Sun. Mar 21, 2021

Room 23

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

[A23-3pm] 01. Education and History of Chemistry

Chair:Sekai Iwama, Shuichi Takahara
1:00 PM - 3:00 PM Room 23 (Online Meeting)

[A23-3pm-01] Analysis with the Systematized Survey on the History of Technology: Planetarium, Magnetic tape, Power system, Writable optical disc, Rolling bearings for automotive applications and Related technologies

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

1:00 PM - 1:20 PM

[A23-3pm-02] Chemical education in the Times of Post Covid-19

○Sekai Iwama[1,2,3], Fumiyoshi Asahi[2,6,3], Ryu Takahashi[2,4,3], Tsugane Sasaki[5] (1. Kumamoto Gakuen University, 2. Specified Nonprofit Corporation Otaru Kagakugizyutsu no Me wo Sodateru Kai, 3. Otaru-city science education network, 4. Otaru City Council, 5. Specified Nonprofit Corporation Nextday, 6. Namara Farm)

1:20 PM - 1:40 PM

[A23-3pm-03] Cu Plating with Sn and Subsequent Bronze Formation under Mild Conditions

○Takahiro Suzuki[1,2], Masayuki Inoue[3] (1. Graduate School of Science, Tokyo University of Science, 2. Sakado High School of Saitama Prefecture, 3. Faculty of Science, Tokyo University of Science)

1:40 PM - 2:00 PM

[A23-3pm-04] Study of experimental teaching materials on molecular polarity

○Shuichi Takahara[1] (1. Okayama University of Science)

2:00 PM - 2:20 PM

[A23-3pm-05] Theoretical Study on Complex Ions composed of Tartrate and Cu(Ⅱ) in Feling's solution

○Koyo Morisaki[1], Gondoh Yoshinobu[1], Noguchi Daisuke[2,1], Tomohiro Hashimoto[3], Suehiro Iwata[4,5] (1. Nagasakinishi high school, 2. Graduate School of Engineering, Nagasaki University, 3. Faculty of Regional Studies, Gifu University, 4. Institute for Molecular Science, 5. Graduate University of Advanced Study)

2:20 PM - 2:40 PM

[A23-3pm-06] A New Chemical Structural Formula gives us an Essential Chemical Image of a Molecule

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

2:40 PM - 3:00 PM

Room 4

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

[A04-3pm] 03. Physical Chemistry -Structure-

Chair:Kazunobu Sato, Tomoko Inose
1:00 PM - 3:00 PM Room 4 (Online Meeting)

[A04-3pm-01] Ion-trajectory simulation for evaluation of an ion-density distribution in a linear multipole ion trap

○Takefumi Handa[1], Akira Terasaki[1] (1. Kyushu Univ.)

1:00 PM - 1:20 PM

[A04-3pm-02] Controlling Molecular Arrangement of Porphyrin Derivative in a Thin Film Using Intermolecular Coordination Bonds

○Kazutaka Tomita[1], Nobutaka Shioya[1], Takafumi Shimoaka[1], Takeshi Hasegawa[1] (1. ICR, Kyoto Univ.)

1:20 PM - 1:40 PM

[A04-3pm-03] ESR analyses of high spin cobalt(II) complexes with large zero-field splitting parameters

○Takeshi Yamane[1], Kenji Sugisaki[1], Kazunobu Sato[1], Kazuo Toyota[1], Daisuke Shiomi[1], Takeji Takui[1] (1. Osaka City Univ.)

1:40 PM - 2:00 PM

[A04-3pm-04] Direct observation of H2 dissociation and spillover process on Pd/Cu Single Atom Alloy Catalyst surface by spectroscopic method

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

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2:00 PM - 2:20 PM

[A04-3pm-05] Mechanism of carbon nanotubes chemically unzipping into graphene nanoribbons

○Tomoko Inose[1], Shuichi Toyouchi[2], Shinnosuke Hara[3], Shoji Sugioka[4], Yasuhiko Fujita[5,2], Steven De Feyter[2], Hirofumi Tanaka[3], Hiroshi Uji-i[2,4] (1. Kyoto University, 2. KU Leuven, 3. Kyushu institute of technology, 4. Hokkaido University, 5. Toray Reserach Center, Inc)

2:20 PM - 2:40 PM

[A04-3pm-06] Invesitgation of distance dependence on vibrational energy transfer in proteins using periodical character of alpha helices

○Satoshi Yamashita[1], Misao Mizuno[1], Yasuhisa Mizutani[1] (1. Osaka university)

2:40 PM - 3:00 PM

Room 7

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

[A07-3am] 04. Physical Chemistry -Properties-

Chair:Takane Imaoka, Kohei Imura
9:00 AM - 11:40 AM Room 7 (Online Meeting)

[A07-3am-02] Structure dependence of the Surface-enhanced Raman spectra observed on a single-molecule junction of the disubstituted benzene derivative

○Satoshi Kaneko[1,2], Koji Yasuraoka[1], Shuji Kobayashi[1], Tomoaki Nishino[1] (1. Tokyo Institute of Technology, 2. JST PRESTO)

9:20 AM - 9:40 AM

[A07-3am-03] In situ detection of Pt subnano particles by dual-isolated nanostar-enhanced Raman Spectroscopy

○Yuansen Tang[1], Akiyoshi Kuzume[2,3], Kimihisa Yamamoto[1,2] (1. Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 2. JST-ERATO in Tokyo Institute of Technology, 3. Clean Energy Research Center, Yamanashi University)

9:40 AM - 10:00 AM

[A07-3am-04] STM study of on-surface adsorption process of 3d transition metal atom into organic molecule

○Toyo Kazu Yamada[1] (1. Chiba Univ.)

10:00 AM - 10:20 AM

[A07-3am-05] Structure and Electrical Properties of a New Molecular Memory Element with an Alternating Circular Array of Dipolar Rotors and Rotation Suppressors

○Takuya Miyazaki[1,3], Yoshiaki Shoji[1], Shintaro Fujii[2], Tomoaki Nishino[2], Chi Zhang[3], Emiko Kazuma[3], Yousoo Kim[3], Takanori Fukushima[1] (1. Lab. Chem. &Life Sci., Tokyo Tech., 2. School of Science, Tokyo Tech., 3. RIKEN)

10:20 AM - 10:40 AM

[A07-3am-06] Structural and magnetic properties of iron-based ultrasmall particles using arc plasma deposition

○Yumi Ida[1,2], Makoto Tanabe[1,2], Kimihisa Yamamoto[1,2] (1. Tokyo Institute of Technology, 2. JST-ERATO)

10:40 AM - 11:00 AM

[A07-3am-07] Multimodal Detection of Circulating Tumor Cells Using Multifunctional Silica Particles

○Jeladhara Sobhanan[1], Yuta Takano[1,2], Vasudevanpillai Biju[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

11:00 AM - 11:20 AM

[A07-3am-08] Interaction of gold nanoparticle assembly with dye molecules at liquid-liquid interface

○Atsuko Jimbo[1], Kohei Imura[1] (1. Waseda Univ.)

11:20 AM - 11:40 AM

Room 3

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

[A03-3am] 04. Physical Chemistry -Properties-

Chair:Yasutaka Kitagawa, Ryohei Kishi
9:00 AM - 11:20 AM Room 3 (Online Meeting)

[A03-3am-01] Magnetism of Pseudobinary $SmFe_{12}$ Compound

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

9:00 AM - 9:20 AM

[A03-3am-02] Theoretical study on the electronic state of honeycomb framework composed of

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phenelenyl units

○Kyohei Yoneda[1] （1. National Institute of Technology, Nara College）

9:20 AM - 9:40 AM

[A03-3am-03] Synthesis and Excited-state Dynamics of Pentracene-Modified Au_{25} nanoclusters

○Hayato Sakai[1], Yasunaga Hosokawa[2], Nikolai Tkachenko[3], Yuichi Negishi[2], Taku Hasobe[1] （1. Keio University, 2. Tokyo University of Science, 3. Tampere University）

9:40 AM - 10:00 AM

[A03-3am-04] Ligand Effect of Precisely Synthesized Gold Clusters in the Ultrafast Carrier Dynamics

○Daichi Eguchi[1], Naoto Tamai[1] （1. Kwansi Gakuin University）

10:00 AM - 10:20 AM

[A03-3am-05] Coherent-interaction-enhanced hot-electron generation under modal strong coupling conditions

○Yen-En Liu[1], Xu Shi[1], Tomoya Oshikiri[1], Shuai Zu[1], Quan Sun[1], Keiji Sasaki[1], Hiroaki Misawa[1,2] （1. Hokkaido University, 2. National Chiao Tung University, Taiwan）

10:20 AM - 10:40 AM

[A03-3am-06] Electrochemical tuning of coupling strength in strong coupling system between lattice plasmon and molecular excitons

○Takahiro Hayashi[1], Shunpei Oikawa[1], Hiro Minamimoto[2], Kei Murakoshi[2] （1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Department of Chemistry, Faculty of Science, Hokkaido University）

10:40 AM - 11:00 AM

[A03-3am-07] Local Structures and Molecular Motions in Proton-Conducting PVPA-*x*Im Composites Investigated by Molecular Dynamics Simulations

○Yuta Hori[1], Toshiya Suetake[2], Tomonori Ida[2], Motohiro Mizuno[2], Yasuteru Shigeta[1] （1. University of Tsukuba, 2. Kanazawa University）

11:00 AM - 11:20 AM

Room 5

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

[A05-3pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair:Akihiro Furube, Yuta Takano

1:00 PM - 3:40 PM Room 5 (Online Meeting)

[A05-3pm-01] Signal Enhancement in Pump-Repump-Probe Spectroscopy Using a Sequential Pulse Train

○Hikaru Sotome[1], Masafumi Koga[1], Tomoya Sawada[1], Hiroshi Miyasaka[1] （1. Osaka University）

1:00 PM - 1:20 PM

[A05-3pm-02] The molecular mechanism of light-driven inward proton pump, schizorhodopsin, from Asgard archaea

○Keiichi Inoue[1], Wataru Shihoya[1], Masae Konno[1,2], Akimitsu Higuchi[1], Tajima Seiya[3], Yuji Furutani[4], Yuma Kawasaki[1], Takashi Nagata[1], Hiromu Yawo[1], Izuru Kawamura[3], Hideki Kandori[4], Osamu Nureki[1] （1. The Univ. of Tokyo, 2. JST PRESTO, 3. Yokohama Natl. Univ., 4. Nagoya Inst. of Tech.）

1:20 PM - 1:40 PM

[A05-3pm-03] Defect-filling in lead halide perovskite crystals revealed by single-particle electroluminescence microspectroscopy

○Sankaramangalam Balachandran Bhagyalakshmi[1], Yuta Takano[1,2], Vasudevanpillai Biju[1,2] （1. Graduate School of Environmental Science, Hokkaido University , 2. Research Institute for Electronic Science, Hokkaido University）

1:40 PM - 2:00 PM

[A05-3pm-04] Spin Dynamics Study of Photo-Carrier Generation in TIPS-Pentacene Film by Electrically Detected Magnetic Resonance

○Ken Kato[1], Yoshio Teki[1] （1. Osaka City Univ.）

2:00 PM - 2:20 PM

[A05-3pm-05] Non-linear emission dynamics of a $CH_3NH_3PbBr_3$ microcrystal measured by femtosecond trainsient absorption microscopy

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

2:20 PM - 2:40 PM

[A05-3pm-06] Trapping Photogenerated Charge Carriers in Perovskite Nanocrystal Films

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by Doping with Electron Scavengers

○Sachith Bhagyashree Mahesha[1], Yuta Takano[1,2], Vasudevanpillai Biju[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

2:40 PM - 3:00 PM

[A05-3pm-07] Photoinduced Electron Transfer Reaction and Solvent Effect of a Bridging Molecule between Flavin and Tryptophan

○Yoshimi Oka[1] (1. Oita Univ.)

3:00 PM - 3:20 PM

[A05-3pm-08] Controlling the nonadiabatic electron-transfer reaction rate through molecular-vibration polaritons in the ultrastrong coupling regime

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

3:20 PM - 3:40 PM

Room 6

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

[A06-3am] 06. Analytical Chemistry

Chair:Yuko Nishimoto, Masahito Uchikoshi
9:00 AM - 11:00 AM Room 6 (Online Meeting)

[A06-3am-01] X-ray elemental analysis of Ge quantum dots on a Si substrate using an X-ray induced force change through X-ray aided atomic force microscopy (XANAM)

○Shushi Suzuki[1], Shingo Mukai[2], Wang Jae Chun[3], Masaharu Nomura[4], Syuntarou Fujimori[1], Mitsuhisa Ikeda[1], Katsunori Makihara[1], Seiichi Miyazaki[1], Kiyotaka Asakura[2] (1. Nagoya University, 2. Hokkaido University, 3. International Christian University, 4. KEK)

9:00 AM - 9:20 AM

[A06-3am-02] Harmful Reagent-free Separation/Concentration of Boron and Arsenic in Environmental Water

○Masaru Arai[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

9:20 AM - 9:40 AM

[A06-3am-03] Specific interaction between two-dimensional semiconductor MoS_2 and amide molecules under contaminating solution

○Akito Fukui[1], Hiroaki Onoe[2], Shun Itai[2], Keiko Ishikura[2], Hidekazu Ikeno[1], Takahiro Nagata[3], Yuh Hijikata[4], Jenny Pirillo[4], Takeshi Yoshimura[1], Atsushi Ashida[1], Norifumi Fujimura[1], Daisuke Kiriya[1] (1. Osaka Prefecture Univ., 2. Keio Univ., 3. NIMS, 4. Hokkaido Univ.)

9:40 AM - 10:00 AM

[A06-3am-04] Negative Differential Resistance in a Nanopore under Salt Gradient: Models of Surface Charge Effect

○IAT WAI LEONG[1], Makusu Tsutsui[1], Masateru Taniguchi[1] (1. ISIR, Osaka Univ.)

10:00 AM - 10:20 AM

[A06-3am-05] Removal and quantification of biological CO in mammals using a synthetic heme protein model compound.

○Qiyue Mao[1], Hiroaki Kitagishi[1] (1. Doshisha University)

10:20 AM - 10:40 AM

[A06-3am-06] Determination of the distribution and the structures of cupric chloro species in hydrochloric acid solutions using factor analysis of absorption spectra and ab initio calculation

○Masahito Uchikoshi[1], Takatoshi Matsumoto[1] (1. Tohoku University)

10:40 AM - 11:00 AM

Room 7

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

[A07-3pm] 07. Inorganic Chemistry

Chair:Sayaka Uchida, Eisuke Yamamoto
1:00 PM - 2:40 PM Room 7 (Online Meeting)

[A07-3pm-01] Synthesis of antimony polyoxocation crystal with highly acidic protons

○Yuki Watanabe[1], Takafumi Yamamoto[1], Masayoshi Yabuuchi[1], Olesia Karakulina[2], Yasuto Noda[1], Hyeon-Deuk Kim[1], Masanobu Higashi[1], Osamu Tomita[1], Jingxin Xia[1], Craig Brown[3], Takashi Honda[4], Kazutaka Ikeda[4], Toshiya Otomo[4], Yuto Shimoyama[5], Naoki Ogiwara[5], Joke hadermann[2], Artem Abakumov[2], Sayaka Uchida[5], Ryu Abe[1], Hiroshi Kageyama[1] (1. Kyoto Univ., 2. Univ. of Antwerp, 3. NIST, 4. KEK, 5. The Univ. of Tokyo)

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1:00 PM - 1:20 PM

[A07-3pm-02] Photocatalytic Reduction of Ketones by Visible-Light-Responsive Polyoxometalate Catalysts

○Hiroki Sano[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

1:20 PM - 1:40 PM

[A07-3pm-03] Sequential Synthesis and Structural Transformation of Silver Nanoclusters within a Ring-shaped Polyoxometalate

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

1:40 PM - 2:00 PM

[A07-3pm-04] Synthesis of a New Keggin-Type Divacant Lacunary Polyoxomolybdate [γ-$PMo_{10}O_{36}$]$^{7-}$ and its Use for Synthesis of an Inorganic-Organic Hybrid

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

2:00 PM - 2:20 PM

[A07-3pm-05] Exfoliation of layered bismuth oxyfluorides into nanosheets and their stability

○Tsubasa Tasaka[1], Makoto Kobayashi[2], Eisuke Yamamoto[2], Minoru Osada[2,3] (1. Graduate school of Nagoya University, 2. Institute of Materials and Systems for Sustainability, 3. National Institute for Materials Science)

2:20 PM - 2:40 PM

Room 8

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

[A08-3pm] 08. Catalysts and Catalysis

Chair:Zen Maeno, Xiongjie Jin

1:00 PM - 3:20 PM Room 8 (Online Meeting)

[A08-3pm-01] PdAg alloy nanoparticles encapsulated in N-doped microporous hollow carbon spheres for hydrogenation of CO2 to formate

○Guoxiang Yang[1], Yasutaka Kuwahara[1,2,3], Kohsuke Mori[1,2], Catherine Louis[4], Hiromi Yamashita[1,2] (1. Osaka University, 2. Kyoto University, 3. JST PRESTO, 4. Sorbonne University)

1:00 PM - 1:20 PM

[A08-3pm-02] The Roles of Rh and Pt in Electrochemical Toluene Hydrogenation on Rh-Modified Pt Nanoparticle-Loaded Carbon Catalysts

○Toyoki Imada[1], Masanobu Chiku[1], Eiji Higuchi[1], Hiroshi Inoue[1] (1. Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University)

1:20 PM - 1:40 PM

[A08-3pm-03] Preparation of high loading Pd-CHA by dispersion of bulk Pd and its NO adsorption/desorption property

○Shunsaku Yasumura[1], Taihei Ueda[1], Hajime Ide[1], Takashi Toyao[1,2], Zen Maeno[1], Ken-ichi Shimizu[1,2] (1. Institute for Catalysis, Hokkaido Univ., 2. Elements Strategy Initiative for Catalysts and Batteries Kyoto (ESICB))

1:40 PM - 2:00 PM

[A08-3pm-04] Aerobic Dehydrogenation of Saturated Ketones Using CeO_2-Supported Pd-on-Au Bimetallic Nanoparticle Catalysts

○Daisuke TAKEI[1], Takafumi YATABE[1], Tomohiro YABE[1], Kazuya YAMAGUCHI[1] (1. The Univ. of Tokyo)

2:00 PM - 2:20 PM

[A08-3pm-05] Speciation and Ethane Dehydrogenation Catalysis of Isolated Indium Hydrides in CHA Zeolites

○Zen Maeno[1], Shunsaku Yasumura[1], Xiaopeng Wu[1], Takashi Toyao[1,2], Ken-ichi Shimizu[1,2] (1. Institute for Catalysis, Hokkaido University, 2. Elements Strategy Initiative for Catalysts and Batteries, Kyoto University)

2:20 PM - 2:40 PM

[A08-3pm-06] Effects of MgO on direct amination of alcohols over Ru catalysts

○Yusuke Kita[1], Midori Kuwabara[1], Keigo Kamata[1], Michikazu Hara[1] (1. MSL, Tokyo Tech)

2:40 PM - 3:00 PM

[A08-3pm-07] Selective hydrogenolysis of phenols to arenes by metal– support cooperation

○Rio Tsukimura[1], Xiongjie Jin[1], Takeshi Aihara[2], Hiroki Miura[2], Tetsuya Shishido[2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. Tokyo Metropolitan University)

3:00 PM - 3:20 PM

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Room 12

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

[A12-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Tohru Wada, Mio Kondo, Hisashi Shimakoshi
9:00 AM - 11:20 AM Room 12 (Online Meeting)

[A12-3am-01] Photochemical Water Oxidation Reaction Catalyzed by a Doubly N-Confused Hexaphyrin Dinuclear Cobalt Complex

○Takashi Nakazono[1], Tohru Wada[1] (1. Rikkyo University)

9:00 AM - 9:20 AM

[A12-3am-02] Alkane Oxidation with m-CPBA Catalyzed by B_{12} Complex

○Cheng Jiamin[1], Yoshio Hisaeda[1], Hisashi Shimakoshi[1] (1. Kyushu university)

9:20 AM - 9:40 AM

[A12-3am-03] Substituent Effects of Bipyridine Ligands on Oxygen Reduction Reaction Catalyzed by Dinucelar Cobalt Complexes

○Hiroaki Arima[1], Takashi Nakazono[1], Tohru Wada[1] (1. Rikkyo University)

9:40 AM - 10:00 AM

[A12-3am-04] Catalytic Hydrodehalogenation of Aryl Halides Mediated by a Long-Range Metal-Ligand Cooperation of Cobalt(I) Complexes Bearing a Tetradentate PNNP Ligand

○Nai-Yuan Jheng[1,2], Yuki Naganawa[1], Yumiko Nakajima[1,2] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. University of Tsukuba)

10:00 AM - 10:20 AM

[A12-3am-05] Photochemical CO_2 Reduction and Formic Acid Dehydrogenation Promoted by a Pentanuclear Cobalt Complex

○Takuya Akai[1], Yutaka Saga[1], Mio Kondo[1], Shigeyuki Masaoka[1] (1. Osaka University)

10:20 AM - 10:40 AM

[A12-3am-06] Isotope-labeling Studies on Water Oxidation Reaction Catalyzed by a Monocobalt Polymolybdate

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

10:40 AM - 11:00 AM

[A12-3am-07] Electrochemical Polymerization Provides a Function-Integrated System for Water Oxidation

○Hikaru Iwami[1,2,3], Mio Kondo[1], Shigeyuki Masaoka[1] (1. Osaka Univ., 2. SOKENDAi, 3. IMS)

11:00 AM - 11:20 AM

Room 13

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

[A13-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Wataru Kosaka, Koji Nakabayashi, Takuya SHIGA
9:00 AM - 11:40 AM Room 13 (Online Meeting)

[A13-3am-01] Syntheses and Properties of Mixed-valence One-dimensional Assembles Consisting of Polyoxometalate and Tetranuclear Platinum Complexes

○Kazuhiro Uemura[1], Haruka Hasegawa[1], Atsushi Takamori[2] (1. Faculty of Engineering, Gifu University, 2. Graduate School of Engineering, Gifu University)

9:00 AM - 9:20 AM

[A13-3am-02] Magnetic phase switch accompanied with the suppression of structural disorder by Gas-adsorption in a layered assembly of paddlewheel [Ru2] units and TCNQ

○Yoshie Hiwatashi[1], Wataru Kosaka[1,2], Jun Zhang[2], Hitoshi Miyasaka[1,2] (1. Department of Chemistry, Graduate School of Science, Tohoku University, 2. Institute for Materials Research, Tohoku University)

9:20 AM - 9:40 AM

[A13-3am-03] Elucidation of ion insertion/desertion behavior using one-dimensional lanthanoid-phthalocyaninato double-decker complexes

○Tetsu Sato[1], Keiichi Katoh[2], Brian Breedlove[1], Shinya Takaishi[1], masahiro yamashita[1] (1. The Univ. of Tohoku, 2. The Univ. of Josai)

9:40 AM - 10:00 AM

[A13-3am-04] Octacyanidotungstate-based Thermofluorochromic Magnets

○Olaf Stefanczyk[1], Kunal Kumar[1], Shin-ichi Ohkoshi[1] (1. The Univ. of Tokyo)

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10:00 AM - 10:20 AM

[A13-3am-05] Cyanido-Bridged Ho^{III}-M^{III} (M = Co, Rh, and Ir) Dinuclear Molecules Showing Slow Magnetic Relaxation and Luminescence Thermometry Based on Re-Absorption Effect

○Junhao Wang[1], Jakub Zakrzewski[2], Mikolaj Zychowicz[2,3], Veacheslav Vieru[3,4], Liviu Chibotaru[3], Koji Nakabayashi[1], Szymon Chorazy[2], Shin-ichi Ohkoshi[1] (1. the University of Tokyo, 2. Jagiellonian University, 3. Katholieke Universiteit Leuven, 4. Maastricht University)

10:20 AM - 10:40 AM

[A13-3am-06] Magnetic circularly polarized luminescence (MCPL) from iridium (Ir) and platinum (Pt) complexes by applying an external magnetic field

○Kana Matsudaira[1], Junichi Hotei[2], Ken-ichi Yamashita[3], Yoshirou Kondou[4], Satoko Suzuki[4], Shigeyuki Yagi[2], Michiya Fujiki[5], Yoshitane Imai[1] (1. Kindai University, 2. Osaka Prefecture University, 3. Osaka University, 4. JASCO, 5. NAIST)

10:40 AM - 11:00 AM

[A13-3am-07] Toward Iridium Complexes with High Oxidation States through All-carbon Ligated Pincer Ligand-type Aryl-substituted Dipyrido-annulated Carbenes

○Kazuki Nakanishi[1], Rong Shang[1], Masaaki Nakamoto[1], Yohsuke Yamamoto[1], Hiroto Yoshida[1], J. Oscar C. Jimenez-Halla[2] (1. Graduated School of Advanced Science and Engineering, Hiroshima University, 2. Division of Natural and Exact Sciences, University of Guanajuato,)

11:00 AM - 11:20 AM

[A13-3am-08] Synthesis and Characterization of N-Fused Porphyrin Iridium Complexes

○Jibin Alex Abraham[1], Masatoshi Ishida[1], Hiroyuki Furuta[1] (1. Kyushu University)

11:20 AM - 11:40 AM

Room 15

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

[A15-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair:Takuya Kochi, Tomohiro Iwai

1:00 PM - 3:40 PM Room 15 (Online Meeting)

[A15-3pm-01] Iron-Catalyzed Cross-Coupling of Organoboron Reagents with Propargyl Electrophiles

○Siming Lu[1], Ryosuke Agata[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto University)

1:00 PM - 1:20 PM

[A15-3pm-02] Iron-Catalyzed ortho C– H Homoallylation of Aromatic Ketones Using Methylenecyclopropanes

○Naoki Kimura[1], Shiori Katta[1], Yoichi Kitazawa[1], Takuya Kochi[1], Fumitoshi Kakiuchi[1] (1. Keio University)

1:20 PM - 1:40 PM

[A15-3pm-03] Highly Active Cross-Metathesis of Tetrafluoroethylene with a Seven-membered NHC-Ruthenium Catalyst

○Midori Akiyama[1], Kenta Mori[1], Ko Inada[2], Yutaka Imamura[2], Yuichiro Ishibashi[2], Yusuke Takahira[2], Kyoko Nozaki[1], Takashi Okazoe[1,2] (1. The University of Tokyo, 2. AGC Inc.)

1:40 PM - 2:00 PM

[A15-3pm-04] Ruthenium-Catalyzed Enantioselective Propargylic Reduction of Propargylic Alcohols with Hantzsch Esters

○Haowei Ding[1], Shogo Kuriyama[1], Ken Sakata[2], Yoshiaki Nishibayashi[1] (1. University of Tokyo, 2. Toho University)

2:00 PM - 2:20 PM

[A15-3pm-05] Asymmetric Remote C– H Bond Borylation with a Modular Iridium Catalyst

○Ronald Lazo Reyes[1,2], Miyu Sato[2], Tomohiro Iwai[2], Kimichi Suzuki[1], Satoshi Maeda[1,2], Masaya Sawamura[1,2] (1. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, 2. Chemistry Department, Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

[A15-3pm-06] Imidazole-Directed Ir(III)-catalyzed Direct Intermolecular α-Amidation of Masked Aliphatic Acids: A Facile Route to α-Amino Acids

○Sanjit Kumar Mahato[1], Nozomi OHARA[1], Naoto CHATANI[1] (1. Faculty of Engineering, Osaka

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University)
2:40 PM - 3:00 PM

[A15-3pm-07] Reaction of H_2 with mitochondria-relevant metabolites using a single-metal-site (PNNP)iridium complex
○Shota Yoshioka[1], Sota Nimura[1], Masayuki Naruto[1], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)
3:00 PM - 3:20 PM

[A15-3pm-08] Iridium(III)-Catalyzed Regioselective Branch Alkenylation of Aniline with Alkenes
○Shrikant Manmathappa Khake[1], Naoto Chatani[1] (1. Faculty of Engineering, Osaka University)
3:20 PM - 3:40 PM

Room 16

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

[A16-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair:Koji Hirano, Kei Murakami
1:00 PM - 3:40 PM Room 16 (Online Meeting)

[A16-3pm-01] Solid-State Cross-Coupling Reactions of Insoluble Aryl Halides Using Mechanochemistry
○Tamae Seo[1], Naoki Toyoshima[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

[A16-3pm-02] Palladium-Catalyzed Regioselective C-H Alkenylation and Alkynylation of Allylic Alcohols by Phenanthroline-Type Bidentate Auxiliary
○Shibo Xu[1], Koji Hirano[1], Masahiro Miura[1] (1. Osaka University)
1:20 PM - 1:40 PM

[A16-3pm-03] The Intermolecular 1,2-Alkylborylation of Unactivated Olefins through Copper(I)-Catalyzed Radical Relay Reation
○Sota Akiyama[1], Natsuki Oyama[1], Tsubura Endo[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)
1:40 PM - 2:00 PM

[A16-3pm-04] Cross-Couplings of Acyl Halides with Potassium Perfluorobenzoates via Decarboxylation and Decarbonylation
○Liyan Fu[1], Qiang Chen[1], Jingwen You[1], Yasushi Nishihara[2] (1. Grad. Sch. of Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayama Univ.)
2:00 PM - 2:20 PM

[A16-3pm-05] Palladium-Catalyzed Addition of Acylsilanes to Olefins via the Cleavage of a Carbon-Silicon Bond
○Shun Sakurai[1], Tetsuya Inagaki[1], Takuya Kodama[1], Mamoru Tobisu[1] (1. The Univ. of Osaka)
2:20 PM - 2:40 PM

[A16-3pm-06] Synthesis of alpha-Amino Acid Derivatives by Copper-Catalyzed Electrophilic Amination
○Soshi Nishino[1], Toshimichi Kobayashi[2], Koji Hirano[1], Masahiro Miura[1] (1. Graduate School of Engineering, Osaka University, 2. Osaka University)
2:40 PM - 3:00 PM

[A16-3pm-07] Base-free Suzuki– Miyaura cross-coupling reaction
○Takashi Niwa[1], Yuta Uetake[2], Miki Nakaoka[1], Tadashi Takimoto[1], Hidehiro Sakurai[2,3], Takamitsu Hosoya[1,4] (1. RIKEN BDR, 2. Grad. Sch. Eng., Osaka Univ., 3. OTRI, Osaka Univ., 4. IBB, Tokyo Med. &Dent. Univ.)
3:00 PM - 3:20 PM

[A16-3pm-08] Mechanistic study on base-free Suzuki–Miyaura cross-coupling reaction
○Yuta Uetake[1], Takashi Niwa[2], Takamitsu Hosoya[2,3], Hidehiro Sakurai[1,4] (1. Grad. Sch. Eng., Osaka Univ., 2. RIKEN BDR, 3. IIB, Tokyo Med. &Dent. Univ., 4. OTRI, Osaka Univ.)
3:20 PM - 3:40 PM

Room 17

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

[A17-3pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair:Shinji Toyota, Takeshi Kawase

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1:00 PM - 3:40 PM Room 17 (Online Meeting)

[A17-3pm-01] Synthesis of Unsubstituted Polyarylenes
○Shusei Fujiki[1], Akiko Yagi[1], Kenichiro Itami[1] (1. Graduate School of Science, Nagoya University)
1:00 PM - 1:20 PM

[A17-3pm-02] Synthesis and properties of twisted alkene-inserted cycloparaphenylenes
○Tomoaki Terabayashi[1], Eiichi Kayahara[1], Tatsuhisa Kato[1], Shigeru Yamago[1] (1. Institute for Chemical Research, Kyoto University)
1:20 PM - 1:40 PM

[A17-3pm-03] A new synthetic method for cycloparaphenylenes via a macrocyclic gold(I) complex: from mechanism to application
○Yoshitaka Tsuchido[1], Naoki Narita[1], Yohei Tanji[1], Tomohito Ide[3], Kohtaro Osakada[2], Hidetoshi Kawai[1] (1. Tokyo University of Science, 2. Tokyo Institute of Technology, 3. National Institute of Technology, Tokyo College)
1:40 PM - 2:00 PM

[A17-3pm-04] Synthesis of π-Extended [2n+1]Helicenes: Helically Twisted Wire Molecules with Large Effective Conjugation Length
○Yusuke Nakakuki[1], Takashi Hirose[2], Hikaru Sotome[3], Hiroshi Miyasaka[3], Kenji Matsuda[1] (1. Grad. Sch. of Eng. Kyoto Univ. , 2. ICR, Kyoto Univ., 3. Grad. Sch. of Eng. Sci. Osaka Univ.)
2:00 PM - 2:20 PM

[A17-3pm-05] Synthesis, Structure, and Reactivity of Thiophene-fused 1,4-Diazapentalene
○Junichi Usuba[1], Aiko Fukazawa[2] (1. Graduate School of Science, Nagoya University, 2. Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University)
2:20 PM - 2:40 PM

[A17-3pm-06] Development of Benzo[*de*]isoquinolino[1,8-*gh*]quinoline Diimide n-Type Organic Semiconductors with Asymmetric Substituents
○Craig Yu[1], Shohei Kumagai[1], Hiroyuki Ishii[2], Go Watanabe[3], Hiroki Sugiura[4], Yukio Tani[4], Tetsuya Watanabe[4], Jun Takeya[1,5,6], Toshihiro Okamoto[1,5,7] (1. The University of Tokyo, 2. University of Tsukuba, 3. Kitasato Univeresity, 4. FujiFilm Corp., 5. OPERANDO-OIL, AIST-UTokyo, 6. WPI-MANA, NIMS, 7. PRESTO, JST)
2:40 PM - 3:00 PM

[A17-3pm-07] π-Electronic Ion Pairs: Ordered Arrangement Based on Noncovalent Interaction
○Hiroki Tanaka[1], Yohei Haketa[1], Hiromitsu Maeda[1] (1. Ritsumeikan Univ.)
3:00 PM - 3:20 PM

[A17-3pm-08] Synthesis of Thiophene-Based Twisted Bistricyclic Aromatic Ene with Tricoordinate Boron
○Yohei Adachi[1], Takanori Nomura[1], Shion Tazuhara[2], Hiroyoshi Naito[2], Joji Ohshita[1] (1. Hiroshima University, 2. Osaka Prefecture University)
3:20 PM - 3:40 PM

Room 9

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

[A09-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair:Masayuki Takeuchi, Tomoki Ogoshi
1:00 PM - 3:40 PM Room 9 (Online Meeting)

[A09-3pm-01] Synthesis and Cooperative Molecular Recognition of Homoditopic Host Molecule with Rebek’ s Cavitands
○Haruna Fujimoto[1], Daisuke Shimoyama, Takehiro Hirao[1], Takeharu Haino[1] (1. Hiroshima University)
1:00 PM - 1:20 PM

[A09-3pm-02] Triaxially Woven Hydrogen-Bonded Network of Tetrakis(carboxybiphenyl)ethene: Structure and Mechanochromic Behavior
○Yuto Suzuki[1], Norimitsu Tohnai[2], Ichiro Hisaki[1] (1. Graduate School of Engineering Science, Osaka University, 2. Graduate School of Engineering, Osaka University)
1:20 PM - 1:40 PM

[A09-3pm-03] Host– guest chemistry and optical properties of porous molecular crystals
○Hiroshi Yamagishi[1] (1. Univ. of Tsukuba)
1:40 PM - 2:00 PM

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[A09-3pm-04] Base-/Acid-Induced Multi-Step Fluorescence of Trefoil Azine

○Noriho Taniguchi[1], Masaya Naito[1], Shinobu Miyagawa[1], Yuji Tokunaga[1] (1. University of Fukui)

2:00 PM - 2:20 PM

[A09-3pm-05] ^{129}Xe NMR structural analysis of continuous porosity of columnar liquid crystal composed of stacked macrocycles

○Shin-ichiro Kawano[1], Takahiro Taki[1], Hiroaki Yoshimizu[2], Kentaro Tanaka[1] (1. Nagoya University, 2. Nagoya Institute of Technology)

2:20 PM - 2:40 PM

[A09-3pm-06] Conformational Control of Aliphatic Oligoketones by Pillar[5]arene and its Application

○Yumehiro Manabe[1], Keisuke Wada[2], Yudai Baba[2], Tomoki Yoneda[1], Tomoki Ogoshi[3,4], Yasuhide Inokuma[1,5] (1. Grad. Sch. Eng., Hokkaido Univ., 2. Grad. Sch. Eng. Sci. Tech., Kanazawa Univ., 3. Grad. Sch. Eng., Kyoto Univ., 4. WPI-NanoLSI, Kanazawa Univ., 5. WPI-ICReDD, Hokkaido Univ.)

