・Andrew Tarzia[4]・Christopher Coleman[4]・Christian J. Doonan[4]・高橋 雅英[1]
Oriented growth of COF crystals on metal-hydroxides thin film ([1]*Graduate School of Engineering, Osaka Prefecture University*, [2]*Graduate School of Engineering, Hiroshima University,* [3]*Faculty of Education, Shiga University,* [4]*The University of Adelaide*) ○Ken Ikigaki,[1] Kenji Okada,[1] Naoki Tarutani,[2] Yomei Tokuda,[3] Andrew Tarzia,[4] Christopher Coleman,[4] Christian J. Doonan,[4] Masahide Takahashi,[1]

Thin films of oriented covalent organic framework (COF) crystals over cm-scale substrates are one of the promising candidates for the carrier transport materials of organic electronic devices by hosting the functional molecules due to the ideal π-electron systems and 1D pore channels. However, the oriented COF thin films reported so far exhibited only a face-on orientation, where the long-range interconnected pore/framework structure of COF which can work as conductive or diffusion paths are terminated by a substrate. In the present work, oriented COF-1 ($(C_3H_2BO)_6 \cdot (C_9H_{12})$) thin films with an edge-on geometry were successfully fabricated by one-pot synthesis approach on a unique substrate consisting of aligned $Cu(OH)_2$ nanobelts, in which the surface hydroxyl groups on the $Cu(OH)_2$ nanobelts support the oriented growth of COF-1 crystallites as the ”molecular guideline”.
Keywords : Metal hydroxides; Oriented Growth; Covalent organic framework

基板上へ形成した配向 Covalent organic framework (COF)薄膜は、COF のベンゼン環に由来したπ-π積層構造や 1 次元細孔構造によって発現する異方的な伝導性を利用できる点で新規有機エレクトロニク材料として注目されている。しかし、一般的な配向 COF 薄膜はフェイスオン配向しており、COF 骨格や細孔を利用したキャリアの拡散方向を基板で阻害している点が課題とされてきた。本研究では、発表者らが Metal-organic framework(MOF)結晶の足場として利用してきた $Cu(OH)_2$ 配向薄膜[1)]を用いて、溶液プロセスによる COF 配向薄膜の形成を試みた。基板全面で配向した $Cu(OH)_2$ の表面水酸基は、COF を構成するボロン酸と相互作用する異方的な足場とみなす事ができ、基板面内(in-plane)で COF 結晶が整列しエッジオン配向した COF 薄膜の形成が期待される。本研究発表では、代表的な COF として知られる COF-1($(C_3H_2BO)_6 \cdot (C_9H_{12})$)の配向薄膜の形成およびその成長様式を明らかにすることで、種々の COF 系へ応用可能なエッジオン配向薄膜の合成手法を報告する。



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Development of Efficient Triplet-DNP system Using Metal-Organic Frameworks

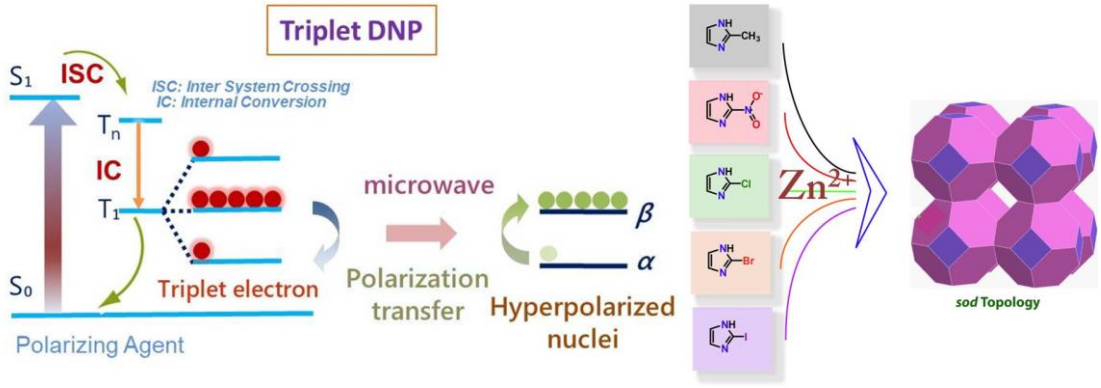
([1]*Graduate School of Engineering, Kyushu University,* [2]*Center for Molecular Systems (CMS), Kyushu University*, [3]*JST-PRESTO*) ○ Arijit Mallick,[1] Saiya Fujiwara,[1] Hironori Kouno[1] Biplab Joarder,[1] Nobuo Kimizuka,[1,2] Nobuhiro Yanai[1,2,3]

Keywords: Dynamic Nuclear Polarization; Triplet Electrons; Nuclear Magnetic Resonance; Metal−Organic Frameworks; Host-Guest Chemistry.

NMR spectroscopy and MRI are powerful methods for the non-destructive analysis of microscopic structures and human body. Sensitivity of NMR and MRI is poor under the conventional conditions due to low nuclear spin polarization. In order to enhance the NMR/MRI sensitivity, dynamic nuclear polarization (DNP) has attracted great attention. High nuclear spin polarization has been achieved by using radical electrons as polarization source, but it requires the sample cooling to very low temperature around 1 K.

To overcome this problem, DNP using photo-excited triplet electrons becomes the focus of research. In triplet-DNP, hyperpolarization of nuclear spins can be achieve at room temperature by transferring triplet electron polarization to nuclear polarization. Presently triplet-DNP mainly uses dense host matrices. However, in order to not only polarize many kinds of molecules but also suppress the spin relaxation effectively, the development of new triplet-DNP system with accessibility of target molecules is required.

Here, we report a series of functionalized porous metal−organic frameworks with *sod*-topology[1] for triplet-DNP. We thoroughly studied the relationship between structure and spin-lattice relaxation time of protons in these compounds, and then introduced polarizing agents into these frameworks. This would show ^{1}H NMR signal enhancement over thermal equilibrium.[2]



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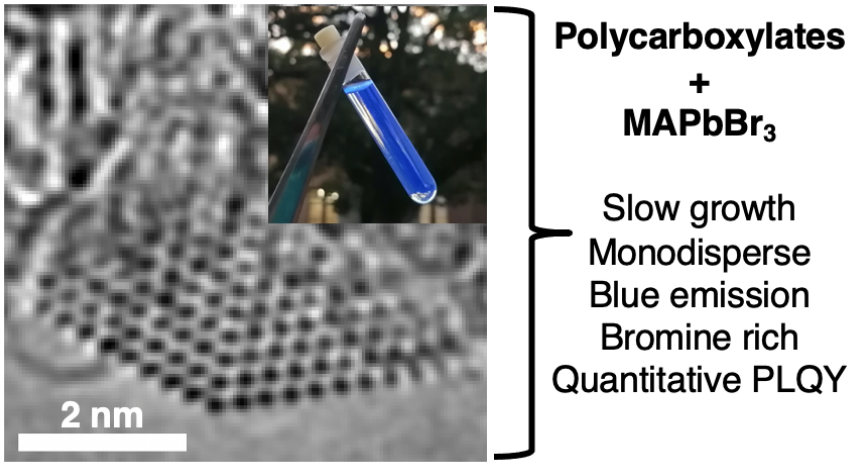
Polycarboxylates as synthetic tools for small and efficient perovskite quantum dots

○Olivier Chevalier[1], Takayuki Nakamuro[1], Rui Shang[1], Eiichi Nakamura[1] (1. Molecular Technology Innovation, Department of Chemistry, The University of Tokyo)

Keywords: Quantum Dots, Perovskite, Ligand

Nanosized lead halide perovskites have gained tremendous interest for light emitting applications over the past few years due to their easy synthesis and color tunability over the entire visible spectra[1]. More precisely, blue light emission is usually achieved via chloride-bromide mixed systems, or by an increase in the confinement of pure bromide quantum dots. However, small pure bromide quantum dots are still lackluster performance-wise with poor stability[2], or require numerous post-treatments[3].

Here we developed a new synthetic method based on polycarboxylates used as replacement to the standard Oleic Acid. By sharply decreasing the kinetics of dots' formation, we drastically improved the performances of the material. Our method yields small (2.5nm in diameter), deep blue perovskite quantum dots with quantitative quantum yield and enhanced stability. We attributed the excellent performances to an in-situ bromine enrichment, enabled by the polycarboxylate. We investigated the role of the ligand and found out polycarboxylates are weakly bound to the edges of the dots and act solely as synthetic aids. Our results highlight the critical impact of polydentate ligands onto quantum dot formation mechanisms leading to dramatic changes in the performances of the resulting dots.



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Synthesis and structure of porous ionic crystals based on delta-Keggin-type aluminum polyoxocation

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

Keywords: Polyaluminum Hydroxide; Polyoxometalates; Ionic Crystal

Aluminum is the third most abundant element in the earth's crust and has complex solution chemistry. The hydrolysis of aluminum salts in water produces an array of polyoxoaluminum clusters with various sizes, widely used in catalysis, water treatment, and as pillaring agents.[1] Among the polyoxoaluminum clusters, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (**Al_{13}**) has five possible isomers of the Baker–Figgis–Keggin (Keggin) structure: α, β, γ, δ, and ε. We have previously obtained all-inorganic porous ionic crystals (PICs) by combining oppositely charged molecular ions (macroions) with T_d symmetry, ε-Keggin-type cation $[\varepsilon\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (ε-**Al_{13}**) and α-Keggin-type anions (e.g., $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$).[2] However, isomers/derivatives of δ-**Al_{13}** have been rarely reported in recent years. The present study describes the synthesis and structural characterization of a PIC of $[\delta\text{-}Al_{13}O_4(OH)_{25}(H_2O)_{11}][\alpha\text{-}CoW_{12}O_{40}]\cdot 29H_2O$ [**I**].

The all-inorganic PIC of **I** crystallized through a dissolution−recrystallization reaction in water for 3 days. Single crystal X-ray diffraction analysis reveals that oppositely charged macroions are combined, δ-**Al_{13}** with C_{3v} symmetry (Figure 1a) and $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ with T_d symmetry (Figure 1b). Compound **I** contains 1D-channels with large apertures (ca. 13 Å × 6.5 Å) along the *b*-axis (Figure 1c) and is applicable as a solid catalyst in environmentally friendly acid reactions. To the best of our knowledge, this is the first example of isolating δ-**Al_{13}** polycation without capping sodium ions in the solid-state.[3,4]

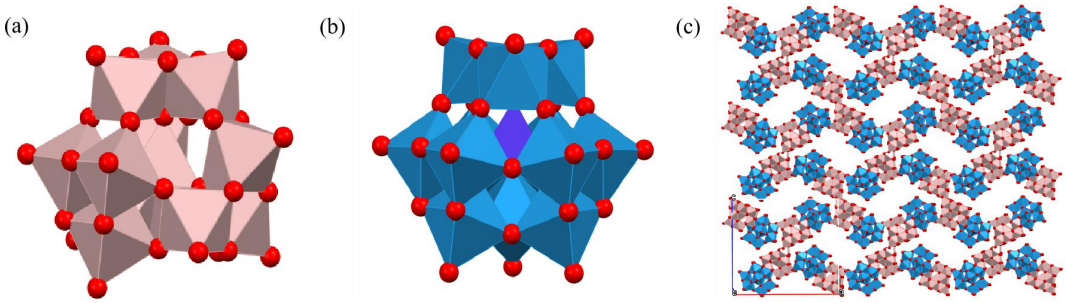

Figure 1.The crystal structure of (a) δ-Al_{13} (b) α-$CoW_{12}O_{40}^{6-}$ and (c) **I** along *b*-axis

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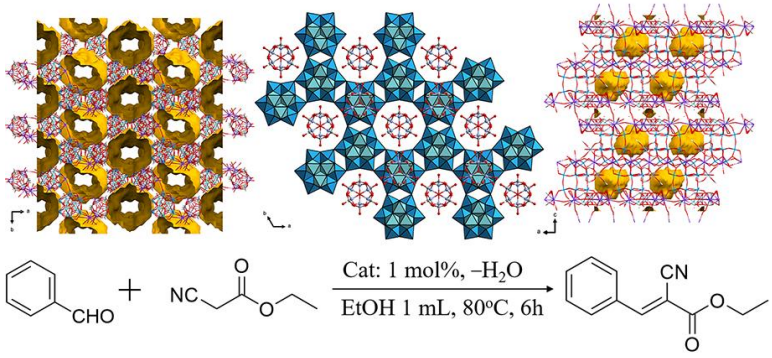
Porous ionic crystals composed of Nb/W mixed-addenda polyoxometalates as solid base catalysts

(*Department of Basic Science, School of Arts and Sciences, The University of Tokyo*) ○Zhewei Weng, Sayaka Uchida

Keywords: Porous Ionic Crystals, Polyoxometalates, Niobium, Mixed-Addenda, Base Catalysis

Polyoxometalates (POMs), which are robust, discrete, and structurally well-defined oxide cluster anions, are widely used as acid and oxidation catalysts, while base catalysis of POMs remains an ongoing challenge. It has been reported that POMs composed of group V elements (V, Nb, Ta) act as base catalysts in CO_2 fixation and Knoevenagel reactions because the surface oxygen atoms become more basic with an increase in the negative charges.[1] We have been working on the design, synthesis and functions of porous ionic crystals (PICs), which are crystalline porous composites of POMs with macrocations,[2] while there are no reports of Nb containing PICs.

In this work, three PICs composed of Dawson-type Nb/W mixed-addenda POMs of mono-substituted $[P_2W_{17}(NbO_2)O_{61}]^{7-}$ or tri-substituted $[P_2W_{15}(NbO_2)_3O_{59}]^{9-}$ with $[Cr_3O(OOCH)_6(H_2O)_3]^+$ ($K_5H[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{17}NbO_{62}](NO_3)\cdot 34H_2O$, **1**; $K_5[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{17}NbO_{62}]\cdot 18H_2O$, **2**; $K_6H[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{15}(NbO_2)_3O_{59}]\cdot 17H_2O$, **3**) were synthesized and tested in Knoevenagel condensation. As a result, **3** exhibited the highest yield (78%) and selectivity (99%) with good reusability, showing that the substitution of W with Nb leads to increased catalytic activity. Furthermore, the catalytic mechanism was studied with ^{31}P solid-state NMR, which indicated that the exposure of terminal oxygen atoms of Nb to the pore surface is crucial to the catalytic performance.



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

[A07-4pm] 08. Catalysts and Catalysis

Chair:Hiroyuki Asakura, Kazuya Yamaguchi

Mon. Mar 22, 2021 1:00 PM - 3:20 PM Room 7 (Online Meeting)

[A07-4pm-01] Direct catalytic arylation of cubane and bicyclo[1.1.1]pentane

○Ryo Okude[1], Genki Mori[1], Akiko Yagi[1], Kenichiro Itami[1] （1. Nagoya University ）

1:00 PM - 1:20 PM

[A07-4pm-02] Iron-Catalyzed Regioselective Thienyl C– H/C– H Coupling and Polycondensation

○Takahiro Doba[1], Laurean Ilies[2], Rui Shang[1], Eiichi Nakamura[1] （1. The University of Tokyo, 2. RIKEN）

1:20 PM - 1:40 PM

[A07-4pm-03] Accessing 1*H*-Indenyl and Dihydro-*s*-Indacenyl Magnesium Reagents via Iron-catalyzed C– O Activation/Acetylenic Cyclization with Magnesium Powder

○MENGQING CHEN[1], Rui Shang[1], Eiichi Nakamura[1] （1. The University of Tokyo）

1:40 PM - 2:00 PM

[A07-4pm-04] Oxygen Reduction Reaction Activity and Characterization of Fe/N/C Catalysts Prepared by Pyrolysis of Fe Complexes Containing 1,12-Diazatriphenylene as a Ligand Structure

○Koki Matsumoto[1], Akira Onoda[2], Takashi Hayashi[1] （1. Graduate school of Engineering, Osaka University, 2. Faculty of Environmental Earth Science, Hokkaido University）

2:00 PM - 2:20 PM

[A07-4pm-05] Water electrolysis in saturated phosphate buffer at neutral pH

○Takahiro Naito[1], Tatsuya Shinagawa[1], Kazuhiro Takanabe[1] （1. The University of Tokyo）

2:20 PM - 2:40 PM

[A07-4pm-07] Highly Stable and Active Solid-Solution-Alloy Three-Way Catalysts by Utilizing the Entropy Effect

○Kohei Kusada[1], Dongshuang Wu [1], Yusuke Nanba[2], Michihisa Koyama[2], Tomokazu Yamamoto[3], Takaaki Toriyama[3], Xuan Tran[3], Syo Matstumura[3], Katsutoshi Sato[1], Katsutoshi Nagaoka[4], Hiroshi Kitagawa[1] （1. Kyoto University, 2. Shinshu University, 3. Kyushu University, 4. Nagoya Universtiy）

3:00 PM - 3:20 PM

キュバンおよびビシクロ[1.1.1]ペンタンの触媒的直接アリール化反応の開発

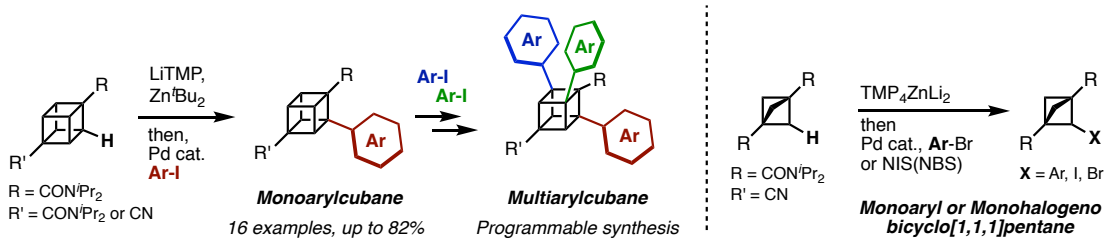
（名大院理[1]・名大 WPI-ITbM[2]）○奥出 諒[1]・森元気[1]・八木 亜樹子[1,2]・伊丹 健一郎[1,2]

Direct catalytic arylation of cubane and bicyclo[1.1.1]pentane ([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*) ○Ryo Okude,[1] Genki Mori,[1] Akiko Yagi,[1,2] Kenichiro Itami[1,2]

Creation of three-dimensional (3D) molecules is an important guiding principle in recent drug design[1]. Among 3D carbon frameworks, cubane and bicyclo[1.1.1]pentane (BCP) have attracted significant attention because they act as bioisosteres of benzene ring[2]. A number of methods for the functionalization of these molecules have been reported so far. However, there are few reports for the direct C–H functionalization of cubane and BCP due to their highly strained structure. Herein we report the programmable synthesis of multiply arylated cubanes through direct *ortho*-metalation and palladium-catalyzed arylation[3]. In addition, we succeeded in direct bridge-C–H functionalization of BCP, which has been rarely reported, by applying the arylation of cubane.

Keywords : Cubane; Bicyclo[1.1.1]pentane; Zincate; Arylation; Palladium

医農薬開発において、近年では分子の三次元性が重要視されている。分子における sp^3 混成炭素の含有率を高めることで医農薬候補となる確率が向上すると期待され[1]、多様なケミカルスペースの構築や溶解性向上において有利な立体分子が求められている。キュバンやビシクロ[1.1.1]ペンタンは、ベンゼン環などの生物学的等価体とされる立体分子であり、創薬での活躍が期待されることから誘導体合成も多数報告されてきた[2]。一方で、大きな歪みを有するため、その C–H 結合を直接変換する例は限られている。本研究では、オルトメタル化を経由したキュバンの触媒的アリール化反応の開発を行なった。さらに、異なるアリール基を複数導入できるマルチアリールキュバンのプログラム合成法の開発に成功した[3]。また、同手法をビシクロ[1.1.1]ペンタンにも応用することで、架橋部の C–H 結合を直接修飾することにも成功した。



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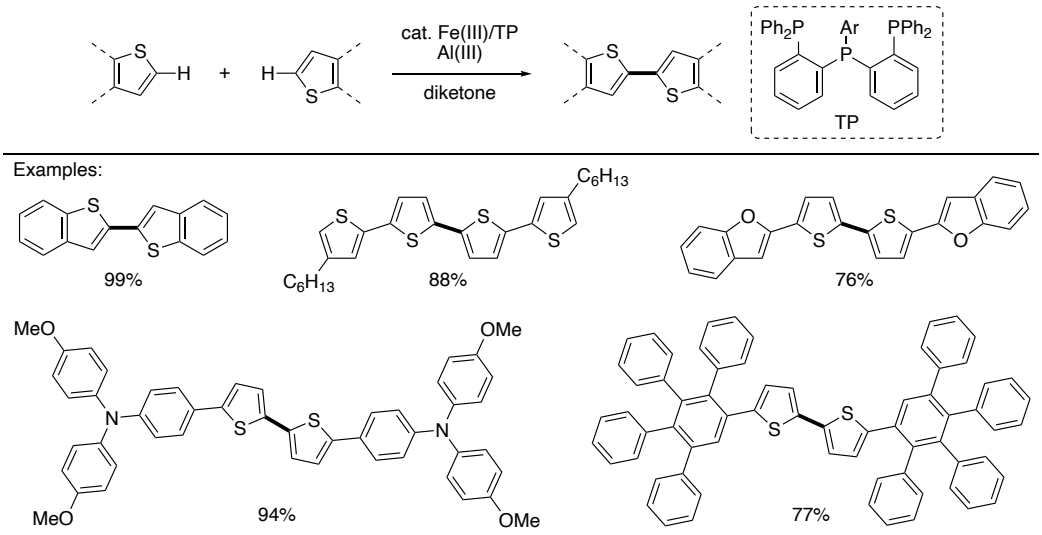
Iron-Catalyzed Regioselective Thienyl C–H/C–H Coupling and Polycondensation

([1] *Molecular Technology Innovation, Department of Chemistry, The University of Tokyo*, [2] *RIKEN Center for Sustainable Resource Science*) ○Takahiro Doba,[1] Laurean Ilies,[2] Rui Shang,[1] Eiichi Nakamura[1]

Keywords: Iron catalysis; C–H/C–H coupling; Thiophene; Polymer; Organic electronics

Direct C–H/C–H coupling to connect two aromatic molecules has attracted attention as one of the most straightforward methods to synthesize biaryls. However, such methods reported so far require strongly oxidizing conditions either to generate reactive cationic radical species (e.g. Scholl reaction, oxidative aromatic coupling)[1] or to turnover catalyst (e.g. palladium catalysis)[2], which limit their synthetic versatility.

Herein, we report that iron(III)/tridentate phosphine catalyst[3] in combination with $AlMe_3$ and a latent oxidant, diketone, enables efficient and selective thienyl C–H/C–H coupling under mildly oxidative conditions. Furthermore, thienyl C–H/C–H polycondensation, which requires high catalytic efficiency, was achieved by the use of a newly designed tridentate phosphine ligand with a modification on the central aryl group. The reaction is compatible with various π-motifs found in optoelectronic materials and allows direct synthesis of dimeric, oligomeric, and polymeric thiophene materials of importance in energy device applications from simple thiophene C–H substrates.



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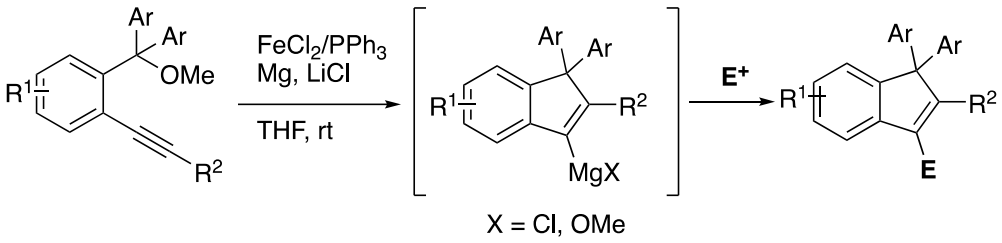
Accessing 1*H*-Indenyl and Dihydro-*s*-Indacenyl Magnesium Reagents via Iron-catalyzed C–O Activation/Acetylenic Cyclization with Magnesium Powder

([1]*Graduate School of Science, The University of Tokyo*) ○Mengqing Chen,[1] Rui Shang,[*1] Eiichi Nakamura[*1]

Keywords Iron; 1*H*-Indenyl; Dihydro-*s*-Indacenyl; Magnesium

Carbon-bridged phenylene vinylene structure, previously reported by our group has found to be applicable in prototype organic photovoltaic device regarding its remarkable photophysical properties and stability.[1] The conventional linear synthesis started from commercially available 1-bromo-2-iodobenzene via 3-lithioindene intermediate using lithium naphthalenide, which guarantees high reactivity while severely limits the substrate scope. Transition-metal catalyzed nucleophilic addition and cross-coupling reactions involving functionalized organometallic reagents are of great importance for carbon–heteroatom or carbon–carbon bond formation in a mild manner[2].

Here we report a mild and effective synthesis of new indenes and indacenes via iron-catalyzed C–O activation and acetylenic cyclization. An arylalkyne substrate possessing methoxy group was successfully cyclized via 1*H*-Indenyl and Dihydro-*s*-Indacenyl magnesium intermediate using magnesium as a reductant, lithium chloride as an additive and catalytic amount of iron(II) chloride and triphenylphosphine ligand. A few examples of indenes trapped with various electrophiles are presented.



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Oxygen Reduction Reaction Activity and Characterization of Fe/N/C Catalysts Prepared by Pyrolysis of Fe Complexes Containing 1,12-Diazatriphenylene as a Ligand Structure

(*[1]Graduate School of Engineering, Osaka University*, *[2]Faculty of Environmental Earth Science, Hokkaido University*) ○Koki Matsumoto[1,2], Akira Onoda[2], Takashi Hayashi[1]

Keywords: Electrode catalyst; Oxygen reduction reaction; Iron complex; Diazahexabenzocoronene; Pyrolysis

Fe/N/C catalysts prepared by pyrolysis of iron and nitrogen sources have been attracted much attention as highly active and durable electrocatalysts for oxygen reduction reaction (ORR) in which the Fe–N_x coordination structures have been proposed as the active sites.[1] Recently, we have reported that thermally durable π-expanded precursors are advantageous for the construction of the Fe–N_x active sites to improve the ORR activity.[2,3] To further control the generation of the Fe–N_x active sites during pyrolysis, preventing the formation of the by-products such as iron carbides, iron oxides and metal iron, and maximizing conversion from the iron precursor is needed. In this work, we designed iron complexes with π-expanded ligands containing 1,12-diazatriphenylene structure (**L1**–**L3**) as a precursor to achieve precise construction of the Fe–N_x active sites. The ligands contain phenyl rings, which are designed to be intramolecularly graphitized during pyrolysis, and the bulkiness of the ligands in its iron complex was found out to prevent the generation of by-products. XRD, XPS and elemental analysis reveal that the Fe–N_x structures were efficiently generated in the Fe/N/C catalysts using Fe complexes of **L1**–**L3**, suggesting that the bromide groups in the ligand structure assist intermolecular graphitization during pyrolysis. More importantly, the tridentate coordination structure in **L3** forming an [Fe(**L3**)$_2$] complex facilitates the construction of the Fe–N_x active sites with higher conversion from the precursor. Rotating ring disk electrode (RRDE) measurements show that the Fe/N/C catalysts have high ORR activity.

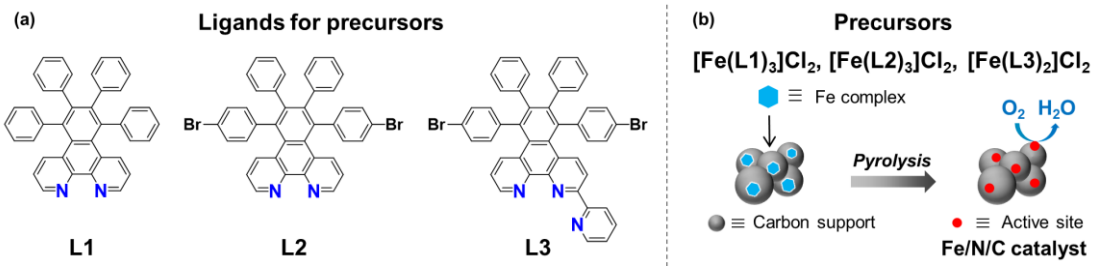


Figure 1. (a) Chemical structure of ligands and (b) schematic illustration of preparation of the Fe/N/C catalyst.

1) M. Shao, Q. Chang, J. P. Dodelet, R. Chenitz, *Chem. Rev.* **2016**, *116*, 3594. 2) Y. Tanaka, A. Onoda, S. Okuoka, T. Kitano, K. Matsumoto, T. Sakata, H. Yasuda, T. Hayashi, *ChemCatChem*, **2018**, *10*, 743. 3) K. Matsumoto, A. Onoda, T. Hayashi, 7th Asian Conference on Coordination Chemistry (2019)

Water Electrolysis in Saturated Phosphate Buffer at Neutral pH

([1]*Graduate School of Engineering, The University of Tokyo*) ○Takahiro Naito,[1] Tatsuya Shinagawa,[1] Kazuhiro Takanabe[1]

Keywords: Electrocatalysis; Energy conversion; Water electrolysis; Phosphate solutions; Heterogeneous catalysis

Adopting the renewable energy is a prerequisite to achieve the sustainability in our society, which is majorly impeded by its spatiotemporal fluctuations. Electrocatalytic processes in this context has regained worldwide interests, whereby we can convert the renewably generated electric power into chemical energy for the use of an energy carrier. Among a variety of energy carriers, hydrogen stands out owing to its high weight energy density.[1] However, conventional polymer exchange membrane (PEM) and alkaline water electrolyzers produce the hydrogen only at a cost economically inferior to those based on fossil fuels.[1] We consider the near-neutral pH electrolyte as the next generation electrolyte medium for the electrolysis,[2] whose milder condition than the conventional electrolyzer offers broader options for materials, which would decrease the capital cost of the electrolyzer. Particularly, densely buffered near-neutral pH medium would enable large mass-transport fluxes and in turn higher efficiency during the electrolysis. Nevertheless, the fundamental understanding as to the physicochemical properties of such electrolyte has been lacking, requiring research activity in this direction.

This presentation reports and analyzes physicochemical properties of densely buffered solutions at neutral pH, and demonstrates water electrolysis in such solutions.[3] Our quantitative analysis validated the applicability of the existing model dealing with the diluted solutions[2] to dense solutions, which allowed for determination of mass-transport fluxes and associated losses during water electrolysis. In the thus identified electrolyte that minimizes the mass-transport losses at pH 7, i.e., saturated K-phosphate solution, water electrolysis was examined using model electrodes at elevated temperatures as in **Figure 1**. The figure revealed that the performance at neutral pH is not only comparable to but also more stable than the extreme pH conditions, demonstrating the potential of the densely buffered electrolyte for the water electrolysis.

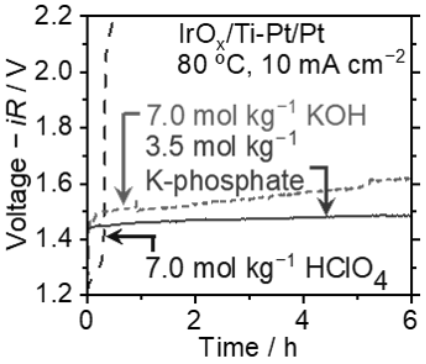


Figure 1. Water electrolysis performance. Chronopotentiometry (CP) profile performed at 10 mA cm^{-2} and 80 °C in electrolyte solutions of 7.0 mol kg^{-1} KOH, 7.0 mol kg^{-1} $HClO_4$, and 3.5 mol kg^{-1} K-phosphate (pH 7.0 at 25 °C) under Ar bubbling.

1) S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, *Catal. Today* **2007**, *120*, 246. 2) T. Shinagawa, K. Takanabe, *ChemSusChem* **2017**, *10*, 1318. 3) T. Naito, T. Shinagawa, T. Nishimoto, K. Takanabe, *ChemSusChem* **2020**, 13, 5921.

Highly Stable and Active Solid-Solution-Alloy Three-Way Catalysts by Utilizing the Entropy Effect

([1]*Grad. Sch. Sci., Kyoto Univ.*, [2]*Hakubi Cent. Adv. Res., Kyoto Univ.*, [3]*iCeMS, Kyoto Univ.*, [4]*JST PRESTO*, [5]*Res. Init. Supra-Materials, Shinshu Univ.*, [6]*URC, Kyushu Univ.*, [7]*Grad. Sch. Eng., Kyushu Univ.*, [8]*ESICB, Kyoto Univ.*, [9]*Grad. Sch. Eng., Nagoya Univ.*) ○Kohei Kusada,[1, 2, 3, 4] Dongshuang Wu,[1] Yusuke Nanba,[5] Michihisa Koyama,[5] Tomokazu Yamamoto[6], Takaaki Toriyama,[6] Xuan Quy Tran,[7] Syo Matsumura[6, 7], Katsutoshi Sato,[8] Katsutoshi Nagaoka,[9] Hiroshi Kitagawa[1]

Keywords: *Alloy nanoparticles*; *Three-way catalyst; Entropy; Rhodium; NO_x reduction*

A three-way catalyst (TWC) that concurrently converts three harmful gases, carbon monoxide, hydrocarbons, and nitrogen oxides (NO_x) is an essential technique for a sustainable society. Rh has been an essential element in TWC because only Rh can efficiently catalytically reduce NO_x. However, since Rh is scarce metal and its price is very fluctuating, significant efforts have been made to develop alternative TWC catalysts to Rh. Nevertheless, Rh is still irreplaceable, and very recently, the price of Rh marked a record high. We reported that solid-solution alloy NPs of Pd and Ru, which are located next to Rh in the periodic table of elements, exhibit an excellent NO_x reduction activity in the TWC reaction superior to Rh.[1] However, the PdRu homogeneous solid-solution alloy structure is transformed at high temperatures into an equilibrium segregated structure due to the immiscibility of Pd and Ru, and the catalyst loses its excellent NO_x reduction activity. To overcome this thermal stability issue, we have focused on the high-entropy effect. Recently, bulk high-entropy alloys consisting of five or more elements with equal or relatively large compositions have drawn much attention as a new type of structural material with high phase stability at higher temperatures.[2] Here, we introduced a third element (M) to stabilize the solid-solution structure in the form of PdRuM NPs at high temperatures (Figure). We demonstrated that PdRuM ternary solid-solution alloy nanoparticles exhibit a highly durable and active TWC performance. Our work provides insights into the design of highly durable and efficient alloy catalysts, guiding how to take the most advantage of the configurational entropy in addition to the mixing enthalpy.

1) a) K. Kusada et al., *J. Am. Chem. Soc*. **2014**, 136, 1864. b) K. Sato et al., *Sci. Rep.* **2016**, *6*, 28265. 2) J.-W. Yeh et al., *Adv. Eng. Mater.* **2004**, *6*, 299.

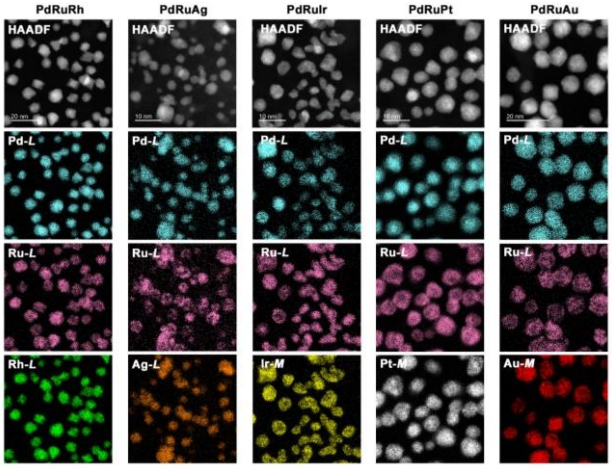


Figure HAADF-STEM images, Pd-L, Ru-L, and M elemental maps.

[A12-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Kyoko Nozaki, Hajime Ito, Hiroaki Kotani

Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 12 (Online Meeting)

[A12-4am-01] Probing Key Reaction Steps in Ce(IV)-driven Water Oxidation Catalyzed by a Mononuclear Ruthenium Complex

○Yutaro Aimoto[1], Alexander Parent[2], Kenton Rodgers[2], Kosei Yamauchi[1], Ken Sakai[1] (1. Dept. Chem. Kyushu Univ., 2. North Dakota State University)

9:00 AM - 9:20 AM

[A12-4am-02] Mechanistic Investigations and Photocatalytic Properties of CO_2-reduction Using Supramolecular Photocatalyst Fixed on Solid Surface

○Daiki Saito[1], Osamu Ishitani[1] (1. Tokyo Institute of Technology)

9:20 AM - 9:40 AM

[A12-4am-03] Control over Catalytic Activity of a Multinuclear Metal Complex Using a Encapsulated Hydrogen Ion

○Misa Tomoda[1,2,3], Yutaka Saga[1], Mio Kondo[1], Shigeyuki Masaoka[1] (1. Osaka University, 2. IMS, 3. SOKENDAI)

9:40 AM - 10:00 AM

[A12-4am-04] Luminescence intensity enhancement for Ir(Ⅲ) complex in dimethyl sulfoxide under photoirradiation

○Shuntaro Hirata[1], Shingo Hattori[1], Kazuteru Shinozaki[1] (1. Yokohama City Univ.)

10:00 AM - 10:20 AM

[A12-4am-05] Regio- and Stereoselective Synthesis of Multi-Alkylated Allylic Boronates through Borylative Coupling of 1,1-Disubstituted Allenes and Alkyl Halides

○Yu Ozawa[1], Kohei Endo[1], Hajime Ito[1,2] (1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)

10:20 AM - 10:40 AM

[A12-4am-06] Aerobic Oxidation Activity of Cu(Phen) Embedded in Hydrophobic Environment

○Shoko Kume[1], Shota Shimizu[2] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. Graduate School of Science, Hiroshima University)

10:40 AM - 11:00 AM

[A12-4am-07] Analysis of Catalytic Performance by Machine Learning for Understanding of Ethylene/Methyl Acrylate Copolymerization Catalyzed by Palladium/Phosphine– Sulfonate Complexes

○Shumpei Akita[1], Jin-Yao Guo[2], Sigman M Sigman[2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. The University of Utah)

11:00 AM - 11:20 AM

[A12-4am-08] Cleavage of C– H Bonds by Cyclopentadienone Iridium Complex

○Takuya Higashi[1], Shuhei Kusumoto[1,2], Kyoko Nozaki[1] (1. Graduate School of Engineering, the University of Tokyo, 2. JST PRESTO)

11:20 AM - 11:40 AM

Probing Key Reaction Steps in Ce(IV)-driven Water Oxidation Catalyzed by a Mononuclear Ruthenium Complex

([1]*Dept. Chem., Kyushu Univ.,* [2]*North Dakota State Univ.*)
○Yutaro Aimoto,[1] Alexander Parent,[2] Kenton Rodgers,[2] Kosei Yamauchi,[1] Ken Sakai[1]
Keywords: Oxidation reaction; Oxygen evolution; Reaction intermediates; Artificial photosynthesis

Water splitting is a promising way to solve energy and environmental problems. Water oxidation (WO) corresponds to the half reaction of water splitting, considered as the bottleneck reaction, because it requires removal of four protons and four electrons ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). It is thus important to clarify the mechanism of WO to develop efficient catalysts for this reaction. In this context, we previously reported that a mononuclear ruthenium complex ($[Ru(tpy)(bpy)(OH_2)]^{2+}$) serves as a molecular catalyst in the WO driven by Ce^{4+} (Ceric Ammonium Nitrate; CAN) as an oxidizing reagent.[1,2]

In this study, we have succeeded in isolating a high valent ruthenium(IV) oxo intermediate $[Ru^{IV}(O)(tpy)(bpy)]^{2+}$ (**Ru^{IV}=O**), as judged by elemental analysis, EDX, ESI-TOF-MS, IR, EPR and Raman spectroscopy. Square wave voltammograms of **Ru^{IV}=O** and CAN recorded in acetonitrile solution indicate that the outer-sphere electron transfer (ET) from **Ru^{IV}=O** to Ce^{4+} is thermodynamically unfavorable, implying that the oxidation of **Ru^{IV}=O** by CAN is likely to proceed via the inner-sphere ET path (**Figure 1**). **Figure 2** shows the UV-Vis spectral change for the reaction between **Ru^{IV}=O** (0.05 mM) and CAN (0.05 mM) at 21°C. The Eyring plot, developed by measuring the temperature dependence of the observed first-order rate constant, afforded the activation parameters of $\Delta H^{\ddagger}$ = 75 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −40 J K^{-1} mol^{-1}. The negative $\Delta S^{\ddagger}$ value is consistent with promotion of an inner-sphere ET, assignable to the adduct formation of **Ru^{IV}=O** and CAN presumably having a Ru^{IV}-O-Ce^{IV} core. We will also discuss the mechanism of WO based on the inner-sphere ET from **Ru^{IV}=O** to CAN in detail.

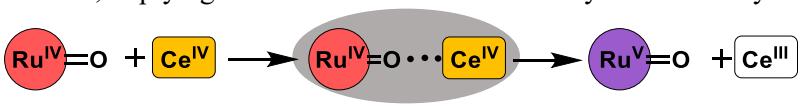


Figure. 1. Inner-sphere electron transfer between **Ru^{IV}=O** and CAN.

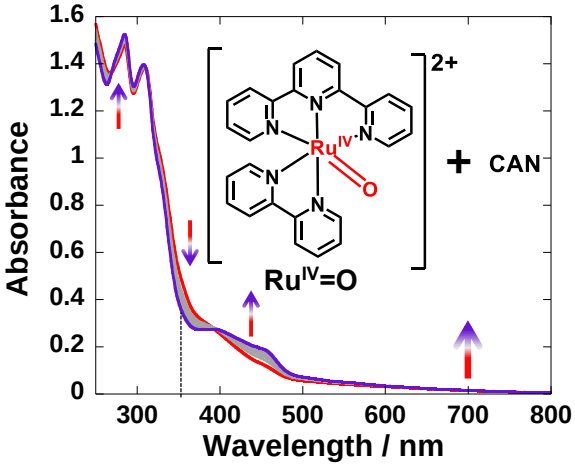


Figure 2. UV-Vis spectral change during the reaction of **Ru^{IV}=O** with CAN in acetonitrile.

1) M. Yoshida, S. Masaoka, J. Abe, K. Sakai, *Chem. Asian J.,* **2010**, *5*, 2369.
2) A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka, K. Sakai, *Chem. Commun*. **2012**, *48*, 239.

Mechanistic Investigations of CO_2-reduction Using Supramolecular Photocatalyst Fixed on Solid Surface

(*Sch. Sci., Tokyo Tech.*) ○Daiki Saito, Osamu Ishitani

Keywords: Supramolecular photocatalyst; Heterogeneous catalyst; CO_2 reduction

CO_2-reduction photocatalysts play a crucial role for developing artificial photosynthesis. Ru(II) metal complexes have been investigated as catalysts to reduce CO_2 and produce CO and HCOOH[1,2]. However, the reaction mechanisms of these metal complexes are still unclear. In this study CO_2 reduction mechanism of a supramolecular photocatalyst consisting of Ru(II) photosensitizer and Ru(II) catalyst units[3] was investigated (**RuRu**, Figure 1). **RuRu** was fixed on Al_2O_3 particles to prevent intermolecular collisions and its photocatalysis was investigated in detail by changing adsorbing density and photocatalytic reaction conditions for CO_2 reduction.

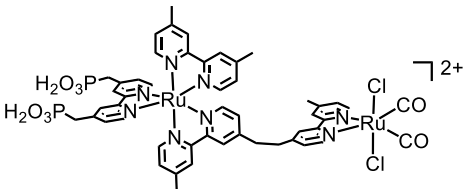


Figure 1. Structure of **RuRu**

The **RuRu** supramolecular photocatalysts were adsorbed on alumina particles by stirring in MeCN for 7 days. The adsorption density of **RuRu**/Al_2O_3 was controlled at 5 μmol g^{-1} where the distance between the neighboring **RuRu** molecules on the Al_2O_3 is much larger than the molecular length of **RuRu**. The **RuRu**/Al_2O_3 particles were dispersed into a dimethylacetamide-triethanolamine (DMA-TEOA) mixed solution containing 0.1 M of 1-benzyl-1,4-dihydronicotinamide (BNAH) as a one-electron donor and irradiated at $\lambda > 480$ nm under CO_2 atmosphere. Both CO and HCOOH was photocatalytically produced. The selectivity of HCOOH formation increased (from 91% to 94%) at lower irradiated light intensity. This strongly suggests that lower efficiency of the electron injection from the one-electron-reduced Ru photosensitizer unit to the Ru catalyst unit predominates the formation of HCOOH. On the other hand, CO selectivity (S_{CO} = CO/(HCOOH+CO) ×100) dramatically increased from 11% to 76% by decreasing the concentration of TEOA from 1.5 M to 0 M (Figure 2). We discuss about the photocatalytic reaction mechanism of CO_2 reduction.

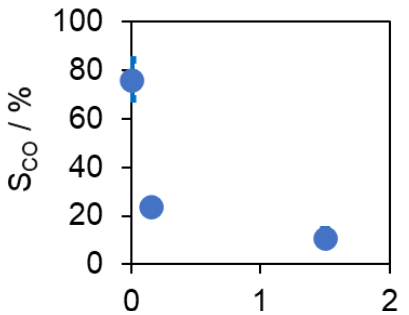


Figure 2. The relationship between TEOA concentration and CO selectivity.

[1] Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1988**, 339.

[2] Kuramochi, Y.; Itabashi, J.; Fukaya, K.; Enomoto, A.; Yoshida, M.; Ishida, H. *Chem. Sci.*, **2015**, *6*, 3063.

[3] Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. *Proc. Natl. Acad. Sci. U. S. A.*, **2012**, *109*, 15673.

Control over Catalytic Activity of a Multinuclear Metal Complex Using an Encapsulated Hydrogen Ion

([1]*Graduate School of Engineering, Osaka University*, [2]*Institute for Molecular Science,* [3]*SOKENDAI*, [4]*JST PRESTO*) ○Misa Tomoda,[1,2,3] Yutaka Saga,[1] Mio Kondo,[1,4] Shigeyuki Masaoka[1]

Keywords: Heterometallic Multinuclear Complex; Proton Trapping; Control of Catalytic Activity; Hydrogen Evolution Reaction

Proton transfer reaction plays important roles both in biological and artificial systems for acquiring their unique functions. Therefore, the development of molecules which can control the behavior of protons is an attractive research target for obtaining novel functional materials. In this work, we discovered that a heterometallic pentanuclear complex, which composed of 3,5-bis(pyridyl)pyrazole (Hbpp) and ruthenium and cobalt ions, can encapsulate a proton in its structure. We also found that the encapsulated proton greatly affects catalytic activity for hydrogen production.

Synthesis of heterometallic pentanuclear complexes was performed by the step-wise complexation of metal ions with Hbpp. Initially, $[Ru(Hbpp)_3](ClO_4)_2$ was synthesized as a precursor. The obtained complex was further reacted with 5 eq. of $Co(OAc)_2 \cdot 4H_2O$ and $[Ru_2Co_3OH(bpp)_6](ClO_4)_3$ (**Ru_2Co_3OH**, Figure 1 (left)) was obtained. The deprotonated form of the complex, $[Ru_2Co_3O(bpp)_6](ClO_4)_2$ (**Ru_2Co_3O**, Figure 1 (right)), was also obtained by treating **Ru_2Co_3OH** with a base.

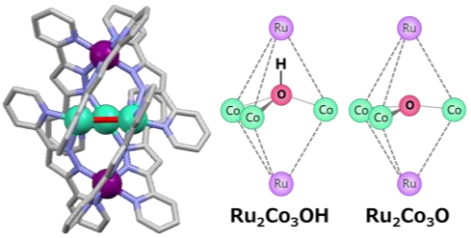


Fig. 1. The structures of heterometallic pentanuclear complexes, **Ru_2Co_3OH** (left) and **Ru_2Co_3O** (right).

Subsequently, we investigated electrochemical properties of **Ru_2Co_3OH** and **Ru_2Co_3O** (Figure 2). In cyclic voltammograms (CVs) of **Ru_2Co_3OH**, two reversible oxidation and three reversible reduction waves were observed. On the other hand, CVs of **Ru_2Co_3O** exhibited four reversible oxidation and two reversible reduction waves. In addition, we explored the catalytic activity of **Ru_2Co_3OH** and **Ru_2Co_3O**. As a result, it was suggested that the encapsulated hydrogen ion can largely influence the catalytic activity of **Ru_2Co_3** complexes.

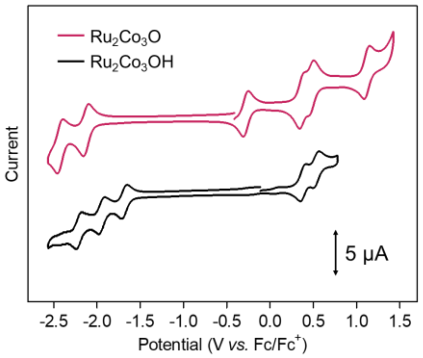


Fig. 2. CVs of **Ru_2Co_3** complexes.

光照射に伴うジメチルスルホキシド中の Ir(III)錯体の発光増強

（横浜市大院生命ナノ）○平田 俊太郎・服部 伸吾・篠﨑 一英
Luminescence Intensity Enhancement for Ir(III) Complex in Dimethyl Sulfoxide under Photoirradiation (*Graduate School of NanoBioscience, Yokohama City University*) ○Shuntaro Hirata, Shingo Hattori, Kazuteru Shinozaki

Luminescent Ir(III) complexes have been applied to organic light-emitting diodes (OLEDs) and photocatalysts. In recent years, the studies on organic synthesis and photodynamic therapy (PDT) using Ir(III) complex as a photosensitizer have been reported. In many cases, dimethyl sulfoxide (DMSO) is employed as a solvent for the photoreactions. Recently, we found that luminescence intensity of *fac*-Ir(ppy)$_3$ (ppy= 2-phenylpyridine), a typical of Ir(III) complex, in aerated DMSO is increased by continuous photoirradiation. This luminescence enhancement was observed only using DMSO as a solvent and of which rate was found to depend on excitation wavelength. In addition, an action spectrum produced by a plot of enhancement rate vs. excitation wavelength was in good agreement with the excitation spectrum of *fac*-Ir(ppy)$_3$ emission. These results suggest that the luminescence enhancement is induced by some O_2 consuming reaction photosensitized by *fac*-Ir(ppy)$_3$. Here, we propose the luminescence enhancement mechanism for *fac*-Ir(ppy)$_3$ based on this photoreaction.
Keywords : Iridium Complex; Luminescence Enhancement; Photosensitization; Singlet Oxygen

発光特性を有する Ir(III)錯体は有機 EL 材料や光触媒へ応用されており、近年では、Ir(III)錯体を光増感剤として用いた有機合成法や光線力学療法についても盛んに研究が行われている。加えて、このような研究分野において、ジメチルスルホキシド(DMSO)を溶媒として使用した報告例が多数挙げられている。

今回我々の研究では、未脱気の DMSO 中における *fac*-Ir(ppy)$_3$ (ppy= 2-フェニルピリジン)が光照射に伴い、発光増強する現象を観測した。発光増強現象は酸素を含む DMSO を溶媒に用いた場合に観測された。さらにこの発光増強は励起波長に依存し、その発光増強速度と励起波長から成るアクションスペクトルが、*fac*-Ir(ppy)$_3$ の励起スペクトルと良く一致することが判明した。これらの結果より、*fac*-Ir(ppy)$_3$ 自身が光増感剤として作用することで、何らかの溶存酸素の消費反応が起き、発光増強現象が観測されていると示唆された。以上の結果に加え、本研究では、各種分光測定及び量子化学計算により、光照射に伴う DMSO 中の *fac*-Ir(ppy)$_3$ の発光増強機構を提唱する。

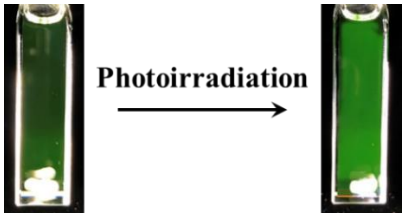


Figure Luminescence enhancement of *fac*-Ir(ppy)$_3$ in DMSO under photoirradiation.

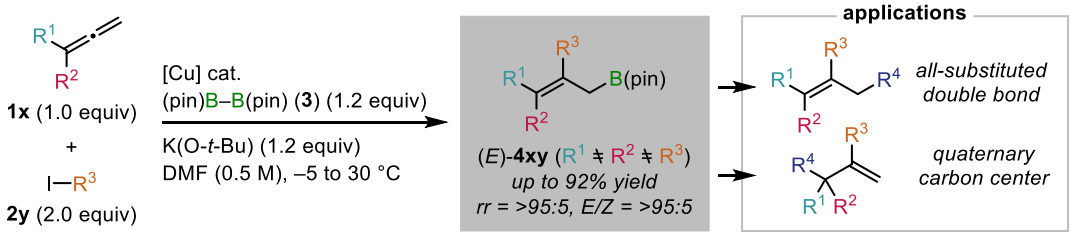
Regio- and Stereoselective Synthesis of Multi-Alkylated Allylic Boronates through Borylative Coupling of 1,1-Disubstituted Allenes and Alkyl Halides

([1]*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University*, [2]*WPI-Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University*) ○Yu Ozawa,[1] Kohei Endo,[1] Hajime Ito[1,2]

Keywords: Copper(I) catalyst, Diboron reagent, Allyl boronates, Stereoselective, DFT calculation

Allylic boronates are recognized as versatile intermediates because of their high stability under ambient conditions and their reactivity of the α- and γ-position for the stereospecific formation of a new C–C bond. In particular, multi-substituted ones are attractive building blocks for constructing sterically demanding carbon skeletons such as multi-substituted alkenes and quaternary carbon centers.[1] Herein, we describe a new approach to the acyclic allyl boronates bearing three different alkyl groups on its alkene moiety. Inspired by Tsuji's, Hoveyda's, and our previous studies,[2] we successfully developed a copper(I)-catalyzed three-component coupling between allenes, alkyl halides, and a diboron reagent. The product was obtained in high yield with high regio- and stereoselectivity (up to 92% yield, rr = >95:5, *E*/*Z* = >95:5).

Given the optimized conditions, the substrate scope was investigated with some allenes and alkyl halides. The copper(I) catalyst could differentiate the bulkiness of two substituents of allenes (R^1 and R^2); e.g. methyl and primary alkyl groups, primary and secondary alkyl groups, primary and tertiary alkyl groups, etc. However, we found some limitations of alkyl halides. Although primary alkyl halides could be applied to the reaction, no product was obtained from secondary alkyl halides due to their low reactivity to S_N2 type reaction. Furthermore, stereospecific transformations were performed to obtained all-substituted alkenes and quaternary carbon centers through α- and γ-substitution of the boryl group, respectively.



1) Diner, C.; Szabó, K. J. *J. Am. Chem. Soc.* **2017**, *139*, 2.

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Aerobic Oxidation Activity of Cu(phen) Embedded in Hydrophobic Environment

(*[1]Graduate School of Advanced Science and Engineering, Hiroshima University, [2]Graduate School of Science, Hiroshima University*) ○Shoko Kume[1], Shota Shimizu[2]

Keywords: aerobic oxidation, alcohol oxidation, hydrophobic environment, phenanthroline

Facile oxygen activation by Cu coordination compounds has led the development of catalysts for aerobic oxidation of organic molecules. These catalysts exploits Cu(II)/(I) electron transfer coupled with organic redox additives, especially TEMPO,[1)] or with redox-active ligands to perform two (or more) electrons oxidation. Several cases of the additive-free aerobic oxidation by copper catalyst have been reported, but its reactivity is elusive, and a lot of articles concluded that the aerobic oxidation is not effective when the redox-additive is removed from the reaction system. We found that the simple Cu(phen) coordination catalysts can act as an effective catalyst in aerobic oxidation of alcohols in hydrophobic solvents. Also, the product yield can be improved by introduction of hydrophobic substituents to the catalyst structure.

The reaction can be divided into three phases, i) induction ii) active period and iii) deactivation. While the hydrophobic environment seems to prolong the induction period due to low solubility of the catalyst, but once it was activated, the oxidation proceeded efficiently. The oxidation proceeds within 1 hour at room temperature, and terminated by deactivation. Therefore, the inhibition of deactivation seems crucial for versatile application of additive-free aerobic oxidation.

The XAFS analysis of the deactivated species revealed binuclear Cu(II) structure, possibly bridged by oxygen. The Cu centers likely to be bridged in the process of oxygen activation and subsequent alcohol oxidation due to the requirement of two-electron electron transfer process.[2)] The introduced hydrophobic group seems to add flexibility to the copper compound even in hydrophobic solvents, which promotes induction and hydrogen abstraction process in oxidation. It can also inhibit deactivation by preventing the binuclear Cu species from aggregation, to bring out the intrinsic oxidation activity of Cu centers.

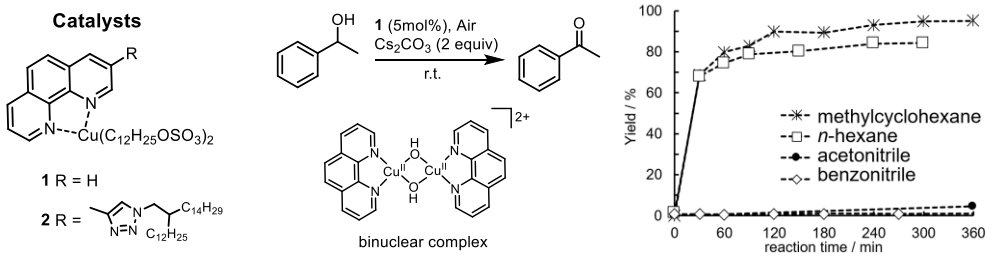


Figure 1. Catalysts and aerobic oxidation profile of 1-phenylethanol in various organic solvents.

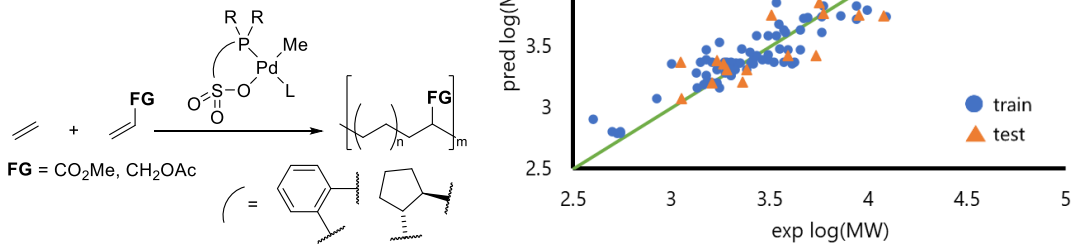
1) S. Stahl *et al.*, *Angew. Chem. Int. Ed.*, **2014**, *53*, 8838. 2) X. Yang *et al.*, *Catal. Sci. Technol.*, **2020**, *10*, 2183.