2:40 PM - 3:00 PM

[A09-3pm-07] Building Heterodimer Porphyrin Capsules Bearing Different Number of Hydrogen bond Function and Application to Aromatic Multi-Layer Structure

○Masahiro Ueda[1], Ban Hayato[1], Kimura Masaki[1], Miyagawa Shinobu[1], Naito Masaya[1], Tokunaga Yuji[1] (1. University of Fukui)

3:00 PM - 3:20 PM

[A09-3pm-08] Selective inclusion of regioisomers of disubstituted aromatic compounds with crystals of *p-tert*-butylcalix[4]arene: Mechanistic consideration for guest selectivity and application for separation

○Tomoaki Matsumoto[1], Atsuya Sakamoto[1], Takuro Sasaki, Naoya Morohashi[1], Tetsutaro Hattori[1] (1. The University of Tohoku)

3:20 PM - 3:40 PM

Room 21

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

[A21-3am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair:Hiroshi Ikeda, Yoichi Kobayashi
9:00 AM - 11:40 AM Room 21 (Online Meeting)

[A21-3am-01] A Mechanism for Opening an Unusual Reaction Pathway in the Mechanochemical Synthesis of Dibenzophenazine

○Naoki Haruta[1,2,3], Paulo Filho Marques de Oliveira[4,5], Alain Chamayou[4], Tohru Sato[1,2,3], Kazuyoshi Tanaka[1,2], Michel Baron[4] (1. FIFC, Kyoto Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. ESICB, Kyoto Univ., 4. IMT Mines Albi, 5. Univ. of São Paulo)

9:00 AM - 9:20 AM

[A21-3am-02] Development of Radical Difunctionalization of Ethylene Gas Predicted by Quantum Chemical Calculations

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

9:20 AM - 9:40 AM

[A21-3am-03] Development of Diversity-Oriented Synthesis Methodologies for Lactones via Activation of Molecular Iodine by Visible Light

○Saki Maejima[1], Eiji Yamaguchi[1], Akichika Itoh[1] (1. Gifu Pharmaceutical University)

9:40 AM - 10:00 AM

[A21-3am-04] Ratiometric fluorescent force probe that works in gels

○Takuya Yamakado[1], Shohei Saito[1] (1. Grad. Sch. of Sci., Kyoto Univ.)

10:00 AM - 10:20 AM

[A21-3am-05] Non-classical control of magnetic circularly polarized luminescence (MCPL) of pyrene and phenanthrene luminophores by electron donor and acceptor effects

○Nobuyuki Hara[1], Maho Kitahara[1], Takaharu Sugimura[1], Hayato Toda[1], Motohiro Shizuma[2], Akari Itou[3], Makoto Miyasaka[3], Michiya Fujiki[4], Yoshitane Imai[1] (1. Kindai University, 2. Osaka Research Institute of Industrial Science and Technology, 3. Tokyo Denki University;, 4. Nara Institute of Science and Technology)

10:20 AM - 10:40 AM

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[A21-3am-06] Singlet Fission in Tetracene Dimers and Oligomers

○Shunta Nakamura[1], Hayato Sakai[1], Masaaki Fuki[2], Yasuhiro Kobori[2], Nikolai V. Tkachenko[3], Taku Hasobe[1] (1. Faculty of Science and Technology, Keio University, 2. Molecular Photoscience Reserch Center, Kobe University, 3. Tampere University)

10:40 AM - 11:00 AM

[A21-3am-07] Preparation and Application of Novel Pt Nanoparticles Supported on TiO_2 Photocatalyst

○Yuki Wada[1], Toshiki Akiyama[1], Kazuo Harada[1], Tetsuo Honma[2], Hiroshi Naka[3], Susumu Saito[3], Mitsuhiro Arisawa[1] (1. Graduate School of Pharmaceutical Sciences, Osaka University, 2. Japan Synchrotron Radiation Research Institute, SPring-8, 3. Graduate School of Science, Nagoya University)

11:00 AM - 11:20 AM

[A21-3am-08] Mg-Promoted Reductive CO_2 Fixation of Propenyl Ketones

○Suhua ZHENG[1], Tianyuan ZHANG[1], Hirofumi MAEKAWA[1] (1. Nagaoka Univ. of Tech.)

11:20 AM - 11:40 AM

Room 10

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

[A10-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair:Mao Minoura, Takeshi Fujita
1:00 PM - 3:20 PM Room 10 (Online Meeting)

[A10-3pm-01] Photocatalytic redox-neutral hydroxyalkylation of *N*-heteroaromatics with aldehydes

○Hiromu Fuse[1], Hiroyasu Nakao[1], Yutaka Saga[2], Arisa Fukatsu[3], Mio Kondo[2], Shigeyuki Masaoka[2], Harunobu Mitsunuma[1], Motomu Kanai[1] (1. The Univ. of Tokyo, 2. Osaka Univ., 3. Inst. for Molecular Science)

1:00 PM - 1:20 PM

[A10-3pm-02] Phosphorus-Based Organocatalysis for Dehydrative Cyclization of *N*-(2-Hydroxyethyl)amides into 2-Oxazolines

○Farzaneh Soleymani-Movahed[1], Siong Wan Foo[1], Saeko Ogawa[1], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

1:20 PM - 1:40 PM

[A10-3pm-03] Acid-Mediated C– F/C– H Coupling of Fluorobenzofurans with Arenes

○Ryutaro Morioka[1], Takuya Fukuda[1], Takeshi Fujita[1], Junji Ichikawa[1] (1. University of Tsukuba)

1:40 PM - 2:00 PM

[A10-3pm-04] Design, Synthesis, and Properties of TEtraQuinoline (TEQ)

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

2:00 PM - 2:20 PM

[A10-3pm-05] Synthesis of Water-Soluble 3-Acyl-2-alkoxyindolizines for Red Light-Induced Release of Bioactive Carboxylic Acids

○Kenji Watanabe[1], Nodoka Terao[1], Takashi Niwa[1], Takamitsu Hosoya[1,2] (1. RIKEN, 2. TMDU IBB)

2:20 PM - 2:40 PM

[A10-3pm-06] Mild Hydrogenation of Arenes/Heteroarenes

○Nao Tanaka[1], Toyonobu Usuki[1] (1. Sophia University)

2:40 PM - 3:00 PM

[A10-3pm-07] Synthesis and Reaction of Dipotassiodisilene and -digermene Bearing Extended Triptycyl Groups

○Ryohei Nishino[1], Mao Minoura[1] (1. College of Science, Rikkyo Univ.)

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

[A19-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair:Yoshiaki Tanabe, Tatsuhiko Yoshino
1:00 PM - 3:40 PM Room 19 (Online Meeting)

[A19-3pm-01] Silane- and peroxide-free hydrogen atom transfer hydrogenation using ascorbic acid and cobalt-photoredox dual catalysis

○Masahiro Kojima[1], Yuji Kamei[1], Yusuke Seino[2],

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Yuto Yamaguchi[2], Tatsuhiko Yoshino[1], Satoshi Maeda[3,4,5], Shigeki Matsunaga[1,6] (1. Graduate School of Pharmaceutical Sciences, Hokkaido University, 2. Faculty of Pharmaceutical Sciences, Hokkaido University, 3. WPI-ICReDD, 4. Department of Chemistry, Graduate School of Science, Hokkaido University, 5. JST-ERATO, 6. GI-CoRE)

1:00 PM - 1:20 PM

[A19-3pm-02] Enantioselective Radical Cation-induced [4+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Effect of Photoirradiation

○Shuhei Ohmura[1], Takahiro Horibe[1], Kazuaki Ishihara[1] (1. Nagoya Univ.)

1:20 PM - 1:40 PM

[A19-3pm-03] Palladium- and Photoredox-Catalyzed Alkylation-Cyclization Reactions of Iodoalkenes with 4-Alkyl-1,4-dihydropyridines and Mechanistic studies

○Yulin Zhang[1], Yoshiaki Tanabe[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo)

1:40 PM - 2:00 PM

[A19-3pm-04] Addition of C(sp^3)– H Bonds to Styrenes via Hydrogen Atom Transfer to Aqueous Hydroxyl Radical under Photocatalysis

○Shogo Mori[1], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

2:00 PM - 2:20 PM

[A19-3pm-05] Switching from Biaryl Formation to Amidation with Convoluted Polymeric Nickel Catalysis

○Abhijit Sen[1], Raghu, N Dhital[1], Takuma Sato[1], Aya Ohno[1], Yoichi M. A. YAMADA[1] (1. RIKEN)

2:20 PM - 2:40 PM

[A19-3pm-06] Pot-Economical Synthesis of Prostaglandins

○Nariyoshi Umekubo[1], Yujiro Hayashi[1] (1. Univ. of Tohoku)

2:40 PM - 3:00 PM

[A19-3pm-07] Development of Nitrogen-doped Carbon Incarcerated Rhodium Nanoparticles for Asymmetric Insertion of Carbenoids and Application for Efficient Continuous Synthesis of Chiral Amino Acids

○Ryusuke Masuda[1], Tomohiro Yasukawa[1], Shū Kobayashi[1] (1. The University of Tokyo)

3:00 PM - 3:20 PM

[A19-3pm-08] Zinc-Catalyzed Phosphonylation of Alcohols with Alkyl Phosphites

○Soomin Cho[1], Luca Alessandro Danieli[1], Akira Matsunaga[1], Yuki Saito[1], Shū Kobayashi[1] (1. University of Tokyo)

3:20 PM - 3:40 PM

Room 22

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

[A22-3am] 16. Natural Products Chemistry, Chemical Biology

Chair:Gosuke Hayashi, Kiichiro Totani
9:00 AM - 11:40 AM Room 22 (Online Meeting)

[A22-3am-01] Total Synthesis of Antibiotic Cyclic Peptide Hytramycin V

○Tetsuya Inaba[1], Yoshimasa Ishizaki[2], Masayuki Igarashi[2], Masahito Yoshida[1], Hideo Kigoshi[1] (1. Graduate School of Pure and Applied Sciences, University of Tsukuba, 2. Institute of Microbial Chemistry)

9:00 AM - 9:20 AM

[A22-3am-02] Peptide ligation between α-amidonitrile and N-terminal cysteine

○Xiaoling Wang[1], Jing Li[1], Yujiro Hayashi[1] (1. Tohoku University, Graduate School of Science)

9:20 AM - 9:40 AM

[A22-3am-03] Structure and biological activity of iezoside, a novel peptide-polyketide hybrid compound from marine cyanobacteria

○Naoaki Kurisawa[1], Arihiro Iwasaki[1], Kiyotake Suenaga[1] (1. Keio university)

9:40 AM - 10:00 AM

[A22-3am-04] New spumigin analogues from a cyanobacterium *Dolichospermum* sp.

○Chin-Soon Phan[1], Andrea Roxanne J. Anas[1], Jakia Jerin Mehjabin[1], Tatsufumi Okino[1] (1. Hokkaido University)

10:00 AM - 10:20 AM

[A22-3am-05] Synthetic study of *N*-glycan from hyperthermophilic archaeon *Thermococcus kodakarensis*

○Kohtaro Hirao[1], Yoshiyuki Manabe[1], Immacolata Speciale[2], Haruyuki Atomi[3], Antonio

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Molinaro[2], Cristina De Castro[2], Koichi Fukase[1]
（1. Graduate School of Science, Osaka University, 2. University of Napoli Federico II, 3. Graduate School of Engineering, Kyoto University）
10:20 AM - 10:40 AM

[A22-3am-06] Opened-Fmoc group: protecting group activated by gold-catalyst
○Tomoya Yamamoto[1], Katsunori Tanaka[1,2,3]（1. RIKEN CPR, 2. Sch. Mater. &Chem. Tech., Tokyo Tech., 3. A. Butlerov Inst. of Chem., KFU）
10:40 AM - 11:00 AM

[A22-3am-07] Development of receptor subtype selective ligands via focused library screening composed of stereoisomers of coronatine
○Kengo Hayashi[1], Nobuki Kato[1], Haruna Nomoto[1], Misuzu Nakayama[1], Takuya Kaji[1], Raku Watanabe[2], Rina Saito[2], Yousuke Takaoka[1], Koji Miyamoto[3], Hideo Inagaki[3], Kazunori Okada[4], Minoru Ueda[1,2]（1. Graduate School of Science, Tohoku University, 2. Graduate School of Life Science, Tohoku University, 3. Graduate School of Science and Engineering, Teikyo University, 4. Biotechnology Research Center, The University of Tokyo）
11:00 AM - 11:20 AM

[A22-3am-08] Creation of H_2O_2-Activatable Photosensitizer based on Hypocrellin B
○Takashi Kitamura[1], Hirotaka Nakata[1], Daisuke Takahashi[1], Kazunobu Toshima[1]（1. Fac. Sci. Tech., Keio Univ.）
11:20 AM - 11:40 AM

Room 26

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

[A26-3am] 17. Biofunctional Chemistry, Biotechnology

Chair:Atsushi Shimoyama, Katsunori Tanaka
9:00 AM - 11:40 AM Room 26 (Online Meeting)

[A26-3am-01] Development of highly functionalized lipid A for self-adjuvanting vaccines.
○Yusuke Yamanaka[1], Atsushi Shimoyama[1], Koichi Fukase[1]（1. Graduate School of Science, Osaka University）
9:00 AM - 9:20 AM

[A26-3am-02] Preparation of Bone-like Hydroxyapatite and its application for cell culture
○Hiroki Miyajima[1], Hiroki Touji[1], Yuanyi Chen[1], Taichi Furukawa[1], Shoji Maruo[1], Kazutoshi Iijima[1]（1. Yokohama National University）
9:20 AM - 9:40 AM

[A26-3am-03] Molecular Dynamics Simulation of Interaction between Polysaccharides and Fabrication of Cell Scaffolds
○Kazutoshi Iijima[1], Makoto Yamazaki[1], Makoto Yabe[2]（1. Yokohama Natl. Univ., 2. Mol Processing）
9:40 AM - 10:00 AM

[A26-3am-04] Spatial and Temporal Regulation of Cellular Morphology using a Photo-Responsive Mechanical DNA Polymer
○Soumya Sethi[1], Tomoko Emura[1], Kumi Hidaka[1], Masayuki Endo[1,2], Hiroshi Sugiyama[1,2]（1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Sciences ,Kyoto University）
10:00 AM - 10:20 AM

[A26-3am-05] Structural basis for membrane receptor activity of ganglioside GM3 regulated by lipid-lipid interactions
○Katsuaki Sasaki[1], Shinya Hanashima[1], Yuuichi Umegawa[1], Michio Murata[1]（1. Osaka University）
10:20 AM - 10:40 AM

[A26-3am-06] *In situ* Detection of Penicillin and Avermectin in Microbes by Raman Microspectroscopy and Multivariate Analysis
○Shumpei Horii[1,2], Masahiro Ando[3], Takuji Nakashima[1], Ashok Zachariah Samuel[3], Yoko Takahashi[1], Haruko Takeyama[1,2,3,4]（1. The Univ. of Waseda, 2. CBBD-OIL, AIST-Waseda Univ., 3. Res. Org. Nano Life Innov., The Univ. of Waseda, 4. Inst. Adv. Res. Biosyst. Dynam., Waseda Res. Inst. Sci. Eng., The Univ. of Waseda）
10:40 AM - 11:00 AM

[A26-3am-07] Development of a Drug Encapsulated Micelle Loaded Photoresponsive Platform for the Treatment of Coronary Stenosis

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○Hayato Laurence Mizuno[1], Yasutaka Anraku[1], Ichiro Sakuma[1], Yuki Akagi[1] (1. The Univ. of Tokyo)

11:00 AM - 11:20 AM

[A26-3am-08] Lysosome-targeting magnetic-plasmonic hybrid nanoparticles for the imaging and isolation of intact lysosomes

○The Son Le[1], Mari Takahashi[1], Yuichi Hiratsuka[1], Kazuaki Matsumura[1], Tomohiko Taguchi[2], Shinya Maenosono[1] (1. Japan Advanced Institute of Science and Technology, 2. Tohoku University)

11:20 AM - 11:40 AM

Room 27

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

[A27-3pm] 18. Polymer

Chair:Takahiro Kakuta, Michio Matsumoto
1:00 PM - 3:20 PM Room 27 (Online Meeting)

[A27-3pm-01] Synthesis of π-conjugated two-dimensional polymers and their electronic properties

○Michio Matsumoto[1] (1. National Institute for Materials Sceince)

1:00 PM - 1:20 PM

[A27-3pm-02] Design of temperature-responsive polymer-gold nanoparticle hybrids using novel gold nanoparticle monomers and regulation of reduction activity

○Takashi Miyata[1], Yoshiko Oota[1], Atsushi Saka[1], Akifumi Kawamura[1] (1. Kansai Univ.)

1:20 PM - 1:40 PM

[A27-3pm-03] Preparation and properties of polysilsesquioxane membrane with proton conductivity

○Hiroshi Fujioka[1] (1. Tokyo University of Science)

1:40 PM - 2:00 PM

[A27-3pm-04] Development of Two-Dimensional Nanostructured Virus Filtration Membranes Based on Gemini Smectic Liquid Crystals

○Kazuma Hamaguchi[1], Rino Ichikawa[1], Satoshi Kajiyama[1], Shotaro Torii[1], Yusuke Hayashi[1], Hiroyuki Katayama[1], Takashi Kato[1] (1. Sch. Eng., The Univ. of Tokyo)

2:00 PM - 2:20 PM

[A27-3pm-05] Development of Halogen-Sensitive Solvatochromism Materials Using Phenolic Polymers

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

2:20 PM - 2:40 PM

[A27-3pm-06] Polarization-Responsive Behavior in Nonlinear Optical Effect of Polymer-Stabilized Dye-Doped Liquid Crystals

○Kohsuke Matsumoto[1], Koji Usui[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

[A27-3pm-07] Metallo-supramolecular polymers: electrochromic and supercapattery device application

○Masayoshi Higuchi[1], Sanjoy Mondal[1], Manas Kumar Bera[1] (1. National Institute for Materials Science)

3:00 PM - 3:20 PM

Room 1

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

[A01-3pm] 19. Colloid and Interface Chemistry

Chair:Atsuhiro Fujimori, Takuya Nakashima
1:00 PM - 3:40 PM Room 1 (Online Meeting)

[A01-3pm-01] Prediction of surface energy and surface wettability assisted by machine learning

○Yuki Tokura[1], Yasuhiko Igarashi[2,3], Hiroaki Imai[1], Yuya Oaki[1,3] (1. Keio Univ., 2. Univ. of Tsukuba, 3. JST PRESTO)

1:00 PM - 1:20 PM

[A01-3pm-02] Control Factor of the Molecular Optical Trapping at Solid-Liquid Interface

○Nobuaki Oyamada[1], Hiro Minamimoto[2], Kei Murakoshi[2] (1. Grad. Sch. of Chem. Sci. and Eng. Hokkaido Univ., 2. Fac. of Sci. Hokkaido Univ.)

1:20 PM - 1:40 PM

[A01-3pm-03] Switchable surface properties induced by photo/thermal responsive molecular layer consisted with anthracene moieties

○Miho Aizawa[1], Haruhisa Akiyama[1], Yoko Matsuzawa[1] (1. National Institute of Advanced

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Industrial Science and Technology (AIST))
1:40 PM - 2:00 PM

[A01-3pm-04] Monolayer of polyethoxylated alkyl amine functionalized gold nanoparticles
○Md. Abdullah Al Nahid[1], Ken-ichi Iimura[1] (1. Utsunomiya University)
2:00 PM - 2:20 PM

[A01-3pm-05] Fabrication of photocathode using modal coupling between plasmon and Fabry– Pé rot nanocavity
○Tomoya Oshikiri[1], Xu Shi[1], Hiroaki Misawa[1,2] (1. Hokkaido University, 2. National Chiao Tung University)
2:20 PM - 2:40 PM

[A01-3pm-06] Self-organization of organic-inorganic hybrid dendrimer with a magnetic Fe_3O_4 nanocore
○Takehiro Yachi[1], Masaki Matsubara[2,1], Atsushi Muramatsu[1], Kiyoshi Kanie[1] (1. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, 2. National Institute of Technology, Sendai College)
2:40 PM - 3:00 PM

[A01-3pm-07] Development of highly functional oriental lacquer for suppression of rash and improvement of light resistance
○Masaki MATSUBARA[1,2], Tetsuo SATO[1], Akiko TOKUTAKE[1], Atsushi MURAMATSU[2], Kiyoshi KANIE[2] (1. National Institute of Technology, Sendai College, 2. IMRAM, Tohoku University)
3:00 PM - 3:20 PM

[A01-3pm-08] Magnetically Controllable Phage Assembly with Centimeter Sizescale
○shuxu wang[1,2], Yasuhiro Ishida[2], Noriyuki Uchida[2], Takuzo Aida[1,2] (1. the Univ. of Tokyo, 2. CEMS, Riken)
3:20 PM - 3:40 PM

Room 2

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

[A02-3pm] 19. Colloid and Interface Chemistry

Chair:Tsuyoshi Asahi, Makoto Tanabe
1:00 PM - 3:40 PM Room 2 (Online Meeting)

[A02-3pm-01] Spontaneous formation and dynamic structural evolution of nanoparticle superstructure during the growth process of copper sulfide nanoparticles
○Masaki Saruyama[1], Fumiko Nakagawa[1], Ryo Takahata[1], Ryota Sato[1], Toshiharu Teranishi[1] (1. Institute for Chemical Research, Kyoto Univeristy)
1:00 PM - 1:20 PM

[A02-3pm-02] Control over the regioselectivity in ligand exchange reaction of a Au_{25} cluster
○Wataru Suzuki[1], Ryo Takahata[1], Toshiharu Teranishi[1] (1. Institute of Chemical Research, Kyoto University)
1:20 PM - 1:40 PM

[A02-3pm-03] Synthesis and Optical Properties of *C*1-$PtIn_2$ Plasmonic Nanoalloys
○Haruka Takekuma[1], Ryota Sato[1], Kenji Iida[2], Tokuhisa Kawawaki[3], Mitsutaka Haruta[1], Hiroki Kurata[1], Toshiharu Teranishi[1] (1. Kyoto Univ., 2. Hokkaido Univ., 3. TUS)
1:40 PM - 2:00 PM

[A02-3pm-04] Mixed oleic acid and oleylamine as the matrix for synthesizing metal nanoparticles by sputter deposition
○Mai Thanh Nguyen[1], Tetsu Yonezawa[1] (1. Hokkaido University)
2:00 PM - 2:20 PM

[A02-3pm-05] Tuning of the responsive temperature of gold nanoparticle assembly by surface modification with oligo(ethylene glycol)-based molecules
○KUN XIONG[1], Hideyuki Mitomo[2,3], Yier Shi, Yusuke Yonamine[2,3], Kuniharu Ijiro[2,3] (1. Graduate School of Life Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University, 3. Global Institution for Collaborative Research and Education, Hokkaido University)
2:20 PM - 2:40 PM

[A02-3pm-06] Copper-Metal Oxide Hybrid Subnanoparticles for Catalytic Selective Oxidations
○Hiromu Koizumi[1], Tetsuya Kambe[1,2], Makoto Tanabe[2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-ERATO)
2:40 PM - 3:00 PM

[A02-3pm-07] Dependence of Plasmon-Induced Charge

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Separation on the Resonance Mode of Silver Nanocubes

○Hiroyasu Nishi[1], Tetsu Tatsuma[1] （1. The University of Tokyo）

3:00 PM - 3:20 PM

[A02-3pm-08] Structural analysis of AOT/water/organic solvent mixed emulsion systems containing silver nanoparticles by SAXS/SANS

○Masafumi Harada[1], Miho Yamamoto[1] （1. Nara Women's University）

3:20 PM - 3:40 PM

Room 22

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

[A22-3pm] 20. Materials Chemistry -Basic and Application-

Chair:Tsuyohiko Fujigaya, Shinya Maenosono
1:00 PM - 3:20 PM Room 22 (Online Meeting)

[A22-3pm-01] Thermoelectric Properties of Paracostibite Fabricated using Chemically Synthesized Co– Sb– S Nanoparticles as Building Blocks

○Mari Takahashi[1], Shujie Fei[1], Masanobu Miyata[1], Pratibha Dwivedi[1], Wei Zhou[2], Michihiro Ohta[2], Shinya Maenosono[1] （1. Japan Advanced Institute of Science and Technology, 2. National Institute of Advanced Industrial Science and Technology ）

1:00 PM - 1:20 PM

[A22-3pm-02] Carbonization of polyacrylonitrile chains in coordination nanospaces

○XIYUAN ZHANG[1], Ryoto HONGU[2], Takashi KITAO[1,3], Takashi UEMURA[1,3] （1. Graduate School of Frontier Sciences, the University of Tokyo, 2. Graduate School of Engineering, Kyoto Univiveristy, 3. Graduate School of Engineering, the University of Tokyo）

1:20 PM - 1:40 PM

[A22-3pm-03] Metal-nitrogen co-doped carbon materials with different metal speciation as electrocatalysts for carbon dioxide reduction

○Kazuyuki Iwase[1], Kazuhide Kamiya[2], Juan Herranz[3], Kathrin Ebner[3], Justus Diercks[3], Takashi Harada[2], Itaru Honma[1], Shuji Nakanishi[2] （1. Tohoku Univ., 2. Osaka Univ., 3. Paul Scherrer Institut）

1:40 PM - 2:00 PM

[A22-3pm-04] Near Infrared Photoluminescence Properties of Diarylethene-functionalized Single-walled Carbon Nanotubes

○Tomohiro Shiraki[1,2], Yasuto Nakagawa[1], Takuya Nakashima[3], Tsuyoshi Kawai[3], Tsuyohiko Fujigaya[1,2,4] （1. Kyushu Univ., 2. I2CNER, Kyushu Univ., 3. NAIST, 4. CMS, Kyushu Univ.）

2:00 PM - 2:20 PM

[A22-3pm-05] Non-linear optical properties of magnetic fluoroscent Ytterbium complexes

○KUNAL KUMAR[1], Olaf Stefanczyk[1], Koji Nakabayashi[1], Kosuke Nakagawa[1], Yurie Oki[1], Shin-ichi Ohkoshi[1] （1. University of Tokyo）

2:20 PM - 2:40 PM

[A22-3pm-06] Direct Determination of Optical Isomers for Carbon Nanotubes

○Issei Tomotsuka[1], Nobuya Mamizu[2], Hiromitsu Furukawa[2], Koji Harano[1], Eiichi Nakamura[1] （1. The University of Tokyo, 2. System in Frontier Inc.）

2:40 PM - 3:00 PM

[A22-3pm-07] Solvatochromism of near infrared photoluminescence from molecularly functionalized carbon nanotubes

○Yoshiaki Niidome[1], Tsuyohiko Fujigaya[1,2,3], Tomohiro Shiraki[1,2] （1. Department of Applied Chemistry, Kyushu Univ., 2. WPI-I2CNER, 3. CMS）

3:00 PM - 3:20 PM

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

[A23-3pm] 01. Education and History of Chemistry

Chair:Sekai Iwama, Shuichi Takahara

Sun. Mar 21, 2021 1:00 PM - 3:00 PM Room 23 (Online Meeting)

[A23-3pm-01] Analysis with the Systematized Survey on the History of Technology: Planetarium, Magnetic tape, Power system, Writable optical disc, Rolling bearings for automotive applications and Related technologies

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

1:00 PM - 1:20 PM

[A23-3pm-02] Chemical education in the Times of Post Covid-19

○Sekai Iwama[1,2,3], Fumiyoshi Asahi[2,6,3], Ryu Takahashi[2,4,3], Tsugane Sasaki[5] （1. Kumamoto Gakuen University, 2. Specified Nonprofit Corporation Otaru Kagakugizyutsu no Me wo Sodateru Kai, 3. Otaru-city science education network, 4. Otaru City Council, 5. Specified Nonprofit Corporation Nextday, 6. Namara Farm）

1:20 PM - 1:40 PM

[A23-3pm-03] Cu Plating with Sn and Subsequent Bronze Formation under Mild Conditions

○Takahiro Suzuki[1,2], Masayuki Inoue[3] （1. Graduate School of Science, Tokyo University of Science, 2. Sakado High School of Saitama Prefecture, 3. Faculty of Science, Tokyo University of Science）

1:40 PM - 2:00 PM

[A23-3pm-04] Study of experimental teaching materials on molecular polarity

○Shuichi Takahara[1] （1. Okayama University of Science）

2:00 PM - 2:20 PM

[A23-3pm-05] Theoretical Study on Complex Ions composed of Tartrate and Cu(Ⅱ) in Feling's solution

○Koyo Morisaki[1], Gondoh Yoshinobu[1], Noguchi Daisuke[2,1], Tomohiro Hashimoto[3], Suehiro Iwata[4,5] （1. Nagasakinishi high school, 2. Graduate School of Engineering, Nagasaki University, 3. Faculty of Regional Studies, Gifu University, 4. Institute for Molecular Science, 5. Graduate University of Advanced Study）

2:20 PM - 2:40 PM

[A23-3pm-06] A New Chemical Structural Formula gives us an Essential Chemical Image of a Molecule

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

2:40 PM - 3:00 PM

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技術の系統化調査による分析：プラネタリウム，磁気テープ，電力系統，書込型光ディスク及び自動車用ベアリングの技術開発を中心に

（独立行政法人 国立科学博物館）○亀井 修

Analysis with the Systematized Survey on the History of Technology: Planetarium, Magnetic tape, Power system, Writable optical disc, Rolling bearings for automotive applications and Related technologies.

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

The Center of the History of Japanese Industrial Technology (CHJI) with the National Museum of Nature and Science, Japan (NMNS) has been studying the systematized survey on the history of industrial technology which include the viewpoints of the Anthropocene. At this time, the analysis of the development tendency with following issues are described; Planetarium technologies, Magnetic tape technologies, Power system technologies in Japan, Writable optical disc technologies, Rolling bearing technologies for automotive applications and related technologies. The followings are confirmed; technological development starting with product imports model, technology development led by the world of ideas and important technologies model, and the difference between "technological innovation" and "innovation".

Keywords : History of Technology; History of Industrial technology; Technological innovation; Innovation; Anthropocene

国立科学博物館・産業技術史資料情報センターでは，現在が地球規模の考察が必要な「人新世（アントロポシーン）」である [1]との視点も導入し，企業や学協会等の協力や実際の技術開発の現場に携わった専門家による日本の技術開発の歴史を系統的に記録・調査・公開してきている [2]。本報告では，プラネタリウム技術 [3]，磁気テープ技術 [4]，電力系統技術 [5]，書込型光ディスク技術 [6]，自動車用ベアリング技術 [7]の各分野の技術開発史の系統化調査に基づく分析を行った。その結果，従前の検討 [8] [9]と同様な「完成品輸入→模倣・ノックダウン・技術導入→国産化→改善・独自技術の開発→世界をリードするトップランナー」といった進展や，DVD 技術や MIDI 技術の開発のように発想や重要技術が海外に先行あるいは並行して開発され，ステップ・アップされた進展の技術分野があること，「技術革新」と「イノベーション」の違いを確認した。今回検討を行ったいずれの技術分野においても従前の科学技術白書で指摘されたような技術開発（技術革新）の停滞がイノベーションの停滞となる関係を確認することはできなかった。

1) Museums in the Anthropocene - Toward the History of Humankind within Biosphere & Technosphere -, Edited by Osamu KAMEI and *et al.*, 国立科学博物館, **2016**. (http://sts.kahaku.go.jp/english/diversity/document/symposium/system/pdf/104_e.pdf)
2) 国立科学博物館産業技術史資料情報センター, http://sts.kahaku.go.jp, (2019/11/03). 各報告書は PDF 版でも公開.
3) 児玉光義, *技術の系統化調査報告*, 国立科学博物館, **2020**, *29*, 1−106.
4) 齊藤真二, *ibid.*, 107−193.
5) 鈴木浩, *ibid.*, 195−272.
6) 武田立, *ibid.*, 273−330.
7) 室谷周良, *技術の系統化調査報告 共同研究編*, 国立科学博物館・北九州産業技術保存継承センター, **2020**, *13*, 1−106.
8) 科学技術白書に見る「技術革新」の意味合いの変遷，有賀 暢迪; 亀井 修, ***Bull. Natl. Mus. Nat. Sci., Ser. E***, **2014**, *37*, 1-17.
9) 日本の技術革新とイノベーション―国立科学博物館の技術の系統化調査と科学技術白書を中心に―，亀井 修，有賀 暢迪, *JASC 研究会（150830）予稿集*, **2015**, 7-8.

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ポスト COVID-19 社会における化学教育

（熊本学園大商学部[1]・NPO 法人小樽青少年科学技術の芽を育てる会[2]・小樽市議会[3]・NPO 法人 Nextday[4]・なまらファーム[5]・小樽市科学教育ネットワーク[6]）
○岩間世界[1,2,6]・旭史悦[2,5,6]・高橋龍[2,3,6]・佐々木束[4]

Chemical education in the Times of Post Covid-19

（[1]*Department of Commerce, Kumamoto Gakuen Univ.,* [2]*Specified Nonprofit Corporation Otaru Kagakugizyutsu no Me wo Sodateru Kai,* [3]*Otaru City Council,* [4] *Specified Nonprofit Corporation Nextday,* [5]*Namara Farm,* [6]*Otaru-city science education network,*）
○IWAMA, Sekai[1,2,6]; ASAHI, Fumiyoshi[2,5,6]; TAKAHASHI, Ryu[2,3,6]; SASAKI, Tsugane[4]

Hear we report the current situation and problems of science education for the children under COVID-19 calamity in Otaru city. Otaru city is a mid-west part city of Hokkaido with a population of 112,000 in end of 2020 is suffering from depopulation from 1960s (It has been halved in 50 years; middle of 1960s had 210,000 population.). We report practical examples that the face-to-face science experience held while taking care of the COVID-19.

Keywords :Science Education for Post Covid-19; Face-to-face Experience; Overcoming Population Decline; Regional Disparities of Science Education; Specified Nonprofit Corporation Activity

2020 年は新型コロナウイルス感染症(COVID-19)の影響により、これまでの教育環境の変容を余儀なくされた。飛沫感染という特徴は、学校教育はもちろんのこと、社会教育における科学体験・工作教室等の実施にあたり「三密（密閉、密集、密接)」の回避が事業実施における感染拡大防止に配慮した環境として必須条件になった。

学校教育における「三密」回避の方策としては、20 年 2 月の一斉休校要請に前後して、種々の非対面型授業の導入が進んだ。大学においては、ほぼ全てが ICT 技術を使用したものであった[1)]。一方で、公立小中学校においては、ICT を利用した非対面型授業の実施は設置市町村数の 35%程度、特に会議ソフトを使用した同時双方向型オンライン指導については、小学校 8%、中学校 10%であった[2)]。ICT を活用した事例においても、自律的な学びの支援や児童・生徒との関係構築における課題などが報告されている[3)]。

発表者らが活動する小樽市内の小中学校においては、「市内共通学習課題のプリント配布（市 HP からも DL 可能）・テレビ放送の活用・分散登校」が実施され、積極的な ICT の活用はなされなかった。これは、市内家庭におけるネット接続可能な PC 保有率が平均 40%程度（低位所得層:37%;中位所得層:41%;上位所得層:53%; n=1060）であることが考慮されたと考えられる[4)]。このような地域状況において、社会教育としての化学（科学）教育において ICT を導入した場合、参加する子ども達の生活実態が参加への障壁となることが示唆される。本発表では 20 年度の小樽市における実験・工作教室の具体例とその考え方から、ポスト COVID-19 社会における化学（科学）教育の展望について報告する。

1) 文部科学省, 今後の国立大学法人等施設の整備充実に関する調査研究協力者会議（第 5 回）資料 2-1，2020 年 9 月 24 日
2) 文部科学省, 新型コロナウイルス感染症の影響を踏まえた公立学校における学習指導等に関する状況について（令和 2 年 6 月 23 日時点）, 2020 年 7 月 17 日
3) 東洋館出版, 理科の教育令和 2 年 11 月号, **2020**, 820(69), pp 5-29.
4) 小樽市, 平成 30 年度小樽市子どもの生活実態調査報告書, pp79, 2019 年 3 月

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温和な条件での銅板のスズめっきと青銅めっきへの誘導

（東理大院理 [1,2]・東理大理 [3]）○鈴木　崇広 [1,2]・井上　正之 [3]
Cu Plating with Sn and Subsequent Bronze Formation under Mild Conditions ([1]*Graduate School of Science, Tokyo University of Science,* [2]*Sakado High School of Saitama Prefecture* [3]*Faculty of Science, Tokyo University of Science*) ○Takahiro Suzuki,[1] Masayuki Inoue[2]

In a well-known bronze plating experiment, a Cu coupon is subjected to Sn plating and heating with a Bunsen burner. In previous methods, NaOH aq or HCl aq is typically used as the plating solution; however, the use of a strong acid or base provides operational risks. Herein, we introduce a modified method utilizing $NaHSO_4$ aq as the plating solution. This method reduces the operational risks and allows for the smooth deposition of silver-white Sn onto the Cu coupon in a higher yield than that of the HCl method.
Keywords :　Oxidation/Reduction, Electrochemistry, Metals, Tin plating

銅にスズめっきを施した後，青銅めっきに誘導する実験として，めっき液に 3 mol/L 水酸化ナトリウム水溶液や 3 mol/L 塩酸を用いる方法が報告されているが，これらの方法には操作上の危険が懸念される [1]。本研究では，電解質水溶液として硫酸水素ナトリウム水溶液を用いる方法を検討した。(a)めっき液を 0.10 mol/L 硫酸水素ナトリウム水溶液に変更し，(b)めっき後の銅板を強火のブンゼンバーナーの酸化炎で強熱し，水道水で急冷する方法を試みた。その結果，従来法より温和な実験条件であるにも関わらず，赤銅色の銅板に銀白色のスズが円滑に析出し，さらに加熱と急冷によって黄金色の青銅めっきに誘導することが可能となった。本法によって，実験室環境への負担と操作上の危険が少ない実験ができるようになった（Fig.1）。

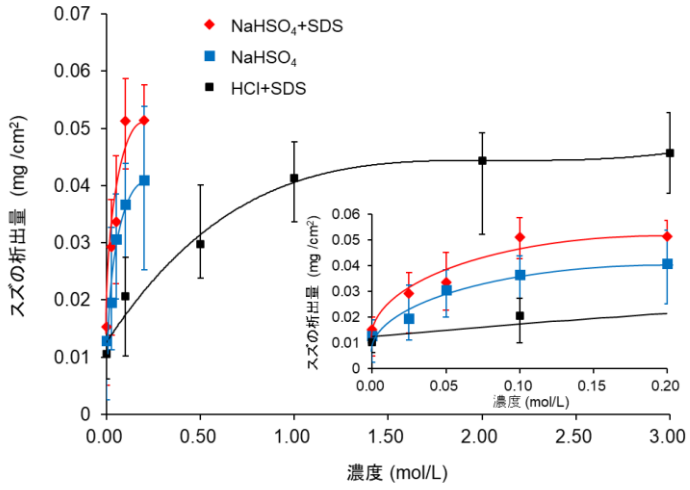


Fig. 1　スズ析出量の比較

1)　堀　葉月，井上正之，化学と教育 **2015**, *63*, 508.