Analysis of Catalytic Performance by Machine Learning for Understanding of Ethylene/Methyl Acrylate Copolymerization Catalyzed by Palladium/Phosphine–Sulfonate Complexes

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Department of Chemistry, The University of Utah*) ○Shumpei Akita,[1] Jing-Yao Guo,[2] Matthew S. Sigman,[2] Kyoko Nozaki,[1]
Keywords: machine learning; catalyst performance prediction; coordination–insertion polymerization; palladium complex; phosphine–sulfonate ligand

Various types of palladium complexes bearing phosphine-sulfonate ligands have been developed for the coordination–insertion copolymerization of olefins with polar monomers.[1] Characteristic features of the ligands, such as electronic[2] and steric[3] properties were discussed in relation to their catalytic performance: for example, the stronger electron-donation from the phosphine to the metal center[2] and the larger B5 parameter of the substituents on the phosphorus atom,[3] both increased the molecular weight of the obtained polyethylene. Aiming at further analysis of the obtained data for the copolymerization of ethylene and methyl acrylate, we developed prediction methods for molecular weight, catalytic activity, and incorporation of methyl acrylate using machine learning.

The result of prediction for molecular weight of the copolymer is shown below. In the prediction, R^2 and Q^2 are larger than 0.85 and 0.80, respectively, suggesting their good agreement. The important parameters for prediction of molecular weight were clarified to be Sterimol B5 parameter of the substituents on phosphorus atom, %Vbur, and occupancy of d_{z2} orbital in palladium.



1) For a review, see: A. Nakamura, T. M. J. Anselment, J. Claverie, B. Goodall, R. F. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. Van Leeuwen, K. Nozaki, *Acc. Chem. Res.* **2013**, *46*, 1438. 2) P. Wucher, V. Goldbach, S. Mecking, *Organometallics* **2013**, *32*, 4516. 3) Y. Ota, S. Ito, J. Kuroda, Y. Okumura, K. Nozaki, *J. Am. Chem. Soc.* **2014**, *136*, 11898.

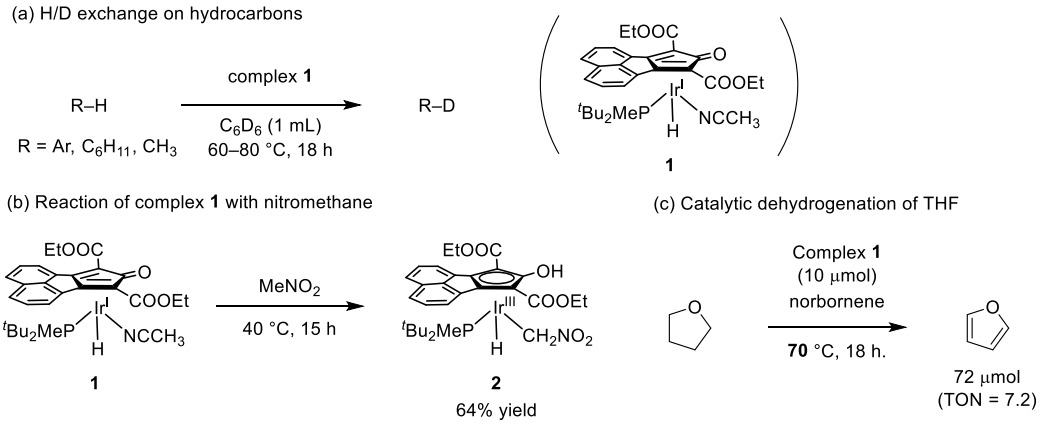
Cleavage of C–H Bonds by Cyclopentadienone Iridium Complex

([1]*Graduate School of Engineering, the University of Tokyo,* [2]*JST PRESTO*) ○ Takuya Higashi,[1] Shuhei Kusumoto,[1,2] Kyoko Nozaki[1]

Keywords: Oxidative Addition; C–H Activation; Cyclopentadienone; Metal–Ligand Cooperation; Iridium

Oxidative addition of C–H bonds, which generates reactive intermediates with metal–carbon bonds, has played an essential role in the field of organometallic chemistry.[1] Previously, we reported a new type of sp^3 C–H bond *forming* reaction, "Metal-Ligand cooperative reductive elimination of sp^3 C–H bonds", which takes place at a hydroxycyclopentadienyl dimethylplatinum(IV) complexes.[2] Herein we prepared an iridium(I) hydride complex **1** bearing electron-deficient cyclopentadienone ligand toward sp^3 C–H bond oxidative addition. Complex **1** catalyzed H/D exchange of sp^2 C–H bonds in toluene, and sp^3 C–H bonds in hexane and methane in the presence of C_6D_6 (**Scheme 1a**). When complex **1** was treated with nitromethane, hydroxycyclopentadienyl nitromethyliridium(III) complex **2** was formed (**Scheme 1b**), showing the novel elementary reaction, *metal–ligand cooperative C–H bond oxidative addition.* In this reaction, we found that the more electron-deficient the cyclopentadienone ligand is, the more favorable the reaction becomes, in sharp contrast to the classical metal-centered oxidative addition.[1] This trend shows good agreement with the proposed mechanism where the C–H bond cleavage is accompanied by two-electron transfer from the metal center to the cyclopentadienone ligand.[3] Complex **1** was further applied to catalytic transfer-dehydrogenation of THF, where 7.2 of catalytic turnover was achieved at 70 °C, the lowest temperature ever reported (**Scheme 1c**).

Scheme 1



1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932. 2) Higashi, T.; Ando, H.; Kusumoto, S.; Nozaki, K. *J. Am. Chem. Soc.* **2019**, *141*, 2247–2250. 3) a) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400–7402. b) Higashi, T.; Kusumoto, S.; Nozaki, K. *Angew. Chem. Int. Ed.* 10.1002/anie.202011322.

[A13-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Shouhei Tashiro, Takane Imaoka, Yukatsu Shichibu, Takashi Fukushima
Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 13 (Online Meeting)

[A13-4am-01] Concentration dependence of absorption and emission spectra of Pt(II) and Au(I) complexes oligomers in aqueous solutions

○Munetaka Iwamura[1], Koichi Nozaki[1], Rina Urayama[1], Airi Fukui[1] (1. Univ. of Toyama)
9:00 AM - 9:20 AM

[A13-4am-02] Spectroscopic properties of aggregates composed of square-planar platinum(II) complexes

○Shingo Hattori[1], Rina Owada[1], Kazuteru Shinozaki[1] (1. Yokohama City Univerisity)
9:20 AM - 9:40 AM

[A13-4am-03] Synthesis of a chiral-at-Pt(II)-Cu(I) complex with a bisphenanthroline macrocycle

○Shun Shimizu[1], Shohei Tashiro[1], Mitsuhiko Shionoya[1] (1. The University of Tokyo)
9:40 AM - 10:00 AM

[A13-4am-04] Syntheses, Crystal Structures, and Properties of Paramagnetic Multinuclear Assembles with Trans Pt-M-Pt Trinuclear Complexes

○Atsushi Takamori[1], Kazuhiro UemuraUemura[2] (1. Graduate School of Engineering, Gifu University, 2. Faculty of Engineering, Gifu University)
10:00 AM - 10:20 AM

[A13-4am-05] Synthesis and Catalytic Properties of Platinum and Platinum Alloy Sub-nanoparticles with Single-Digit Atomicity

○Yuki Akanuma[1], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-ERATO)
10:20 AM - 10:40 AM

[A13-4am-06] Thin film formation of thiolate-protected Au_{25} cluster through inter-cluster covalent linking

○Yuki Saito[1], Yukatsu Shichibu[1,2], Katsuaki Konishi[2,1] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)
10:40 AM - 11:00 AM

[A13-4am-07] Heteropolymetallic Pd/Cu and Pt/Cu for metal-metal cooperative bond activation

○Shubham Deolka Deolka[1], Orestes Rivada wheelaghan[1], Govindarajan ramadoss[1], Eugene Khaskin[1], Julia Khusnutdinova[1] (1. OIST ,JAPAN)
11:00 AM - 11:20 AM

[A13-4am-08] Preparation and Reactivity of Molybdenum Complexes Bearing Pyrrole-Based PNP-Type Pincer Ligand

○Yoshiaki Tanabe[1], Yoshiya Sekiguchi[1], Shogo Kuriyama[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo)
11:20 AM - 11:40 AM

Concentration dependence of absorption and emission spectra of Pt(II) and Au(I) complexes oligomers in aqueous solutions

([1]*Graduate School of Science and Engineering, University of Toyama,* [2]*Faculty of Science, University of Toyama*) ○Munetaka Iwamura,[1,2] Rina Urayama,[2] Airi Fukui,[2] Koichi Nozaki[1,2]

Keywords: Metallophilic interaction; Emissive molecular assembly; Ionic strength; Aggregate induced emission;

Metallophilic oligomers of gold and platinum complexes have been attracted because their emission colors widely vary depending on the degree of oligomerization. The assignments of the absorption and emission bands of oligomers of $[Pt(CN)_4^{2-}]_n$, one of the most primal metallophilic oligomers, were made by Schindler and other workers based on the concentration dependence of the band intensity in aqueous solutions.[1] However, the effects of ionic strength were not considered in their works though the equilibrium constants for oligomer formation of charged species may depend strongly on the ionic strength in the solutions. In this work, the concentration dependence of emission and absorption spectra for $[Pt(CN)_4]^{2-}$ and $[Au(CN)_2]^-$ in aqueous solutions were re-investigated with controlled ionic strength to determine the photophysical properties of the oligomeric species.

An absorption band at 300 nm for $K_2[Pt(CN)_4]$ solutions was assigned to dimer because its intensity is proportional to the square of the analytical concentration under a controlled ionic strength (Figure 1a and b), though assigned to trimer in the previous work.[1] Emission bands at 350 nm and 407 nm were assigned to fluorescence from S_1 dimer and trimer, respectively, based on the concentration dependence of the populations of the emitting species (Figure 1c and d). These assignments also differ from those for uncontrolled ionic strength.[1]

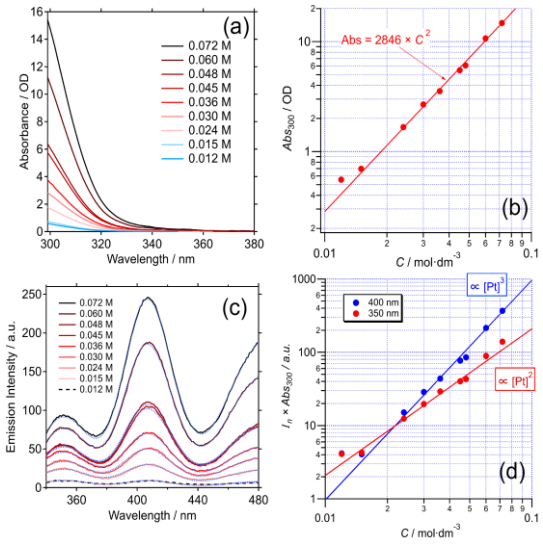


Figure 1. Concentration dependence of absorption spectra (a) and absorbance at 300 nm (b) of $K_2[Pt(CN)_4]$ aqueous solution. (c) Steady-state fluorescence spectra of $K_2[Pt(CN)_4]$ aqueous solution at various concentrations. (d) Concentration dependence of $I_n \times Abs_{300}$ (the product of intensities of the 407-nm or 350-nm emission band and absorbance at 300 nm). ([Pt] = 0.012-0.072 mol/dm^3, μ = 1.8 mol/dm^3, λ_{ex} = 300 nm d = 1 mm)[2]

1) J. W. Schindler, R. C. Fukuda, A. W. Adamson, *J. Ame. Chem. Soc.* **1982**, *104*, 3596-3600.

2) M. Iwamura, A. Fukui, K. Nozaki, H. Kuramochi, S. Takeuchi, T. Tahara, *Angew. Chem. Int. Ed.* **2020,** 59. 23154..

平面型白金(II)錯体からなる会合体の分光学的性質

（横浜市大院生命ナノ）○服部 伸吾・大和田 李奈・篠﨑 一英

Spectroscopic Properties of Aggregates Composed of Square-Planar Platinum(II) Complexes

(*Graduate School of Nanobioscience, Yokohama City University*) ○Shingo Hattori, Rina Owada, Kazuteru Shinozaki

It is known that cyclometalated platinum(II) complexes showing high luminescent efficiencies at room temperature form excited aggregates owing to metallophilic interactions and π-π interactions. In our laboratory, we have succeeded in observing an excited dimer and an excited trimer in the luminescence of cyclometalated platinum complexes.[1,2] Here, we report spectroscopic properties of a newly found water-soluble cyclometalated platinum(II) complex ([Pt(dpb)(sol)]$^+$OTf$^-$, Figure 1), which forms ground state aggregates in water.

Figure 2 shows the electronic absorption spectrum of [Pt(dpb)(sol)]$^+$OTf$^-$ in aqueous solution. The complex showed a π-π* transition of the ligand at around 200-300 nm, a charge transfer transition at around 300-400 nm. While these characteristic bands are of monomeric cyclometalated Platinum(II) complex, another absorption band was observed at 1000 nm in [Pt(dpb)(sol)]$^+$OTf$^-$. It can be attributed to be a MMLCT transition originated from the aggregate formation of [Pt(dpb)(sol)]$^+$OTf$^-$.

Keywords : Square-Planar Platinum(II) Complex; Aggregates; Electronic Absorption Spectrum; Emission Spectrum

室温で高効率な発光を示すシクロメタレート型白金(II)錯体は、分子間のスタッキングや白金間相互作用により、励起会合体を形成することが知られている。当研究室では、シクロメタレート型白金(II)錯体において、励起二量体、励起三量体からの発光の観測に成功している[1,2]。本研究では、水溶液において基底会合体を形成するシクロメタレート型白金(II)錯体（[Pt(dpb)(sol)]$^+$OTf$^-$, Figure 1）を新たに発見したため、その分光学的性質を報告する。

Figure 2 に水溶液における[Pt(dpb)(sol)]$^+$OTf$^-$の電子吸収スペクトルを示す。200-300 nm 付近に配位子のπ-π*遷移、300-400 nm 付近に電荷移動遷移が観測された。これらの吸収帯は中性のシクロメタレート型白金(II)錯体と同様であった一方、[Pt(dpb)(sol)]$^+$OTf$^-$では 1000 nm 付近にブロードな吸収帯が観測された。これは、[Pt(dpb)(sol)]$^+$OTf$^-$の会合形成による MMLCT 遷移に由来すると考えられる。

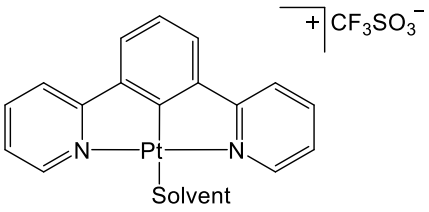


Figure 1 A molecular structure of [[Pt(dpb)(sol)]$^+$OTf$^-$.

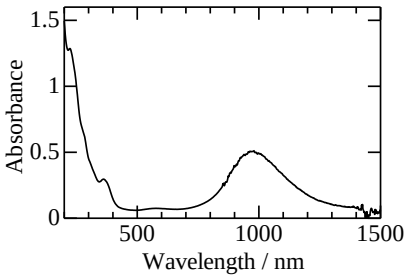


Figure 2 The electronic absorption spectrum of [Pt(dpb)(sol)]$^+$OTf$^-$.

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Synthesis of a chiral-at-Pt(II)-Cu(I) complex with a bisphenanthroline macrocycle

(*Graduate School of Science, The University of Tokyo*) ○Shun Shimizu, Shohei Tashiro, Mitsuhiko Shionoya

Keywords: Macrocycle; Platinum; Copper; Heterodinuclear complex; Chirality

Chiral-at-metal complexes have been extensively studied due to their potential applications for chiroptical materials and enantioselective catalysts. Among them, chiral-at-metals multinuclear complexes are of particular interest due to some synergetic effects between the metal centers, but the examples are still limited especially for heteronuclear metal complexes due to the difficulty in controlling the product selectivity. In this regard, we have developed a novel method for synthesizing chiral-at-bimetals heterodinuclear complexes from bisphenanthroline macrocyclic ligands with two inward coordination sites. The heterodinuclear structure was constructed by first introducing a kinetically-stable cyclometalated Pt(II) center and then coordinating to the Cu(I) ion. Subsequently, ligand exchange with a C_s symmetrical 5-Ph-dpp ligand at the Cu(I) center afforded chiral-at-Pt(II)-Cu(I) heterodinuclear complexes (Figure 1a). Notably, the crystal structure of the [PtCuCl(H$_{-1}$**2**)(5-Ph-dpp)](BF$_4$) complex showed unprecedented diastereoselectivity for $(R)_{Cu}(S)_{Pt}$/$(S)_{Cu}(R)_{Pt}$-isomers with chirality at both metal centers (Figure 1b–d). We also report the effect of the substituent at the 5-position of the dpp ligand on diastereoselectivity based on crystallographic and ^{1}H NMR spectroscopy.

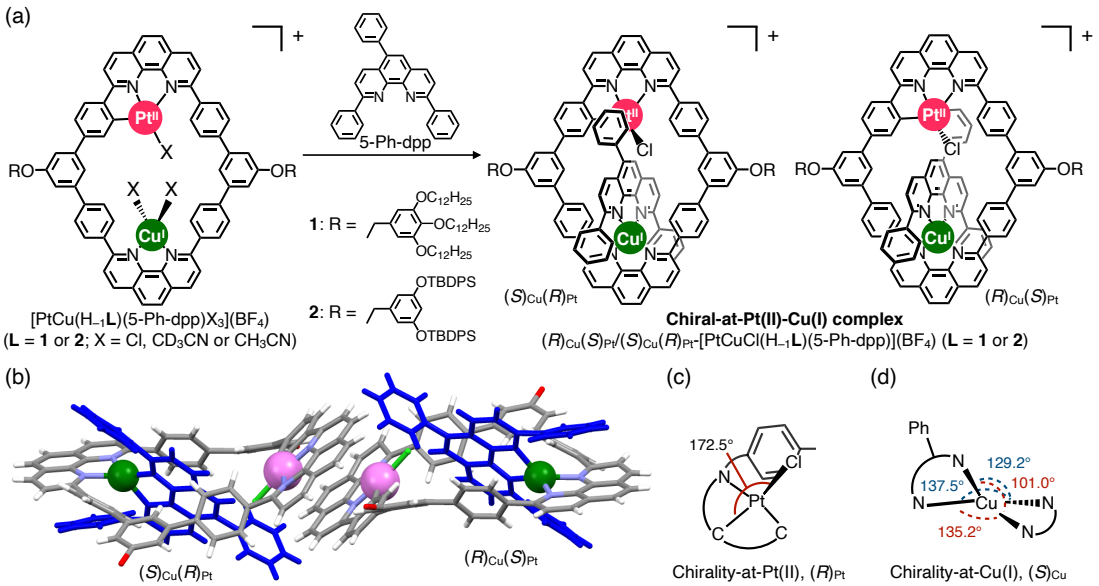

Figure 1. (a) Synthetic scheme for chiral-at-Pt(II)-Cu(I) complexes; (b) crystal structure of $(R)_{Cu}(S)_{Pt}$/$(S)_{Cu}(R)_{Pt}$-[PtCuCl(H$_{-1}$**2**)(5-Ph-dpp)]$^+$ (5-Ph-dpp ligands are highlighted in blue.); (c) schematic representation of the chiral-at-Pt(II) structure; (d) schematic representation of the chiral-at-Cu(I) structure.

トランス架橋白金-異種金属三核錯体を用いた常磁性多核集積体の構造と物性

(岐阜大院工[1]・岐阜大工[2]) ○高森 敦志[1]・植村 一広[2]
Syntheses, Crystal Structures, and Properties of Paramagnetic Multinuclear Assembles with Trans Pt–M–Pt Trinuclear Complexes ([1]*Graduate School of Engineering, Gifu University*, [2] *Faculty of Engineering, Gifu University*) ○Atsushi Takamori,[1] Kazuhiro Uemura[2]

We have synthesized heterometallic one-dimensional chains linked by metal–metal bonds utilized with HOMO-LUMO interaction at dz^2 orbitals between two kinds of metal complexes. Here, we will show novel multinuclear assembles containing Pt–M–Pt trinuclear complexes (M = first transition metal) where each metal is bridged by amidate ligands with trans fashions. The Pt–M–Pt trinuclear complexes, where M have high-spin sates, are dimerized in the crystal, showing magnetic interaction through –Pt---Pt–bonds.
Keywords : Multinuclear Complex; One-dimensional Chain; Hetero-metal; Magnetic Behavior

当研究室では、2 種類の金属錯体間の HOMO-LUMO 相互作用を用いて、複数の金属種からなる異種金属一次元鎖錯体を合成してきた[1)]。例えば、dz^2 軌道に HOMO をもつ *cis*-$[Pt_2M(NH_3)_4(piam)_4]X_n$（M = 第一遷移金属, piam = pivalamidate, X = アニオン）と、LUMO をもつ$[Rh_2(O_2CCH_3)_4]$を混合すると、–Rh–Rh–Pt–M–Pt–と並んだ異種金属一次元鎖錯体が得られる[2,3)]。本研究では、異種金属結合をもつ新しい常磁性集積体構築を目標に、*trans*-$[Pt_2M(NH_3)_4(piam)_4]X_n$ を合成し、諸物性測定をした。

trans-$[Pt(NH_3)_2(piam)_2]$と MCl_2 もしくは $MClO_4$（M = Mn, Fe, Co, Ni, Cu）を混合して、*trans*-$[Pt_2M(NH_3)_4(piam)_4]X_n$ を得た。単結晶 X 線構造解析の結果、piam がトランス架橋し、Pt–M–Pt と並んだ三核錯体であった。金属間距離は、Pt–Mn = 2.68 Å、Pt–Fe = 2.59 Å、Pt–Co = 2.62 Å、Pt–Ni = 2.59 Å、Pt–Cu = 2.66 Å であった。組成から、鉄以外の金属酸化数は+2、鉄は+3 と考えられる。また、鉄以外の三核錯体は、結晶中で Pt–M–Pt---Pt–M–Pt と二量化していた（図 1）。磁化率および ESR 測定から、すべての三核錯体中の第一遷移金属は高スピン状態をとることを確認した。シス架橋との比較と、$[Rh_2(O_2CCH_3)_4]$との多核集積体についても発表する予定である。

1) K. Uemura, Dalton Trans., 2017, 46, 5474–5492. 2) K. Uemura, J. Mol. Str., 2018, 1162, 31–36. 3) K. Uemura, R. Miyake, Inorg. Chem., 2020, 59, 1692–1701.

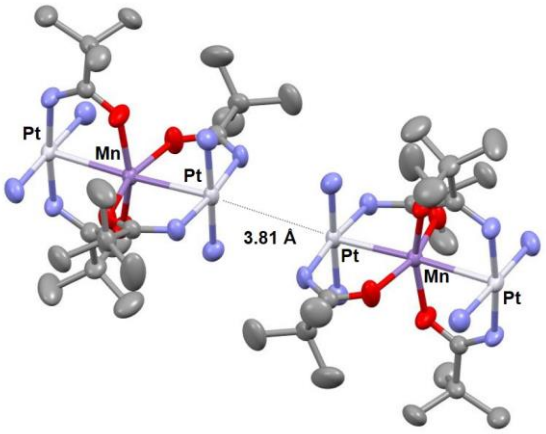

図 1. 二量化した *trans*-$[Pt_2Mn(NH_3)_4(piam)_4]^{2+}$の構造

数原子からなる白金及びその合金サブナノ粒子の合成と触媒特性

(東工大化生研[1]・JST-ERATO[2]) ○赤沼 友貴[1]・今岡 享稔[1,2]・山元 公寿[1,2]

Synthesis and Catalytic Properties of Platinum and Platinum Alloy Sub-nanoparticles with Single-Digit Atomicity

([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology,* [2]*JST-ERATO*) ○Yuki Akanuma,[1] Takane Imaoka,[1,2] Kimihisa Yamamoto[1,2]

Particles with sizes below a few nanometers, which are known as subnano-particles or clusters, can exhibit unique physical and chemical properties that change with atomicity. In this study, a synthetic route to platinum and its alloy cluster was studied by using platinum-thiolate complexes as the precursor, to achieve chemical synthesis of subnano-particles at one atom precision. Pt_n (n = 5-12) supported on carbon were synthesized by using platinum-thiolate complexes, $[Pt(SC_8H_{17})_2]_n$ (n = 5-12), as the precursor. This method was further applied to the synthesis of heterometal doped clusters. The silver ion inclusion complex was applied to the synthesis of silver doped platinum cluster. This synthetic method could open up a new horizon for the study of clusters, enabling a more realistic and practical application in catalysis.

Keywords : Cluster; Platinum; Multinuclear Complex

数個から十数個の金属原子で構成されるクラスターは、バルク結晶やナノ粒子とは異なる物性や触媒機能が期待される。本研究では環状白金チオラート多核錯体を前駆体とした白金及びその合金クラスターの合成と触媒活性評価を行った。

環状白金チオラート多核錯体$[Pt(SC_8H_{17})_2]_n$ (n = 5-12) の合成を行い、サイズ分離カラムクロマトグラフィーにより単離した。単離した白金錯体をカーボン担体に担持、焼成することによって、原子数の制御された白金クラスターPt_n (n = 5–12) を得た。走査透過型電子顕微鏡 (STEM) 観察により、原子数に制御された Pt_n (n = 5–12) のクラスターの生成を確認した。また、環状白金チオラート多核錯体の内部空間を利用した金属包接機能の探索と、包接錯体を前駆体として合金クラスターの合成を行った。白金及び銀白金クラスターの触媒活性および構成原子数依存性について報告する。

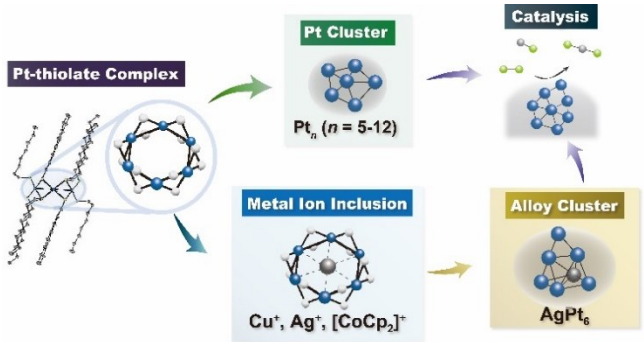

Figure 1. Conversion of platinum-thiolate complexes to platinum and its metal alloy cluster.

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[2] Y. Akanuma, T. Imaoka, H. Sato, K. Yamamoto, *Angew. Chemie Int. Ed.*, 2021, in press.
DOI:https://doi.org/10.1002/anie.202012921

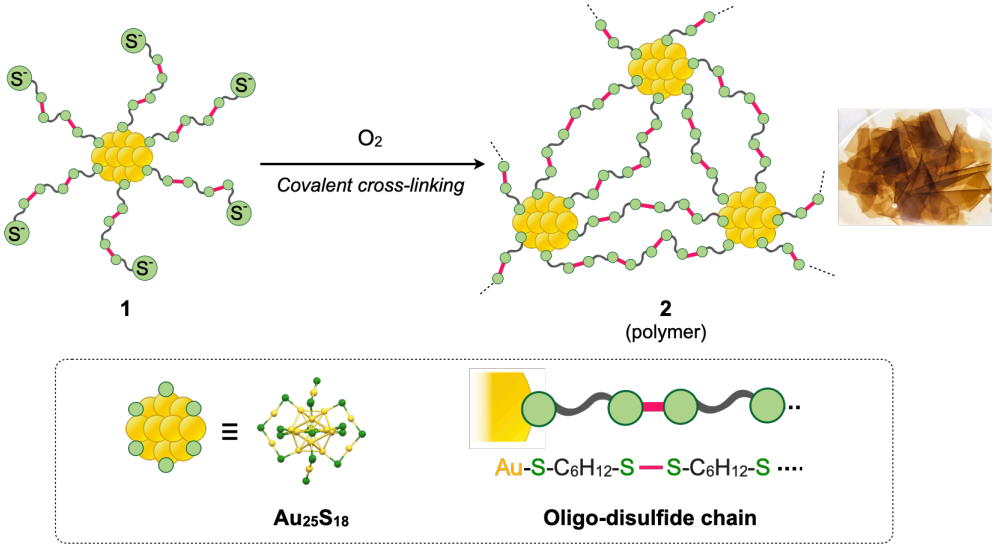
Thin-film formation of thiolate-protected Au_{25} cluster through inter-cluster covalent linking

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Yuki Saito,[1] Yukatsu Shichibu,[1,2] Katsuaki Konishi,[1,2]

Keywords: Gold cluster; Disulfide; Film formation; Singlet oxygen

Ligand protected gold clusters show unique optical and catalytic properties, and thus they have great potentials for solid materials.[1] In such situations, an incorporation of cluster compounds into films is one of the promising strategies for further applications. However, preparation of cluster-based film is limited to dispersion of cluster compounds into polymer matrices, which inhibits the emergence of unique cluster-based properties.[2] In this study, we present a facile synthesis of thiolated-Au_{25} cluster film, in which the clusters are covalently cross-linked with retention of the original Au_{25} framework.

We first synthesized 1,6-hexanedithiolate-protected Au_{25} cluster by a conventional method. After purification, absorption spectrum showed the characteristic pattern of $Au_{25}S_{18}$ framework. In addition, elemental analysis and ^{1}H-NMR measurements revealed that the cluster surface is coated with oligo-disulfide chains derived from 1,6-hexanedithiols, having thiolate anions (S^-) at the terminal of the chains (**1**). The as-synthesized Au_{25} cluster (**1**) is soluble in common organic solvents, however, it turned into insoluble polymer films (**2**) upon the exposure to oxygen in solid state. This film formation is associated with the inter-cluster covalent cross-linking as a result of the oxidation of the terminal thiolates. We also demonstrated that the obtained Au_{25} film can be used as a photosensitizer for singlet oxygen generation and an adsorbent for small organic molecules.



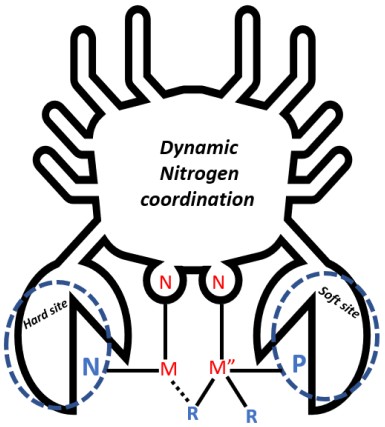
1) R. Jin *et al., Chem. Rev.* **2017**, *117,* 8208. 2) T. Goodson III *et al., ACS Nano* **2016**, *10*, 562.

Heteropolymetallic Pd/Cu and Pt/Cu for metal-metal cooperative bond activation

([1]*Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University;* [2] *Arbuzov Institute of Organic and Physical Chemistry, FCR Kazan Scientific Center, Russian Academy of Sciences)* ○Shubham Deolka,[1], Orestes Rivada-Wheelaghan, Govindarajan Ramadoss, Eugene Khaskin,[1] Robert R. Fayzullin,[2] Julia R. Khusnutdinova*[1].

Keywords: Platinum; Palladium; Copper; Small-molecule activation.

Catalytically active Pd complexes are frequently used in combination with base metal additives in many examples of organometallic catalysis, such as the Wacker process, C-H bond functionalization and C-C coupling reactions. Although the involvement of both metals[1] in key bond activation steps is sometimes proposed, the mechanistic studies of such reactions are challenging due to difficulties in detecting heteromultimetallic reaction intermediates.



In the currently presented work, we recently reported[2] an unsymmetrical ditopic ligand scaffold based on a naphthyridine framework that can selectively incorporate two different metals due to different "soft" and "hard" binding sites on the ligand.
We explored possible bimetallic cooperative effects by inclusion of both Pt and Cu centers inside the ligand framework and tested the resulting complexes in common organometallic reactions. We used these dinucleating unsymmetrical ligand scaffolds for the stepwise formation of heterobimetallic Pt/Cu organometallic complexes with pre-defined, close Pt-Cu distances, leading to unusual cooperative coordination modes of the common alkyl, aryl and acetylide ligands between two metal centers.
Further we extended our strategy for formation of polynuclear Pd/Cu complexes. We developed an unsymmetrical multinucleating ligand based on a naphthyridine framework with a "soft" phosphine terminus, which can bridge up to four metal centers in a linear fashion. Here we demonstrates a stepwise and systematic approach to build tetranuclear and binuclear complexes based on palladium and copper metals center. The nuclearitiy of these complexes is controlled by the nature of the ligands or anions: coordinating anions lead to binuclear Pd/Cu species, while non-coordinating counter anions leads to a tetranuclear compound. We have also found that this ligand can support tetra-palladium chains that can be deprotonated leading to naphthyridine dearomatization.

We have tested the reactivity of these complexes in reactions with alkynes. Interestingly, bimetallic Pd/Cu cooperation is involved in a reaction with a terminal alkyne leading to disassembly of the Pd/Cu chain at the same time, alkyne dimerization catalyzed by these and similar complexes did not require Pd/Cu cooperation. We have also studied the effect of Cu on C-O formation at the aryl palladium center in these heteromultimetallic complexes using common and cheap oxidants.

References:
1. Rudd, P. A.et.al, Angew. Chem., Int. Ed. 2013, 52, 4449−4452.
2. Deolka, S.et.al, Chem. Sci., 2020, 11, 5494-5502.

ピロール骨格 PNP 型ピンサー配位子を有するモリブデン錯体の合成と反応性

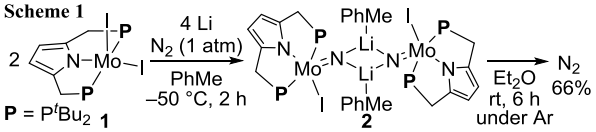
（東大院工）○田辺 資明・関口 義也・栗山 翔吾・西林 仁昭
Preparation and Reactivity of Molybdenum Complexes Bearing Pyrrole-Based PNP-Type Pincer Ligand (*School of Engineering, The University of Tokyo*) ○Yoshiaki Tanabe, Yoshiya Sekiguchi, Shogo Kuriyama, Yoshiaki Nishibayashi

We have recently succeeded in the catalytic transformation of N_2 into NH_3 under ambient conditions by using SmI_2 and H_2O as a reducing reagent and a proton source, respectively, where Mo complexes bearing *N*-heterocyclic carbene-based PCP-type pincer ligands work as best catalysts. On the other hand, a series of transition metal complexes bearing anionic pyrrole-based PNP-type pincer ligands have been shown to work as effective catalysts for the catalytic reduction of N_2 under mild conditions. Here, we have newly prepared a series of Mo analogues, and have revealed that nitrido complexes are obtained by the N≡N triple bond cleavage of N_2, whereas N_2 is regenerated via the coupling of these nitrido complexes. Further investigation on their catalytic activity has demonstrated that these Mo complexes have shown to act as catalysts toward the conversion of N_2 into NH_3 under ambient conditions.
Keywords : Ammonia; Dinitrogen; Nitrogen Fixation; Pincer Ligand; Pyrrolide

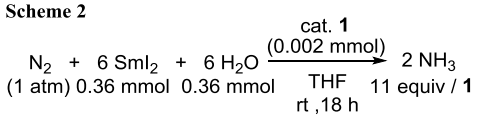
当研究室では、常温常圧で窒素分子をアンモニアへと触媒的に変換反応において、SmI_2 を還元剤として用いることで、水をプロトン源とする触媒反応の開拓に成功している [1]。中でも *N*-ヘテロサイクリックカルベン骨格を基盤とする PCP 型ピンサー配位子を有するモリブデン錯体がもっとも高い触媒活性を示した。一方で当研究室ではアニオン性のピロール骨格を基盤とする PNP 型ピンサー配位子を有する種々の遷移金属錯体を用いることで、温和な条件下で窒素をアンモニアなどに触媒的に変換する反応の開拓にも成功して来た。そこで本研究では対応するモリブデン錯体を合成し、その反応性を検討した [2]。

ピロール骨格 PNP 型ピンサー配位子を有する Mo(III)ジヨード錯体 **1** を新規に合成し、これを窒素下トルエン中リチウムで還元したところ、窒素窒素三重結合の開裂反応が進行し、リチウムイオン架橋二核 Mo(IV)(ヨード)(ニトリド)錯体 **2** が生成した (Scheme 1)。**2** をアルゴン下で撹拌したところ、一度開裂したニトリドからの窒素分子の再生が進行した。続いて得られた錯体を用いて、常温常圧で窒素をアンモニアへと変換する反応を検討したところ、錯体 **1** 当たり 11 当量のアンモニアが生成し (Scheme 2)、ピロール骨格 PNP 型ピンサー配位子を有するモリブデン錯体が窒素固定触媒として働くことを明らかにした。

Scheme 1



Scheme 2



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[A16-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair:Yoichi Hoshimoto, Kohei Takahashi

Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 16 (Online Meeting)

[A16-4am-01] Ni-Catalyzed Aryl Transfer Reaction Between Two Different Aromatic Compounds

○Ryota Isshiki[1], Miki Kurosawa[1], Naomi Inayama[1], Kei Muto[1], Junichiro Yamaguchi[1] （1. Waseda University ）

9:00 AM - 9:20 AM

[A16-4am-02] Solar-Driven Hydrogenation Using Ethanol as Hydrogen Source

○Naoki Ishida[1], Yoshiki Kamae[1], Keigo Ishizu[1], Yuka Kamino[1], Hiroshi Naruse[1], Masahiro Murakami[1] （1. Kyoto University）

9:20 AM - 9:40 AM

[A16-4am-03] Nickel-Catalyzed C-O/N-H, C-S/N-H and C-CN/N-H Annulation of Aromatic Amides with Alkynes

○Yasuaki Iyori[1], Rina Ueno[1], Aoi Morishige[1], Naoto Chatani[1] （1. Faculty of Engineering, Osaka University）

9:40 AM - 10:00 AM

[A16-4am-04] Nickel-Catalyzed Cross-Coupling Reaction of Acyl Fluorides with Terminal alkynes

○Qiang Chen[1], Liyan Fu[1], Jingwen You[1], Yasushi Nishihara[2] （1. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayama Univ.）

10:00 AM - 10:20 AM

[A16-4am-05] Asymmetric Coupling of 1,3-Dienes and C-Nucleophiles by Ni/Cu Cooperative Catalysts Bearing Planer Chiral Diphosphine Ligand

○Takahiro Hirai[1], Jingzhao Xia[1,2], Shoichiro Katayama[1], Haruki Nagae[1], Wanbin Zhang[2], Kazushi Mashima[1] （1. Department of Chemistry, Graduate School of Engineering Science, Osaka University, 2. Shanghai Jiao Tong University）

10:20 AM - 10:40 AM

[A16-4am-06] Synthesis of (hydrosilyl)boranes via Si– H monoborylation of dihydrosilanes

○Takumi Takeuchi[1,2], Ryosuke Shishido[1,2], Koji Kubota[1,2], Hajime Ito[1,2] （1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University）

10:40 AM - 11:00 AM

[A16-4am-07] Mechanism of Asymmetric Coupling of 1,3-Dienes and C-Nucleophiles by Ni/Cu Cooperative Catalysts by DFT Calculations

○Haruki Nagae[1], Jingzhao Xia[1,2], Shoichiro Katayama[1], Takahiro Hirai[1], Wanbin Zhang[2], Kazushi Mashima[1] （1. Osaka University, 2. Shanghai Jiao Tong University）

11:00 AM - 11:20 AM

[A16-4am-08] Catalytic Cycloaddition Reactions between Propargylic Alcohols Derivatives and Hydrazones

○Shiyao Liu[1], Yoshiaki Tanabe[1], Shogo Kuriyama[1], Ken Sakata[2], Yoshiaki Nishibayashi[1] （1. The University of Tokyo, 2. Toho University）

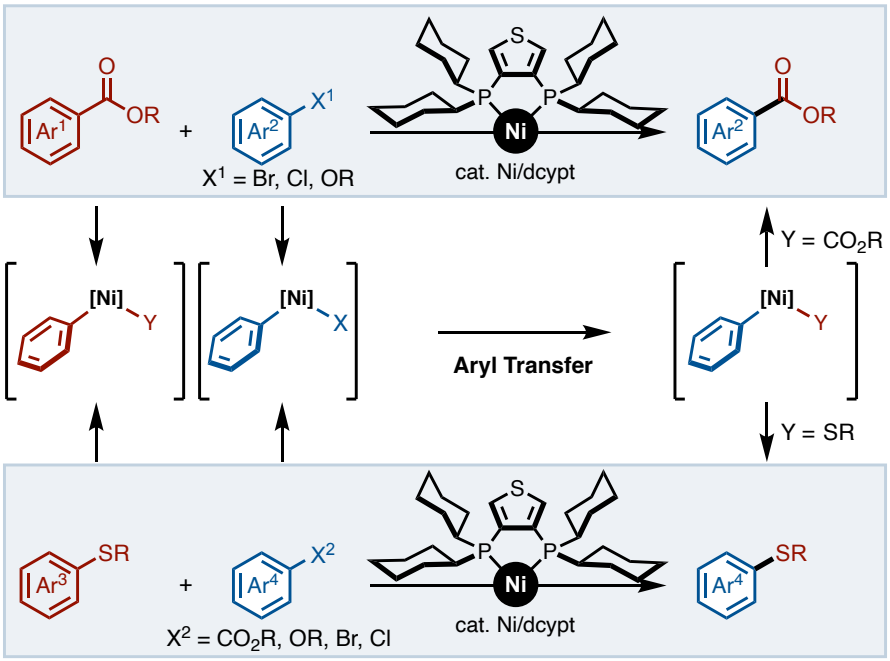
11:20 AM - 11:40 AM

Ni-Catalyzed Aryl Transfer Reaction between Two Different Aromatic Compounds

(*Graduate School of Advanced Science and Engineering, Waseda University*)
○Ryota Isshiki, Miki B. Kurosawa, Naomi Inayama, Kei Muto, Junichiro Yamaguchi
Keywords: Nickel; Aromatic Esters; Haloarenes; Aryl Sulfides; Phenol Derivatives

Development of catalytic functionalization of aromatic compounds is one of the most important topics in organic chemistry. Transition-metal-catalyzed cross-coupling such as Buchwald–Hartwig amination and Ullmann condensation are commonly known as a representative method. In recent years, metal-catalyzed aryl transfer reactions between two different aromatic compounds have been developed as a novel arene functionalization approach.[1] The key of these reactions is the use of catalyst capable to both cleave and form two distinct chemical bonds appropriately.

Herein, we have developed two types of Ni-catalyzed aryl transfer reactions of aromatic compounds. We found that Ni/dcypt catalyst enabled an aryl transfer reaction between aromatic esters (Ar^1–CO_2R) and haloarenes or phenol derivatives (Ar^2–X^1) to afford Ar^2–CO_2R.[2] It was also discovered that a similar reaction takes place between aryl sulfides (Ar^3–SR) and aromatic esters, phenols, or haloarenes (Ar^4–X^2), giving Ar^4–SR. In both cases, the use of our Ni/dcypt catalyst was critically important for the reaction progress.



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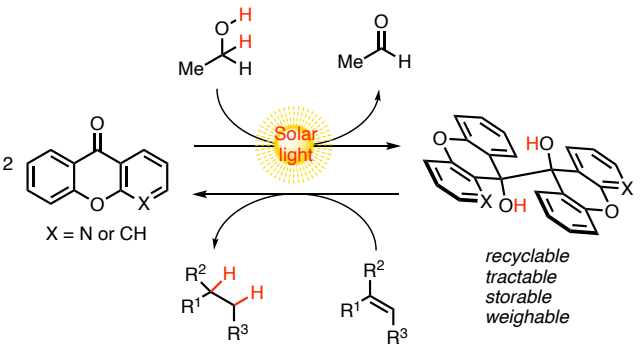
エタノールを水素源とする太陽光エネルギー駆動型水素化反応

（京大院工）○石田直樹・釜江祥希・石津啓伍・上農悠花・成瀬啓司・村上正浩
Solar-Driven Hydrogenation Using Ethanol as Hydrogen Source (*Graduate School of Engineering, Kyoto University*) ○Naoki Ishida, Yoshiki Kamae, Keigo Ishizu, Yuka Kamino, Hiroshi Naruse, Masahiro Murakami

Hydrogenation of unsaturated functionalities is arguably one of the most fundamental transformations in organic synthesis. Typical methods for hydrogenation utilize gaseous hydrogen, most of which is currently supplied from processes reforming fossil resources such as natural gas and oil. However, the ongoing escalation of global concerns about environmental issues strongly demands to replace any fossil resource-based technologies with more sustainable schemes. Thus, it is highly desired to develop a new system for hydrogenation exploiting renewable resources. Ethanol can be produced from bio-based raw materials by fermentation, and has attracted much attention as an alternative and renewable fuel as well as a hydrogen source. We here report a sustainable, safe, and convenient system for hydrogenation using biorenewable ethanol as the source of hydrogen and solar light as the ultimate source of energy. The present system can be applied to asymmetric hydrogenation of a dehydroamino acid derivative.
Keywords : Solar, Hydrogen, Biomass, Ethanol, Hydrogenation

不飽和官能基の水素化反応は有機合成化学における基本的な反応の一つである。通常は水蒸気改質法によって化石資源から合成された水素ガスが用いられているが、持続可能性の観点から、再生可能な原料を用いた手法を開発することが望まれている。本発表では、バイオマス資源から合成されるエタノールを水素供与体として用いる太陽光駆動の簡便な水素化反応について述べる。本手法は二つの段階で構成される。第一段階では、芳香族ケトンのエタノール溶液に太陽光を照射して、立体歪みを有する1,2-ジオールを合成する。エネルギー的にアップヒルな反応であり、太陽光のエネルギーを歪みエネルギーとしてジオールに蓄えている。第二段階では、1,2-ジオールに蓄えられた歪みエネルギーの開放を駆動力として利用して、遷移金属触媒の作用で1,2-ジオールの水素原子をアルケンへ移動させると同時に芳香族ケトンを再生する。再生した芳香族ケトンは回収して、ジオール合成に再利用できる。また、ジオールから水素ガスを発生させることもでき、これをデヒドロアミノ酸の不斉水素化に応用することもできた。

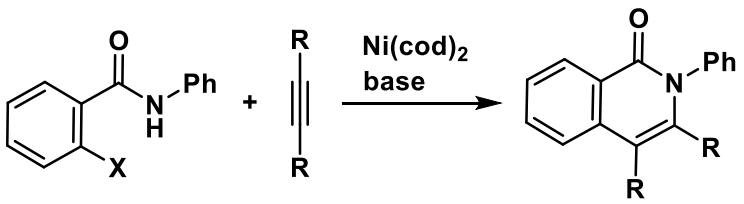


Nickel-Catalyzed C-O/N-H, C-S/N-H and C-CN/N-H Annulation of Aromatic Amides with Alkynes

(*Faculty of Engineering, Osaka University*) ○Yasuaki Iyori, Rina Ueno, Aoi Morishige, Naoto Chatani

Keywords: Nickel Catalyst; Carbon-Oxygen Bond Cleavage; Aromatic Amide; Alkyne; Annulation

C-O bond activation reactions have been widely explored as an efficient tool for the transformation of phenol derivatives which are inexpensive and readily available.[1] The cleavage of the C-O bond required a high reaction temperature and the addition of a strong donor ligand. We recently reported the C-F/N-H annulation of aromatic amides with alkynes in the presence of a nickel catalyst, which gave isoquinolin-1(2*H*)-ones.[2] This reaction proceeded via the cleavage of the C-F bond without a ligand even at low temperature. A key to the success of the reaction is the addition of a base. The base abstracts a N-H proton from the substrate to generate the amide anion, which reacts with nickel to give catalytically active species. We hypothesized that C-O bond activation can be achieved by this methodology. After some examinations, it was found that benzamides bearing an alkoxy group at the *ortho* position reacts with alkynes to give the annulation product via the cleavage of the C-O bond.[3] This reaction proceeded even in the absence of a ligand at low temperature, which tolerates various kinds of functional groups under the reaction conditions. This methodology is also applicable to the activation of other unreactive bonds, such as C-S and C-CN bonds.



(X = OPh, $OCONR_2$, SMe, CN)

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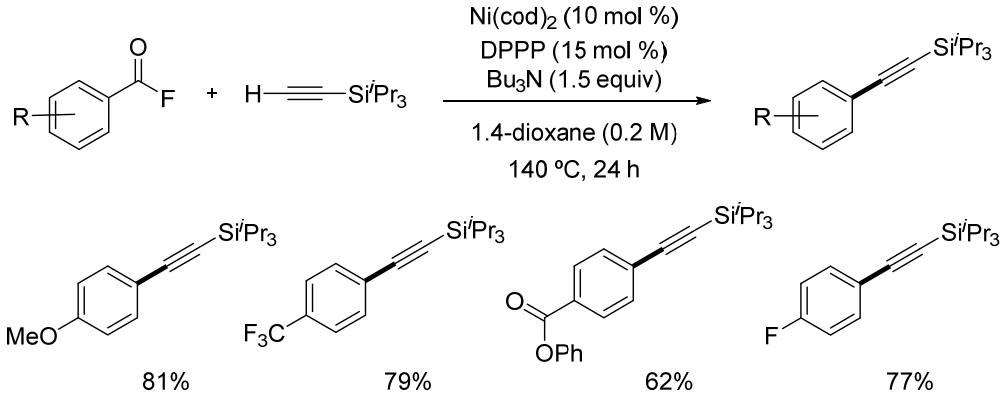
Nickel-Catalyzed Cross-Coupling Reaction of Acyl Fluorides with Terminal Alkynes

([1]*Graduate School of Natural Science and Technology, Okayama University*, [2]*Research Institute for Interdisciplinary Science, Okayama University*)
○Qiang Chen,[1] Liyan Fu,[1] Jingwen You,[1] Yasushi Nishihara[2]
Keywords: Nickel; Alkynylation Reaction; Acyl Fluorides; Decarbonylation

Sonogashira–Hagihara (S–H) reaction[1] is known to be an effective method for the preparation of a variety of conjugated arylethynes and enynes, and a large number of applications of this reaction have been reported. One of the most important purposes regarding this reaction is to replace the common aryl and vinyl (pseudo)halides with naturally abundant coupling partners. Recently, acyl fluorides have attracted much attention due to their ease of preparation, moderate stability and reactivity in cross-coupling reactions.[2] We have successfully developed a Pd/Cu-co-catalyzed decarbonylative sila-S–H reaction of acyl fluorides with silylated internal alkynes through direct C–Si bond activation.[3] With the aim of further expanding the substrate scope, we have developed the nickel-catalyzed decarbonylative alkynylation using terminal alkynes under copper-free conditions.

The reaction of an array of acyl fluorides with ethynyl(triisopropyl)silane under optimized conditions afforded the desired products in 62-81% yields. Further investigation of the substrate scope revealed that various acyl fluorides bearing ether, fluoride, cyano, ketone, and ester functional groups as well as nitrogen, oxygen, and sulfur-containing heterocyclic compounds were applicable to this reaction.



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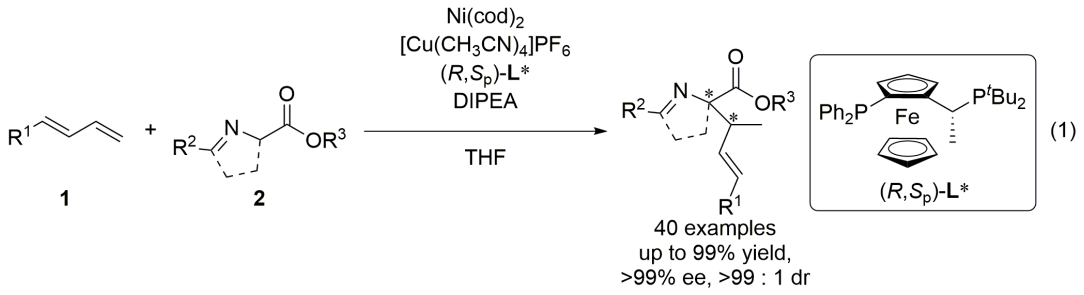
Asymmetric Coupling of 1,3-Dienes and *C*-Nucleophiles by Ni/Cu Cooperative Catalysts Bearing Planer Chiral Diphosphine Ligand

([1]*Graduate School of Engineering Science, Osaka University*, [2]*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University*) ○Takahiro Hirai,[1] Jingzhao Xia,[1,2] Shoichiro Katayama,[1] Haruki Nagae,[1] Wanbin Zhang,[2] Kazushi Mashima[1]

Keywords: Nickel; Copper; π-Allyl Complex; Enolate Complex; Asymmetric Allylic Alkylation

Asymmetric hydrofunctionalization of 1,3-dienes with *C*-nucleophiles is one of atom- and step-economical reactions to construct a chiral quaternal carbon center in high yield and high enantioselectivity. Such the reaction has mainly been demonstrated by using noble Pd and Rh catalysts,[1] and the catalytic system using earth abundant metals such as first-row transition metals is highly demanded.[2] Herein, we report that a combination of two metals, Ni and Cu, in the presence of chiral JOSIPHOS-type diphosphine ligand **L*** became a cooperative catalyst for asymmetric coupling of 1,3-dienes **1** and low-activated *C*-nucleophiles **2** to generate vicinal stereocenters in high yields and high stereoselectivities (eq. 1). We propose a reaction mechanism through two catalytic cycles, *i.e.*, the Ni cycle for activation of diene **1** to form allylic intermediate, and the Cu cycle for deprotonation of *C*-nucleophiles **2** based on controlled experiments and kinetics. In fact, we isolated a cationic Ni(II) π-allyl complex by treating $Ni(cod)_2$ with **L***, diene **1**, and ammonium salt, and a Cu(I) enolate complex by reacting Cu(I) precursor, **L***, and the potassium enolate of **2**. Their solid structures were characterized by spectral data along with X-ray single crystal analyses. Stoichiometric reaction of these isolated Ni and Cu complexes gave the desired coupling product under room temperature, indicating that the both two complexes were key reaction intermediates. In addition, we conducted kinetic studies and control experiments using a deuterated *C*-nucleophile.



1) For reviews, see, Adamson, N. J.; Malcolmson, S. J. *ACS Catal.* **2020**, *10*, 1060. 2) For examples of Ni catalyzed reactions, see, (a) Cheng, L.; Li, M.-M.; Xiao, L.-J.; Xie, J.-H.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2018**, *140*, 11627; (b) Shao, W.; Besnard, C.; Guénée, L.; Mazet, C. *J. Am. Chem. Soc.* **2020**, *142*, 16486.

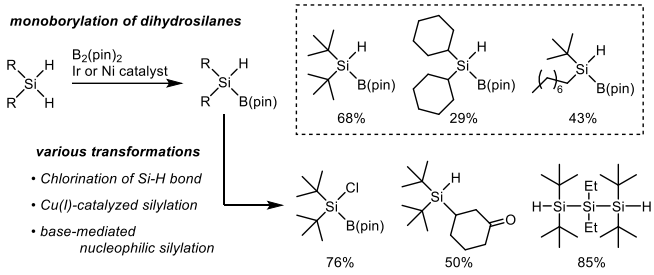
Synthesis of (hydrosilyl)boranes via Si–H monoborylation of dihydrosilanes

([1]*Division of Applied Chemistry, Graduate school of Engineering*, Hokkaido University, [2]*WPI-ICReDD, Hokkaido University*) ○Takumi Takeuchi,[1,2] Ryosuke Shishido,[1,2] Koji Kubota,[1,2] Hajime Ito[1,2]

Keywords: Silylboranes; (Hydrosilyl)borane; Borylation; Iridium; Nickel

Silylboranes can be easily activated by nucleophiles or transition-metal catalysts to construct carbon-silicon and carbon-boron bonds they thus have been used as useful synthetic reagents. The conventional synthetic method for accessing silylboranes involves a stoichiometric reaction between a silyl anion and a boron electrophile. Since silyl anion is produced by the reduction of chlorosilanes with alkali metals, the substituents on silicon atom are largely limited. Therefore, the alternative synthetic method is required. In 2008, the Hartwig group developed the pioneering Si–H borylation reaction catalyzed by an iridium complex[1)]. This could be considered as one of the most direct synthetic method for silylboranes. Recently, we reported rhodium or platinum catalyst can be applied to much broader substrates[2)]. In particular, the functional-group-containing silylboranes can be obtained by platinum-catalyzed borylation. Thus, the discovery of new catalysts for Si–H borylation reactions would allow accessing to novel silylboranes.

During the research of our Si-H borylation reaction, we found that monoborylation of dihydrosilanes catalyzed by a nickel or an iridium complex to afford silylboranes, (hydrosilyl)boranes, bearing a hydrogen atom on silicon atom[3)]. In the case of *t*-Bu_2SiH_2, the corresponding (hydrosilyl)borane was obtained in high yield (68%). Although the steric bulkiness of substituents on silicon atom is essential for the stability of silylboranes, even less bulky (hydrosilyl)boranes are obtained in moderate yield. Additionally, they can be derived into various silicon compounds via subsequent transformations, including a chlorination of Si–H bond, a Cu(I)-catalyzed conjugated silylation, and a base-mediated nucleophilic silylation.



1) Boebel, T. A.; Hartwig, J. F. *Organometallics* **2008**, *27*, 6013–6019.
2) Shishido, R.; Uesugi, M.; Takahashi, R.; Mita, T.; Ishiyama, T.; Kubota, K.; Ito, H. *J. Am. Chem. Soc.* **2020**, *142*, 14125–14133.
3) Takeuchi, T.; Shishido, R.; Kubota, K.; Ito, H. *manuscript in preparation.*

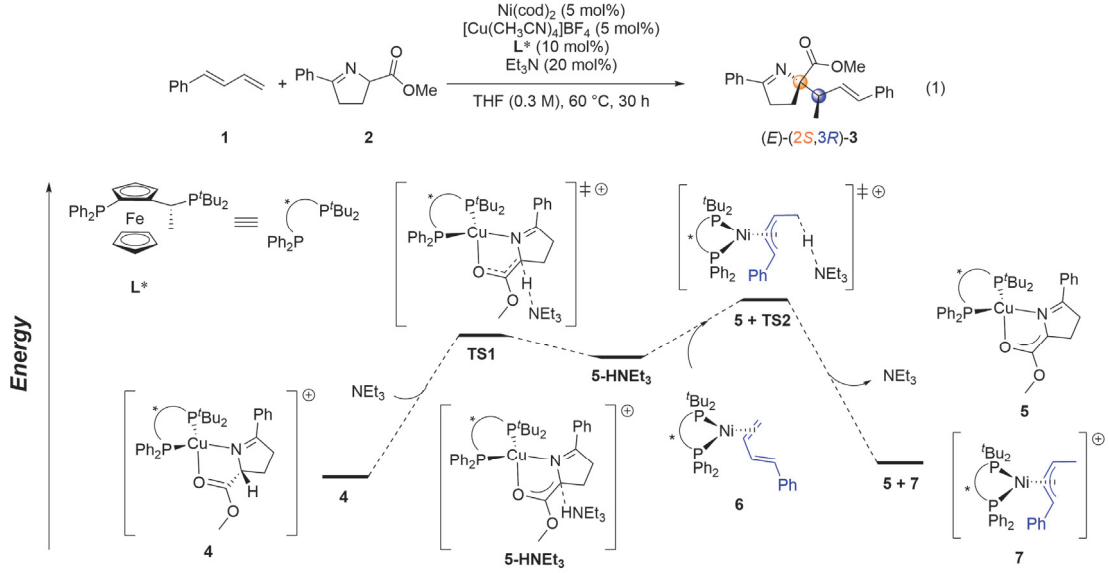
Mechanism of Asymmetric Coupling of 1,3-Dienes and C-Nucleophiles by Ni/Cu Cooperative Catalysts by DFT Calculations

([1]*Graduate School of Engineering Science, Osaka University*, [2]*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University*) ○Haruki Nagae,[1] Jingzhao Xia,[1,2] Shoichiro Katayama,[1] Takahiro Hirai,[1] Wanbin Zhang,[2] Kazushi Mashima[1]

Keywords: Nickel; Copper; π-Allyl Complex; Enolate Complex; Asymmetric Allylic Alkylation

Asymmetric hydrofunctionalization of 1,3-dienes with *C*-nucleophiles has been paid considerable attentions as atom- and step-economical reactions for constructing vicinal two stereocenters in one step.[1] Such the coupling reaction has mainly been demonstrated by novel Pd and Rh catalysts, and the catalytic systems using earth abundant metals such as first-row transition metals suffered from the low diastereoselectivity.[2] We found that the cooperative catalyst system of Ni and Cu with a chiral JOSIPHOS-type bisphosphine ligand **L*** exhibited the high catalytic activity with high enantio- and diastereoselectivity toward the asymmetric coupling of 1,3-diene **1** and *C*-nucleophile **2** to give the corresponding product (2*S*,3*R*)-**3** (eq. 1). Herein, we report the details of the reaction mechanism for the asymmetric coupling based on the experimental results and the DFT calculations.

The first step of the asymmetric coupling is deprotonation of Cu complex **4** by Et_3N to give an intermediate **5-HNEt$_3$** *via* a transition state **TS1**. The ammonium cation is transferred to Ni complex **6**, and complex **6** is protonated *via* **TS2** to afford the key intermediates, Cu enolate complex **5** and π-allyl Ni complex **7**. The highest activation barrier of the proton transfer step in this reaction pathway suggested that the proton transfer step is the rate determining step. Next, α-carbon of enolate moiety of **5** attacks to the 3-position of π-allyl moiety of **7** to yield the corresponding product (2*S*,3*R*)-**3** with vicinal two stereocenters. In addition, we discuss how the Ni/Cu catalyst system controls the stereoselectivity of this asymmetric coupling reaction.



1) Adamson, N. J.; Malcolmson, S. J. *ACS Catal.* **2020**, *10*, 1060. 2) (a) Cheng, L.; Li, M.-M.; Xiao, L.-J.; Xie, J.-H.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2018**, *140*, 11627; (b) Shao, W.; Besnard, C.; Guénée, L.; Mazet, C. *J. Am. Chem. Soc.* **2020**, *142*, 16486.

Catalytic Cycloaddition Reactions between Propargylic Alcohols Derivatives and Hydrazones

([1]*School of Engineering, The University of Tokyo*, [2]*Faculty of Pharmaceutical Sciences, Toho University*) ○ Shiyao Liu,[1] Yoshiaki Tanabe,[1] Shogo Kuriyama,[1] Ken Sakata,[2] Yoshiaki Nishibayashi[1]

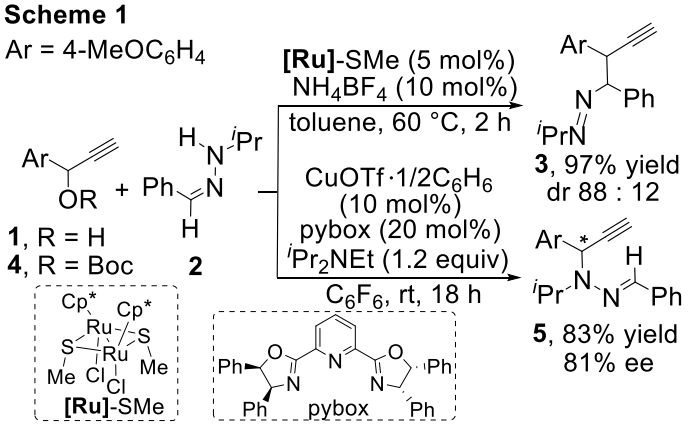
Keywords: Cycloaddition reaction; Propargylic alcohol derivatives; Hydrazones; Ruthenium complexes; Copper complexes

Transition metal-catalyzed propargylic substitution reactions of propargylic alcohol derivatives with nucleophiles have been attracting much attention as synthetic tools for the carbon–carbon and carbon–heteroatom formation in organic synthesis.[1] On the other hand, hydrazones are known to serve not only as nitrogen-centered nucleophiles but also as carbon-centered nucleophiles, leading to multiple applications in organic synthesis in recent years.[2] As an extensive study, we have focused on the use of hydrazones as nucleophiles for the transition metal-catalyzed propargylic substitution reactions of propargylic alcohol derivatives, and further examined their application to cycloaddition reactions.

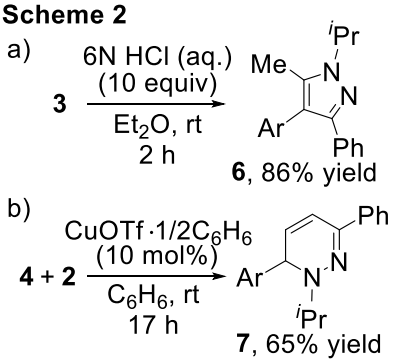
The reaction of a propargylic alcohol (**1**) with a hydrazone (**2**) in the presence of 5 mol% of thiolate-bridged diruthenium complex **[Ru]**-SMe and 10 mol% of NH_4BF_4 in toluene at 60 °C for 2 h gave the corresponding *C*-propargylic substituted product (**3**) in 97% yield, whereas the reaction of a propargylic ester (**4**) with **2** in the presence of 10 mol% of CuOTf·1/2C_6H_6 and 20 mol% of a chiral pybox in hexafluorobenzene at room temperature for 18 h gave the corresponding *N*-propargylic substituted product (**5**) in 83% yield with 81% ee (Scheme 1).

Further treatment of **3** with 10 equiv of HCl in ether at room temperature for 2 h brought about the intramolecular cycloaddition to afford a 5-methyl-1*H*-pyrazole derivative (**6**) in 86% yield (Scheme 2a). In contrast, the reaction of **4** with **2** in the presence of 10 mol% of CuOTf·1/2C_6H_6 in benzene at room temperature for 17 h gave a 1,6-dihydropyridazine derivative (**7**) in 65% yield (Scheme 2b). The difference in the reactivity of hydrazone toward the ruthenium- and copper-catalyzed reaction systems was also investigated in details.

Scheme 1



Scheme 2



1) K. Sakata, Y. Nishibayashi, *Catal. Sci. Technol*. **2018**, *8*, 12. 2) M. G. Retamosa, E. Matador, D. Monge, J. M. Lassaletta, R. Fernández, *Chem. Eur. J.* **2016**, *22*, 13430.

[A15-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair:Yoshihiro Nishimoto, Sobi Asako

Mon. Mar 22, 2021 9:00 AM - 11:20 AM Room 15 (Online Meeting)

[A15-4am-01] Synthesis of Alkynylsilanes by Catalytic Decarboxylation of Silyl Alkynoates

○Takahiro Kawatsu[1], Keiya Aoyagi[1], Sho Kataoka[2], Yumiko Nakajima[1], Norihisa Fukaya[1], Jun-Chul Choi[1], Kazuhiko Sato[1], Kazuhiro Matsumoto[1] （1. AIST, IRC3, 2. AIST, CPT）

9:00 AM - 9:20 AM

[A15-4am-02] Development of Silylsilanolates as New Silylating Reagents

○Hiroki Yamagishi[1], Jun Shimokawa[1], Hideki Yorimitsu[1] （1. Kyoto University）

9:20 AM - 9:40 AM

[A15-4am-03] Development of 7-Membered Dialkoxysilyl Group and Its Application to Organic Synthesis

○Hayate Saito[1], Jun Shimokawa[1], Hideki Yorimitsu[1] （1. Kyoto Univ.）

9:40 AM - 10:00 AM

[A15-4am-04] Borylation Reactions with Novel Borylstannanes via Radical Mechanism

○Kensuke Suzuki[1], Yoshihiro Nishimoto[1], Makoto Yasuda[1] （1. Osaka University）

10:00 AM - 10:20 AM

[A15-4am-05] Solvent-less mechanochemical synthesis of magnesium-based carbon nucleophiles and their application to organic synthesis

○Rina Takahashi[1], Anqi Hu[2], Yadong Pang[2], Tamae Seo[1], Koji Kubota[1,2], Hajime Ito[1,2] （1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University）

10:20 AM - 10:40 AM

[A15-4am-06] Organic Synthesis Using Sodium Dispersion

○Ikko Takahashi[1], Hirotaka Nakajima[2], Laurean Ilies[1], Yoshiaki Murakami[3], Sobi Asako[1,2], Kazuhiko Takai[2] （1. RIKEN Center for Sustainable Resource Science, 2. Graduate School of Natural Science and Technology, Okayama University, 3. KOBELCO ECO-Solutions Co., Ltd.）

10:40 AM - 11:00 AM

[A15-4am-07] Sodium-Metal-Promoted 1,2-Dimagnesiation and 1,2-Dialumination of Alkynes

○Fumiya Takahashi[1], Hideki Yorimitsu[1] （1. Kyoto University）

11:00 AM - 11:20 AM

日本化学会 第101春季年会 (2021)

シリルアルキノエートの触媒的脱炭酸を用いたアルキニルシランの合成

（産総研）○河津 貴大・青柳 圭哉・片岡 祥・中島 裕美子・深谷 訓久・崔 準哲・佐藤 一彦・松本 和弘

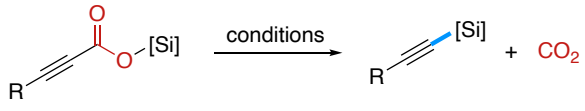
Synthesis of Alkynylsilanes Using Catalytic Decarboxylation of Silyl Alkynoates (*National Institute of Advanced Industrial Science and Technology*) ○Takahiro Kawatsu, Keiya Aoyagi, Sho Kataoka, Yumiko Nakajima, Norihisa Fukaya, Jun-Chul Choi, Kazuhiko Sato, Kazuhiro Matsumoto

Alkynylsilanes are important building blocks in organic synthesis. Generally, they are synthesized by nucleophilic substitution or cross-coupling reactions using terminal alkynes and silicon electrophiles. In this study, we developed two catalytic systems, CuCl/PCy_3 and TBAT, for decarboxylation of silyl alkynoates to alkynylsilanes.

Keywords : Synthetic Chemistry; Organosilicon Compounds; Catalytic Reactions; Decarboxylation; Alkynylsilanes

アルキニルシランは有機合成において重要なビルディングブロックである。一般的に、アルキニルシランは末端アルキンとシリル化剤を用いた求核置換反応もしくはクロスカップリング反応により合成されるが、アルキニルシラン合成の別のアプローチとしてシリルアルキノエートの脱炭酸がある。脱炭酸は副生成物が二酸化炭素のみであるため、上述した手法と比べてシリル化剤由来の廃棄物がでないなどの利点があるが、これまでに開発された手法では適用可能なシリルアルキノエートは極めて限られている [1]。そこで本研究では、シリルアルキノエートの触媒的脱炭酸を用いたアルキニルシランの合成について、一般的な基質に適用できる手法の開発を行った。

その結果、触媒量の CuCl と PCy_3 の存在下、シリルアルキノエートの脱炭酸が円滑に進行することを見出し、対応するアルキニルシランを良好な収率で得ることに成功した (condition A) [2]。一方、この条件ではトリイソプロピルシリル基のようにケイ素原子上の置換基がかさ高い場合には収率が大きく低下したが、テトラブチルアンモニウムジフルオロトリフェニルシリケート (TBAT)を触媒に用いたところ、かさ高い基質でも収率良く脱炭酸が進行することも見出した (condition B)。



condition A
CuCl (0.5 mol%), PCy_3 (1.0 mol%) in DMF, 80 ˚C

condition B
TBAT (5.0 mol%) in DMF, 150 ˚C

1) G. Simchen, H. H. Hergott, *Chimia*, **1985**, *39*, 53.
2) T. Kawatsu, K. Aoyagi, Y. Nakajima, J.-C. Choi, K. Sato, K. Matsumoto, *Organometallics*, **2020**, *39*, 2947.

謝辞：この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構（ＮＥＤＯ）の委託業務の結果得られたものです。

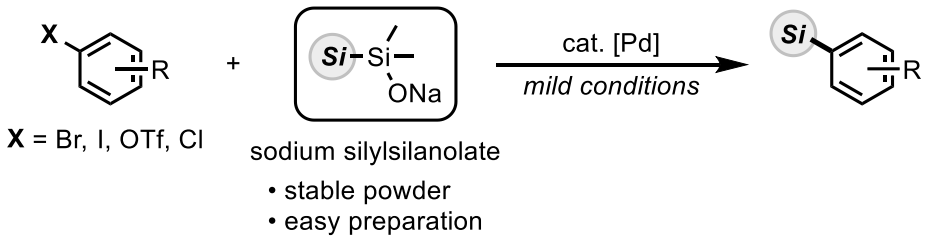
Development of Silylsilanolates as New Silylating Reagents

(*Graduate School of Science, Kyoto University*) ○Hiroki Yamagishi, Jun Shimokawa, Hideki Yorimitsu

Keywords: *Silylsilanolate; Silylation; Silylpalladium*

Arylsilanes are gathering significant attention in the areas of material, agrochemical, and pharmaceutical sciences. One of the most reliable methods for the synthesis of arylsilanes is the alkali metal-halogen exchange of aryl halides followed by trapping with silicon electrophiles. This method suffers from low functional group tolerance because of the high reactivity of arylmetal intermediates. Thus, the silylation of aryl halides using transition metal catalysts and silylating reagents has been employed in recent years. Although these transition metal-catalyzed silylation reactions proceed under relatively mild conditions, conventional silylating reagents leave much room for improvement in terms of stability, reactivity for transmetalation, and handling.

We have developed silylsilanolates as new silylating reagents. Most of these reagents are stable solids with easy preparation and handling. Application of silylsilanolates to palladium-catalyzed silylation of aryl halides afforded silylated products under very mild conditions. A variety of silylsilanotes could be prepared, which enabled the introduction of various silyl groups. This silylation reaction could be applied to a broad scope of aryl iodide, bromide, chloride, and pseudohalides such as triflate. Silylation is amenable to even complex molecules which were previously considered difficult to silylate. Our ^{31}P and ^{19}F NMR experiments disclosed that the Pd(II) complex bearing silylsilanolate substituent is the key precursor of the silylpalladium intermediate. The reaction mechanism of this palladium-catalyzed silylation was also studied by using DFT calculation to reveal how the silyl groups on silylsilanolates migrate to the palladium atom.



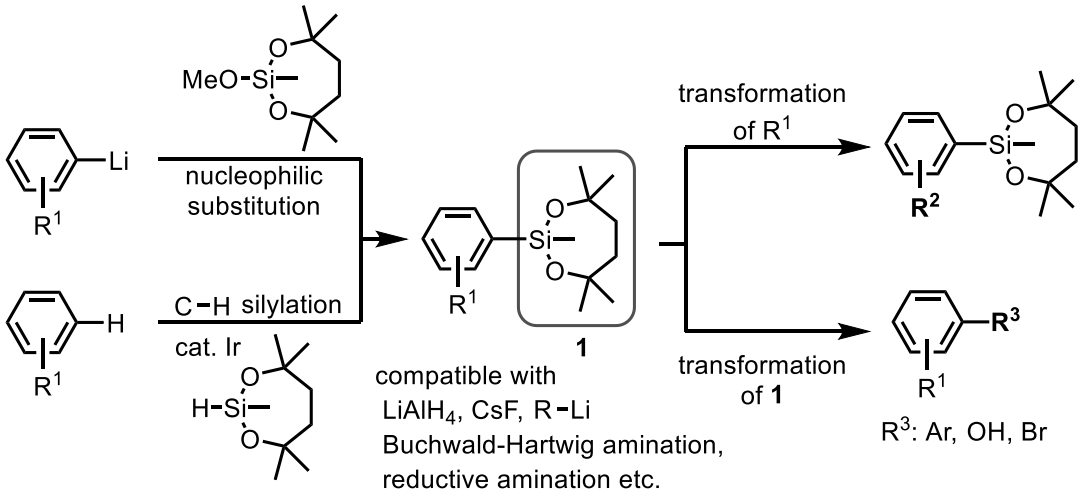
Development of 7-Membered Dialkoxysilyl Group and Its Application to Organic Synthesis

(*Graduate School of Science, Kyoto University*) ○Hayate Saito, Jun Shimokawa, Hideki Yorimitsu

Keywords: Organosilicon; Silyl Group; Steric Protection; Cyclic Structure

Even modestly reactive organometallic compounds such as organoboronate esters and alkoxysilanes are often difficult to purify and to selectively modify at another functional group in the compounds while maintaining the organometallic moieties. For example, $ArSi(OMe)_3$ has good reactivity for cross-coupling reactions whereas it easily undergoes hydrolysis of the Si–OMe moieties and does not survive under various reaction conditions. Thus, a stable organometallic moiety that can be reliably activated under specific conditions would be highly desirable as a powerful tool for organic synthesis.

In an attempt to develop a new alkoxysilyl group that is orthogonal to various functional group transformations, a 7-membered dialkoxysilyl group **1** was found to be compatible with strong nucleophiles such as CsF, organolithiums, and even $LiAlH_4$.[1] Computational studies revealed that the 7-membered structure is highly stabilized not only kinetically but also thermodynamically. While **1** showed the excellent stability, the C–Si bond in arylsilanes bearing **1** could be transformed with the aid of an appropriate activator. In addition, **1** was easily introduced onto arenes with retaining various functional groups by iridium-catalyzed C–H silylation with the corresponding hydrosilane. Nucleophilic substitution of the corresponding methoxysilane with aryllithiums also afforded a series of arylsilanes. To prove the advantages of silyl group **1** in organic synthesis, we conducted a shorter synthesis of a bioactive molecule employing iterative halogen-lithium exchanges, which other conventional alkoxysilyl groups cannot endure.



1) H. Saito, J. Shimokawa, H. Yorimitsu, *submitted*.

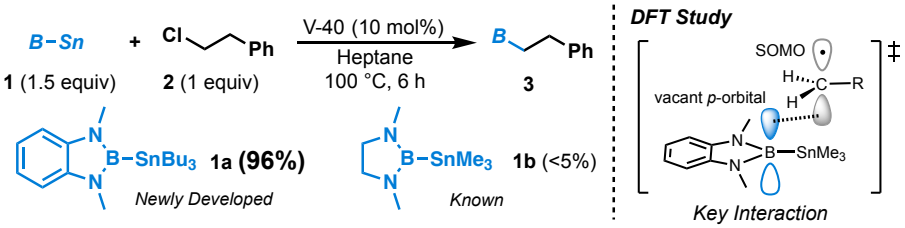
Borylations with Novel Borylstannanes via Radical Mechanism

(Graduate School of Engineering, Osaka University) ○ Kensuke Suzuki, Yoshihiro Nishimoto, Makoto Yasuda

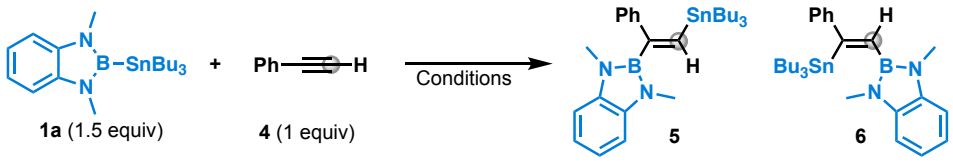
Keywords: Radical Reactions; Borylstannane; Tin; Borylation

Organoboron compounds represent valuable synthetic intermediates in organic synthesis. Recently, radical approach for preparing organoboron compounds has been merging because of the functional group tolerance.[1] Diborons are mainly used for radical acceptors forming the borylated products. However, applicable substrates are limited because of the inefficiency of radical chain reactions by boryl radical. Therefore, the development of new efficient borylation reagents is necessary. Herein, novel type of borylstannanes were newly invented and applied to radical borylations.

In the reaction of borylstannane **1** with 1-chloro-2-phenylethane **2** in the presence of V-40 as a radical initiator, borylstannane **1a** was found to be a significantly effective reagent, which afforded the borylated compound **3**.[2] The known borylstannane **1b**[3] did not work for the acceptor of the alkyl radical intermediate. DFT calculation disclosed that the phenylenediamino structure plays a crucial role in accepting the radical because benzo-fusion lowers its LUMO level including the vacant *p*-orbital on the boron atom to enhance the ability to accept alkyl radicals.



Moreover, borylstannane **1a** was employed for borylstannation of alkynes under radical mechanism. The reaction of borylstannane **1a** with phenylacetylene **4** in the presence of AIBN gave the addition product **5** exclusively. While the conventional method using a palladium catalyst gave the product **6**,[3] our radical system showed the different regioselectivity and stereoselectivity.



This Work	AIBN (5 mol%), 60 °C	**96%**	0%
(ref. 2)	$Pd(PPh_3)_4$ (1 mol%), RT	0%	48%

1) A. Studer, *Chem. Sci.* **2019**, *10*, 8503. 2) K. Suzuki, Y. Nishimoto, M. Yasuda, *Chem. Eur. J.* doi.org/10.1002/chem.202004692. 3) M. Tanaka, *Organometallics* **1996**, *15*, 5450.

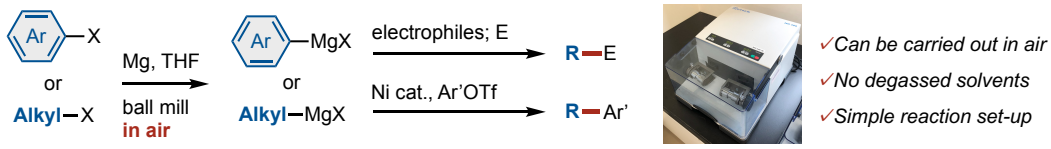
Solvent-less mechanochemical synthesis of magnesium-based carbon nucleophiles and their application to organic synthesis

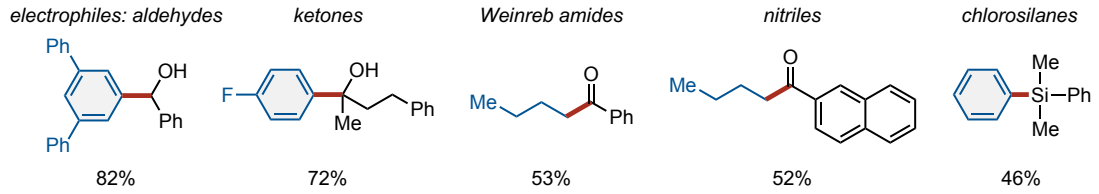
([1]*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*) ○Rina Takahashi,[1] Anqi Hu,[2] Yadong Pang,[2] Tamae Seo,[1] Koji Kubota[1,2], Hajime Ito[1,2]

Keywords: Grignard Reagents; Carbon Nucleophiles; Nucleophilic Additions; Mechanochemistry; Ball Milling

Grignard reagents are magnesium-based carbon nucleophiles that have been used in organic synthesis since their discovery in 1900.[1] One of the preferred methods for the preparation of Grignard reagents is direct insertion of magnesium into organic halides.[2] However, several drawbacks limit the practical application. Large amounts of dry organic solvents and Schlenk-line techniques are needed for preparation of the Grignard reagents because these reagents are often air- and moisture-sensitive. In addition, magnesium metal surface may be covered with an unreactive oxide layer, which sometimes requires a pre-activation process. These requirements are major drawbacks from both an environmental and a cost perspective.

Herein we report a novel method for the synthesis of magnesium-based carbon nucleophiles in air under solvent-less mechanochemical conditions using ball milling machine.[3] This protocol is simple and cost-effective, which does not require synthetic techniques and any special precautions. The key to the success of the developed protocol is the addition of stoichiometric amounts of liquid ethers. We demonstrated that the carbon nucleophiles so formed can be used for direct one-pot nucleophilic addition to various organic electrophiles, nickel-catalyzed Kumada-Tamao-Corriu cross-coupling reactions, and metal-mediated selective addition to conjugated enones under mechanochemical conditions.





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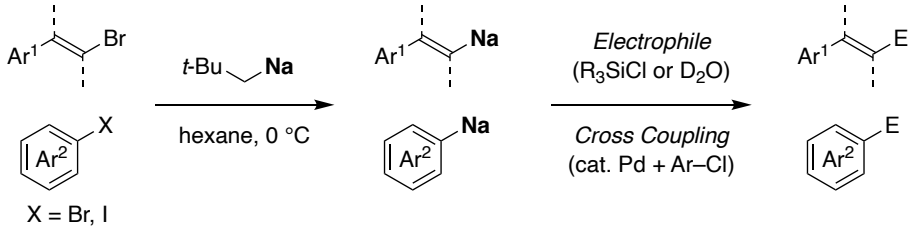
Organic Synthesis Using Sodium Dispersion

([1]*RIKEN Center for Sustainable Resource Science*, [2]*Graduate School of Natural Science and Technology, Okayama University*, [3]*KOBELCO ECO-Solutions Co., Ltd.*) ○Ikko Takahashi,[1] Hirotaka Nakajima,[2] Laurean Ilies,[1] Yoshiaki Murakami,[3] Sobi Asako,[1,2] Kazuhiko Takai[2]

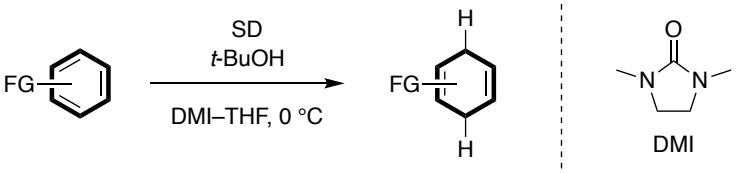
Keywords: sodium; dispersion; organosodium; halogen–sodium exchange; Birch reduction

During the last century, organolithium chemistry has played a dominant role in organic synthesis, both for laboratory and industry. However, lithium is an unevenly distributed resource that is gradually depleting and its cost is increasing. With the aim of finding sustainable alternatives to lithium, we have been reexploring organosodium chemistry using sodium dispersion (SD),[1,2] and we report herein the development of halogen–sodium exchange[3] and ammonia-free Birch reduction.

Scheme 1. Halogen–Sodium Exchange with Neopentylsodium[3]



Scheme 2. Birch Reduction using DMI solvent



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2) Asako, S.; Kodera, M.; Nakajima, H.; Takai, K. *Adv. Synth. Catal.* **2019**, *361*, 3120.

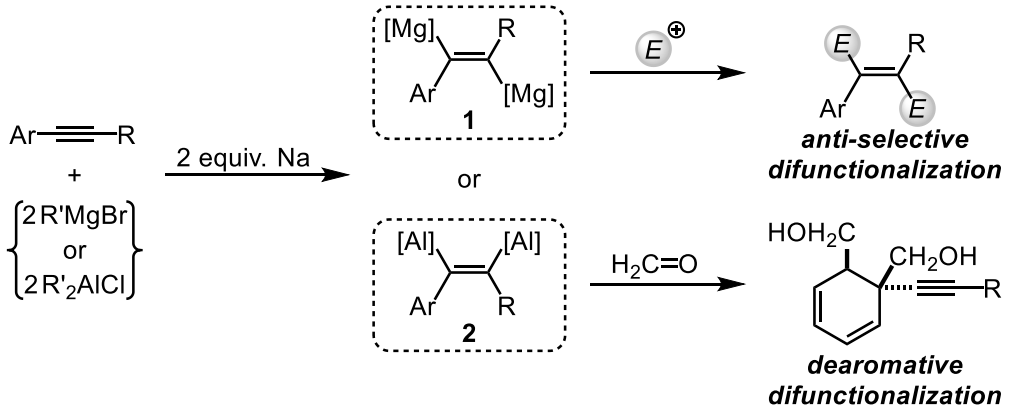
3) Asako, S.; Takahashi, I.; Nakajima, H.; Ilies, L.; Takai, K. *ChemRxiv* **2020**, 10.26434/chemrxiv.12378104.v1

Sodium-Metal-Promoted 1,2-Dimagnesiation and 1,2-Dialumination of Alkynes

(*Graduate School of Science, Kyoto University*) ○Fumiya Takahashi, Hideki Yorimitsu
Keywords: Sodium Metal; Alkyne; 1,2-Dimagnesiation; 1,2-Dialumination; Dearomatization

Recently, we have been interested in the development of sodium-metal-promoted functionalizations of unsaturated hydrocarbons.[1] For example, the 1,2-*syn*-diboration of arylacetylenes proceeds with the aid of sodium metal and trimethoxyborane.[1c] The key to the success of these reactions is the use of reduction-resistant electrophiles such as trimethoxyborane. In this context, we envisioned that organomagnesium or organoaluminium compounds would also be suitable electrophiles and that the resulting 1,2-dimetalloethenes would show unique reactivities. Here, we report that arylacetylenes undergo the sodium-metal-promoted 1,2-dimetallation to give the corresponding 1,2-dimagnesioethenes **1** or 1,2-dialuminoethenes **2**.

In the presence of 2 equivalents of alkylmagnesium bromide, arylacetylenes reacted with 2 equivalents of sodium metal to afford **1**. The subsequent one-pot addition of electrophiles gave 1,2-*anti*-difunctionalized ethene derivatives with high stereoselectivity. When dialkylaluminium chlorides were used instead of alkylmagnesium bromides, the subsequent one-pot addition of paraformaldehyde to the resulting 1,2-dialumino-1-arylethenes **2** induced an unexpected dearomatization of the aryl moiety to provide the corresponding dearomatized 1,4-diols. The mechanism of the dearomatization was investigated by means of DFT calculation.



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

[A17-4pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair:Soji Shimizu, Yohei Haketa

Mon. Mar 22, 2021 1:00 PM - 3:20 PM Room 17 (Online Meeting)

[A17-4pm-01] Metalation-Induced Formation of Novel Fused Porphyrinoid Dimers from Tetrabromo-[36]octaphyrin *via* Transannular Bond Formation

○Akito Nakai[1], Takayuki Tanaka[1], Atsuhiro Osuka[1,2] (1. Kyoto University, 2. Ritsumeikan University)

1:00 PM - 1:20 PM

[A17-4pm-02] Modulation of Physicochemical Properties for Thiophene-fused Naphthodiphospholes by Precise Fusion of Heterole Rings

○Keiichi Ishida[1], Tomohiro Higashino[1], Hiroshi Imahori[1,2] (1. Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ.)

1:20 PM - 1:40 PM

[A17-4pm-03] Synthesis of novel peripherally fused corannulenes based on quintuple amination reactions and their structural and electronic perturbations

○Koki Kise[1], Shota Ooi[1], Takayuki Tanaka[1], Atsuhiro Osuka[1] (1. Kyoto University)

1:40 PM - 2:00 PM

[A17-4pm-04] Synthesis of Covalently Linked Norcorrole Dimers and Their Association Behavior

○Siyu Liu[1], Norihito Fukui[1], Hiroshi Shinokubo[1] (1. Nagoya Univ.)

2:00 PM - 2:20 PM

[A17-4pm-05] Synthesis of xanthene derivative exhibiting twisted intramolecular charge transfer emission

○Taro Koide[1], Shohei Iwamori[1], Satoshi Koga[2], Yasutaka Suzuki[2], Jun Kawamata[2], Yoshio Hisaeda[1] (1. Kyushu University, 2. Yamaguchi University)

2:20 PM - 2:40 PM

[A17-4pm-06] Synthesis and Properties of Pyrrole-Bridged Quinones

○Shinya Sugiura[1], Hiromitsu MAEDA[1] (1. Ritsumeikan Univ.)

2:40 PM - 3:00 PM

[A17-4pm-07] Borole-Embedded Polycyclic π-Electron Systems and Photoresponsive Behavior of their B– P Lewis Adducts

○Naoki Ando[1], Takuya Yamada[1], Hiroki Narita[1], Niels Oehlmann[2], Matthias Wagner[2], Shigehiro Yamaguchi[1,3] (1. Grad. Sch. Sci., Nagoya Univ. , 2. Goethe-Universität Frankfurt, 3. ITbM, Nagoya Univ.)

3:00 PM - 3:20 PM

Metalation-induced formation of novel fused porphyrinoid dimers from tetrabromo-[36]octaphyrin *via* transannular bond formation

([1]*Graduate School of Science, Kyoto University*, [2]*Research Organization of Science and Technology, Ritsumiekan University*) ○Akito Nakai,[1] Takayuki Tanaka,[1] Atsuhiro Osuka,[1,2]
Keywords: global aromaticity; N-confused porphyrin; octaphyrin; porphyrin(2.1.1.1); transannular reaction

Porphyrin tapes have been targets of extensive studies because of their remarkably red-shifted absorptions, multi-charge responsibility, and electric conductivity.[1] A variety of porphyrin tape variants have also been created to display perturbed photophysical properties being characteristic of constituent porphyrin(oid) units. Such tape-like porphyrinoid arrays are synthesized mostly by oxidative fusion of the corresponding singly-linked precursors.

Here we found that tetrabromo-[36]octaphyrin was transformed to novel fused porphyrin dimers such as porphyrin(2.1.1.1) dimer **2** and N-confused porphyrin dimer **3** through metalation-induced transannular C–C bond formation. Tetrabromo-[36]octaphyrin **1** was synthesized as a novel *meso*-free type octaphyrin. Zn^{II} complexation of **1** afforded bis-Zn(II) complex **2** through C_{meso}–C_{meso} bond formation. The complex **2** exhibits a diatropic ring-current effect due to its 36π Möbius aromaticity.[2] On the other hand, Ni^{II} complexation of **1** caused C_{meso}–C_{β} bond formation with concomitant debrominations. Bis-Ni^{II} complex **3** shows a paratropic ring-current effect due to its global 36π antiaromaticity.

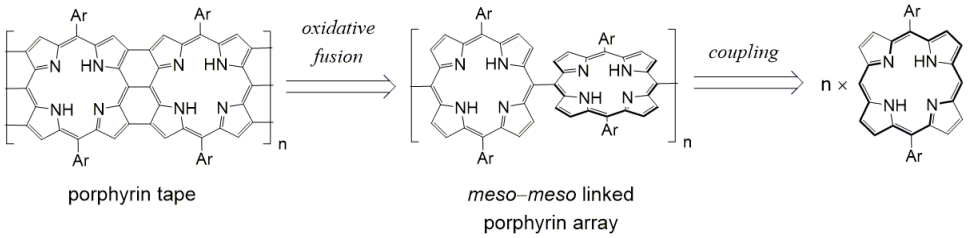
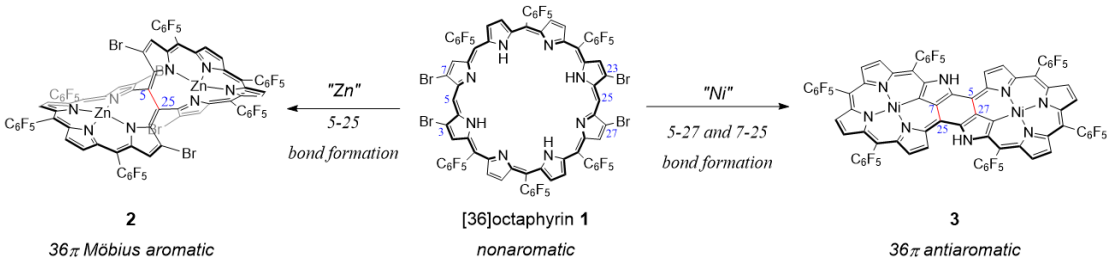


Figure 1. Typical synthetic route of porphyrin tape.



Scheme 1. Synthesis of **2** and **3**.

1) T. Tanaka, A. Osuka, *Chem. Soc. Rev.* **2015**, *44*, 943. 2) T. Tanaka, A. Osuka, *Chem. Rev.* **2017**, *117*, 2584; D. Kim, A. Osuka *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 681.

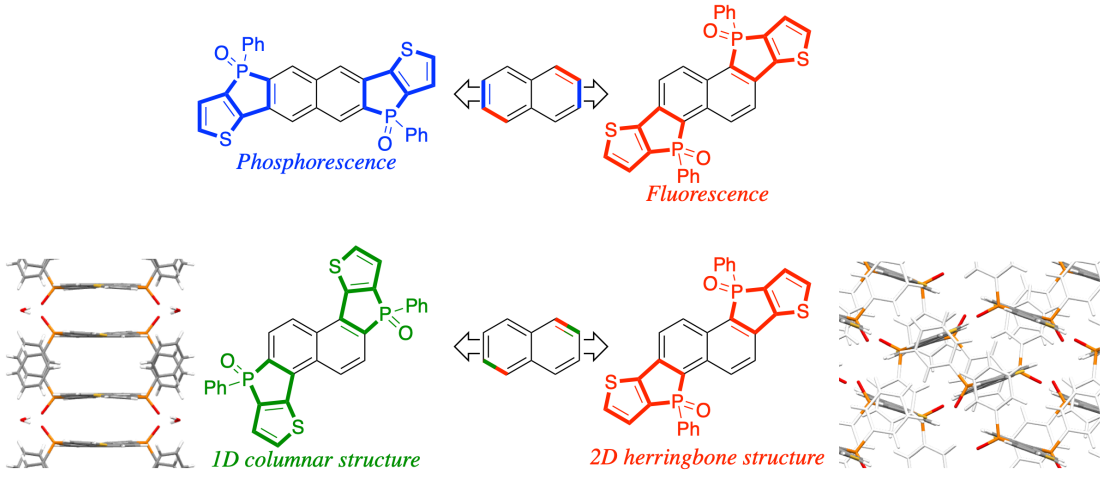
Modulation of Physicochemical Properties of Thiophene-fused Naphthodiphospholes by Precise Fusion of Heterole Rings

([1]*Graduate School of Engineering, Kyoto University*, [2]*WPI-iCeMS, Kyoto University*) ○ Keiichi Ishida,[1] Tomohiro Higashino,[1] Hiroshi Imahori[1,2]

Keywords: *Phosphole, Thiophene, Fluorescence, Phosphorescence*

Fused polycyclic aromatics have been vigorously pursued over the years because of their attracting structural, electronic, and photophysical features associated with the rigid and planar π-conjugated frameworks. For polycyclic aromatics with heterole-fused structures, the orientation of fused heterole rings as well as the geometry of their fused structures has a large impact on the physicochemical properties. In this regard, we expected that introducing two phosphorus atoms into polycyclic aromatics would provide an assortment of isomers originated from not only the position and orientation of the phosphole rings, but also the orientation of substituents on the phosphorus atoms (i.e., *trans*/*cis* configurations).

Herein, we designed and synthesized a series of six isomers of thiophene-fused naphthodiphospholes based on our envision. The isomers with fused structures on 2,3/6,7-positions showed phosphorescence due to enhanced spin-orbit coupling, whereas the isomers with fused structures on 1,2/5,6-positions displayed intense fluorescence. In addition, the *cis* isomers with 1,2/5,6-fused structure exhibited different packing structure in the solid states (i.e., 1D columnar structure and 2D herringbone structure) according to the orientation of fused heterole rings. Therefore, we demonstrated that the positions of heterole rings are of utmost importance to tune their electronic properties, and the orientations of heterole rings and substituents on the phosphorus atoms play critical roles in the molecular arrangements in the solid states.[1]



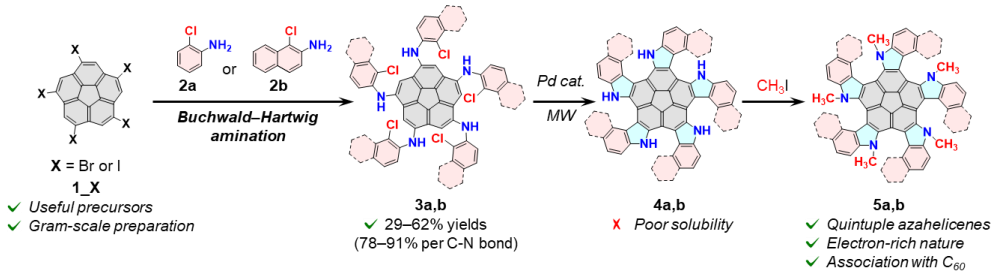
1) Ishida, K.; Higashino, T.; Wada, Y.; Kaji, H.; Saeki, A.; Imahori, H. *ChemPlusChem*, *in press*.

Synthesis of Novel Peripherally Fused Corannulenes via Quintuple Amination Reactions and Their Structural and Electronic Perturbations

(*Graduate School of Science, Kyoto University*) ○Koki Kise, Shota Ooi, Takayuki Tanaka, Atsuhiro Osuka

Keywords: Heteronanographene; Heterohelicene; Amination; Solid-state fluorescence; Association behavior with fullerene

Structural and electronic properties of polycyclic aromatic hydrocarbons (PAHs) can be controlled by incorporation of heteroatoms at the periphery of the PAHs. Especially, corannulene, that is a fragment of fullerene, is an attractive research target due to its bowl-shaped structure and electron-deficient nature. Recent reports on nitrogen-embedded corannulenes have been attracting great attention due to the unique stereochemistry and effective electronic perturbation.[1] In this work, we first prepared *sym*-pentabromocorannulene **1_Br** and *sym*-pentaiodocorannulene **1_I** as promising substrates for palladium-catalyzed amination reaction. Then, we synthesized pentaaminocorannulenes **3a**,**b** in which five nitrogen atoms are peripherally incorporated. Subsequently, we synthesized pentaindolocorannulene **4a** and pentakis(benzoindolo)corannulene **4b** via intramolecular cyclization reactions under palladium catalysis, and subsequent *N*-methylation reaction afforded **5a**,**b** which possess quintuple azahelicene scaffolds.[2] Owing to the electron-rich nature, fused aminocorannulenes **5a**,**b** showed multi-step oxidations by cyclic voltammetry and larger association constants with fullerene C_{60} compared with previously reported corranulene-based PAHs.[3]



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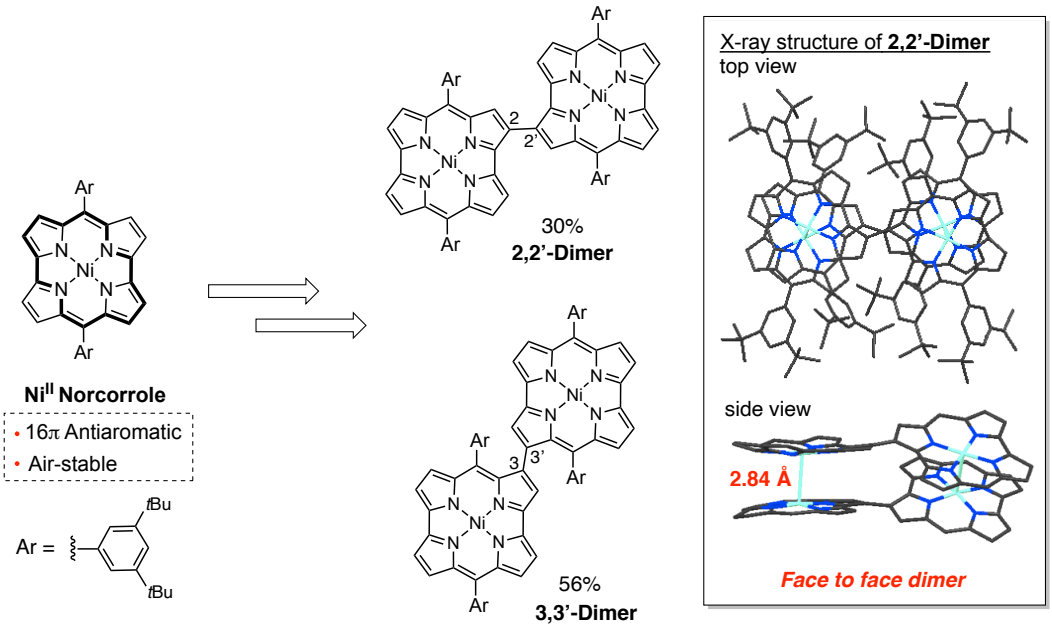
Synthesis of Covalently Linked Norcorrole Dimers and Their Association Behavior

(*Graduate School of Engineering, Nagoya University*) ○Si-Yu Liu, Hiroyuki Kawashima, Norihito Fukui, Hiroshi Shinokubo

Keywords: Antiaromaticity; Supramolecule; Electronic Interaction; Association Behavior; Covalent Linkage

The use of π–π stacking between aromatic π-systems is an important guideline to design supramolecular assemblies because such assemblies are useful for the development of novel electronic and optoelectronic materials.[1] However, the interplanar distances between conventional π–π stacking are usually longer than that the sum of van der Waals radii of two carbon atoms (3.4 Å). In addition, the electronic repulsion among π-electrons usually results in an offset or slipped π-stacking rather than perfect face-to-face alignment. These structural features are not suitable for the effective intermolecular electronic interaction.

In 2016, our group reported that norcorrole, an antiaromatic porphyrinoid, tends to form a face-to-face dimer with a remarkably short interplanar distance (3.05 Å).[2] Such a close stacking is attributed to strong frontier orbital interactions between the antiaromatic cores. In this work, we synthesized several covalently linked norcorrole dimers. These molecules spontaneously assembled to form molecular architectures with effective electronic interactions. In this presentation, we will discuss the structures of these supramolecular assemblies.



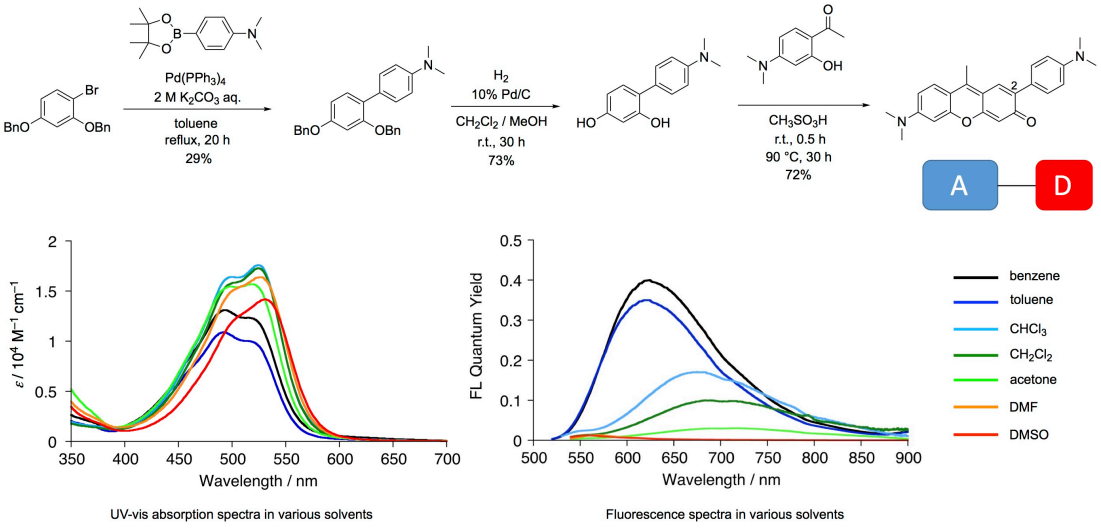
1) N. Martin *et al*. *Chem. Soc. Rev*. **2015**, *44*, 6425.
2) H. Shinokubo *et al*. *Nat. Commun*. **2016**, *7*, 13620.

ねじれ型分子内電荷移動発光を示すキサンテン誘導体の合成

(九大院工[1]・山口大理[2]) ○小出 太郎[1]・岩森 頌平[1]・古賀 訓[2]・鈴木 康孝[2]・川俣 純[2]・久枝 良雄[1]
Synthesis of xanthene derivative exhibiting twisted intramolecular charge transfer emission ([1]*Graduate School of Engineering, Kyushu University*, [2]*Faculty of Science, Ymaguchi University*) ○ Taro Koide,[1] Shohei Iwamori,[1] Satoshi Koga[2], Yasutaka Suzuki[2], Jun Kawamata[2], Yoshio Hisaeda[1]

Xanthene derivatives are dyes that have been studied for a long time, but it is difficult to synthesize regioselectively modified derivatives and to control Stokes shift. In this study, we succeeded in synthesizing a new xanthene derivative showing twisted intramolecular charge transfer (TICT) by introducing a rotatable electron-donating aryl group at the 2-position of the xanthene skeleton selectively. It was clarified that this compound shows a large solvent effect on the changes of structural and luminescence characteristics.
Keywords : xanthene, twisted intramolecular charge transfer, solvent effect

キサンテン誘導体は古くから研究されている色素であるが、位置選択的に修飾した誘導体の合成や、ストークスシフトの制御などが難しい化合物群であった。今回、キサンテン骨格の 2 位に回転可能な電子供与性アリール基を選択的に導入することで、ねじれ型分子内電荷移動（TICT）を示す新規誘導体の合成に成功した。また、この化合物が大きな溶媒効果を示し、構造や発光特性の変化を示すことを明らかにしたので報告する。



UV-vis absorption spectra in various solvents　　Fluorescence spectra in various solvents

1) Synthesis of 2,6,9-substituted xanthen-3-one and solvent effect on structural and photophysical properties, T. Koide, S. Iwamori, S. Koga, Y. Suzuki, J. Kawamata, Y. Hisaeda, *Dyes and Pigments* **2020**, in press. Available online: https://doi.org/10.1016/j.dyepig.2020.108667

ピロール架橋型キノンの合成と物性

（立命館大生命科学）○杉浦 慎哉・前田 大光
Synthesis and Properties of Pyrrole-Bridged Quinones (*College of Life Sciences, Ritsumeikan University*) ○Shinya Sugiura, Hiromitsu Maeda

π-Extended quinoid molecules, exhibiting diradical properties and near-infrared absorptions, have been of interest in various fields. Controlling electronic and optical properties of quinoid units exhibiting tautomerism would provide materials responsive to external stimuli. In this study, pyrrole-bridged quinones were synthesized and their tautomeric behaviors depending on external stimuli were evaluated. Pyrrole-based quinoidal derivatives were obtained by the deprotection and oxidation of di(acetoxyphenyl)pyrroles. In CH_2Cl_2, β-unsubstituted **1a** provided the UV/vis absorption maximum (λ_{max}) at 626 nm, which was ascribable to the quinoid form. In contrast, β-bromo **1b** in CH_2Cl_2 gave a dark red solution derived from the hydroxy form with the λ_{max} at 428 nm. Furthermore, in CH_2Cl_2, **1a** exhibited Cl^- binding and also deprotonation by bases, resulting in near-infrared absorption.
Keywords : π-conjugated systems; pyrrole; quinones; tautomerism; anion binding

拡張π電子系キノン誘導体は、ジラジカル特性や長波長領域の吸収を示すことから、広い分野で注目されている。さらに、キノイド構造を基盤とした互変異性による電子・光物性の変調を制御することで、刺激応答性材料の開発が期待できる。本研究では、ピロール架橋した新規キノン誘導体の合成および外部刺激に依存した互変異性の評価をおこなった。ジ（アセトキシフェニル）ピロール誘導体に対し、過剰量の無水 $FeCl_3$ を用いて脱保護および酸化することでキノン誘導体 **1a–c** を得た（Figure 1）。理論計算や ^{1}H NMR から、**1a** は CH_2Cl_2 中でキノイド構造 $\mathbf{1a}_{NH}$ であることが明らかになった（λ_{max} = 625 nm）。一方で、**1b**,**c** は溶媒の極性に依存して溶液の色が変化し、**1b** は CH_2Cl_2 中で OH 体を形成することで、褐色の溶液を示した（$\mathbf{1b}_{OH}$: λ_{max} = 428 nm）（Figure 2a）。さらに、**1a** は CH_2Cl_2 中で Cl^-会合能（K_a = 260 M^{-1}）を示し、塩基を用いた脱プロトン化によって近赤外領域の吸収（λ_{max} = 773 nm）が観測された（Figure 2b）。[1)]

Figure 1

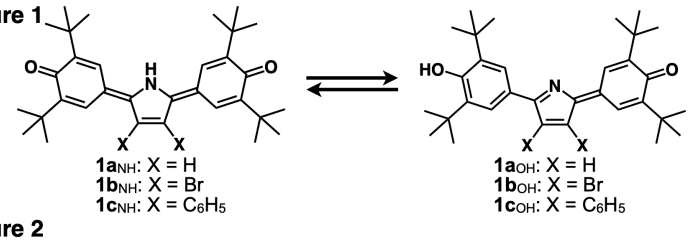
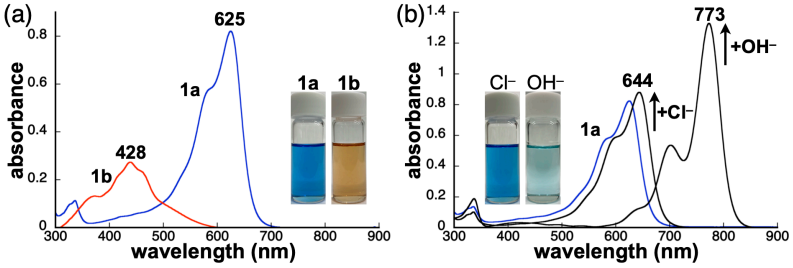


Figure 2



1) Sugiura, S.; Maeda, H. to be submitted.

ボロールを含む多環π電子系の創製とホウ素ーリン錯体の光応答性

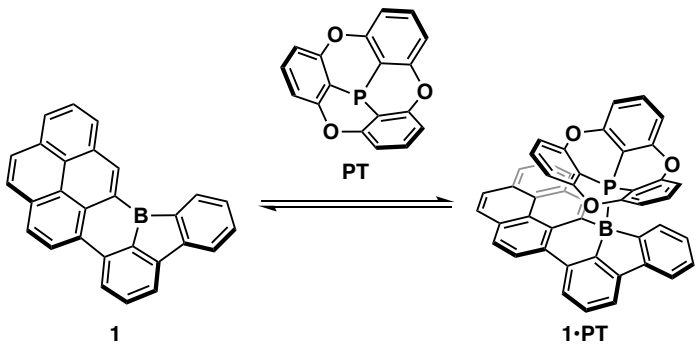
（名大院理[1]・Goethe-Universität[2]・名大 ITbM[3]）○安藤 直紀[1]・山田 卓弥[1]・成田 皓樹[1]・Niels Oehlmann[2]・Matthias Wagner[2]・山口 茂弘[1,3]

Borole-Embedded Polycyclic π-Electron Systems and Photoresponsive Behavior of their B–P Lewis Adducts ([1]*Graduate School of Science, Nagoya University*, [2]*Goethe-Universität Frankfurt am Main*, [3]*Institute of Transformative Bio-Molecules (ITbM), Nagoya University*) ○ Naoki Ando,[1] Takuya Yamada,[1] Hiroki Narita,[1] Niels Oehlmann,[2] Matthias Wagner,[2] Shigehiro Yamaguchi[1,3]

We have previously reported the synthesis of planarized triarylboranes consisting of a 4π-antiaromatic borole substructure. Herein, we studied the Lewis acidity of the borole-embedded polycyclic π-electron systems, which showed one of the highest Lewis acidity among the hitherto known planarized triarylboranes and formed a Lewis acid–base adduct even with a polycyclic compound containing a phosphorous atom. Notably, the B–P bond in the Lewis acid–base adduct cleaved upon UV irradiation. In this presentation, we will discuss the fundamental properties of the borole-embedded polycyclic compounds, control of their molecular orientation in the crystalline state by substituents, and photodissociation behavior of the B–P Lewis acid–base adducts.

Keywords : Boron; Borole; Antiaromaticity; Lewis Acid; Photodissociation

我々は、これまでに4π反芳香族性を示すボロール骨格を組み込んだ多環式化合物を合成し、これがかさ高い置換基をもたないにもかかわらず、空気中で取り扱えるだけの安定性を示すことを報告している。今回、π拡張した誘導体 **1** について、そのLewis 酸性を評価したところ、既報の平面固定トリアリールボランと比較して、**1** が顕著に高いLewis 酸性を示すことが明らかとなった。そこで、**1** と種々のLewis 塩基との錯形成を検討したところ、リンを中心にもつトリアンギュレン誘導体 **PT**[1]ともLewis 酸・塩基錯体 **1**・**PT** を形成することがわかった。また、このLewis 酸・塩基錯体は、光照射下でホウ素ーリン結合の開裂に起因した特異な発光挙動を示した。本発表では、一連の誘導体について、物性、置換基による結晶中での分子配向の制御、ホウ素–リン錯体の発光挙動について報告する。



[1] (a) F. C. Krebs, P. S. Larsen, J. Larsen, C. S. Jacobsen, C. Boutton, N. Thorup, *J. Am. Chem. Soc.* **1997**, *119*, 1208−1216. (b) M. Yamamura, T. Nabeshima, *Bull. Chem. Soc. Jpn.* **2016**, *89*, 42–49.