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分子の極性に関する実験教材の研究

（岡山理科大学）○高原 周一
Study of experimental teaching materials on molecular polarity
(*Okayama University of Science*) ○Shuichi Takahara

As an experimental teaching material to show the polarity of molecule, the phenomenon that the liquid flow is bent by a charged body is sometimes used. As a result of investigating this phenomenon for various liquids, it was confirmed that there is a correlation between the polarity of the molecule and the bending angle, but the charging of the liquid was also observed for the liquid showing a large bending angle. This result suggests that the cause of this phenomenon is electrostatic induction rather than dielectric polarization. Therefore, it is inappropriate to use this phenomenon as a teaching material showing the polarity of molecule.
Keywords : Polarity of Molecule, Dielectric Polarization, Electrostatic Induction

分子の極性を示すための実験教材として、液流が帯電体によって曲がるという現象が用いられることがある[1]。この教材を検証するため、水および種々の有機液体について、ビュレットから滴下した液流に正に帯電した金属棒（電位 3 kV）を近づけたときの曲がり角 α を測定した。その結果、液体の誘電率 ε が大きいほど α が大きくなることがわかった（図 1）。ジクロロベンゼンで α が小さめになっているのは液体の密度が大きいためと考えられる。一方で、液流は負に帯電しており、帯電量 Q が大きいほど α が増えるという結果も得られた（図 2）。このことは、液流が帯電体によって曲がる原因が、誘電分極（分子の極性）ではなく、静電誘導（荷電粒子の移動による電荷分離）である可能性を示唆している。その場合、この現象を分子の極性に関する教材として用いるのは不適当ということになる。現在、α が Q によって再現できるか定量的な計算を進めており、当日はその結果も紹介する予定である。

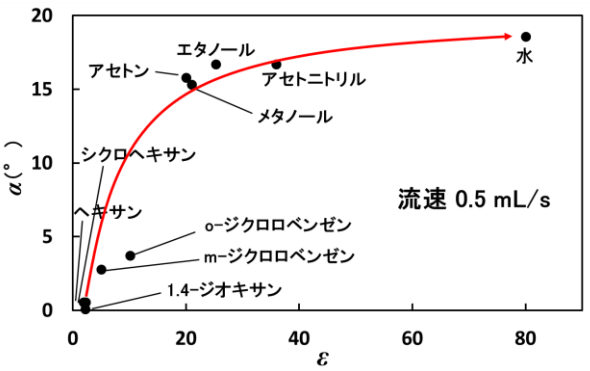


図 1　液体の誘電率 ε と曲がり角 α の関係

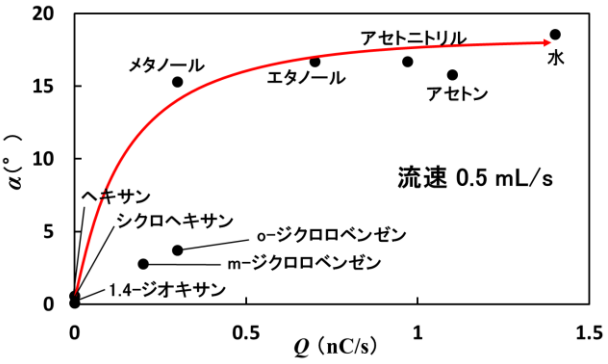


図 2　液体の帯電量 Q と曲がり角 α の関係

1) 例えば、啓林館の高校「物理」の教科書
星野泰也, 視覚でとらえるフォトサイエンス化学図録, 数研出版, p30 (2010)

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フェーリング溶液中における酒石酸と銅の錯イオンに関する理論的研究

(長崎県立長崎西高等学校 [1]、長崎大学大学院工学研究科 [2]、岐阜大学地域科学部 [3]、分子科学研究所 [4]、総合研究大学院大学 [5]) ○森崎 皓陽 [1]、川原 惟人 [1]、麻生 遥史 [1]、浜口 天真 [1]、赤坂 一成 [1]、江頭 基靖 [1]、岩本 崇弘 [1]、権藤 好信 [1]、野口 大介 [1,2]、橋本 智裕 [3]、岩田 末廣 [4,5]

Theoretical Study on Complex Ions Composed of Tartrate and Cu(II) in Fehling's Solution

Koyo Morisaki[1], Tadato Kawahara[1], Haruhumi Aso[1], Tenma Hamaguchi[1], Issei Akasaka[1], Motoyasu Egasira[1], Takahiro Iwamoto[1], Yoshinobu Gondoh[1], Daisuke Noguchi[2,1], Tomohiro Hashimoto[3], Suehiro Iwata[4,5] ([1] Nagasakinishi High School, [2]Graduate School of Engineering, Nagasaki University, [3]Faculty of Regional Studies, Gifu University, [4]Institute of Molecular Science, [5]Graduate University of Advanced Study)

Fehling's test is widely used to detect reducing substances such as aldehydes[1)]. However, there are few theoretical studies on complex ions composed of tartaric acid and Cu(II), which are principal species involved in Fehling's solution. Hörner et al. have proposed several structures of copper tartrate complexes using various functionals such as B3LYP and TZVP basis set[2)]. In this work, we studied geometric and electronic structures of the complex ions *in silico*, and compared UV-Vis absorption spectra in solution with those calculated by TDDFT. As a result, it was found that the mononuclear complex proposed by Hörner et al. (Fig.1) does not cause d-d transition due to its high symmetry. It was also revealed that the structure shown in Fig.2 causes strongest d-d transition among the binuclear complexes whose symmetry is broken.

Keywords : Fehling's solution; Cu(Ⅱ) complex; TDDFT; UV-Vis absorption spectra; d-d transition

フェーリング試験はアルデヒド類の還元性確認に広く用いられる [1)]。しかし、フェーリング反応に関与している酒石酸(LH_4)と銅(II)の錯イオンについての理論的研究例は非常に少なく、形成される錯イオンの構造については、いまだ不明な部分が多い。Hörner らは、B3LYP などの様々な汎関数と基底関数に TZVP を用いて、酒石酸と銅の錯イオンの様々な構造を提案している [2)]。本研究では、TDDFT 計算による UV-Vis スペクトルを実験値と比較することで、溶液中における酒石酸と銅の単核及び 2 核の錯イオンの様々な構造を解析した。その結果、Fig. 1 で示される Hörner がフェーリング液中で存在するとしている単核錯体の構造では、対称性の高さから d-d 遷移を起こさないことが分かった。また、対称性が壊れる 2 核錯体の中では、Fig. 2 に示される構造が、もっとも強い d-d 遷移を引き起こすことが分かった。

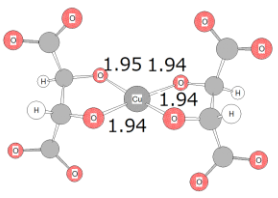


Fig. 1 $[Cu(L^{4-})_2]^{6-}$

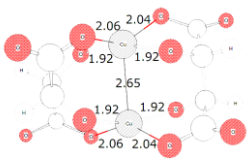


Fig. 2 $[Cu_2(L^{4-})_2]^{4-}$

1) 野口大介 化学と教育 **2019**, *67*, 254-257
2) Hörner et al. *Eur. J. Inorg. Chem.* **2016**, 1798-1807

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日本化学会 第101春季年会 (2021)

新構造式は分子の本質的な化学イメージを提供する

（地球エネルギーシステム研究所）○佐野 寛

A New Chemical Structural Formula gives us an Essential Chemical Image of a Molecule

(LOGES) SANO Hirosi

[Key Words]: New chem-formula, chem-property visualization, shape of π electron cloud, πbond modelling

The new chem-formula can directly show the shape of **π** bonding electron distribution, at a side of the bond. It visualizes a chemical reactivity of a molecule. Traditional **molecule model** only shows a **geometric shape of atoms.** On the other hand, a chemical reactivity owes to a vast expanse of electron distribution shown by the pictorial electron-model. Such a pictorial electron-model of molecule makes a chemical education free from a rote memorization.

＜概要＞

新構造式は**π結合を結合側面に直示**する。それは分子の**化学活性の可視化**に直結する。古典的な分子モデルは**原子の幾何学的**位置表現である。ところが、化学活性は(原子ではなく)**電子 or 空軌道**の位置により決まる。**∴電子モデルを絵画的に表せば**、化学活性を直示し,化学活性を推理できるので、**化学教育を暗記から解放**すると期待できる。

しかし**電子**の位置は**点**ではなく拡がり（＝波動関数 ϕ^2）を持つ分布なので**原子組立モデル的な固定描画は困難**である。だが、**π結合関連**では下記のように、比較的**容易に描画できる**ので、感覚的に**優れた化学教材**を提供できる。

＜**π結合の表示**：構造式から絵画表示まで＞

C=C、 C=C-C=C ↠ (エチレン) (ブタジエン) ↠ *従来型構造式*	C-C-C-C、 C—C (ブタジエン) (エチレン) *新式 a(印刷体)*	C-C、 C-C ——　〜 *新式 b、 新式 c*	C-C、 C-C ⬭　⬬ *描画 a, 描画 b*

構造式印刷を一行で収めたい場合には「アンダライン利用表記」（新式 a）が便利。だが実態のπ電子**張出し長**さは,**σ結合長**さと同程度なので新 b がより近似性が高いモデル;さらにπ電子の揺らぎを取込める新 c がより高い近似・・・となる(=手描きの良さ)。

π電子の横長さを**σ結合**に揃える表示(古典的な C=C)は,実態の学習に有害である。隣接原子への**π電子分布**はみ出し(**共役性**の可視化)理解には、ブタジエン例を示した。

＜C=C-X の**π結合電子の偏移**＞

電子偏移性が,σ結合とπ結合が独立に挙動することは,有機電子論の運用で重要。しかし旧構造式ではσとπが区別できない。一方、新構造式では自然に形で表示されている。

C ═ C→—C̄l　　C ═ C→—C̄l *従来型構造式　(C=C 間結合電子は右へ偏移？)*	C⟶C→—Cl　　C→C→—Cl *新構造式（σ系電子は右偏移；π系は左偏移）*

塩化ビニルでは C-Cl が右へ偏るのに,C^+の攻撃を受ける(＝電子リッチ)2 重結合は左端。ビニルアルコール（C=C—OH）が不安定,アセトアルデヒド（HC—C=O）になる予測も可能。

＜逆配位＞置換基が電子的に「σで吸引しπで供与」する現象の、他の数例を紹介する。

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

[A04-3pm] 03. Physical Chemistry -Structure-

Chair:Kazunobu Sato, Tomoko Inose

Sun. Mar 21, 2021 1:00 PM - 3:00 PM Room 4 (Online Meeting)

[A04-3pm-01] Ion-trajectory simulation for evaluation of an ion-density distribution in a linear multipole ion trap

○Takefumi Handa[1], Akira Terasaki[1] （1. Kyushu Univ.）

1:00 PM - 1:20 PM

[A04-3pm-02] Controlling Molecular Arrangement of Porphyrin Derivative in a Thin Film Using Intermolecular Coordination Bonds

○Kazutaka Tomita[1], Nobutaka Shioya[1], Takafumi Shimoaka[1], Takeshi Hasegawa[1] （1. ICR, Kyoto Univ.）

1:20 PM - 1:40 PM

[A04-3pm-03] ESR analyses of high spin cobalt(II) complexes with large zero-field splitting parameters

○Takeshi Yamane[1], Kenji Sugisaki[1], Kazunobu Sato[1], Kazuo Toyota[1], Daisuke Shiomi[1], Takeji Takui[1] （1. Osaka City Univ.）

1:40 PM - 2:00 PM

[A04-3pm-04] Direct observation of H2 dissociation and spillover process on Pd/Cu Single Atom Alloy Catalyst surface by spectroscopic method

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

2:00 PM - 2:20 PM

[A04-3pm-05] Mechanism of carbon nanotubes chemically unzipping into graphene nanoribbons

○Tomoko Inose[1], Shuichi Toyouchi[2], Shinnosuke Hara[3], Shoji Sugioka[4], Yasuhiko Fujita[5,2], Steven De Feyter[2], Hirofumi Tanaka[3], Hiroshi Uji-i[2,4] （1. Kyoto University, 2. KU Leuven, 3. Kyushu institute of technology, 4. Hokkaido University, 5. Toray Reserach Center, Inc）

2:20 PM - 2:40 PM

[A04-3pm-06] Invesitgation of distance dependence on vibrational energy transfer in proteins using periodical character of alpha helices

○Satoshi Yamashita[1], Misao Mizuno[1], Yasuhisa Mizutani[1] （1. Osaka university）

2:40 PM - 3:00 PM

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イオン軌道シミュレーションを用いた線形イオントラップ内のイオン密度分布の解析

（九大院理）○飯田　岳史・寺嵜　亨

Ion-Trajectory Simulation for Evaluation of an Ion-Density Distribution in a Linear Multipole Ion Trap (*Department of Chemistry, Kyushu University*) ○Takefumi Handa, Akira Terasaki

An ion-density distribution in a linear rf ion trap is quantitatively simulated by the SIMION software. Considering a space charge and ion–buffer He collisions, we were able to reproduce a ring profile of an ion distribution experimentally observed[1] for a linear octopole trap at a high density of ions close to the space-charge limit. In contrast, a quadrupole trap was found to locate ions around the central axis of the trap. The present study aims at optimizing the ion density in the trap for a specific experiment, e.g., laser spectroscopy, of gas-phase clusters.
Keywords: Linear Ion Trap; Ion Density Distribution; Space Charge; SIMION

希薄な気相クラスターの試料密度を向上し、分光計測などを可能とする実験技術の一つにイオントラップがある。本研究は、イオントラップ内のイオン雲をシミュレーションで解析し、計測に最適なイオン密度および分布形状を実現することを目的とした。先行研究で、八極子トラップ内に空間電荷制限値に近い 5.5×10^8 個の Ag_2^+ を導入し、その空間分布をレーザー光解離実験で測定した Fig. 1 の結果が報告されており [1]、まずこの実測結果の再現を試みた。イオン光学系解析ソフト SIMION を利用し、イオン間反発や緩衝ガスとの衝突を考慮したイオン飛跡シミュレーションを行った結果、Fig. 2 のようにリング状の分布が再現され、イオン密度やリング径など、定量性も確認された。このリング形状は、八極子が作る比較的平坦なポテンシャルの中に閉じ込められた多数のイオンが互いに反発しあって形成されたと考えられる。発表では、イオンが中心部に分布する四極子トラップも紹介し、捕捉イオン量や、円筒もしくは双曲面など、電極面の形状の違いによるイオン分布の変化についても議論する。

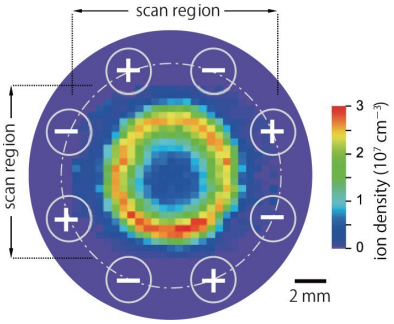


Fig.1 Spatial distribution of Ag_2^+ in a linear octopole trap measured by experiment.[1] The eight circles represent electrodes of the ion trap.

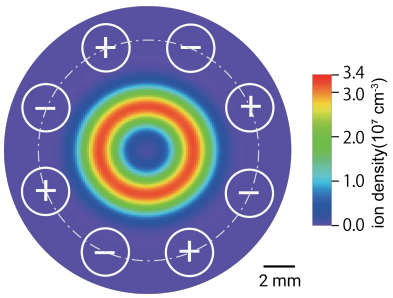


Fig.2 Trajectory simulation of Ag_2^+ in a linear octopole trap reproducing the experimental result in Fig. 1.

1) T. Majima, G. Santambrogio, C.Bartels, A.Terasaki, T. Kondow, J. Meinen, T. Leisner, *Phys. Rev. A* **2012**, *85*, 053414.

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ポルフィリン誘導体の中心金属との配位結合を利用した分子配列制御法の確立: pMAIRS 法と GIXD 法による解析

（京大化研）○冨田 和孝・塩谷 暢貴・下赤 卓史・長谷川 健

Controlling Molecular Arrangement of Porphyrin Derivative in a Thin Film Using Intermolecular Coordination Bonds (*Institute for Chemical Research, Kyoto University*)

Kazutaka Tomita, Nobutaka Shioya, Takafumi Shimoaka, Takeshi Hasegawa

Porphyrin derivatives are promising materials which are used for various thin film devices. The previous studies of 'single crystal structure' reveal that the molecular aggregation structure of the porphyrin derivatives can be controlled by changing the combination of the center metal atom and the functional groups attached to the porphyrin ring.[1,2] In this study, the molecular aggregation structure of tetrapyridylporphyrin (TPyP, Fig. 1) is controlled in a 'thin film,' via the structural analysis using the p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) [3] and grazing incidence X-ray diffraction (GIXD) techniques. When Cu or two H atoms are chosen for the porphyrin center atom, the C–H/N intermolecular interaction between the porphyrin ring and the pyridyl ring gives a lying orientation of the porphyrin ring as shown in Fig. 2. In contrast, when Fe is chosen, the intermolecular coordination bonds between the N atom of the pyridyl groups and the center metal atom realizes a standing orientation of the ring (Fig. 2).

Keywords: Porphyrin; Molecular Orientation; pMAIRS

有機薄膜太陽電池やガスセンサーなど，さまざまな薄膜デバイスへの用途をもつポルフィリン誘導体は，置換基や中心金属を選択することによって，分子集合構造を制御できるという特徴をもつ[1,2]．本研究では，tetrapyridylporphyrin（Fig. 1）に着目し，中心金属とピリジル基との配位結合を利用して薄膜中で分子凝集構造を制御した．pMAIRS 法[3]と GIXD 法による構造解析の結果，中心金属のない H_2TPyP や，配位結合を形成しにくい CuTPyP の薄膜では，C–H/N 分子間相互作用によって作られたシート状の凝集構造[1]が，基板に対して平行に形成されることがわかった（Fig. 2）．このシート面はポルフィリン環とほぼ平行であるため，ポルフィリン環が基板に対して寝た Face-on 配向膜となる．一方で，銅(II)よりも強い配位結合を形成できる鉄(II)を導入した FeTPyP の場合には，Fe/N 配位結合による 2 次元フレームワーク構造[2]が基板に沿って形成され，環が基板に対して立ち上がった Edge-on 配向膜となった（Fig. 2）．

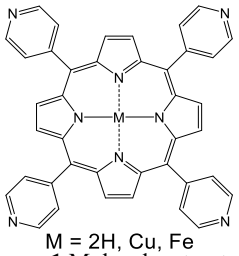


Figure 1 Molecular structure of tetrapyridylporphyrin

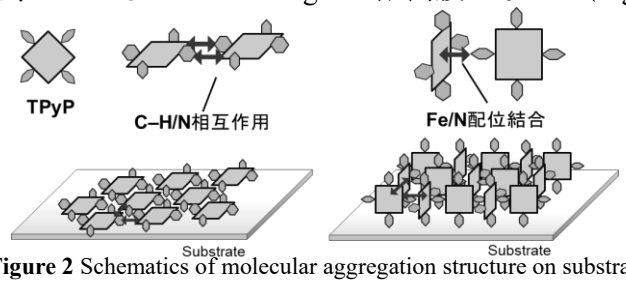


Figure 2 Schematics of molecular aggregation structure on substrate

1) S. M. Yoon, et al. *Angew. Chem. Int. Ed.* **2009**, *48*, 2506. 2) L. Pan. et al. *Chem. Commun.* **2002**, *20*, 2334. 3) T. Hasegawa, *Anal. Chem.* **2007**, *79*, 4385.

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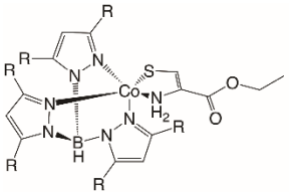
大きいゼロ磁場分裂定数を持つ高スピンコバルト(II)錯体の ESR スペクトルにおける一般解析法

（阪市大院理[1]・JST さきがけ[2]）○山根 健史[1]・杉崎 研司[1,2]・佐藤 和信[1]・豊田 和男[1]・塩見 大輔[1]・工位 武治[1]
ESR analyses of high spin cobalt(II) complexes with large zero-field splitting parameters ([1]*Graduate School of Science, Osaka City University*, [2]*JST PRESTO*) ○Takeshi Yamane[1], Kenji Sugisaki[1,2], Kazunobu Sato[1], Kazuo Toyota[1], Daisuke Shiomi[1], Takeji Takui[1]

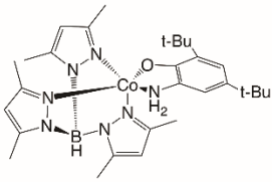
A fictitious spin-1/2 Hamiltonian approach is a putative method to analyze ESR spectra from high spin complexes with sizable zero-field splitting (ZFS) parameters. In this approach, the analyses result in the effective magnetic parameters such as *g*- and *A*-values (g^{eff}, A^{eff}), which are far from the theoretical true *g*- and *A*-values (g^{true}, A^{true}) obtainable from reliable quantum chemical calculations. We established the analytical procedure for analyzing the ESR spectra of high spin Co(II) complexes (S = 3/2, I = 7/2) with sizable ZFS tensors. Our generalized method, which is applicable to non-collinear cases among **D**-, **g**- and **A**-tensors, is based on the analytically derived relationships between the fictitious spin-1/2 and true spin Hamiltonians.
Keywords : Electron Spin Resonance Spectroscopy, High Spin Metallocomplex, Cobalt Complex, Zero-Field Splitting Parameter, Quantum Chemical Calculation

ゼロ磁場分裂（ZFS）定数の大きい高スピン金属錯体は，生体内において重要な役割を果たしているだけでなく磁気材料への応用も期待されている．このような系の ESR スペクトル解析は，仮想スピン 1/2 ハミルトニアンに基づいて行われてきた．しかし，得られた磁気的パラメータ（g^{eff}, A^{eff}）は，系本来のスピン量子数に基づく量子化学計算によるパラメータ（g^{true}, A^{true}）とかけ離れており，直接比較ができなかった．我々はこれまでにスピン量子数 $S \leq 7/2$ までの錯体に対して，スピンハミルトニアンの厳密解析解を用いて g^{eff}–g^{true} 関係式を導出し，種々の遷移金属錯体の ESR スペクトル解析に適用した[1)]．

本研究では，超微細相互作用定数に対する関係式を導出し，確立した ZFS 定数の大きいコバルト錯体（S = 3/2, I = 7/2）の ESR スペクトルの一般解析法を 3 種類の錯体[2,3)]に適用した．この手法は **D**, **g** および **A** テンソルの主軸が共軸でない場合にも適用可能である．スピンハミルトニアンの厳密エネルギー解に基づいて計算した A^{true} の E/D 依存性から理論的 A^{true} を決定し，関係式の妥当性を裏付けることができた．



1 (R = Ph)[2)]
2 (R = Me)[2)]



3[3)]

1) T. Yamane, et al., *Phys. Chem. Chem. Phys.* **2017**, *19*, 24769.; T. Yamane, et al., *Dalton. Trans.* **2018**, *47*, 16429. 2) A. A. Fischer, et al., *Dalton. Trans.* **2017**, *46*, 13229. 3) P. Kumar, et al., *J. Am. Chem. Soc.* **2019**, *141*, 10984.

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Direct observation of H_2 dissociation and spillover process on Pd/Cu single atom alloy catalyst surface by spectroscopic method

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

Keywords: Hydrogen; Single atom alloy catalyst; Dissociative adsorption; X-ray photoelectron spectroscopy; Infrared reflection absorption spectroscopy

The dissociation of hydrogen molecules on the catalyst surface is an important elementary reaction in various industrial processes. For example, Cu-based catalysts in methanol synthesis reactions show low H_2 dissociation activity, and thus a high temperature is required. However, it is unfavorable for exothermic methanol generation from CO_2 and H_2. More active catalysts for H_2 dissociation are indispensable for efficient hydrogenation reactions. For this purpose, Pd/Cu single atom alloy catalyst (SAAC) is one of the attractive solution, in which a few percent of Cu surface atoms are replaced with Pd atoms. It has been reported that H_2 is dissociated on the Pd/Cu SAAC surface even at low temperatures, and that H atoms spillover onto the Cu host surface[1]. In this study, the processes of hydrogen dissociation and spillover on Pd/Cu SAAC surface was investigated using high-resolution X-ray photoelectron spectroscopy (XPS) and infrared reflection absorption spectroscopy (IRAS).

For XPS experiments, the Pd/Cu(977) SAAC was prepared in which the coverage of Pd(θ_{Pd}) was 0.07 ML. The peak of $Pd3d_{5/2}$ was observed at 335.3 eV on the clean SAAC surface. As a function of exposure to H_2 at 80 K, the $Pd3d_{5/2}$ peak was shifted to 335.6 eV and 336.5 eV in two steps(Fig. 1 (a)).

For IRAS experiments, the ML Pd/Cu(111) SAAC was prepared(θ_{Pd} = 0.01 ML). Time-resolved IRAS measurements were performed during H_2 exposure at 83 K. The H-Cu vibrational peak appeared at 1143 cm^{-1} about 300 s after starting H_2 exposure[2], and it developed with elapsed time (Fig. 1 (b)).

These results directly indicated the processes of hydrogen dissociaion, adsorption and spillover on the Pd/Cu SAAC surface. The Pd atoms act as a site for H_2 dissociation and initial H adsorption, and the spillover to Cu sites occurs only after Pd sites are saturated with H atoms.

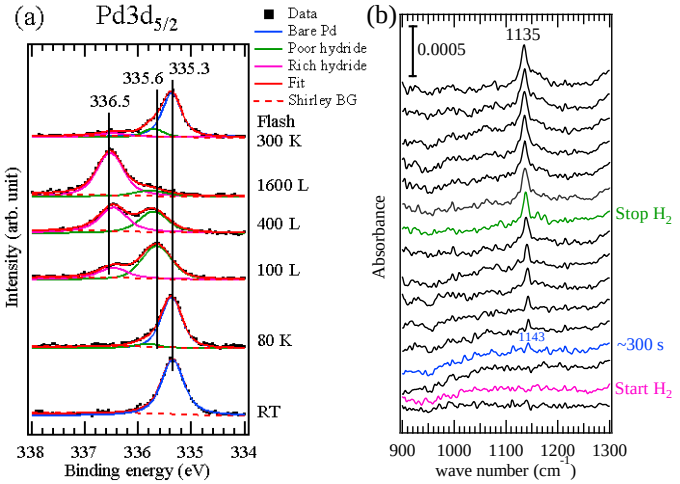


Fig. 1 Results of (a) XPS, *hv* = 680 eV. (b) IRAS, 4 cm^{-1} of resolution, 500 scans.

1) G. Kyriakou *et al*, *Science* **2012**, *335*, 1209. 2) K. Mudiyanselage *et al*, *J. Chem. Phys.* **2013**, *139*, 044712.

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探針増強ラマン分光法を用いた化学的アンジップグラフェンナノリボン生成機構解明

(京大高等研究院[1]・ルーバン大学[2]・九工大[3]・北大電子研[4]・東レリサーチセンター[5])○猪瀬 朋子[1]・豊内 秀一[2]・原 慎之介[3]・杉岡 祥治[4]・藤田 康彦[5]・Steven De Feyter[2]・田中 啓文[2]・雲林院 宏[2,4]

Mechanism of carbon nanotubes chemically unzipping into grapheen nanoribbons ([1]*KUIAS, Kyoto Univ.*, [2]*Leuven Univ.*, [3]*Kyutech*, [4]*RIES, Hokkaido Univ.*, [5]*TRC, Inc.*) ○Tomoko Inose,[1] Syuichi Toyouchi,[2] Shinnosuke Hara,[3] Shoji Sugioka,[4] Yasuhiko Fujita,[5] Steven De Feyter,[2] Hirofumi Tanaka,[3] Hiroshi Uji-i[2,3]

Graphene is a graphite layer with a thickness of one atom, which shows excellent carrier mobility, thermal conductivity, transparency, mechanical strength, and flexibility. Graphene shows conductive property without a bandgap. However, when the sheet-like graphene is changed to a fine ribbon-like graphene nanoribbon (GNR), a bandgap could be formed by a quantum confinement effect while keeping the physicochemical properties of graphene. GNR is thus a promising candidate for next-generation semiconductor materials. Such GNR can be produced by unzipping of carbon nanotube. Despite the promising method to fabricate GNR, the chemical structures at the edge of unzipped GNR is still unclear. The purpose of this work is to elucidate the electronic state and edge structure of chemically unzipped GNR using tip-enhanced Raman scattering(TERS) microscope capable of obtaining molecular information at nanoscale.

Keywords：Graphene nanoribbon; Tip-enhanced Raman spectroscopy (TERS)

グラフェンナノリボン(GNR)は、厚みが単原子層の黒鉛で、伝導率が銅の 1000 倍程を示す良伝導体である。GNR は、ダウンサイズの限界が近づく微細化の分野において、さらなる微細化の可能性を有する有望な次世代微細配線材料の候補である。GNR 作製方法のうち、カーボンナノチューブに欠陥を入れてアンジップすることで GNR を得る方法は、大量合成可能な方法として注目されている。これまでに我々のグループでは、ダブルウォールカーボンナノチューブ(DWNT)を用いて化学的アンジップを行うことで質の高い GNR が得られることを報告している。[1]一方、化学的アンジップ法では DWNT に欠陥を入れることで GNR を作成しているが、得られた GNR にどの程度の欠陥が入っているのかについて、その詳細は不明であった。本研究では、探針増強ラマン分光法(TERS)を用い[2]、GNR1 本の AFM 像と対応するラマンマッピング像を同時取得することで、GNR 1 本に含まれる欠陥の不均一性を評価した。特に、GNR 作製中間体として得られる y 字型の GNR の TERS 測定を行うことで、DWNT の外側に由来する GNR には多くの欠陥が含まれ、内側に由来する DWNT からは欠陥が非常に少なく質の高い GNR が得られることが明らかになった。

1) Method for controlling electrical properties of single-Layer graphene nanoribbons via adsorbed planar molecular nanoparticles. H. Tanaka *et al.*, *Sci. Rep.* **2015**, *5*, 12341.
2) Facilitating Tip-Enhanced Raman Scattering on Dielectric Substrates via Electrical Cutting of Silver Nanowire Probes, H. Uji-i *et al.*, *Nanoscale*, **2018**, *9*, 7117.

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A study of distance dependence on vibrational energy transfer in proteins taking advantage of the periodic character of α helices

([1]*Graduate School of Science, Osaka University*) ○Satoshi Yamashita,[1] Misao Mizuno,[1] Yasuhisa Mizutani[1]

Keywords : vibrational energy relaxation; resonance Raman spectroscopy; hemeproteins

We investigated vibrational energy transfer from heme in heme proteins by observing intensity changes of anti-Stokes Raman bands of a tryptophan (Trp) residue.[1-2] In our previous study, we observed energy transfer using Trp residues at different distances from heme in globular proteins.[1] However, it is impossible to observe distance dependence without altering orientation between heme and Trp because globular protein has complex folding structure. In this study, we systematically observed distance dependence on energy transfer in protein taking advantage of the periodic character of α helices.

Cytochrome b_{562} has four anti-parallel helices (Figure 1a). Taking advantage of the periodic character of α helices, distance between heme and Trp can be changed with equal intervals by introducing a Trp residue to one-turn separated positions of the same helix. The schematic structures of the cytochrome b_{562} mutants are shown in Figure 1b.

In time-resolved anti-Stokes spectra of five mutants, W18, W17, and W16 bands due to the introduced Trp residue were observed at 770, 877, and 1010 cm^{-1}, respectively. We compared the temporal changes in the anti-Stokes W18 band intensities among five Trp residues (Figure 1c). The intensity changes of W18 band decreased and the rise of W18 band intensity became slower as the heme-Trp distance increased. These results are qualitatively consistent with the prediction from the classical thermal diffusion. This indicates that, due to highly dense nature of protein structure, vibrational energy flows in protein moiety mainly through atomic contacts. However, the intensity changes of W18 band was not quantitatively reproduced by those calculated on the basis of a one-dimensional classical diffusion model. Moreover, the Trp residues in the different helices showed different intensity changes even though their distances from heme are almost the same (Figure 1c, light and dark blue curves). This result means that the protein moiety is not uniform as a thermal conductor and/or that contacts of the residues to solvent water affect the energy relaxation.

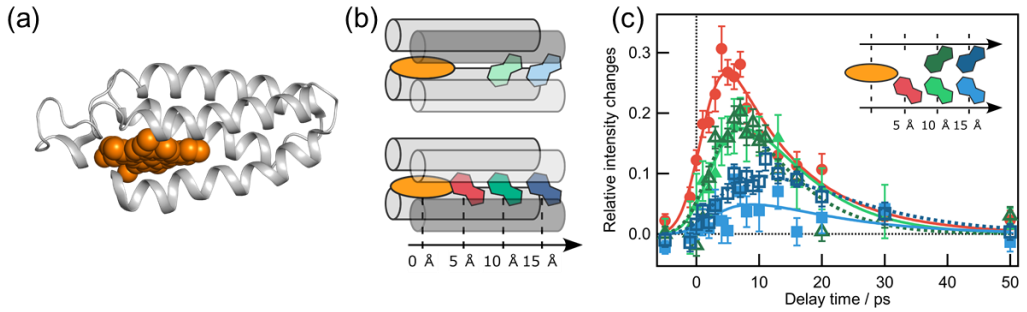


Figure 1 (a) Crystal structure of the cytochrome b_{562}. Orange spheres represent heme. (b) Position of five introduced Trp residues into cytochrome b_{562}.mutants depicted as a schematic structure. Trp is represented by a polygon. (c) Temporal changes of relative intensity in the W18 bands.

1) N. Fujii, et al, *J. Phys. Chem. B* **2011**, *115*, 13057. 2) S. Yamashita, et al, *J. Phys. Chem. B* **2018**, *122*, 5877.