[A08-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair:Takashi Hirano, Kenta Kokado
Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 8 (Online Meeting)

[A08-4am-01] A novel platform for crystalline molecular rotor based on NHC metal complexes

○Mingoo Jin Jin[1,2], Rempei Ando[4], Marcus J. Jellen[3], Miguel A. Garcia-Garibay[3], Hajime Ito[1,2] （1. Hokkaido Univ. Dep. Eng., 2. Hokkaido Univ. WPI-ICReDD, 3. University of California Los Angeles, 4. Hokkaido Univ. Sch. Chem.）

9:00 AM - 9:20 AM

[A08-4am-02] Organofullerene Nano- and Microspheres Containing Inorganic and Biological Nanoparticles: Self-Assembly and Electron Tomography

○Ryosuke Sekine[1], Prince Ravat[1], Haruaki Yanagisawa[2], Chao Liu[1], Masahide Kikkawa[2], Koji Harano[1], Eiichi Nakamura[1] （1. Grad. School of Sci., The Univ. of Tokyo, 2. Grad. School of Med., The Univ. of Tokyo）

9:20 AM - 9:40 AM

[A08-4am-03] Identification and thermodynamics of rim binding modes of cyclodextrins by atomic-resolution electron microscopy

○Hiroki Hanayama[1], Junya Yamada[1], Koji Harano[1], Eiichi Nakamura[1] （1. The University of Tokyo）

9:40 AM - 10:00 AM

[A08-4am-04] Quantitative Evaluation of Noncovalent Interactions at the C_{60} Surface

○Michio Yamada[1], Haruna Narita[1], Yutaka Maeda[1] （1. Tokyo Gakugei University）

10:00 AM - 10:20 AM

[A08-4am-05] Linear momentum of a microfluid realizes an anisotropic reaction at the ends of a supramolecular nanofiber

○Chisako Kanzaki[1], Arinori Inagawa[2], Gaku Fukuhara[3,4], Tetsuo Okada[3], Tetsuya Narushima[5], Hiromi Okamoto[5], Munenori Numata[1] （1. Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, 2. Graduate School of Regional Development and Creativity, Utsunomiya University, 3. Department of Chemistry, Tokyo Institute of Technology, 4. JST, PRESTO, 5. Institute for Molecular Science）

10:20 AM - 10:40 AM

[A08-4am-06] Asymmetric benzoin condensation reaction involving dynamic crystallization

Aoi Washio[1], Yasushi Yoshida[1], ○Takashi Mino[1], Masami Sakamoto[1] （1. Graduated school of engineering, chiba University）

10:40 AM - 11:00 AM

[A08-4am-07] Rotaxane-based supramolecular mechanophores exhibiting reversible/irreversible change in their fluorescence property

○Tatsuya Muramatsu[1], Yoshimitsu Sagara[1,2] （1. School of Materials and Chemical Technology, Tokyo Institute of Technology, 2. JST PRESTO）

11:00 AM - 11:20 AM

[A08-4am-08] Relationship between Cooperative Photodimerization Reaction Process and Size Change of 9-Methylanthracene Single Crystal

○Kohei Morimoto[1], Daichi Kitagawa[1], Fei Tong[2], Christopher J. Bardeen[2], Seiya Kobatake[1]
（1. Grad. Sch. Eng., Osaka City Univ., 2. Department of Chemistry, University of California, Riverside）

11:20 AM - 11:40 AM

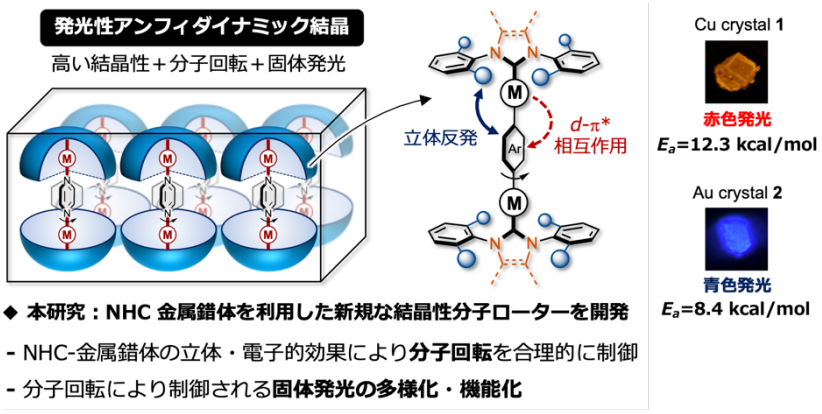
NHC 金属錯体を基軸とした結晶性分子ローターの新規プラットフォーム

（北大院工[1]・北大化学反応創成研究拠点[2]・カルフォニア州立大学ロスアンゼルス校[3]・北大総化[4]）○陳旻究[1,2]・安藤 廉平[4]・Jellen Marcus[3]・Garcia-Garibay M.A.[3]・伊藤 肇[1,2]

A novel platform for crystalline molecular rotor based on NHC metal complexes ([1]*Hokkaido Univ. Dep. Eng.*, [2]*Hokkaido Univ. WPI-ICReDD*, [3]*University of California Los Angeles*, [4]*Hokkaido Univ. Sch. Chem.*) ○Mingoo Jin,[1,2] Rempei Ando,[4] Marcus Jellen,[3] Miguel A. Garcia-Garibay,[3] Hajime Ito[1,2]

Recently, several novel approaches for controlling/modulating the solid-state functional properties by using molecular rotation in solid have been demonstrated. However, the reported platform for the crystalline media still has limitations to design the molecular dynamics in solid-state due to its high dependency on intermolecular packing manner in crystals. Here, we will describe a newly designed platform for crystalline molecular rotors by using NHC metal complexes and those features on molecular rotations and photophysical properties in solid-state.
Keywords : Crystalline molecular rotor; Solid-state luminescence; N-heterocyclic carbene; Transition metal

最近、「固体中の分子回転」を利用した様々な固体物性を制御する例が報告されているが、固体物性と分子回転を合理的に設計・制御することは未だ困難である。本発表では、我々がごく最近成功した豊富な化合物ライブラリーを持つ N-ヘテロ環式カルベン(NHC)金属錯体を基軸とした新たなアンフィダイナミック結晶の開発について紹介する[1]。合成された NHC 錯体は、回転部位の 1,4-pyrazine に対し、両側の窒素原子に銅(I)および金(I)が配位し、その末端には嵩高い NHC 配位子が導入されたカチオン錯体である。単結晶 XRD、固体 NMR 測定など種々の検討により NHC 金属錯体が持つ立体・電子的効果により分子回転が精密に制御されることが明らかとなった。



Jin, M.*, Ando R., Jellen, M., Garcia-Garibay, M.A., Ito, H.*, ***J. Am. Chem. Soc. 2020**, just accepted.*

1) **Jin, M.***; Ando, R.; Jellen, M. J.; Garcia-Garibay, M. A.; Ito, H.* *J. Am. Chem. Soc.* **2020**, *Just Accepted.*

Organofullerene Nano- and Microspheres Containing Inorganic and Biological Nanoparticles: Self-Assembly and Electron Tomography

([1]*Graduate School of Science, The University of Tokyo*, [2]*Graduate School of Medicine, The University of Tokyo*) ○Ryosuke Sekine,[1] Prince Ravat,[1] Haruaki Yanagisawa,[2] Chao Liu,[1] Masahide Kikkawa,[2] Koji Harano,[1] Eiichi Nakamura[1]

Keywords: Fullerene; Amorphous particle; Electron microscopy; Sample preparation; Structural analysis

Organofullerene amphiphiles show diverse behaviors in water, forming vesicles, micelles, Langmuir-Blodgett film, and anisotropic nanostructures. We found that gradual in situ protonation of an organic solution of (4-heptylphenyl)$_5C_{60}^-K^+$ (**C7K**, Figure a) by water or buffer generates the corresponding protonated molecule, (4-heptylphenyl)$_5C_{60}H$ (**C7H**), which self-assembles to form a nano- and microsphere of organofullerene. The diameter is controlled by the preparation or pH of the buffer in range between 30 nm to 2.5 μm. By using an aqueous solution of organic dye, or aqueous dispersion of inorganic nanoparticle, protein, and virus, we encapsulated these entities in the fullersphere. This approach through self-assembly is distinct from other preparations of organic core-shell particles that generally require polymerization for construction of a robust shell. We found that the rigid spherical shape is suitable for electron tomography (ET), which is an analytical method to reconstruct three-dimensional (3D) structures of target nanomaterials. The spheres sticked out to vacuum (Figure b) enable us to collect the transmission electron microscope (TEM) images from various angles in a constant contrast, and 3D structures and coordinate can be reconstructed on the incorporated specimens (Figure c).

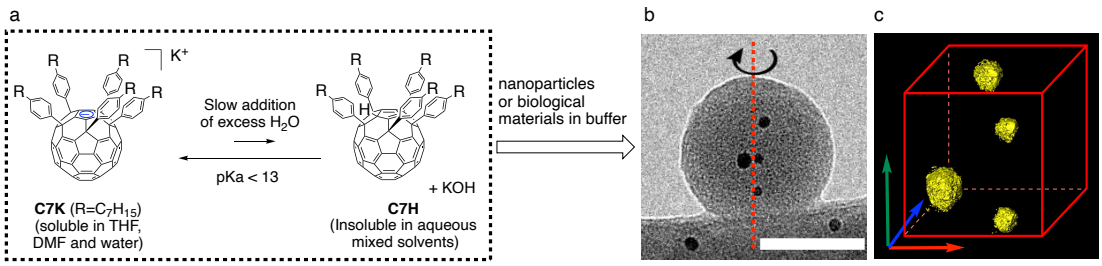


Figure. Preparation of self-assembled multiple-component nanospheres by utilizing an equilibrium of organofullerenes in water and structural analysis of incorporated specimens with ET. (a) An equilibrium between **CnH** and **CnK**. (b) TEM image of gold nanoparticles (AuNPs) in an organofullerene nanosphere. Scale bar: 50 nm. (c) The reconstructed volume data of incorporated AuNPs.

原子分解能電子顕微鏡を用いたシクロデキストリンの口縁部による結合モードの同定と熱力学解析

（東大院理[1]）○花山 博紀[1]・山田 純也[1]・原野 幸治[1]・中村 栄一[1]
Identification and thermodynamics of rim binding modes of cyclodextrins by atomic-resolution electron microscopy ([1]*Graduate School of Science, The University of Tokyo*) ○Hiroki Hanayama,[1] Junya Yamada,[1] Koji Harano,[1] Eiichi Nakamura[2]

Cyclodextrins are widely applied in industry because they encapsulate and solubilize molecules in water. In this study, the interaction between CD and the tip of conical carbon nanotubes with a wide size distribution, which are almost continuously distributed widely from smaller sizes than the cavity of γ-CD to far larger sizes, was statistically analyzed by atomic-resolution electron microscopy (EM). The size distribution of CD-bound tips not only revealed the presence of size-selective binding to larger curvature than cavity using their two kinds of rims but also reflected the thermodynamics of each binding mode. Thermodynamic analysis by variable-temperature experiments showed that rim binding occurred as effectively as cavity binding in the similar thermodynamic characters. This result suggests that the rim binding modes contribute to the binding solely assigned as inclusion binding in some cases.
Keywords : Cyclodextrin; Molecular recognition; Transmission electron microscopy; Thermodynamics; Nanocarbon

シクロデキストリン(CD)は空孔に難溶性分子を包接し水に可溶化する性質を有し，広く産業に応用されている．今回，γ-CD の空孔よりも小さいサイズから大きなサイズまでほぼ連続的に広いサイズ分布を持つコーン型カーボンナノチューブ（NT）をゲストとして，CD との結合構造を原子分解能電子顕微鏡で統計解析した（図 a）．CD が結合した NT 先端のサイズ分布（図 b）は，CD 内孔への包接に加え，CD が 2 種類の口縁部を用いて空孔よりも大きな曲率のゲストにもサイズ選択的に結合することを明らかにした．温度可変実験による熱力学解析では，口縁部による結合が包接と同様の熱力学的特性で起こることが示され，これまで包接のみと考えられていた CD による疎水性分子との結合に口縁部による結合が寄与している可能性を示唆している．

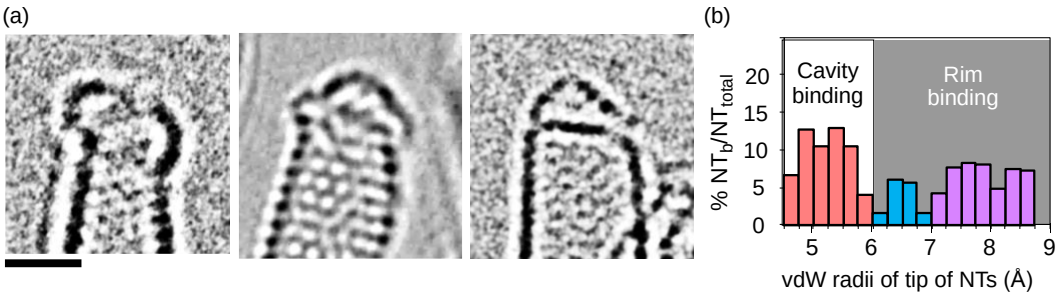


図. TEM による CD の結合モードの解析．（a）様々なサイズの NT 先端に結合するγ-CD の TEM 像．（b）γ-CD が結合した NT 先端のサイズ分布．

C_{60} 表面に働く非共有結合性相互作用の定量的な評価

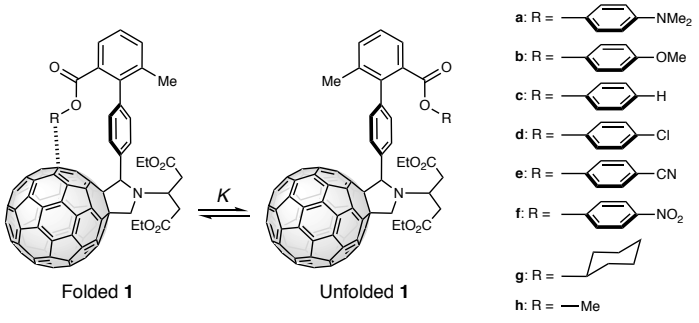
（学芸大教）○山田 道夫・成田 陽菜・前田 優

Quantitative Evaluation of Noncovalent Interactions at the C_{60} Surface ([1]*Department of Chemistry, Tokyo Gakugei University*) ○Michio Yamada,[1] Haruna Narita,[1] Yutaka Maeda[1]

Fullerenes are unique molecules with spherical hydrophobic structures and curved π-electron systems, and they are expected to find widespread use in a variety of applications in the materials science and medicinal chemistry fields. Quantitative investigations of the noncovalent interactions at the fullerene surface, which are often very weak, are essential for understanding the assembled molecular systems of fullerenes as well as its molecular recognition events. In this study, we designed, synthesized, and characterized the first model system of a fullerene-based molecular balance to quantitative analyze the noncovalent interactions at the C_{60} surface. We found two conformers corresponding to the folded and unfolded states are observable based on their ^{1}H NMR spectra, allowing us to determine the thermodynamic parameters corresponding to the noncovalent interactions occurring on the fullerene surface.

Keywords : Conformational Analysis; Electrostatic Interactions; London Dispersion Force; π–π Interactions; Fullerenes

C_{60} は球状のπ電子共役系構造をもつ特異な疎水性分子であり、物質化学や医薬品化学などの分野で広く注目されている。C_{60} からなる分子集合体や C_{60} の分子認識における性質を理解する上では、C_{60} 分子の表面に働く非共有結合性相互作用を定量的に評価することが重要であるが、非常に弱い分子間力の計測は容易ではない。本研究ではねじり天秤分子を設計・合成し、C_{60} 表面と種々の置換基との間に働く相互作用を計測・評価したので報告する [1)]。本研究で設計・合成したねじり天秤分子（**1**）について、Folded 型配座および Unfolded 型配座からなる二種類の配座異性体の相互変換が ^{1}H NMR から観測することができた。そこで、この配座異性の解析により、フラーレン表面と種々の置換基の間に働く相互作用に対応する熱力学パラメータの算出を行い、それらは非常に弱いものの、観測可能であることが明らかとなった。



1) A fullerene-based molecular torsion balance for investigating noncovalent interactions at the C_{60} surface, M. Yamada, H. Narita, Y. Maeda, *Angew. Chem. Int. Ed.* **2020**, *59*, 16133.

マイクロ流体の力学的エネルギーを利用した異方的な超分子成長とそのメカニズムの解明

（京都府大院 生命環境 [1]・宇都宮大院 地域創生科学 [2]・東工大理 [3]・JST さきがけ [4]・分子研 [5]）○神崎千沙子 [1]・稲川有徳 [2]・福原学 [3,4]・岡田哲男 [3]・成島哲也 [5]・岡本裕巳 [5]・沼田宗典 [1]

Kinetic energy in a microfluid realizes an anisotropic reaction at the ends of a supramolecular nanofiber ([1]*Graduate School of Life and Environmental Sciences, Kyoto Prefectural University*, [2]*Graduate School of Regional Development and Creativity, Utsunomiya University*, [3]*Department of Chemistry, Tokyo Institute of Technology*, [4]*JST, PRESTO*, [5]*Institute for Molecular Science*) ○Chisako Kanzaki,[1] Arinori Inagawa,[2] Gaku Fukuhara,[3,4] Tetsuo Okada,[3] Tetsuya Narushima,[5] Hiromi Okamoto,[5] Munenori Numata[1]

In artificial supramolecular systems, molecular assemblies occur generally under thermodynamic processes and structural varieties of the resultant assemblies are restricted. Herein, we demonstrate that the use of microflow system to precisely regulate the self-assembling field enables control over the pathway for kinetic self-assembly processes. In the present study, we employed tetrakis(4-sulfonatophenyl)porphyrin (TPPS) as a model compound. We demonstrated that the porphyrin molecules spontaneously self-assembled in microflow space.

Keywords : Supramolecular structures; Kinetic control; Supramolecular polymerization; Microflow; Non-equilibrium

複雑性と階層性を内在した超分子材料の創製には、複数の分子間相互作用を的確な位置とタイミングで形成させる必要がある。我々はこの課題に挑戦するため、分子集積場としてマイクロフロー空間の利用を提案してきた [1)]。マイクロフロー空間における迅速かつ均質な分子拡散は、通常形成が困難である複雑な超分子構造の効率的な創出を実現すると期待される。本研究では会合挙動が既知であるアニオン性ポルフィリン Tetrakis(4-sulfonatophenyl)porphyrin (TPPS)をモデル分子として用いた（図 1a）。マイクロフロー空間において TPPS 水溶液と酸溶液を混合すると、通常の溶液混合過程と比較して会合効率が大幅に向上した。このメカニズムを検証するため、リアルタイム蛍光および直線偏光二色性 (LD) 測定を実施した（図 1b）。その結果、マイクロフロー空間における速度論的な分子間相互作用の制御機構を明らかとしたので報告する [2)]。

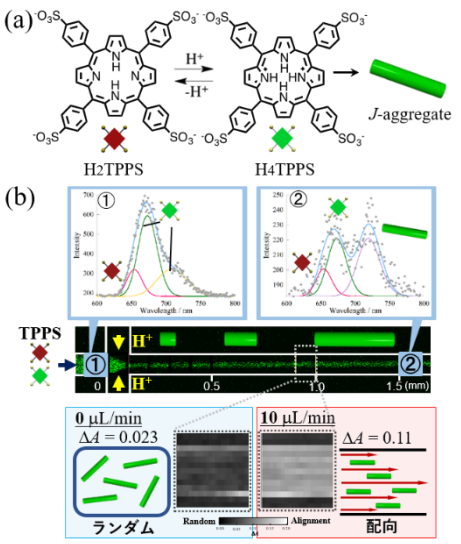


図 1: (a) TPPS の構造 (b) マイクロフロー空間を流れる TPPS 溶液の蛍光イメージ像：①②における空間分解蛍光スペクトル (ex.473 nm) 及び中間点における LD 吸収イメージ

1) M. Numata, *Chem. Asian J.*, **2015**, *10*, 2574.

2) C. Kanzaki et al., *Bull. Chem. Soc. Jpn*, in press.

動的結晶化を伴う不斉ベンゾイン縮合反応

（千葉大院工）○鷲尾 葵・吉田 泰志・三野 孝・坂本 昌巳
Asymmetric benzoin condensation reaction involving dynamic crystallization (*Graduate School of Engineering, Chiba University*)○Aoi Washio, Yasushi Yoshida, Takashi Mino, Masami Sakamoto

Absolute asymmetric synthesis has attracted many researchers because it is closely related to the homochirality of biomolecules in nature. Similarly, dynamic crystallization is an attractive research project because it does not require an external chiral source. In this study, we have focused on absolute asymmetric synthesis of benzoins involving benzoin condensation followd by dynamic crystallization (**Figure 1**). In order to perform dynamic crystallization, it is necessary for the target compound to racemize. We investigated the racemization conditions of anisoin. As a result, racemization of anisoin was confirmed under basic conditions. Based on these results, we attempted to synthesize chiral anisoin involving benzoin condensation using achiral vitamin B_1 followed by dynamic crystallization. As a result, we succeeded in the asymmetric synthesis of anisoin in 99% ee. *Keywords : Benzoin condensation; Dynamic crystallization; Asymmetric amplification; Asymmetric control; Anisoin*

化学的不斉源を用いずに光学活性体を合成する絶対不斉合成は，自然界のホモキラリティーの発現と深く関連しており，多くの研究者を魅了してきた。同様に，コングロメレートの自然分晶を利用した動的結晶化法は，外的不斉源を必要とせず，一方の鏡像異性体のみが得られるため，魅力的な課題である [1]。本研究では，ベンゾイン縮合と，動的結晶化を伴うベンゾイン類の絶対不斉合成を試みた (**Figure 1**)。今回，既知のコングロメレートである Anisoin (space group: $P2_12_12_1$)を目的物として選択した。

動的結晶化法を行うための条件として，目的物が母液中でラセミする必要がある。そのため，Anisoin のラセミ化条件を調査した。その結果，塩基性条件下にて，Anisoin のラセミ化が確認され，さらにラセミ化速度の塩基性度および溶媒極性依存性が観測された。以上の結果を基に，ベンゾイン縮合と，動的結晶化による不斉 Anisoin 合成を試みた。触媒として天然に存在するアキラルな Vitamin B_1 を使用した。反応を開始して 24 時間後には，Anisoin 結晶が析出し，そのまま動的結晶化を行うことで，99% ee 以上の光学純度の Anisoin 合成に成功した。本研究ではさらに，D または L-valine を添加した Anisoin の不斉制御についても検討を行った。

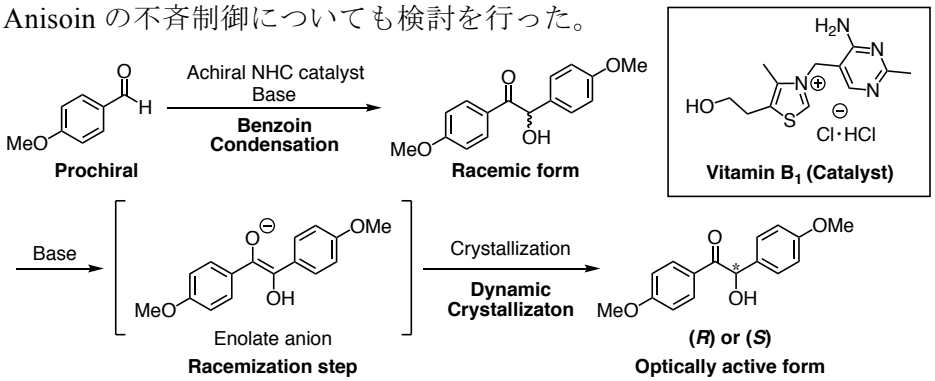


Figure 1. Asymmetric anisoin synthesis involving benzoin condensation followed by dynamic crystallization.

1) M. Sakamoto, Asymmetric Synthesis Involving Dynamic Enantioselective Crystallization, in *Advances in Organic Crystal Chemistry*, *Comprehensive Reviews 2020*, M. Sakamoto, H. Uekusa eds, Splinger, **2020**, 433.

可逆・不可逆な発光特性の変化を示すロタキサン型超分子メカノフォア

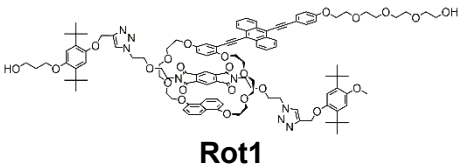
（東工大物質[1]・JST さきがけ[2]）○村松 達也[1]・相良 剛光[1,2]
Rotaxane-based supramolecular mechanophores exhibiting reversible/irreversible change in their fluorescence property ([1]*Department of Materials Science and Engineering, Tokyo Institute of Technology*, [2]*JST-PRESTO*) ○Tatsuya Muramatsu,[1] Yoshimitsu Sagara[1,2]

Recently, mechanophores that show various responses to mechanical stress have attracted much interest.[1)] Our group has developed rotaxane-based supramolecular mechanophores, which are composed of a cyclic molecule featuring a luminophore and a dumbbell-shaped molecule having a quencher and two stoppers.[2-4)] Because the cycle is located around the quencher in the initial state, the fluorescence is quenched. When a force is applied to the rotaxane, the separation of the cycle from the quencher occurs. Consequently, the fluorescence is observed. After the removal of the force, the cycle returns to the vicinity of the quencher and the fluorescence is quenched again. In this study, we synthesized a rotaxane-based supramolecular mechanophore **Rot1** with a smaller cycle and smaller stoppers compared to the rotaxane-based mechanophores that we have reported. **Rot1** was covalently embedded into the polyurethane main chain (**Rot1PU**) and the mechanoresponsive luminescence behavior of the obtained polyurethane film was examined. **Rot1PU** films showed reversible changes in emission intensity upon stretching for initial several times. However, **Rot1PU** films exhibited strong emission in the relaxed state after stretching more than 50 times. We proved that this irreversible behavior is attributed to dethreading of the cycle from the dumbbell-shaped molecule. Once dethreading of the cycle occurs, the luminophore attached to the cycle can't return to the vicinity of the quencher.

Keywords : Mechanophore; Rotaxane; Stimuli-responsive luminescent material; Polyurethane; Supramolecular chemistry

近年、機械的刺激を可視化・評価するメカノフォアが盛んに研究されている[1)]。我々はロタキサンを用いて、可逆的な発光特性変化を示す超分子メカノフォアを開発してきた[2-4)]。ロタキサン型超分子メカノフォアは、消光団と 2 つのストッパーを有するダンベル状分子と、蛍光団を有する環状分子から構成される。力を印加していない状態では、消光団が環状分子に包接され、蛍光団からの蛍光が消光される。いったん、力を印加すると、環状分子と消光団が離れ、蛍光が観察されるようになる。印加した力を除くと、環状分子は消光団近傍に戻り、蛍光は再び消光される。

本研究では、環状構造とストッパーの大きさを従来のものよりも小さくしたロタキサン型メカノフォア **Rot1** を開発した。合成した **Rot1** を、共有結合を介してポリウレタン中に導入し（**Rot1PU**）、機械的刺激に対する発光特性変化を精査した。得られた **Rot1PU** フィルムでは、従来のロタキサン型メカノフォアと同様に、フィルムの伸縮に伴い、蛍光強度が可逆的に変化した。しかし、繰り返し伸縮すると、力を印加していない状態でも **Rot1PU** フィルムが蛍光を示すようになった。この不可逆的な発光特性変化は、機械的刺激を受けたいくつかのロタキサンにおいて、環状分子がストッパー部位をすり抜けたことが原因であると考えられる。



Rot1

1) D. A. Davis *et al.*, *Nature* **2009**, *459*, 68–72. 2) Y. Sagara *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 1584–1587. 3) Y. Sagara *et al.*, *ACS Cent. Sci.* **2019**, *5*, 874–881. 4) T. Muramatsu *et al.*, *ACS Appl. Mater. Interfaces* **2019**, *11*, 24571–24576.

Relationship between Cooperative Photodimerization Reaction Process and Size Change of 9-Methylanthracene Single Crystal

([1]*Graduate School of Engineering, Osaka City University*, [2]*Department of Chemistry, University of California, Riverside*) ○Kohei Morimoto,[1] Daichi Kitagawa,[1] Fei Tong,[2] Christopher J. Bardeen,[2] Seiya Kobatake[1]

Keywords: Anthracene; Organic Crystal; [4+4] Photodimerization; Photomechanical Effect; Cooperative Effect

It is important to understand the mechanism of the photomechanical effect in photoreactive organic crystals based on photoreaction kinetics. In most cases, the photochemical reaction in the crystalline phase follows kinetics similar to a photochemical reaction in solution. However, the photoreaction of some molecules such as cinnamic acid and anthracene in the crystalline state follows the cooperative kinetics represented by the sigmoidal curve showing nucleation and growth.[1] In this study, we investigated the relationship between the cooperative photoreaction process and the photomechanical effect using a thin single crystal of 9-methylanthracene (**9MA**).

9MA is a representative compound that undergoes [4+4] photodimerization in the crystalline phase. **9MA** thin crystals were prepared by the seeded-growth method.[2] The decay of absorption originated from monomer molecules by UV irradiation indicated the sigmoidal curve shown in Figure 1. During photodimerization, the size changes in **9MA** single crystal were observed as shown in Figure 2(a) and showed a clear sigmoidal curve having the induction period as shown in Figure 2(b). By the measurement of both the monomer absorbance decay and the crystal length change at the same time, it was revealed that the crystal shape change relative to the conversion ratio from the monomer pair to the dimer has a linear relationship. This result indicates that the sigmoidal change in the photoinduced crystal shape is induced by the additive accumulation of the internal strain due to the cooperative photodimerization reactions of **9MA** molecules.

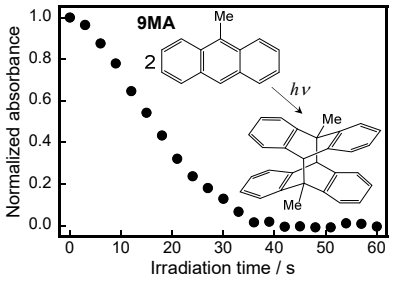


Fig. 1 Photoinduced absorbance change of monomer (irradiation wavelength: 365 nm and power: 2.4 mW cm^{-2})

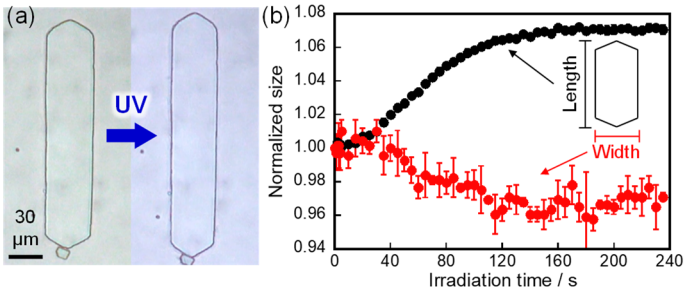


Fig. 2 (a) Photoinduced crystal shape change and (b) photoinduced crystal size change upon irradiation with 405 nm light. (irradiation power: 1.6 mW cm^{-2})

1) F. Tong *et al.*, *Phys. Chem. Chem. Phys.* **2016**, *18*, 31936–31945.
2) F. Tong *et al.*, *Angew. Chem. Int. Ed.* **2018**, *57*, 7080–7084.

[A09-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair:Seiya Kobatake, Hiroshi Katagiri
Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 9 (Online Meeting)

[A09-4am-01] Accuracy of intermolecular interaction energies of molecules including hetero atoms using Grimme’ s dispersion corrections

○Seiji Tsuzuki[1], Tadafumi Uchimaru[1] （1. National Institute of Advanced Industrial Science and Technology）

9:00 AM - 9:20 AM

[A09-4am-02] Control of stacking patterns of two-dimensional molecular layers in hydrogen-bonded cocrystals composed of 2-pyrrolidone and anilic acids

○Masaki Donoshita[1], Yukihiro Yoshida[1], Mikihiro Hayashi[1], Ryuichi Ikeda[1], Kunihisa Sugimoto[2], Shogo Kawaguchi[2], Yasuhisa Yamamura[3], Kazuya Saito[3], Hiroshi Kitagawa[1] （1. Kyoto University, 2. JASRI/SPring-8, 3. University of Tsukuba）

9:20 AM - 9:40 AM

[A09-4am-03] Crystalline-state chemiluminescence property of 1,2-dioxetanes conjugated with a strongly fluorescent chromophore

○Chihiro Matsuhashi[1], Hironaga Ohyama[2], Hidehiro Uekusa[2], Ayana Sato-Tomita[3], Kouhei Ichiyanagi[4], Shojiro Maki[1], Takashi Hirano[1] （1. The Univ. of Electro-Communications, 2. Tokyo Tech, 3. Jichi Medical Univ., 4. KEK）

9:40 AM - 10:00 AM

[A09-4am-04] Control of Molecular Orientation in Organic Semiconductors Using Weak Iodine-Iodine Interactions

○Amane Matsunaga[1], Yuta Ogawa[1], Daisuke Kumaki[2], Shizuo Tokito[2], Hiroshi Katagiri[1] （1. Graduate School of Science and Engineering, Yamagata University, 2. Graduate School of Organic Materials Science, Yamagata University）

10:00 AM - 10:20 AM

[A09-4am-05] Design of photo-functional soft crystals based on degree of protonation in the acid-base complexes

○Yoshio Yano[1], Ono Toshikazu[1,2], Hisaeda Yoshio[1,2] （1. Grad. Sch. Eng., Kyushu Univ., 2. Center for Molecular Systems, Kyushu Univ.）

10:20 AM - 10:40 AM

[A09-4am-06] Development of Thermo-responsive Solid-State Luminescent Materials Utilizing Intermolecular Interactions between Carboranes and Nitrogen Atoms

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

10:40 AM - 11:00 AM

[A09-4am-07] Thermo- and Mechanoresponsive Turn-On Phosphorescence of Thienyl Diketone Crystal

○Yosuke Tani[1], Takuji Ogawa[1] （1. Osaka University）

11:00 AM - 11:20 AM

[A09-4am-08] Synthesis and Photophysical Properties of Extended Pyrazinacenes

○Gary James Richards[1,2], Jonathan Hill[2], Shinji Yamada[3], Katsuhiko Ariga[2], Akiko Hori[1] （1. Shibaura Institute of Technology, 2. National Institute of Materials Science, 3. Ochanomizu University）

11:20 AM - 11:40 AM

Grimme の分散力補正 DFT 法で計算したヘテロ原子の分散力の精度

（産総研機能材料）○都築 誠二・内丸 忠文

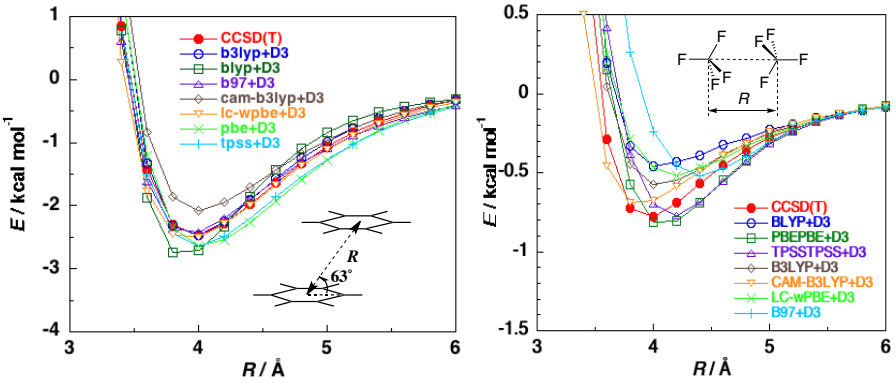
Accuracy of intermolecular interaction energies of molecules including hetero atoms using Grimme's dispersion corrections

(*Research Center for Computational Design of Advanced Functional Materials, National Institute of Advanced Industrial Science and Technology*) ○Seiji Tsuzuki, Tadafumi Uchimaru

Intermolecular interaction potentials for 11 complexes were calculated using several functionals with Grimme's dispersion correction methods of the D2, D3 and D3BJ versions. The calculated potentials were compared with the CCSD(T) level potentials to evaluate the accuracy of the dispersion corrected DFT methods for calculating the intermolecular interaction energies. The performance of the calculations depends strongly on the choice of functional and dispersion correction method. Neither combination of the functionals and the dispersion correction methods can reproduce well the CCSD(T) level interaction potentials of all the 11 complexes. The improvement of the functionals from GGA to hybrid GGA or meta GGA is not essential for improving the performance. The interaction potentials for the benzene and CF_4 dimers calculated by the dispersion corrected DFT methods are shown in Figure. The dispersion-corrected DFT potentials for hydrocarbons often well reproduce CCSD(T) calculations well, while those for molecules including heteroatoms often do not match well.

Keywords : Intermolecular interaction, Dispersion correction, DFT calculation, Hetero atom, Accuracy of calculation

種々の汎関数と Grimme の D2, D3, D3BJ 分散力補正法を使い 11 種の会合体の分子間相互作用ポテンシャルを計算し、計算精度を検討するために CCSD(T) 法で計算した相互作用ポテンシャルと比較した。計算精度は汎関数と分散力補正法の選択に強く依存した。どの汎関数と分散力補正を組み合わせても 11 種の会合体全ての CCSD(T) 法での相互作用ポテンシャルを良く再現することはできなかった。また、汎関数を GGA から hybrid GGA やメタ GGA に改良しても必ずしも CCSD(T) 計算との一致は改善しなかった。図のベンゼンのように炭化水素では多くの組み合わせが CCSD(T) 計算をよく再現したが、ヘテロ原子が入った CF_4 等の分子では再現の困難な場合がある。



Control of stacking patterns of two-dimensional molecular layers in hydrogen-bonded cocrystals composed of 2-pyrrolidone and anilic acids

([1]*Graduate School of Science, Kyoto University*, [2]*JASRI/SPring-8*, [3]*Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba*)
○Masaki Donoshita,[1] Yukihiro Yoshida,[1] Mikihiro Hayashi,[1] Ryuichi Ikeda,[1] Kunihisa Sugimoto,[2] Shogo Kawaguchi,[2] Yasuhisa Yamamura,[3] Kazuya Saito,[3] Hiroshi Kitagawa[1]
Keywords: Molecular Crystal; Layered Compound; Hydrogen Bond; Nuclear Magnetic Resonance

In two-dimensional (2D) layered compounds, the stacking pattern of layers plays an important role in determining the chemical and physical properties. Therefore, it is desired to establish the methodology of controlling the stacking patterns. Assemblies of organic molecules can be an ideal platform for such a study because of tunable intermolecular interactions with diverse directionalities and strengths. We have investigated the structural phase transitions of a cocrystal PyCA (**Fig. 1**) composed of 2-pyrrolidone (Py) and chloranilic acid (CA)[1]. The cocrystal consists of molecular layers (**Fig. 1b,c**) involving one-dimensional (1D) hydrogen-bonded (HB) tapes (**Fig. 1a**). In PyCA, the competition of various interlayer interactions such as π···π and lone pair···π as well as the out-of-plane molecular motion of Py plays a crucial role in structural phase transitions resulting in four kinds of different stacking patterns including metastable ones. In this study, we prepared halogen-substituted cocrystals (PyFA, PyBA, and PyIA) using appropriate anilic acids (FA, BA, and IA, **Fig. 1a**) and investigated the substitution effect on the stacking pattern of the 2D layers. Single-crystal X-ray diffraction (SCXRD) revealed that all the halogen-substituted cocrystals adopt the 2D layers identical to PyCA, although they showed no structural phase transition in 100-298 K. Based on the results of ^{35}Cl nuclear quadrupole resonance experiments and the calculation of intermolecular interactions in addition to the SCXRD results, the effect of halogen substitution is discussed in terms of changes in atomic polarizability and bulkiness of halogens as well as the motion of Py, and the phase transition behavior characteristic of PyCA is attributed to the balance of these factors.

1) M. Donoshita *et al. Chem. Commun.* **2018**, *54*, 8571.

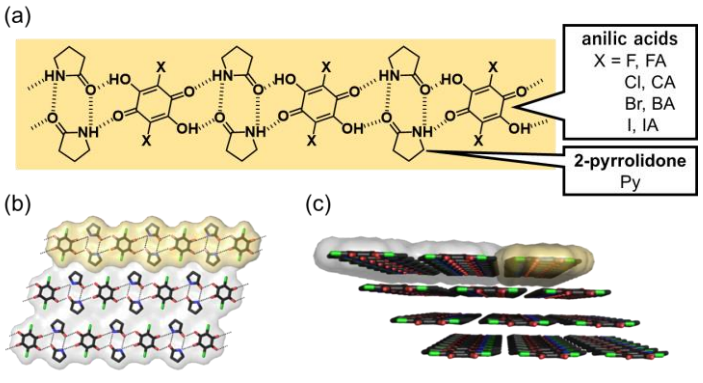


Figure 1. (a) 1D HB tape of cocrystals and (b) 2D assembly and (c) crystal structure of PyCA.

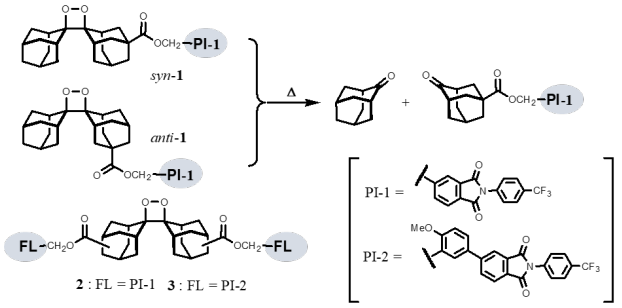
強発光蛍光団を連結したアダマンチリデンアダマンタン 1,2-ジオキセタンの結晶化学発光特性評価

（電通大[1]・東工大理学院[2]・自治医大医[3]・高エネ機構[4]）○松橋 千尋[1]・大山 滉永[2]・植草 秀裕[2]・佐藤 文菜[3]・一柳 光平[4]・牧 昌次郎[1]・平野 誉[1]
Crystalline-state chemiluminescence property of 1,2-dioxetanes conjugated with a strongly fluorescent chromophore ([1] *The University of Electro-Communications*, [2]*Tokyo Institute of Technology,* [3] *Jichi Medical University*, [4]*High Energy Accelerator Research Organization (KEK)*) ○Chihiro Matsuhashi[1], Hironaga Ohyama[2], Hidehiro Uekusa[2], Ayana Sato-Tomita[3], Kouhei Ichiyanagi[4], Shojiro Maki[1], Takashi Hirano[1]

As a “soft crystal” chemiluminescence (CL) system, we investigated the crystalline-state CL property of adamantylideneadamantane 1,2-dioxetane (Adox) derivatives conjugated with a fluorophore and found that the CL properties and kinetics were well correlated with the crystal structures. In this study, we prepared Adox derivatives with a strongly fluorescent chromophore and found that the luminescent properties of crystalline-state CL provide information on the reaction field in crystals. The reaction mechanism of the characteristic CL in crystals will be discussed.

Keywords :　Organic molecular crystal; Chemiluminescence; 1,2-Dioxetane; Fluorophore

ソフトクリスタル[1)]の性質を示す化学発光系構築のために、本研究ではアダマンチリデンアダマンタン-1,2-ジオキセタン（Adox）を化学励起部位に用い、アダマンタン骨格の 5 位に蛍光団を連結してエネルギー移動するように設計した誘導体を合成して結晶状態における化学発光特性を調査している。蛍光団としてフタルイミド PI-1[2)]を連結した Adox 誘導体 **1** では、*syn*-**1** と *anti*-**1** の異性体で対照的な結晶構造の違いを示し、この結晶構造の特徴が化学発光特性と反応性に反映することを見出した[3)]。更なる分子構造／結晶構造／発光特性の相関についての知見を得るため、PI-1 と蛍光性を強めた PI-2 を 2 個連結した誘導体 **2**,**3** に展開し、結晶化学発光特性を調査した結果、結晶内特有の化学発光特性や反応性、反応進行に伴う結晶内環境の変化に関する知見が得られた。これらの結晶内反応機構について議論する。



1) Kato, M.; Ito, H.; Hasegawa, M.; Ishii, K., *Chem. Eur. J.*, **2019**, *25*, 5105.
2) Nakayama, H.; Nishida, JI.; Takada, N.; Sato, H.; Yamashita, Y. *Chem Mater.*, **2012**, *24*, 671.
3) Matsuhashi, C.; Ueno, T.; Uekusa, H.; Sato-Tomita, A.; Ichiyanagi, K.; Maki, S.; Hirano, T. *Chem. Comm.,* **2020**, *56*, 3369.

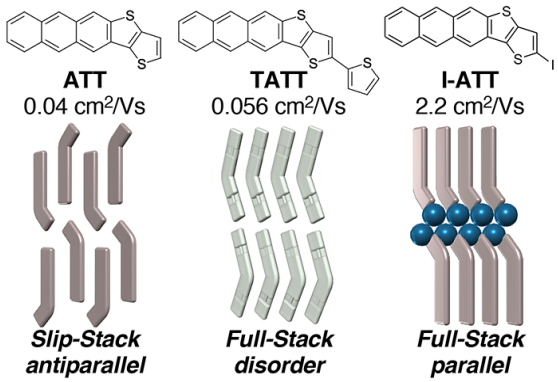
Control of Molecular Orientation in Organic Semiconductors Using Weak Iodine–Iodine Interactions

([1]*Graduate School of Science and Engineering, Yamagata University,* [2]*Graduate School of Organic Materials Science, Yamagata University*) ○ Amane Matsunaga,[1] Yuta Ogawa,[1] Daisuke Kumaki,[2] Shizuo Tokito,[2] Hiroshi Katagiri[1]

Keywords: Organic Field-Effect Transistor; Halogen-Halogen Interaction; Herringbone Structure; Thienoacene; Charge Transfer

Organic field-effect transistor (OFET) materials require high molecular orientation for efficient charge transport in thin films. In this study, we report the semiconductor characteristics of asymmetric thienoacene (ATT; anthra[2,3-*b*]thieno[2,3-*d*]thiophene) derivatives that exhibit both high solubility and high molecular orientation.[1] Herein, we systematically investigated the crystal structure changes and charge transport properties of asymmetric thienoacenes(ATT), the thienyl derivative (TATT), and the monoiodinated derivative (I-ATT)[2].

TATT and I-ATT were synthesized via the regioselective α-lithiation of ATT. OFET devices of I-ATT fabricated by drop-casting method showed higher p-type semiconductor characteristics than those of ATT and TATT (ATT: 0.04 cm^2/Vs, TATT: 0.056 cm^2/Vs, and ATT: 2.2 cm^2/Vs). Single crystal X-ray diffraction analysis revealed that ATT formed a slip-stack antiparallel structure and TATT formed a full-stack disorder structure with enhancement of molecular symmetry and dispersion force. In contrast, I-ATT formed a full-stack parallel structure with a large orbital overlapping. These results suggest that a weak iodine–iodine interaction as an intermolecular force stabilizes the molecular arrangement favorable for charge transport. Thin film X-ray diffraction, which was fabricated in the same manner as the OFET device, gave profiles characteristic of the in-plane herringbone structure and the end-on orientation in the out-of-plane direction in all molecules. The d-spacing calculated from the out-of-plane direction corresponded to one molecular length for ATT and TATT, and head-to-head dimers for I-ATT. These results indicate that the iodine–iodine interaction is effective for controlling molecular orientation in solution-processable OFET materials.



1) Y. Ogawa, *et al*., *ACS Appl. Mater. Interfaces* **2017**, *9*, 9902–9909.
2) A. Matsunaga, *et al.*, *J. Phys. Chem. Lett.* **2021**, *12*, 111–116.

Design of photo-functional soft crystals based on degree of protonation in the acid-base complexes

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

Keywords: Organic crystals; Multicolor fluorescence; Acid-base reaction; Stimuli response; Protonation

In terms of crystal engineering, there has been significant interest in differentiating salts and cocrystals, and where appropriate position of the proton in the continuum in the systems. It is generally accepted that ΔpK_a value (pK_a (protonated base) – pK_a (acid)) and the crystalline environment determine the extent of proton transfer. The pK_a value is greater than 4, a salt is expected to form and the pK_a value is less than -1 lead toward co-crystals forms. However, when ΔpK_a is in the range of $-1 < \Delta pK_a < 4$, the crystals result in molecular salt, cocrystal or disordered solid with partial proton transfer forms, and the location of the acidic proton depends on the specific crystal packing environment.

Here we report that the three states (salts/cocrystals/salt–cocrystal continuum) can be distinguished by solid–state photoluminescent color changes based on acid-base complexes consisting of a pyridine-modified pyrrlo[3,2-*b*]pyrrole derivative (**1**)[1] which shows intramolecular charge–transfer (ICT) character and organic acids such as phenol, carboxylic acid and sulfonic acid derivatives (**a**-**h**) (**Figure 1**). The results proved that the multicolor photoluminescent properties were observed from blue, green, and yellow depends on the ΔpK_a value between the **1** and the organic acids (**a**–**h**). In addition, the salt–cocrystal continuum ($-1 < \Delta pK_a < 4$) showed vapochromism /vapofluorochromism against CH_2Cl_2[2]. Single crystal neutron diffraction measurements supported that the optical property modulation resulted from difference of the extent of proton transfer to the pyridyl moiety of the dye by inclusion and desorption of CH_2Cl_2.

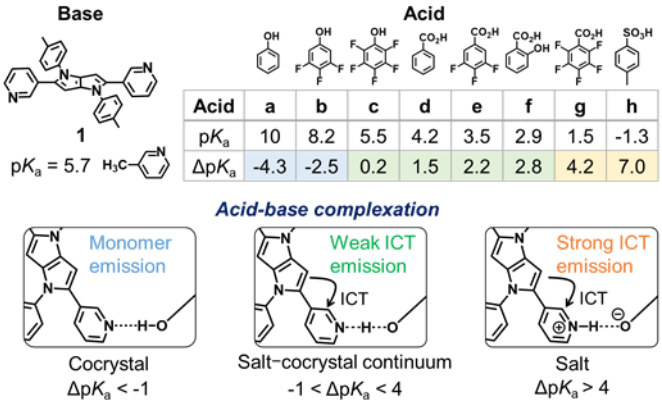


Figure 1. Chemical structure of two-component crystal motifs and suggested mechanism for photofunction modulation by increasing the ICT strength.

1) Y. M. Poronik, L. M. Mazur, M. Samoc, D. Jacquemin and D. T. Gryko, *J. Mater. Chem. C*, **2017**, *5*, 2620. 2) Y. Yano, T. Ono, S. Hatanaka, D. T. Gryko and Y. Hisaeda, *J. Mater. Chem. C*, **2019**, *7*, 8847.

Development of Thermo-responsive Solid-State Luminescent Materials Utilizing Intermolecular Interactions between Carboranes and Nitrogen Atoms

(*Graduate School of Engineering, Kyoto University*)
○Junki Ochi, Kazuo Tanaka
Keywords: Carborane; Solid state emission; Thermochromic property

o-Carborane is an icosahedral cluster composed of ten boron and two carbon atoms with three-center two-electron (3c2e) bonds. Its three-dimensionally delocalized skeletal electrons through 3c2e bonds can be an origin of various unique luminescent properties.[1] Moreover, the electronically polarized structure has the potential to form electrostatic interactions and therefore to be a versatile scaffold to develop functional materials (Fig. 1).

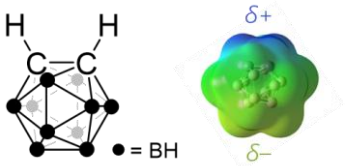


Fig. 1 Chemical structure of *o*-carborane (left). Electrostatic potential map of *o*-carborane (right).

In this research, we synthesized three types of acridine-modified compounds **Ac-M1**, **Ac-E1**, and **Ac-E2** (Fig. 2). From single-crystal X-ray analyses, it was revealed that the nitrogen-containing acridine unit induced intermolecular CH···N interactions. All three compounds formed a dimer structure and each dimer was π-stacked via acridine moieties (Fig. 3). They showed structureless broad emission bands with long emission lifetimes from the crystalline samples. After the series of measurements under various conditions, we attributed those broad emission bands to solid-state excimer emission derived from the π-stacking in the crystalline state. In addition, crystalline acridine-modified *o*-carboranes showed thermochromic luminescence (Fig. 3). The fluorescence band shifted continuously depending on the temperature, probably because the degree of π-stacking could be gradually changed. These results strongly indicate that CH···N interaction-induced dimer formation should be a powerful tool for designing thermochromic luminescence materials.

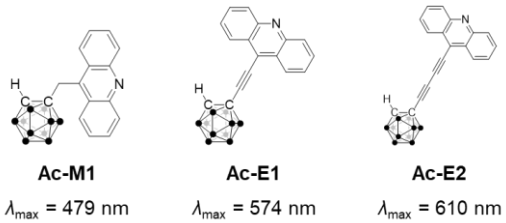


Fig. 2 Chemical structure and fluorescence wavelengths of acridine-modified *o*-carboranes.

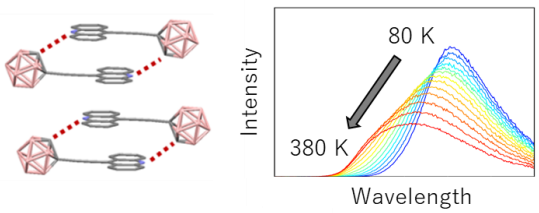


Fig. 3 Single-crystal X-ray structure (left) and thermochromic luminescence (right) of **Ac-E1**.

1) Tanaka, K. *et al. Angew. Chem. Int. Ed.*, **2019**, *59*, 9841.

熱および機械刺激応答型ターンオンりん光を示すチエニルジケトン結晶

（阪大院理）○谷 洋介・小川琢治
Thermo- and Mechanoresponsive Turn-On Phosphorescence of Thienyl Diketone Crystal (*Graduate School of Science, Osaka University*) ○Yosuke Tani, Takuji Ogawa

Phosphorescence is a spin-forbidden emission from triplet excitons. Room-temperature phosphorescence (RTP) of metal-free organic molecules has gained significant interest and has been achieved mainly in the rigid crystalline state.[1)] Recently, we found thienyl diketone derivatives exhibiting RTP in amorphous states, and reported their mechanoresponsive behavior.[2)] Herein, we report RTP that is brighter under looser environment. The crystal of a thienyl diketone was non-emissive, and application of mechanical stimuli turned the solid emissive. Moreover, melting the solid and cooling to room temperature afforded supercooled liquid, which exhibited higher phosphorescence quantum yield at room temperature under air.
Keywords : Room-Temperature Phosphorescence; Supercooled Liquid; Organic Crystals; Stimuli-Responsiveness; Thermoresponsive Materials

りん光は三重項励起子の発光であり、スピン反転を伴う禁制遷移である。イリジウムなどの貴金属を含まない有機分子の室温りん光は特に困難な課題だが、近年、結晶など剛直な環境に分子をおくことで実現可能であることが示されてきた[1)]。一方我々は、チエニルジケトンがアモルファス固体でも効率よく室温りん光を示す優れたりん光色素骨格であることを見出し、その機械刺激応答性について報告してきた[2)]。

本研究では、環境が柔軟になるほど強く発光する有機りん光分子の開発に成功した（図 1）。トリエチルシリル基を有するチエニルジケトン誘導体を合成したところ、その結晶は非発光性であった。この結晶は、機械刺激を加えアモルファス化するとりん光性を獲得する Turn-on 応答を示した。りん光強度は機械刺激を加えるほど増大し、室温大気下でのりん光量子収率は最大 4.5%となった。さらに、融点である 64 °C 以上に加熱し融解させ室温まで放冷すると過冷却液体が得られ、量子収率は 5.2%まで向上した。すなわち、同分子は熱刺激に応答した Turn-on りん光も示すことがわかった。発表では過冷却液体の量子収率向上の要因を含め詳細に議論する。

図 1 室温大気下での刺激応答型 Turn-on りん光（左：可視光下、右：UV 照射下）。

1) S. Hirata *Adv. Opt. Mater.* **2017**, *5*, 1700116. 2) a) Y. Tani, M. Terasaki, M. Komura, T. Ogawa, *J. Mater. Chem. C* **2019**, *7*, 11926.; b) Y. Tani, M. Komura, T. Ogawa, *Chem. Commun.* **2020**, *56*, 6810.

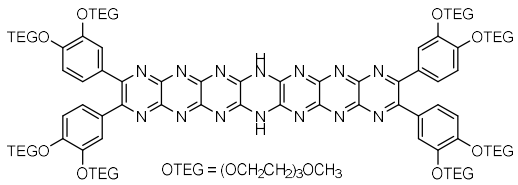
Synthesis and Photophysical Properties of Extended Pyrazinacenes

([1]*Department of Applied Chemistry, Shibaura Institute of Technology,* [2]*National Institute of Materials Science,* [3]*Ochanomizu University*) ○Gary James Richards[1,2], Jonathan Hill[2], Shinji Yamada[3], Katsuhiko Ariga[2], Akiko Hori[1]

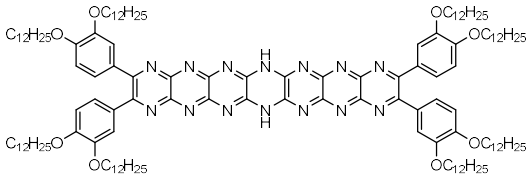
Keywords: Acenes, Pyrazinacenes, Near Infrared Emission, Fluorescence, Amphiprotism

Pyrazinacenes consist of rectilinearly fused 1,4-pyrazine units and can be considered as highly nitrogenated analogues of conventional acenes. Higher analogues tend to contain a single reduced dihydropyrazine unit which often improves their photoluminescence quantum yields when compared to their fully oxidized congeners.

In this presentation, we will discuss our investigations into higher pyrazinacenes containing 6 and 7 consecutively fused pyrazine rings. We have previously demonstrated that higher pyrazinacenes can exhibit highly efficient deep red and near infrared (NIR) photoluminescence.[1] Here we show how the solubility of these compounds can be tuned by addition of different alkoxy substituents to give derivatives that are soluble in solvents with a wide range of polarity from hexane to water. In addition, we describe the synthesis of a previously unreported dodecaazahexacene containing six consecutively fused pyrazine rings. We will discuss the photophysical properties of these compounds in different solvents as well as their amphiprotic properties.



WATER SOLUBLE



HEXANE SOLUBLE

1) G. J. Richards *et al*, *J. Am. Chem. Soc*., **2019**, 141, *50*, 19570-15974.

[A18-4pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair:Takashi Koike, Shinji Yamada
Mon. Mar 22, 2021 1:00 PM - 3:40 PM Room 18 (Online Meeting)

[A18-4pm-01] Mechanoredox C-H functionalization reactions

○YADONG PANG[2], JOO WON LEE[1], KOJI KUBOTA[1,2], HAJIME ITO[1,2] (1. Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

1:00 PM - 1:20 PM

[A18-4pm-02] Substituent effects on gas-phase stabilities of 2-phenyl-1,3-dehydroadamantane-5,7-diyliums

○Kazuhide Nakata[1], Mizue Fujio[2] (1. Hosei University, 2. Kyushu University)

1:20 PM - 1:40 PM

[A18-4pm-05] Photocatalytic reductive cleavage C-O bond of ether using carbazole catalyst

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

2:20 PM - 2:40 PM

[A18-4pm-06] Photocarboxylation of aromatic amine derivatives by fixing CO_2 driven via excited-state hydrogen detachment

○Akinobu Nakada[1,2], Kanae Abe[1], Ho-Chol Chang[1] (1. Chuo University, 2. PRESTO/JST)

2:40 PM - 3:00 PM

[A18-4pm-07] Synthesis of Propargyl Silanes from Propargyl Pivalates via C-O Bond Cleavage by Ca-Promoted Reductive Silylation

○Tianyuan Zhang[1], Hirofumi Maekawa[1] (1. Nagaoka Univ. of Tech.)

3:00 PM - 3:20 PM

[A18-4pm-08] Electrolyte-coordination-induced electrochemical multiple electron oxidation of 2,5-diarylthiophenes and following unprecedented dimerization reaction to give sulfonium salt

○Naoki Shida[1,2], Takuma Maekawa[2], Ikuyoshi Tomita[2], Shinsuke Inagi[2] (1. Yokohama National University, 2. Tokyo Institute of Technology)

3:20 PM - 3:40 PM

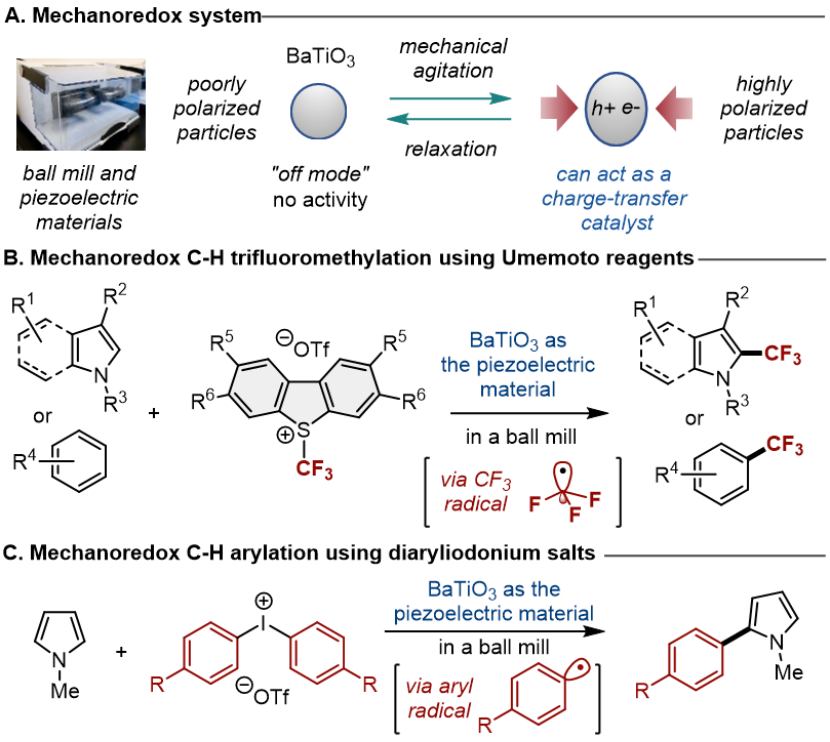
日本化学会 第101春季年会 (2021)

Mechanoredox C–H functionalization reactions

([1]*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*) ○Yadong Pang,[2] Joo Won Lee,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Keywords: ball milling; piezoelectric material; redox reaction; trifluoromethylation; arylation

Recently, we reported that agitation of piezoelectric materials *via* ball milling generates a temporary electrochemical potential that can reduce aryl diazonium salts to give the corresponding aryl radicals.[1] This mechanoredox system can be applied to arylation and borylation reactions under mechanochemical conditions. This approach may complement existing photoredox transformations because mechanoredox reactions can be carried out without the use of large amounts of dry and degassed organic solvents in air, and do not require special operating conditions. In this study, we have developed a C–H trifluoromethylation of aromatic compounds using a mechanoredox system.[2] This reaction presumably proceeds *via* the formation of trifluoromethyl radical, which is generated by a piezoelectric effect-induced single electron reduction of the Umemoto reagents, to yield trifluoromethylated aromatic compounds in good yield with high regioselectivity. Furthermore, we found that this mechanoredox system can be applied to a C–H arylation of aromatic compounds with diaryliodonium salts.



1) K. Kubota, Y. Pang, A. Miura, H. Ito, *Science* **2019**, *366*, 1500. 2) Y. Pang, J. W. Lee, K. Kubota, H. Ito, *Angew. Chem. Int. Ed.* **2019**, 59, 22570.

日本化学会 第101春季年会 (2021)

2-フェニル-1,3-デヒドロアダマンタン-5,7-ジイリウムの気相安定性に及ぼす置換基効果

（法大自然科学セ[1]・九大先導研[2]）○中田 和秀[1]・藤尾瑞枝[2]

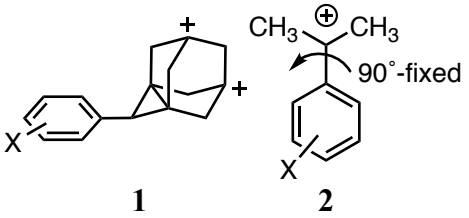
Substituent Effects on Gas-Phase Stabilities of 2-Phenyl-1,3-dehydroadamantane-5,7-diyliums

([1]*Science Research Center, Hosei University*, [2]*IMCE, Kyushu University*) ○ Kazuhide Nakata,[1] Mizue Fujio[2]

In the previous work, we computationally determined substituent effects on stabilities of dications that have one cationic center at the benzylic position and compared them one another. It was suggested that substituent effects of highly electron-deficient dications can be correlated by an extended Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + s^+\Delta\bar{\sigma}_s^+)$) (1) implementing the third term. In this research, substituent effects on the stabilities of 2-phenyl-1,3-dehydroadamantane-5,7-diyliums (**1**) were computationally determined to examine the validity of Eq. (1). Obtained substituent effects were compared with those of α,α-dimethylbenzyl cations (**2**) having 90˚-fixed dihedral-angle between the cationic side chain and the benzene ring that have been used as a reference system of σ^0. In the comparison, plots of *meta*-EDGs gave an excellent linear correlation with the correlation coefficient of 0.998. While plots of *para*-EDGs are on the correlation line, those of EWGs are deviated above the correlation line. These facts reveal that a certain amount of the electronic effects quantified by the third term of Eq. (1) are operating on the stabilities of **1** although the through-resonance effects are negligible. Independent change of these electronic effects shows the validity of Eq. (1).

Keywords : Dication; Gas-Phase Stability; Substituent Effect; DFT calculation; Extended Yukawa-Tsuno Equation

前回、ベンジル位にカチオン中心を持つ種々のジカチオンについて、気相安定性に及ぼす置換基効果を計算化学によって決定し、互いに比較した。その結果、高度に電子不足のジカチオンの置換基効果は、新たな電子効果を相関する第三項を導入した拡張湯川−都野式（$-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + s^+\Delta\bar{\sigma}_s^+)$）(1)によって精度良く相関されることが示唆された。本研究では、式(1)の妥当性を検証する目的で、2-フェニル-1,3-デヒドロアダマンタン-5,7-ジイリウム(**1**)を選択し、置換基効果を計算化学によって検討した。得られた **1** の置換基効果を、σ^0 基準系である側鎖とベンゼン環のなす角度を 90˚に固定したα,α-ジメチルベンジルカチオン(**2**)の置換基効果と比較した。全てのプロットでは劣った直線相関（*R*=0.984）を示す一方で、*meta*-EDG のプロットは優れた直線相関（*R*=0.998）を与えた。また、*para*–R 基のプロットは、この相関線上に位置する一方、EWG のプロットは相関線から上方への片寄りを示した。この事実は、**1** の安定性に直接共鳴効果は寄与しない一方で、第三の電子効果が寄与していることを示す。両効果は種々のジカチオンで互いに独立した値を取ることが明らかになり、式(1)の妥当性が示された。



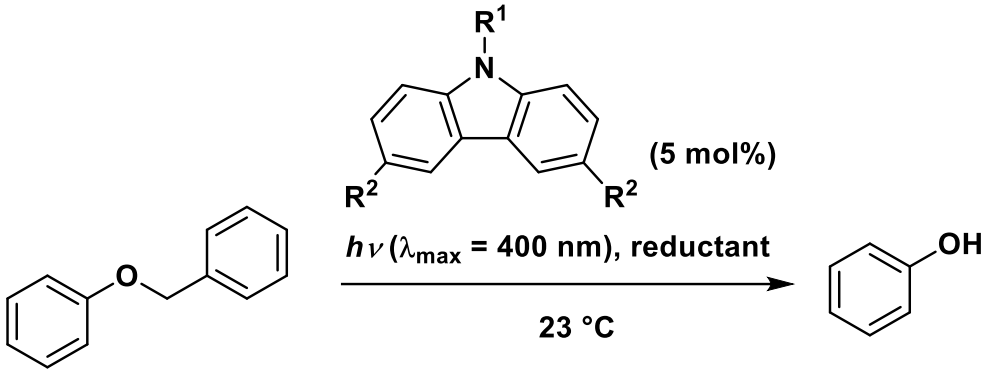
1 **2**

カルバゾール光触媒を用いたエーテル C-O 結合の還元反応

（神戸大院理）○藪田 達志・林 昌彦・松原 亮介
Photocatalytic reductive cleavage C-O bond of ether using carbazole catalyst (*Faculty of Science, Kobe University*) ○Tatsushi Yabuta, Masahiko Hayashi, Ryosuke Matsubara

The ether C-O bond is abundant functional group in natural and synthetic molecules. Thus, methods to activate the relatively stable ether bonds and convert them to other functional groups are desirable. However, the examples to transform the ether bond are rare due to the stability under various conditions. We have developed carbazole-based photocatalyst with high reducing ability and reported the reductive cleavage of C-Cl bond to form C-H and C-C bonds. Herein, we report the photochemical reduction of relatively stable ether C-O bond using carbazole photocatalyst with high reducing ability.
Keywords : Organic photocatalyst, Carbazole, Aryl alkyl ether, Reduction, Single electron transfer

エーテル結合は天然資源や合成化学品に多く含まれる結合であり合成も容易であるため、合成原料としての潜在的価値が高い。しかし、エーテル結合は安定で強固な結合であるため、その変換反応の例は乏しい。当研究室では高い還元能力を持つカルバゾール光触媒の開発を行っており、以前 C-Cl 結合などの不活性な結合の変換反応を報告している [1)]。今回はカルバゾール光触媒を用いて安定なエーテル結合の効率的な還元的切断反応を達成したことを報告する [2)]。



1) Matsubara, R.; Yabuta, T.; Idros, U. M.; Hayashi, M.; Ema, F.; Kobori, Y.; Sakata, K. *J. Org. Chem.* **2018**, *83*, 9381-9390. 2) Yabuta, T.; Hayashi, M.; Matsubara, R. *J. Org. Chem.* in print (doi: 10.1021/acs.joc.0c02663)

励起状態水素脱離により駆動する芳香族アミン誘導体の CO_2 光固定型カルボキシル化反応

(中大理工[1]・JST さきがけ[2]) ○中田 明伸[1,2]・阿部 叶[1]・張 浩徹[1]
Photocarboxylation of aromatic amine derivatives by fixing CO_2 driven via excited-state hydrogen detachment ([1]*Faculty of Science and Engineering, Chuo University*, [2]*PRESTO/JST*)
○Akinobu Nakada,[1,2] Kanae Abe,[1] Ho-Chol Chang[1]

Exploring new types of photochemical reactions is of great interest in the field of synthetic chemistry. Although excited-state hydrogen detachment (ESHD) represents a promising prospective template for additive-free photochemical reactions, applications of ESHD in a synthetic context remains scarce. Herein, we applied this photochemical for regioselective aromatic C(sp^2)–H photocarboxylation. In these reactions, the selectivity can be controlled by judicious choice of the functional groups.

Keywords : CO_2 fixation, Photocarboxylation, Excited-state hydrogen detachment, Hydrogen radical, Aromatic amine

光エネルギーにより進行する有機反応の開拓は、エネルギーや環境負荷低減の観点から重要である。例えば、環境負荷が懸念される一方で重要な C1 炭素源となり得る CO_2 を活用した光カルボキシル化反応において、芳香族 C(sp^2)–H 結合の直接的光カルボキシル化の例はなく新たな光反応の適用が不可欠である (Fig. 1)。本反応では、芳香族アミン誘導体の励起状態水素脱離(ESHD)[1]により駆動する芳香族 C(sp^2)–H 結合の CO_2 による光カルボキシル化 (Fig. 1e) について報告する[2]。

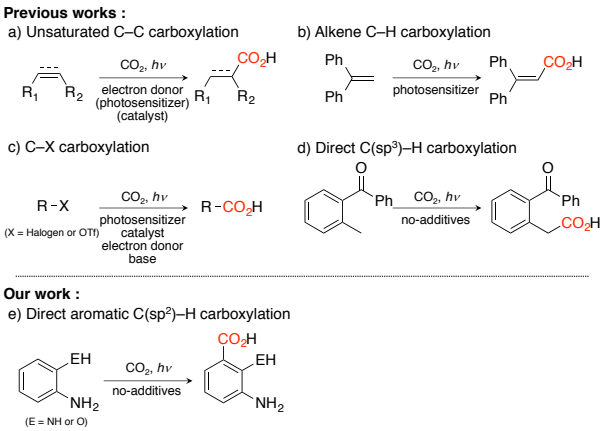


Fig. 1 (a-d) Previously reported and (e) our photocarboxylation using CO_2.

o-アミノフェノール (*o*-apH_2) に CO_2 下、300 nm の光照射を行うと、OH 基の *o* 位隣接位にカルボキシル基が導入された 3-アミノ-2-ヒドロキシ安息香酸 (3A2H) が生成した。本光カルボキシル化反応は、金属触媒、還元剤や塩基などの添加物を一切必要としない。さらに、基質の置換基-EH (NH_2, OH; Fig. 1e)の種類に依存してカルボキシル化の位置選択性を変調でき、アミノフェノールのアミノ基、ヒドロキシ基の位置によって反応効率が大幅に変化することが明らかとなった。発表では、これら反応性に与える置換基効果について報告する。

1) A. Nakada, T. Koike, T. Matsumoto, H.-C. Chang, *Chem. Commun.* **2020**, *56*, 15414.
2) K. Abe, A. Nakada, T. Matsumoto, D. Uchijo, H. Mori, H.-C. Chang, *J. Org. Chem.* **2021**, *86*, 959.

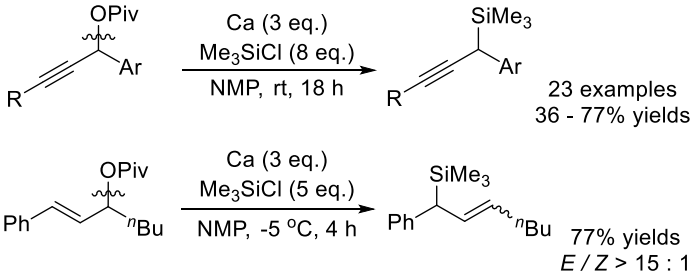
Synthesis of Propargyl Silanes from Propargyl Pivalates via C-O Bond Cleavage by Ca-Promoted Reductive Silylation

(*Nagaoka University of Technology*[1]) ○ Tianyuan Zhang,[1] Hirofumi Maekawa[1]

Keywords: Electron Transfer Reaction; Calcium; Reductive Silylation; Propargyl Pivalates; Propargyl Silanes

Cross-coupling reactions via C-O bond cleavage have been utilized as a versatile yet powerful method for forming complex organic molecules. Many efforts have been undertaken on silylation via less reactive C-O bond cleavage to date.[1)] However, the development of useful silylation strategies via less reactive C-O bond cleavage, especially silylation of less reported C(sp3)-O electrophiles under catalyst-free conditions, has remained a challenge. We previously reported the reductive silylation of activated vinyl triflates with chlorotrimethylsilane by electron transfer from magnesium.[2)] With our continuous interest in organosilicon chemistry, we herein present our efforts towards propargyl and allyl silanes from the readily accessible propargyl and allyl pivalates via calcium-promoted C(sp3)-O bond cleavage.

Calcium is a vastly abundant, inexpensive, air-stable, and commercially available metal. The use of calcium metal for reductive coupling reactions is unexplored to date. In this study, we commenced our study by choosing propargyl pivalate prepared from 1-hexyne, benzaldehyde, and pivaloyl chloride as the model substrate. As a result, the reductive coupling reaction of propargyl pivalate with chlorotrimethylsilane in the presence of calcium granules gave a propargyl silane in 77% isolated yield. The optimized reaction conditions were fully studied and applied to diverse propargyl pivalates to give a series of propargyl silanes in 36-77% yields. In addition, the reaction of aromatic allyl pivalate also gave the corresponding allyl silane in good yields via allylic arrangement. This reaction provides an efficient approach to synthesize various propargyl and allyl silanes with good yields under mild reaction conditions. Reaction mechanism will be also presented in detail.



1) a) C. Zarate, R. Martin, *J. Am. Chem. Soc.* **2014**, *136,* 2236. b) J. Zhang, Y. Zhang, S. Geng, S. Chen, Z. Liu, X. Zeng, Y. He, Z. Feng, *Org. Lett.* **2020**, *22*, 2669. 2) H. Maekawa, K. Noda, K. Kuramochi, T. Zhang, *Org. Lett.* **2018**, *20*, 1953.

電解質配位に基づく 2,5-ジアリールチオフェンの電気化学的多電子酸化とそれに続く二量化反応によるスルホニウム塩形成

(横国大院工 [1]・東工大物質理工 [2]) ○信田 尚毅 [1,2]・前川 拓磨 [2]・冨田 育義 [2]・稲木 信介 [2]

Electrolyte-coordination-induced electrochemical multiple electron oxidation of 2,5-diarylthiophenes and following unprecedented dimerization reaction to give sulfonium salt

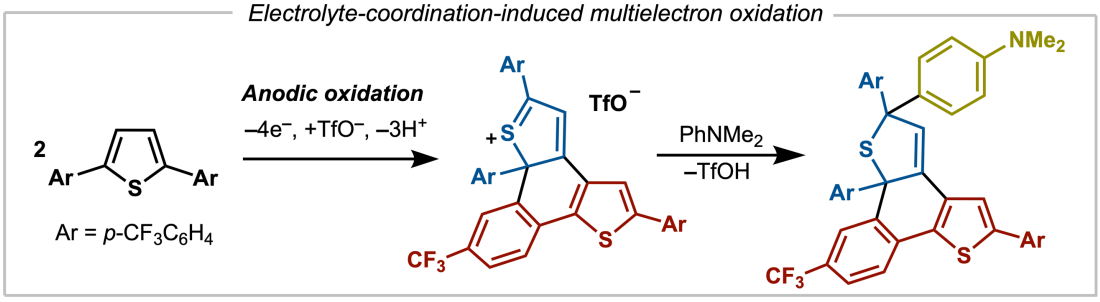
([1]*Department of Chemistry and Life Science, Yokohama National University*, [2]*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Naoki Shida,[1,2] Takuma Maekawa,[2] Ikuyoshi Tomita,[2] Shinsuke Inagi[2]

We report that the electrochemical redox behavior of 2,5-diarylthiophene varies significantly depending on the coordination of the electrolyte. We have found that the coordination of the electrolyte alters the number of electrons in the oxidation of 2,5-diarylthiophene. It was also found that the species generated by the multiple electron transfer showed a unique reactivity, and proceeded to an unprecedented dimerization reaction to give S(IV)-species.

Keywords : Electrosynthesis; Thiophene; Oxidation reaction; Conjugated molecule; Sulfonium salt

16 属元素を含む芳香族化合物であるカルコゲノフェンは電気化学的な酸化が容易であり、様々な分子変換が報告されている。一方、共役によりカチオン性やラジカルが安定化するπ拡張カルコゲノフェン類を用いる場合、電子移動反応を利用した合成反応は本質的に困難となる。一方最近、我々はπ拡張テルロフェン類の酸化において電解液の設計による1電子/2電子酸化のスイッチングを報告している[1]。

本研究では、2,5-ジアリールチオフェンの電気化学的酸化還元挙動が電解質の配位により変化することを新たに見出したので報告する。具体的には、電解質の配位が2,5-ジアリールチオフェンの電解酸化過程における反応電子数を変化させることを明らかとした。1電子移動により生じたラジカルカチオンが安定化し反応性を示さなかった一方で、配位により誘起される多電子移動により発生した化学種においてはこれまでに報告例のない二量化反応が進行し、S(IV)を含む塩を与えることを見出した。さらに、このS(IV)化合物の反応性についても併せて報告する。



1) N. Shida, H. Nishiyama, F. Zheng, S. Ye, D. S. Seferos, I. Tomita, S. Inagi, *Commun. Chem.* **2019**, *2*, 124.

[A11-4pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair:Koji Hirano, Akihiro Orita
Mon. Mar 22, 2021 1:00 PM - 3:20 PM Room 11 (Online Meeting)

[A11-4pm-01] Study of the mechanism of selective recognition of p-*tert*-butylcalix[4]thiacrown-5 for organic mercury(II) compounds

○Tatsuya Takimoto[1], Yuu Hashimoto[1], Gen Inoue[1], kazuhito Hioki[1], Hideaki Sasaki[1] (1. Kobegakuin University)

1:00 PM - 1:20 PM

[A11-4pm-02] One-pot enantiodivergent synthesis of axially chiral biaryls using organocatalyst

○Seitaro Koshino[1], Tohru Taniguchi[2], Kenji Monde[2], Eunsang Kwon[1], Yujiro Hayashi[1] (1. Tohoku University,Graduate School of Science , 2. Hokkaido University, FrontierResearch Center of Advanced Material andLife Science Faculty of Advanced Life Science)

1:20 PM - 1:40 PM

[A11-4pm-04] Synthesis of Benzophosphole Derivatives via Phosphenium Dication Mediated Sequential Bond Forming Reaction

○Kazutoshi Nishimura[1], Koji Hirano[1], Masahiro Miura[1] (1. Graduate School of Engineering, Osaka University)

2:00 PM - 2:20 PM

[A11-4pm-05] Dearomative Activation of Fused Aromatic Compounds toward Achieving Regioselective Annulative π-Extension (APEX)

○Wataru Matsuoka[1], Hideto Ito[1], David Sarlah[3], Kenichiro Itami[1,2] (1. Nagoya Univ., 2. Institute of Transformative Bio-Molecules, 3. University of Illinois)

2:20 PM - 2:40 PM

[A11-4pm-06] Synthesis and Properties of a New Element-Substituted Pentalene Derivative

○Junki Kashida[1], Yoshiaki Shoji[1], Yasuhiro Ikabata[2], Hideo Taka[3], Hayato Sakai[4], Taku Hasobe[4], Hiromi Nakai[2], Takanori Fukushima[1] (1. CLS, Tokyo Tech, 2. Facul. Sci. and Eng., Waseda Univ., 3. Konica Minolta, 4. Facul. Sci. and Technol., Keio Univ.)

2:40 PM - 3:00 PM

[A11-4pm-07] Base- and Process-Controlled Regiodivergent [4+2] Benzannulation of Phosphoryl Ynamine

○Yasuhiro Okuda[1], Kazunori Masuda[1], Nobuyuki Akagi[1], Akihiro Orita[1] (1. Fac. of Eng., Okayama Univ. of Sci.)

3:00 PM - 3:20 PM

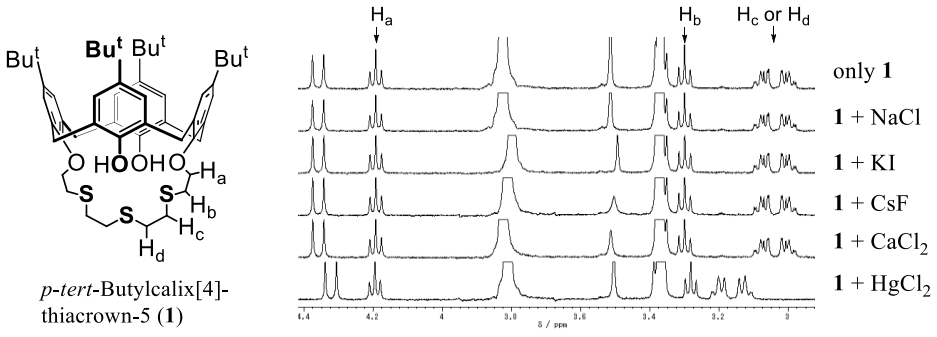
Study of the Mechanism of Selective Recognition of *p-tert*-Butylcalix[4]thiacrown-5 for Organic Mercury(II) Compounds

(*Faculty of Pharmaceutical Sciences, Kobe Gakuin University*) ○Tatsuya Takimoto, Yuu Hashimoto, Gen Inoue, Kazuhito Hioki, Hideaki Sasaki

Keywords: *p-tert*-Butylcalix[4]thiacrown-5; Selective Trapping of Organic Mercury(II) Compounds; ^{1}H-NMR Titration; Binding Constant; Computational Simulation

We have synthesized calix[4]thiacrown derivatives[1] and investigated their recognition abilities to mercury(II) picrate dissolved in water solution by solid-liquid absorption experiment.[2] To research more easily the abilities, the behavior of ^{1}H-NMR chemical shifts of the thiacrown moieties in the coexistence of ion species is followed at present.[1] In this study, we investigated the affinity of the thiacrown moiety of *p-tert*-Butylcalix[4]-thiacrown-5 (**1**) to alkali, alkaline-earth metal, and some mercury(II) ions (Fig. 1). In addition, the binding constants of **1** to mercury(II) compounds, $HgCl_2$, $HgBr_2$, and $Hg(CH_3COO)_2$ were estimated. Finally, the recognition ability of **1** for mercury(II) compounds was discussed by using computational simulation.

As shown Fig. 1, the affinity of the thiacrown moiety of **1** was investigated to some inorganic compounds, NaCl, KCl, $CsCl_2$, $CaCl_2$, $HgCl_2$ in ^{1}H-NMR study. In the presence of the only $HgCl_2$, some chemical shifts of the thiacrown moiety of **1** moved into the low magnetic field. Furthermore, the binding constants were estimated to **1**-mercury(II) complexes using ^{1}H-NMR titration. The calix[4]thiacrown exhibited the highest affinity to $Hg(CH_3COO)_2$ among the three compounds, and the binding constant was 6.3 x 10^4 M^{-1}. That shows the calix[4]thiacrown trapped organic mercury(II) compounds specifically. The reason for the selective affinity of **1** to ones was discussed by the conformations predicted from the ^{1}H-NMR spectral analysis and computational simulation of **1**-mercury(II) complexes.



p-tert-Butylcalix[4]-thiacrown-5 (**1**)

Figure 1. ^{1}H-NMR spectra of **1** in the presence of various inorganic compounds.

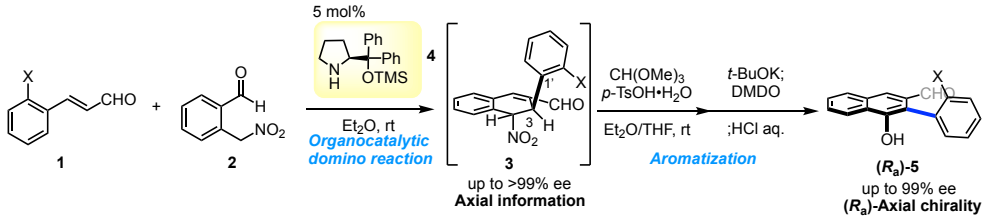
1) T. Takimoto, H. Tsue, H. Takahashi, *Heterocycles*, **2014**, *88*, 911. 2) T. Takimoto, H. Tsue, R. Tamura, H. Sasaki, *Heterocycles*, **2015**, *90*, 842.

One-pot enantiodivergent synthesis of axially chiral biaryls using organocatalyst

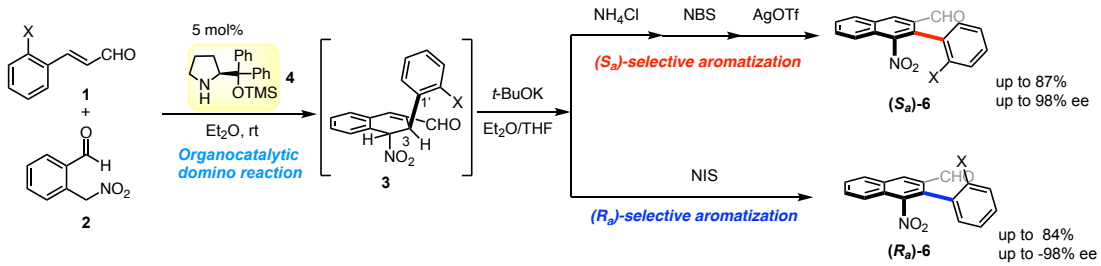
([1]*Graduate School of Science, Tohoku University*, [2]*Faculty of Advanced Life Science, Hokkaido University*) ○Seitaro Koshino,[1] Tohru Taniguchi,[2] Kenji Monde,[2] Eunsang Kwon,[1] Yujiro Hayashi[1]

Keywords: Axial chirality; Enantioselective synthesis; Organocatalyst; One-pot;

Axially chiral biaryls have broad utility for not only chiral ligands and organocatalysts, but also bioactive molecules in nature. Thus, it is important to develop a new methodology for the enantioselective construction of axially chiral molecules. We have already reported that axially chiral biaryl **5** was obtained with excellent enantioselectivity and complete axial inversion by removal of the central chirality from the enantio-enriched dihydronaphthalene **3**,[1)] which was synthesized as a single axial conformer from nitroaldehyde **2** and unsaturated aldehyde **1** using organocatalyst **4**.[2)] In this presentation, we will report a one-pot enantiodivergent synthesis of axially chiral biaryls using a catalytic amount of the chiral source.



The organocatalyst mediated domino Michael/aldol reaction afforded the enantio-enriched dihydronaphthalene **3**, which was converted to axially chiral biaryl **(*S*$_a$)-6** with excellent enantioselectivity by sequential treatment of *t*-BuOK/NH_4Cl/NBS/AgOTf in one-pot. On the other hand, the treating of **3** with *t*-BuOK/NIS afforded **(*R*$_a$)-6** with excellent enantioselectivity in one-pot. These axially chiral compound **6** were useful as a new chiral building block and could be transformed into other axially chiral biaryls without losing the enantiopurity. The reaction mechanism of enantiodivergence is also investigated by isolation of intermediates and investigation of their reactivities. The plausible reaction mechanism will be proposed.



1) D. Enders, C. Wang, J. W. Bats, *Synlett,* **2009**, *11*, 1777.

2) S. Koshino, A. Takikawa, K. Ishida, T. Taniguchi, K. Monde, E. Kwon, S. Umemiya, Y. Hayashi, *Chem. Eur. J.* **2020**, *26*, 4524.

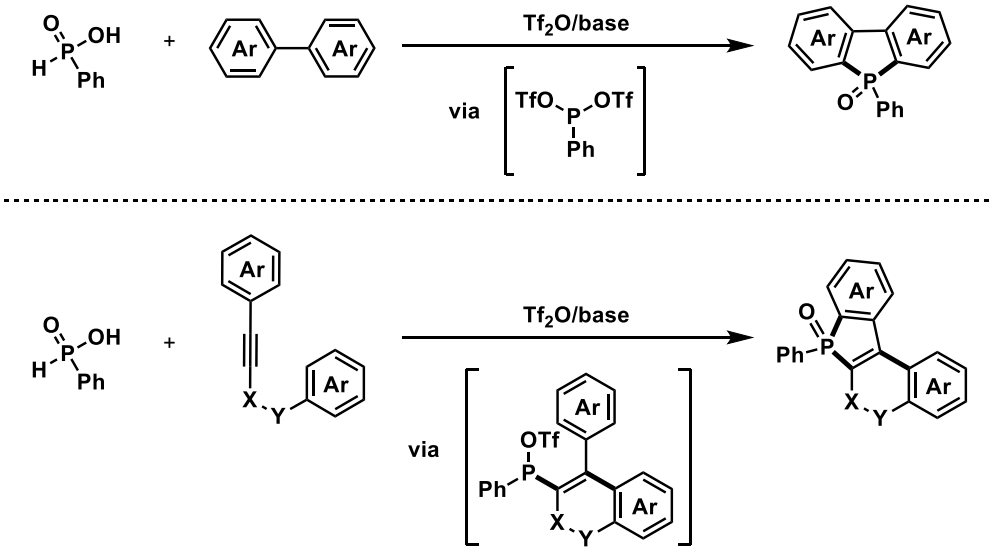
Synthesis of Benzophosphole Derivatives via Phosphenium Dication Mediated Sequential Bond Forming Reaction

(Graduate School of Engineering, Osaka University) ○Kazutoshi Nishimura, Koji Hirano, Masahiro Miura

Keywords: Phosphenium dications; Dibenzophospholes; Benzophospholes; C-P bond formation; C-C bond formation

Dibenzophosphole derivatives have now received significant attention in various fields of organic chemistry because of their unique physical, optical, and electronic properties, as exemplified by impressive application to photovoltaic cells. However, the reported synthetic protocols still suffer from tedious multistep procedures and use of unstable and toxic starting materials/reagents, and low reaction efficiency. On the other hand, we recently developed the unique method for generation of highly reactive phosphenium cations from readily available and easy-to-handle secondary phosphine oxides and its application to several new C–P bond forming reactions.[1]

Herein, we report one-step synthesis of dibenzophospholes from simple biaryls and phosphinic acids by simultaneous C–P bond formation via phosphenium dication equivalents.[2] The synthesis of benzophospholes from aryl alkynes and phosphenium dications via sequential C–P/C–C bond formation is also described.



1) a) Y. Unoh, K. Hirano, M. Miura, *J. Am. Chem. Soc.* **2017**, *139*, 6106.
b) K. Nishimura, Y. Unoh, K. Hirano, M. Miura, *Chem. Eur. J.* **2018**, *24*, 13089.
c) K. Nishimura, K. Hirano, M. Miura, *Org. Lett.* **2019**, *21*, 1467.
2) K. Nishimura, K. Hirano, M. Miura, *Org. Lett.* **2020**, *22*, 3185.

脱芳香族化による縮環芳香族化合物の活性化と位置選択的縮環π拡張(APEX)反応の開発

（名大院理[1]・JST-ERATO[2]・イリノイ大学[3]・名大 WPI-ITbM[4]）○松岡 和[1]・伊藤 英人[1,2]・David Sarlah[3]・伊丹健一郎[1,2,4])

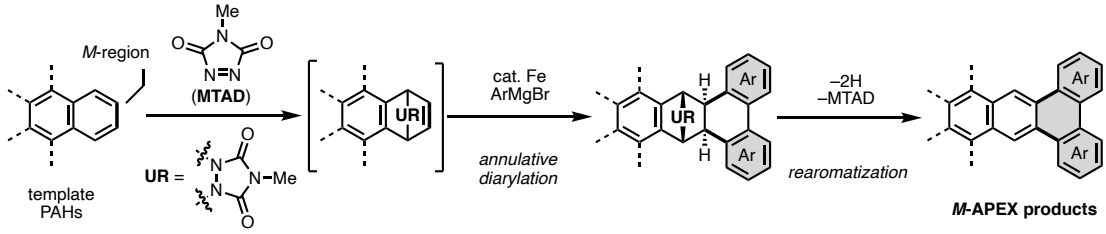
Dearomative Activation of Fused Aromatic Compounds toward Achieving Regioselective Annulative π-Extension (APEX)

([1]*Graduate School of Science, Nagoya University*; [2]*ERATO, JST*; [3]*University of Illinois*; [4]*WPI-ITbM, Nagoya University*) ○Wataru Matsuoka,[1] Hideto Ito,[1,2] David Sarlah,[3] Kenichiro Itami[1,2,4]

Fused aromatics such as polycyclic aromatic hydrocarbons (PAHs) and nanographenes are one of the most important classes of compounds in the field of materials science, especially in optoelectronics. To streamline the synthesis of these molecules, we have previously proposed the synthetic concept of annulative π-extension (APEX). [1] We herein describe a novel APEX reaction on *M*-region of polycyclic aromatic compounds.[2] 4-Methyl-1,2,4-triazoline-3,5-dione (MTAD) participates in regioselective Diels–Alder reactions with PAHs. Treatment of the resulting cycloadducts with Grignard reagents in the presence of iron catalyst afforded diarylated compounds, which are easily rearomatized to give *M*-region-APEX products. In the presentation, the optimization of reaction conditions and substrate scope including the application to rubrene, one of the most-studied organic semiconductors, will be described.

Keywords : Annulative π-extension; Nanographene; Dearomatization; Rubrene; Organic semiconductor

ナノグラフェンに代表される縮環芳香族化合物は、有機エレクトロニクス材料などへの応用が期待される重要な分子群である。これまでに我々は、縮環芳香族化合物の効率的な合成を指向した縮環π拡張(APEX)反応の合成概念を提唱し反応開発を行ってきた[1]。今回我々は、多環芳香族炭化水素(PAH)の *M* 領域選択的 APEX 反応を開発した[2]。まず、PAH とメチルトリアゾリンジオン(MTAD)の脱芳香族的 Diels–Alder 反応により生成する環化付加体に対し、鉄触媒の存在下で Grignard 反応剤を作用させることにより、ジアリール化反応が進行した。得られた生成物は容易に酸化・再芳香族化され、目的の *M* 領域 π 拡張生成物を与えた。発表では反応条件の最適化、基質適応範囲の検討結果に加え、代表的な有機半導体材料であるルブレンへの応用について報告する。



1) (a) Ozaki, K.; Kawasumi, K.; Shibata, M; Ito, H.; Itami, K. *Nat. Commun*. **2015**, *6*, 6251. (b) Matsuoka, W.; Ito, H.; Itami, K. *Angew. Chem., Int. Ed.* **2017**, *56*, 12224.
2) 松岡和、伊藤英人、David Sarlah、伊丹健一郎、第 66 回有機金属化学討論会、2019 年 9 月 14 日、O1-12

新規元素置換ペンタレン誘導体の合成および性質

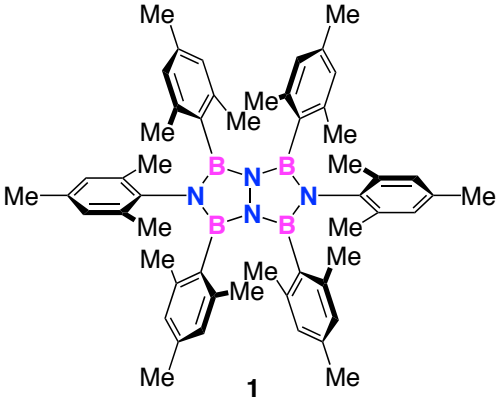
(東工大化生研[1]・早稲田大理工学術院[2]・コニカミノルタ[3]・慶大理工[4]) ○菓子田 惇輝[1]・庄子良晃[1]・五十幡 康弘[2]・高 秀雄[3]・酒井 隼人[4]・羽曾部 卓[4]・中井 浩巳[2]・福島 孝典[1]

Synthesis and Properties of a New Element-Substituted Pentalene Derivative ([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*; [2]*Research Institute for Science and Engineering, Waseda University;* [3]*Konica Minolta;* [4]*Department of Chemistry, Faculty of Science and Technology, Keio University*) ○ Junki Kashida,[1] Yoshiaki Shoji,[1] Yasuhiro Ikabata,[2] Hideo Taka,[3] Hayato Sakai,[4] Taku Hasobe,[4] Hiromi Nakai,[2] Takanori Fukushima[1]

Element-substitution, *e.g.*, the replacement of C–C bonds with isoelectronic but polar B–N bonds, can endow π-conjugated molecules with new electronic and opto-electronic properties.[1] We recently demonstrated that an element-substituted cyclobutadiene (CBD) derivative, in which its C–C bonds are replaced by B–N bonds, displays unique excited-state properties.[2] Here we report the synthesis of a new element-substituted BN-pentalene derivative (**1**) and its detailed molecular structure revealed by single-crystal X-ray crystallography. Similar to the case of the element-substituted CBD, **1** can emit high-energy phosphorescence from a T_1 state. We also show the fabrication and properties of OLED devices using **1** as a host material.

Keywords : BN-Containing π-Conjugated Molecule; Element Substitution; Pentalene; Phosphorescence; Host Material

π 電子系化合物の炭素–炭素 (C–C) 結合を、等電子的かつ分極したホウ素–窒素 (B–N) 結合に置き換える元素置換は、新たな電子・光電子物性を実現させるための有効なアプローチである[1]。我々は最近、C–C 結合を B–N 結合に置換したシクロブタジエン誘導体が特異な励起状態特性を示すことを報告している[2]。今回、同様の元素置換により、新規 BN ペンタレン誘導体（**1**）を合成し、単結晶 X 線構造解析により分子構造の詳細を明らかにした。また **1** が、無機 CBD と同様に、エネルギーの高い T_1 状態からの燐光発光を示すことを見出した。本発表では、**1** の分子・電子構造の詳細とともに、**1** をホスト材料として用いた OLED 素子の特性についても報告する。



1

[1] a) P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074. b) Z. X. Giustra, S.-Y. Liu, *J. Am. Chem. Soc*. **2018**, *140*, 1184.

[2] (a) 庄子良晃, Ryzhii Ivan, 五十幡康弘, 王祺, 中井浩巳, 生駒忠昭, 福島孝典 日本化学会第 99 春季年会, 3H1-49. (b) Ryzhii Ivan, 庄子良晃, 三浦智明, 福島孝典, 生駒忠昭 日本化学会第 99 春季年会, 3H1-51.

塩基および合成プロセスの制御によるホスホリルイナミンの位置選択的[4+2]芳香環形成

（岡山理大工）奥田 靖浩、益田 和法、赤木 伸行、折田 明浩
Base- and Process-Controlled Regiodivergent [4+2] Benzannulation of Phosphoryl Ynamine
(Fac. of Eng., Okayama Univ. of Sci.) ○Yasuhiro Okuda, Kazunori Masuda, Nobuyuki Akagi, Akihiro Orita

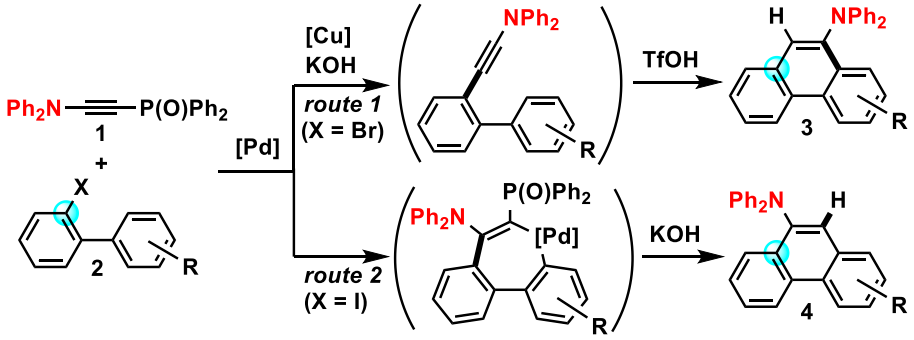
Polycyclic aromatic amines (PAAs) are widely utilized in organic electronics due to their superior fluorescent and hole-transporting properties. Although palladium-catalyzed cross-coupling is widely used in syntheses of aromatic amines, this technology does not work well for PAAs due to extremely low solubility of the corresponding starting materials, aryl halides. In this work, we developed dephosphorylation process-controlled regiodivergent synthesis of PAAs via [4+2] benzannulation of 2-bromobiphenyls with phosphoryl ynamine.

When a mixture of phosphoryl ynamine **1** and 2-bromobiphenyl (**2**) were treated with palladium and copper catalysts in the presence of KOH, consecutive dephosphorylation and Sonogashira coupling proceeded, and subsequent TfOH-catalyzed Friedel-Crafts cyclization of the resulting biphenylethyne provided the desired PAA **3** (route 1). In contrast, Pd(II)-catalyzed direct annulation between **1** and **2** in a basic condition gave amino-regioisomer **4** via dephosphorylation (route 2).

Keywords : Ynamine; Aromatic Amine; π-Extension; Regioselective Synthesis; Optical Property

多環式アミンは優れた発光特性、正孔輸送性を発現することから有機エレクトロニクス産業で幅広く利用されている。芳香族アミンを合成するには、ハロゲン化アリールとアミンとのクロスカップリング反応が頻繁に用いられるが、π拡張したハロゲン化アリールの溶解性が著しく乏しいため、多環式アミンの合成は、一般に困難である。最近我々は、ホスホリル置換したイナミン **1** と 2-ハロゲン化ビフェニルとの [4+2] 環化反応を用いて，位置選択的な多環式アミン合成法を開発した。

ホスホリルイナミン **1** の脱ホスホリル化、2-ブロモビフェニル(**2**)との薗頭カップリング、続く Friedel-Crafts 型渡環反応を連続的に行ったところ、いずれの反応も速やかに進行し、多環式アミン **3** が得られた (route 1)。一方、パラジウム触媒による **1** と **2** との直截環化、続く脱ホスホリル化からは、アミノ基の置換異性体 **4** が選択的に得られた (route 2)。



[A19-4pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair:Takuya Kodama, Muhammet Uyanik
Mon. Mar 22, 2021 1:00 PM - 2:40 PM Room 19 (Online Meeting)

[A19-4pm-01] Phosphine-Catalyzed Carbofluorination of Alkynes via a P(V) Intermediate

○Hayato Fujimoto[1], Takuya Kodama[1], Masahiro Yamanaka[2], Mamoru Tobisu[1] (1. Osaka University, 2. Rikkyo University)

1:00 PM - 1:20 PM

[A19-4pm-02] Reductive Cyclization of α-Iminocarbonyl Compounds Catalyzed by Organosuperbase

○Azusa Kondoh[1], Masahiro Terada[1] (1. Tohoku University)

1:20 PM - 1:40 PM

[A19-4pm-03] Amine-catalyzed asymmetric Mannich reaction or conjugate addition using alkynyl *Z*-ketimines

○Chihiro Homma[1], Taichi Kano[1], Keiji Maruoka[2] (1. Graduate School of Science, Kyoto University, 2. Graduate School of Pharmaceutical Sciences, Kyoto University)

1:40 PM - 2:00 PM

[A19-4pm-04] Helix Inversion of Chiral Poly(quinoxaline-2,3-diyl)s through Nonbonding Interaction with Specific Haloalkanes

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

2:00 PM - 2:20 PM

[A19-4pm-05] Hypoiodite-catalyzed Chemoselective Oxidative Cyclization of Indole Derivatives

○Hiroki Tanaka[1], Muhammet Uyanik[1], Kazuaki Ishihara[1] (1. Nagoya University)

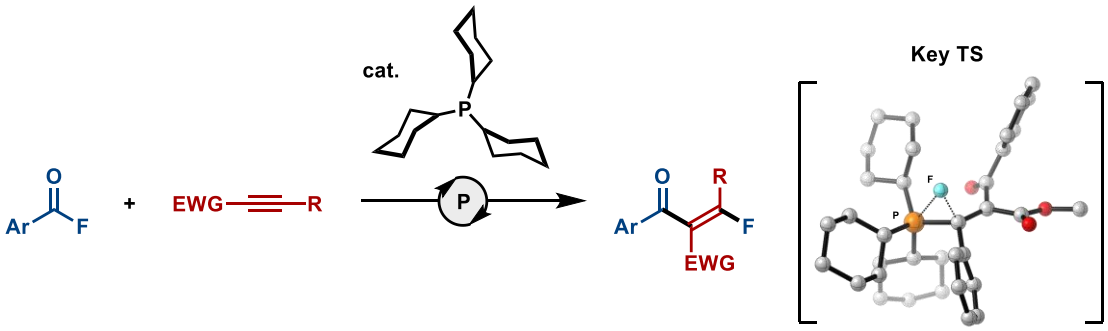
2:20 PM - 2:40 PM

Phosphine-Catalyzed Carbofluorination of Alkynes via a P(V) Intermediate

([1]*Graduate School of Engineering, Osaka University*, [2]*Faculty of Science, Rikkyo University*) ○Hayato Fujimoto,[1] Takuya Kodama,[1] Masahiro Yamanaka,[2] Mamoru Tobisu[1]

Keywords: Phosphine-Catalyst; Carbofluorination; Acyl Fluoride; Monofluoroalkene; Metal-Free

Fluorinated molecules occupy an important place in the pharmaceutical, agrochemical and material sciences.[1] Among the various fluorinated motifs, monofluoroalkene derivatives are of particular interest, partly because of their utility as a peptide bond isostere. Therefore, straightforward methods for the synthesis of monofluoroalkenes via C–F bond formation are in great demand.[2] The carbofluorination of alkynes, which proceeds via the concomitant formation of C–C and C–F bonds, is a powerful method for the synthesis of monofluoroalkenes. Although some methods for the catalytic carbofluorination of alkynes have recently been developed,[3] these methods are restricted to intramolecular reactions in which transition-metal catalysts are used. In this presentation, we report on the phosphine-catalyzed intermolecular carbofluorination of alkynes using acyl fluorides as fluorinating reagents.[4] This reaction promises to be a useful method for the synthesis of highly substituted monofluoroalkene derivatives, since acyl fluorides can be easily prepared from the corresponding carboxylic acid derivatives and the reaction proceeds under ambient conditions without the need for a transition-metal catalyst. Experimental and computational studies indicate that a five-coordinated fluorophosphorane is involved as the key intermediate in the fluorination step.



1) a) K. Muller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881. b) M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2004**, *44*, 214. c) G. Landelle, M. Bergeron, M. O. Turcotte-Savard, J. F. Paquin, *Chem. Soc. Rev.* **2011**, *40*, 2867. 2) P. A. Champagne, J.-D. Hamel, M. Vandamme, J.-F. Paquin, *Chem. Rev.* **2015**, *115*, 9073. 3) a) H. Peng, G. Liu, *Org. Lett.* **2011**, *13*, 772. b) Q. Tian, B. Chen, G. Zhang, *Green Chem.* **2016**, *18*, 6236. 4) H. Fujimoto, T. Kodama, M. Yamanaka, M. Tobisu, *J. Am. Chem. Soc.* **2020**, *142*, 17323.

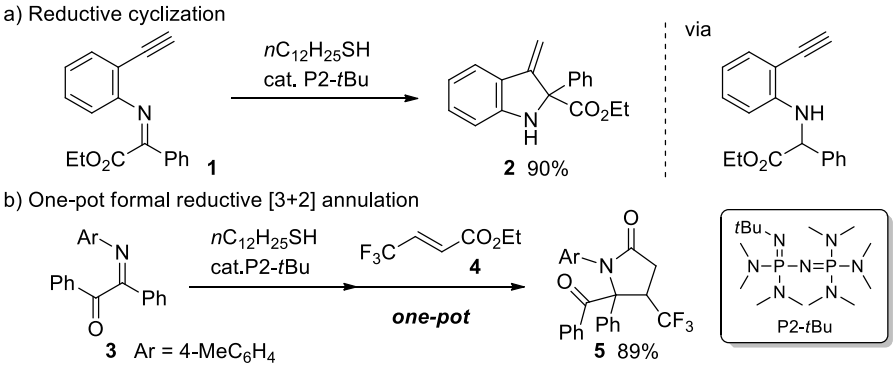
有機超強塩基触媒による α-イミノカルボニル化合物を用いた還元的環化反応

（東北大院理）○近藤 梓・寺田 眞浩
Reductive Cyclization of α-Iminocarbonyl Compounds Catalyzed by Organosuperbase
(*Graduate School of Science, Tohoku University*) ○Azusa Kondoh, Masahiro Terada

During the course of our study on the development of Brønsted base catalyzed reactions, we serendipitously found that a Brønsted base catalyzed the reduction of *α*-iminocarbonyl compounds with thiols as a reductant. We envisioned utilizing the newly found reduction as an elementary process in tandem reactions under Brønsted base catalysis. The reduction of *α*-iminocarbonyl compounds generates an acidic proton at the position *α* to the carbonyl moiety, which would be further transformable through a conventional elementary process initiated by the deprotonation, such as nucleophilic addition to an electrophile. Thus, we developed a reductive cyclization of *N*-(2-alkynylaryl)-*α*-iminoesters. We also investigated the one-pot formal reductive [3+2] annulation of 4,4,4-trifluorocrotonate and α-iminoketones.
Keywords : Base Catalysis; Reduction; Cyclization; Tandem Reaction; Organocatalysis

我々は、ブレンステッド塩基触媒を用いた分子変換反応の開発を行っている過程で、ブレンステッド塩基がチオールを還元剤として *α*-イミノカルボニル化合物のイミノ基の還元を触媒することを見いだした。この還元により生じる *α*-アミノカルボニル化合物は、カルボニル基の *α* 位に酸性プロトンを有しており、脱プロトン化を起点としたさらなる変換が可能である。そこで、この新たな還元反応と *α*-アミノカルボニル化合物の求電子剤への付加反応を組み合わせた触媒的連続反応の開発に取り組んだ。

具体的にはまず、有機超強塩基 P2-*t*Bu を触媒、ドデカンチオールを還元剤として用い、窒素上のアリール基にアルキン部位を有する *α*-イミノエステル **1** を基質とする分子内環化反応の開発を行った [1)]。また、*α*-イミノケトン **3** の還元と 4,4,4-トリフルオロクロトン酸エチル(**4**)への分子間付加を組み合わせた形式的[3+2]環化反応の開発にも取り組んだ [2)]。



1) A. Kondoh, M. Terada, *Org. Lett.* **2018**, *20*, 5309.
2) A. Kondoh, M. Terada, *Chem. Eur. J.* **2021**, *27*, 585.

Amine-catalyzed Asymmetric Mannich Reaction or Conjugate Addition Using Alkynyl *Z*-Ketimines

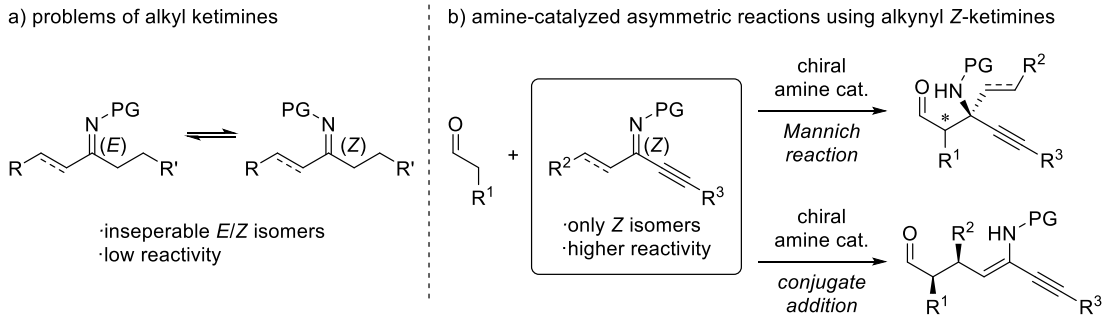
([1]*Graduate School of Science, Kyoto University*, [2]*Graduate School of Pharmaceutical Sciences*) ○Chihiro Homma,[1] Taichi Kano,[1] Keiji Maruoka[2]

Keywords: Asymmetric Reaction; Amine Catalyst; Mannich Reaction; Conjugate Addition; Ketimine

Imines are key structural components to synthesize chiral amines. Among imines, aldimines derived from aldehydes are widely used for asymmetric reactions; however, the use of ketimines derived from ketones is rather scarce despite their synthetic utility. The difficulty in developing asymmetric Mannich reactions of ketimines can be attributed in part to the intrinsic property of ketimines. In the case of asymmetric reaction of ketimines, the geometry of the *N*-substituent of the ketimine affects the enantioselectivity. However, ketimines that bear both alkyl and alkenyl groups or two alkyl groups on the imine carbon exist as inseparable mixtures of *E* and *Z* isomers and their stereoselective synthesis is quite difficult due to the rapid *E*/*Z* isomerization. Additionally, ketimines are in general less reactive towards nucleophilic additions than aldimines owing to electronic effects and steric hindrance in the C–C bond-forming step.

We then became interested in alkynyl-substituted ketimines that exist as *Z* isomers.[1] These *Z*-ketimines can be used as synthetic equivalents of alkyl-substituted ketimines because alkynyl groups can be converted into alkyl groups by simple hydrogenation. In addition, the alkynyl ketimines would be expected to show higher reactivity than alkyl ketimines due to the electron-withdrawing and sterically less hindered alkynyl group.

In this research, we have developed the amine-catalyzed asymmetric Mannich reaction and conjugate addition using alkynyl *Z*-ketimines.



1) a) T. Kano, R. Kobayashi, K. Maruoka, *Org. Lett.* **2016**, *18*, 27. b) T. Kano, Y. Aota, K. Maruoka, *Angew. Chem., Int. Ed.* **2017**, *56*, 16293.

Helix Inversion of Chiral Poly(quinoxaline-2,3-diyl)s through Nonbonding Interaction with Specific Haloalkanes

(*Graduate School of Engineering, Kyoto University*) ○Takaya Fujie, Takeshi Yamamoto, Michinori Suginome

Keywords: Molecular Recognition; Organocatalyst; Circular Dichroism; Catalytic Asymmetric Synthesis; Noncovalent Interaction

Solvent-dependent switch of the helical conformation of dynamic helical macromolecules is one of the most attractive bases for the development of chirality-switchable functional materials.[1] However, the need for two different solvents for the switch of chirality often meets with non-mirror image outputs due to the inherent solvent effect on the functions, such as enantioselectivities in asymmetric catalysis. Herein, we disclose that addition of less than 1 mol% of haloalkane in cyclohexane switches the helical conformation of poly(quinoxaline-2,3-diyl)s through their specific nonbonding interactions.

(*R*)-**PQX1** bearing chiral (*R*)-2-octyloxymethyl side chains[2] formed *P*-helix in cyclohexane, showing a positive CD signal at 366 nm. The helicity of (*R*)-**PQX1** was inverted to *M*-helix by addition of >8 mol% of 1,3-DCP to cyclohexane, as judged by a negative CD signal (Figure 1). Addition of 1,2-DCE (>5 mol%) or 1,2-DBE (>2 mol%) induced *M*-helix more efficiently than 1,3-DCP. Notably, highly responsive *M*-helix induction was achieved by using 1,1,2-TCE (>0.9 mol%) and 4-CBN (>0.3 mol%). These results indicate that the presence of specific interactions between **PQX1** and particular haloalkanes. Further details of the screening and application to the chirality-switchable helical polymer catalyst will also be discussed.

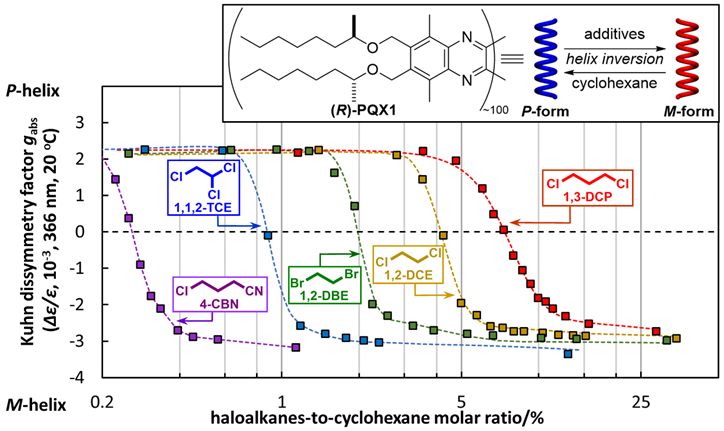


Figure 1. Helix inversion of (*R*)-**PQX1** with various haloalkanes in cyclohexane

1) Yashima, E.; Ousaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. *Chem. Rev.* **2016**, *116*, 13752.
2) Nagata, Y.; Yamada, T.; Adachi, T.; Akai, Y.; Yamamoto, T.; Suginome, M. *J. Am. Chem. Soc.* **2013**, *135*, 10104.