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

[A07-3am] 04. Physical Chemistry -Properties-

Chair:Takane Imaoka, Kohei Imura

Sun. Mar 21, 2021 9:00 AM - 11:40 AM Room 7 (Online Meeting)

[A07-3am-02] Structure dependence of the Surface-enhanced Raman spectra observed on a single-molecule junction of the disubstituted benzene derivative

○Satoshi Kaneko[1,2], Koji Yasuraoka[1], Shuji Kobayashi[1], Tomoaki Nishino[1] （1. Tokyo Institute of Technology, 2. JST PRESTO）

9:20 AM - 9:40 AM

[A07-3am-03] In situ detection of Pt subnano particles by dual-isolated nanostar-enhanced Raman Spectroscopy

○Yuansen Tang[1], Akiyoshi Kuzume[2,3], Kimihisa Yamamoto[1,2] （1. Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 2. JST-ERATO in Tokyo Institute of Technology, 3. Clean Energy Research Center, Yamanashi University）

9:40 AM - 10:00 AM

[A07-3am-04] STM study of on-surface adsorption process of 3d transition metal atom into organic molecule

○Toyo Kazu Yamada[1] （1. Chiba Univ.）

10:00 AM - 10:20 AM

[A07-3am-05] Structure and Electrical Properties of a New Molecular Memory Element with an Alternating Circular Array of Dipolar Rotors and Rotation Suppressors

○Takuya Miyazaki[1,3], Yoshiaki Shoji[1], Shintaro Fujii[2], Tomoaki Nishino[2], Chi Zhang[3], Emiko Kazuma[3], Yousoo Kim[3], Takanori Fukushima[1] （1. Lab. Chem. &Life Sci., Tokyo Tech., 2. School of Science, Tokyo Tech., 3. RIKEN）

10:20 AM - 10:40 AM

[A07-3am-06] Structural and magnetic properties of iron-based ultrasmall particles using arc plasma deposition

○Yumi Ida[1,2], Makoto Tanabe[1,2], Kimihisa Yamamoto[1,2] （1. Tokyo Institute of Technology, 2. JST-ERATO）

10:40 AM - 11:00 AM

[A07-3am-07] Multimodal Detection of Circulating Tumor Cells Using Multifunctional Silica Particles

○Jeladhara Sobhanan[1], Yuta Takano[1,2], Vasudevanpillai Biju[1,2] （1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University）

11:00 AM - 11:20 AM

[A07-3am-08] Interaction of gold nanoparticle assembly with dye molecules at liquid-liquid interface

○Atsuko Jimbo[1], Kohei Imura[1] （1. Waseda Univ.）

11:20 AM - 11:40 AM

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二置換ベンゼン誘導体を用いた単分子接合における表面増強ラマン散乱スペクトルの架橋構造依存性

（東工大理[1]・JST PRESTO[2]）○金子哲[1,2]・安楽岡浩司[1]・小林柊司[1]・西野智昭[1]
Structure Dependence of the Surface-Enhanced Raman Spectra Observed on a Single-Molecule Junction of the Disubstituted Benzene Derivative ([1]*School of Science, Tokyo Institute of Technology,* [2]*JST PRESTO*) ○ Satoshi Kaneko,[1,2] Koji Yasuraoka,[1] Shuji Kobayashi,[1] Tomoaki Nishino[1]

Structural identification of the single-molecule junctions (SMJs) is an important topic because of their potential for the ability to induce unique chemical reactions. However, it has been difficult to identify the junction structure due to the difficulty in the identification of the trapped single molecule. In this study, we observe the surface-enhanced Raman scattering (SERS) spectral changes of 1,4-benzenedithiol (BDT) SMJs depending on the adsorption structure by combining them with current-voltage measurements. Analyzing SERS and *I-V* response we detected the adsorption state of BDT-SMJ.[1] Furthermore, we detected spectral change induced by bias voltage and external force. [2,3] The observed change in the vibration energy is considered to originate from the modulation of the electronic state induced by the structural change.
Keywords : surface enhanced Raman scattering, single-molecule junction, 1,4-benzenedithiol, bias modulation.

単分子接合は特異な電子状態を持つため新規反応の探索場として注目を集めており、その架橋構造の解明は重要な課題の一つである。走査型トンネル顕微鏡(STM)や表面増強ラマン散乱(SERS)スペクトル計測により金属表面の吸着構造は盛んに研究が行われているが、単分子接合形成時における接合構造の解明は困難であった。そこで本研究では電流ー電圧計測と表面増強ラマン散乱(SERS)を組み合わせることにより、1,4-ベンゼンジチオール(BDT)の単分子接合の吸着構造変化を SERS スペクトル変化により検出することを目指した。SERS 及び電流ー電圧計測の解析により、単分子接合形成時における吸着構造を同定した。[1] また、接合構造を保持した状態で電極間距離及び印加電圧を変調させた所、接合構造の変化に由来した振動エネルギー変化を観測することができた(Figure 1)。[2,3] 振動エネルギー変化は摂動による接合構造変化により架橋した分子の電子状態が変化したためであると考えられる。

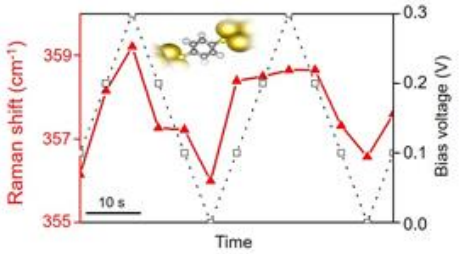


Figure 1 BDT 分子接合における振動エネルギー印加電圧依存性

1) S. Kaneko, *et al., Chem. Sci.*, 10, 6261 (2019). 2) K. Yasuraoka, *et al*., *J. Phys. Chem. C*, 123, 15267 (2019).
3) S. Kobayashi, *et al*., *J. Phys. Chem. Lett.*, 11, 6712, (2020).

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In situ detection of Pt subnano particles by dual-isolated nanostar-enhanced Raman Spectroscopy

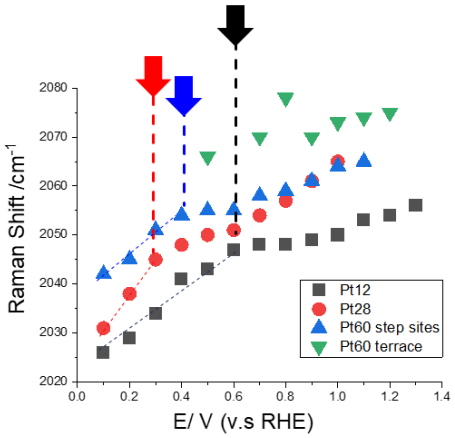
([1] Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, [2] JST-ERATO in Tokyo Institute of Technology, [3] Clean Energy Research Center, Yamanashi University) ○Yuansen Tang,[1] Akiyoshi Kuzume,[2,3] Kimihisa Yamamoto[1,2]

Keywords: Surface-enhanced Raman spectroscopy; Au nanoparticles; *in situ* analysis; subnano particles; electrochemistry

Subnano particles[1] with a size about 1 nm in diameter show unique physical and chemical properties as well as higher catalytic performance than that of conventional nano-materials, based on their high surface-to-volume ratio, specific electronic states and amorphous atomic structures. However, it is not easy to characterize subnano substances due to its small size, which is far beyond the detection limit of most conventional analytic methods. High sensitivity shell-isolated nano-star enhanced Raman spectroscopy (HS-SHINERS) is one of the advanced surface enhanced Raman spectroscopic techniques, where anisotropic Au nanoparticles, employed as optical amplifiers, were coated by a thin silica layer to block direct contact of samples with Au surfaces revealing intrinsic vibrational properties of samples[2].

Here, further optimizations were carried out to use Au surface electrode to improve the enhancement properties of shell-isolated nanostar-enhanced Raman spectroscopy in electrochemical setup. In this context, Au surface was coated by thin graphene oxide film by the Langmuir-Blodgett method.

In this presentation, a carbon monoxide was utilized as a probe to characterize Pt-subnano particles due to its strong interaction with Pt. Stretching modes of CO adsorbed on Pt surface were observed to shift to high wavenumber during anodic potential scan due to the Stark effect. By comparing Pt subnano particles with different size, Raman spectra of CO adsorbed on subnano particles showed the different behaviours during the CO electro oxidation.



1) Yamamoto K, et al. *Chemical Reviews*, 2019, 120(2): 1397-1437.

2) Li J F, Huang Y F, Ding Y, et al. *Nature*, **2010**, 464(7287): 392. *40*, 3835.

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真空表面上の有機分子への３ｄ遷移金属原子吸着プロセスの STM 研究

（千葉大院工 [1]）○山田 豊和 [1]
STM study of on-surface adsorption process of 3d transition metal atom into organic molecule
([1]*Graduate School of Engineering, Chiba University*) ○Toyo Kazu Yamada[1]

Well-known organic molecular magnets such as iron phthlocyanines (FePc) or cobalt porphyrins (CoTPP) have been synthesized via chemical reaction of [2HPc + Fe -> FePc + H_2 (gas)]. On the other hand, our recent scanning tunneling microscopy (STM) results obtained in ultrahigh vacuum (UHV) showed generation of precursol adcomplex via [2HPc + Fe -> Fe-2HPc] without dehydrogenation [1], which provided new molecular electronic structures because of the presence of hydrogen atoms. Variation of 2HPc and 2HTPP electronic structures due to Fe and Co adsorption will be shown. Further, we will show Co adsorption process on a well-ordered crown ether molecular array grown on Cu(111) [2,3].

Keywords : Scanning Tunneling microscopy; Phthalocyanine; Crownether; Transition metal

鉄フタロシアニン(FePc)やコバルトポルフィリン(CoTPP)に代表される有機分子磁石は、[2HPc + Fe -> FePc + H_2 (gas)]反応で合成できる。しかし、最近の真空環境での走査トンネル顕微鏡(STM)研究から、水素脱離を伴わない precursol adcomplex: [2HPc + Fe -> Fe-2HPc]を作製できることが分かってきた [1]。 特徴的な点は、水素分子が残留することで、新たな分子電子状態を発現できる点にある。2HPc および 2HTPP 分子への磁性金属 Fe, Co 吸着による電子状態変化を報告する。

また、環状クラウンエーテル(Br-CR)分子への 3d 遷移金属吸着プロセスの STM および角度分解紫外光電子分光結果についても報告する [2,3]。Br-CR 分子は１個の分子内に「環」を内包する。溶液中では環に金属イオンをトラップできると報告されているが、真空環境での基板表面上での報告はない。我々は Cu(111)基板表面上での Br-CR 分子規則配列構造の解明と、コバルト吸着による不規則化と生成物の詳細を報告する。

1) Direct Imaging of Precursor Adcomplex States during Cryogenic-Temperature On-Surface Metalation: Scanning Tunneling Microscopy Study on Porphyrin Array with Fe Adsorption at 78.5 K. E. Inami, M. Yamaguchi, R. Nemoto, H. Yorimitsu, P. Krueger, T. K. Yamada, *J. Phys. Chem. C* **2020**, *124*, 3621.
2) Well-Ordered Monolayer Growth of Crown-Ether Ring Molecules on Cu(111) in Ultra-High Vacuum: An STM, UPS, and DFT Study. R. Nemoto, P. Krueger, A. N. P. Hartini, T. Hosokai, M. Horie, S. Kera, T. K. Yamada, *J. Phys. Chem. C* **2019**, *123*, 18939.
3) Room-Temperature Deposition of Cobalt Monolayer on (7×4) Crown-Ether Ring Molecular Array: Ultra-High Vacuum STM and UPS Study. R. Nemoto, P. Krueger, T. Hosokai, M. Horie, S. Kera, T. K. Yamada, *表面と真空* **2020**, *63*, 465.

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双極性回転ユニットと回転抑制ユニットの環状配列を有する新しい分子メモリの構造および電気特性評価

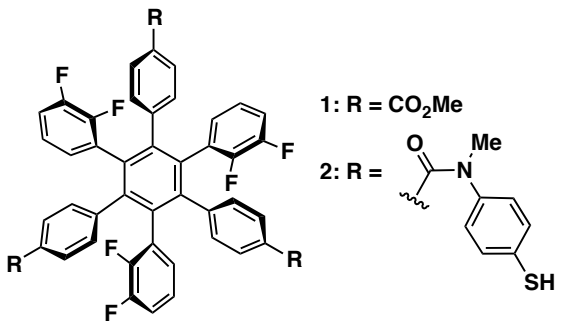
（東工大化生研[1]・東工大理学院[2]・理研[3]）○宮崎 拓也[1,3]・庄子 良晃[1]・藤井 慎太郎[2]・西野 智昭[2]・張 弛[3]・數間 恵弥子[3]・金 侑洙[3]・福島 孝典[1]

Structure and Electrical Properties of a New Molecular Memory Element with an Alternating Circular Array of Dipolar Rotors and Rotation Suppressors ([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology;* [2]*Graduate School of Science, Tokyo Institute of Technology;* [3]*Riken*) ○ Takuya Miyazaki[1,3], Yoshiaki Shoji[1], Shintaro Fujii[2], Tomoaki Nishino[2], Chi Zhang[3], Emiko Kazuma[3], Yousoo Kim[3], Takanori Fukushima[1]

We have reported that a new hexaarylbenzene derivative (**1**) with an alternating circular array of dipolar rotating units and rotation suppressors serves as a new element for an electric-field-responsive molecular memory.[1] Here we report detailed analysis of the structure and electrical properties of **1**. We performed the STM break junction measurement of **2**, a new derivative of **1** with three thiol groups, and found that its rotational isomers show significantly different *I–V* characteristics. We also successfully visualized rotational isomers of **1** at the molecular level by the ultra-high-vacuum STM measurement of a monolayer film of **1**.

Keywords：Hexaarylbenzene; Molecular Memory; Electric Field-Response; Conformational Isomerism

我々は、電場に応答して分子レベルで構造および電気双極子の方向を制御可能な分子システムの開発を目指した研究を推進している。この目的を具現化する分子として、回転可能な双極性ジフルオロフェニル基を1,3,5-位に導入した新規なヘキサアリールベンゼン誘導体 **1** を設計し、その電場応答型分子メモリ機能を報告している[1]。化合物 **1** には、ジフルオロフェニル基の回転により生じる、単離可能な二つの異性体が存在する。これまでに、化合物 **1** の配向多層膜に対して電場を印加すると、電場のバイアスに依存して表面電位が可逆に変化し保持されることを明らかにしている[1]。今回、**1** にチオール基を導入した新規誘導体（**2**）を合成し、STM-ブレイクジャンクション測定を行ったところ、回転異性体間で大きく異なる電流-電圧特性を示すことを見出した。また **1** の単分子膜を作製し、超高真空STMを用いた分子解像度でのイメージングにより回転異性体の可視化に成功したので報告する。



[1] T. Miyazaki, Y. Shoji, F. Ishiwari, T. Kajitani, T. Fukushima, *Chem. Sci.* **2020**, *11*, 8388.

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プラズマ蒸着による鉄を主元素とする極小粒子の構造評価と磁気特性

（東工大 IIR[1]・JST-ERATO[2]）○井田 由美[1,2]・田邊 真[1,2]・山元 公寿[1,2]
Structural and magnetic properties of iron-based ultrasmall particles using arc plasma deposition ([1] *Institute of Innovative Research, Tokyo Tech*, [2] *JST-ERATO*) ○Yumi Ida,[1,2] Makoto Tanabe,[1,2] Kimihisa Yamamoto[1,2]

The magnetic properties of ultrasmall particles remain unexplored due to the difficult structural analysis. A challenging issue is to develop a preparation method for size-controlled iron oxide particles (IOPs) and to determine the dependence of magnetic properties on the morphology and crystallinity. However, synthetic approaches to obtain IOPs, regarded as one of the new fields of magnetic nanoparticles, have been significantly limited. We developed a synthetic method to prepare IOPs using arc plasma deposition (APD), which clarified the finely-controlled formation of IOPs on graphene nanosheets. Structural characterization of the IOPs revealed the formation of crystalline γ-Fe_2O_3 ultrasmall particles with oxygen deficiency. The pulsed APD method for IOPs is the first simple and convenient technique to not only prevent significant aggregation and contamination by organic compounds and avoid the need for thermal pretreatment, but also provide uniform crystalline nano-order particles. We also present the subjects of magnetic properties on multimetallic particles with Fe, Ni, and Al.
Keywords :Iron oxide; Magnetic Properties; Graphene; Cluster; Arc Plasma Deposition (APD)

2 nm 以下の微小粒子は、従来のナノ粒子と大きく異なり、特異な幾何構造や電子状態が支配した化学特性及び磁気特性を示すため、新物質群として注目を集めている。しかし、微小粒子の磁気特性に関する研究は、その粒子の構造解析が困難であることから未開拓の領域である。サイズ制御された酸化鉄粒子の合成方法を開発し、粒子の形態に対する磁気特性の依存性について調査した。合成方法には、アークプラズマ蒸着（APD）法を用いた。微小酸化鉄粒子のサイズ制御に適した担体を探索するために、様々なカーボン担体を用いて検討し、サイズ制御に有効な担体はグラフェン類縁体であることが分かった。グラフェンナノプレートレットに蒸着した微小酸化鉄粒子は、各種分光法（XPS、XAFS など）から γ-Fe_2O_3 に類似した形態をもつことを明らかにした。さらに、磁気測定において同程度のサイズの結晶性の高い酸化鉄粒子の磁気パラメータと比較的よい一致を示した。微小領域における粒子はアモルファス挙動を示すことが知られているが、APD 法を用いて作製した粒子は結晶性の高い粒子を簡便に合成できることを実証した[1)]。APD 法は熱処理を施さずに、均一な結晶性を有する粒子を提供するための便利な手法である。

これらの知見から、微小粒子の作製には平面の基材を用いることが有用であると推測される。取り扱いに容易なカプトンフィルムを用いて、Fe、Ni、Al を用いた多元系の微小粒子の組成比の変化に対する磁気特性について報告する。

1) Y. Ida, A. Okazawa, M. Tanabe, K. Yamamoto, et al. *RSC Advances*, **2020**, *10*, 41523.

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Multimodal Detection of Circulating Tumor Cells Using Multifunctional Silica Particles

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Research Institute for Electronic Science, Hokkaido University*) ○ Jeladhara Sobhanan,[1] Yuta Takano,[1,2] Vasudevanpillai Biju[1,2]

Keywords: Circulating Tumor Cells (CTCs), Multifunctional Silica, Fluorescence Imaging, Microscopic Detection

Circulating tumor cells (CTCs) have a vital role in the field of liquid biopsy for the early stage detection, isolation, and molecular or genomic identification of various cancers. CTCs serve as potential biomarkers for prognosis and diagnosis by providing useful therapeutic information to determine the cancer recurrence and chemotherapeutic efficiency.[1] The extreme rarity of CTC demands accurate and convenient strategies for its isolation and detection. Recently, different technologies have been developed for CTC enrichment and isolation, which are often supplemented by various optical detection techniques. Yet, the low recovery rate, less purity, and the poor sample holding capacity (throughput) add limitations to these technologies.[2]

In this study, we introduce a multi-modal CTC detection method based on fluorescence microscopic imaging and spectrally and temporally resolved fluorescence detection technique for the detection (Figure 1). We successfully capture CTCs from among the blood cells by carefully pre-labeling the cells with the desired antibodies (Figure 1A), and using the large-size, and antibody-functionalized silica particles. Besides, as an alternative to EpCAM-based CTC capturing, we focus on the transmembrane glycoprotein, CD44, a stem cell marker, present abundantly in metastasized cells. Therefore, we present a highly sensitive and error-free CTC detection method to enable an advanced cancer screening and post-surgical/ therapeutic clinical follow up.

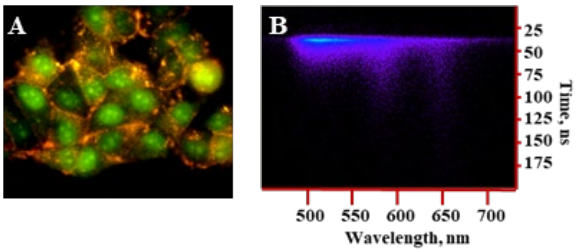


Figure 1 (A) A fluorescence image of MCF7 cells triply stained with SYTO-13, QD655 labeled anti-EpCAM-Ab, and QD585 labeled anti-CD44-Ab (λex = 465 nm, λem >500 nm). (B) The time and energy dispersed photocount histogram of the labeled cells (λex = 400 nm, λem >500 nm).

1) D. E. Campton, A. B. Ramirez, J. J. Nordberg, N. Drovetto, A. C. Clein, P. Varshavskaya et al., *BMC Cancer* **2015**, *15*, 360. 2) A. Albuquerque, I. Kubisch, G. Breier, G. Stamminger, N. Fersis, A. Eichler, S. Kaul, U. Stolzel, *Oncology* **2012**, *82*, 3.

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Interaction of gold nanoparticle assembly with dye molecules at liquid-liquid interface

(*Graduate School of Advanced Science and Engineering, Waseda University*)
○Atsuko Jimbo, Kohei Imura
Keywords: Plasmonics; Gold nanoparticles

Plasmon resonance excited in metal nanoparticle confines light spatially and generates enhanced optical fields. Gold nanoparticle (AuNP) assemblies exhibit giant enhanced fields at the gap between the AuNPs and have been utilized for various applications, such as surface enhanced Raman scattering (SERS) and photochemical reactions. In most of the studies, the assemblies have been prepared on a solid substrate. Optical properties of the assemblies are permanent and less controllable once the assemblies are fabricated on the substrate. The restriction is overcome by preparing the assemblies at liquid-liquid interface. In this study, we prepared AuNP assembly at water-hexane interface and used them to reveal chemical interaction of the assembly with dye molecules dissolved in solvents.

To control optical properties and chemical environment of the assemblies, surface of the AuNP was chemically modified with linker molecules; cysteine (Cys) or glutathione (GSH). We found from linear and non-linear spectroscopy that optical properties of the assemblies are dependent on the linker molecule. Observed results indicate that gap distance between the particles varies due to physical size of the linker molecule and/or chemical interaction of the molecules with the particle. To reveal the role of the linker molecule in detail, rhodamine 6G (R6G) is dissolved in the water and SERS of the dye is excited with 633 nm. Figure 1 shows SERS spectra of R6G observed on the assembly prepared with the Cys and the GSH. SERS intensity for the Cys modified assembly is stronger than that for the GSH. The result indicates that gap distance for the Cys is smaller than for the GSH, since the SERS enhancement become large with decrease of the gap distance. We also performed two-photon induced isomerization of diarylethene in the vicinity of the assembly and found that magnitude of the enhancement was dependent not only on the enhanced field intensity but on the affinity between the linker molecules and the dyes. We revealed from these observations that the AuNP assembly prepared at the interface enables to reveal chemical interaction between the surface modified AuNP and dye molecules with ultrahigh sensitivity.

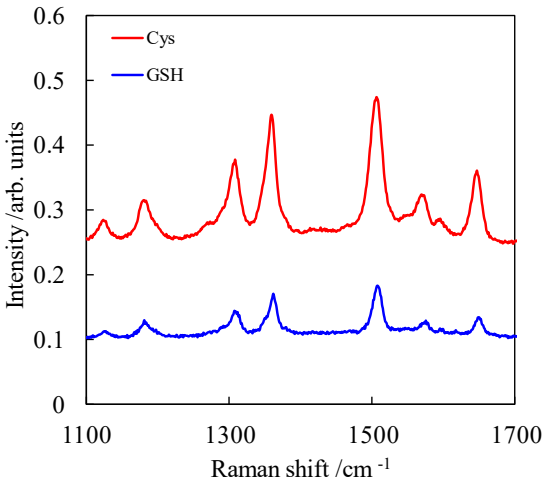


Figure 1. (a) SERS spectra of R6G with linker molecules. Red: Cys, blue: GSH.

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

[A03-3am] 04. Physical Chemistry -Properties-

Chair:Yasutaka Kitagawa, Ryohei Kishi

Sun. Mar 21, 2021 9:00 AM - 11:20 AM Room 3 (Online Meeting)

[A03-3am-01] Magnetism of Pseudobinary $SmFe_{12}$ Compound

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

9:00 AM - 9:20 AM

[A03-3am-02] Theoretical study on the electronic state of honeycomb framework composed of phenelenyl units

○Kyohei Yoneda[1] (1. National Institute of Technology, Nara College)

9:20 AM - 9:40 AM

[A03-3am-03] Synthesis and Excited-state Dynamics of Pentracene-Modified Au_{25} nanoclusters

○Hayato Sakai[1], Yasunaga Hosokawa[2], Nikolai Tkachenko[3], Yuichi Negishi[2], Taku Hasobe[1] (1. Keio University, 2. Tokyo University of Science, 3. Tampere University)

9:40 AM - 10:00 AM

[A03-3am-04] Ligand Effect of Precisely Synthesized Gold Clusters in the Ultrafast Carrier Dynamics

○Daichi Eguchi[1], Naoto Tamai[1] (1. Kwansi Gakuin University)

10:00 AM - 10:20 AM

[A03-3am-05] Coherent-interaction-enhanced hot-electron generation under modal strong coupling conditions

○Yen-En Liu[1], Xu Shi[1], Tomoya Oshikiri[1], Shuai Zu[1], Quan Sun[1], Keiji Sasaki[1], Hiroaki Misawa[1,2] (1. Hokkaido University, 2. National Chiao Tung University, Taiwan)

10:20 AM - 10:40 AM

[A03-3am-06] Electrochemical tuning of coupling strength in strong coupling system between lattice plasmon and molecular excitons

○Takahiro Hayashi[1], Shunpei Oikawa[1], Hiro Minamimoto[2], Kei Murakoshi[2] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Department of Chemistry, Faculty of Science, Hokkaido University)

10:40 AM - 11:00 AM

[A03-3am-07] Local Structures and Molecular Motions in Proton-Conducting PVPA-*x*Im Composites Investigated by Molecular Dynamics Simulations

○Yuta Hori[1], Toshiya Suetake[2], Tomonori Ida[2], Motohiro Mizuno[2], Yasuteru Shigeta[1] (1. University of Tsukuba, 2. Kanazawa University)

11:00 AM - 11:20 AM

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Magnetism of Pseudobinary $SmFe_{12}$ Compound

([1]*Institute for Chemical Research, Kyoto University*) ○T. Thuy Trinh,[1] Ryota Sato,[1] Toshiharu Teranishi[1]

Keywords: Samarium-Iron Intermetallics; $ThMn_{12}$; Permanent Magnetic Materials

The physics of magnetism is based on the distinction between intrinsic and extrinsic properties related to atomic origin and the microstructure of materials, respectively. Our elementally strategic research has explored new economically viable permanent magnetic materials, namely $(Sm_{1-x}Zr_x)(Fe_{1-y}Co_y)_{12-z}Ti_zH$ ($ThMn_{12}$, $I4/mmm$, Fig. 1): partial substitution of Fe with Co and Ti has stabilized the highly tetragonal lattice in bulk and resulted in large saturation magnetization M_s, large anisotropy field H_a, and high Curie temperature T_c; hydrogen interstitial doping has strongly stabilized the easy *c*-axis anisotropy and significantly enhanced the H_a and T_c of the materials. The resulting intrinsic magnetic properties (e.g., $\mu_0 M_s$ = 1.36 T, $\mu_0 H_a$ = 9.2 T, and T_c = 750 K) were comparable or superior to those of the current high-end $Nd_2Fe_{14}B$ permanent magnetic materials, depending on the substituent concentration.

The combination of controllable chemical synthesis and reduction-diffusion process in a bottom-up approach has opened horizons for optimization of the microstructure of the materials, resulting in the enhancement of their magnetic performance (e.g., coercivity $\mu_0 H_c$ = 0.45 T, energy product $(BH)_{max}$ = 166 kJ/m^3 at RT). The details of structural analysis and magnetic properties will be discussed on the bases of characterization using a wide range of techniques and models and first-principle calculations.

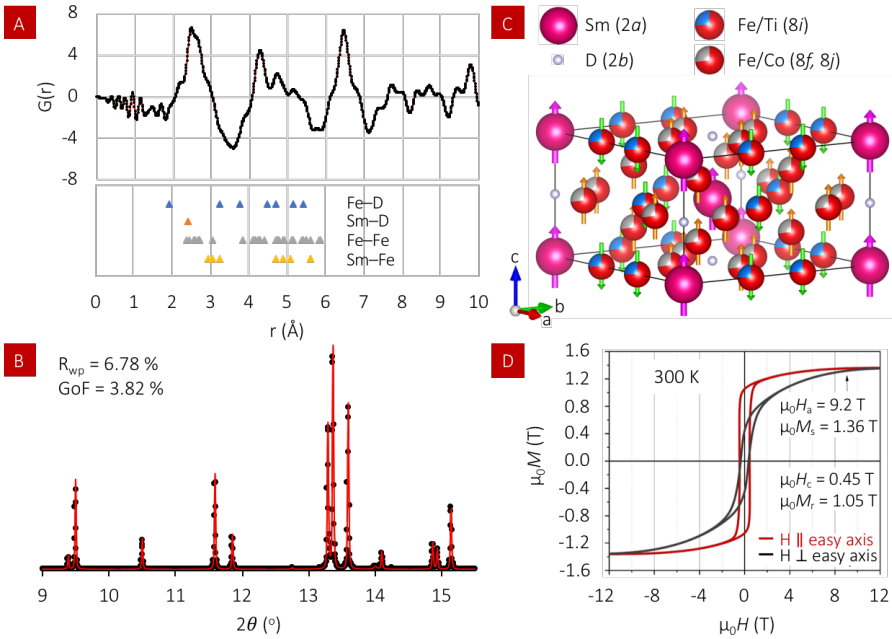


Fig. 1 Structural analysis and magnetic properties of chemically synthesized $Sm(Fe_{0.8}Co_{0.2})_{11}TiH$ mesoscopic particles: (A) Neutron diffraction-pair distribution function G(r), (B) Rietveld refinement synchrotron XRD pattern, (C) Crystal structure and direction of magnetic moments, and (D) M–H curves.

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日本化学会 第101春季年会 (2021)

フェナレニルユニットからなるハニカム骨格の電子構造に関する理論研究

（奈良高専物質）○米田 京平
Theoretical study on the electronic states of giant molecules composed of phenelenyl units
(*Department of Chemical Engineering, National Institute of Technology, Nara College*)
○Kyohei Yoneda

Phenalenyl molecule, which is a D_{3h} symmetric π conjugated molecule, is a monoradical system. The SOMO is delocalized over the whole molecule. Therefore, in the giant molecule composed of a number of the phenalenyl molecules, each phenalenyl molecule is expected to show similar behavior to the one sp2 hybrid carbon atom. In this research, using the density functional theory method, the electronic state of planar honeycomb framework composed of the phenalenyl units.

Keywords : Phenalenyl Molecule; Quantum Chemical Calculation; Open-Shell

カーボンナノチューブやグラフェンをはじめとするナノカーボン材料は、軽量性から構造部材への応用、高い電気伝導性や熱伝導性により導電材料や放熱部材への応用、そして高い電子移動度から高速トランジスタへの応用などが期待されているが、このような特異な電子特性は sp^2 炭素原子特有のπ共役に起因する。近年、共役電子系を持つ新規カーボン材料の構成要素としてフェナレニルラジカル（PLY）[Fig. 1(a)]が注目されている。PLY は D_{3h} 対称性を持つモノラジカル分子であり、安定なラジカル軌道と優れた電子の授受能ゆえに、様々な分野での応用が期待されている[1]。

PLY の SOMO は分子全体に非局在化しており、複数の PLY が連結した巨大分子中では、1 つ 1 つのフェナレニル分子単体が 1 つの sp2 炭素原子と近い振る舞いを示す可能性が予測される。そこで本研究では、PLY をアセチレンにより Fig. 1(b) に示す、PLY を構成単位としたハニカム骨格を持つ平面構造体を対象とし、この電子状態を密度汎関数法に基づいて解析する。計算には LDA 汎関数（PW92）を用い、平面波のカットオフエネルギーは 18 Hartree とした。Fig. 2 の結果より PLY ハニカム骨格では、その Fermi 準位近傍においてグラフェンシートと同様の線形バンド構造が現れることが確認された。

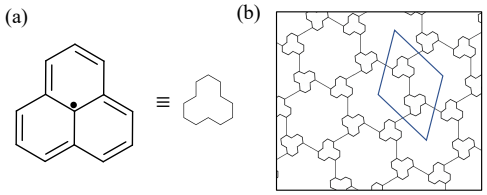


Fig. 1 PLY(a)およびそのハニカム骨格構造(b)

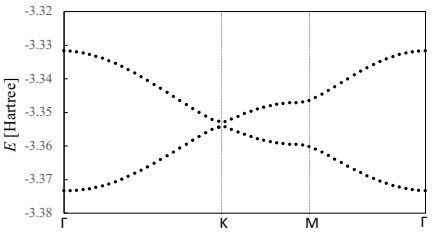


Fig. 2 PLY ハニカム骨格のバンド構造

[1] T. Kubo et al., *Angew. Chem. Int. Ed.* **44**, 6564 (2005); Y. Morita et al., *Nat. Mater.* **7**, 48 (2008); V. Morita et al., *Nat. Chem.* **3** 197 (2011); K. Uchida, T. Kubo, *J. Synth. Org. Chem., Jpn.* **74**, 1069 (2016).

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ペンタセン-Au_{25}ナノクラスター連結体の合成と励起ダイナミクス評価

（慶大理工 [1]・東理大理 [2]・タンペレ大学 [3]）○酒井 隼人 [1]・細川 泰長 [2]・Tkachenko Nikolai[3]・根岸 雄一 [2]・羽曾部 卓 [1]

Synthesis and Excited-state Dynamics of Pentracene-Modified Au_{25} nanoclusters ([1]*Faculty of Science and Technology, Keio University*, [2]*Faculty of Science, Tokyo University of Science,* [3]*Chemistry and Advanced Materials Group, Faculty of Engineering and Natural Sciences Tampere University*) ○Hayato Sakai,[1] Yasunaga Hosokawa,[2] Nikolai Tkachenko[3], Yuichi Negishi,[2] Taku Hasobe[1]

Generally, it is quite difficult to observe excited states such as luminescence in gold nanoclusters composed of more than 100 atoms. Additionally, in the case of organic dyes-modified gold nanoclusters, the fluorescence of dye molecules is significantly quenched by surface energy transfer. On the other hand, regarding small nanoclusters such as Au_{25} nanocluster, the discretization of the energy levels leads to the spectroscopic observation of excited-state dynamics such as near-infrared luminescence. In this study, based on the above concept, pentracene-modified Au_{25} nanoclusters were newly synthesized and triplet-related energy transfer from Au_{25} nanocluster to pentacene was successfully observed.

Keywords : Pentacene; Gold Nanocluster; Excited-State Dynamics; Energy Transfer; Triplet Excited State

有機配位子によって修飾された金クラスターはバルクな状態とは異なり、有機配位子や金属コアのサイズに依存した光物性を示す。一般に、金原子数 100 以上の金ナノクラスターでは発光などの励起状態から基底状態への遷移過程を直接的に観測することは困難である。また、配位子として有機色素を用いて化学修飾すると、有機色素の蛍光は金クラスターへのエネルギー移動等によって大幅に消光される。一方、金 25 原子体(Au_{25}) のような微小な金ナノクラスターは量子サイズ効果による電子構造の離散化により、近赤外発光などの励起ダイナミクスが発現される。しかしながら、Au_{25} の電子構造と関連する励起ダイナミクスについては未だ議論が尽きない。一方、5 つのベンゼン環を直線状で縮環したペンタセンは最低励起一重項状態のエネルギー (S_1) が 2.1 eV であるのに対し、励起三重項状態のエネルギー (T_1) は 0.8 eV であり、他の有機分子と比較すると極めて小さい。したがって、ペンタセンと Au_{25} を組み合わせることで Au_{25} の三重項状態が関与する励起ダイナミクスの観測が期待できる。そこで本研究では、Au_{25} に TIPS ペンタセン (Pc) 一分子のみを異なるアルキル鎖長により連結した TIPS ペンタセン連結 Au_{25} (Pc-C$_n$S-Au$_{25}$: n = 5, 11) を合成した (Figure 1)。Pc-C$_n$S-Au$_{25}$ の Pc を光励起したフェムト秒過渡吸収測定では Pc の S-S 吸収の減衰とともに Au_{25} の励起状態に由来するスペクトルが観測され、Pc から Au_{25} へ一重項状態の関与するエネルギー移動が確認できた。一方、ピコ秒過渡吸収測定では逆に Au_{25} から Pc へエネルギー移動が進行し、最終的に Pc の三重項状態 ($^3Pc^*$) が観測できたため Au_{25} における項間交差の進行が示唆された。

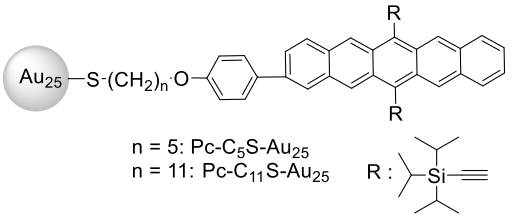


Figure 1. Pc 連結 Au_{25} ナノクラスターの構造

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Ligands Effect of Precisely Synthesized Gold Clusters in the Ultrafast Carrier Dynamics

(*Graduate School of Science and Technology, Kwansei Gakuin University*)
○Daichi Eguchi, Naoto Tamai
Keywords: Gold Cluster; Ligand Effect; Ultrafast Spectroscopy

Gold clusters (AuCs) are promising photo-energy conversion materials due to their composition and geometric structure dependence of electronic structures. Understanding the carrier dynamics of AuCs is a key for these applications, and the electronic and geometric structures affect the carrier dynamics. Although the main contribution of electronic structures in AuCs is derived from the core, it has been reported that electronic structures are perturbed by organic ligands owing to their large surface-to-volume ratio.[1] However, a comprehensive understanding of the effect of ligands on the electronic and geometric structures, and the carrier dynamics of AuCs is still unclear. In this study, we systematically studied the ligand effect of triphenylphosphine derivatives on the carrier dynamics of AuCs by using femtosecond transient absorption (TA) spectroscopy.