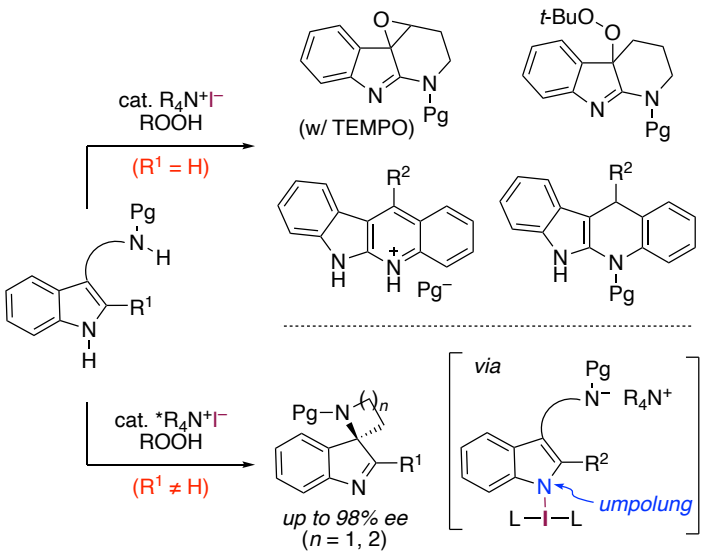
Hypoiodite-catalyzed Chemoselective Oxidative Cyclization of Indole Derivatives

(*Graduate School of Engineering, Nagoya University*) ○Hiroki Tanaka, Muhammet Uyanik, Kazuaki Ishihara

Keywords: *Hypoiodite catalysis; Oxidation; Cyclization; Indole; Alkaloids*

Indole derivatives are key structural units of several biologically active compounds. To date, numerous synthetic methods for those compounds have been developed. Among them, oxidative cyclization of indoles is one of the most powerful tools for the synthesis of spiro or polycyclic indole derivatives.[1] However, previous methods often rely on the use of toxic and expensive transition metal catalysts.[1] On the other hand, quaternary ammonium hypoiodite salt catalysis has been developed for the environmentally benign oxidative coupling reactions in our laboratory.[2] In this catalytic oxidation system, hypoiodite salts are generated *in situ* from the corresponding quaternary ammonium iodides in the presence of hydrogen peroxide or alkyl hydroperoxides as an environmentally benign oxidant.

Here, we succeeded in the ammonium hypoiodite-catalyzed oxidative cyclization reactions of indole derivatives. For example, a number of pyridoindole derivatives, precursors of various natural products, could be obtained in high yield from the reaction of *C*2-nonsubstituted indoles *via* cyclization at *C*2-position.[3,4] On the other hand, spiroindolenine derivatives could be synthesized from *C*2-substituted indoles *via* dearomative spirocyclization at *C*3-position. In addition, enantioselective dearomative spiroamination of indoles using chiral quaternary ammonium iodide as a catalyst gave the corresponding spiroindolenines with high enantioselectivity. Moreover, mechanistic studies suggested the umpolung reactivity of indoles by iodination of indole nitrogen atom. We anticipated that this unusual "electrophilic" indole strategy would allow to significantly improve the synthetic portfolio for indole manipulation.



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(2) M. Uyanik, K. Ishihara, *ChemCatChem* **2012**, *4*, 177.
(3) M. Uyanik, H. Tanaka, K. Ishihara, *Org. Lett.* **2020**, *22*, 8049.
(4) M. Uyanik, H. Tanaka, K. Ishihara, *Asian J. Org. Chem.* **2021**, 10.1002/ajoc.202000570.

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

[A22-4am] 16. Natural Products Chemistry, Chemical Biology

Chair:Kaname Sasaki, Akihiro Ishiwata

Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 22 (Online Meeting)

[A22-4am-01] Synthetic Studies on Ikoamide, a highly *N*-methylated linear lipopeptide

○YUNG-HAN LO[1] （1. Keio University）

9:00 AM - 9:20 AM

[A22-4am-02] Discovery of a cyclotide-based coagulation Factor XIIa inhibitor by mRNA display

○Wenyu LIU[1], Simon J. de Veer[2], Yen-Hua Huang[2], Toby Passioura[1], Hiroaki Suga[1], David Craik[2] （1. Department of Chemistry, Graduate School of Science, the University of Tokyo, 2. Institute for Molecular Bioscience, The University of Queensland）

9:20 AM - 9:40 AM

[A22-4am-03] One Pot-Chemical Synthesis of Glycoproteins and Their Glycan-Hydration Effect

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

9:40 AM - 10:00 AM

[A22-4am-04] Semisynthetic Study of Interleukin-6 (IL-6)

○Yanbo Liu[1], Ryo Okamoto[1], Yuta Maki[1], Yasuhiro Kajihara[1] （1. Grad. Sch. Sci., Osaka Univ.）

10:00 AM - 10:20 AM

[A22-4am-05] Development of High-mannose Glycan Library Synthesized by Dendritic Glycosylation

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

10:20 AM - 10:40 AM

[A22-4am-06] Synthesis of Oligoglucosamine Analogues Equipped with Trimethylammonium Glycoside

○Md Azadur Rahman[1], Shuji Takahashi[1], Toshiki Nokami[1] （1. Tottori University）

10:40 AM - 11:00 AM

[A22-4am-07] Systematic Synthesis of Squaryl Group Modified Glycolipid Analogues as Potential Ligands of GPR55

○Junpei Abe[1], Adam Tsuda Guy[2], Feiqing Ding[3], Peter Greimel[2], Yoshio Hirabayashi[4], Hiroyuki Kamiguchi[2], Yukishige Ito[1,4] （1. Grad. Sch. Sci. Osaka Univ. , 2. RIKEN CBS, 3. Sch. Pharm. Sci. SunYat-sen Univ., 4. RIKEN CPR）

11:00 AM - 11:20 AM

[A22-4am-08] Diosgenin-induced physicochemical effects on phospholipid bilayers in comparison with cholesterol

○Joan Candice Ondevilla[1] （1. Osaka University）

11:20 AM - 11:40 AM

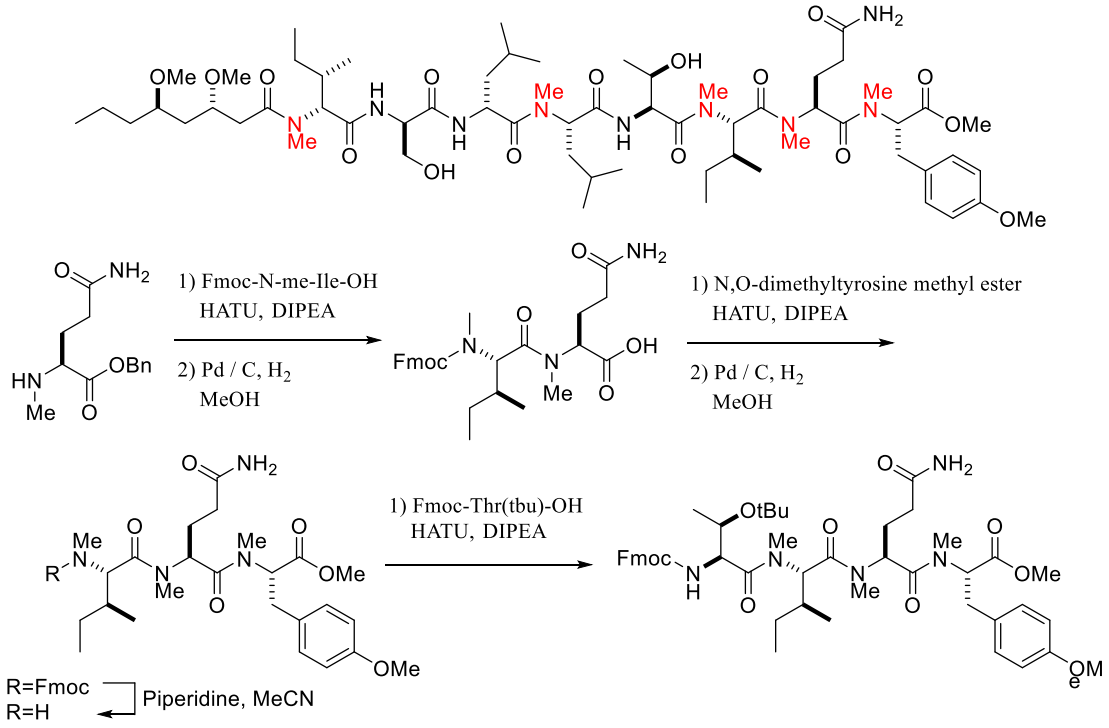
Synthetic Studies on Ikoamide, a highly *N*-methylated linear lipopeptide

Yung-Han Lo, Keitaro Iwasaki, Arihiro Iwasaki, and Kiyotake Suenaga

Faculty of science and technology, Keio university

Ikoamide was a highly *N*-methylated linear lipopeptide isolated from a marine cyanobacterium collected at Kuroshima Island, Okinawa. Ikoamide shows weak cytotoxicity against HeLa cells (IC_{50} 9.9 μM) and also shows growth inhibitory activity against malaria parasite *plasmodium falciparum* (IC_{50} 0.14 μM). The gross structure was elucidated by spectroscopic analyses, and the absolute configuration was determined by chiral HPLC analyses of acid hydrolysate and synthetic means. Since ikoamide is available a trace amount from natural resources, we began to study on the total synthesis of ikoamide for a supply for further biological tests. Starting from L-tyrosine, L-glutamine, and L-isoleucine, *N,O*-dimethyltyrosine methyl ester, *N*-methylglutamine, and *N*-methylisoleucine were prepared, respectively. Condensations of prepared *N*-methyl amino acids and *O*-tert-butylthreonine provided tetrapeptide. Further condensation reactions are now in progress.

Keyword：Total Synthesis, Ikoamide, *N*-methylated linear lipopeptide



Discovery of a cyclotide-based coagulation Factor XIIa inhibitor by mRNA display

([1]*Department of Chemistry, Graduate School of Science, the University of Tokyo,* [2]*Institute for Molecular Bioscience, The University of Queensland,* [3]*Department of Biochemistry, Graduate School of Medicine, Yokohama City University*) ○Wenyu LIU,[1] Simon J. de Veer,[2] Yen-Hua Huang,[2] Toby Passioura,[1] Toru Sengoku,[3] David Craik[2], Hiroaki Suga[1]

Keywords: Disulfide-rich cyclic peptide; FXIIa inhibitor; mRNA display

Cyclotides are plant-derived disulfide-rich cyclic peptides characterized by their head-to-tail cyclic backbone and cystine knot core, which make them attractive pharmaceutical candidates with promising enzymatic stability and cell permeability.[1] Engineering potent bioactivity against human pharmaceutical targets into cyclotides is of interest, however, has proven to be challenging due to the structural complexity.

In this work, we report the rapid discovery of potent and selective cyclotide-based coagulation factor XIIa (FXIIa) inhibitors using mRNA display. A cyclotide-based peptide library containing 12 randomized amino acids was synthesized and screened against FXIIa by mRNA display, which affords high library diversity (more than 10^{12} compounds) (Figure 1a). 5 of the most abundant selected peptides were synthesized by solid phase peptide synthesis (SPPS). Surface plasma resonance (SPR) and *in vitro* inhibitory assay revealed the most potent binder, cMCoFx1, which exhibits exceptional binding affinity (K_D = 0.9 nM) and inhibitory activity (K_i = 0.37 nM) towards FXIIa. Further inhibitory profiling with a panel of structurally and functionally related serine proteases showed high selectivity of cMCoFx1 towards FXIIa. X-ray analysis of co-crystal of cMCoFx1 and FXIIa revealed tight binding of the peptide to the enzyme in a substrate-like manner, with insertion of Arg at the peptide P1 site to the enzymatic S1 pocket (Figure 1b). These results elucidate the capability of mRNA display for identifying cyclotide-based FXIIa inhibitors, which are appealing candidates for therapeutic development.

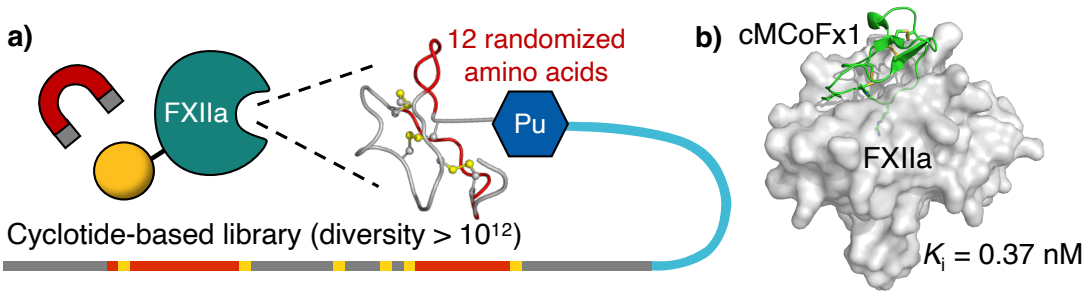


Figure 1 a) Discovery of cyclotide-based FXIIa inhibitors using mRNA display. b) Co-crystal structure of cMCoFx1 binding to FXIIa.

1) S. J. De Veer, J. Weidmann, D. J. Craik, *Acc. Chem. Res.* **2017**, *50*, 1557.

One Pot-Chemical Synthesis of Glycoproteins and Their Glycan-Hydration Effect

([1]*Graduate School of Science and* [2]*Project Research Center for Fundamental Science, Osaka University*) ○Hiroyuki Shibata[1], Yuya Tanaka[1], Donglin Zhao[1], Yuta Maki[1, 2], Yasuhiro Kajihara[1, 2], Ryo Okamoto[1, 2]

Keywords: Glycoprotein, Hydration, HDX, One-Pot

The glycosylation of proteins is one of the most abundant posttranslational modifications of proteins. Due to the intrinsic structural complexity, the function of oligosaccharides on glycoproteins is still unclear at a molecular level. We have been studying the function of oligosaccharides on glycoproteins by using homogeneous glycoproteins prepared by chemical synthesis. Our results suggested that the unique hydration of oligosaccharides attenuates the function of glycoproteins[1)]. We hypothesized that the hydration of oligosaccharides affects the molecular recognition of protein moiety of glycoproteins. However, there was no systematic study for the elucidation of the hydration volume of various oligosaccharides on glycoproteins. In order to address this question, we need to prepare a variety of glycoproteins having different oligosaccharides as key probes.

In this study, we set out the synthesis of chemokine glycoprotein CCL1[2)3)] having a variety of oligosaccharide. We newly developed one-pot peptide coupling reactions using peptidyl-2-aminothiazoline (peptide-AT). We found that peptide-AT is interconvertible with peptide-thioester, and thereby enabling regioselective peptide coupling. With the unique reactivity of peptide-AT, we successfully assembled the full length of CCL1 through a sequential peptide coupling reaction in one-pot manner. This synthetic strategy allowed us the efficient preparation of CCL1 having different oligosaccharides. By using the homogeneous glycosyl CCL1, we also conducted the hydrogen deuterium exchange mass spectrometry (HDX-MS) of the resultant glycoproteins to address the hydration region of oligosaccharides on glycoproteins. In this presentation, we would present the detail of the new synthesis and the results of HDX-MS.

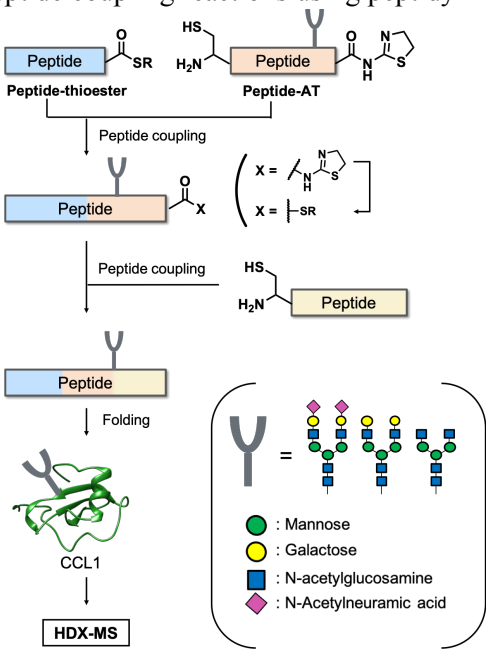


Fig. 1 The synthesis of CCL1 using One-Pot method

1) Y. Maki, et. al, *J. Am. Chem. Soc.* **2020**, 142, 49, 20671; 2) R. Okamoto, et. al, *Angew. Chem*. Int. Ed. **2014,** 53, 5188; 3) R. Okamoto, et. al, *Angew. Chem*. Int. Ed. **2014,** 126, 5288

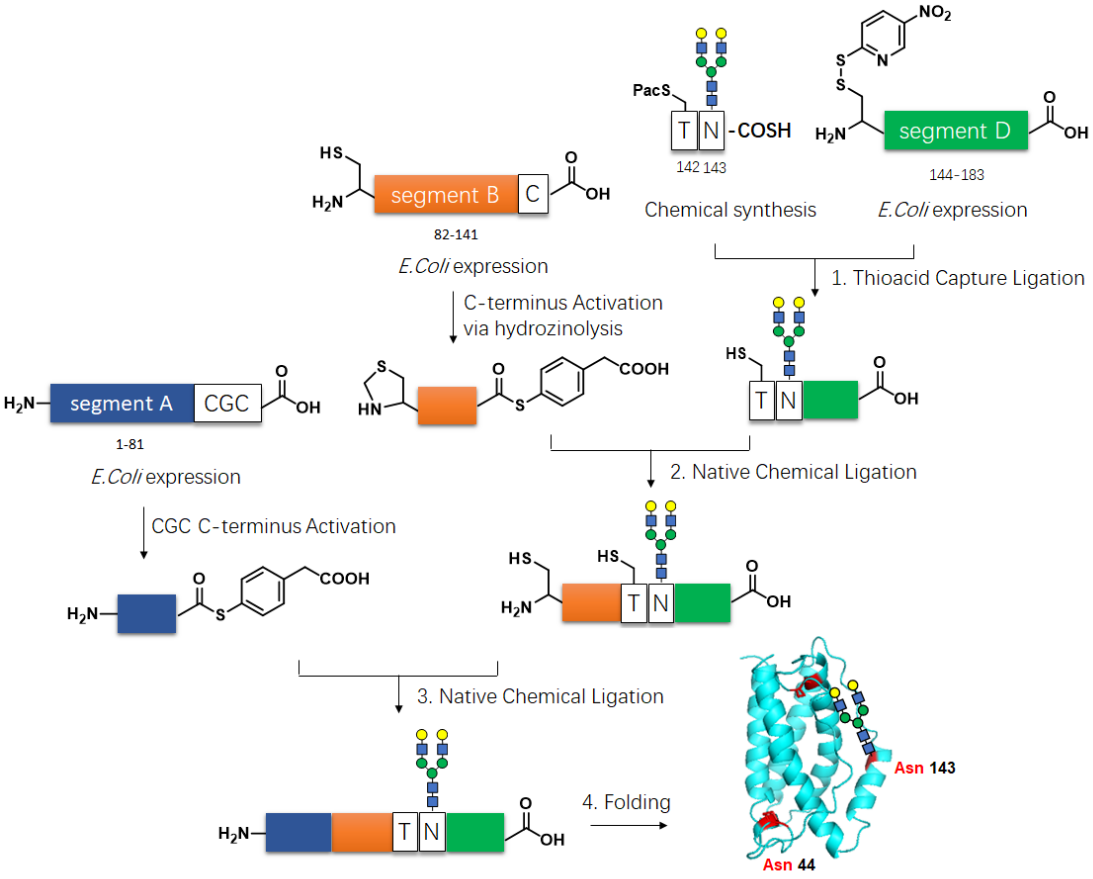
Semisynthestic Study of Interleukin-6 (IL-6)

(*[1]Graduate School of Science and [2]Project Research Center for Fundamental Science, Osaka University*) ○Yanbo Liu[1], Ryo Okamoto[1,2], Yuta Maki[1,2], Yasuhiro Kajihara[1,2]

Keywords: glycoprotein; semi-synthesis; interleukin-6; thioacid capture ligation; thioesterification

Preparation of glycoproteins having homogeneous oligosaccharides is essential approach for understanding the glycan function at molecular level. However, current mammalian cell expression system is usually not able to yield such homogeneous form. Moreover, total chemical synthesis using solid phase peptide synthesis (SPPS) is time-consuming.

In this research project, we have been developing a novel semisynthetic strategy without using SPPS in order to obtain homogeneous glycoprotein within a few chemical conversion steps. In this strategy, peptide-thioester is prepared by E. coli expression system followed by selective activation of peptidyl-Cys or peptidyl-Cys-Gly-Cys, which were developed in our laboratory. The key glycopeptide is prepared by thioacid capture ligation using glycosyl dipeptide thioacid and an expressed peptide. So far, we have synthesized two N-terminus peptides after C terminal activation of expressed peptide, and C-terminus glycopeptide ready for native chemical ligation (NCL). In this presentation, we would like to present our investigation of the C-terminal activation.



1) Ryo Okamoto, Kota Nomura, Yuta Maki, Yasuhiro Kajihara, *Chemistry Letters*, **2019**, *48*, 1391-1393

樹状型グリコシル化法を利用した高マンノース型糖鎖ライブラリーの構築研究

（成蹊大理工）○碓井 瑠智雄・樺澤 恵・栗原 大輝・戸谷 希一郎

Development of High-mannose Glycan Library Synthesized by Dendritic Glycosylation

(*Facurity of Science and Technology, Seikei University*) ○Ruchio Usui, Megumi Kabasawa, Taiki Kuribara, Kiichiro Totani

Various high-mannose-type glycans on glycoprotein play major roles in glycoprotein quality control. However, the study of the functions is still problematic because of the difficulty in both biological samples and chemical synthesis to obtain a sufficient amount of high-mannose-type glycans. To overcome the issue, we developed the facile methodology called dendritic glycosylation to assist the branched synthesis of various high-mannose-type glycans.

In this study, we examined the application of the dendritic glycosylation aimed to obtain the full set of natural high-mannose-type glycans library. In detail, we synthesized $Man_3GlcNAc_2$ (M3)-type tri-OH accepter giving $Man_6GlcNAc_2$ (M6) structure by the first dendritic glycosylation (Figure 1). In the second dendritic glycosylation starting with the deprotected M6-type tri-OH acceptor, we estimated the intentional interruption of the glycosylation for yields the eight types of high-mannose-type glycans in one-pot.

Keywords : High-mannose-type glycans; Endoplasmic reticulum glycoprotein folding quality control; Dendritic Glycosylation; One-pot Synthesis; Glycoform

糖タンパク質上の多様な高マンノース型糖鎖は、小胞体糖タンパク質品質管理において重要な役割を担う。これらの機能解析には多種の高マンノース糖鎖が必要となるが、生物試料・化学合成のどちらの供給源においても十分量の糖鎖の入手は困難である。この課題に対し、我々は先行研究において標的糖鎖の部分構造をモデルとし、複数の分岐鎖骨格を同一系内で効率的に合成する樹状型グリコシル化法を開発した。

これを踏まえ、本研究では、樹状型グリコシル化法による 8 種類の高マンノース型分岐鎖（M6～M9）の合成を検討し、多様な高マンノース型糖鎖のライブラリー構築を目指した。具体的には、$Man_3GlcNAc_2$ (M3) 構造を有した tri-OH 型アクセプターを合成し、樹状型グリコシル化により $Man_6GlcNAc_2$ (M6) 骨格を合成した (Figure 1)。さらに脱保護した M6 型 tri-OH アクセプターに対する二回目の樹状型グリコシル化において、意図的に伸長反応を中断させ、八種類の高マンノース型分岐鎖をワンポットで合成する系を検討した。

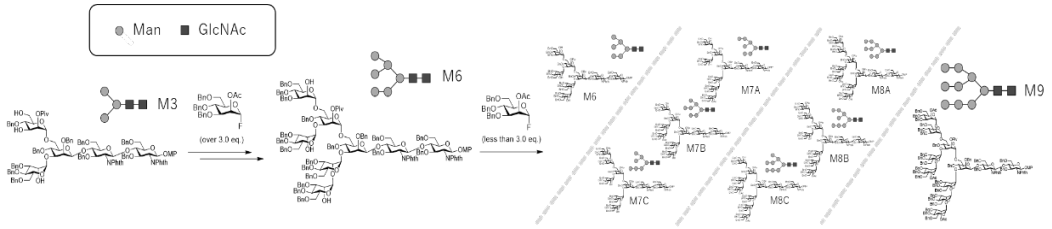


Figure 1. Synthesis of high-mannose glycans library by dendritic glycosylation

Synthesis of Oligoglucosamine Analogues Equipped with Trimethylammonium Glycoside

([1]*Graduate School of Engineering, Tottori University,* [2]*GSC Center, Tottori University*)
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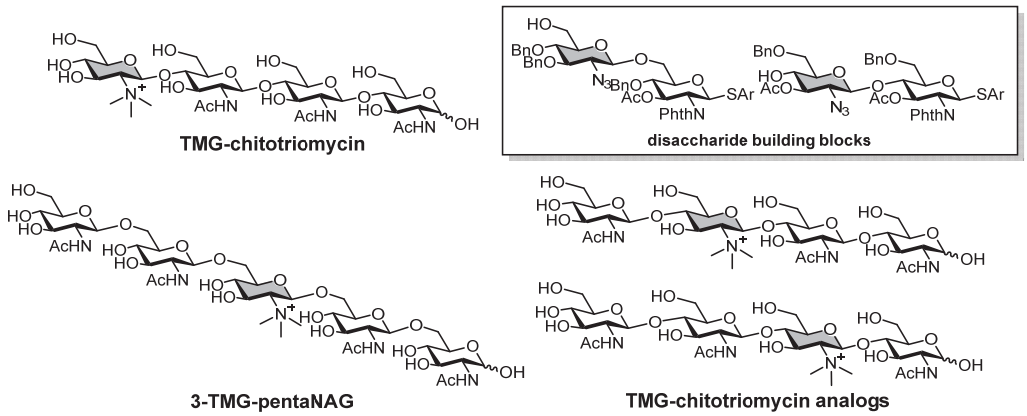
Keywords: Oligosaccharide, Inhibitor, Glucosamine, Trimethylammonium, Electrochemical Glycosylation

Oligoglucosamins are abundant and important oligosaccharides for living things such as plants, fungi, insects, and other organisms. **TMG-chitotriomycin** with the *N*,*N*,*N*-Trimethyl-D-glucosaminyl (TMG) unit showed potent and selective inhibition of insect and fungal GlcNAcases with no inhibition of mammalian and plant GlcNAcases.[1] Synthesis of TMG-chitotriomycin has been achieved by us using an automated electrochemical synthesizer.[2] We have been interested in the inhibitory activity of oligoglucosamine analogs with the TMG unit.

Initially, we synthesized two disaccharide building blocks under conventional and mixed-electrolyte conditions.[3] We obtained the precursor **3-TMG-pentaNAG**, which is a β-1,6-oligoglucosamine, using the [1+1+2+1] strategy for automated electrochemical assembly. The precursor was converted to **3-TMG-pentaNAG** by conventional manipulation of functional groups. For the preparation of TMG chitotriomycin analogs another disaccharide building block with β-1,4-glycosidic linkage was used. Positions of the TMG unit in precursors of TMG-chitotriomycin analogs can be changed by changing strategies for automated electrochemical assembly. These precursors tetrasaccharide can be synthesized by [1+2+1] and [1+1+2] strategies in reasonable yields and converted into TMG-chitotriomycin analogs by global deprotection according to the reported method.[2b]



1) H. Kanzaki, et al. *J. Am. Chem. Soc.* **2008**, *130*, 4146. 2) a) T. Nokami, et al. *Org. Lett.* **2015**, *17*, 1525. b) Y. Isoda, et al. *Beilstein J. Org. Chem.* **2017**, *13*, 919. 3) Y. Isoda, et al. *ChemElectroChem* **2019**, *6*, 4149.

新規な GPR55 リガンドの開発に向けたスクアリル基修飾型糖脂質類縁体の系統的合成

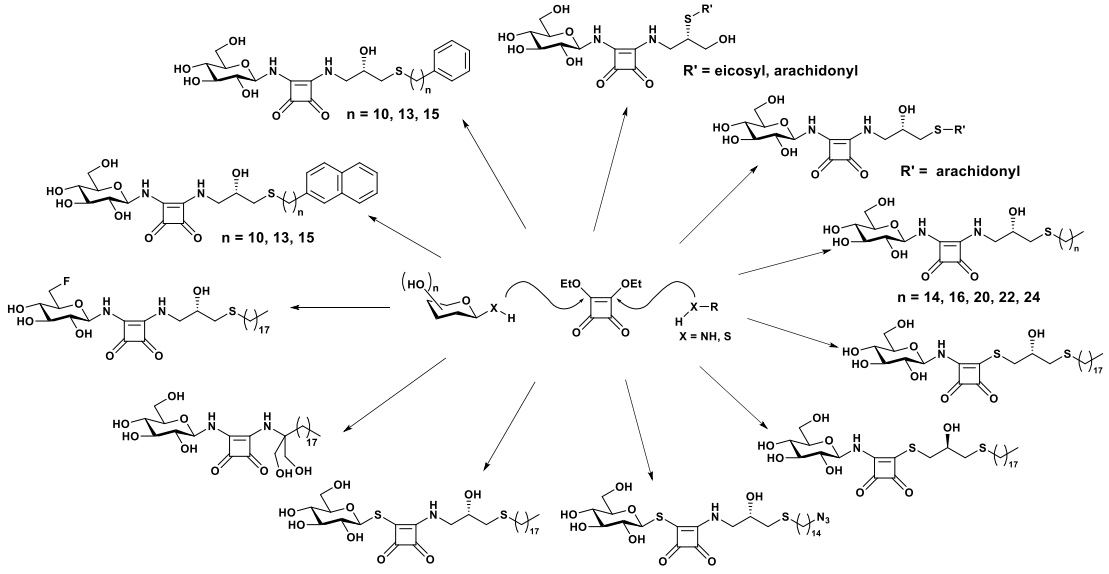
(阪大院理[1]・RIKEN CBS[2]・中山大學[3]・RIKEN CPR[4]・阪大院理基礎理学プロジェクト研究センター[5]) ○阿部　純平[1]・Guy Adam[2]・Ding Feiqing[3]・Greimel Peter[2]・平林　義雄[4]・上口　裕之[2]・伊藤　幸成[1,4,5]

Systematic Synthesis of Squaryl Group Modified Glycolipid Analogues as Potential Ligands of GPR55 ([1]*Grad. Sch. Sci., Osaka Univ.*, [2]*RIKEN CBS*, [3]*Sch. Pharm. Sci., Sun Yat-sen Univ.*, [4]*RIKEN CPR*, [5]*Grad. Sch. Sci. PRC, Osaka Univ.*) ○Junpei Abe[1], Adam Tsuda Guy[2], Feiqing Ding[3], Peter Greimel[2], Yoshio Hirabayashi[4], Hiroyuki Kamiguchi[2], Yukishige Ito[1,4,5]

A G protein-coupled receptor GPR55, is known to play various biological roles and promising as a pharmaceutical target. As it is known to recognize lysophosphatidyl-β-D-glucoside (LPGlc) as endogenous agonist, our group has developed novel LPGlc analogues possessing a squaryldiamide group as a surrogate of phosphodiester which showed similar activity to LPGlc. These compounds can be obtained in a highly facile manner because the synthesis can be carried out without recourse of protection/deprotection of the sugar component. We applied this method to systematically create various analogues of LPGlc as potential agonists or antagonists of GPR55.

Keywords : GPR55; lysophosphatidyl-β-D-glucoside; squaryl diamide

創薬標的として重要な GPR55 は、リゾホスファチジルグルコシド(LPGlc)を内因性アゴニストの１つとする G タンパク質共役型受容体である[1)]。我々はリン酸ジエステル基をスクアリルジアミド基で置換した類縁体が LPGlc と類似の活性を示すことを見出した[2)]。その合成では糖・側鎖アルキル基の保護・脱保護工程なしに最終物を得ることができる。これを広範な GPR55 リガンド候補となる LPGlc 類縁体合成に展開した[3), 4)]。



1) A. T. Guy, *et al*. *Science*, **2015**, *349*, 974-977. 2) F. Ding, *et al*. *Chem. Commun*. **2018**, *54*, 8470-8473. 3) J. Abe, *et al. Org. Biomol. Chem.* **2020**, *18*, 8467-8473. 4) A. T. Guy, *et al. ACS Chem. Neurosci*. **2020**, *11*, 3635−3645.

Diosgenin-Induced Physicochemical Effects on Phospholipid Bilayers in Comparison with Cholesterol

(*Graduate School of Science, Osaka University*)
○Joan Candice Ondevilla, Shinya Hanashima, Yuichi Umegawa, Michio Murata

Keywords: Diosgenin, Cholesterol, Solid-state NMR, Laurdan, Diphenylhexatriene

Diosgenin (DGN), a plant sterol isolated from *Dioscorea* family, has gained pharmacological importance for its anti-cancer, anti-inflammatory and cardioprotective effects.[1] DGN has a structural similarity to cholesterol (Cho). In particular, they possess an identical tetracyclic backbone but the spiro-acetal structure of DGN is significantly different from the linear C_8 sidechain of Cho. [Figure 1]

In this study, the membrane effects of DGN was investigated and compared to Cho using membrane fluorescent probes, differential scanning calorimetry (DSC) and solid state NMR. We examined the effects of the common tetracyclic cores and the different sidechains on the physicochemical properties in phosphatidylcholine (PC) lipid bilayer membranes. DSC thermograms showed that DGN and Cho reduce membrane cooperativity of DMPC to a similar extent. On the other hand, an equimolar mixture of DGN and Cho revealed a weaker effect on the reduction of cooperativity. In ^{2}H NMR, deuterated-DGN and Cho showed similar quadrupolar coupling values in POPC bilayers. These spectra revealed that DGN is oriented parallel to the membrane normal like Cho. It was also suggested that the affinity of DGN-Cho in the membrane is stronger than that of DGN-DGN or Cho-Cho interaction. ^{31}P NMR of POPC in bilayers revealed that, unlike Cho, DGN altered the interactions of POPC headgroups at concentrations over 30 mol%. In DPH anisotropy experiments, DGN up to 30 mol% stably bound to the POPC bilayers and induced a similar ordering effect on POPC to Cho. Measurement of membrane hydration using laurdan and prodan also revealed a similar tendency for Cho and DGN. These results suggest that DGN below 30 mol% has comparable effects with Cho on basic biomembrane properties.

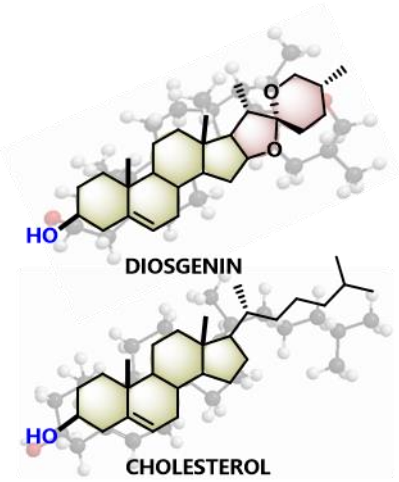


Figure 1. Chemical structures of the two sterols

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b) Patel, K.; Gadewar, M.; Tahilyani, V.; Patel, D. K. *Nat. Prod. Bioprospecting* **2012**, *2* (2), 46–52.
c) Raju, J.; Mehta, R. *Nutr. Cancer* **2008**, *61* (1), 27–35.
d) Lv, Y.; Yang, J.; Yao, F.; Xie, W.; Tang, Y.; Ouyang, X.; He, P.; Tan, Y.; Li, L.; Zhang, M.; Liu, D.; Cayabyab, F. S.; Zheng, X.-L.; Tang, C. *Atherosclerosis* **2015**, *240* (1), 80–89.

[A25-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair:Ryosuke Ueki, Kou Okuro

Mon. Mar 22, 2021 1:00 PM - 3:00 PM Room 25 (Online Meeting)

[A25-4pm-01] A DNA aptamer that inhibits aberrant receptor signaling in cancer cells

○Akihiro Eguchi[1], Ayaka Ueki[1], Keiko Kuwata[2], Yoko Chikaoka[3], Takeshi Kawamura[3], Satoru Nagatoishi[4], Kouhei Tsumoto[1,4], Ryosuke Ueki[1], Shinsuke Sando[1] （1. Grad. Sch. Eng., The Univ. of Tokyo, 2. WPI-ITbM, Nagoya University,, 3. ISC, The University of Tokyo, 4. IMS, The University of Tokyo, ）

1:00 PM - 1:20 PM

[A25-4pm-02] Photoreactive molecular glue for immobilizing DNA aptamer onto targeted proteins

○Ai Kohata[1], Kou Okuro[2], Takuzo Aida[1] （1. The University of Tokyo, 2. University of Hong Kong）

1:20 PM - 1:40 PM

[A25-4pm-03] Studies on Synthesis and Property of Chimeric Artificial Nucleic Acid Conjugated with DNA for Catalytic Target RNA Cleavage

○Akira Yano[1], Masahito Inagaki[1], Tsuyoshi Yamamoto[2], Masaki Nishijima[1], Yasuyuki Araki[1], Asako Yamayoshi[2], Satoru Ishibashi[3], Takanori Yokota[3], Takehiko Wada[1] （1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Department of Chemistry of Biofunctional Molecules, School of Pharmaceutical Sciences, Nagasaki University, 3. Department of Neurology and Neurological Science, Tokyo Medical and Dental University）

1:40 PM - 2:00 PM

[A25-4pm-04] X-ray crystal structure analysis of a reverse binding orientation cyclic-PIP and DNA complex and structural comparison with forward binding orientation complex

○Katsuhiko Abe[1], Yuki Hirose[1], Haruhiko Eki[1], Kazuki Takeda[1], Endo Masayuki[1], Bando Toshikazu[1], Hiroshi Sugiyama[1] （1. Kyoto University）

2:00 PM - 2:20 PM

[A25-4pm-05] Elucidation of mechanism and function of TERRA aggregates

○Tatsuki Masuzawa[1], Kentaro Takahama[1], Ayako Okushima[1], Riki Kurokawa[2], Takanori Oyoshi[1] （1. Shizuoka University, 2. Saitama Medical University）

2:20 PM - 2:40 PM

[A25-4pm-06] Development of large-scale analytical system for RNA alkylation reactions

○Kazumitsu Onizuka[1], Kaoru Richard Komatsu[2], Shunya Ishikawa[1], Yutong Chen[1], Kanna Ojima[1], Hirotaka Murase[1], Ryosuke Nagasawa[1], Mamiko Ozawa[1], Emi Miyashita[2], Hirohide Saito[2], Fumi Nagatsugi[1] （1. Tohoku Univ., 2. Kyoto Univ.）

2:40 PM - 3:00 PM

A DNA aptamer that inhibits aberrant receptor signaling in cancer cells

([1]*Grad. Sch. Eng., The Univ. of Tokyo,* [2]*WPI-ITbM, Nagoya Univ.,* [3]*Isotope Science Center, The Univ. of Tokyo,* [4]*The Institute of Medical Science, The Univ. of Tokyo,*) ○Akihiro Eguchi,[1] Ayaka Ueki,[1] Keiko Kuwata,[2] Yoko Chikaoka,[3] Takeshi Kawamura,[3] Satoru Nagatoishi,[4] Kouhei Tsumoto,[1,4] Ryosuke Ueki,[1] Shinsuke Sando[1]

Keywords: Aptamers, Receptors, Signal transduction, Cancer, Inhibitors

Aptamers have been attracting attention as an alternative to antibodies in diagnostic and therapeutic settings due to their high affinity and specificity of binding to their targets.[1] To date, various aptamers have been generated by *in vitro* selection targeting cancer-related biomarkers.[2] Growth factor receptors are key cancer biomarkers because their aberrant signaling is associated with cancer malignancy. Gene amplification and resultant overexpression of growth factor receptors often cause the formation of ligand-independent receptor dimers and resultant aberrant signaling.[3]

Aptamers have been utilized as tools to control the activity of growth factor receptors. Although there have been many reports of aptamers that function as antagonists and inhibit ligand-dependent activation of growth factor receptors,[4] no aptamer has been demonstrated to inhibit ligand-independent activation that often causes the aberrant signaling and resultant cancer development and progression. In this presentation, we will talk about a DNA aptamer that targets a growth factor receptor and inhibits the constitutive aberrant activation of the target receptor.[5] The inhibition leads to the inhibition of the downstream signaling and cell growth of a cancer cell. A series of experiments indicates that the aptamer exerts the inhibitory function by preventing the ligand-independent dimer formation of the receptor on cancer cell surface.

1) H. Ma *et al. Chem. Soc. Rev.* **2015**, *44*, 1240. 2) J. Zhou, J. Rossi, *Nat. Rev. Drug Discov.* **2017,** *16*, 181. 3) a) R. Worthylake, L. K. Opresko, H. S. Wiley, *J. Biol. Chem.* **1999,** *274*, 8865.; b) N. Shinomiya *et al. Cancer Res.* **2004,** *64*, 7962.; c) N. Turner *et al. Cancer Res.* **2010,** *70*, 2085.; 4) a) N. Li *et al. PLoS One* **2011,** *6*, e20299.; b) R. Ueki, S. Sando, *Chem. Commun.* **2014,** *50*, 13131.; c) P. Kanlikilicer, *et al. Mol. Ther. Nucleic Acids* **2017,** *9*, 251.; d) N. Kamatkar *et al. Mol. Ther. Nucleic Acids* **2019,** *17*, 530.; 5) A. Eguchi *et al. ChemRxiv* **2020,** DOI: https://doi.org/10.26434/chemrxiv.12925175.v1.

Photoreactive Molecular Glue for Immobilizing DNA Aptamer onto Targeted Proteins

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Faculty of Science, The University of Hong Kong*) ○Ai Kohata,[1] Kou Okuro,[2] Takuzo Aida[1]

Keywords: Molecular Glue; Photo-immobilization; DNA Aptamer; Protein

Because of high target-selectivity and synthetic accessibility, DNA aptamers are promising as an alternative to antibodies. However, many of the DNA aptamers so far developed do not have sufficient binding affinity to the target and therefore have not been applied for practical use. Previously, we developed water-soluble molecular glues bearing multiple guanidinium (Gu^+) ion units that can strongly adhere to biomacromolecules through multiple salt-bridge interactions with oxyanions.[1]

In the present study, we developed "photoreactive molecular glue" that can immobilize a DNA aptamer onto the target protein by light. The molecular glue tightly adheres to a DNA aptamer/protein complex and covalently crosslinks it upon photoirradiation. By means of this molecular glue-mediated photo-crosslinking, we successfully enhanced the inhibitory effect of a DNA aptamer, which binds to receptor protein c-Met,[2] against its interaction with hepatocyte growth factor (HGF; Figure 1). Without the UV exposure, molecular glue readily comes off the aptamer, resulting in the negligibly weak inhibition of the HGF/c-Met interaction.

1) R. Mogaki, P. K. Hashim, K. Okuro, T. Aida, *Chem. Soc. Rev.* **2017**, *46*, 6480. 2) R. Ueki, S. Sando, *Chem. Commun.* **2014**, *50*, 13131.

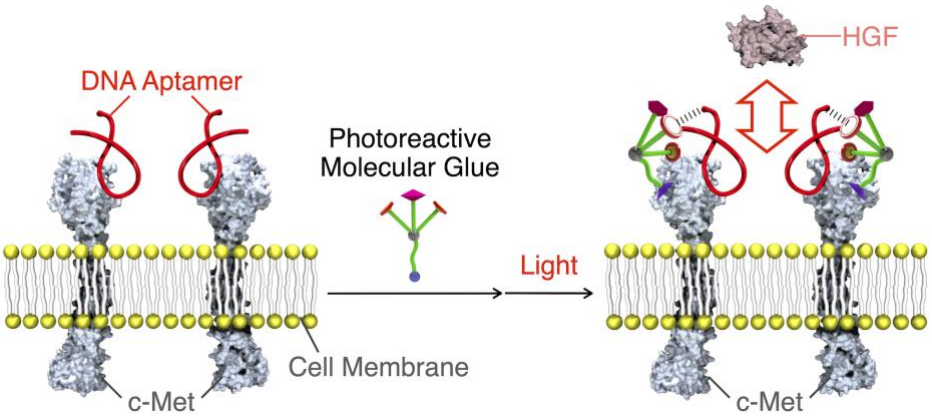


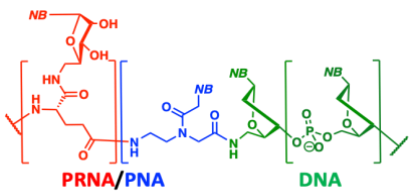
Fig. 1 Schematic illustration of immobilization of a DNA aptamer onto the target protein (c-Met) via photoreactive molecular glue by light, resulting in the enhanced inhibition of HGF/c-Met interaction.

触媒的標的 RNA 切断機能を有する新規人工核酸の開発
－ 癌治療を志向したキメラ人工核酸の合成と機能評価 －

（東北大多元研 [1]・長崎大薬 [2]・東京医科歯科大学 [3]）○矢野 輝 [1]・稲垣 雅仁 [1]・山本 剛史 [2]・西嶋 政樹 [1]・荒木 保幸 [1]・山吉 麻子 [2]・石橋 哲 [3]・横田 隆徳 [3]・和田 健彦 [1]
Studies on Synthesis and Property of Chimeric Artificial Nucleic Acid Conjugated with DNA for Catalytic Target RNA Cleavage ([1]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, [2]Department of Chemistry of Biofunctional Molecules, School of Pharmaceutical Sciences, Nagasaki University, [3]Department of Neurology and Neurological Science, Tokyo Medical and Dental University) ○Akira Yano,[1] Masahito Inagaki,[1] Tsuyoshi Yamamoto,[2] Masaki Nishijima,[1] Yasuyuki Araki,[1] Asako Yamayoshi,[2] Satoru Ishibashi,[3] Takanori Yokota,[3] Takehiko Wada,[1]

Oligonucleotide therapeutics have been attracting attention as next-generation molecularly targeted drugs, but there is a need to improve the issues of low therapeutic effect mostly originated by extremely low intracellular concentrations of the compounds. In this study, we designed artificial nucleic acid for targeting Vasohibin 2, which mainly appeared in the cancer cell and contributed to angiogenesis. We have proposed and demonstrated the improved target RNA cleavage efficiency by the chimeric artificial nucleic acids consisted of PNA/PRNA conjugated with DNA with RNase H. In the strategy, we focused on the thermal stabilities of the hybrids before and after RNA cleavage. To improve the catalytic cleavage efficiency, drastic stability change of the hybrid down to physiological temperature after RNA cleaved should be a key factor, due to promoting the rapid dissociation of the RNA cleaved hybrid from RNase H complex. For this purpose, we have proposed the position selective cleavage of the target RNA by a non-sequence selective endonuclease, RNase H with the chimeric artificial nucleic acids. To realize the issue, we designed and synthesized the chimeric artificial nucleic acid, which consisted of DNA moiety to bind the positive channel of RNase H conjugated with PNA/PRNA moiety for improving the stability of the hybrid with the target RNA. In the presentation, we'll report the demonstration of the target RNA cleavage efficiency with UV/CD melting experimental and gel electrophoresis studies.
Keywords : Artificial Nucleic Acid, Catalytic Oligonucleotide Therapeutics, RNase H

現在注目されている核酸医薬は、細胞内極低濃度に起因する低治療力価問題さえ改善できれば、幅広い疾患への適用が期待されている。本研究では、主に癌細胞に発現し、血管新生に関与する Vasohibin 2[1)]を標的としたキメラ人工核酸を設計・合成し、治療力価向上に資する RNase H による標的 RNA の高効率触媒的切断を検討した。RNase H による標的 RNA の高効率切断を実現する為、切断後の DNA/RNA 複合体の迅速な解離を誘起し得る位置での RNase H による RNA 選択切断を発案した。標的 RNA の位置選択切断には、RNase H の塩基性チャネル [2)]への選択的結合可能な負電荷骨格 DNA と、電荷を有しないアミド骨格 PNA/PRNA[3)]を融合したキメラ人工核酸が有効であると仮説し、設計・合成、特性解析に取り組んだ。発表では、同配列を有する天然型 DNA、チオエステル修飾 S-oligo との機能比較も併せて発表する。



1) Sato, Y., *J. Biochem.* **2013**, *153*, 1, 5. 2) Yang, W. *et. al., Mol. Cell* **2007**, *28*, 2, 264. 3) Wada, T. *et al. J. Am. Chem. Soc.* **2000**, *122*, 29, 6900. (Selected reference)

X-ray crystal structure analysis of a reverse binding orientation cyclic-PIP and DNA complex and structural comparison with forward binding orientation complex

(*Graduate School of Science, Kyoto University*) ○ Abe Katsuhiko, Hirose Yuki, Eki Haruhiko, Takeda Kazuki, Endo Masayuki, Bando Toshikazu, Sugiyama Hiroshi

Pyrrole imidazole polyamide (PIP) is a molecule that binds to the DNA duplex in a sequence-specific manner, and because of this property it shows promise in drug discovery applications. PIP contains an N-terminus and a C-terminus, and when the N-terminus is oriented toward the 5' side of the DNA strand, it is called forward orientation, and when the C-terminus is oriented toward the 5' side of the DNA strand, it is called reverse orientation. Depending on the design of the PIP, there are some PIPs that cannot recognize this orientation and combine in both types of orientation. To design a PIP that specifically recognizes only a single orientation, it is necessary to elucidate the bonding mode in both orientations at the atomic level. The X-ray crystal structure of the forward binding orientation of the cPIP-DNA complex has been reported[1,2], but that of the reverse binding orientation has not been reported yet. In this presentation, we will report X-ray crystal structure analysis for the reverse binding orientation of cPIP-DNA[3]. In addition, comparisons were made with forward-oriented structures, and similarities and differences were highlighted. Based on this result, the factors of orientation priority were also considered using modeling.

Keywords : X-ray crystal structure analysis; DNA; PIP

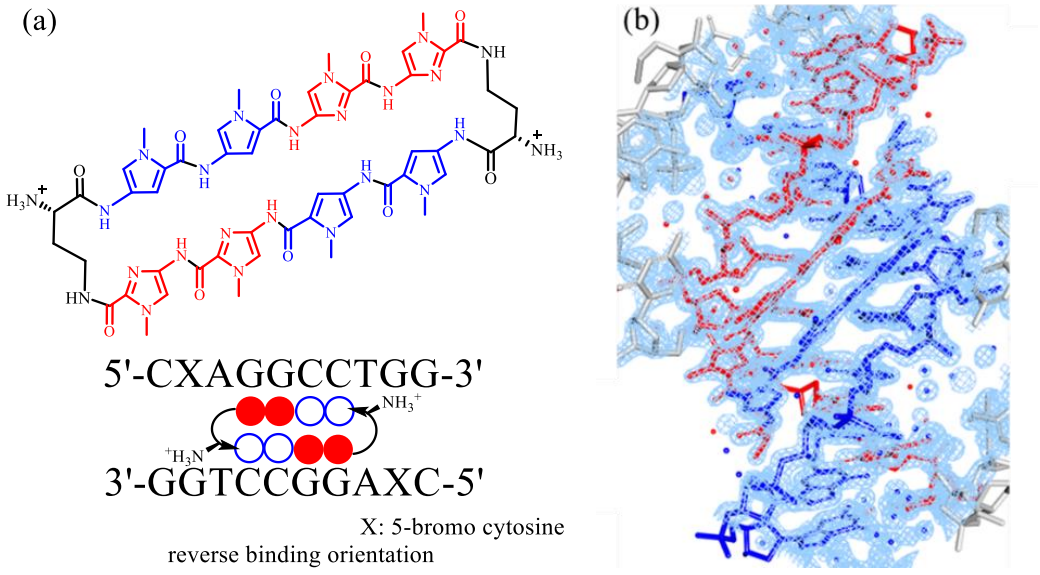


Figure 1. (a) Chemical structure and ball and stick notation of a cyclic PIP. (b) The crystal structure of the reverse binding orientation cPIP-DNA complex.

1) D. M. Chenoweth. *et al.*, *Proc. Natl. Acad. Sci.* **2009**, *106*, 13175-13179.
2) D. M. Chenoweth. *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 14521-14529.
3) K. Abe. *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 10544–10549.

TERRA の凝集体の形成機構とその機能の解明

（静大創造科学技術大学院 [1]・静大院理 [2]・埼玉医科大ゲノム医学研究センター[3]）○増澤樹 [1]・高濱謙太朗 [2]・奥島彩子 [2]・黒川理樹 [3]・大吉崇文 [1,2]
Elucidation of mechanism and function of TERRA aggregates ([1]*Graduate School of Science and technology, Shizuoka University*, [2]*Graduate school of Science, Shizuoka University,* [3]*Research Center for Genomic Medicine, Saitama Medical University*)○Tatsuki Masuzawa,[1] Kentaro Takahama,[2] Ayako Okushima,[2] Riki Kurokawa[3], Takanori Oyoshi[1,2]

Recently, it is known that noncoding RNAs form assemblies such as a paraspeckle with RNA binding proteins, and this assemblies regulates expression of target gene[1)]. TERRA (Telomeric repeat-containing RNA) which transcribed from telomere region also forms clusters with RNA binding proteins *in vivo*[1,2)]. Although TERRA relates with tri-methylation of H3K9 in telomere region, the relationship between TERRA clusters and histone modification is elusive. Therefore, we aimed to elucidate formation mechanism of TERRA clusters and its functions. In result, TERRA formed droplets depending on G-quadruplex RNA binding proteins such as TAF15 (TATA-box binding protein associated factor 15). Furthermore, formation of TERRA clusters repressed histone modifications in telomere region (Fig. 1). These findings suggest that TERRA clusters with the G-quadruplex binding protein can regulate epigenetics through histone modifications.
Keywords : G-quadruplex; TERRA; RNA binding protein; liquid-liquid phase separation; histone modification

近年、非コード RNA は RNA 結合タンパク質とパラスペックルなどの構造体を形成して、標的遺伝子の発現を制御していることが報告されている [1)]。テロメア領域から転写される非コード RNA の一種である TERRA(Telomeric repeat-containing RNA)は、細胞内で RNA 結合タンパク質と共にクラスターを形成する [1,2)]。一方で、TERRA はテロメア領域のヘテロクロマチン化にかかわることが報告されているが、クラスター形成との関連は不明である。そこで、TERRA のクラスター形成機構と機能の解明を目的とした。その結果、TERRA はグアニン四重鎖結合タンパク質である TAF15(TATA-box binding protein associated factor 15)依存的に液滴を形成することが分かった。さらに、TERRA のクラスター形成により、テロメア領域のヒストン修飾を抑制することが分かった（図 1)。

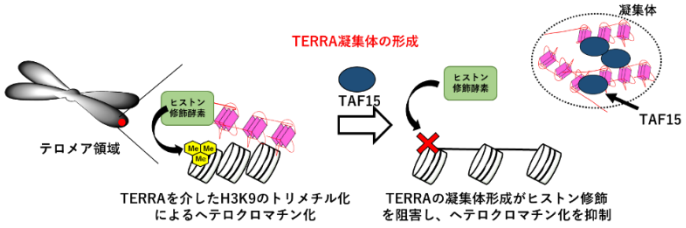


図1：TERRA凝集体の細胞内での作用モデル

1)*Science*, 2007, 318, 789-801
2)*Nat. Commun.*, 2010, 33, 1-10

RNA を標的としたアルキル化反応の大規模解析技術開発

（東北大多元研[1]・東北大院理[2]・京大 CiRA[3]）○鬼塚和光[1,2]・小松リチャード馨[3]・石川竣也[1,2]・Yutong Chen[1,2]・小嶋かんな[1,2]・村瀬裕貴[1]・長澤瞭佑[1,2]・小澤眞美子[1]・宮下映見[3]・齊藤博英[3]・永次史[1,2]
Development of large-scale analytical system for RNA alkylation reactions ([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,* [2]*Graduate School of Science, Tohoku University*, [3]*CiRA, Kyoto University*) ○ Kazumitsu Onizuka,[1,2] Kaoru Richard Komatsu,[3] Shunya Ishikawa,[1,2] Yutong Chen,[1,2] Kanna Ojima,[1,2] Hirotaka Murase,[1] Ryosuke Nagasawa,[1,2] Mamiko Ozawa,[1] Emi Miyashita,[3] Hirohide Saito,[3] Fumi Nagatsugi[1,2]

RNA is the attractive medicinal targets for the gene-related and infectious diseases. Defining the binding- and alkylation-selectivity of small molecules for various types of RNA structures is often overlooked due to the lack of tested numbers and species of RNAs. Practically, it is difficult to show the actual selectivity of RNA-binding and RNA-alkylating molecules toward various types of RNA structures because a large-scale analysis with diverse RNA structures has been challenging. In this presentation, we will report a new system to analyze small molecule-RNA interactions and RNA alkylation on a large scale.
Keywords : RNA; Alkylation; Large-scale analysis; DNA Microarray

RNA 標的創薬は近年、オリゴ核酸に加え、経口投与可能な小・中分子でも効果を期待できる標的が増え、飛躍的に進展している。RNA 標的医薬の中には、重篤な遺伝性疾患に対して治療効果が期待できるものもあり、遺伝性・難治性疾患に対する新しい治療法として期待されている。一方で、RNA は同種の高次構造でも配列が変われば、その微細構造も変わるため、RNA 結合分子やアルキル化分子の真の選択性の評価には、数百以上の網羅的な解析が不可欠である。しかし、これまで効率的な解析手法は報告されていなかった。我々は RNA 結合性小分子およびアルキル化分子の真の結合・反応選択性の調査を目的に、RNA-小分子間相互作用やアルキル化反応を大規模に解析する新しい技術の開発を行った。本研究では、マイクロアレイ技術を利用することで、RNA ライブラリ [1]（数千配列）に対する RNA-小分子間の結合親和性およびアルキル化反応性のランク化を一挙に行うことに成功した。本発表では、得られた親和性・反応性情報およびそれらの検証に関して報告する予定である。

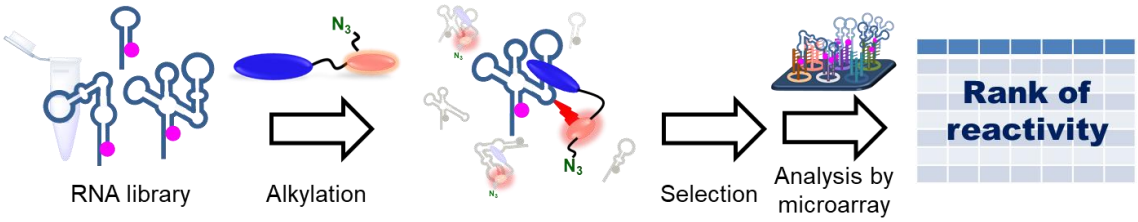


Fig. 1 Large-scale analytical system for RNA alkylation reactions with the RNA structure library.

1) H. Saito, *et. al.*, *Nat. Commun.* **2020,** *11,* 6275.

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

[A24-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair:Yuki Goto, Rie Wakabayashi

Mon. Mar 22, 2021 1:00 PM - 3:20 PM Room 24 (Online Meeting)

[A24-4pm-01] Total Chemical Synthesis and Investigation of Modified Linker Histone H1.2 and HP1α Utilizing Ru catalyst

○Naoki Kamo[1], Tomoya Kujirai[2], Hitoshi Kurumizaka[2], Hiroshi Murakami[3], Gosuke Hayashi[3], Akimitsu Okamoto[1,4] （1. Grad. Sch. Eng., The Univ. of Tokyo, 2. IQB, The Univ. of Tokyo, 3. Grad. Sch. Eng., Nogoya Univ., 4. RCAST, The Univ. of Tokyo）

1:00 PM - 1:20 PM

[A24-4pm-02] Ribosomal synthesis of helical peptide libraries containing cyclic β-amino acids and its application to drug screening

○Marina Kawai[1], Takayuki Katoh[1], Hiroaki Suga[1] （1. The University of Tokyo）

1:20 PM - 1:40 PM

[A24-4pm-03] *In vitro* selection of a library of pseudo-natural prenylated peptides

○Sumika Inoue[1], RIka Okuma[1], Yuki Goto[1], Hiroaki Suga[1] （1. The Univ. of Tokyo）

1:40 PM - 2:00 PM

[A24-4pm-04] Rebuilding ring-type decameric assembly of peroxiredoxin by chemical modification

○Tomoki Himiyama[1], Tsutomu Nakamura[1] （1. National Institute of Advanced Industrial Science and Technology）

2:00 PM - 2:20 PM

[A24-4pm-05] Entropy-driven ring-opening polymerization of the cyclic hemoglobin monomer containing a high molecular weight PEG

○Takashi Matsuhira[1], Hiromi Sakai[1] （1. Nara Medical University）

2:20 PM - 2:40 PM

[A24-4pm-06] Controlled co-assembly of peptide amphiphiles and its cell adhesion

○Rie Wakabayashi[1], Rino Imatani[1], Noriho Kamiya[1], Masahiro Goto[1] （1. Kyushu University）

2:40 PM - 3:00 PM

[A24-4pm-07] Development of protein nanoparticles displaying IgG binding domain and luciferase

○Gaoyang Wang[1], Yasumasa Mashimo[1], Masayasu Mie[1], Eiry Kobatake[1] （1. Tokyo Institute of Technology）

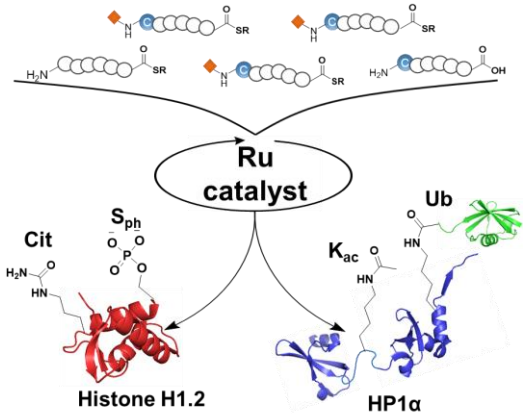
3:00 PM - 3:20 PM

Total Chemical Synthesis and Investigation of Modified Linker Histone H1.2 and HP1α Utilizing Ru catalyst

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute for Quantitative Biosciences, The University of Tokyo*, [3]*Graduate School of Engineering, Nagoya University*, [4]*Research Center for Advanced Science and Technology, The University of Tokyo*)
○ Naoki Kamo,[1] Tomoya Kujirai,[2] Hitoshi Kurumizaka,[2] Hiroshi Murakami,[3] Gosuke Hayashi,[3] Akimitsu Okamoto[1,4]
Keywords: Chemical Protein Synthesis; Ru catalyst; Post-Translational Modification

Chemical protein synthesis has facilitated the preparations of target proteins bearing site-specific post-translational modifications (PTMs).[1] Recently, applications of metal complexes for protein synthesis have been focused using those transformative powers, but significant amounts of metal complexes were required to achieve chemical reactions on proteins. Therefore, the synthetic strategy based on metal-catalyzed reactions on proteins has been demanded to avoid wasting expensive organometallic compounds and minimize the possibility of the absorption of metal on proteins.

Here, we report one-pot multiple peptide ligation strategy assisted by an organoruthenium catalyst, which showed more than 50-fold catalytic activity than previous palladium complexes, to eliminate cumbersome purification steps and synthesize proteins of interest with PTMs efficiently. Utilizing the ruthenium catalyst, we accomplished chemical synthesis of heterochromatin factors, histone H1.2 and heterochromatin protein 1α (HP1α), bearing various patterns of PTMs such as phosphorylation, ubiquitination, citrullination. We found that the citrullination at R53 in H1.2 reduced the stability of chromatosomes due to lack of the electrostatic interaction between Arg and DNA. Furthermore, we identified a key phosphorylation region in HP1α to control its binding toward DNA. It was envisaged that our strategy using Ru chemistry would facilitate the preparation of a variety of biologically significant proteins with PTMs and contribute to the elucidation of biological phenomena.



1) V. Agouridas *et al*., *Chem. Rev*. **2019**, *119*, 7328−7443.

Ribosomal synthesis of helical peptide libraries containing cyclic β-amino acids and its application to drug screening

[1]*Graduate School of Science, Department of Chemistry, The University of Tokyo* ○Marina Kawai[1], Takayuki Katoh[1], Hiroaki Suga[1]

Keywords: peptide drug; non-natural amino acid; drug screening; foldamer; helical structure

Peptides are an attractive drug development platform for their low manufacturing cost and little side effect. However, peptides consisting of only canonical L-α-amino acids often suffer from low target binding affinity, cell permeability, and rapid proteolytic degradation due to their flexible backbone structures. In contrast, introduction of sterically constrained nonproteinogenic amino acids, such as cyclic β-amino acids (cβaas), induces highly restricted structures of peptides, and thereby improved binding affinity against target molecules, cell permeability, and protease resistance, making them more attractive drug candidates.[1] For instance, peptides bearing periodical 2-amino-cyclopentane carboxylic acid (2-ACPC) exhibit a well-defined helical structure called 10/11/11 helix (Fig. 1a). Recently, we succeeded in ribosomal incorporation of diverse cβaas by utilizing a reconstituted *E. coli* translation system.[2] By means of this technology, we constructed a 10/11/11-helical peptide library containing 2-ACPC at every third position and applied it to an mRNA display-based screening methodology referred to as the Random non-standard Peptide Integrated Discovery (RaPID) system (Fig. 1b). The affinity screening was performed against Nrf2, which is related to the proliferation of cancer cells. As a result, we were able to obtain potent peptides with high binding affinity to Nrf2 as well as enhanced proteolytic stability compared to their α-Ala mutant counterparts. Circular Dichroism spectrometry measurement revealed that all of the discovered peptides were folded into 10/11/11 helices, showing that our strategy is practically applicable to developing a novel class of peptide drugs bearing 10/11/11-helical structures.

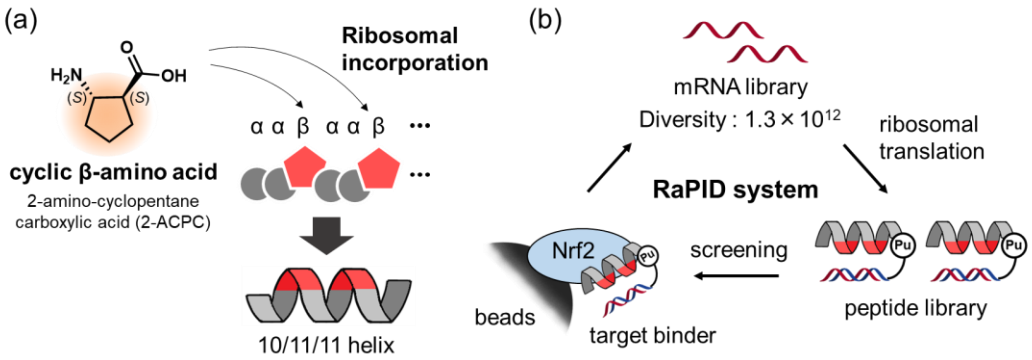


Figure 1 (a) Structure of a cyclic β-amino acid and ribosomal synthesis of 10/11/11-helical peptides. (b) The scheme of the RaPID system using a 10/11/11-helical peptide library.

[1] Gellman, S. H. et al. *Chem. Rev.*, **2001**, *101*, 3219.
[2] Katoh, T. et al. *Nat. Chem.*, **2020**, *12*, 1081.

In vitro selection of a library of pseudo-natural prenylated peptides

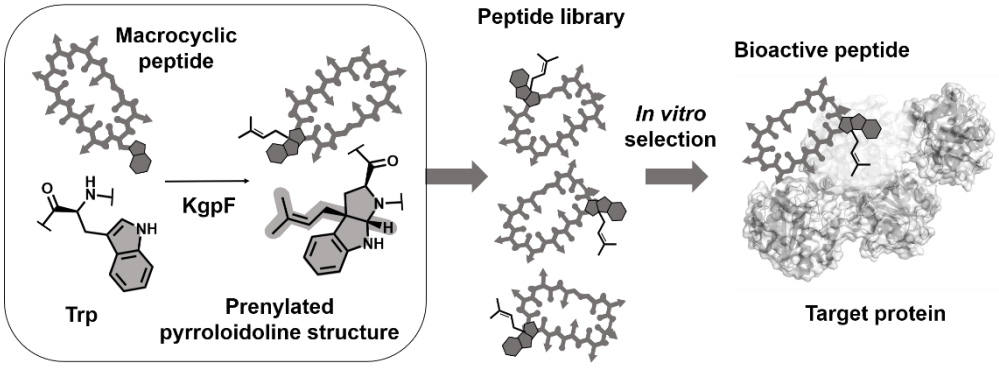
(*Graduated school of Science, The University of Tokyo*) ○Sumika Inoue, Rika Okuma, Yuki Goto, Hiroaki Suga

Keywords*:* Peptide library; Natural product; Post-translational modification; Prenylated peptide

In nature, peptides undergo post-translational modification (PTM) to acquire highly complex structures distinct from 20 proteinogenic amino acids. Prenylation is a typical PTM in peptidic natural products produced by cyanobacteria, and is expected to increase membrane permeability, biostability, and rigidity of peptides. In this study, a library of pseudo-natural prenylated peptides, artificial peptides containing naturally occurring prenylated structure, was constructed. The library was applied for selection experiments to develop *de novo* bioactive peptides.

For construction of the library, an engineered *in vitro* translation system was combined with enzymatic prenylation. KgpF is a member of the prenyltransferase family involved in cyanobactin biosynthesis and utilized in this study. KgpF mediates stereospecific transfer of a dimethylallyl group to a tryptophan (Trp) and backbone ring closure, giving a tricyclic hydrophobic pyrroloindoline structure in peptides[1,2]. The previous experiments in our laboratory demonstrated that KgpF exhibits remarkably broad substrate tolerance. This characteristic of KgpF enabled prenylation of more than 10^{14} types of artificial thioether macrocyclized peptides by a simple operation.

Using this library, ligands against multiple therapeutic target proteins were successfully obtained. These ligands exhibited strong affinity with Kd values of low nM level. In this talk, details about the design of the library, the *in vitro* selection experiments, and unique functionalities of the obtained bioactive pseudo-natural peptides will be described.



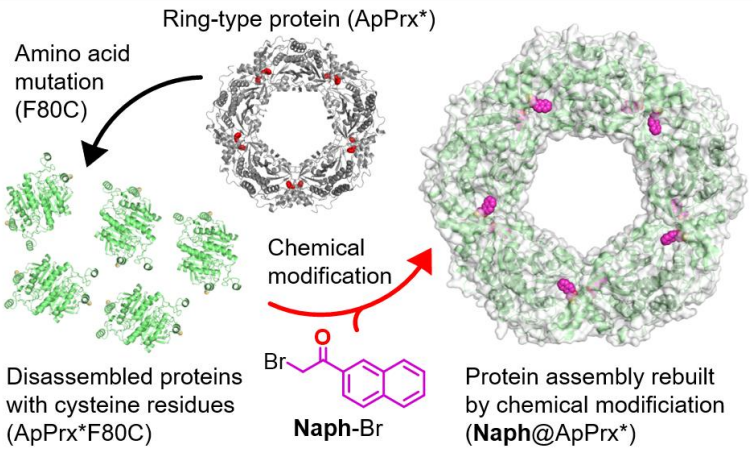
1) *Angew. Chem. Int. Ed.,* 55, 3596-3599 (2016). 2) *Org. Biomol. Chem.*, 14, 9639-9644 (2016).

Rebuilding ring-type decameric assembly of peroxiredoxin by chemical modification

(*Biomedical Research Institute, National Institute of Advanced Industrial Science and Technology (AIST)*) ○Tomoki Himiyama, Tsutomu Nakamura
Keywords: Peroxiredoxin; Chemical Modification; Protein Assembly

The quaternary structure (QS) of proteins is generated through specific supramolecular interactions among protein domains, resulting in highly sophisticated architectures such as spheres, tubes, ring-like conformations, and bacterial compartments and viruses.[1] Direct control of protein QS is still challenging owing to the complexity of protein structure. As a protein with a characteristic QS, peroxiredoxin (Prx) is an antioxidant enzyme expressed in most living organisms.[2] It uses cysteine as a catalytic residue and forms characteristic QS including dimers, square octamers, pentagonal decamers, and hexagonal dodecamers. Such structural variations render Prx a noteworthy target for studying protein assembly and its application in nanotechnology. For example, Prx from *Aeropyrum pernix* K1 (ApPrx) forms a characteristic ring-type decamer via the assembly of five dimers.

In this work, we disrupted and reconstituted ApPrx QS via amino acid mutations and chemical modifications targeting hot spots for protein assembly (Figure).[3] Hydrophobic interactions are essential for the ApPrx dimers to associate. The decameric QS of an ApPrx* mutant, wherein all cysteine residues in wild-type ApPrx were mutated to serine, was destructed to dimers via an F80C mutation destructing the hydrophobic interactions. The dimeric ApPrx*F80C mutant was then modified with small molecules and successfully assembled as a decamer by modifying the protein with a naphthalene derivative. Structural analysis confirmed that an artificially installed chemical moiety potentially facilitates suitable protein-protein interactions to rebuild a native structure. This study describes a facile method to regulate protein assembly state.



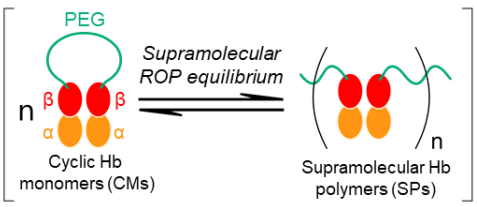
1) B. J. G. E. Pieters, M. B. van Eldijk, R. J. M. Nolte, J. Mecinović, *Chem. Soc. Rev.* **2016**, *45*, 24. 2) A. Perkins, K. J. Nelson, D. Parsonage, L. B. Poole, P. A. Karplus, *Trends. Biochem. Sci.* **2015**, *40*, 435. 3) a) T. Himiyama, T. Nakamura, *Protein Sci.* **2020**, *29*, 1138. b) T. Himiyama, Y. Tsuchiya, Y. Yonezawa, T. Nakamura, *Bioconjugate Chem.* Article ASAP. doi: 10.1021/acs.bioconjchem.0c00587

Entropy-driven ring-opening polymerization of the cyclic hemoglobin monomer containing a high molecular weight PEG

(*Department of Chemistry, Nara Medical University*) ○Takashi Matsuhira, Hiromi Sakai
Keywords: Hemoglobin; Polyethylene Glycol; Cross-Linking; Thermodynamic Parameters; Blood Substitutes

A hemoglobin (Hb) molecule consists of an $\alpha_2\beta_2$ tetramer which dissociates reversibly into two αβ dimers ($2\alpha\beta \leftrightarrows \alpha_2\beta_2$). We previously reported that an exchange reaction of dimeric αβ subunits proceeds between native Hb and Cys-93(β) PEGylated Hb at a sub-millimolar concentration although they fundamentally favor stable $\alpha_2\beta_2$ tetrameric structures.[1] Moreover, we revealed that a cyclic Hb monomer (CM), in which two Cys-93(β) residues in an $\alpha_2\beta_2$ tetramer were connected through a flexible PEG chain, undergoes ring-opening polymerization (ROP) to form a linear supramolecular polymer (SP) with Hb−PEG alternating structure through the reversible inter-molecular exchange of αβ subunits (Fig. 1).[2] In the present work, thermodynamics of supramolecular ROP was evaluated for four CMs containing high molecular weight PEGs (2, 5, 10, or 20 kDa).

The equilibrated mixture of the produced SPs and the remained CMs were quantified by covalent fixing method[1,2] using site-specific ββ-cross-linker, bis(3,5-dibromosalicyl) fumarate (DBBF). The ββ-cross-linking was conducted at different monomer concentrations $[M]_0$ and at different temperatures. Then, the cross-linked products were quantified using size exclusion chromatography. When DBBF was reacted at a lower $[M]_0$, a fixed CM was obtained mainly. In contrast, a reaction with DBBF at a higher $[M]_0$ generated dominantly a fixed SP. The results indicate the existence of ROP equilibrium depending on $[M]_0$. We found that the critical monomer concentration $[M]_{crit}$, a threshold for starting ROP, decreased with increasing of the ring size. Additionally, Van't Hoff plots for ROP equilibrium constant at $[M]_0$ = 1 mM revealed negligibly small enthalpy changes (ΔH_p < 1 kJ·mol^{-1}) and considerably positive entropy changes that increased with the ring size (ΔS_p = 26.8−33.2 J·mol^{-1}·K^{-1}) (Fig. 1). These results indicate that the entropy-driven mechanism governs supramolecular ROP, and a CM with a larger ring size prefers to convert to a SP.



Cyclic Hb monomers (CMs)	$[M]_{crit}$ (mM)	ΔH_p (kJ·mol^{-1})	ΔS_p (J·mol^{-1}·K^{-1})
Hb-PEG2k	0.86	< 1	26.8
Hb-PEG5k	0.33	< 1	27.3
Hb-PEG10k	0.13	< 1	28.5
Hb-PEG20k	0.063	< 1	33.2

Fig. 1 Supramolecular ring-opening polymerization (ROP) equilibrium of cyclic Hb monomers (CMs) and supramolecular Hb polymers (SPs), and summary of their thermodynamic parameters.

(1) Matsuhira, T.; Kure, T.; Yamamoto, K.; Sakai, H. *Biomacromolecules* **2018**, *19(8)*, 3412–3420.
(2) Matsuhira, T.; Yamamoto, K.; Sakai, H. *Biomacromolecules* **2019**, *20(4)*, 1592–1602.

自己組織化ペプチドの共集合制御と細胞接着性

（九大院工 [1]）○若林 里衣 [1]・今谷 梨乃 [1]・神谷 典穂 [1]・後藤 雅宏 [1]

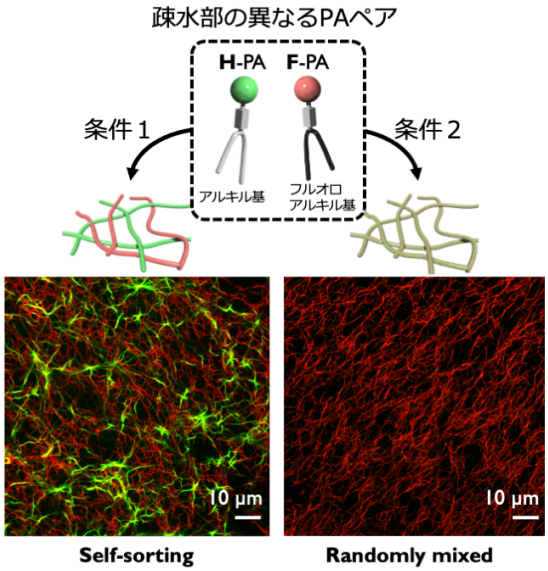
Controlled co-assembly of peptide amphiphiles and its cell adhesion

([1]*Graduate School of Engineering, Kyushu University*)
○Rie Wakabayashi,[1] Rino Imatani,[1] Noriho Kamiya,[1] Masahiro Goto[2]

This study aimed to control co-assembly formation of peptide amphiphiles (PAs) when more than two kinds of PAs were mixed and to realize novel functions. PAs bearing alky and fluoroalkyl groups as the hydrophobic groups did not mix each other but formed self-sorted assembly. The co-assembly behavior could be controlled by the temperature and additives. In the presentation, we will report the co-assembly behavior under various conditions and the cell adhesion of the assemblies when cell adhesive ligand was introduced.

Keywords : Co-assembly; Peptide amphiphiles; Cell adhesion

本研究は、二種類以上の両親媒性ペプチド (peptide amphiphile, PA) を混合した際の共集合の制御と機能発現を目的としている。類似の分子骨格を持つが疎水部にそれぞれアルキル基とフルオロアルキル基を有する PA はいずれもファイバー状構造体を形成するが、両者を混合すると、互いに混ざり合わず、PA 同士が独立して自己組織化する self-sorting[1)]という現象が観察された。しかし混合の際の温度条件や第三成分の添加により、共集合の様式が変化した。水中で働く疎水性相互作用と疎フルオロ性のバランスにより、この共集合の変化が生じていることが示唆された。末端に細胞接着性因子を有する PA を導入した場合、混合する PA との相溶性の違いにより、ファイバーへの細胞接着性に変化が生じた。本講演では、各条件下における共集合の様式と、細胞接着性因子を導入した際の細胞接着性の発現に関し報告する。



1) I. Hamachi *et al*., *Nat. Chem., 8*, 743, 2016; D. J. Adams *et al., Nat. Commun.,* 4:1480, 2013.

Development of protein nanoparticles displaying IgG binding domain and luciferase

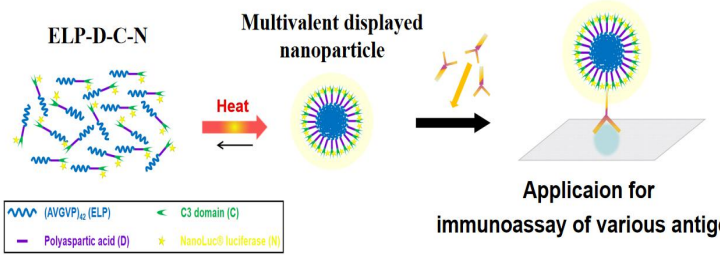
(*School of Life Science and Technology, Tokyo Institute of Technology*) ○Gaoyang Wang , Yasumasa Mashimo , Masayasu Mie , Eiry Kobatake

Keywords: Temperature responsive nanoparticles; Bioluminescence; Immunoassay

Immunoassays play an important role in clinical, pharmaceutical and scientific researches. Especially the enzyme-linked immunosorbent assay (ELISA) is widely used due to its low background, wide dynamic range, simple operation and high specificity. However, the sensitivity of ELISA still has the potential to be improved.

In our previous research, we developed a fusion protein composed of elastin-like polypeptide (ELP) and polyaspartic acid (D). ELP is an amphipathic temperature-responsive recombinant protein. By incubating over the phase transition temperature, it can self-assemble into spherical nanoparticles with a hydrophobic core. In this study, we developed a new fusion protein ELP-D-C-N, ELP-D fused with IgG binding protein (C) and bright blue light-emitting luciferase NanoLuc (N). Based on the fusion protein ELP-D-C-N formed nanoparticles, a highly sensitive immunedetection system has been developed. The nanoparticle displays IgG binding domain and NanoLuc multivalently on its surface. Compared with traditional reporter enzyme-labeled monovalent constructs, multivalent antibody constructs can react with the antigen through an excess of labeled antibodies, and convert trace amounts of antigen into antigen-antibody complexes that can be detected by the reporter molecule. The apparent binding affinity is increased from several times to several hundred times, thereby more directly and significantly improving the sensitivity of the assay. In addition, the bioluminescence produced by Nanoluc through interaction with the substrate is a chemical process that does not require irradiation, which may increase the background signal, so a luminescence-based detection system may achieve a more sensitive ELISA.

The results of the application of the ELP-D-C-N protein nanoparticle in the immunoassay system showed that it increased the LOD from 341.19 pg/mL in the monomer by 10-fold to 34.8 pg/mL.



Schematic of preparation of ELP-D-C-N nanoparticle and the ELP-D-C-N nanoparticle-based ELISA

[A23-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair:Shinichi Sato, Tomonori Tamura

Mon. Mar 22, 2021 1:00 PM - 3:00 PM Room 23 (Online Meeting)

[A23-4pm-01] A new reactive peptide tag-probe pair for the site-specific incorporation of designer chemical probes into proteins

○Vikram Thimaradka[1], Jae Hoon Oh[2], Christina Heroven[3,4], Radu Aricescu[3,4], Michisuke Yuzaki[5], Tomonori Tamura[1], Itaru Hamachi[1,2] （1. Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, JAPAN., 2. ERATO (Exploratory Research for Advanced Technology, JST), Sanbancho, Chiyodaku, Tokyo, 102-0075, JAPAN., 3. Division of Structural Biology, University of Oxford, Oxford OX3 7BN, UK., 4. Neurobiology Division, MRC Laboratory of Molecular Biology, Cambridge CB2 0QH, UK., 5. Department of Physiology, Keio University School of Medicine, Tokyo 160-8582, JAPAN.）

1:00 PM - 1:20 PM

[A23-4pm-02] Ligand-directed two-step labeling to quantify AMPA-type glutamate receptor trafficking

○Kento Ojima[1], Kyohei Soga[2], Itaru Hamachi[1,3], Shigeki Kiyonaka[2] （1. Kyoto Univ., 2. Nagoya Univ., 3. ERATO JST）

1:20 PM - 1:40 PM

[A23-4pm-03] Extra-cellular loop (ECL) engineering for GPCR-chemogenetics (3): Allosteric control of metabotropic glutamate receptor signaling

○Tomohiro Doura[1], Kanta Hasegawa[1], Shigeki Kiyonaka[1] （1. Graduate school of engineering, Nagoya University）

1:40 PM - 2:00 PM

[A23-4pm-04] Investigation on the local structural effects on chemical modification of cysteine residues on protein surface

Ryosei Tamaki[1], Teruyuki Miyake[1], Shun Hirota[1], ○Takashi Matsuo[1] （1. Nara Institute of Science and Technology）

2:00 PM - 2:20 PM

[A23-4pm-05] Development of photocatalyst-proximity protein labeling for profiling protein-protein interaction in intracellular microenvironment

○Michihiko Tsushima[1,2], Shinichi Sato[3], Hiroyuki Nakamura[1] （1. Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 2. School of Life Science and Engineering, Tokyo Institute of Technology,, 3. Frontier Research Institute for Interdisciplinary Sciences, Tohoku University）

2:20 PM - 2:40 PM

[A23-4pm-06] *De novo* design of transmembrane coiled-coil peptide channels

○Ai Niitsu[1], Andrew R Thomson[2], Alistair J Scott[2], Jason T Sengel[3], Yuji Sugita[1], Mark I Wallace[3], Hagan Bayley[4], Derek N Woolfson[2] （1. Riken, 2. Univ. of Bristol, 3. KCL, 4. Univ. of Oxford）

2:40 PM - 3:00 PM

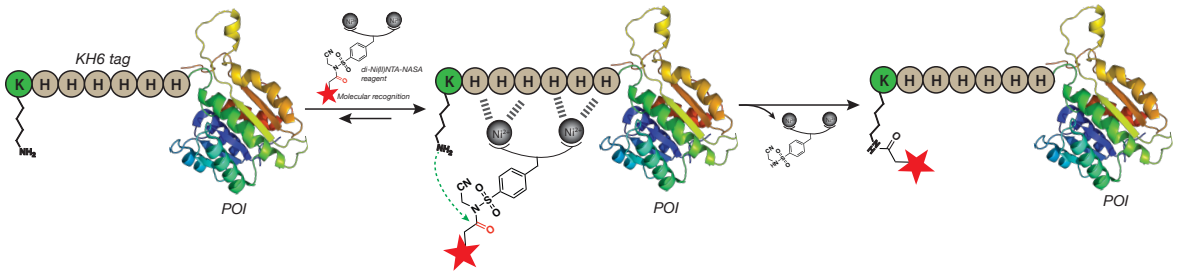
A new reactive peptide tag-probe pair for the site-specific incorporation of designer chemical probes into proteins

([1]*Graduate School of Engineering, Kyoto University*, [2]*JST, ERATO*, [3]*University of Oxford, UK*, [4]*MRC LMB, Cambridge, UK*, [5]*Keio University School of Medicine, Tokyo*) ○Vikram Thimaradka,[1] Jae Hoon Oh,[2] Christina Heroven,[3,4] Radu Aricescu,[3,4] Michisuke Yuzaki,[5] Tomonori Tamura,[1] Itaru Hamachi[1,2]

Keywords: Bioconjugation; Protein modification; Peptide tag.

Installation of desired chemical functionality on protein of interest (POI) provides numerous downstream applications in biology and medicine. Albeit several powerful enzymatic methods, such as SNAP-tag and Halo tag, has been established, the large protein tag domain could perturb natural function and/or behavior of POI. In this context, short peptide tag-probe pairs are promising alternatives for site-specific covalent modification of proteins with minimum perturbation to the inherent protein functions. Our lab had previously developed reactive peptide tag-probe pair system involving a di-Ni(II)NTA–His_6 tag interaction for recruiting a cysteine-reactive alpha chloroacetamide towards tag fused POI.[1] However, oxidation of Cys residues to form disulfide linkages often hinders the labeling in true biological contexts.

Herein, we report a new reactive peptide tag-probe pair employing Lys containing His_6 tag (KH_6/H_6K) with di-Ni(II)NTA tethered *N*-alkyl-*N*-acyl sulfonamide (NASA) reagent, a cleavable electrophile for Lys side chain modification.[2,3] The proximity induced by di-Ni(II)NTA–His_6 interaction facilitates a reaction between a Lys residue of the tag and the NASA group to covalently and site-specifically incorporate a desired reporter into the tag with concomitant removal of di-Ni(II)NTA part. We characterized the labeling kinetics and site specificity using model peptides and several proteins containing the tag sequence *in vitro*. Further, we succeeded in the labeling of the tag-fused EGFR and Neuroligin-1 expressed in live cells.



1) S. Uchinomiya *et al. Chem. Commun.,* 49, 5022 (2013) 2) V. Thimaradka *et al. Bioorg. Med. Chem.,* 30, 115947 (2020) 3) T. Tamura *et al. Nat. Commun.,* 9, 1870 (2018).

Ligand-directed two-step labeling to quantify AMPA-type glutamate receptor trafficking

([1]*Graduate School of Engineering, Kyoto University*, [2]*ERATO, JST, Graduate School of Engineering, Nagoya University*) ○Kento Ojima,[1] Kyohei Soga,[3] Itaru Hamachi,[1,2] Shigeki kiyonaka[3]

Keywords: Ligand-directed Chemistry; IEDDA reaction; AMPA receptor

AMPA-type glutamate receptor (AMPAR) is a subtype of the ionotropic glutamate receptors, which mediates fast excitatory neurotransmission in the central nervous system. The number of AMPARs on the postsynaptic surface changes dramatically during synaptic plasticity, a cellular mechanism of memory and learning. Impaired membrane trafficking of AMPARs causes cognitive impairment and psychiatric disturbance such as anxiety and depression. Therefore, analyzing the trafficking of AMPAR is indispensable for elucidation of the molecular mechanism of memory, learning and neurological diseases.

Our laboratory developed ligand-directed acyl imidazole (LDAI) chemistry, a chemical labeling method for cell-surface proteins in live cells[1]. Although this technique is powerful for labeling endogenous AMPARs[2], there are some restrictions for analyzing trafficking of AMPARs. First, live cells need to be kept at low temperatures (17 °C) during labeling to suppress the internalization of labeled AMPARs. Second, the culture medium needs to be exchanged for serum-free medium or buffered saline during labeling to decrease non-specific labeling of serum proteins such as albumin. The relatively long-term exposure (1–4 h) to these non-physiological conditions may interfere with neuronal activity or survival. Ideally, neurons should be kept under physiological conditions during chemical labeling.

Here, we develop a method for the rapid and selective labeling of AMPARs under physiological temperature in culture medium by ligand-directed two-step labeling combining LDAI chemistry and inverse-electron demand Diels-Alder (IEEDA) reaction[3]. This method allowed us to label AMPARs within a few minutes under cell-friendly condition. Furthermore, we successfully analyzed lifetime of AMPARs for long time without neuronal death, and quantified the fast recycling dynamics of AMPARs in the cultured neuron.

1) Fujishima, S.*et al.* Ligand-directed acyl imidazole chemistry for labeling of membrane-bound proteins on live cells. *J. Am. Chem. Soc.* 2012, **134**, 3961-3964

2) Wakayama, S. *et al.* Chemical labeling for visualizing native AMPA receptors in live neurons. *Nat Commun.* 2017, **8**, 14850

3) Ojima, K. *et al.* Ligand-directed two-step labeling to quantify neuronal glutamate receptor trafficking. *Nat. Commun.* (in press)

細胞外ループ工学による GPCR 化学遺伝学(3): アロステリックサイトに着目した代謝型グルタミン酸受容体の活性制御

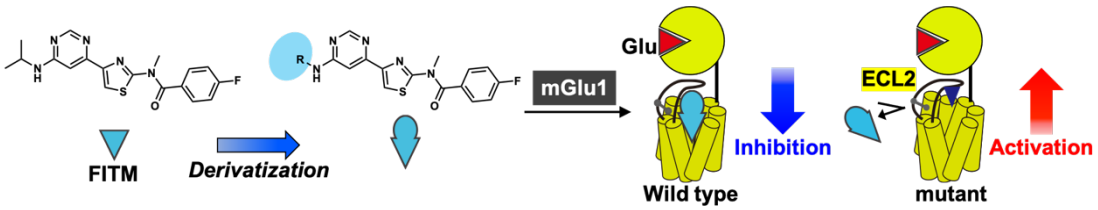
（名大院工）○堂浦 智裕・長谷川 寛太・清中 茂樹
Extra-cellular loop (ECL) engineering for GPCR-chemogenetics (3): Allosteric control of metabotropic glutamate receptor signaling (*Graduate School of Engineering, Nagoya University*) ○Tomohiro Doura, Kanta Hasegawa, Shigeki Kiyonaka

Metabotropic glutamate receptors belong to class C GPCRs that mediate excitatory neurotransmission in the central nervous system. Class C GPCRs contain 7 transmembrane (7TM) domain and extracellular ligand-binding domain (LBD). Endogenous ligands such as glutamate bind the LBD, while some subtype-selective allosteric modulators bind the 7TM domain.

The aim of this research is the regulation of metabotropic glutamate receptor 1 (mGlu1) having essential roles in motor learning. We implemented mutagenesis at the extracellular loop 2 (ECL2) near the allosteric ligand binding site, and derivatization of FITM, a mGlu1-selective allosteric modulator. Screening assays led to the identification of a combination of mGlu1 mutant and FITM derivative, which allowed chemogenetic control of mGlu1. In addition, binding assays of FITM derivatives to mGlu1 provided knowledge relevant to the mechanism of the chemogenetic regulation. In this presentation, we report the results of this chemogenetic research.
Keywords: GPCR; Chemogenetics; Neurotransmitter receptor; Allosteric control

代謝型グルタミン酸受容体は中枢神経系において興奮性神経伝達に関わる class C に属する GPCR である。Class C GPCR には 7 回膜貫通（7TM）ドメインに加えて細胞外にリガンド結合ドメイン（LBD）が存在する。グルタミン酸のような内在リガンドは LBD に結合するが、7TM ドメインに結合するサブタイプ選択的なアロステリックリガンドも知られている。

本研究では運動学習に関与する代謝型グルタミン酸受容体 1（mGlu1）の活性制御を目標に、アロステリックリガンド結合部位近傍の細胞外ループ 2（ECL2）への変異導入と mGlu1 選択的アロステリックリガンド FITM の誘導体化を行い、スクリーニングより mGlu1 の活性制御を可能にする変異体と FITM 誘導体の組み合わせを見出した。また、mGlu1 と FITM 誘導体の結合実験より、当該誘導体の mGlu1 活性制御のメカニズムに関する知見を得た。本発表ではこれらの知見について報告する。



Investigation on the local structural effects on chemical modification of cysteine residues on protein surface

(*Division of Materials Science, Nara Institute of Science and Technology*) Ryosei Tamaki, Teruyuki Miyake, Shun Hirota, ○Takashi Matsuo

Keywords: Chemical modification; Cysteine; Local structural effect; Adenylate kinase

Adenylate kinase (Adk), a phosphoryl transfer enzyme for ATP/AMP and ADP, shows the conformational interconversion between OPEN and CLOSED forms. Using this characteristic, we previously constructed a photo-switching system of pyrene, where two pyrene molecules were conjugated onto cysteine residues of the mutant Adk (A55C/C77S/V169C).[1)] Furthermore, the reactivity of the thiol at Cys55 was found to be higher than that of the thiol at Cys169 although both cysteine residues are located on the protein surface. In general, the regioselective modification of cystine residues on the protein surface is difficult. Assuming that local structural effects of acidic amino acid residues (Asp54 and Glu170) located nearby these cysteine residues may provide the reactivity difference, we conducted the following molecular dynamics (MD) simulation and mutation studies. The MD simulation for the mutant Adk demonstrated that Glu170 tends to face to Cys169, whereas Asp54 took away from Cys55 to form a salt bridge with Lys50. Accordingly, we studied the reactivities of cysteine thiols for another mutant K50A/A55C/C77S/V169C because the removal of the salt bridge may bring about a similar situation for Asp54 and Glu170. In contrast to our expectation, the reactivity of the thiol at Cys55 was further enhanced on the mutation at Lys50. Lys/Ala50 and Asp54 are on a α-helix, whereas Cys55 is located on the edge of the α-helix. The Lys50Ala mutation causes the increase in the flexibility of the α-helix, and the structural perturbation is transmitted to Cys55. The finding indicates that the local flexibility near the chemical modification site influences the reactivities of cysteine thiols on the protein surface.[2)]

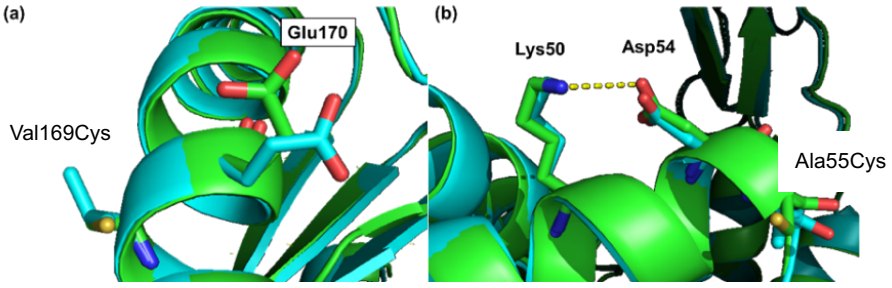


Figure 1. Local structures around Cys/Val169 (figure (a)) and Cys/Ala55 (figure (b)) obtained by MD simulation (blue backbone: the wild-type Adk; green backbone: mutant Adk (A55C/C77S/V169C)).

1) A. Fujii, S. Hirota, T. Matsuo, *Bioconjugate Chem.* **2013**, *24*, 1218. 2) T. Miyake, R. Tamaki, M. Asanuma, Y. Fukada, S. Hirota, T. Matsuo, *Bioconjugate Chem.* **2020**, *31*, 794.

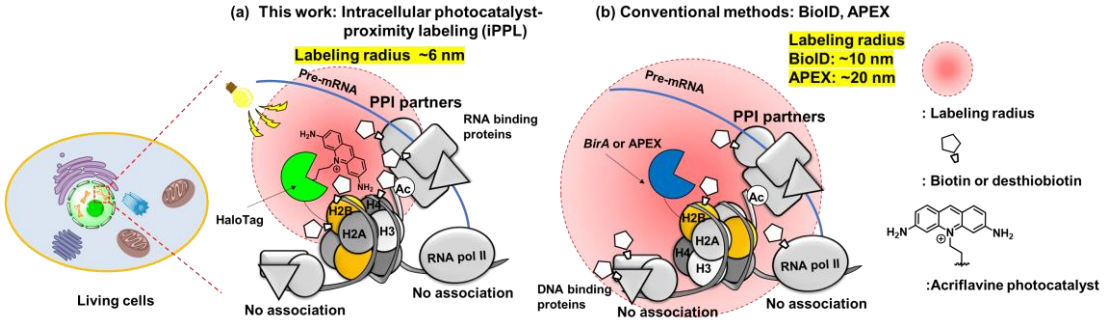
Development of photocatalytic-proximity protein labeling for profiling protein-protein interaction in intracellular microenvironments

([1]*Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology,* [2]*School of Life Science and Engineering, Tokyo Institute of Technology,* [3]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University*) ○Michihiko Tsushima,[1,2] Shinichi Sato,[3] Hiroyuki Nakamura[1]

Keywords: photocatalyst; Proximity labeling; chromatin; protein-protein interaction

Protein–protein interactions (PPIs) are a key component of molecular interaction networks, and thus, techniques for analyzing PPIs can yield key elucidations of biological pathways. Although proximity labeling techniques utilizing genetically expressed proteins of interest (POIs) fused to enzymes such as *BirA* (BioID)[1] and engineered ascorbate peroxidase (APEX)[2] were useful for clarification of protein dynamics and localization in living cells, it is difficult to apply them to focused PPIs profiling due to their large labeling radius (BioID: ~10 nm, APEX: ~20 nm).

In this study, we developed intracellular photocatalytic-proximity labeling (iPPL). Acriflavine was found to be an efficient cell-membrane-permeable photocatalyst for introduction into genetically fused HaloTag for photocatalyst-mediated labeling with 1-methyl-4-arylurazole (MAUra)[3] within a few-nanometer labeling radius. We demonstrated the photocatalyst-proximity labeling of H2B as a POI with MAUra in the intracellular environment of HaloTag-H2B expressed HEK293FT cells. Endogenous histone components (H2A, H2B, H3, and H4) and RNA-binding proteins that directly interact with histone were selectively labeled using the iPPL approach, revealing that iPPL has approximately 6 nm labeling radius which is smaller than those of BioID and APEX.



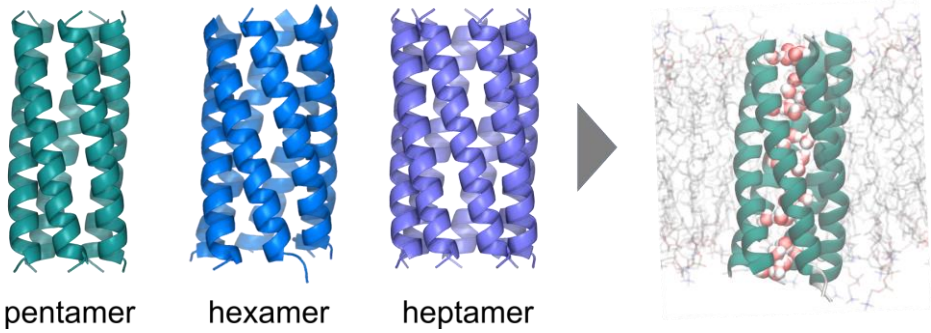
1) K. J. Roux, D. I. Kim, M. Raida, B. Burke, *J. Cell Biol.* **2012**, *196*, 801−10. 2) H-W. Rhee, P. Zou, N. D. Udeshi, J. D. Martell, V. K. Mootha, S. A. Carr, A. Y. Ting, *Science*, **2013**, *339,* 1328-1331. 3) S. Sato, K. Hatano, M. Tsushima and H. Nakamura, *Chem. Commun.,* **2018**, *54*, 5871–5874.

膜貫通コイルドコイルペプチドチャネルの *de novo* 設計

(理化学研究所[1]、ブリストル大[2]、ロンドン大キングスカレッジ[3]、オックスフォード大[4]) ○新津 藍[1]、Andrew Thomson[2]、Alistair Scott[2]、Jason Sengel[3]、杉田 有治[1]、Mark Wallace[3]、Hagan Bayley[4]、Derek Woolfson[2]
De novo design of transmembrane coiled-coil peptide channels ○Ai Niitsu[1], Andrew R Thomson[2], Alistair J Scott[2], Jason T Sengel[3], Yuji Sugita[1], Mark I Wallace[3], Hagan Bayley[4], Derek N Woolfson[2] ([1]Riken, [2]Univ. of Bristol, [3]KCL, [4]Univ. of Oxford)

De novo design of membrane proteins requires deep understandings of their sequence-to-structure relationship[1]. To address this challenge, focusing on coiled-coil structures based on stable helix-helix packing, we rationally design and synthesize transmembrane coiled-coil peptide-based ion channels. Through computational peptide design and structure prediction along with experimental structural analysis and single channel current recording of the designed peptide channels, we shed light on general principles of coiled-coil formation in membrane.
Keywords : Transmembrane Peptide, Protein Design, Single Channel Recording, Molecular Dynamics

膜タンパク質の *de novo* 設計を達成するためには、膜タンパク質のアミノ酸配列－構造相関を理解することが不可欠である[1]。そこで本研究では、安定なαヘリックス会合構造として知られるコイルドコイル構造に着目し、イオンチャネルを形成するコイルドコイルペプチドを設計・合成した。計算機を用いたペプチド理論設計と構造予測、およびペプチド会合体の構造分析、一分子チャネル電流測定より得られた、膜貫通コイルドコイル構造の形成機序について報告する。



1) Membrane-spanning α-helical barrels as tractable protein-design targets. A. Niitsu, J.W. Heal, K. Fauland, A.R. Thomson, D.N. Woolfson, *Phil. Trans. R. Soc. B* **2017**, *372*, 20160213

[A02-4am] 19. Colloid and Interface Chemistry

Chair:Kensuke Akamatsu, Masafumi Harada

Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 2 (Online Meeting)

[A02-4am-01] Threading Ultra-long Polymer into MOF: Synthesis and Physical Properties

○Tomoya Iizuka[1], Etsuhiro Miwa[2], Nobuhiko Hosono[1], Takashi Uemura[1,2] (1. Grad. Sch. of Front. Sci., Univ. of Tokyo, 2. Grad. Sch. of Eng., Univ. of Tokyo)

9:00 AM - 9:20 AM

[A02-4am-02] Novel redox and optical properties of thiolate-protected gold superatom $Au_{25}(SR)_{18}$ induced by bulky ligands

○Tsubasa Omoda[1], Shinjiro Takano[1], Tatsuya Tsukuda[1,2] (1. Grad. Sch. Sci., The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)

9:20 AM - 9:40 AM

[A02-4am-03] Shape memory behaviour of Cu1.8S nanoparticles during cation exchange reaction

○ZHANZHAO LI[1], Masaki Saruyama[2], Toshiharu Teranishi[2] (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Chemical Research, Kyoto University)

9:40 AM - 10:00 AM

[A02-4am-04] Fabirication of aqueous nanoparticle colloids of metal porphyrins and photosensitized singlet oxygen generation by visible light irradiation.

○Tsuyoshi Asahi[1], Eiji Yukihiro[1], Taisei Himeda[1], Tamotsu Zako[1] (1. Ehime University)

10:00 AM - 10:20 AM

[A02-4am-05] Synthesis of Mo and Ru solid-solution alloy NPs and their hydrogen evolution reaction activity

○Shinya Okazoe[1], Kohei Kusada[1], Dongshuang Wu[1], Tomokazu Yamamoto[2], Takaaki Toriyama[2], Syo Matsumura[2], Shogo Kawaguchi[3], Yoshiki Kubota[4], Hiroshi Kitagawa[1] (1. Kyoto Univ., 2. Kyushu Univ., 3. JASRI/SPring-8, 4. Osaka Pref. Univ.)

10:20 AM - 10:40 AM

[A02-4am-06] Crystal-structure-controlled solid-solution alloy nanoparticles and their hydrogen evolution reaction performance

○QUAN ZHANG[1], Kohei Kusada[1], Dongshuang Wu[1], Tomokazu Yamamoto[2], Syo Matsumura[2], Yoshiki Kubota[3], Susan Meñez Aspera[4], Hiroshi Nakanishi[4], Hiroshi Kitagawa[1] (1. Kyoto University, 2. Kyushu University, 3. Osaka Prefecture University, 4. Akashi College)

10:40 AM - 11:00 AM

[A02-4am-07] Synthesis and Structural Transformation of Ternary Alloy Nanoparticles Containing Boron: Pd–*TM*– B

○Keigo KOBAYASHI[1], Kohei KUSADA[1], Dongshuang WU[1], Naoki OGIWARA[1], Hirokazu KOBAYASHI[1,2], Mitsutaka HARUTA[3], Hiroki KURATA[3], Tomokazu YAMAMOTO[4], Takaaki TORIYAMA[4], Syo MATSUMURA[4,5], Satoshi HIROI[6,7], Okkyun SEO[6,8], Chulho SONG[8], Yanna CHEN[6,8], Jaemyung KIM[8], Akhil TAYAL[8], Osami SAKATA[6,7,8,9], Koji OHARA[7], Tetsuo HONMA

[7], Hiroshi KITAGAWA[1] （1. Graduate School of Science, Kyoto University, 2. JST PRESTO, 3. Institute of Chemical Research, Kyoto University, 4. Ultramicroscopy Research Center, Kyushu University, 5. Graduate School of Engineering, Kyushu University, 6. Research Center for Advanced Measurement and Characterization, NIMS, 7. JASRI, 8. Synchrotron X-ray Station at SPring-8, NIMS, 9. School of Materials and Chemical Technology, Tokyo Institute of Technology）

11:00 AM - 11:20 AM

[A02-4am-08] Vapor phase synthesis of bimetal nanoparticles with different nanostructures

○Naomi Sakono[1], Kazuki Omori, Koki Yamamoto, Naru Ishikuro （1. National Institute of Technology, Toyama College）

11:20 AM - 11:40 AM

Threading Ultra-long Polymer into MOF: Synthesis and Physical Properties

([1]*Grad. Sch. of Frontier Sci., The Univ. of Tokyo*, [2]*Grad. Sch. of Eng., The Univ. of Tokyo*)
○Tomoya Iizuka,[1] Etsuhiro Miwa,[2] Nobuhiko Hosono,[1] Takashi Uemura,[1, 2]
Keywords: *Metal-organic framework, Ultra-long polymer, Polymer composite*

Metal-organic frameworks (MOFs) have attracted great interest for decades in various research fields from gas storage to catalyst due to their regular structure and designable nanopores. In our previous research, it was demonstrated that even polymeric guests, such as polyethylene glycol (PEG), can be incorporated into one-dimensional (1D) MOF nanochannels, and each polymer chain exists in a stretched form inside the 1D channel.[1] In the case of these previous studies, host MOF crystals that are much larger than the length of guest polymer chains have been used. A question arises here about what we can expect if this size correlation between MOF and gust polymer was reversed, namely, in the case of that the guest polymer is much longer than the MOF crystal diameter (Fig. 1a). To answer this question, we attempted to insert ultra-long PEG chains into MOF crystals whose diameter is smaller than the polymer chains. This configuration would give a novel form of host-guest complex between MOF and polymers, in which the long polymers thoroughly penetrate through the MOF crystals, providing a supramolecularly crosslinked network structure.

In this study, ultra-long PEG (M_w ~ 4,000,000, PEG4M, persistent length = 30 μm) and down-sized MOF, [$Cu_2(bdc)_2(bpy)$] (**1**, bdc = 1,4-benzenedicarboxylate, bpy = 4,4'-bibyridyl, averaged diameter = 500 nm) were employed. **1** is known to undergo structure transformation from nonporous closed phase to porous open phase upon guest inclusion.[2] This phase transformation of **1** was observed when PEG4M was introduced to **1** (Fig. 1b), demonstrating that even such a long polymer can be incorporated into MOFs.[2] Since PEG4M chains are long enough compared to the diameter of **1** crystal, a rotaxane-like structure that PEG chains are penetrating through MOFs is anticipated. Details of synthesis and properties of the MOF/PEG hybrid materials will be discussed in the presentation.

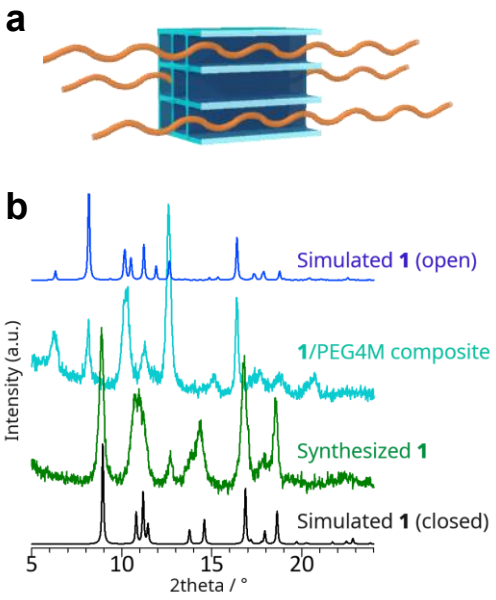


Fig. 1. (a) A schematic image of insertion of ultra-long polymers into MOF channels. (b) XRPD patterns of simulated and synthesized **1** and the **1**/PEG4M composite.

1) T. Uemura *et al.*, *Nat. Commun.*, **2010**, *1*, 83. 2) Y. Sakata *et al.*, *Science*. **2013**, *339*, 193.

Novel redox and optical properties of thiolate-protected gold superatom $Au_{25}(SR)_{18}$ induced by bulky ligands

([1]*Graduate School of Science, The University of Tokyo*, [2]*ESICB, Kyoto University*)
○Tsubasa Omoda,[1] Shinjiro Takano,[1] Tatsuya Tsukuda,[1,2]

Keywords: Ligand-protected gold cluster; Superatom; X-ray absorption fine structure; Single crystal X-ray diffraction; Density functional theory calculation

Thiolate (RS)-protected superatom $[Au_{25}(SR)_{18}]^-$ is a ubiquitous system that has an isotropic icosahedral (Ih) Au_{13} core and prefers the charge state of –1 with a closed electron configuration $(1S)^2(1P)^6$ (Figure 1a).[1] Conventionally, it is believed that their structures and associated properties are not affected appreciably by the R groups. In this study, $Au_{25}(SR)_{18}$ having novel optical and redox properties was synthesized by using bulky thiols with a secondary α-carbon in the R groups.

(1) $[Au_{25}(SPG)_{18}]^-$ (PGSH = *N*-(2-mercaptopropionyl)glycine)[2]

Optical spectral profile of $[Au_{25}(SPG)_{18}]^-$ was significantly different from that of conventional $[Au_{25}(SR)_{18}]^-$. Extended X-ray absorption fine structure analysis elucidated that $[Au_{25}(SPG)_{18}]^-$ has an anisotropic Au_{13} core. We theoretically proposed a model structure formulated as $Au_{13}[Au_1(SPG)_2]_2[Au_2(SPG)_3]_2[Au_3(SPG)_4]_2$ with the electron configuration of $(1S)^2(1P)^4(1D)^2$ (Figure 1b). The different optical absorption in $[Au_{25}(SPG)_{18}]^-$ is ascribed to the reordering of superatomic orbitals by the deformation of Au_{13} core probably induced by the stress of the interaction between PGS ligands such as steric hinderance and/or hydrogen bonding.

(2) $[Au_{25}(ScHex)_{18}]^0$ (cHexSH = cyclohexanethiol)[3]

Optical absorption spectroscopy and single-crystal X-ray diffraction analysis indicated that $[Au_{25}(ScHex)_{18}]^0$ prefers a neutral state with an open electron configuration $(1S)^2(1P)^5$ and has a Jahn-Teller distorted Ih Au_{13} core (Figure 1c). The resistance to the formation of a closed electron configuration $(1S)^2(1P)^6$ is probably because the Au_{13} core is forced to be remained distorted by the steric hindrance between the cHexS ligands.

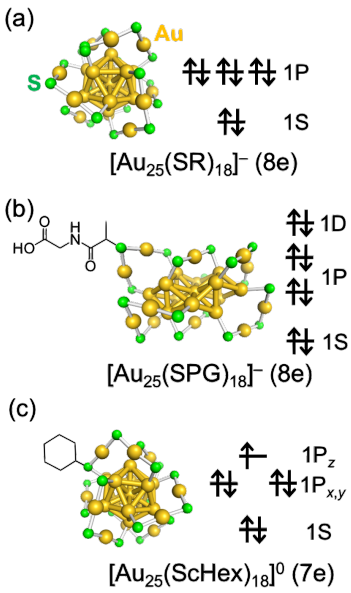


Figure 1. Structures of (a) conventional $[Au_{25}(SR)_{18}]^-$, (b) a model of $[Au_{25}(SPG)_{18}]^-$, and (c) $[Au_{25}(ScHex)_{18}]^0$. R groups are omitted or schematically shown for clarity.

1) X. Kang *et al.*, *Nanoscale* **2018**, *10*, 10758. 2) T. Omoda *et al.*, *J. Phys. Chem. C* **2018**, *122*, 13199. 3) T. Omoda *et al.*, *Chem. Lett.* **2019**, *48*, 885.

“Scrap and Build” of Semiconductor Nanoplates during Cation Exchange Reaction

([1]*Department of Chemistry, Graduate School of Science, Kyoto University*, [2]*Institute for Chemical Research, Kyoto University*) ○Zhanzhao Li,[1] Masaki Saruyama,[2] Toshiharu Teranishi[2]

Keywords: Cation exchange; Ionic nanocrystals; crystalline decomposition

Cation exchange (CE) reaction of colloidal ionic nanocrystals (NCs) is a powerful methodology to create new and complicated nanomaterials. Preservation of the initial morphology of host NCs during CE reaction is a general concept because the gust cations just replace the host cations progressively and the overall morphology of host NCs is maintained during total CE process. [1-2] Here, we found the unique evolution process of morphology and composition of metal sulfide nanoplatelets (NPLs) via CE reaction. During CE, the Cu^{+} cations in $Cu_{1.8}S$ NPLs were replaced by Mn^{2+} cations to form the wurtzite MnS phase. At the intermediate stage of the reaction, unique bow-type $Cu_{1.8}S$/MnS nanoheterostructures were dominantly observed. After the CE proceeded, however, hexagonal plate-shape could be observed again, and the final product was assigned to wurtzite MnS NPLs. Further investigation of bow-type $Cu_{1.8}S$/MnS nanoheterostructure presents MnS and $Cu_{1.8}S$ phases mainly located on the ‘bow body’ and ‘bow line’ part respective with liner interface of MnS(100)//$Cu_{1.8}S$(040) between them. Considering the initial stage of CE reaction starting from the dual plate surface of the $Cu_{1.8}S$ plate, we concluded that the bow-like shaped NPLs NCs were constituted by central $Cu_{1.8}S$ crystalline protected by MnS phase in the ‘bow line’ part and occasional scattered $Cu_{1.8}S$ domains inside of MnS plate in the ‘bow back’ part. These study provides a deep understanding of the evolution of morphology and composition of ionic NCs during CE.