To investigate the ligand effect on the carrier dynamics of AuCs, we synthesized the AuCs coordinated by triphenylphosphine derivatives with different substitution groups at para-position (TPP-R/Au_{11}: R= CF_3, F, H, CH_3, OMe). Single-crystal X-ray diffraction (SCXRD) measurements showed that the structures of TPP-R/Au_{11} consisted of seven phosphines and three bromides ligate all ten gold atoms on the surface of the AuCs (Figure 1a). Femtosecond TA measurements of AuCs were performed to understand the carrier dynamics. Upon excitation at 510 nm, excited-state absorption (ESA) across the visible region was observed, and the kinetic trace exhibited the decay process of TPP-CF_3/Au_{11} was slower than that of TPP-OMe/Au11, indicating that the degree of overlap between the HOMO and LUMO is different dependent on the substitution groups of TPP (Figure 1b).

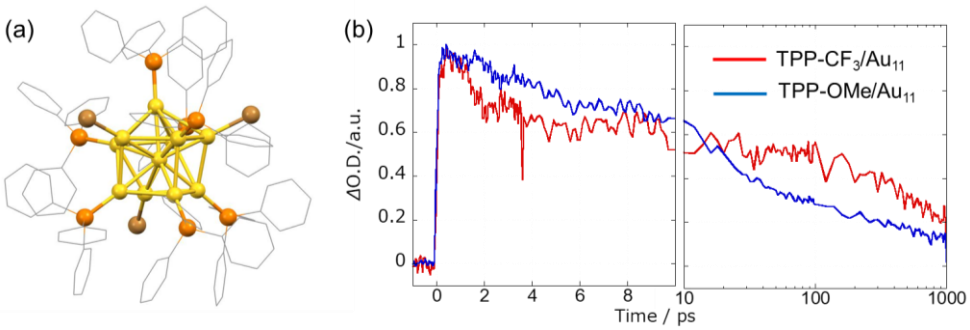


Figure 1. (a) Crystal structure of TPP-H/Au_{11}. Hydrogen atoms and solvent molecules were omitted for clarify. Decay dynamics of ESA in TPP-CF_3/Au_{11} and TPP-OMe/Au_{11} with excitation at 510 n

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

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Coherent-interaction-enhanced hot-electron generation under modal strong coupling conditions

([1]*Research Institute for Electronic Science, Hokkaido University*, [2]*Center for Emergent Functional Matter Science, National Chiao Tung University, Taiwan*) ○Yen-En Liu,[1] Xu Shi,[1] Tomoya Oshikiri,[1] Shuai Zu,[1] Quan Sun,[1] Keiji Sasaki,[1] Hiroaki Misawa[1,2]

Keywords: Localized surface plasmon, Fabry–Pérot nanocavity, Modal strong coupling, Coherent coupling, Transient absorption

Modal strong coupling between Fabry–Pérot (FP) nanocavity and localized surface plasmon resonance of Au nanoparticles has recently been demonstrated to improve the quantum efficiency of the photoelectrochemical reaction.[1] In the present study, we explored the optical properties and the hot carrier generation/transfer of the modal strong coupling system with various coverage ratio (CR) of Au nanodisks (Au NDs) on thin-film TiO_2/Au-film nanocavity (ATA).[2] The CR is proportional to the number density of Au ND and obtained by dividing the gold coverage area by the total surface area.

In an ensemble strong coupling between molecules and an FP cavity, it is known that the magnitude of splitting energy is proportional to the square root of the number of molecules in the cavity.[3] In our modal strong coupling, the magnitude of the split energy was plotted against the square root of CR, and it was shown that the splitting energy increases in proportion to the square root of CR in the region where CR is low. From this plot, we were able to calculate the split energy for a single Au ND. Furthermore, it was revealed that the area calculated from the CR value of the single Au ND is several times larger than the extinction cross-section of the Au ND. Additionally, neither absorption nor near-field intensity were enhanced with the increasing CR. These phenomena could be explained as the LSPRs of Au NDs coherently interacted with the FP nanocavity under modal strong coupling conditions. Under the coherent interaction between the Au NDs and the cavity, the energy and optical properties exchange with other Au NDs, causing saturation of both absorption and near-field intensity. We call the effective area of the coherent interaction to be the coherence area, which was calculated from the CR of single Au ND as above. Furthermore, the transient measurement was also carried out to further understand how the modal strong coupling affects the charge generation and charge transfer on Au/TiO_2. The transient absorption signal at 3500 nm, which corresponds to the absorption of the injected electron in the TiO_2 conduction band,[4] was monitored under excitation of the upper and lower branches of the ATA. From the transient curves, the maximum ΔOD (ΔOD_{max}) was normalized by the extinction of the structure to realize the hot electron generation/injection efficiency. Interestingly, the normalized ΔOD_{max} increased with the increasing CR. We considered that the coherent behavior between the Au NDs is promoted in the ATA with high CR of Au NDs, which might enhance the hot-electron injection from Au NDs to TiO_2 or suppress charge recombination and eventually contribute to efficient charge carrier generation in the conduction band of TiO_2.

1) X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki and H. Misawa, *Nat. Nanotechnol.* **2018**, 13, 953
2) T. W. Ebbesen, *Acc. Chem. Res.* **2016**, 49, 2403
3) Y. Liu, X. Shi, T. Oshikiri, S. Zu, Q. Sun, K. Sasaki, H. Misawa, *Light: Sci. Appl.* under revision.
4) L. C. Du, W.D. Xi, J. B. Zhang, H. Matsuzaki, A. Furube, *Chem. Phys. Lett.* **2018**, 701, 126

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Electrochemical tuning of coupling strength in strong coupling system between lattice plasmons and molecular excitons

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○Takahiro Hayashi,[1] Shunpei Oikawa,[1] Hiro Minamimoto,[2] Kei Murakoshi[2]
Keywords: Lattice Plasmon; Strong Coupling; Molecular Exciton

It is well known that the strong electric field forms in the vicinity of the metal nanoparticles under the visible light illumination due to the excitation of plasmon resonance. In such plasmonic fields, various interesting photochemical phenomena, including the formation of the strong coupling states, have been reported. The strong coupling between plasmons and molecular excitons leads to the generation of the new hybridized states via the coherent light energy exchange.[1] However, the relatively shorter lifetime of the plasmon derived from the radiative energy loss often limits to its application. On the other hand, the two dimensionally arranged metal lattice structure has been receiving much attention because such structure can suppress the radiative damping due to the interaction between the collective electron oscillation and the diffractive light, resulting in the excitation of the lattice plasmon mode.[2] In this study, we have focused on the longer lifetime of lattice plasmon mode to construct strong coupling system using Au lattice structures and organic dye molecules. In addition, we have tried to control the coupling strength of strong coupling via electrochemical potential control.

The Au lattice structures were fabricated on the conductive glass substrate by electron beam lithography method. To construct strong coupling system, the Nafion thin film with dye molecules (S0366) absorbed by the cation-exchange method was prepared on the lattice structure. The new energy states, indicating the formation of the strong coupling regime, has been successfully observed as the peak splitting on angle-resolved extinction spectra. In addition, we revealed that the peak splitting of the strong coupling system was reversibly tuned by the electrochemical potential as shown in the figure. This result suggests that electrochemical potential control is effective for active tuning of the coupling strength of the strong coupling system.

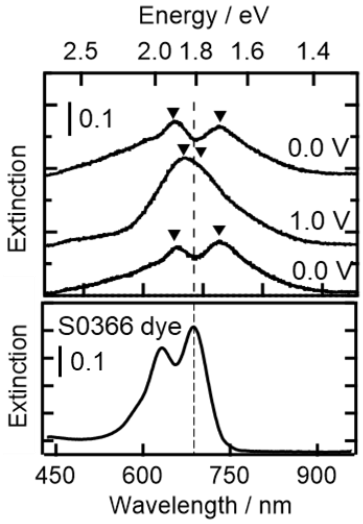


Fig 1. Extinction spectra of S0366 dye molecule(bottom) and S0366 dye supported Au lattice structure under electrochemical potential control(top). Potential sweep direction is upper direction.

1) J. A. Hutchison *et al.*, *Angew. Chem. Int. Ed*. **2012**, 51, 1592 –1596.
2) T. Hayashi *et al*., *J. Phys. Chem. C.,* **2018**, 122, 25, 14162-14167.

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分子動力学計算によるプロトン伝導性 PVPA-*x*Im 複合体の局所構造と分子ダイナミクス

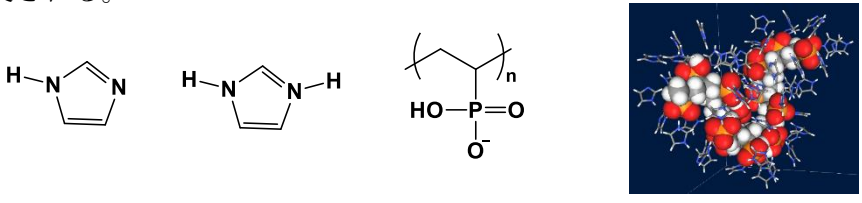
（筑波大 CCS[1]・金沢大院自然 [2]）○堀 優太 [1]・末武 鋭也 [2]・井田 朋智 [2]・水野 元博 [2]・重田 育照 [1]

Local Structures and Molecular Motions in Proton-Conducting PVPA-*x*Im Composites Investigated by Molecular Dynamics Simulations ([1]*Center for Computational Sciences, University of Tsukuba*, [2]*Graduate School of Natural Science and Technology, Kanazawa University*) ○Yuta Hori,[1] Toshiya Suetake,[2] Tomonori Ida,[2] Motohiro Mizuno,[2] Yasuteru Shigeta[1]

Poly(vinylphosphonic acid)-imidazole (PVPA-*x*Im) exhibits high proton conductivity above 100 °C. The elucidation of the proton conduction mechanism leads to the design of future high-temperature polymer electrolyte membrane fuel cells. This work examines the local hydrogen-bond structures and dynamics of Im for PVPA-*x*Im by using molecular dynamics simulations. Radial distribution functions and diffusion coefficients showed that the intercalation of Im and imidazolium into PVPA reduces the translational motion of Im in PVPA-2Im. The activation energy of the internal motion of Im is lower than that of the translational motion, indicating that proton conduction in PVPA-2Im occurs via a Grotthuss-type mechanism. This study shows that the internal motion of Im enhances proton conduction in PVPA-*x*Im composites.
Keywords : Poly(vinylphosphonic acid)-Imidazole; Proton Conduction; Molecular Dynamics Simulation

ポリビニルホスホン酸（PVPA）とイミダゾール（Im）の複合体（PVPA-*x*Im）は、100℃以上の温度領域で高いプロトン伝導性を示す無水プロトン伝導物質であり、その伝導機構の理解は、固体燃料電池の電解質材料を設計する上で重要となる。本研究では、PVPA-*x*Im 複合体中のプロトン伝導機構を明らかにするために、分子動力学計算を用いることにより、複合体中の水素結合構造や Im の分子ダイナミクスを調べた。

動径分布関数の結果から、複合体中では PVPA–Im 間および Im–Im 間で水素結合を形成することがわかった。一方、Im の拡散係数や回転相関関数の結果から、PVPA–Im 間に比べて Im–Im 間の水素結合領域に存在する Im の運動性が大きいことがわかった。拡散運動と回転運動の活性化エネルギーから、回転運動の方が起こりやすいことがわかった。よって PVPA-*x*Im 中では、Grotthuss 型機構でプロトン伝導が起こることが示唆される。



1) Y. Hori, T. Suetake, Y. Shigeta, T. Ida, M. Mizuno, *Chem. Lett.* **2021**, *50*, 17. 2) Y. Hori, T. Suetake, Y. Shiota, K. Yoshizawa, Y. Shigeta, T. Ida, M. Mizuno, **2020**, *2*, 1561.

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[A05-3pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair:Akihiro Furube, Yuta Takano

Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 5 (Online Meeting)

[A05-3pm-01] Signal Enhancement in Pump-Repump-Probe Spectroscopy Using a Sequential Pulse Train

○Hikaru Sotome[1], Masafumi Koga[1], Tomoya Sawada[1], Hiroshi Miyasaka[1] (1. Osaka University)

1:00 PM - 1:20 PM

[A05-3pm-02] The molecular mechanism of light-driven inward proton pump, schizorhodopsin, from Asgard archaea

○Keiichi Inoue[1], Wataru Shihoya[1], Masae Konno[1,2], Akimitsu Higuchi[1], Tajima Seiya[3], Yuji Furutani[4], Yuma Kawasaki[1], Takashi Nagata[1], Hiromu Yawo[1], Izuru Kawamura[3], Hideki Kandori[4], Osamu Nureki[1] (1. The Univ. of Tokyo, 2. JST PRESTO, 3. Yokohama Natl. Univ., 4. Nagoya Inst. of Tech.)

1:20 PM - 1:40 PM

[A05-3pm-03] Defect-filling in lead halide perovskite crystals revealed by single-particle electroluminescence microspectroscopy

○Sankaramangalam Balachandran Bhagyalakshmi[1], Yuta Takano[1,2], Vasudevanpillai Biju[1,2] (1. Graduate School of Environmental Science, Hokkaido University , 2. Research Institute for Electronic Science, Hokkaido University)

1:40 PM - 2:00 PM

[A05-3pm-04] Spin Dynamics Study of Photo-Carrier Generation in TIPS-Pentacene Film by Electrically Detected Magnetic Resonance

○Ken Kato[1], Yoshio Teki[1] (1. Osaka City Univ.)

2:00 PM - 2:20 PM

[A05-3pm-05] Non-linear emission dynamics of a $CH_3NH_3PbBr_3$ microcrystal measured by femtosecond trainsient absorption microscopy

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

2:20 PM - 2:40 PM

[A05-3pm-06] Trapping Photogenerated Charge Carriers in Perovskite Nanocrystal Films by Doping with Electron Scavengers

○Sachith Bhagyashree Mahesha[1], Yuta Takano[1,2], Vasudevanpillai Biju[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

2:40 PM - 3:00 PM

[A05-3pm-07] Photoinduced Electron Transfer Reaction and Solvent Effect of a Bridging Molecule between Flavin and Tryptophan

○Yoshimi Oka[1] (1. Oita Univ.)

3:00 PM - 3:20 PM

[A05-3pm-08] Controlling the nonadiabatic electron-transfer reaction rate through molecular-vibration polaritons in the ultrastrong coupling regime

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

3:20 PM - 3:40 PM

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Signal Enhancement in Pump-Repump-Probe Spectroscopy Using a Sequential Pulse Train

([1]*Graduate School of Engineering Science, Osaka University*) ○ Hikaru Sotome,[1] Masafumi Koga,[1] Tomoya Sawada,[1] Hiroshi Miyasaka[1]

Keywords: Transient Absorption Spectroscopy; Pump-Repump-Probe Spectroscopy; Multiphoton Process

Pump-repump-probe spectroscopy using two excitation pulses is a powerful tool for investigating reaction dynamics in higher excited states (S_n states). The pump pulse excites the ground state molecule into the intermediate state, which is further pumped up to the higher excited state by the repump pulse, and the resultant dynamics therein is monitored by the probe pulse. The transient signals, however, are rather weak (typically ~10^{-3} OD) and often difficult to detect due to the limited portion of molecules populated into the higher excited state upon the two sequential excitations. In the present study, we have developed a method for enhancing the transient signal using a sequential pulse train and demonstrated its application to photoionization dynamics of perylene in solution. Figure 1a shows schematic diagram of signal enhancement in pump-repump-probe spectroscopy. We generated a collinear 32-pulse train with 5 birefringent crystals and used it as the pump beam, thereby enabling us to increase the excitation portion of the intermediate without undesirable nonlinear optical effects. Figure 1b shows transient absorption spectra of perylene in acetonitrile excited with a pulse train at 400 nm (pump) and a subsequent pulse at 700 nm (repump). The delay time is defined as an interval between the repump and probe pulses, and ΔΔAbsorbance is differential absorbance between in the presence and absence of the repump pulse. At the time zero, negative and positive bands, which are respectively ascribable to the S_1 bleaching and absorption from the S_n state, are observed at 690 and 500 nm with signal intensity of -0.15 and +0.03 OD. This result clearly shows that the transient signals are amplified by a factor of a few tens under the present excitation condition.

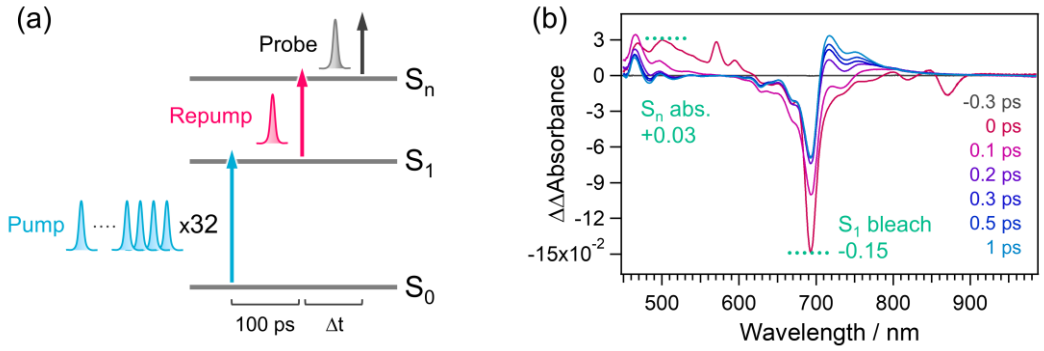


Figure 1. (a) Photoexcitation scheme with a sequential pulse train. (b) Transient absorption spectra of perylene in acetonitrile excited with the pump (400 nm, 3 μJ) and repump (700 nm, 300 nJ) pulses.

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The Molecular Mechanism of Light-Driven Inward Proton Pump, Schizorhodopsin, from Asgard Archaea

([1]Inst. Solid State Phys., Univ. Tokyo, [2]Grad. Sch. Sci., Univ. Tokyo, [3]PRESTO, JST, [4]Grad. Sch. Eng. Sci., Yokohama Natl. Univ., [5]Grad. Sch. Eng., Nagoya Inst. Tech., [5]OptoBioTechnol. Res. Ctr., Nagoya Inst. Tech.) ○Keiichi Inoue[1]、Wataru Shihoya[2]、Masae Konno[1,3]、Akimitsu Higuchi [2]、Seiya Tajima[4]、Yuji Furutani[5,6]、Yuma Kawasaki[1]、Takashi Nagata[1,3]、Hiromu Yawo[1]、Izuru Kawamura [4]、Hideki Kandori[5,6]、Osamu Nureki[2]

Keywords: Schizorhodopsin; Crystal structure; Photocycle; FTIR spectroscopy; Solid-state NMR spectroscopy

Microbial rhodopsins are the heptahelical photo-receptive membrane proteins using retinal chromophore. The functions of microbial rhodopsins are very diverse, and light-driven outward H^+ pump rhodopsins most ubiquitously exist in nature. Recently, we identified new types of light-driven inward H^+ pumping microbial rhodopsin, schizorhodopsin (SzR), in Asgard archaea, the living prokaryote closest to the last common ancestor of eukaryotes[1]. Here, H^+-transport mechanism of SzR was spectroscopically and structural biologically studied. The first X-ray crystallographic structure of SzR was determined at 2.1 Å resolution[2] (Fig. 1). It revealed that the transmembrane helices (TMs) of SzR is significantly shorter compared with other microbial rhodopsins. The short TMs are considered to be important for efficient H^+ release to the cytoplasmic milieu. Furthermore, the cyclic photoreaction involving the multi-step H^+ transfer between the Schiff base linkage of the retinal chromophore and large conformational change of protein moiety were revealed by laser flash photolysis and step-scan FTIR spectroscopy (Fig. 2). Also, the hydrogen bonding network around the retinal Schiff base, Asp184 and Tyr71 was investigated by NMR spectroscopy.

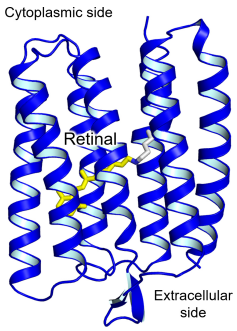


Fig. 1. The crystal structure of SzR

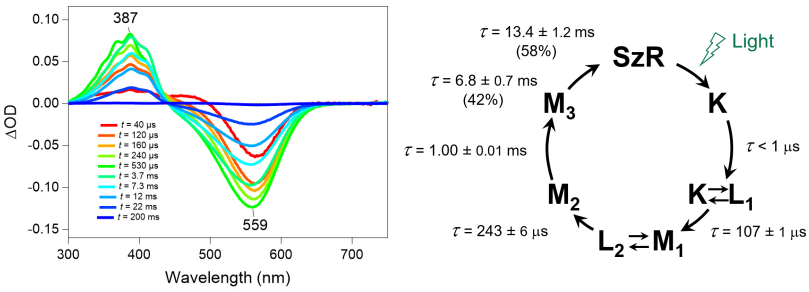


Fig. 2. Transient absorption spectra (left) and the photocycle of SzR (right)

1) K. Inoue, S. P. Tsunoda, M. Singh, S. Tomida, S. Hososhima, M. Konno, R. Nakamura, H. Watanabe, P.-A. Bulzu, H. L. Banciu, A.-Ş. Andrei, T. Uchihashi, R. Ghai, O. Béjà, H. Kandori *Sci. Adv.* **2020**, *6*, eaaz2441. 2) A. Higuchi, W. Shihoya, M. Konno, T. Ikuta, H. Kandori, K. Inoue, O. Nureki *bioRxiv*, **2020**, doi.org/10.1101/2020.07.28.224907.

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Defect-filling in Lead Halide Perovskite Crystals Revealed by Single-Particle Electroluminescence Microspectroscopy

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Keywords: Halide Perovskites; Electroluminescence; Blinking; Halide Vacancy; Single-Particle Study

Lead halide perovskites emerge into a new class of semiconductor materials for potential applications to solar cells, LEDs, lasers, and photodetectors. However, photoluminescence (PL) and electroluminescence (EL) blinking caused by nonradiative losses through defects in the bandgap adversely affects the efficiencies of perovskite devices.[1,2] We clarify the mechanism of EL blinking in lead halide perovskite and understand the role of bromide vacancies in blinking.

Methylammonium lead bromide ($MAPbBr_3$) perovskite microcrystals with varying bromide composition are synthesized by using the precursors (MABr: $PbBr_2$) in the stoichiometric or under stoichiometric ratio. In a sample synthesized with the lower bromide ratio than required for $MAPbBr_3$, the EL blinking is associated with the linear power-law behavior for the ON- and OFF-time probability distributions (Figure 1a,b). On the other hand, the crystals synthesized by using a stoichiometric precursor solution shows EL blinking characterized by a truncated power-law behavior (Figure 1c,d). Single particle electroluminescence studies suggest that the trap-assisted quenching of emission and the type-B blinking dominate in a sample with higher density of halide vacancy.

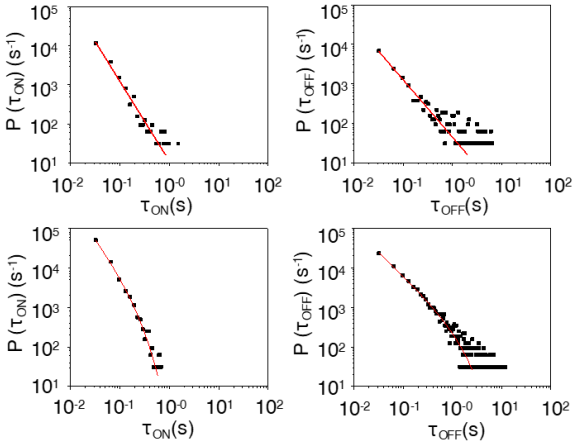


Figure 1. ON- and OFF-time probability distributions at 8V of $MAPbBr_3$ perovskite crystal prepared from precursor solutions with (a,b) under stoichiometric and (c,d) stoichiometric amounts of precursors.

1) T. Kim, *Small*. **2019**,15, 1900355. 2) D. K. Sharma, *Nat. Commun.* **2019,** 10, 4499.

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Spin Dynamics Study of Photo-Carrier Generation in TIPS-Pentacene Film by Electrically Detected Magnetic Resonance

(*Graduate School of Science, Osaka City University*) ○Ken Kato, Yoshio Teki

Keywords: Electrically Detected Magnetic Resonance, Spin Dynamics, Electron-Hole Pair, TIPS-Pentacene, Photocurrent

The spin dynamics of the electron-hole pair (e–h pair) in the photo-carrier generation is important for understanding the carrier dynamics and the performance of organic semiconductors. The aim of this study is to clarify the spin dynamics and the photo-charrier generation mechanism of the vacuum vapor deposition film of 6,13-bis(triisopropylsilyl-ethynyl)pentacene (TIPS-Pentacene) by photocurrent and electrically detected magnetic resonance (EDMR) measurement.

The TIPS-pentacene film was fabricated on a custom-made interdigitated platinum electrode by a vacuum deposition method. The photocurrent of the film sample was measured under the 1.5 V applied vias voltage and white light irradiation (100 mW) using xenon lamp. Figure 1 shows temperature dependence of EDMR spectra and the signal intensity. The intensity increased from 80 to 200 K and then decreased from 200 to 310 K. To understand the temperature dependence of EDMR, we discussed about the excited-state dynamics and carrier generation process with a model of e–h pair as illustrated in Scheme 1. The thermally active barrier was assumed from the e–h pair to carrier, which was determined to be E/k_B = 1103 K by temperature measurement of photocurrent. The temperature dependence was calculated using quantum mechanical simulations of the excited state and carrier dynamics of the e–h pair as well as the analytical solution for the kinetic rate equation using model of Scheme 1.[1]

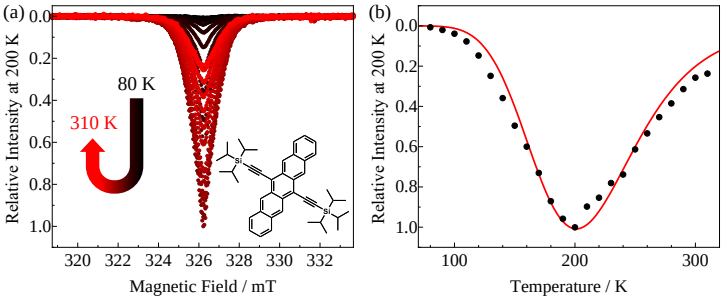
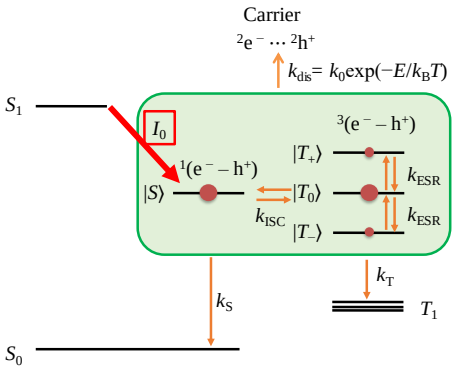


Figure 1. Temperature dependence of the photocurrent-detected EDMR. (a) EDMR spectra. (b) Temperature dependence of the signal intensity (black dots) and the simulation curve (red line).



Scheme 1. Excited-state dynamics and carrier generation process in TIPS-Pentacene film.

1) K. Kato, Y. Teki, *Phys. Chem. Chem. Phys.* **2021**, in press [DOI: 10.1039/D0CP05125J].

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フェムト秒顕微過渡吸収スペクトル測定法による $CH_3NH_3PbBr_3$ 単一微結晶の非線形発光ダイナミクス計測

（徳大院理工）○片山 哲郎・赤木 裕一郎・藤田 優真・古部 昭広

Non-linear emission dynamics of a $CH_3NH_3PbBr_3$ microcrystal measured by femtosecond transient absorption microscopy

(*Graduate School of Science and Engineering, Tokushima University*)
○Tetsuro Katayama, Yuichiro Akagi, Yuma Fujita, Akihiro Furube

Lead halide perovskites have attracted much attention for their applications for solar cells and optoelectronics devices, and have been reported to exhibit nonlinear emission at low threshold. To understand the nonlinear emission dynamics, we used a femtosecond transient absorption spectroscopy system for a $CH_3NH_3PbBr_3$ microcrystal. As a result, we observed a significant spectral interference signal immediately after excitation above the threshold, as shown in Fig.1. We will discuss the origin of the interference signal along with the density-dependent carrier dynamics.

Keywords : Carrier dynamics, Polariton, Organic-inorganic lead halide perovskite, Transient absorption microscopy

近年、ハロゲン化鉛ペロブスカイトは太陽電池、オプトエレクトロニクスへの応用が期待され、注目を集めている。特に結晶系では低発振閾値で誘導放出増幅（ASE）、レージングを示し、比較的高い励起光強度では隠れた電子状態が観測され[1)]、低閾値発振機構について光とキャリアの相互作用状態であるポラリトン、プラズモンが重要なことを示唆する結果が報告されてきている。この非線形ダイナミクスを理解するため本研究では、非線形発光を示す $CH_3NH_3PbBr_3$ 結晶に対してフェムト秒顕微過渡吸収スペクトル測定を行った。

Fig.1 に過渡吸収スペクトルの形状変化を示す。時間原点前では観測されなかった干渉信号が時間原点からスペクトル全体に顕著に観測された。また、励起光強度を非線形発光の発振閾値以上の条件では、577 nm 付近の負の信号が増大し、4 ps の時定数で減衰する挙動が観測された。発表では、過渡吸収スペクトルの形状変化から非線形発光挙動について議論する。

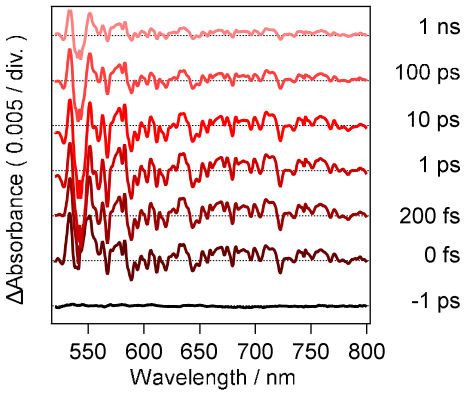


Fig.1 Femtosecond transient absorption spectra of a $CH_3NH_3PbBr_3$ microcrystal (Ex. 400 nm, 4.2 μJcm^{-2}).

1) T. Katayama, H. Suenaga, T. Okuhata, S. Masuo, N. Tamai, *JPC.C,* **2018**, 122**,** 5209.

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Trapping Photogenerated Charge Carriers in Perovskite Nanocrystal Films by Doping with Electron Scavengers

([1]*Graduate School of Environmental Science,* [2]*Research Institute for Electronic Science, Hokkaido University*) ○Bhagyashree Mahesha Sachith,[1] Yuta Takano,[1,2] Vasudevanpillai Biju[1,2]
Keywords: Halide Perovskite; Nanocrystals; Fullerene; Electron Transfer; Photoluminescence

Perovskite nanocrystals (PNCs) become attractive due to their excellent photoluminescence (PL) and electronic properties. Thus, these perovskites show great promise to optical, electronic, and photovoltaic applications. Both PL lifetime and transient absorption measurements in the presence of electron- and hole-accepting materials reveal the high charge mobility in perovskite films.[1]We synthesize $CsPbBr_3$ and $FAPbBr_3$ PNCs by the hot injection[2] and ligand assisted reprecipitation[3] methods, respectively, and subsequently investigate the PL properties of these PNCs in the presence and absence of electron scavengers such as fullerene (C_{60}). We evaluate the effect of C_{60} on the PL of PNCs in solutions and thin films. Interestingly, the PL intensity of a PNC solution is continuously decreased with an increase in the concentration of C_{60}, indicating efficient electron transfer from PNC to C_{60}. However, the corresponding changes to the PL lifetime are not comparable to the decrease in PL intensity. Thus, the contribution of the static component to the PL quenching is considered. We record the transient absorption spectrum of a PNC solution supplemented with C_{60}, which shows electron transfer from PNCs to C_{60} and the formation of C_{60} radical anion.

To evaluate the diffusion of charge carriers in a PNC film, we dope one-half of the film with high-density C_{60} and record the PL decays at every 100 μm distance from the interface region of PNC and C_{60}. As we move away from the interface region to the PNC only region, the PL lifetime is increased, showing long-range diffusion of photogenerated charge carriers in the PNC film, whereas the electrons near the interface region are efficiently captured by C_{60}. The corresponding plot of the distance and photocounts or the PL lifetime suggests that the contribution of the static component to the PL quenching is much lower than the dynamic component. PL spectra, PL decays, and the corresponding plot of the distance vs photocounts or the PL lifetime suggest the contributions by the dynamic and static electron transfer components to the PL quenching of PNCs. We hypothesize that the hydrophobic nature of C_{60} enables it to closely interact with the PNCs capped with hydrophobic ligands. An interfacial electron transfer from PNC to C_{60} can be rationalized with the detailed investigations of PNC films.

1) J. S. Manser, et al. *Nat. Photon*, **2014**, *9*, 737. 2) L. Protesescu, et al. *Nano Lett.*, **2015**, *15*, 3692. 3) V. C. Nair, et al. *Angew. Chem. Int. Ed*, **2017**, *56*, 1214.

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フラビンートリプトファン連結分子の光誘起電子移動反応と溶媒効果

（大分大全学研究推進機構）○岡 芳美

Photoinduced Electron Transfer Reaction and Solvent Effect of a Bridging Molecule between Flavin and Tryptophan

(*Research Promotion Institute, Oita University*) ○Yoshimi Oka

A possibility that flavoprotein cryptochrome functions as a sensitive magnetic sensor in biological system is strongly suggested. The mechanism is that when flavin adenine dinucleotide (FAD) in cryptochrome is excited by blue light, electron transfer occurs between FAD and tryptophan (Trp), and the resulting radical pair is estimated to detect the magnetic field as the difference in reaction efficiency. The relative positions of flavin and Trp are important for the magnetic sensing of cryptochrome, and for this purpose of precise control, this study used an approach to design and synthesize a bridging structure for flavin–Trp molecule. Here, the synthesis, crystal structure and reaction dynamics of photoinduced electron transfer, measured by fluorescence lifetime and time-resolved electron spin resonance (TR-ESR) spectroscopy, of a flavin-Trp molecule bridged by a *p*-phenylamide linker will be presented. Solvent effect on the reaction dynamics will be also discussed.[1]

Keywords : Flavoprotein Model, Photoinduced Electron Transfer, Solvent Effect, Precise Synthesis, Time-Resolved Electron Spin Resonance Spectroscopy

生体内で、フラビンタンパク質クリプトクロムが高感度磁気センサーとして働いている可能性が強く示唆されている。その機構は、クリプトクロム中のフラビンアデニンジヌクレオチド（FAD）が青色光により励起されたとき、アミノ酸（トリプトファン、Trp）との間で電子移動が起こり、その結果生じるラジカルペアのために、微弱磁場であっても反応効率の差として検出できると推定されている。クリプトクロムの磁気センシングにおいて、フラビンと Trp の相対位置が重要であり、その精密制御を目的として、本研究では、フラビンーTrp 連結分子を対象にリンカー構造を設計、合成するアプローチをとった。本講演では、*p*-フェニルアミド・リンカーで連結したフラビンーTrp 分子の合成と結晶構造、蛍光寿命と時間分解電子スピン共鳴（TR-ESR）測定による光誘起電子移動反応のダイナミクス、その溶媒効果[1]について報告する。

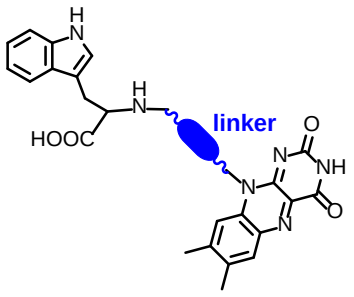


図１ フラビンートリプトファン連結分子

1) Y. Oka, *ACS Omega* **2020**, *5*, 21226–21230.

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Controlling the Nonadiabatic Electron-Transfer Reaction Rate through Molecular-Vibration Polaritons in the Ultrastrong Coupling Regime

Nguyen Thanh Phuc
Kyoto University

Controlling chemical reactions is one of the ultimate goals in the field of chemistry. Recent experiments showed that the chemical reactions can be modified, either increased or decreased, by strongly coupling a nuclear vibration mode to the single mode of an optical cavity [1]. Motivated by these experiments, we investigated how the rate of a nonadiabatic electron-transfer reaction changes by varying the molecule-cavity coupling strength in the hitherto unexplored ultrastrong coupling regime, where the coupling strength is comparable in magnitude with both the vibrational and the cavity frequencies.

We found two main factors that determine the modification of the reaction rate: the relative shifts of the energy levels induced by the coupling, and the mixing of ground and excited states of molecular vibration in the ground state of the hybrid molecule-plus-cavity system [2]. The former is the dominant factor if the molecule-cavity coupling strengths for the reactant and product states differ significantly from each other, and it gives rise to an increase in the reaction rate over a wide range of system's parameters. The latter dominates if the coupling strengths and energy levels of the reactant and product states are close to each other, and it leads to a decrease in the reaction rate. The effect of the mixing of molecular vibrational states on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton. In contrast, the effect of the relative shifts of the energy levels should be essentially independent of the number of molecules coupled to the cavity.