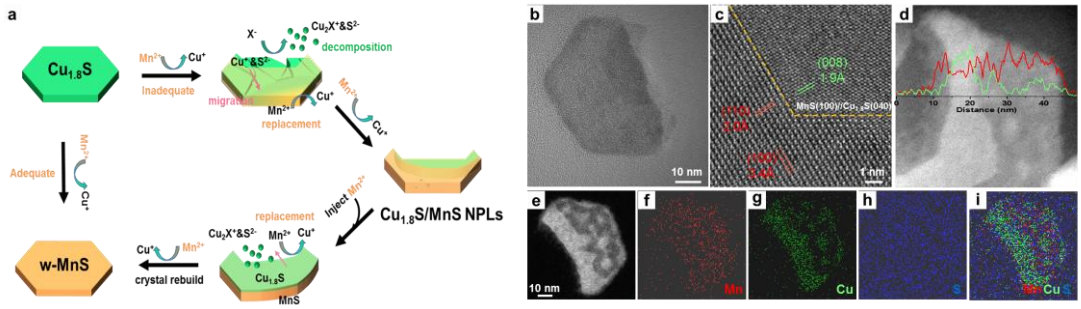


Fig. (a) Schematic of Mn^{2+} CE route for $Cu_{1.8}S$ NPLs. (b, c) TEM and HRTEM images, (d-i) HAADF-STEM images and corresponding line scanning and element mapping analysis of bow-type $Cu_{1.8}S$/MnS nanoheterostructure NPLs.

1) L. De Trizio, L. Manna, *Chem. Rev.* **2016**, *116*, 10852. 2) B. C. Steimle, J. L. Fenton, R. E. Schaak, *Science* **2020**, *367*, 418.

金属ポルフィリンナノ粒子コロイドの作製と光増感一重項酸素発生

（愛媛大院理工）○朝日 剛、行広 英二、姫田 泰聖、座古 保

Fabrication of aqueous nanoparticle colloids of metal porphyrins and photosensitized singlet oxygen generation by visible light irradiation

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Aqueous nanoparticle colloids of metal octaethyl porphyrins （MOEPs）were prepared by nanosecond pulse laser ablation of microcrystalline powder in an aqueous solution of Pluronic® F127 (0.1 wt%). The nanoparticles (about 100-nm size in diameter) were dispersed stably in water and a cell culture medium. We examined the photosensitized singlet oxygen generation of by visible light irradiation for several metalloporphyrin complexes with Pt, Pd, Co, Cu, and Zn. Among them, the Pt complex nanoparticle exhibited the most efficient photosensitization effect. The results of photodynamic therapy effects for the rat pheochromocytoma PC12 cells will be also reported.

Keywords : Nanoparticle colloid; Porphyrin, Singlet oxygen generation, Photodynamic therapy, Laser Ablation

近年、可視・近赤外波長域に強い吸収を有するナノ粒子コロイドは、バイオイメージングや光線力学療法への応用が期待されている。本研究では、液中レーザーアブレーション法により細胞培地中でも安定に分散する金属ポルフィリンナノ粒子を作製し、光線力学療法への応用の観点から、可視光増感一重項酸素発生を検討した。中心金属の異なるオクタポルフィリン錯体（Fig., MOEP:M = Pt, Pd, Co, Cu, Zn）の微結晶粉末 (20 mwt%)を中性界面活性剤 Pluronic® F127(Fig.1, F127) 水溶液(0.1 wt%)に懸濁させ、ナノ秒 Nd^{3+}:YAG レーザーの第二高調波(波長：532 nm、パルス幅 6ns)を照射した結果、分散安定性の高いナノ粒子コロイド（平均サイズは約 100nm）が得られた。また、吸収スペクトル形状から、MOEP と F127 が混ざり合った複合ナノ粒子であることが示唆された。可視光(波長 532nm)照射による光増感一重項酸素発生を中心金属の異なる MOEP について比較した結果、PtOEP が最も高い光増感作用を示しすことが分かった。一方 CoOEP、CuOEP では一重項酸素発生が確認されなかった。PtOEP ナノ粒子コロイドについて、ラット副腎褐色細胞腫 PC12 に対する効果を調べた結果、暗所では細胞毒性が全くなく、可視光照射による光線力学療法効果があることが確認された。

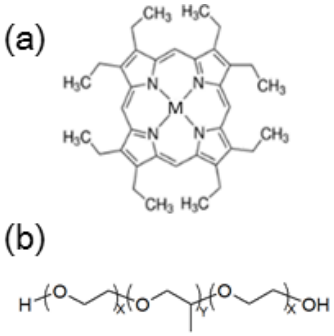

Fig. 1 Molecular structure of (a) MOEP and (b) Pluronic® F127

Synthesis of Mo and Ru solid-solution alloy NPs and their hydrogen evolution reaction activity

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Keywords: *Nanoparticle, Alloy, Hydrogen evolution reaction, Molybdenum, Ruthenium*

The platinum group metals (PGMs) nanoparticles (NPs) are known as efficient catalysts for various reactions. Although their properties are quite attractive, their usage needs to be reduced because they are not abundant elements on Earth. Alloying allows fine-tuning of the electronic structures of catalysts and can improve the catalytic properties of PGMs. Solid-solution alloy NPs where constituent atoms exist uniformly were synthesized by bottom-up methods such as liquid-phase reduction. However, most of solid-solution alloy NPs involved combinations with late transition metals, and there are fewer reports with abundant early transition metals.[1] Alloying PGMs with early transition metals is still a challenging task due to their large negative redox potentials. Among the various combinations of early-transition metals and PGMs, we have focused on Mo–Ru system. According to Mo–Ru phase diagram, although there are miscible regions in both rich compositions in the bulk,[2] there are few reports on MoRu solid-solution NPs.

In this work, we report on the synthesis of MoRu solid-solution alloy NPs and their hydrogen evolution reaction (HER) activity.[3] The MoRu solid-solution alloy NPs were synthesized by a thermal decomposition using triruthenium-dodecacarbonyl and molybdenum-hexacarbonyl in oleylamine. The solid-solution structure was confirmed by high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM)-energy-dispersive X-ray (EDX) spectroscopy (Figure 1). The synthesized MoRu NPs were loaded onto carbon and tested HER performance in 1 M KOH aqueous solution. The catalytic activity of MoRu NPs overtook that of Pt NPs which is known as the best catalyst for monometallic catalyst (Figure 2). As a charge transfer from Mo to Ru occurs in the MoRu solid-solution alloy NPs, the hydrogen adsorption energy on Ru sites could be weakened, resulting in the enhancement of Ru HER activity.

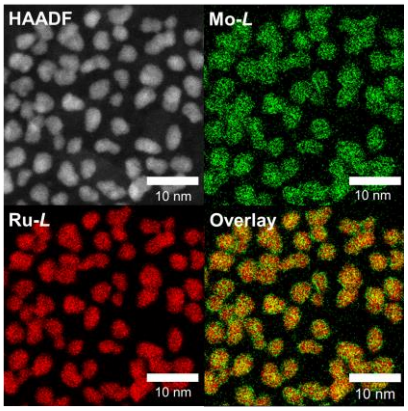

Figure 1. HAADF-STEM image and EDX maps of MoRu NPs.

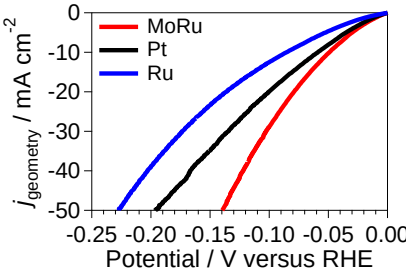

Figure 2. Polarization curves of MoRu, Pt, and Ru NPs catalysts in 1 M KOH solution.

1) K. Kusada *et. al.*, *Chem. Eur. J.*, **2020**, *26*, 5105, 2) E. Anderson and W. H. Rothery, *J. Less Common Met.*, **1960**, *2*, 443 3) S. Okazoe *et. al.*, *Chem. Commun.*, **2020**, *56*, 14475

Crystal-structure-controlled solid-solution alloy nanoparticles and their hydrogen evolution reaction performance

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Keywords: Crystal structure control, catalytic, solid-solution alloy nanoparticle, hydrogen evolution reaction

The size, shape, composition, and crystal phase of alloy nanoparticles (NPs) are key factors in determining their physical and chemical properties. Among them, the size-, shape-, and composition-controlled syntheses of alloy NPs have been well established so far to improve their properties. Crystal structure, that is, the arrangement of the atoms in a solid is the most important parameter affecting its physicochemical properties. However, as for solid-solution alloy, once its constituent elements and composition are fixed, the crystal structure is uniquely determined and hardly changed. Therefore, crystal-structure control of solid-solution alloy is still a great challenge and has not been freely used to control physical and chemical properties of alloy NPs.

Here, by fine-tuning the reduction process of the metal precursors, we succeeded in selectively synthesizing face-centered cubic (fcc) and hexagonal close-packed (hcp) binary (Pt–Ru and Ir–Ru) and ternary (Pt–Ir–Ru) solid-solution alloy NPs with the same composition, size, and morphology through a chemical reduction method. The structures of the obtained NPs were confirmed by powder X-ray diffraction analysis and atomic resolution scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy.

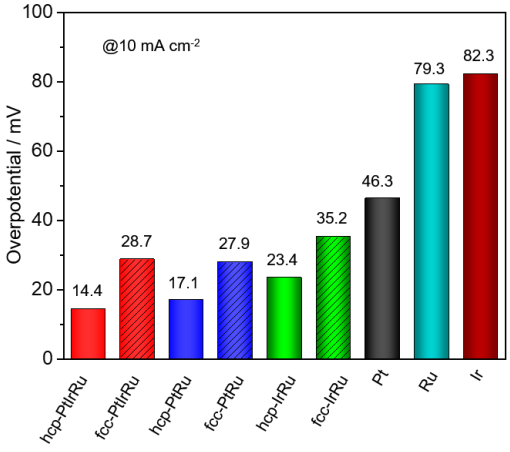

Figure. Catalytic performance of alloy NPs with fcc and hcp structures for hydrogen evolution reaction.

The electrocatalytic hydrogen-evolution-reaction catalytic performance of the alloy NPs with two different crystal structures was investigated. The catalytic performance of the alloy NPs showed an obvious dependence on their crystal structure. The hcp alloy NPs show an improved catalytic activity compared to the fcc alloy NPs and commercial Pt (Figure). Our work provides a new controllable parameter, crystal structure, to improve the catalytic performance of solid-solution alloy NPs.

Synthesis and Structural Transformation of Ternary Alloy Nanoparticles Containing Boron: Pd–*TM*–B

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Keywords: Ternary Alloy Nanoparticles; Palladium; Boron; Structural Transformation; Amorphous

It is known that metal nanoparticles (NPs) exhibit different structures or chemical and physical properties from those in bulk metals. For examples, palladium (Pd) and ruthenium (Ru), which are immiscible in the bulk state, are mixed homogeneously at the atomic level by the nanosize effect.[1] To date, novel solid-solution alloy NPs have been developed mainly by a combination of transition metals (TMs). But researches on the alloy NPs composed of TMs and light elements remain uninvestigated. Previously, we presented an external boron (B) doping method for a novel fabrication of alloy NPs containing B, via novel structured Pd–B nanocrystals.[2] This method has a probability to be adapted to obtain Pd–TM–B ternary alloy NPs. Here, we demonstrate the versatility of the synthetic method by using Pd–Ru and copper (Cu)–Pd alloy NPs as starting materials. Firstly, Pd–Ru and Cu–Pd solid-solution NPs were prepared in a liquid-phase reduction method, as previously reported.[1,3] Then, B doping was performed by adding borane-tetrahydrofuran complex solution into the prepared NPs under inert condition. Elemental mapping suggested successful introduction of B into metal NPs. Powder X-ray diffraction (PXRD) patterns of the NPs drastically changed (Figure) after the reaction, indicating the formation of amorphous structure in both cases.

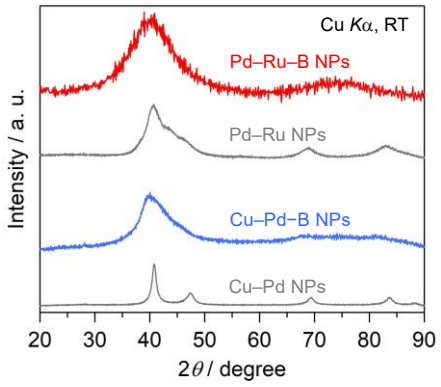


Figure PXRD patterns of the NPs.

1) K. Kusada *et al.*, *J. Am. Chem. Soc.* **2014**, *136*, 1864. 2) K. Kobayashi *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 6578. 3) S. Ma *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 47.

ナノ構造の異なる二元金属ナノ粒子の気相合成

（富山高専）○迫野 奈緒美・大森一樹・山本紘希・石黒成琉
Vapor Phase synthesis of bimetal nanoparticles with different nanostructures (*National Institute of Technology, Toyama College*) ○Naomi Sakono, Kazuki Omori, Koki Yamamoto, Naru Ishikuro

Composite nanoparticles composed of multiple metals have optical properties and electromagnetic properties different from those of single metal nanoparticles, and the properties largely depend on nanostructures such as alloy type and core-shell type [1,2]. In this study, we attempted to separate composite nanoparticles with different nanostructures by using the evaporation/condensation method, which is one of the vapor phase synthesis methods for nanoparticles.

From the mapping analysis results by EDS, bright spots corresponding to Au and Ag atoms were found in the same particle. This suggests that the synthesized nanoparticles are composed of both elements. In addition, the results of line analysis by EDS suggested that the nanostructure composed of gold and silver changed significantly depending on the combination of electric furnaces. Furthermore, the difference in nanostructures also appeared as the difference in SPR absorption wavelength, indicating a correlation between nanostructures and functional expression. From the above, it is considered that the synthesis of composite nanoparticles by the evaporation/condensation method can be a means for producing materials having a defined nanostructure.

Keywords : Composite nanoparticles; Vapor phase synthesis; structure analysis;

複数金属で構成されるコンポジットナノ粒子は、単一金属ナノ粒子とは異なる光学特性や電磁気特性を持ち、その特性は、合金型やコア-シェル型等、ナノ構造に大きく依存することが明らかにされつつある [1,2]。本研究では、気相合成法の 1 つである蒸発濃縮法を用いて、ナノ構造の異なるコンポジットナノ粒子の作り分けを試みた。

石英管を通した管状電気炉を 2 台連結し、温度の異なる各電気炉に金および銀を配置した。石英管内は窒素ガスを流し、得られたナノ粒子を STEM 観察、EDS による元素分析、光吸収スペクトルにより評価した。

EDS によるマッピング分析結果から、同一粒子内に Au と Ag 原子に対応する輝点が見られた。これにより、合成されたナノ粒子は両元素から構成されている事が示唆された。また、EDS によるライン分析結果から、電気炉の組み合わせの違いにより、金および銀で構成されるナノ構造が大きく変化することが示唆された。さらに、ナノ構造の違いは SPR 吸収波長の違いとしても表れたことから、ナノ構造と機能発現の相関が示された。以上より、蒸発濃縮法によるコンポジットナノ粒子の合成は、ナノ構造を規定した材料作製手段となりうると考えられる。

1) Bimetallic Nanocrystals: Syntheses, Properties, and Applications, K. D. Gilroy, et al., *Chem. Rev.*, **2016**, 116, 10414.
2) Bimetallic catalysts for hydrogen generation, Z. Wei. et. al., *Chem. Soc. Rev.* **2012**, 41, 7994.

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

[A21-4am] 20. Materials Chemistry -Basic and Application-

Chair:Kazunori Matsuura, Shoichi Kubo

Mon. Mar 22, 2021 9:00 AM - 11:40 AM Room 21 (Online Meeting)

[A21-4am-01] Development of Self-healing hydrogels designed based on the Intercalation of Polymeric Ions into Mica.

○Shingo Tamesue[1], Yushin Saito[1] （1. Utsunomiya Uniersity）

9:00 AM - 9:20 AM

[A21-4am-02] Effect of Positional Isomerism of Picenodithiophene Derivatives on Semiconducting Properties

○Zhenfei Ji[1], Hiroki Mori[2], Yasushi Nishihara[2] （1. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayama Univ.）

9:20 AM - 9:40 AM

[A21-4am-03] Photochromism of Imidazole Dimer Bridged by Helical Aromatic Molecule

○Katsuya Mutoh[1], Jiro Abe[1] （1. Aoyama Gakuin University）

9:40 AM - 10:00 AM

[A21-4am-04] Propulsion of DNA microspheres driven by light-induced peptide nanofiber growth

○Hiroshi Inaba[1], Kenji Hatta[1], Kazunori Matsuura[1] （1. Grad. Sch. of Eng., Tottori Univ.）

10:00 AM - 10:20 AM

[A21-4am-05] "Bio-Adhesive" Covalent Organic Framework for Bioapplications

○Hyuna Jo[1], Kou Okuro[1,2], Takuzo Aida[1,3] （1. The Univ. of Tokyo, 2. The Univ. of Hong Kong, 3. Riken Center for Emergent Matter Science）

10:20 AM - 10:40 AM

[A21-4am-06] Investigation of SN-38 Anticancer Nano-prodrugs Intracellular Dynamics

○Farsai Taemaitree[1], Beatrice Fortuni[2], Yoshitaka Koseki[1], Eduard Fron[2], Susana Rocha[2], Johan Hofkens[2,3], Hiroshi Uji-i[2,4], Anh Thi Ngoc Dao[1], Ryuju Suzuki[1], Tomoko Inose[5], Hitoshi Kasai[1] （1. Tohoku University, 2. KU Leuven, 3. Max Planck Institute for Polymer Research, 4. Hokkaido University, 5. Kyoto University）

10:40 AM - 11:00 AM

[A21-4am-07] Fabrication of nano-prodrugs composed of hinokitiol-modified podophyllotoxin

○Keita Tanita[1], Yoshitaka Koseki[1], Takaaki Kamishima[1], Hitoshi Kasai[1] （1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University）

11:00 AM - 11:20 AM

[A21-4am-08] Fabrication of guaiazulene derivatives nano-prodrugs and their structure-activity evaluation

○Kiyotaka Maruoka[1], Keita Tanita[1], Ryuju Suzuki[1], Yoshitaka Koseki[1], Toshihiro Murafuji[2], Hitoshi Kasai[1] （1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Graduate School of Sciences and Technology for Innovation, Yamaguchi University）

11:20 AM - 11:40 AM

マイカへのインターカレーションを利用した自己修復ゲルの作製

（宇都宮大院工 [1]）○為末 真吾 [1]・齋藤 佑槇 [1]

Development of Self-healing hydrogels designed based on the Intercalation of Polymeric Ions into Mica.

([1]*Graduate School of Regional Development and Creativity, Utsunomiya University*)
○Shingo Tamesue,[1] Yushin Saito,[1]

Today, various self-healing materials are developed and reported to use materials in long life spans. Layered inorganic compounds, such as mica, have intercalation properties, which entrap various guest compounds into their interlayers.

In this research, we developed novel self-healing hydrogel materials designed based on the intercalation properties of layered inorganic compound, mica. Mixing mica and a synthesized polymer appending imidazolium cations as side chains, we prepared self-healing hydrogel materials. These self-healing hydrogels showed high environmental durability, such as pH, temperature, and solvents. In particular, the self-healing ability was not lost even in the high salty conditions. This tolerance towards salt will enable us to use the self-healing hydrogel materials practically.

Keywords : Hydrogel; Self-healing; Soft Material; Layered Inorganic Compound; Intercalation

傷を人間の皮膚のように自動的に修復する自己修復材料は、限られた資源の保護や環境保護のため、近年、活発に研究・開発されるようになってきた。しかし、これらの自己修復材料を実用化するためには、様々な環境に対する耐性を材料に持たせる必要がある。

層状無機化合物マイカの層間には、様々なカチオンをインターカレーションによって取り込むことが可能である。

本研究では、イミダゾリウムカチオンを側鎖として有する高分子をラジカル重合によって合成した。この高分子と層状無機化合物マイカの水分散液を混合し、高分子側鎖のイミダゾリウムカチオン間をマイカの層間へインターカレーションした。このようにして、高分子間をマイカによって架橋し、ヒドロゲルを作製した（Figure 1）。得られたヒドロゲルは、塩水中でも利用可能な自己修復性を示し、様々な環境に対する高い耐性を示した。

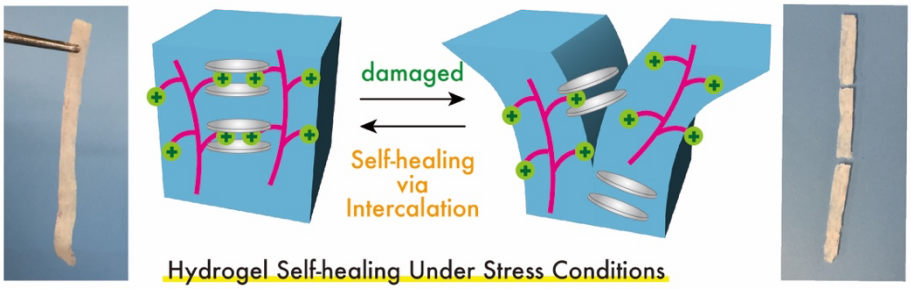


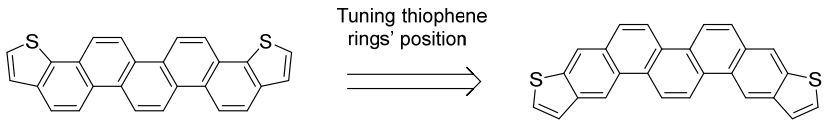
Figure 1. Photograph and schematic illustration of the self-healing hydrogel designed in this research based on the intercalation properties of layered inorganic compound, mica.

Effect of Positional Isomerism of Picenodithiophene Derivatives on Semiconducting Properties

([1]*Graduate School of Natural Science and Technology, Okayama University*, [2]*Research Institute of Interdisciplinary Science, Okayama University*)
○Zhenfei Ji,[1] Hiroki Mori,[2] Yasushi Nishihara[2]
Keywords: Organic Field-Effect Transistors; Organic Semiconducting Materials; Picenodithiophene Derivatives; Positional Isomerism

A number of π-conjugated semiconducting materials have been developed for application in organic field-effect transistor (OFETs).[1] In particular, thienoacenes have received much attention due to their excellent organic semiconducting properties.[2] However, the introduction of thiophene rings into the acene backbone poses new problems due to the formation of various isomers such as stereoisomers and regioisomers, *etc*.[3] Recently, our research group has reported the synthesis of piceno[4,3-*b*:9,10-*b*']dithiophene (PiDT-1) with seven fused rings and a π-extended conjugated system and its transistor properties, which exhibited high hole mobility but relatively larger threshold voltage.[4] In order to achieve higher mobility and low-voltage operation, we report the design, synthesis, physicochemical and FET properties of piceno[3,2-*b*:10,11-*b*']dithiophene PiDT-3, an isomer of PiDT-1.

Initially, PiDT-3 was synthesized by Suzuki-Miyaura coupling reaction of 1,4-phenylenediboronic acid with 5-bromobenzo[*b*]thiophene-6-carbaldehyde as a key step. Subsequently, epoxidation and Lewis acid-catalyzed intramolecular cycloaromatization reactions were carried out to yield PiDT-3. The HOMO level of PiDT-3 increased from −5.6 eV to −5.5 eV with the change in the position of the thiophene rings. Additionally, the UV-vis absorption spectra of the obtained PiDT-3 showed a clear red-shift behavior due to the extended π-conjugation compared to PiDT-1. The OFETs based on PiDT-3 fabricated on FOTS-treated substrates exhibited hole mobility of 1.8×10^{-2} cm^2 V^{-1} s^{-1}. However, the hole mobility of PiDT-3 was found to be lower than that of PiDT-1 despite the surface modification with different types of SAMs. These results highlight the importance of regioisomeric effects on intrinsic electronic and charge transport properties, and indicate the importance of further rationalization of molecular design.



1) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2012**, *112*, 2208. 2) K. Takimiya, S. Shinamura, I. Osaka, E. Miyazaki, *Adv. Mater.* **2011**, *23*, 4347. 3) P. Hu, H. Jiang, *J. Mater. Chem. C*, **2019**, *7*, 5858. 4) K. Hyodo, R. Toyama, H. Mori, Y. Nishihara, *ACS Omega* **2017**, *2*, 308.

らせん状芳香族分子で架橋されたイミダゾール二量体のフォトクロミズム

（青学大理工）○武藤 克也・阿部 二朗
Photochromism of Imidazole Dimer Bridged by Helical Aromatic Molecule (*Dept. Chem., Sch. Sci. Eng., Aoyama Gakuin Univ.*) ○Katsuya Mutoh, Jiro Abe

Biradicaloids have been extensively studied for their characteristic features. Besides, it is expected that the study of the chemical and physical properties of biradicaloids opens up a fundamental insight into the nature of chemical bonds. Recently, the development of the radical species on helical polycyclic aromatic structures has been of interest as a novel platform for organic radicals. We have recently developed photochromic bridged imidazole dimers. The bridged imidazole dimer generates a transient biradical upon UV light irradiation. The transient biradical thermally goes back to the initial imidazole dimer. In this study, we designed and synthesized helicene-bridged imidazole dimer (helicene-ImD). The helicene-ImD generates the biradical upon UV-light irradiation, and the thermal back reaction of the biradical follows the first-order-reaction kinetics. The helicene-bridged imidazole dimer can be also expected as a novel family of fast photochromic molecules.
Keywords : Photochromism; Biradical; Helicene

架橋型イミダゾール二量体は、光照射により着色体としてビラジカルを生成し、ビラジカルは熱的にもとのイミダゾール二量体へ戻る。このフォトクロミック特性は架橋基に依存するため、新たな架橋基の探索は高速フォトクロミック分子の発展においても重要である。本研究では、らせん状芳香族分子の 1 つであるヘリセンを架橋基として用いたヘリセン架橋型イミダゾール二量体（helicene-ImD）を合成し、フォトクロミック特性について詳細に検討した。helicene-ImD に紫外光を照射すると C–N 結合が解離し過渡種であるビラジカルが生成した。ビラジカルの生成は ESR 測定により確認された。過渡吸収スペクトル測定より、ビラジカルは波長 500 nm と 800 nm に極大吸収を示し、吸光度時間減衰曲線よりビラジカルの半減期は 298 K において 29 ms と求められた。これらより、ヘリセン架橋型イミダゾール二量体は高速フォトクロミズムを示すことが明らかとなった。

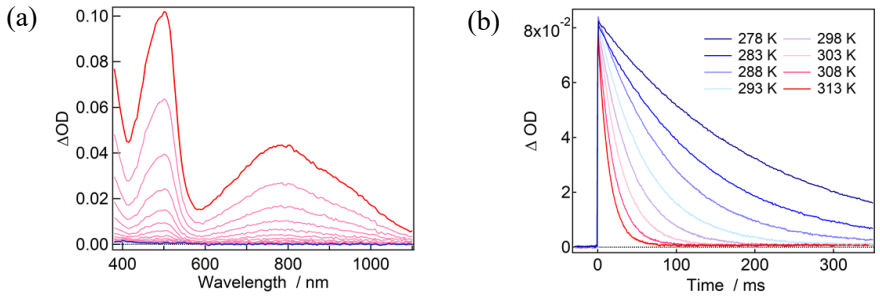


Fig. 1 (a) The transient absorption spectra of helicene-ImD in Ar-bubbled benzene upon 355-nm laser irradiation (3 mJ) at 298 K. (b) The time profiles of the transient absorbance of helicene-ImD in benzene.

光誘起ペプチドナノファイバー成長を駆動力としたDNA球状集合体の運動推進

（鳥取大院工）○稲葉 央・八田 健志・松浦 和則

Propulsion of DNA microspheres driven by light-induced peptide nanofiber growth

(*Graduate School of Engineering, Tottori University*) ○Hiroshi Inaba, Kenji Hatta, Kazunori Matsuura

Light-induced propulsion of microparticles is attracted attention. We have reported the light-induced peptide nanofiber growth by connecting a self-assembling peptide and a DNA via a photocleavable amino acid.[1)] The system was applied for the propulsion of giant liposomes driven by light-induced peptide nanofiber growth.[2)] In this work, we report a light-induced propulsion of DNA microspheres[3)] by introducing the system. Modification of the fluorescent-labeled peptide-DNA conjugate to DNA microspheres and UV light-induced peptide nanofiber growth were observed by confocal laser scanning microscopy (CLSM). By irradiation of UV light, directional propulsion of DNA microspheres was observed.

Keywords : Peptide; Nanofiber; Photocleavable amino acid; DNA microsphere; Propulsion

光刺激によってマイクロサイズの粒子の運動や形状を制御する試みが注目を集めている。我々は、光解離アミノ酸を介して自己集合性ペプチドとDNAを連結したコンジュゲートを開発し、UV光によるペプチドナノファイバー成長システムを構築している[1)]。このシステムを実装することで、ナノファイバー形成を駆動力としたジャイアントリポソームの運動推進に成功した[2)]。本研究では、このシステムを応用することで、自己相補性末端を有する三種のDNAからなる球状集合体[3)]の運動推進を試みた（Fig. 1）。ビオチン修飾されたDNA球状集合体を構築し、ストレプトアビジンとの相互作用、DNAハイブリダイゼーションを利用して、球状集合体表面にコンジュゲートを修飾した。蛍光ラベルコンジュゲートのDNA球状集合体表面への導入および光刺激によるナノファイバー形成を共焦点レーザー顕微鏡（CLSM）により確認した。DNA球状集合体の顕微鏡観察により、光照射方向から逃げるように運動することが明らかとなり、方向性のある運動推進に成功した。

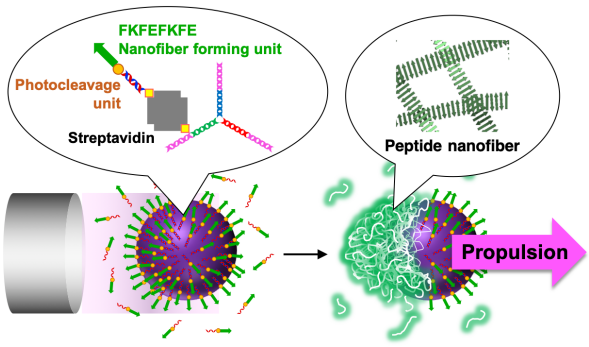


Fig. 1. 光誘起ペプチドナノファイバー成長を利用したDNA球状集合体の運動推進

1) M. Furutani, A. Uemura, A. Shigenaga, C. Komiya, A. Otaka, K. Matsuura, *Chem. Commun.*, **2015**, *51*, 8020. 2) H. Inaba, A. Uemura, K. Morishita, T. Kohiki. A. Shigenaga, A. Otaka, K. Matsuura, *Sci. Rep.*, **2018**, *8*, 6243. 3) K. Matsuura, K. Masumoto, Y. Igami, T. Fujioka, N. Kimizuka, *Biomacromolecules*, **2007**, *8*, 2726.

“Bio-adhesive” Covalent Organic Framework for Bioapplications

(*Graduate School of Engineering, The University of Tokyo*)
○Hyuna Jo, Kou Okuro, Takuzo Aida

Keywords: adhesive material, porous material, substance transfer, photochemistry

Biological channels are molecular gatekeepers that regulate substance transport across cell membranes in response to external stimuli. An intriguing example is a channelrhodopsin-1, an ion channel that opens in response to light, allowing proton transport.[1] Inspired by such biological channels, a variety of photoresponsive synthetic channels have been developed.[2,3] However, the synthetic channels are applicable for limited types of substances such as H^+ and K^+.

Herein, we newly designed a bio-adhesive covalent organic framework (^{Glue}COF) bearing multiple guanidinium ion (Gu^+) pendants. In the nanopores of ^{Glue}COF, we loaded rose bengal (RB), which generates singlet oxygen ($^1O_2$) upon photoirradiation,[4] as a photo-responsive pore-opener (^{Glue}COF⊃RB, Fig 1a). The multiple Gu^+ pendants serve as “molecular glue” to noncovalently adhere to the surface of liposomes via multivalent salt-bridge interactions (Fig 1a).[5] Photo-triggered transfer of a guest fluorescent dye (calcein) between liposomes was achieved (Fig 1b and c). In this presentation, the details of molecular design, substance transfer, and future perspective will be discussed.

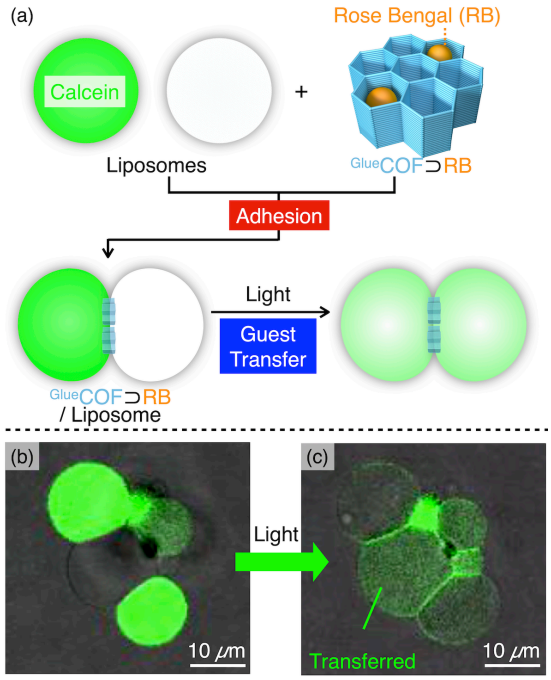


Fig 1. (a) Schematic illustration of guest transfer mediated by ^{Glue}COF⊃RB upon photoirradiation. (b, c) Confocal laser scanning microscopy (λ_{ex} = 488 nm) images of a mixture of calcein-loaded liposomes and guest-free liposomes with ^{Glue}COF⊃RB (b) before and (c) after photoirradiation.

1) G. Nagel, D. Ollig, M. Fuhrmann, S. Kateriya, A. M. Musti, E. Bamberg, P. Hegemann, *Science* **2002**, *296*, 2395. 2) S. Loudwig, H. Bayley, *J. Am. Chem. Soc.* **2006**, *128*, 12404. 3) H. -Q. Liang, Y. Guo, Y. Shi. X. Peng, B. Liang, B. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 7732. 4) D. C. Neckers, *J. Photochem. Photobiol. A* **1989**, 47, 1. 5) R. Mogaki, P. K. Hashim, K. Okuro, T. Aida, *Chem. Soc. Rev.* **2017**, *46*, 6480.

Investigation of SN-38 Anticancer Nano-prodrugs Intracellular Dynamics

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Department of Chemistry, KU Leuven,* [3]*Max Planck Institute for Polymer Research,* [4]*Research Institute for Electronic Science, Hokkaido University,* [5]*Institute for Integrated Cell-Material Sciences, Kyoto University*) ○ Farsai Taemaitree,[1] Beatrice Fortuni,[2] Yoshitaka Koseki,[1] Eduard Fron, [2] Susana Rocha, [2] Johan Hofkens,[2,3] Hiroshi Uji-i, [2,4] Anh Thi Ngoc Dao, [1] Ryuju Suzuki, [1] Tomoko Inose, [5] Hitoshi Kasai[1]

Keywords: Drug delivery systems; Nano-prodrugs; SN-38; FRET; Intracellular dynamics

The majority of the drug delivery systems developed to date use nanocarriers to transport the drug. These nanocarriers, which are considered to cause long-term side-effects and increase the risk of systemic toxicity, are one of the main limitations in the clinical translation of DDSs.[1] To overcome this limitation, researchers started working on alternative carrier-free systems, composed exclusively of hydrophobic drugs or prodrugs. On the path toward clinical application of carrier-free nanoparticle systems, the knowledge of their intracellular fate, degradation, and conversion into active forms after internalization must be established.

In our work, with SN-38 anticancer nano-prodrugs[2] (NPs) as a model system and FRET microscopy as a key analytical strategy (**Figure 1**), we successfully described the behavior of carrier-free NPs after entering the cells.[3] It was revealed that NPs were consistently taken up by cells as intact particles, then translocate into lysosomes, where degradation occurred over time. Surface modification of NPs by PEI greatly enhanced the internalization of NPs and delayed the degradation process by inducing the escape of NPs from lysosomes. Cell viability studies demonstrated that our NPs are highly efficient against liver cancer cells and that their anticancer activity is related to the esterase expression level of the target cell line. This work provides a comprehensive overview of the dynamics of NPs inside cancer cells which are urgently needed for further progress towards their application as the next generation of anticancer drug delivery devices.

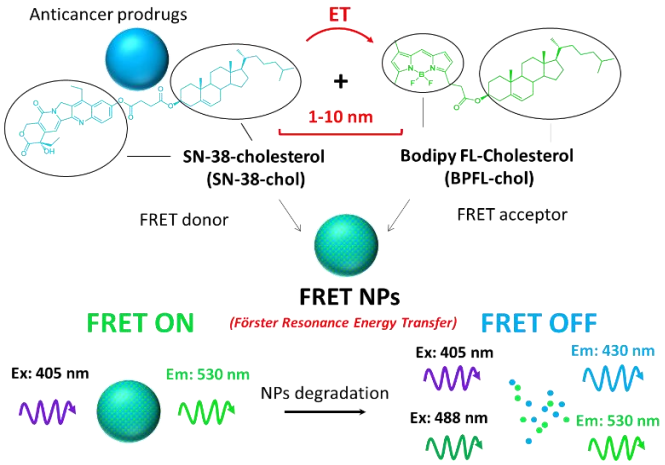


Figure 1. Design of FRET-NPs.

1) J. Junghanns *et al*., *Int. J. Nanomedicine* **2008**, *3*, 295–309. 2) H. Kasai *et al*., *Angew. Chemie - Int. Ed*. **2012**, *51*, 10315–10318. 3) F. Taemaitree *et al*., *Nanoscale* **2020**, *12*, 16710.

Fabrication of nano-prodrugs composed of hinokitiol-modified podophyllotoxin

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*)
○Keita Tanita,[1] Yoshitaka Koseki,[1] Takaaki Kamishima,[1] Hitoshi Kasai[1]
Keywords: Drug delivery system, Reprecipitation method, Anticancer drugs, Hinokitiol

In recent years, nanomedicines made by the usage of nanocarriers such as liposome, polymer micelle, and protein have been applied to drug delivery system for cancer treatment. However, the conventional formulation strategy can lead to several problems, such as undesirable side effects caused by the carriers themselves or their metabolites. To overcome these problems, our group have proposed "nano-prodrugs" which is novel designed nano-drugs without using carriers. We had reported some nano-prodrugs composed various substituent-modified drugs.[1]

In this study, we synthesized hinokitiol-modified anticancer drugs as heterodimeric prodrugs and fabricated their nano-prodrugs by reprecipitation method.[2] Hinokitiol, a natural monoterpenoid, is known for its antibacterial activity and some anticancer activities.[3] These nano-prodrugs possessed high drug loading capacity, and *in vitro* cell cytotoxicity revealed that depends on the length of the carbon chain linker (Figure 1). These nanoparticles also possessed good dispersion stability, and further research revealed that the tropone skeleton of hinokitiol is the key structure for the dispersion stability in our prodrug design.

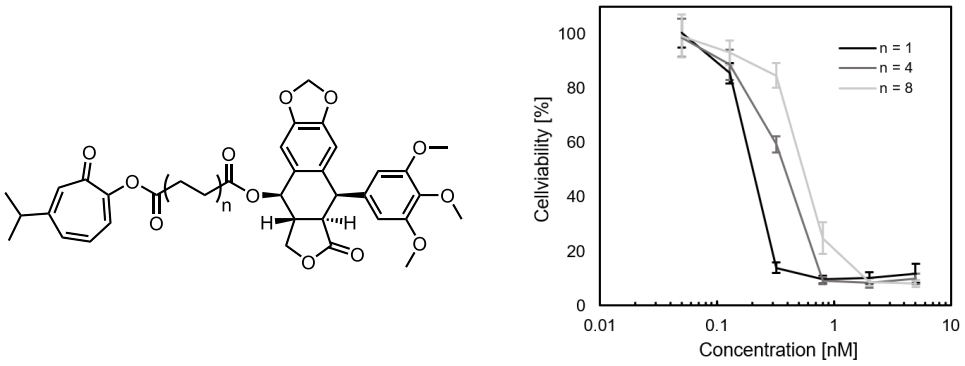


Figure 1. *in vitro* cytotoxicity of hinokitiol-conjugated PPT linked via dicarboxylic acid
All results are indicated as mean ± standard deviation (n = 3).

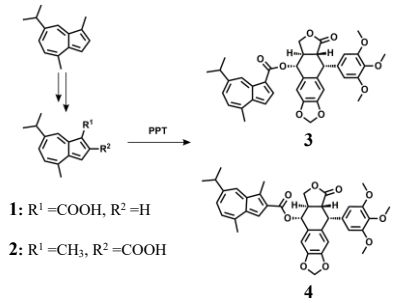
1) K. Tanita *et al*., *Chem. Lett.* **49**, 222 (2020).
2) H. Kasai *et al*., *Jpn. J. Appl. Phys*. **31**, L1132 (1992).
3) D. G. Tu et al., *Oncology Lett*. **11**, 2934 (2016).

Fabrication of guaiazulene derivatives nano-prodrugs and their structure-activity evaluation

([1]*Institute of Multidisciplinary Research for Advanced Materials*, *Tohoku University*, [2]*Graduate School of Science and Technology for Innovation*, *Yamaguchi University*)
○Kiyotaka Maruoka, [1] Keita Tanita, [1] Ryuju Suzuki, [1] Yoshitakta Koseki, [1] Toshihiro Murafuji, [2] Hitoshi Kasai[1]
Keywords: Guaiazulene; Nanoparticles; Anticancer drugs

Combination chemotherapy and nanoparticle drug delivery have shown promising results in the treatment of cancer.[1)] The combination therapy offers modulation of different pathways in cancer, maximizing therapeutic efficacy and overcoming resistance mechanisms such as inflammation. On the other hand, nanoparticle regulate the side effects of drug by selectively delivery drug to the target area without harming healthy tissues.[2)] Herein, we reported the fabrication of nano-prodrugs composed of the conjugated guaiazulene anti-inflammatory agents and podophyllotoxin (PPT) anticancer drug for the delivery of combination chemotherapy by nanoparticle. The effect of prodrug molecular design on nano-prodrugs fabrication, release of therapeutic agents via hydrolysis, and anticancer efficacy will be investigated.

We first synthesized guaiazulene derivatives **1** and **2** having carboxyl group, and then leaded to guaiazulene-modified PPT prodrugs **3** and **4** (**Scheme 1**). Prodrug NPs of as-synthesized derivatives **3** and **4** were successfully fabricated by reprecipitation method,[3)] which had average sizes around 50 nm with high dispersion stability. The obtained prodrug NPs were then incubated with KPL-4 cell line and CHO-K1 cell line for 48 h. As a result, both of derivatives **3** and **4** showed appropriate drug efficacy with different drug release behaviors, which could be affected by bonding positions of guaiazulene (**Fig. 1**). We will also report the hydrolysis behavior of obtained nanoparticles with *in vitro* experiments.



Scheme 1 Synthetic procedure of guaiazulene-modified PPT prodrug

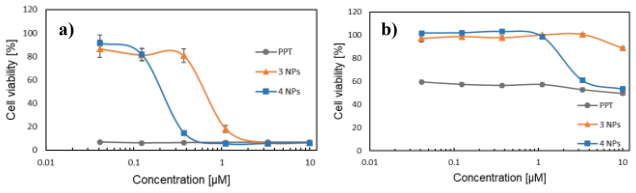


Figure 1 *in vitro* pharmacological activity of guaiazulene-conjugated PPT. a) KPL-4 cell, b) CHO-K1 cell
All results are indicated as mean ± standard deviation (n = 3)

1) R. K. Pathak et al., *J. Am. Chem. Soc.* **2015**, *137*, 8324. 2) Y. Koseki *et al*., *Bull. Chem. Soc. Jpn*. **2016**, *89*, 540. 3) H. Kasai *et al*., *Jpn. J. Appl. Phys*. **1992**, *31*, L1132.

[A04-4am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair:Qing Shen, Masashi Ikegami

Mon. Mar 22, 2021 9:00 AM - 10:40 AM Room 4 (Online Meeting)

[A04-4am-01] Inhibition of Dendrite Growth on Lithium-Metal Negative Electrode for All-Solid-State Rechargeable Batteries Using Porous Current Collector with High Aperture Ratio

○Shota Shinzo[1], Masanobu Chiku[1], Eiji Higuchi[1], Akitoshi Hayashi[1], Hiroshi Inoue[1] (1. Osaka Prefecture University)

9:00 AM - 9:20 AM

[A04-4am-03] Control of ZnO nanowire quality by annealing atmosphere and its influence on $AgBiS_2$ nanocrystal-based solar cells

○Yun Xiao[1], Haibin Wang[1], Takaya Kubo[1], Hiroshi Segawa[1,2] (1. RCAST, The Univ. of Tokyo, 2. Grad. Sch. Arts and Sci. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[A04-4am-04] Dye Molecules Assisted $CsPbIBr_2$ Based All Inorganic Perovskite Solar Cells for Excellent Performance

○Yang Shuzhang[1], Liang Wang[1], Tingli Ma[1] (1. kyushu institute of technology)

10:00 AM - 10:20 AM

[A04-4am-05] Carbon-Free Connected Nanoparticle Catalysts for Oxygen Reduction Reaction in PEFCs

○Hidenori Kuroki[1,2], Takanori Tamaki[1,2], Takeo Yamaguchi[1,2] (1. Tokyo Institute of Technology, 2. Kanagawa Institute of Industrial Science and Technology)

10:20 AM - 10:40 AM

Inhibition of Dendrite Growth on Lithium-Metal Negative Electrode for All-Solid-State Rechargeable Batteries Using Porous Current Collector with High Aperture Ratio

(*Graduate School of Engineering, Osaka Prefecture University*) ○Shota Shinzo, Masanobu Chiku, Eiji Higuchi, Akitoshi Hayashi, Hiroshi Inoue

Keywords: All-solid-state rechargeable battery; Lithium metal negative electrode; Dendrite growth; Current collector

The Li negative electrode in all-solid-state batteries (ASSBs) causes short-circuits due to the dendritic growth of metallic Li, which significantly reduces battery performance. One of factors that accelerate the dendritic growth of Li is the increase in the mechanical stress of the Li metal during its electrochemical plating. However, only a few studies have been attempted to reduce it. During the Li metal plating between a flat current collector and solid electrolyte (SE) fixed by the cell stacking pressure, the mechanical stress of Li metal increases due to its volume expansion. We have reported a porous current collector (PCC) was effective for reducing the mechanical stress because the Li metal growth occurred preferentially in micro-sized pores[1]. However, the effect of suppressing the dendritic growth was limited due to low aperture ratio of the current collector. This study aimed higher tolerance to the dendritic growth of Li using a new PCC with high aperture ratio, commercial electroforming sieve.

The tolerance to the dendritic growth of lithium was evaluated as the critical current density (CCD, the maximum plating/stripping current density without internal short-circuits) and the Coulombic efficiency (CE). The new PCC showed three times as large CCD as a planer Ni foil current collector, suggesting that the high aperture ratio of PCC significantly relieved the stress of Li. The SEM observation of the PCC and SE surfaces after the Li plating/stripping cycling test suggested the side reaction between SE and Li promoted the Li dendritic growth. The CCD was improved by using other SE with high tolerance to the side reaction with Li.

The Au thin layer was coated on the PCC surface to maximize the Li plating/stripping performance. Our previous research demonstrated that the Li deposition behavior depended on the coating material on the PCC, and the Li dendritic growth was effectively suppressed by the Li diffusion in the Au thin layer on the PCC[1]. Consequently, the present Au-coated PCC achieved the record-high CCD over 6 mA cm^{-2}, and, notably, the excellent cycle performance with an extremely high average CE of 98.7 % for 300 cycles. Such the significant improvement clearly demonstrates that the present Au-coated PCC is effective for reversible deposition/dissolution of Li. **【ref. This body consists of 363 words.】**

1) S. Shinzo et al., ACS Appl. Mater. Interfaces (2020), 12, 20, 22798

Control of ZnO nanowire quality by annealing atmosphere and its influence on $AgBiS_2$ nanocrystal-based solar cells

([1]*RCAST, The University of Tokyo,* [2]*Graduate School of Arts and Sciences, The University of Tokyo*) ○Yun Xiao, [1] Haibin Wang, [1] Takaya Kubo, [1] Hiroshi Segawa[1,2]
Keywords: ZnO nanowires; defect; Annealing; Solar cell; $AgBiS_2$

Colloidal quantum dots (CQDs) are promising materials for next-generation solar cells because of size-dependent bandgap and solution-process compatibility. Recently, solar cells using PbS CQDs and ZnO materials have made considerable progress. ZnO electron accepting materials are also important for the solar cells due to their high electron mobility and excellent stability. In particular, ZnO nanowires (NW) were verified essential to improve charge collection and light absorption simultaneously.[1] Thus, we constructed eco-friendly solar cells using infrared-absorbing $AgBiS_2$ nanocrystals (NCs) and ZnO NWs. [2] In this work, we applied annealing treatment on ZnO NWs, and studied how thermal annealing conditions (temperature and atmosphere) influenced the performance of $AgBiS_2$ NC-based solar cells using ZnO NW.

We synthesized ZnO nanowires (NWs) with a length of ~320 nm by a hydrothermal method, and then annealed them under different atmospheres (N_2, O_2 and H_2) and at different temperatures (200 - 500 °C). $AgBiS_2$ NC-based solar cells[1] using the annealed ZnO NWs (inset figure of Fig. 1, denoted as X-Y SC, X: temperature, Y: atmosphere, for example, 400-H_2 SC) were fabricated.

The power conversion efficiency (PCE) of H_2- and N_2-SCs decreased with increasing annealing temperature, respectively, from 3.78% (pristine) to 2.98% (400-H_2 SC) and 1.03% (400-N_2 SC), while PCE of 500-O_2 SC was enhanced to 5.41 from 3.78% (w/o) (table in Fig. 1). Then defect-related photoluminescence (PL) spectra of the annealed ZnO NW, appearing in the visible and near-infrared region, were studied to investigate the influence of annealing on the performance of solar cells. The defect emissions of ZnO NW annealed at all atmospheres were reduced (Fig. 1). After annealing at high temperature, oxygen interstitials (O_i, 1.77 eV) and hydroxyl group (2.05 eV), even though largely reduced, still remained in all ZnO NWs. However, these defect states form only shallow trap sites, they might not the main defects that affect the performance of solar cells. In contrast, Zinc interstitials (Zn_i, 3.15 eV) appearing on the shoulder of the band-to-band emission (3.30 eV) were generated in ZnO NWs annealed only in H_2. Oxygen vacancies (V_O^{2+}, 2.30 eV) were also observed in all the ZnO NWs, but the ratio of PL from V_O^{2+} to the total PL is 0.072 in O_2-treated ZnO compared to 0.13 and 0.16 in N_2- and H_2-treated ZnO. These deep trap sites might explain the annealing condition dependence of the performance of $AgBiS_2$ NC-based solar cells.

Device	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	PCE (%)
W/O	0.384	17.08	57.6	3.78
ZnO-O_2	0.409	22.21	59.6	5.41
ZnO-N_2	0.331	7.17	43.5	1.03
ZnO-H_2	0.379	14.66	53.7	2.98

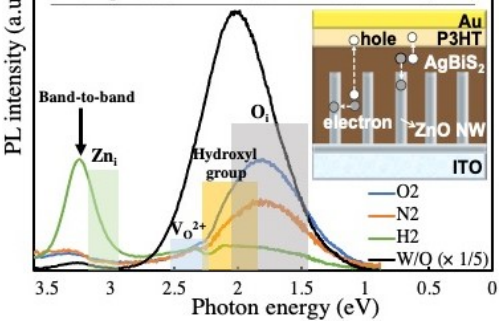


Figure 1. PL spectra of ZnO NW annealed in N_2 and H_2 at 400 °C, in O_2 at 500 °C and without annealing (Inset table: corresponding solar cell performance, inset figure: solar cell structure).

[1] Wang, H.; Kubo, T.; Nakazaki, J.; Kinoshita, T.; Segawa. H., *J. Phys. Chem. Lett.* **2013**, 4, 2455.
[2] Xiao, Y.; Wang, H.; Awai, F.; Shibayama, N.; Kubo, T.; Segawa, H., *ACS Appl. Mater. Inter.* **2021**, DOI: 10.1021/acsami.0c19435.

Dye Molecules Assisted $CsPbIBr_2$ Perovskite Solar Cells for Excellent Performance

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[1] *Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Japan.*

[2] *Department of Materials Science and Engineering, China Jiliang University, China.*

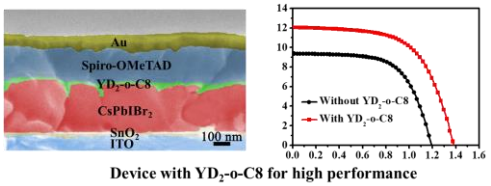
E-mail: tinglima@life.kyutech.ac.jp

Keywords: All inorganic perovskite; broadening absorption spectrum; moisture stability; dye molecular; low energy loss

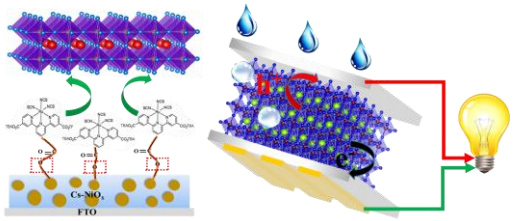
All-inorganic metal halide perovskite solar cells (PSCs) have attracted widespread attention due to excellent thermal stability. The $CsPbIBr_2$, representative all-inorganic perovskite material, has a relatively narrow bandgaps around 2.05 eV and superior thermal, which is considered the best choice due to balance the band gap and stability features.

While the low PCE and poor water stability are main issues limit $CsPbIBr_2$ development, for solving these problems we ingeniously use dye molecule to broaden the absorption spectrum and improve the moisture stability of the device. We demonstrate YD_2-o-C8 has a bifunctional effect, not only as a co-sensitization layer for $CsPbIBr_2$ with broader absorption spectrum, but also reducing the Energy loss by interface passivation. Specifically, the light absorption range of the photoactive layer was broadened from 600 to nearly 680 nm. And record-high open circuit voltage of 1.37 V and short-circuit currents of 12.05 mA/cm^2 were achieved. Meanwhile we introduced another dye moleculer N749 in device the device exhibits extremely high moisture stability that retains 90% of their initial PCE at 1000 h in ambient condition over 65 % RH. Our results prove an efficient way to prepare high-efficient and superior moisture stable all-inorganic PSCs.

The presentation will introduce the results of our group and recent progress in all inorganic $CsPbIBr_2$ PSCs.



Device with YD_2-o-C8 for high performance



Device with N749 for moisture stability

References

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PEFC 酸素還元反応用カーボンフリーナノ粒子連結触媒の開発

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Carbon-Free Connected Nanoparticle Catalysts for Oxygen Reduction Reaction in PEFCs
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To expand the applications of PEFCs, the improvement of the activity and durability of cathode electrocatalysts for oxygen reduction reaction (ORR) is essential. The conventional ORR catalyst (Pt/C) consists of Pt nanoparticles supported on carbon black (Fig. 1a), which shows low ORR activity as well as low durability due to the dissolution and agglomeration of Pt nanoparticles and carbon corrosion during PEFC operations. Our group has developed a carbon-free connected nanoparticle catalyst for ORR, which consists of nanonetwork formed by the connection of Pt-based nanoparticles (Fig. 1b).[1)] The metal nanonetwork possesses high electrical conductivity, leading to the elimination of carbon supports. As shown in Fig. 1c, the ORR specific activity of the connected Pt–Fe catalyst is about 10 times higher than that of Pt/C. Furthermore, the connected Pt–Fe catalyst with a carbon-free structure and a high superlattice degree provides high durability against PEFC operations (start/stop and load cycles).

Keywords : Fuel Cell; Nanonetwork; Platinum-Based Catalyst; Activity; Durability

固体高分子形燃料電池(PEFC)の普及拡大には、酸素還元反応(ORR)触媒の高活性・高耐久化が必要不可欠である。Pt ナノ粒子がカーボン上に担持された従来の ORR 触媒(Pt/C, Fig. 1a)は、ORR 活性が低く、PEFC 運転時に Pt ナノ粒子の溶出・凝集やカーボンの腐食が起こり、電池性能が劇的に低下する。本グループは、新たな ORR 触媒として、Pt 系ナノ粒子が連結したナノネットワークで構成されるカーボンフリーナノ粒子連結触媒(Fig. 1b)を開発した[1)]。金属ナノネットワークは導電性を有するため、カーボン担体を必要としない。開発した超格子 Pt–Fe ナノ粒子連結触媒は、市販の Pt/C よりも約 10 倍高い ORR 表面比活性を示す(Fig. 1c)。さらに、カーボンフリーかつ高い超格子化度を有する本触媒は、燃料電池(起動停止・負荷応答)運転に対する高耐久性を実現できる。

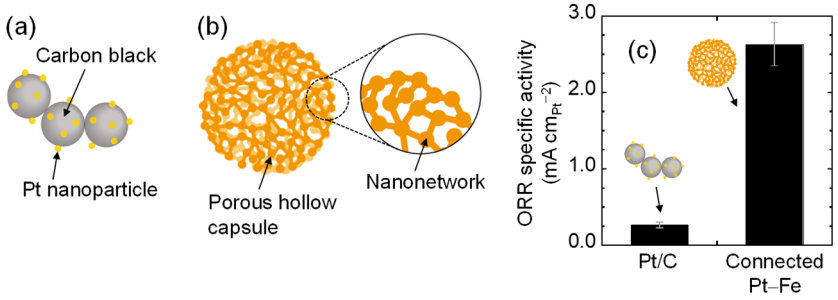

Fig. 1. Schematics of (a) conventional Pt/C and (b) carbon-free connected nanoparticle catalysts. (c) Comparison of ORR specific activity of the catalysts.

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