The rapid progress in the realization of strong and ultrastrong couplings between molecules and optical cavities is likely to open a new door to the physical control of chemical reactions and dynamical processes that, unlike Floquet engineering [3] and other approaches using intense laser fields, is based on the zero-point quantum fluctuation of the vacuum state of the cavity field.

[1] A. Thomas et al., *Angew. Chem. Int. Ed.* **55**, 11462 (2016); A. Thomas et al., *Science* **363**, 615 (2019); H. Hiura et al., *ChemRxiv* 10.26434/chemrxiv.7234721.v2 (2018); J. Lathera et al., *Angew. Chem. Int. Ed.* **58**, 10635 (2019)
[2] N. T. Phuc, P. Q. Trung, and A. Ishizaki, *Scientific Reports* **10**, 7318 (2020).
[3] N. T. Phuc and A. Ishizaki, *J. Phys. Chem. Lett.* **9**, 1243 (2018); N. T. Phuc and A. Ishizaki, *Phys. Rev. B* **99**, 064301 (2019).

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

[A06-3am] 06. Analytical Chemistry

Chair:Yuko Nishimoto, Masahito Uchikoshi

Sun. Mar 21, 2021 9:00 AM - 11:00 AM Room 6 (Online Meeting)

[A06-3am-01] X-ray elemental analysis of Ge quantum dots on a Si substrate using an X-ray induced force change through X-ray aided atomic force microscopy (XANAM)

○Shushi Suzuki[1], Shingo Mukai[2], Wang Jae Chun[3], Masaharu Nomura[4], Syuntarou Fujimori[1], Mitsuhisa Ikeda[1], Katsunori Makihara[1], Seiichi Miyazaki[1], Kiyotaka Asakura[2] (1. Nagoya University, 2. Hokkaido University, 3. International Christian University, 4. KEK)

9:00 AM - 9:20 AM

[A06-3am-02] Harmful Reagent-free Separation/Concentration of Boron and Arsenic in Environmental Water

○Masaru Arai[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

9:20 AM - 9:40 AM

[A06-3am-03] Specific interaction between two-dimensional semiconductor MoS_2 and amide molecules under contaminating solution

○Akito Fukui[1], Hiroaki Onoe[2], Shun Itai[2], Keiko Ishikura[2], Hidekazu Ikeno[1], Takahiro Nagata[3], Yuh Hijikata[4], Jenny Pirillo[4], Takeshi Yoshimura[1], Atsushi Ashida[1], Norifumi Fujimura[1], Daisuke Kiriya[1] (1. Osaka Prefecture Univ., 2. Keio Univ., 3. NIMS, 4. Hokkaido Univ.)

9:40 AM - 10:00 AM

[A06-3am-04] Negative Differential Resistance in a Nanopore under Salt Gradient: Models of Surface Charge Effect

○IAT WAI LEONG[1], Makusu Tsutsui[1], Masateru Taniguchi[1] (1. ISIR, Osaka Univ.)

10:00 AM - 10:20 AM

[A06-3am-05] Removal and quantification of biological CO in mammals using a synthetic heme protein model compound.

○Qiyue Mao[1], Hiroaki Kitagishi[1] (1. Doshisha University)

10:20 AM - 10:40 AM

[A06-3am-06] Determination of the distribution and the structures of cupric chloro species in hydrochloric acid solutions using factor analysis of absorption spectra and ab initio calculation

○Masahito Uchikoshi[1], Takatoshi Matsumoto[1] (1. Tohoku University)

10:40 AM - 11:00 AM

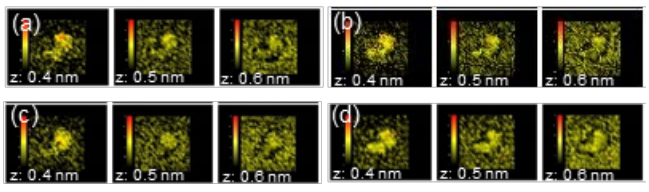
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X 線支援原子間力顕微鏡 XANAM による X 線誘起の力変化を利用した Si 基板上の Ge 量子ドットの X 線元素分析

（名大院工[1]・北大触媒研[2]、ICU[3]、KEK-PF[4]）○鈴木秀士[1]，向井慎吾[2]，田旺帝[3]，野村昌治[4]，藤森俊太郎[1]，池田弥央[1]，牧原克典[1]，宮﨑誠一[1]，朝倉清高[2]
X-ray elemental analysis of Ge quantum dots on a Si substrate using an X-ray induced force change through X-ray aided atomic force microscopy (XANAM) ([1]*Nagoya Univ.*, [2]*Hokkaido Univ.*, [3]*ICU*, [4]*KEK-PF*) Kensuke Kiyokawa,[1] ○Shushi Suzuki[1], Shingo Mukai[2], Wang-Jae Chun[3], Masaharu Nomura[4], Syuntarou Fujimori[1], Mitsuhisa Ikeda[1], Katsunori Makihara[1], Seiichi Miyazaki[1], Kiyotaka Asakura[2]

We developed "X-ray aided atomic force microscopy (XANAM)" for elemental analysis of surface/interface nanostructures. This methodology combines non-contact atomic force microscopy (NC-AFM) and synchrotron radiation X-ray (SR X-ray). We expect to realize X-ray chemical analysis with the same spatial resolution as NC-AFM, assuming that X-rays could change the covalent bond strength in the tip-surface interaction via the excitation of the inner-core shell electrons from the sample. From the previous measurements of Ge surfaces in KEK-PF, it has been confirmed that the tip-surface interaction changed with X-rays near the X-ray absorption edge energies. Here, we observed the Ge quantum dots prepared on a Si substrate. While irradiating X-rays with energies near the Ge-K absorption edge, the X-ray energy dependence of the tip-surface force was acquired three-dimensionally. A clear difference was confirmed between the Ge quantum dot position and the Si substrate position. Therefore, we have succeeded in the elemental mapping of the sample surface with a spatial resolution of at least a few nanometers.
Keywords : X-ray surface chemical analysis; NC-AFM; Germanium Quantum dot; Covalent

我々は、表面／界面のナノ構造の元素分布情報を得る手法として、「X 線支援非接触原子間力顕微鏡(XANAM)」を開発してきた。これは非接触原子間力顕微鏡（NC-AFM）と放射光 X 線（SR X-ray）を組み合わせた手法である。NC-AFM の探針-試料間に生じる共有結合が、試料からの内殻電子励起を介して X 線に応答すると考え、NC-AFM と同等の空間分解能で化学分析を実現することを目指した。これまでの KEK-PF における Ge 表面の測定から、X 線吸収端付近の X 線で原子間力に変化が生じることを確認した。そこで今回、Si 基板上に作成した Ge 量子ドット試料を観察した。Ge-K 吸収端付近のエネルギーの X 線を照射しながら、原子間力の X 線エネルギー依存性を 3 次元に取得し、Ge 量子ドット位置と基板 Si 位置で明確な違いが確認できた。これより試料の元素分布を少なくとも数 nm の空間分解能を達成できた。



1) XANAM images of quantum dots at the tip-surface separation (z) at 0.4, 0.5 0.6 nm. Image size: 40 × 40 nm^2, X-ray energies: (a) 11053 eV, (b) 11103 eV(Ge-K), (c) 11153 eV, amd (d) 11203 eV.

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Harmful Reagents-free Separation/Concentration of Boron and Arsenic in Environmental Water

([1] *Department of Chemistry, Kanagawa University*)
○Masaru ARAI[1], Yuko NISHIMOTO[1]

Keywords: Harmful Reagent-free; Separation and Concentration method; Eutectics; Boron; Arsenic

Alkali halide aqueous solution forms eutectics of salt and water at low temperature. By keeping the temperature at which only the eutectics of salt and water melted at around 0 to -20 ℃, trace elements in water can be concentrated to the eutectic mixture. In the temperature range above the eutectic point and below the melting point of ice, only the eutectic mixture exists as a liquid phase, so it was thought that a new low-temperature separation and concentration method could be constructed. Since the eutectic point depends on the alkali halide, the applicable temperature range is different. In this study we focused on harmful reagents-free freeze concentration method for the purpose of separating and concentrating boron and arsenic in environmental water.

We focused on boron and arsenic which are components of hot springs. Also, environmental standards of boron and arsenic are defined for the protection of human health as environmental standards for water pollution in public water bodies. An aqueous solution was prepared with a boron or arsenic concentration of 0.1 mmol/L as a model solution. In addition, sample was prepared with a NaCl or KCl concentration of 10 mmol/L as a coexisting salt. After freezing 100 mL of the sample at about -30 ℃ for 12 hours or longer, the frozen sample was melted at room temperature and the aqueous phase was separated every 10 mL. The concentration of boron and arsenic was determined by ICP-AES (Hitachi High-Tech Science SPS3510).

The boron and arsenic were concentrated to 10 mL of early stage of melting more than other liquid phases. It was found that 80 % or more of the total boron or arsenic can be concentrated in the early stage of melting up to 30 mL.

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夾雑溶液下における 2 次元半導体 MoS_2 とアミド系分子間の特異的相互作用

（阪府大院工[1]・慶應大院理工[2]・物質・材料研究機構[3]・北海道大 WPI-ICReDD[4]）
○福井暁人[1]・尾上弘晃[2]・板井駿[2]・石倉恵子[2]・池野豪一[1]・長田貴弘[3]・土方優[4]・Jenny Pirillo[4]・吉村武[1]・芦田淳[1]・藤村紀文[1]・桐谷乃輔[1]
Specific Interaction between Two-dimensional Semiconductor MoS_2 and Amide Molecules under Contaminating Solution ([1]*Graduate School of Engineering, Osaka Prefecture University*, [2]*Graduate School of Integrated Design Engineering, Keio University,* [3]*National Institute for Materials Science,* [4]*Institute for Chemical Reaction Design and Discovery, Hokkaido University*) ○Akito Fukui[1], Hiroaki Onoe[2], Shun Itai[2], Keiko Ishikura[2], Hidekazu Ikeno[1], Takahiro Nagata[3], Yuh Hijikata[4], Jenny Pirillo[4], Takeshi Yoshimura[1], Atsushi Ashida[1], Norifumi Fujimura[1], Daisuke Kiriya[1]

N, N-dimethylformamide (DMF) is widely used as a solvent, but it has been reported to be toxic to the human body and cells. However, DMF molecule sensing in solution is not easy due to its stability and the coexistence of other polar molecules. In this study, we found specific and selective interactions between a defective site of molybdenum disulfide (MoS_2), which is a two-dimensional semiconductor, and an amide-based molecule. We also attempted to demonstrate a molecular sensor under a contaminating solution using a field-effect device.

A field-effect transistor with a channel length of 1 μm was fabricated for MoS_2 transferred onto a SiO_2 substrate by mechanical exfoliation. A microchannel using polydimethylsiloxane was bonded on the substrate to hold and exchange the solution. DMF/NaCl aqueous solutions were introduced into the microchannel. The concentration of NaCl was 0.15 M, and the concentration of DMF was changed from 1 μL/mL to 200 μL/mL. By the measurement of the device under the solution, the change of the current value was observed corresponding to the concentration of DMF.

Keywords : Amide Molecules, Molybdenum Disulfide, Biosensors

N,N-ジメチルホルムアミド(DMF)は溶媒として広く用いられているが、人体および細胞に対して毒性を有することが報告されている[1)2)]。しかし、溶液中での DMF 分子センシングは DMF が安定な分子であることや、他の極性分子が存在することから容易ではない。本発表では、2 次元半導体である二硫化モリブデン(MoS_2)の欠陥サイトとアミド系分子間における特異的相互作用を見出し、さらに電界効果型デバイスにより、夾雑溶液下における分子センサの実証を試みたので報告する。

機械的剥離法によって SiO_2 基板上に転写した MoS_2 に対し、チャネル長 1 μm の電界効果トランジスタを作製した。この基板上に、ポリジメチルシロキサンを用いたマイクロ流路を取り付けることで、溶液の保持と交換が可能な機構を作製した。その後、NaCl 濃度が 0.15 M, DMF 濃度が 1 μL/mL から 200 μL/mL になるよう調整した DMF/NaCl 水溶液を流路内に導入したところ、電流値に濃度依存性が確認された。

1) Jamalzadeh. L et al., Avicenna J Med Biochem., 4(1):e33453. (2016)
2) N. Sun et al., Sensors & Actuators: B. Chemical, 261, 153-160 (2018)

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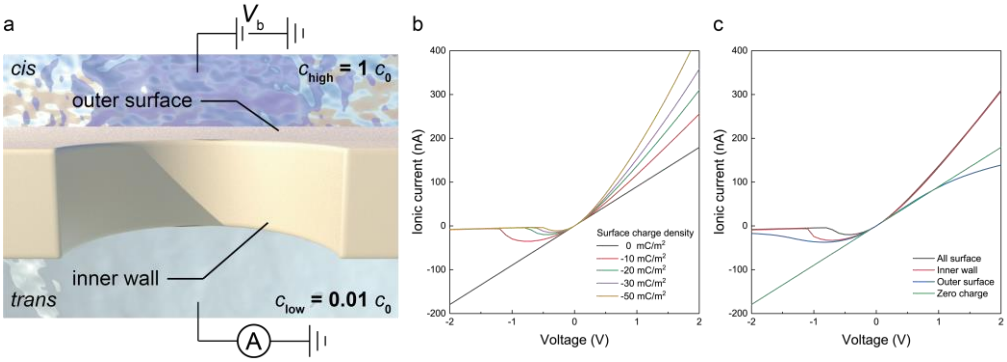
Negative Differential Resistance in a Nanopore Under Salt Gradient: Models of Surface Charge Effect

([1]*The Institute of Scientific and Industrial Research, Osaka University*) ○Iat Wai Leong,[1] Makusu Tsutsui,[1] Masateru Taniguchi[1]

Keywords: Nanopore, Ion transport, Salt gradient, Negative differential resistance

Nanopore technology has been widely used in various bioanalytical applications because of the high spatial sensitivity and simple mechanism. Recently, ionic current rectification (ICR) and negative differential resistance (NDR) were reported for salt-gradient-biased solid-state nanopores showing the potential usage as nanofluidic diodes[1] and memristors.[2] The unique electric characteristics of ICR and NDR presenting asymmetric ion transport is based on the electrical double layers on the charged surface and the associated electroosmotic flow (EOF). In this study, we explored the roles of wall surface charge on the distinct ion transport properties. We performed finite element simulations by solving Poisson-Nernst-Planck and Navier-Stokes equations under different conditions: (i) all surface is charged; (ii) only inner wall is charged; (iii) only pore wall is charged. Those charged patterns were elucidated to change the current-voltage characteristics. Through this method, we show how NDR of low-aspect-ratio nanopore with 50-nm thick SiN_x membrane with salt gradient can be tuned by controlling two important factors: surface charged destiny and it's charged pattern.

In experimental section, a model of 300 nm-diameter and 50 nm-thick membrane under the cis-to-trans ion concentration ratio of 100, is considering in the simulations: charged boundary surface on the outer surface and inner wall are shown in Fig. 1a. When changing the values of surface charge density in the case of (i), simulated current-voltage curves show that nanopore behaves as an ohmic resistor (0 mC/m^2, black curve) and NDR occurs at higher charge density (Fig. 1b). On the other hand, examining the four different regions of the charged surface area, only the case of (i) showed NDR behavior (Fig. 1c). These findings provide a new approach to build nanofluidic devices in many fields such as iontronics, nanosensors, and energy harvesters.



1) I. W. Leong, M. Tsutsui, S. Murayama, Y. H. He, M. Taniguchi, *J. Phys. Chem. B* **2020**, 124, 7086. 2) I. W. Leong, M. Tsutsui, S. Murayama, T. Hayashida, Y. H. He, M. Taniguchi, *ACS Appl. Mater. Interfaces* **2020**, 12, 52175.

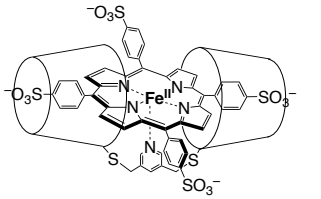
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Removal and quantification of biological CO in mammals using a synthetic heme protein model compound.

(*Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University*) ○Qiyue Mao, Hiroaki Kitagishi

Keywords: Carbon monoxide; hemoprotein; *in vivo*; CO receptor

Carbon monoxide (CO) is known as a toxic and biologically active gas. CO shows high toxicity because of CO strongly binds to hemoglobin and disperses in organs when inhaled in high amounts. The blood carboxyhemoglobin (CO-Hb) level has been established using oximeters. However, it's still a challenge to detect and quantify of CO in organs and tissues.



K_d (O_2) = 17 μM, K_d (CO) = 0.02 nM

Figure 1. Structure of a CO–scavenging agent, hemoCD.

In this study, we established a simple spectrophotometric method for CO detection and quantification using hemoCD, a synthetic heme protein model compound composed of an iron(II)porphyrin and a cyclodextrin dimer (Figure 1)[1]. First, we quantified the amount of CO in rat tissues under normal condition and after inhaling CO gas in a time variation. During 20 min inhalation of rat to CO gas, CO-Hb is linearly increased, however, the amount of CO in organs didn't show significant increase compared to the results after 5 min of inhalation. The kinetic studies on CO-Hb and bio-distribution of CO in tissues after CO gas inhalation suggest a protective effect of circulating Hb in CO intoxication. Second, we followed the decrease of amount of CO in rat organs after ventilation with air and 100% oxygen after exposure to CO gas using hemoCD. Finally, we used the hemoCD as a CO removal agent after exposure of rat to CO gas 80 min. The accumulation of CO in rat tissues include brain were efficiently removed in the rats treated with hemoCD during oxygen ventilation (Figure 2).

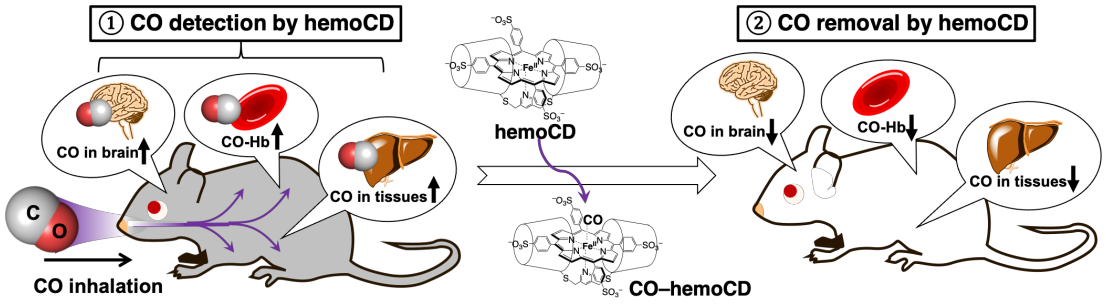


Figure 2. HemoCD used for CO detection and removal *in vivo* after inhalation of CO gas to rats.

1) Q. Mao, A. T. Kawaguchi, S. Mizobata, R. Motterlini, R. Foresti, H. Kitagishi, *bioRxiv*, DOI: https://doi.org/10.1101/2020.10.12.336735.

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日本化学会 第101春季年会 (2021)

紫外可視/X 線吸収分光成分分析および第一原理計算による塩酸水溶液中銅(II)クロロ錯体分布と構造の決定

（東北大多元研 [1]）○打越 雅仁 [1]・松本 高利 [1]

Determination of Distribution and Structures of Cupric Chloro Complexes in Hydrochloric Acid Solutions using Factor Analysis of UV-Vis and X-ray Absorption Spectra and Validation using *ab-initio* Technique

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○Masahito Uchikoshi,[1] Takatoshi Matsumoto[1]

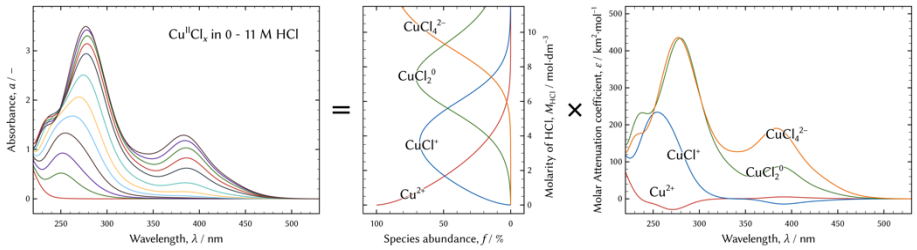
Attention should be paid to conditions of chemical species in aqueous solution employing ion-exchange and solvent extraction in the separation of metals besides extracting agents. Therefore, the distribution of cupric chloro complexes in hydrochloric acid solutions was investigated using factor analysis and validated using *ab-initio* technique.

An empirical estimation of a number of components was proposed. Distribution of cupric chloro complexes based on thermodynamic models was employed to decompose UV-Vis absorption spectra and the most possible thermodynamic model was optimized. The results were applied to X-ray absorption spectra (XAS) and those of the individual species were obtained. The structures of cupric chloro complexes were determined using FEFF fitting. Stable structures of cupric chloro complexes were calculated and compared with the structures determined experimentally. Consequently, the most reasonable distribution was determined; There were four cupric chloro complexes and their formation constants were successfully determined.

Keywords: Cupric chloro complex; Factor analysis; Distribution; ab-initio technique

イオン交換や溶媒抽出で金属を分離する際、官能基だけではなく、水相中のイオンの状態も重要である。本研究では、塩酸水溶液中の銅クロロ錯体の分布を成分分析法により調べ、第一原理計算による検証を実施した。

成分数の新しい推定方法を提案した。熱力学モデルによる錯体分布を用いて、紫外可視吸収スペクトルを分解し、最適化を行った。最適化された熱力学モデルを X 線吸収分光（XAS）の分解に応用し、錯体個別の XAS を得た。FEFF によるフィッティングを実行し、銅クロロ錯体の構造を決定した。実験的に決めた構造と第一原理計算により求めた銅クロロ錯体の安定構造を比較検討し、最も確からしい熱力学モデルを決定した。その結果、4 つの銅クロロ錯体が存在することが分かり、各々の安定度定数を決定した。



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[A07-3pm] 07. Inorganic Chemistry

Chair:Sayaka Uchida, Eisuke Yamamoto

Sun. Mar 21, 2021 1:00 PM - 2:40 PM Room 7 (Online Meeting)

[A07-3pm-01] Synthesis of antimony polyoxocation crystal with highly acidic protons

○Yuki Watanabe[1], Takafumi Yamamoto[1], Masayoshi Yabuuchi[1], Olesia Karakulina[2], Yasuto Noda[1], Hyeon-Deuk Kim[1], Masanobu Higashi[1], Osamu Tomita[1], Jingxin Xia[1], Craig Brown[3], Takashi Honda[4], Kazutaka Ikeda[4], Toshiya Otomo[4], Yuto Shimoyama[5], Naoki Ogiwara[5], Joke hadermann[2], Artem Abakumov[2], Sayaka Uchida[5], Ryu Abe[1], Hiroshi Kageyama[1] （1. Kyoto Univ., 2. Univ. of Antwerp, 3. NIST, 4. KEK, 5. The Univ. of Tokyo）

1:00 PM - 1:20 PM

[A07-3pm-02] Photocatalytic Reduction of Ketones by Visible-Light-Responsive Polyoxometalate Catalysts

○Hiroki Sano[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] （1. The University of Tokyo）

1:20 PM - 1:40 PM

[A07-3pm-03] Sequential Synthesis and Structural Transformation of Silver Nanoclusters within a Ring-shaped Polyoxometalate

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

1:40 PM - 2:00 PM

[A07-3pm-04] Synthesis of a New Keggin-Type Divacant Lacunary Polyoxomolybdate [γ-$PMo_{10}O_{36}$]$^{7-}$ and its Use for Synthesis of an Inorganic-Organic Hybrid

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

2:00 PM - 2:20 PM

[A07-3pm-05] Exfoliation of layered bismuth oxyfluorides into nanosheets and their stability

○Tsubasa Tasaka[1], Makoto Kobayashi[2], Eisuke Yamamoto[2], Minoru Osada[2,3] （1. Graduate school of Nagoya University, 2. Institute of Materials and Systems for Sustainability, 3. National Institute for Materials Science）

2:20 PM - 2:40 PM

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酸性プロトンを有する新規カチオン性アンチモンポリオキソメタレート結晶の合成

Synthesis of antimony polyoxocation crystal with highly acidic protons ([1]*Kyoto University*, [2]*University of Antwarp,* [3]*National Institute of Standards and Technology,* [4]*High Energy Accelerator Research Organization,* [5]*Tokyo Univerisity,* [6]*Skolkovo Institute of Science and Technology*) ○ Yuki Watanabe[1], Takafumi Yamamoto[1], Masayoshi Yabuuchi[1], Olesia Karakulina[2], Yasuto Noda[1], Hyeon-Deuk Kim[1], Masanobu Higashi[1], Osamu Tomita[1], Jingxin Xia[1], Craig Brown[3], Takashi Honda[4], Kazutaka Ikeda[4], Toshiya Otomo[4], Yuto Shimoyama[5], Naoki Ogiwara[5], Joke hadermann[2], Artem Abakumov[2,6], Sayaka Uchida[5], Ryu Abe[1], Hiroshi Kageyama[1]

Polyoxometalates (POMs) are metal oxide ionic clusters composed of a finite number of metal-oxygen polyhedral units. Their diverse structures have a wide range of chemical and physical properties such as catalysis, single-molecule magnets, and selective ion capturing. However, most of POMs are anionic, and cationic POMs are very rare. In recent years, cationic POMs have attracted much attention and several positively charged metal oxide clusters have been synthesized, but most of them focus on the synthesis aspects and not on their properties. In this study, we have synthesized a new cationic antimony POM compound, H-Sb-O-I (Fig.1). The structural analysis electron diffraction tomography and powder X-ray diffraction show that this compound has a cationic antimony POM forming a face-centered close packed lattice, with anionic clusters at the interstitial sites. Protons in H-Sb-O-I on the surface of the cationic clusters are found to be highly acidic, allowing for acid-catalyst reactions.
Keywords: *polyoxometalate, antimony, acid catalyst, lone pair*

金属酸化物多面体が結合して形成されるポリオキソメタレート（POM）は多様な構造と多彩な化学的・物理的性質によって盛んに研究されてきた。しかし、その多くはアニオン性であり、カチオン性の POM というのは極めて珍しい。近年では少しずつ新たなカチオン性の POM も報告され始めているが、その機能に注目するものは未だ少ない。本研究では、偶然にも合成されたカチオン性のアンチモン POM を含む新規な結晶である H-Sb-O-I 系について報告する。この POM の結晶構造は電子線回折トモグラフィーと粉末 X 線回折を組合せて解析することで明らかにした。さらに、この H-Sb-O-I 系中に含まれるプロトンのうち、カチオンクラスター表面に存在するものは酸性度が高く、優れた酸触媒としての機能を有することが明らかとなった。

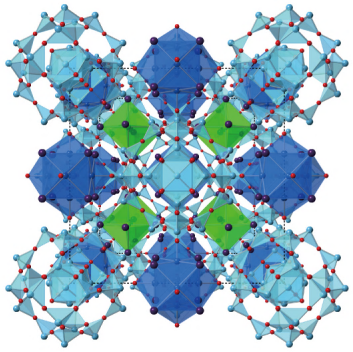


Fig. 1 Crystal structure of H-Sb-O-I

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可視光応答型ポリオキソメタレート触媒を用いたケトンの光還元反応

（東大院工）○佐野 広樹・鈴木 康介・山口 和也
Photocatalytic Reduction of Ketones by Visible–Light–Responsive Polyoxometalate Catalysts (*School of Engineering, The University of Tokyo*) ○Hiroki Sano, Kosuke Suzuki, Kazuya Yamaguchi

Polyoxometalates (POMs) are a class of anionic metal–oxo clusters with a wide range of properties such as multielectron redox properties and photo-responsive properties. In this work, we report photocatalytic reduction of ketones by using lacunary polyoxometalates that show visible-light-responsive photocatalysis in the presence of alcohols. In particular, by controlling the redox potential of S-shaped lacunary silicotungstate via changing protonation states and/or by introducing catalytically active site, photocatalytic reduction of ketones to alcohols efficiently proceeded.
Keywords : Polyoxometalate; Visible-Light-Responsive Catalysis; Photoreduction

アニオン性の金属酸化物クラスターであるポリオキソメタレートは、多電子酸化還元特性や光応答性を有し、これを利用した特異な光触媒特性を示す[1)]。我々は、可視光に応答してアルコールから欠損型ポリオキソメタレートへの多電子移動が進行することを見出し、これを種々の有機基質の選択的還元反応に利用できることを報告してきた。本研究では、アルコールの存在下で可視光応答性を示す欠損型ポリオキソメタレートを利用して、ケトンの光還元反応を行った。特に、S 字型シリコタングステートを用いて、プロトン化状態を変えることによる酸化還元電位の制御や、活性点の導入により、ケトンからアルコールへの光還元反応が効率的に進行することを見出した。

触媒量の S 字型シリコタングステート $TBA_4H_8[Si_2W_{20}O_{70}]$ (**SDimer**, TBA = tetra-*n*-butylammonium)の存在下、アルコールを還元剤として 70℃で可視光を照射することにより、芳香族ケトンの還元反応が進行し対応するアルコールが中程度の収率で生成した。さらに、塩基を添加し、S 字型シリコタングステートのプロトン化状態を変えて光反応を行うと、生成物の収率が向上した。これは、プロトン化状態を変化させることでより還元力の高い POM 種が生成したためであると考えられる。さらに、S 字シリコタングステートの片方の欠損部位に活性点となる Lewis 酸性の金属を導入し検討を行ったところ生成物の収率がさらに向上した。本反応は、可視光を照射することで欠損部位に配位したアルコールから POM への電子・プロトン移動が起こり、生成したポリオキソメタレート還元体により芳香族ケトンの還元反応が進行している。

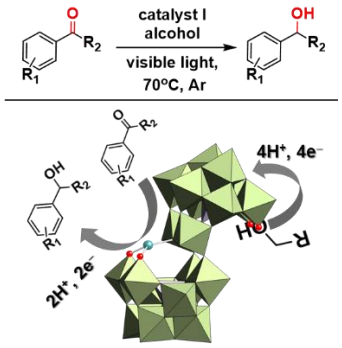


図1 本研究の概要

1) K. Suzuki, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2018**, *8,* 10809−10825

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Sequential Synthesis and Structural Transformation of Silver Nanoclusters within a Ring-shaped Polyoxometalate

([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Science, Tokyo Metropolitan University*) ○Kentaro Yonesato,[1] Kosuke Suzuki,[1] Seiji Yamazoe,[2] Kazuya Yamaguchi[1]

Keywords: Polyoxometalate, Silver Nanocluster, Inorganic Synthesis

Atomically precise silver (Ag) nanoclusters have attracted great interest in diverse fields due to their unique structures, electronic states, and physicochemical properties.[1] In particular, Ag nanoclusters supported on metal oxides are attractive catalysts due to the cooperative catalysis of the Ag nanoclusters and metal oxides. We have recently reported that polyoxometalates (POMs) act as inorganic multidentate ligands that enable the synthesis of ultrastable Ag nanoclusters with unique structures and electronic states.[2] Herein, we report sequential synthesis and structural transformation of the uncovered Ag nanoclusters using a ring-shaped POM that possesses a large cavity (ca. 1 nm in a diameter).[3]

We first synthesized an Ag^+-containing ring-shaped POM (**I**) by the reaction of $[P_8W_{48}O_{184}]^{40-}$ and silver acetate in acetone. Second, the silver nanocluster (**II**) was successfully synthesized within the ring-shaped POM by the reaction of **I**, silver acetate, and a reductant (Figure 1). Furthermore, the reaction of **II** with an additional reductant led the structural transformation into another Ag nanocluster (**III**) in which the Ag atoms were arranged in face-centered-cubic packing. The X-ray absorption near edge structure (XANES) spectra of **II** and **III** revealed that the structural transformation was induced by the reduction of the Ag nanoclusters. The UV-Vis spectrum of **III** exhibited unique absorptions in the visible light region. Although **III** possessed the uncovered Ag surface, **III** exhibited high stability in an organic solvent and the UV-Vis spectrum of the solution remained almost unchanged for about 1 week.

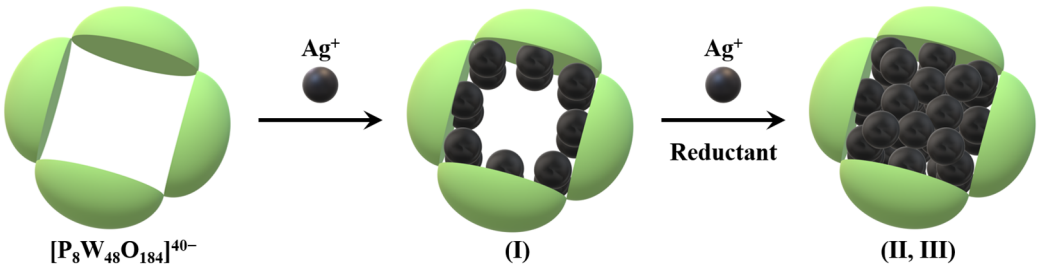


Figure 1. Schematic of sequential synthesis of Ag nanocluster within ring-shaped POM.

1) I. Chakraborty, T. Pradeep, *Chem. Rev.* **2017**, *117*, 8208. 2) a) K. Yonesato, H. Ito, H. Itakura, D. Yokogawa, T. Kikuchi, N. Mizuno, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2019**, *141*, 19550; b) K. Yonesato, H. Ito, D. Yokogawa, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2020**, *59*, 16361. 3) S. Sasaki, K. Yonesato, N. Mizuno, K. Yamaguchi, K. Suzuki, *Inorg. Chem.* **2019**, *58*, 7722.

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Synthesis of a New Keggin-Type Divacant Lacunary Polyoxomolybdate $[\gamma\text{-}PMo_{10}O_{36}]^{7-}$ and its Use for Synthesis of an Inorganic-Organic Hybrid

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

Keywords: Polyoxometalate; Inorganic-Organic Hybrid; Porphyrin; Pyridine

Polyoxometalates (POMs) are a family of discrete anionic metal (W, Mo, V, etc.) oxide clusters that possess enormous structural diversity, which has led to fascinating properties and a wide range of applications in the fields of catalysis, photocatalysis, electrochemistry, sensors, and medicine.[1] For the pursuit of novel POM structures and properties, multivacant lacunary POMs, where more than one $\{MO_x\}$ units are removed from the parent structures, are key precursors.[2] Multivacant lacunary POMs are typically synthesized by empirically controlling the complex equilibrium in aqueous solvents. Unfortunately, despite the excellent catalytic and electrochemical properties of "polyoxomolybdates", only one multivacant lacunary species, i.e., $[A\text{-}\alpha\text{-}PMo_9O_{34}]^{9-}$, has been identified and isolated because multivacant lacunary polyoxomolybdates are typically unstable.

Here we report a ligand-directed approach for the selective formation of an unprecedented lacunary polyoxomolybdate in organic solvents. By structure transformation of a pyridine-coordinated $[A\text{-}\alpha\text{-}PMo_9O_{31}(\mathbf{py})_3]^{3-}$ (**I**, **py** = pyridine, Figure 1),[3,4] a new γ-Keggin-type divacant lacunary polyoxomolybdate $[\gamma\text{-}PMo_{10}O_{34}(\mathbf{py})_2]^{3-}$ was selectively obtained (**II**, Figure 1). Furthermore, this lacunary polyoxomolybdate **II** can act as a synthetic precursor; by reacting **II** with 5,10,15,20-tetra(4-pyridyl)porphyrin (**tpyp**), a POM–organic hybrid structure (**III**, Figure 1) was successfully constructed.[5]

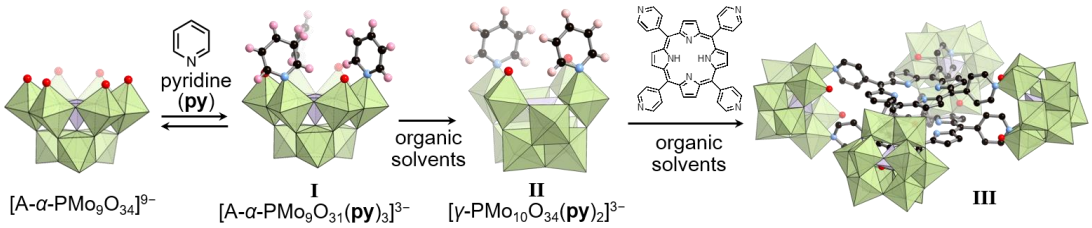


Figure 1. Schematics of the ligand-directed synthesis of a new γ-Keggin-type divacant lacunary polyoxomolybdate **II** bearing pyridine molecules as protecting groups, and its further use as a precursor for the synthesis of a hybrid structure **III**.

1) H. N. Miras, J. Yan, D.-L. Long, L. Cronin, *Chem. Soc. Rev*. **2012**, *41*, 7403. 2) A. Dolbecq, *Chem. Rev.* **2010**, *110*, 6009. 3) C. Li, N. Mizuno, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2019**, *141*, 7687. 4) C. Li, A. Jimbo, K. Yamaguchi, K. Suzuki, *Chem. Sci.* **2021**, DOI: 10.1039/d0sc06133f. 5) C. Li, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2021**, DOI: 10.1002/anie.202016642.

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層状酸フッ化ビスマスの剥離による酸フッ化物ナノシートの合成とその安定性評価

（名大院工[1]・名大未来研[2]・NIMS[3]）○田坂 翼[1]・小林 亮[2]・山本 瑛祐[2]・長田 実[2,3]
Exfoliation of layered bismuth oxyfluorides into nanosheets and their stability ([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute of Materials and Systems for Sustainability, Nagoya University,* [3]*National Institute for Materials Science*) ○ Tsubasa Tasaka,[1] Makoto Kobayashi,[2] Eisuke Yamamoto,[2] Minoru Osada[2,3]

Inorganic nanosheets exhibit unique functionalities inherent from their 2D structure. In contrast to many reports on nanosheets (such as oxides and hydroxides) bearing single anion, the synthesis of mixed-anion nanosheets are still challenging. In this study, we synthesized oxyfluoride nanosheets by delaminating layered oxyfluorides $Bi_2OF_3(NO_3)$ and $Bi_6O_6F_5(NO_3)$[1)], and investigated their stability. Bi-containing oxyfluoride nanosheets with a width of 1 μm and a thickness of 3.5 nm were obtained using formamide as an exfoliating reagent. In the same samples, nanoparticles and holes on nanosheets were observed. When the synthesis was performed under N_2 atmosphere, nanosheets with larger lateral sizes and less holes were confirmed by AFM observation. These results indicated that oxyfluoride nanosheets obtained are not stable and turn into particles under ambient conditions.
Keywords: *nanosheet; oxyfluoride; mixed-anion*

無機ナノシートはその特異な２次元ナノ構造により優れた機能を示す。酸化物、水酸化物といった単アニオン系ナノシートの報告が数多くされる一方で、複合アニオン系ナノシートの合成例は僅少である。本研究では、層状酸フッ化物 $Bi_2OF_3(NO_3)$および $Bi_6O_6F_5(NO_3)$[1)]の剥離による、酸フッ化物ナノシートの合成を試みた。ホルムアミドを剥離剤として用いることで、幅 1 μm、厚さ 3.5 nm の Bi を含む酸フッ化物ナノシートが得られることを AFM および XPS により確認した(Fig. 1(a))。同時に、1 nm 程度のナノ粒子やシートに穴が観察されたことから、より大きく形の整ったシートを調製する条件を検討した。窒素置換したホルムアミドを用いて剥離したナノシートを、窒素雰囲気下で乾燥・保存をした場合、横幅が大気雰囲気で合成したときと比較して、幅が 2 μm 程度大きく穴の少ないナノシートが得られた (Fig. 1(b))。このシートを大気に曝すと、粒子化することを確認した。以上のことから、大気雰囲気下では安定ではないものの、目的とする酸フッ化物ナノシートの合成に成功した。

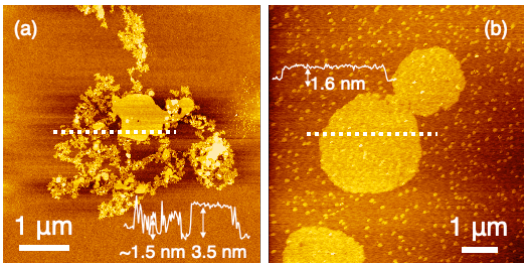


Fig. 1 AFM images and height profiles of nanosheets prepared by exfoliation of $Bi_2OF_3(NO_3)$ (a) under ambient conditions and (b) N_2 atmosphere.

1) Layered Bismuth Oxyfluoride Nitrates Revealing Large Second-Harmonic Generation and Photocatalytic Properties, E. J. Cho *et al.*, *Inorg. Chem.* **2019**, *58*, 2183.

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

[A08-3pm] 08. Catalysts and Catalysis

Chair:Zen Maeno, Xiongjie Jin

Sun. Mar 21, 2021 1:00 PM - 3:20 PM Room 8 (Online Meeting)

[A08-3pm-01] PdAg alloy nanoparticles encapsulated in N-doped microporous hollow carbon spheres for hydrogenation of CO2 to formate

○Guoxiang Yang[1], Yasutaka Kuwahara[1,2,3], Kohsuke Mori[1,2], Catherine Louis[4], Hiromi Yamashita[1,2] （1. Osaka University, 2. Kyoto University, 3. JST PRESTO, 4. Sorbonne University）

1:00 PM - 1:20 PM

[A08-3pm-02] The Roles of Rh and Pt in Electrochemical Toluene Hydrogenation on Rh-Modified Pt Nanoparticle-Loaded Carbon Catalysts

○Toyoki Imada[1], Masanobu Chiku[1], Eiji Higuchi[1], Hiroshi Inoue[1] （1. Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University）

1:20 PM - 1:40 PM

[A08-3pm-03] Preparation of high loading Pd-CHA by dispersion of bulk Pd and its NO adsorption/desorption property

○Shunsaku Yasumura[1], Taihei Ueda[1], Hajime Ide[1], Takashi Toyao[1,2], Zen Maeno[1], Ken-ichi Shimizu[1,2] （1. Institute for Catalysis, Hokkaido Univ., 2. Elements Strategy Initiative for Catalysts and Batteries Kyoto (ESICB)）

1:40 PM - 2:00 PM

[A08-3pm-04] Aerobic Dehydrogenation of Saturated Ketones Using CeO_2-Supported Pd-on-Au Bimetallic Nanoparticle Catalysts

○Daisuke TAKEI[1], Takafumi YATABE[1], Tomohiro YABE[1], Kazuya YAMAGUCHI[1] （1. The Univ. of Tokyo）

2:00 PM - 2:20 PM

[A08-3pm-05] Speciation and Ethane Dehydrogenation Catalysis of Isolated Indium Hydrides in CHA Zeolites

○Zen Maeno[1], Shunsaku Yasumura[1], Xiaopeng Wu[1], Takashi Toyao[1,2], Ken-ichi Shimizu[1,2] （1. Institute for Catalysis, Hokkaido University, 2. Elements Strategy Initiative for Catalysts and Batteries, Kyoto University）

2:20 PM - 2:40 PM

[A08-3pm-06] Effects of MgO on direct amination of alcohols over Ru catalysts

○Yusuke Kita[1], Midori Kuwabara[1], Keigo Kamata[1], Michikazu Hara[1] （1. MSL, Tokyo Tech）

2:40 PM - 3:00 PM

[A08-3pm-07] Selective hydrogenolysis of phenols to arenes by metal– support cooperation

○Rio Tsukimura[1], Xiongjie Jin[1], Takeshi Aihara[2], Hiroki Miura[2], Tetsuya Shishido[2], Kyoko Nozaki[1] （1. The University of Tokyo, 2. Tokyo Metropolitan University）

3:00 PM - 3:20 PM

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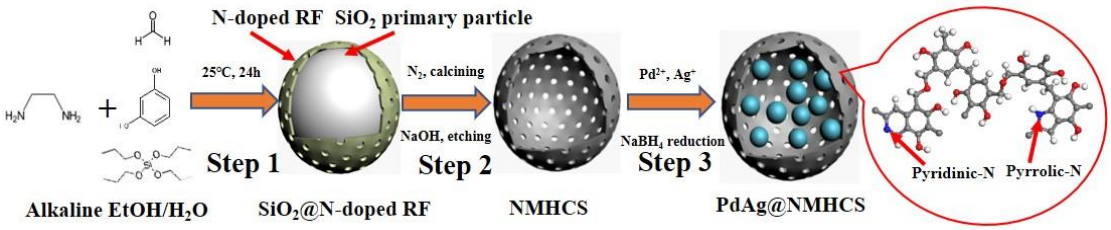
PdAg Alloy Nanoparticles Encapsulated in N-doped Microporous Hollow Carbon Spheres for Hydrogenation of CO_2 to Formate

([1]*Graduate School of Engineering, Osaka University*, [2]*Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University*, [3]*JST, PRESTO*, [4]*Sorbonne University*) ○ Guoxiang Yang,[1] Yasutaka Kuwahara,[1,2,3] Kohsuke Mori,[1,2] Catherine Louis,[4] Hiromi Yamashita[1,2]

Keywords: CO_2 Hydrogenation; Formate; N-doped Microporous Hollow Carbon Spheres; Alloy Nanoparticles

The greenhouse effect is now a global concern. Chemical conversion of CO_2 to beneficial compounds has attracted great interest. Formate has been considered a promising hydrogen storage material because its hydrogen storage capacity is high (53 g L^{-1}). Therefore, the CO_2 hydrogenation catalyst is used to generate formate, which ensures effective CO_2 utilization and achieves economically viable CO_2-mediated hydrogen cycles. Palladium-based heterogeneous catalysts are highly active for the synthesis of formate/formic acid from CO_2.[1,2] Microporous hollow carbon spheres (MHCS) is one of the most ideal carriers for immobilizing metal particles by providing excellent stability. In addition to the porous structure, doped nitrogen as an additional functional group can effectively improve catalytic performance because it can change the polarity and the electron distribution of the carbon matrix.[3]

Herein, we report a general synthesis approach to produce PdAg nanoparticles that are dispersed uniformly within N-doped MHCS (PdAg@NMHCS) as shown in the below Figure for efficient hydrogenation of CO_2 to formate. As a result, thanks to the formation of the ultrafine PdAg alloy nanoparticle size and uniform distribution in the NMHCS, the optimized catalyst shows excellent catalytic activity and good stability in the CO_2 hydrogenation to formate, affording a high turnover number (TON) value of 640 and 2750 at 100 °C after 2 and 24 h, respectively. According to kinetic analyses, NMHCS not only contributed to the adsorption of CO_2 due to the doping of nitrogen but also reduced the activation energy for CO_2 hydrogenation to formate.



1) Y. Kuwahara, Y. Fujie, T. Mihogi, H. Yamashita, *ACS Catal.* **2020**, *10*, 6356. 2) G. Yang, Y. Kuwahara, S. Masuda, K. Mori, C. Louis, H. Yamashita, *J. Mater. Chem. A* **2020**, *8*, 4437. 3) G. Yang, Y. Kuwahara, K. Mori, C. Louis, H. Yamashita, *Appl. Catal. B: Environ.* **2021**, *283*, 119628.

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The Roles of Rh and Pt in Electrochemical Toluene Hydrogenation on Rh-Modified Pt Nanoparticle-Loaded Carbon Catalysts

(*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University*) ○Toyoki Imada, Masanobu Chiku, Eiji Higuchi, Hiroshi Inoue

Keywords: Toluene/methylcyclohexane; Electrochemical hydrogenation; Pt nanoparticle; Rh modification; CO-stripping

A couple of toluene (TL)/ methylcyclohexane (MCH) is a promising candidate of hydrogen carriers for large-scale hydrogen storage/transportation. Electrochemical TL hydrogenation (ETH) can achieve energy saving compared to hydrogenation using molecular hydrogen on appropriate catalysts.[1] We found that the Pt_3Ru alloy catalyst had the highest activity among Pt_xRu/C (x = 1, 3, 4) catalysts.[2] Moreover, in our preliminary experiments, it has been found that Rh was the best partner for Pt among Pt_3M (M = Rh, Au, Pd, Ir) alloy catalysts. Recently, we have found that Rh-modified Pt nanoparticle-loaded carbon ($Rh_x/Pt/C$) catalysts showed higher ETH activity than commercial Pt/C catalyst. However, electrochemical surface areas (ECSAs) of Rh and Pt for Pt-Rh binary catalysts could not be individually determined by hydrogen adsorption/desorption peaks because these peaks of Rh and Pt overlapped each other. In this study, we found how to individually evaluate the ECSAs of Rh and Pt and the Rh coverage (θ_{Rh}) by CO-stripping technique, and discussed the effect of the θ_{Rh} on the ETH activity per ECSA of Pt or Rh to clarify the roles of both components.[3]

HAADF-STEM images and EDX line scanning profiles showed that the distribution of Pt and Rh overlapped each other, and pure Rh particles were not observed, suggesting that Rh was modified only on the Pt nanoparticles. The θ_{Rh} initially increased with the Rh/Pt mole ratio of $Rh_x/Pt/C$, but plateaued at about 0.20, whereas the ECSA of Rh continued increasing. Thus, the accumulation of Rh on the modified Rh surfaces occurred prior to the epitaxial growth of Rh on the Pt surface after θ_{Rh} reached about 0.20. Based on LSVs and Tafel plots, the $Rh_x/Pt/C$ electrodes had higher ETH activity than the Pt/C electrode, and addition of adsorbed atomic hydrogen (H_{ads}) to TL was rate-determining for each electrode. The dependence of geometric reduction current density at 0 V vs. RHE ($j_{geo,0}$) on the Rh/Pt mole ratio was similar to that of θ_{Rh}. Platinum showed higher activity in ETH and lower activity in the hydrogen evolution reaction than rhodium.[1] TL is adsorbed on the Rh surface more strongly than on the Pt surface.[4] Therefore, it is concluded that Rh and Pt sites in ETH work for H_{ads} generation and TL adsorption, respectively, and the enhanced catalytic activity is attributed to the increased coupling of H_{ads} generated on the Rh surface and TL adsorbed on the Pt surface at the interface between Pt and Rh.

1) K. Takano, H. Tateno, Y. Matsumura, A. Fukazawa, T. Kashiwagi, K. Nakabayashi, K. Nagasawa, S. Mitsushima, M. Atobe, *Bull. Chem. Soc. Jpn*. **2016**, *89*, 1178. 2) E. Higuchi, Y. Ueda, M. Chiku, H. Inoue, *Electrocatalysis* **2018**, *9*, 226. 3) T. Imada, M. Chiku, E. Higuchi, H. Inoue, *ACS Catal.* **2020**, 10, 13718. 4) X. Jia, W. An, *J. Phys. Chem. C* **2018**, *122*, 21897.

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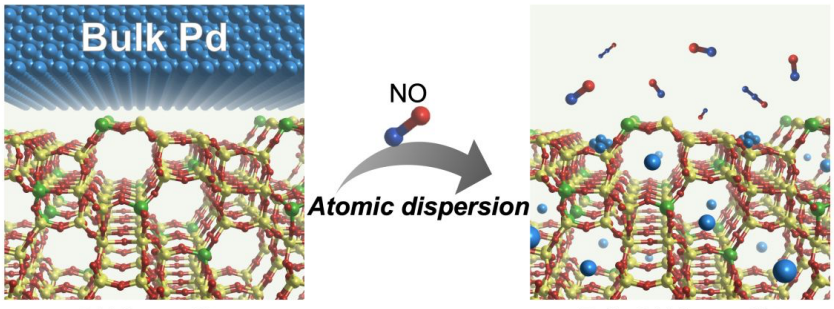
Preparation of high loading Pd-CHA by dispersion of bulk Pd and its NO adsorption/desorption property

([1]*Institute for Catalysis, Hokkaido University*, [2]*Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto*) ○Shunsaku Yasumura,[1] Taihei Ueda,[1] Hajime Ide,[1] Takashi Toyao, [1,2] Zen Maeno[1], Ken-ichi Shimizu[1,2]

Keywords: *Pd loaded CHA zeolite, Passive NOx adsorber, in-situ IR spectroscopy, DFT calculation*

Passive NOx adsorber (PNA) is a promising approach to reduce NOx emission from vehicle engines during a cold-start period (< 200 ˚C) where NOx are trapped at low temperatures and then released at the operating temperature for selective catalytic reduction system (e.g. NH_3-SCR system). Pd-loaded CHA zeolites (Pd-CHA) have recently attracted attention as promising PNAs because of the great hydrothermal stability of CHA zeolite framework and NO adsorption ability of loaded Pd^{2+} cations. However, the preparation of high-loading Pd-CHA is still difficult by a conventional aqueous ion-exchange method due to the strong water solvation of cations, which are too bulky to access the small pores of CHA zeolite.[1)]

In this study, we achieved the preparation of high-loading Pd-CHA based on NO-facilitated atomic dispersion of bulk Pd.[2)] Under a 4% NO flow at 600℃, bulk metal Pd (particle sizes in the 50-100 nm range) outside CHA zeolites effectively disperses, affording Pd^{2+} cations on paired Al sites with concomitant formation of N_2O. The highest Pd loading amount (Pd: 4.1 wt%) was achieved among the previously reported methods. In the NO adsorption/desorption experiment, the desorption temperature for the Pd-CHA with higher loading was higher compared to the one with lower loading (Pd: 0.5 wt%). DFT calculations revealed that the strength of NO adsorption on Pd^{2+} cations depend on the local structure of surrounding paired Al sites.



1) Y. Zheng, L. Kovarik, M. H. Engelhard, Y. Wang, Y. Wang, F. Gao, J. Szanyi, *J. Phys. Chem. C* **2017**, *121*, 15793.
2) S. Yasumura, H. Ide, T. Ueda, Y. Jing, C. Liu, K. Kon T. Toyao, Z. Maeno, K. Shimizu, *JACS Au* **2021**, in press. DOI:10.1021/jacsau.0c00112

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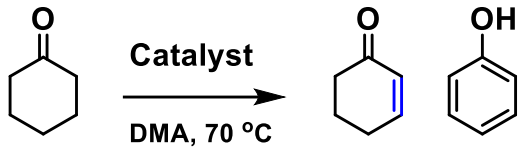
Aerobic Dehydrogenation of Saturated Ketones Using CeO_2-Supported Pd-on-Au Bimetallic Nanoparticle Catalysts

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

Keywords: Aerobic Dehydrogenation; Gold; Palladium; Bimetallic Nanoparticle; Heterogeneous Catalyst

α,β-Unsaturated carbonyl compounds are important in organic synthesis because they are useful as not only bioactive substances but also synthetic intermediates. One of the ideal α,β-unsaturated ketone syntheses is direct α,β-dehydrogenation of saturated carbonyl compounds. The α,β-dehydrogenation was typically performed using a stoichiometric amount of oxidants with the corresponding byproducts. Recently, environmentally-friendly aerobic α,β-dehydrogenations have been developed using homogeneous Pd(II) catalysts.[1,2] However, to our knowledge, there are no reports on selective α,β-dehydrogenation using O_2 in the presence of supported Pd heterogeneous catalysts, although heterogeneously catalyzed systems have many advantages in terms of green chemistry.

In this study, we successfully prepared a dispersed Pd(II)-on-Au bimetallic nanoparticle catalyst supported on CeO_2 (Pd/Au molar ratio = 1/5, Pd/Au/CeO_2), which enabled heterogeneously catalyzed aerobic selective α,β-dehydrogenation of saturated ketones to α,β-unsaturated ketones for the first time.[3] We carried out the dehydrogenation of cyclohexanone, a typical saturated ketone, using supported nanoparticle catalysts (Table 1). While CeO_2-supported Au nanoparticles (Au/CeO_2, entry 2), CeO_2-supported Pd nanoparticles (Pd/CeO_2, entry 3) or physical mixture of Au/CeO_2 and Pd/CeO_2 (entry 4) did not catalyze the aerobic dehydrogenation, Pd/Au/CeO_2 specifically showed a high catalytic activity (TOF = 122 h^{-1} based on Pd) for the α,β-dehydrogenation compared with those of previously reported homogeneous systems (2–3 h^{-1}).[1,2] Besides cyclohexenones, this system has a wide range of substrate scopes; various α,β-unsaturated compounds, including bioactive substances and enaminones, can be synthesized from the corresponding saturated ketones (22 examples).



1a 2a 3a

Entry	Catalyst (mol%)	Yield (%) 2a	3a
1	**Pd/Au/CeO_2 (Pd: 0.6, Au: 3.0)**	**74**	**<1**
2	Au/CeO_2 (3.9)	<1	<1
3	Pd/CeO_2 (4.9)	<1	<1
4	Pd/CeO_2 (2.5) + Au/CeO_2 (2.0)	<1	<1

Table 1. The effect of catalysts

1) M. Tokunaga, S. Harada, T. Iwasawa, Y. Obora, Y. Tsuji, *Tetrahedron Lett.* **2007**, *48*, 6860. 2) T. Diao, S. S. Stahl, *J. Am. Chem. Soc.* **2011**, *133*, 14566. 3) D. Takei, T. Yatabe, X. Jin, T. Yabe, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2020**, *10*, 5057.

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CHA ゼオライト内 In ヒドリドの局所構造解析とエタン脱水素触媒作用

（北大触媒研[1]・京大触媒電池[2]）○前野 禅[1]・安村 駿作[1]・呉 暁鵬[1]・鳥屋尾 隆[1,2]・清水 研一[1,2]

Speciation and Ethane Dehydrogenation Catalysis of Isolated Indium Hydrides in CHA Zeolites ([1]*Institute for Catalysis, Hokkaido University*, [2]*Elements Strategy Initiative for Catalysts and Batteries, Kyoto University*) ○Zen Maeno,[1] Shunsaku Yasumura,[1] Xiaopeng Wu,[1] Takashi Toyao,[1,2] Ken-ichi Shimizu[1,2]

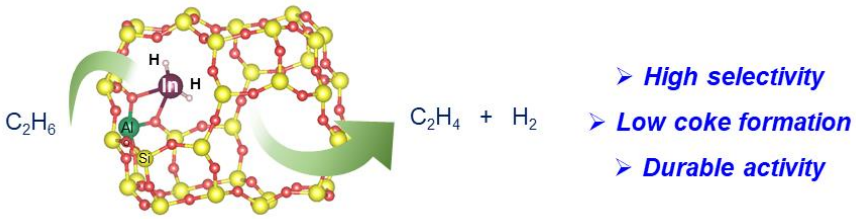
Hydrides in/on solid materials play key roles in heterogeneously-catalyzed hydrogenations and dehydrogenations. However, their characterizations are complicated owing to the complexity and analytical difficulty of solid surfaces. The studies of formation and catalysis of surface hydrides are formidable research subjects.

In this work, we found the formation of isolated In hydrides in CHA zeolite and their unique catalysis for nonoxidative dehydrogenation of ethane by combination of experimental and theoretical studies. The isolated $[InH_2]^+$ ions on Al sites were formed by H_2 treatment of In-exchanged CHA zeolite (In-CHA) at high temperature (> 773 K) as revealed by *in situ* Fourier transform infrared (FTIR) spectroscopy and the vibration analysis using density functional theory (DFT) calculations. The $[InH_2]^+$ ions serve as the catalytically active stie to promote selective ethane dehydrogenation, leading to low coke formation and high durability.

Keywords : Isolated surface hydrides; Indium; CHA zeolite; Ethane dehydrogenation

固体表面に生成する金属ヒドリド種(表面金属ヒドリド)は、固体触媒による水素化・脱水素反応の活性点として重要な表面化学種である。表面金属ヒドリドは一般に不安定であるため、その構造並びに触媒機能の解明は、固体触媒の分野において重要な研究の一つである。

我々は、高温 H_2 雰囲気下にて、In 導入 CHA ゼオライト(In-CHA)に表面ヒドリド種が生成することを見出した。*In situ* 分光と振動数計算から、その構造が$[InH_2]^+$であることが分かった。In-CHA は高選択的なエタン脱水素反応を促進し、90 h 以上の耐久性を示した。速度論解析と遷移状態計算に基づいたメカニズム解析により、ゼオライト内$[InH_2]^+$が高選択的なエタン脱水素反応の活性点であることが示唆された。[1,2)]



1) Z. Maeno, S. Yasumura, X. Wu, M. Huang, C. Liu, T. Toyao, K. Shimizu, *J. Am. Chem. Soc.* **2020**, *142*, 4820.
2) Z. Maeno, X. Wu, S. Yasumura, T. Toyao, Y. Kanda, K. Shimizu, *Catalysts* **2020**, *10*, 807.

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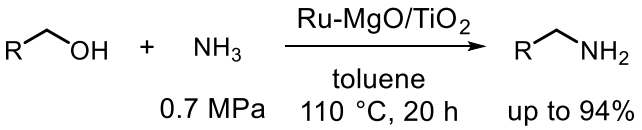
ルテニウム触媒によるアルコールの直接アミノ化における MgO の効果

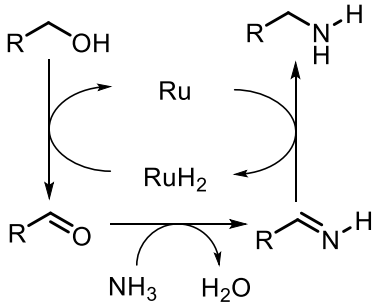
（東工大フロンティア研）○喜多 祐介・桑原 翠・鎌田 慶吾・原 亨和

Effects of MgO on Direct Amination of Alcohols over Ru Catalysts (*Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology*) ○Yusuke Kita, Midori Kuwabara, Keigo Kamata, Michikazu Hara

Direct amination of alcohols requires harsh reaction conditions due to the high stability of alcohols and the low leaving ability of the hydroxy group. Recently, borrowing hydrogen methodology has been extensively explored because of the high atom economy. We developed that the supported Ru catalysts with MgO exhibited high catalytic activity for the direct amination of alcohols with ammonia to produce the corresponding primary amines in high selectivity.[1)] The advantage of the present catalyst is that Ru-MgO/TiO_2 did not require H_2 as opposed to the previously reported heterogeneous Ru catalysts. In this presentation, we will also discuss about the effects of MgO on the catalyst preparation and the reaction.
Keywords : Amination; Primary amine; Ruthenium; Borrowing Hydrogen

１級アミンは様々な変換反応が可能なことから医薬品やポリマーの合成中間体として汎用される化合物である。したがって、１級アミン合成法が数多く開発されている。近年、Borrowing Hydrogen 法と呼ばれるアルコールをアルキル源とするタンデム反応に注目が集まっている。本手法は、アルコールの脱水素、アンモニアとの脱水縮合とイミンの水素化により進行し、水のみを共生成物とすることから環境調和性に優れる。今回、担持ルテニウム触媒に MgO を共担持することにより高い活性と高い１級アミン選択性を示すことを見出した[1)]。既報の担持ルテニウム触媒と異なり水素分子の添加を必要としない長所を有し、バイオマス由来化合物の変換反応にも高活性を示す。MgO の効果について詳細に検討し、ルテニウムの分散度とヒドリド種の水素化能に影響を与えることを明らかとしたので併せて発表する。





1) Effects of ruthenium hydride species on primary amine synthesis by direct amination of alcohols over a heterogeneous Ru catalyst. Y. Kita, M. Kuwabara, S. Yamadera, K. Kamata, M. Hara, *Chem. Sci.* **2020**, *11*, 9884.

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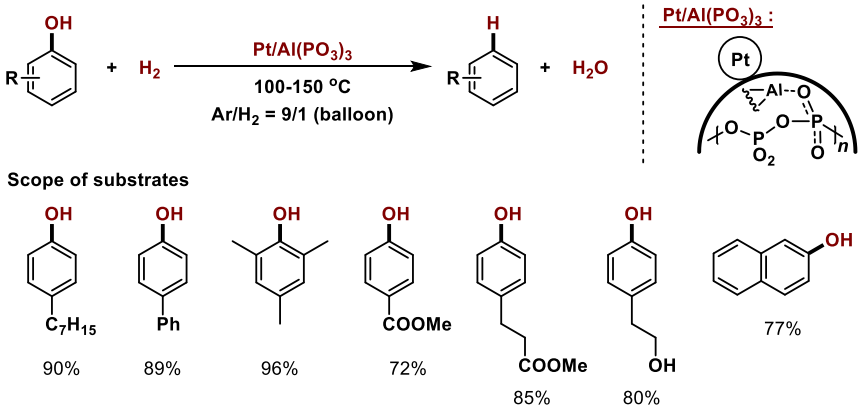
Selective hydrogenolysis of phenols to arenes by metal–support cooperation

([1]*The University of Tokyo*, [2]*Tokyo Metropolitan University*) ○ Rio Tsukimura,[1] Xiongjie Jin,[1] Takeshi Aihara,[2] Hiroki Miura,[2] Tetsuya Shishido,[2] Kyoko Nozaki[1]

Keywords: Hydrogenolysis; Phenols; Platinum; Heterogeneous Catalyst; Aluminum Metaphosphate

Hydrogenolysis of phenols to arenes is useful as a new synthetic route to basic chemical arenes from biomass substances such as lignin. Also, selective hydrogenolysis of functionalized phenols under mild condition is expected to be applied to fine chemical synthesis. Recently, various heterogeneous or homogeneous catalysts[1, 2] have been reported for the hydrogenolysis of phenols to arenes. In general, it is challenging to achieve high conversion by maintaining high selectivity since the C(sp^2)–OH bond is strong and/or the over-reduction to cyclohexanes could be problematic. As far as we know, there have been no reports on widely applicable hydrogenolysis of phenols to arenes with high selectivity under mild condition.

Here we report the use of $Al(PO_3)_3$-supported Pt nanoparticles ($Pt/Al(PO_3)_3$) for the selective hydrogenolysis of phenols to afford arenes under relatively low temperature (<150 °C) and ambient pressure (Ar/H_2 = 9/1, 1 atm). $Pt/Al(PO_3)_3$ could be applicable to various kinds of structurally diverse phenols (including sterically highly demanding phenols and lignin model compounds), giving the corresponding arenes in moderate to high yields. The catalyst was truly heterogeneous and could be reused several times. Mechanistic studies suggested that the metaphosphate anion in $Al(PO_3)_3$ contributes to the high efficiency of $Al(PO_3)_3$ support, likely *via* formation of the surface phenol phosphate species to facilitate the C(sp^2)–O bond cleavage. The present catalyst system could find a broad application in bio-refinery and fine chemical synthesis.



1) M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates, M. R. Rahimpour. *Energ. Environ. Sci.* **2014**, *7*, 103. 2) Z. Qiu, C.-J. Li. *Chem. Rev.* **2020**, *120*, 10454.

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[A12-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Tohru Wada, Mio Kondo, Hisashi Shimakoshi

Sun. Mar 21, 2021 9:00 AM - 11:20 AM Room 12 (Online Meeting)

[A12-3am-01] Photochemical Water Oxidation Reaction Catalyzed by a Doubly N-Confused Hexaphyrin Dinuclear Cobalt Complex

○Takashi Nakazono[1], Tohru Wada[1] (1. Rikkyo University)

9:00 AM - 9:20 AM

[A12-3am-02] Alkane Oxidation with m-CPBA Catalyzed by B_{12} Complex

○Cheng Jiamin[1], Yoshio Hisaeda[1], Hisashi Shimakoshi[1] (1. Kyushu university)

9:20 AM - 9:40 AM

[A12-3am-03] Substituent Effects of Bipyridine Ligands on Oxygen Reduction Reaction Catalyzed by Dinucelar Cobalt Complexes

○Hiroaki Arima[1], Takashi Nakazono[1], Tohru Wada[1] (1. Rikkyo University)

9:40 AM - 10:00 AM

[A12-3am-04] Catalytic Hydrodehalogenation of Aryl Halides Mediated by a Long-Range Metal-Ligand Cooperation of Cobalt(I) Complexes Bearing a Tetradentate PNNP Ligand

○Nai-Yuan Jheng[1,2], Yuki Naganawa[1], Yumiko Nakajima[1,2] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. University of Tsukuba)

10:00 AM - 10:20 AM

[A12-3am-05] Photochemical CO_2 Reduction and Formic Acid Dehydrogenation Promoted by a Pentanuclear Cobalt Complex

○Takuya Akai[1], Yutaka Saga[1], Mio Kondo[1], Shigeyuki Masaoka[1] (1. Osaka University)

10:20 AM - 10:40 AM

[A12-3am-06] Isotope-labeling Studies on Water Oxidation Reaction Catalyzed by a Monocobalt Polymolybdate

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

10:40 AM - 11:00 AM

[A12-3am-07] Electrochemical Polymerization Provides a Function-Integrated System for Water Oxidation

○Hikaru Iwami[1,2,3], Mio Kondo[1], Shigeyuki Masaoka[1] (1. Osaka Univ., 2. SOKENDAi, 3. IMS)

11:00 AM - 11:20 AM

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Photochemical Water Oxidation Reaction Catalyzed by a Doubly N-Confused Hexaphyrin Dinuclear Cobalt Complex

([1]*Department of Chemistry, College of Science, Rikkyo University*)
○Takashi Nakazono, Tohru Wada
Keywords: Water Oxidation, Doubly N-Confused Hexaphyrin, Cobalt Complex

The water oxidation reaction is a four-electron process; therefore, it is important that water oxidation catalysts (WOCs) can undergo multielectron transfer reactions. WOCs having redox-active ligands with a large π-conjugated system such as Co porphyrins are known as highly active water oxidation catalysts.[1,2] Thus, we were interested in evaluating the benefits of the unique structural and electronic features of a related binuclear cobalt complex to develop WOCs with enhanced performance. Doubly N-confused hexaphyrin (DNCH), which is a kind of expanded porphyrin, is a large macrocyclic ligand with a Hückel aromatic 26π system that can accommodate two metal ions. In this study, we report water oxidation activity of a doubly N-confused hexaphyrin dinuclear cobalt complex (Co_2DNCH).

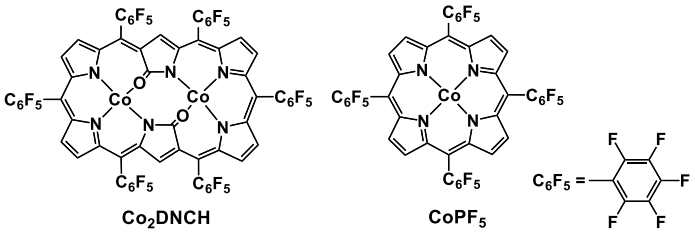


Fig. 1 Strictures of Co_2DNCH and $CoPF_5$.

The water oxidation activity of Co_2DNCH was investigated using $[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ based photosystem. By photoirradiation with visible light (430 nm < λ <510 nm), oxygen was obtained maximum with turnover number (TON) = 1200, turnover frequency (TOF) = 3.9 s^{-1} (Fig. 2).[3] Under the same conditions, $CoPF_5$, which has the same aryl groups as those in Co_2DNCH, also evolved oxygen with TOF = 0.051 s^{-1} and TON = 83. Thus, we revealed that Co_2DNCH is highly efficient WOC. The study of electrochemical water oxidation behavior will also be discussed.

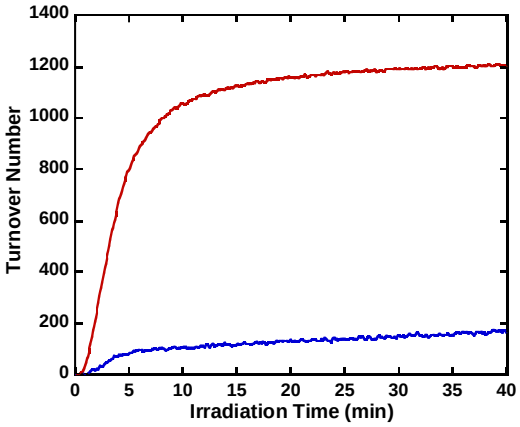


Fig. 2 Photochemical oxygen evolution from a 9:1 water/acetone-d_6 mixture. (Red) Co_2DNCH, (Blue) $CoPF_5$

1) T. Nakazono, A. R. Parent, K. Sakai, *Chem. Eur. J.*, **2015**, *21*, 6723.
2) T. Nakazono, K. Sakai, *Dalton Trans.*, **2016**, *45*, 12649.
3) T. Nakazono, T. Wada, *Inorg. Chem.*, **2021**, ASAP.

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Alkanes Oxidation with *m*-CPBA Catalyzed by B_{12} Complex

([1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University*) ○Cheng Jiamin,[1] Yoshio Hisaeda,[1] Hisashi Shimakoshi[1]

Keywords: Alkane Oxidation; Catalysis; B_{12} Complex; *m*-CPBA; Silica-gel

Alkane oxidation to value-added alcohol and ketone is important for industrial application. Thus, the possibility of converting alkane into alcohols, ketones etc., is a challenging goal in contemporary catalytic chemistry.[1] In previous reports, due to stable nature of C-H bond, higher activation energy is required to carry out this reaction at high temperature. Due to very less solubility of oxygen, high pressure is also desired.[2] In fact, modern industrial methods usually require high pressure and temperature when using soluble cobalt as catalyst. In this work, we first synthesized B_{12} complex as homogeneous catalyst (Fig. 1a) and then immobilized it on silica particles to form heterogenous catalyst (Fig. 1b). The alkanes oxidation reaction was performed in mild conditions under air, using *m*-CPBA as oxidant, catalyzed by homogeneous and heterogenous catalyst. For the model substrate of cyclohexane, total turnover numbers and yields of over 147 and 36% were provided respectively in homogenous (Fig. 2a), over 1200 and 24% were provided respectively in heterogenous (Fig. 2b). It exhibits a good catalytic performance and is the first reported reference for extensive application of vitamin B_{12} in catalytic oxidation reaction. And more kinds of alkane substrates will be checked in the future work.[3]

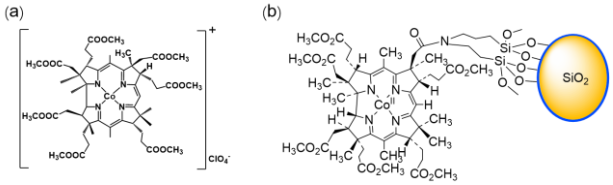


Fig. 1. (a) Structure of $Co^{II}B_{12}$, (b) structure of $Co^{II}B_{12}$-SiO_2.

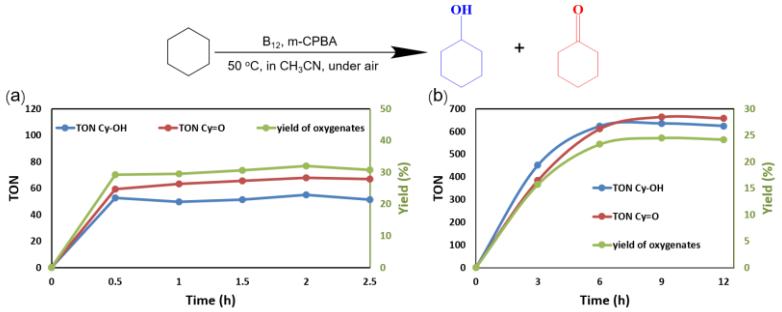


Fig. 2. Time profiles of TON and yield in the (a) $Co^{II}B_{12}$, (b) $Co^{II}B_{12}$-SiO_2 catalyst system.

1) Qiu, Y.; Hartwig, J. F., *J. Am. Chem. Soc.* **2020,** *142* (45), 19239-19248.

2) Yuan, H. X.; Xia, Q. H., et al., *Applied Catal. A: General* **2006,** *304*, 178-184.

3) Ucoski, G. M.; Pinto, V. H. A., et al., *Microporous and Mesoporous Materials* **2018,** *265*, 84-97.

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Substituent Effects of Bipyridine Ligands on Oxygen Reduction Reaction Catalyzed by Dinuclear Cobalt Complexes

(*Department of Chemistry, College of Science, Rikkyo University*) ○ Hiroaki Arima, Takashi Nakazono, Tohru Wada

Keywords: Oxygen Reduction Reaction; Cobalt Complex; Catalyst

Four-electron oxygen reduction reaction (4e$^-$-ORR) is a key step of natural and artificial energy conversion systems. In nature, cytochrome *c* oxidase containing Fe-Cu dinuclear complex as an active center efficiently catalyzes 4e$^-$-ORR in the respiration process. Therefore, the studies of ORR catalyst based on transition-metal complex has been of interest over the past few decades.[1] Previously, we reported dinuclear cobalt polypyridyl complexes bridged by xanthene (**1**), anthraquinone and anthracene[2] as effective 4e$^-$-ORR catalysts. Among them, **1** indicated the highest selectivity (96%) and TOF (5.6×10^2 s^{-1}) for chemical 4e$^-$-ORR. However, **1** required relatively large overpotential of 630 mV for electrochemical ORR.

In this paper, we discuss effects of bipyridine substituents on electrochemical ORR catalyzed by dinuclear cobalt complexes bridged by 1,8-bis(terpyridyl)xanthene (**1**-**6**, Figure 1). Linear sweep voltammetry (LSV) using the complex catalyst modified on glassy carbon (GC) as a working electrode in O_2-saturated phosphate buffer (pH 1.0) showed a catalytic wave at the potential under 0.27 (**1**), 0.24 (**2**), 0.27 (**3**), 0.26 (**4**), 0.23 (**5**), 0.32 (**6**) V vs. SCE (Figure 2). The onset potantial of **6** was more positive than those of **1**–**5**, suggesting that overpotential of ORR was affected by proton relay rather than electron-donating and -withdrawing effects of bipyridine ligands.

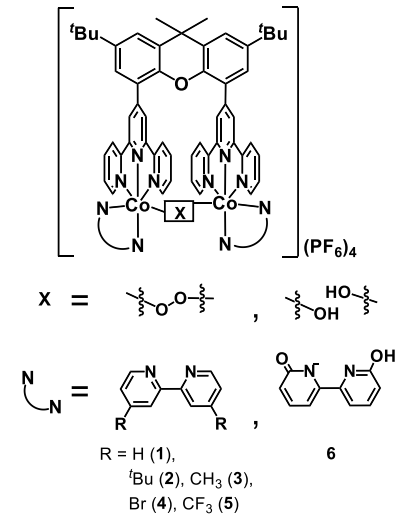


Figure 1. Structures of the xanthene-bridged dinuclear cobalt polypyridyl complexes.

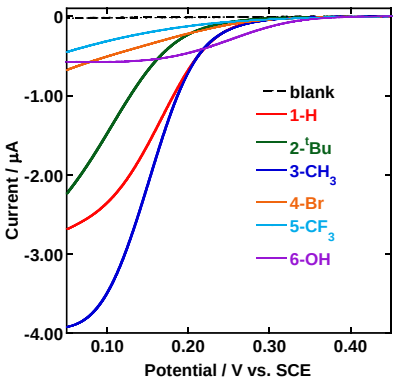


Figure 2. LSVs using a GC modified with complex catalysts (3.0 nmol cm^{-2}) in O_2-saturated phosphate buffer (pH 1.0). Scan rate: 10 mV s^{-1}.

References

1) M. L. Pegis, C. F. Wise, D. J. Martin, J. M. Mayer, *Chem. Rev.* **2018**, *118*, 2340.
2) T. Wada, H. Maki, T. Imamoto, H. Yuki, Y. Miyazato, *Chem. Commun.* **2013**, *49*, 4394.

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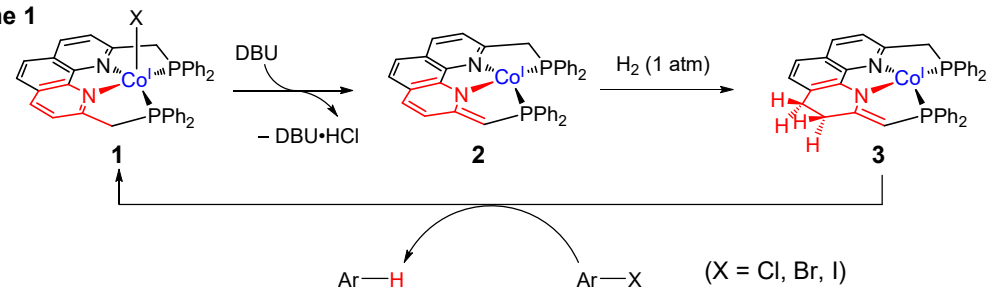
Catalytic Hydrodehalogenation of Aryl Halides Mediated by a Long-Range Metal-Ligand Cooperation of Cobalt(I) Complexes Bearing a Tetradentate PNNP Ligand

([1]*Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST),* [2]*Graduate School of Pure and Applied Sciences, University of Tsukuba*) ○Nai-Yuan Jheng,[1,2] Yuki Naganawa,[1] Yumiko Nakajima[1,2]
Keywords: Cobalt; Metal-ligand Cooperation; PNNP Ligand; Hydrogen Activation

Metal-ligand cooperation (MLC) is recognized as an important key step for construction of various catalytic reactions.[1] In this study, an intrinsic long-range MLC was demonstrated using a well-defined cobalt(I) system supported by a tetradentate PNNP ligand (2,9-bis((diphenylphosphaneyl)methyl)-1,10-phenanthroline).[2]

PNNP-supported Co(I) chloro complex [CoCl(PNNP)] (**1**) easily underwent deprotonation on the treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in polar solvents to form a four-coordinate-cobalt(I) complex coordinated with an asymmetrical PNNP' ligand with a dearomatized phenanthroline backbone, [Co(PNNP')] (**2**) (Scheme 1). Complex **2** cleaved a H–H bond to form **3**, in which two H-termini were added to the endocyclic double bond of the PNNP backbone. Complex **3** reacted with chlorobenzene to give **1** as well as benzene. Thus, an unprecedented long-range MLC, where the PNNP-backbone behaves as a hydrogen reservoir, was demonstrated. By using this reaction strategy, catalytic hydrodehalogenation of aryl halides with H_2 (1 atm) was performed. The reaction efficiently proceeded in the presence of **1** (2 mol%) and DBU (2 equiv), and a broad substrate scope (> 40 entries) was achieved in good to excellent yields. Radical clock study supported the occurrence of the homolysis of C–X bonds during the reaction. The reaction was accelerated by introducing electron-withdrawing substituents to aryl halides. A series of kinetic parameters showed a good Hammett correlation with the σ_p values of substituents ($\rho = 0.86$). Overall, the single-electron transfer mechanism was suggested.

Scheme 1



1) Milstein, D. *et al. Angew. Chem. Int. Ed*. **2015**, *54*, 12236-12273. 2) Nakajima, Y. *et al. Dalton Trans.* **2020**, *49*, 14592-14597.

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Photochemical CO_2 Reduction and Formic Acid Dehydrogenation Promoted by a Pentanuclear Cobalt Complex

([1]*Graduate School of Engineering, Osaka University,* [2]*JST PRESTO*) ○Takuya Akai,[1] Yutaka Saga,[1] Mio Kondo,[1,2] Shigeyuki Masaoka[1]

Keywords: Multinuclear Metal Complex; Photochemical Reaction; CO_2 Reduction; Formic Acid Dehydrogenation

To solve energy and environmental problems, demand for the production of hydrogen gas in a clean manner is increasing. In this context, formic acid can be regarded as an excellent hydrogen career, and the production of formic acid from earth-abundant source and the dehydrogenation of formic acid to produce hydrogen have attracted considerable attention in recent years.

In this work, we developed a novel pentanuclear cobalt complex ($[Co_5OH(bpp)_6]^{3+}$, **Co5**, Hbpp = 3,5-bis(2-pyridyl)pyrazole, **Fig. 1**) and investigated it catalytic activity for the production and dehydrogenation of formic acid. Visible light irradiation of a solution containing **Co5**, $Ir(ppy)_3$ (Hppy = 2-phenylpyridine) as a photosensitizer and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1*H* -benzo[d]imidazole) as a sacrificial electron donor under CO_2 resulted in the formation of carbon monoxide and formic acid.[1] Furthermore, irradiation of visible light to a solution containing **Co5**, $Ir(ppy)_3$, BIH and formic acid (500 *eq. vs.* **Co5**) under Ar atmosphere resulted in the formation of H_2 (**Fig. 2**). Therefore, we demonstrate that **Co5** works as a bicatalyst that promote both photochemical CO_2 reduction and formic acid dehydrogenation.

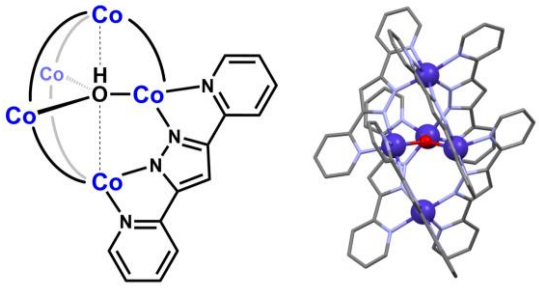


Fig. 1 Structure of the pentanuclear cobalt complex (**Co5**).

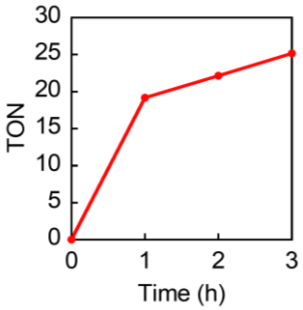


Fig. 2 Photochemical H_2 evolution in the presence of **Co5**, $Ir(ppy)_3$, BIH, and formic acid.

1) T. Akai, M. Kondo, S. K. Lee, H. Izu, T. Enomoto, M. Okamura, Y Saga, S. Masaoka, *Dalton Trans.*, **2020**, *49*, 1384.

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Isotope-labeling Studies on Water Oxidation Reaction Catalyzed by a Monocobalt Polymolybdate

(*Dept. Chem., Kyushu Univ.*) ○Natsuki Taira, Kosei Yamauchi, Ken Sakai
Keywords: Water Oxidation Catalysts; Isotope-labeling Experiments; Polyoxometalates; Cobalt Complexes; Artificial Photosynthesis

The rate-determining step of water oxidation (WO) has been considered as either the inter/intramolecular O-O bond coupling of two metal-oxyl radicals (I2M) or intermolecular O-O coupling via the water nucleophilic attack (WNA) to the metal-oxo species.[1] Polyoxometalates (POMs) are known to be highly active and robust WO catalysts (WOCs) owing to their carbon-free framework. However, their detailed mechanism has not been clarified due to their relatively large size leading to afford various structures during the catalysis.

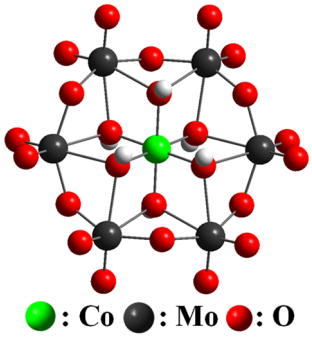
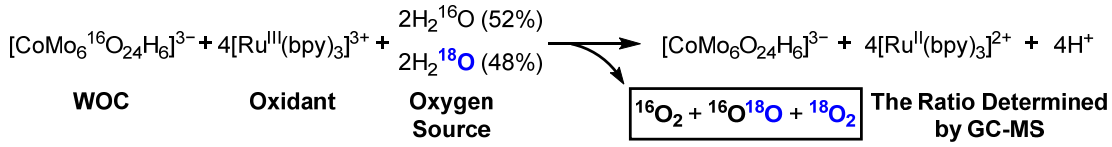


Figure 1. Structure of **Co-POM-Mo**.

In this study, we investigated the mechanism of WO catalyzed by Anderson-type polyoxometalate (**Co-POM-Mo**, **Figure 1**)[2] by reacting it with $[Ru^{III}(bpy)_3]^{3+}$ as an oxidant in an aqueous borate buffer solution. Kinetic traces for $[Ru^{II}(bpy)_3]^{2+}$ generation were spectrophotometrically observed, and the rate constants of WO were determined. Interestingly, the analyses of Eyring plots show a positive activation entropy in any fitting models, suggesting that the rate-determining O-O bond formation takes place in an intramolecular fashion, which must be clearly distinguished from the intermolecular I2M and WNA pathways previously proposed for other WOCs. The isotope-labeling experiments using ^{17}O-NMR were performed to determine the rate for the oxygen exchange with bulk water in **Co-POM-Mo**. The rate constant obtained (k_{ex} = 2.9 × 10^{-5} [s^{-1}]) clearly shows that its exchange is negligible during the analysis of WO. Then, O_2 evolved from 48% ^{18}O-enriched aqueous borate buffer solution was analyzed by the glovebox/GC-MS system developed in our group (see **Scheme 1**). The results obtained are in good agreement with the isotope distribution expected for the intramolecular O-O bond formation within the **Co-POM-Mo** core. Importantly, the DFT results also support the proposed mechanism.



Scheme 1. Isotope-labeling experiments conducted in this study.

1) A. R. Parent, T. Nakazono, Y. Tsubonouchi, N. Taira and K. Sakai, *Adv. Inorg. Chem.*, **2019**, 74, 197. 2) S. Tanaka, M. Annaka and K. Sakai, *Chem. Commun.*, **2012**, 48, 1653.

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Electrochemical Polymerization Provides a Function-Integrated System for Water Oxidation

([1]*Graduate School of Engineering, Osaka University*, [2]*Institute for Molecular Science*, [3]*The Graduate University for Advanced Studies (SOKENDAI)*, [4]*JST PRESTO*) ○ Hikaru Iwami,[1,2,3] Mio Kondo,[1,4] Shigeyuki Masaoka[1]

Keywords: Carbazole; Electrocatalyst; Water oxidation; Cobalt; Ruthenium

Due to the increased demand for a sustainable society, the production of clean chemical fuels from abundant resources is highly required in recent years. Water oxidation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is considered a key process in such a scheme. In nature, the reaction is efficiently catalyzed by a metal-complex based catalytic center, which is surrounded by hole-transporting amino acid residues. In other words, the catalytic center surrounded by hole transporters is essential to achieve efficient water oxidation.

Inspired by the natural system, we have designed two kinds of novel catalyst modules bearing carbazole moieties (Figure 1, left). These modules were polymerized by electrochemical oxidation to afford the materials with biscarbazole moieties (**poly-1** and **poly-2**). Electrochemical impedance analysis indicated that the charge transfer resistance of the polymers is substantially lowered compared to the relevant systems without hole-transporting biscarbazole moieties. Moreover, both **poly-1** and **poly-2** can catalyze water oxidation in phosphate buffer (pH = 7) and O_2 was continuously evolved over 1 h of electrolysis. Notably, the catalytic activity is drastically suppressed in the absence of biscarbazole moieties. These results clearly demonstrated that the integration of catalytic center and hole transporter can be a powerful strategy to construct highly active catalytic system for water oxidation (Figure 1, right).[1] Catalytic properties of **poly-2** will be also discussed in the presentation.

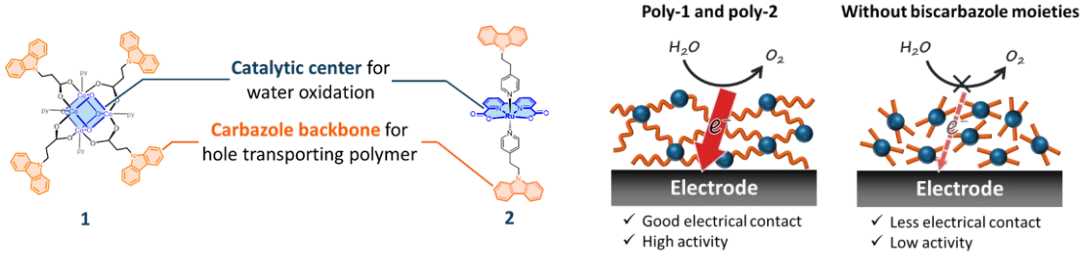


Figure 1 (left) Structures of catalyst modules investigated in this study. (right) Scheme of the comparisons of properties between polymer system and discrete molecular system.

1) H. Iwami, M. Okamura, M. Kondo, S. Masaoka, *Angew. Chem. Int. Ed.* **2020**, *in press*. DOI: 10.1002/anie.202015174.

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[A13-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair:Wataru Kosaka, Koji Nakabayashi, Takuya SHIGA

Sun. Mar 21, 2021 9:00 AM - 11:40 AM Room 13 (Online Meeting)

[A13-3am-01] Syntheses and Properties of Mixed-valence One-dimensional Assembles Consisting of Polyoxometalate and Tetranuclear Platinum Complexes

○Kazuhiro Uemura[1], Haruka Hasegawa[1], Atsushi Takamori[2] (1. Faculty of Engineering, Gifu University, 2. Graduate School of Engineering, Gifu University)

9:00 AM - 9:20 AM

[A13-3am-02] Magnetic phase switch accompanied with the suppression of structural disorder by Gas-adsorption in a layered assembly of paddlewheel [Ru2] units and TCNQ

○Yoshie Hiwatashi[1], Wataru Kosaka[1,2], Jun Zhang[2], Hitoshi Miyasaka[1,2] (1. Department of Chemistry, Graduate School of Science, Tohoku University, 2. Institute for Materials Research, Tohoku University)

9:20 AM - 9:40 AM

[A13-3am-03] Elucidation of ion insertion/desertion behavior using one-dimensional lanthanoid-phthalocyaninato double-decker complexes

○Tetsu Sato[1], Keiichi Katoh[2], Brian Breedlove[1], Shinya Takaishi[1], masahiro yamashita[1] (1. The Univ. of Tohoku, 2. The Univ. of Josai)

9:40 AM - 10:00 AM

[A13-3am-04] Octacyanidotungstate-based Thermofluorochromic Magnets

○Olaf Stefanczyk[1], Kunal Kumar[1], Shin-ichi Ohkoshi[1] (1. The Univ. of Tokyo)

10:00 AM - 10:20 AM

[A13-3am-05] Cyanido-Bridged Ho^{III}-M^{III} (M = Co, Rh, and Ir) Dinuclear Molecules Showing Slow Magnetic Relaxation and Luminescence Thermometry Based on Re-Absorption Effect

○Junhao Wang[1], Jakub Zakrzewski[2], Mikolaj Zychowicz[2,3], Veacheslav Vieru[3,4], Liviu Chibotaru[3], Koji Nakabayashi[1], Szymon Chorazy[2], Shin-ichi Ohkoshi[1] (1. the University of Tokyo, 2. Jagiellonian University, 3. Katholieke Universiteit Leuven, 4. Maastricht University)

10:20 AM - 10:40 AM

[A13-3am-06] Magnetic circularly polarized luminescence (MCPL) from iridium (Ir) and platinum (Pt) complexes by applying an external magnetic field

○Kana Matsudaira[1], Junichi Hotei[2], Ken-ichi Yamashita[3], Yoshirou Kondou[4], Satoko Suzuki[4], Shigeyuki Yagi[2], Michiya Fujiki[5], Yoshitane Imai[1] (1. Kindai University, 2. Osaka Prefecture University, 3. Osaka University, 4. JASCO, 5. NAIST)

10:40 AM - 11:00 AM

[A13-3am-07] Toward Iridium Complexes with High Oxidation States through All-carbon Ligated Pincer Ligand-type Aryl-substituted Dipyrido-annulated Carbenes

○Kazuki Nakanishi[1], Rong Shang[1], Masaaki Nakamoto[1], Yohsuke Yamamoto[1], Hiroto Yoshida[1], J. Oscar C. Jimenez-Halla[2] (1. Graduated School of Advanced Science and

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Engineering, Hiroshima University, 2. Division of Natural and Exact Sciences, University of Guanajuato,）

11:00 AM - 11:20 AM

[A13-3am-08] Synthesis and Characterization of N-Fused Porphyrin Iridium Complexes

○Jibin Alex Abraham[1], Masatoshi Ishida[1], Hiroyuki Furuta[1] （1. Kyushu University）

11:20 AM - 11:40 AM

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ポリオキソメタレートと白金四核錯体からなる混合原子価一次元集積体の合成と物性

(岐阜大工[1]・岐阜大院工[2]) ○植村 一広[1]・長谷川 遥[1]・高森 敦志[2]

Syntheses and Properties of Mixed-valence One-dimensional Assembles Consisting of Polyoxometalate and Tetranuclear Platinum Complexes ([1]*Faculty of Engineering, Gifu University*, [2]*Graduate School of Engineering, Gifu University*) ○Kazuhiro Uemura,[1] Haruka Hasegawa,[1] Atsushi Takamori[2]

The Kegin-type or Dawson-type polyoxometallates were mixed with the one-dimensional amidate bridged platinum tetranuclear complexes to afford one-dimensional assembles, where each was alternately aligned. The crystal structures and various physical measurements revealed that oxidation state of metals in these assembles are mixed-valence. We will show the results of measurements such as electrical conductivity and magnetic susceptibility measurements, discussing their band structures and physical properties.

Keywords : Polyoxometalate; Platinum Blue; One-dimensional; Mixed-valence; Conductivity

アミダート架橋ハーフランタン型白金複核錯体が二量化した四核錯体は、約半世紀前に構造決定された白金ブルーとよばれ、4 つの白金 dz^2 軌道に非局在化した不対電子をもつ。我々は、この白金四核錯体を異種金属結合を用いて一次元状に並べ、その固体物性を追跡してきた。[1] 今回、白金ブルー同様に混合原子価相をとりえるポリオキソメタレート（POM）を用いて一次元状に連結された集積体を合成し、その固体物性を追跡したので報告する。POM に、ケギン型の$[Mo_{12}PO_{40}]^{3-}$、もしくはドーソン型の$[Mo_{18}P_2O_{62}]^{6-}$を選び、白金四核錯体の$[Pt_2(piam)_2(NH_3)_4]_2X_4$（piam = pivalamidate, X = アニオン）と混合すると、青黒色の$[\{Mo_{12}PO_{40}\}\{Pt_2(piam)_2(NH_3)_4\}_2]_n \cdot 6n Me_2CO$、もしくは、緑色の$(NH_4)_n[\{Mo_{18}P_2O_{62}\}\{Pt_2(piam)_2(NH_3)_4\}_2]_n \cdot 3n MeCN$ の単結晶が得られた。単結晶 X 線構造解析の結果、いずれも、POM と白金ブルーが繰り返し並んだ一次元状錯体であることがわかった。当日は、電気伝導度測定と磁化率測定を含め、物性測定の結果を議論する予定である。

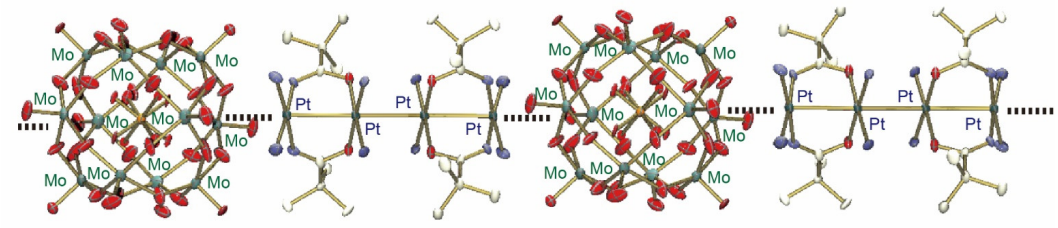


図 1. ケギン型$[Mo_{12}PO_{40}]$と白金四核錯体からなる一次元集積体の構造.

1) K. Uemura, *Dalton Trans.*, **2017**, *46*, 5474–5492.

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Magnetic phase switch accompanied with the suppression of structural disorder by Gas-adsorption in a layered assembly of paddlewheel [Ru_2] units and TCNQ

([1]*Department of Chemistry, Graduate School of Science, Tohoku University*, [2]*Institute for Materials Research, Tohoku University*, [3]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University*)
○Yoshie Hiwatashi,[1] Wataru Kosaka,[1,2] Y Jun Zhang,[2,3] Hitoshi Miyasaka,[1,2]
Keywords: Metal-organic framework; Ferrimagnet; Gas-responsive magnetic property; Paddlewheel-type diruthenium complex; Layered magnet

Charge-transferred metal-organic frameworks composed of electron-donor (D) and -acceptor (A), called as D/A-MOFs, have been attracted much attention because of their high potential applications for tunable electronic/magnetic materials. While the uniformity of pores is usually drawn attention in the class of MOFs, the movability of organic ligands in sufficient interstitial pore spaces, which sometimes results in static/dynamic structural disorders, is one of the intriguing characteristics of MOFs. Such structural disorders are often affected by the guest accommodation, which may cause a modulation of electronic state, consequently physical properties, in the case of D/A-MOFs.

Here, we investigated CO_2 responsibility of magnetic properties of the [Ru_2]-TCNQ layered magnet with T_C = 56 K, {[Ru_2(*o*-$ClPhCO_2$)$_4$]$_2$[$TCNQ(OMe)_2$]} (**1**, *o*-$ClPhCO_2^-$ = *ortho*-chlorobenzoate), because **1** possesses a static structural disorder at the Cl atom on the benzoate moiety, which could be an origin of partial charge fluctuations, although the charge-distribution was basically classified into the one-electron-transferred ionic state (1e-I) formulated as $[Ru_2]^{0.5+}$–$[TCNQ(OMe)_2]^{\bullet-}$–$[Ru_2]^{0.5+}$.[1]

Single-crystal X-ray diffraction (SCXRD) analyses of **1** under CO_2 revealed that the disorder in **1** was disappeared by accommodating one molar amount of CO_2 in a small pore of **1**, forming **1⊃CO₂** (Fig. 1a, b). Compound **1⊃CO₂** also has the 1e-I state, as well as **1**. Magnetic measurements revealed that T_C largely increased to 100 K under CO_2 sorption from 56 K of **1** (Fig. 1c). The IR spectra for **1** at P_{CO2} = 100 kPa revealed that the CN stretching peak at the lowest energy in **1** is disappeared in **1⊃CO₂**, indicating disappearing the partially presented diamagnetic $TCNQ(OMe)_2^{2-}$ species (Fig. 1d). This fact indicates that the electronic state of **1** is not an exact 1e-I state, but is slightly fluctuated as a (1+δ)e-I state. Thus, a drastic increase of T_c was achieved by the suppression of charge fluctuation (δ), which cloud be associated with the structural disorder suppressed by the CO_2 adsorption.

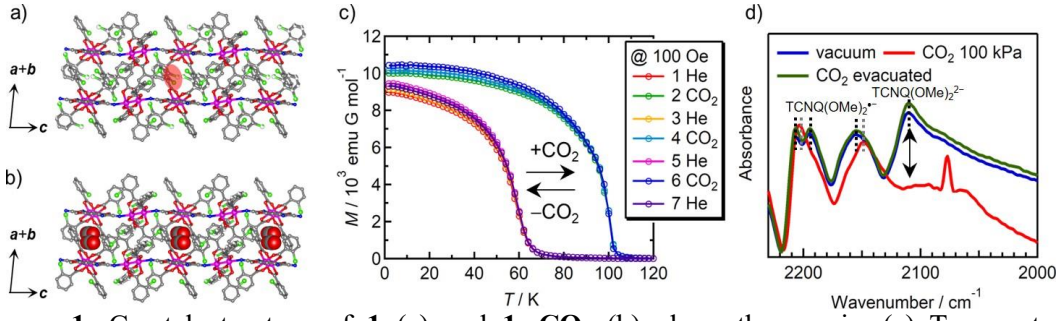


Figure 1. Crystal structure of **1** (a) and **1⊃CO₂** (b) along the *a*-axis. (c) Temperature dependence of magnetization at 100 Oe of **1** (under He) and **1⊃CO₂**. (d) IR spectra under vacuum (blue), 90 kPa CO_2 (red), and evacuated after CO_2 adsorption (green) (200 K).

1) N. Motokawa *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 11943–11951.

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Elucidation of ion insertion/desertion behavior using one-dimensional lanthanoid-phthalocyaninato double-decker complexes

([1]*Graduate School of Science, Tohoku University,* [2]*Josai University*) ○Tetsu Sato,[1] Brian K. Breedlove,[1] Shinya Takaishi,[1] Masahiro Yamashita[1], Keiichi Katoh[2]

Keywords: Phthalocyaninato complex; Lanthanoid; Double-decker; Oxidative insertion; Cyclic voltammetry

Molecular crystals composed of phthalocyaninato (Pc) complexes arranged one-dimensionally have various oxidation numbers depending on the central metal and counter anion. In recent years, a neutral state of a 1-D phthalocyaninato complex (LiPc) has been reported.[1] These crystals have one-dimensional pores with diameters of about 4 Å next to the column of LiPc molecules. Researchers have focused on controlling the physical properties of these compounds by inserting gas molecules or ions into the pores.[2]

In our laboratory, we have reported a double-decker complex (**Figure 1**) with lanthanoid (Ln) ions sandwiched between two Pc ligands and investigated the galvanomagnetic properties of solid crystals. By using electrolytic oxidation, we have obtained a one-dimensional array crystal ($[DyPc_2]I_x$: I = triiodide) suitable for measuring the physical properties. Since robust 1-D pores form after removing I_3^- ions and the crystallinity and electrical conductivity are maintained under ambient conditions, we investigated the possibility of reversible ion insertion by using a chemical/electrochemical method. For these studies, a mixture of Nafion and $[DyPc_2]I_x$ was applied to the working electrode, and solid CV was performed. In cyclic volammograms, oxidation waves were observed derived from the motion of anion (ClO_4^-) (**Figure 2**). In addition, similar waves were observed when a single crystal was attached to the electrode surface, confirming the insertion of ions obtained from the X-ray structural analysis and SEM-EDX. In this presentation, we will report the detailed structure and the electrochemical properties related to anion doping.

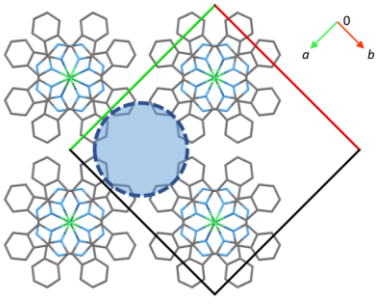


Figure 1 1-D pore of single crystal

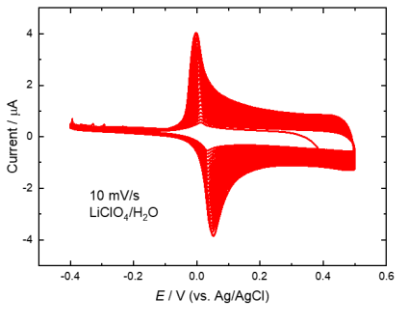


Figure 2 Cyclic voltammogram of single crystal

1) M. Nishi et al., *CrystengComm*., **2020**, *22*, 7528 2) Y. Miyoshi et al., *Chem. Commun*., **2014**, *16* , 9266

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Octacyanidotungstate-based Thermofluorochromic Magnets

([1]*Department of Chemistry, School of Science, The University of Tokyo*) ○ Olaf Stefanczyk,[1] Kunal Kumar,[1] Shin-ichi Ohkoshi,[1]

Keywords: Molecular Magnetism; Fluorescence; Thermochromism; Solvatochromism; Functional Materials

The design of multifunctional materials combining several diverse physicochemical phenomena is one of the greatest goals in chemistry. Presently, we witnessed the galloping progress in the development of functional molecular magnet exhibiting non-trivial magnetic properties, *e.g.*, a long-range magnetic ordering with high critical temperatures for three-dimensional cyanide-bridged networks[1] or a slow magnetic relaxation for lanthanide(III) single ion magnets,[2] and evolution of optical properties (*e.g.*, fluorescence, absorbance) tuned by external physical (*e.g.*, temperature, pressure) or chemical stimuli (*e.g.*, solvent and gas molecules).[3] These assemblies can be applied for the construction of new detectors, as well as model systems to broaden our knowledge about magnetostructural correlations and cross-effects in such materials.

In this presentation, we will introduce a comprehensive studies for octacyanidotungstate salts combining the alternation of long-range antiferromagnetic ordering temperatures, and diverse chromic effects: hygrochromism (the change of color in different relative humidity atmospheres), thermochromism (the alteration of color at diverse temperatures), and thermofluorochromism (the simultaneous modification of luminescence and color at varied temperatures).

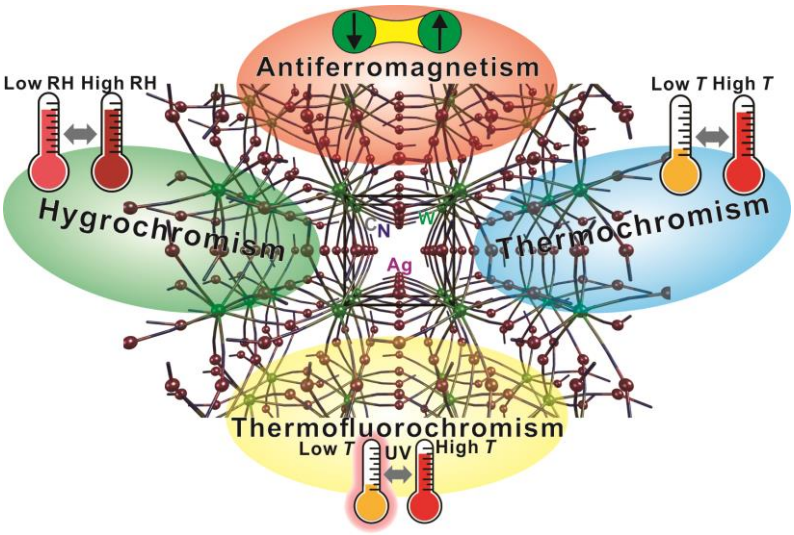


Figure 1. Functionalities present in $M^{I}_{3}[W^{V}(CN)_{8}]\cdot nH_{2}O$ salts.

1) O. Stefańczyk, S. Ohkoshi, *Chem. Eur. J.* **2019**, *25*, 15963. 2) Y. Xin, J. Wang, M. Zychowicz, J. Zakrzewski, K. Nakabayashi, B. Sieklucka, S. Chorazy, S. Ohkoshi, *J. Am. Chem. Soc.* **2019**, *141*, 18211. 3) M. Reczyński, K. Nakabayashi, S. Ohkoshi, *Eur. J. Inorg. Chem.* **2020**, 2669.

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Cyanido-Bridged Ho^{III}-M^{III} (M = Co, Rh, and Ir) Dinuclear Molecules Showing Slow Magnetic Relaxation and Luminescence Thermometry Based on Re-Absorption Effect

([1]*the University of Tokyo*, [2]*Jagiellonian University*, [3]*Katholieke Universiteit Leuven*, [4]*Maastricht University*) ○ Junhao Wang,[1] Jakub Zakrzewski,[2] Mikolaj Zychowicz,[2,3] Veacheslav Vieru,[3,4] Liviu Chibotaru,[3] Koji Nakabayashi,[1] Szymon Chorazy,[2] Shin-ichi Ohkoshi[1]

Keywords: Single Molecule Magnet, Luminescence Thermometry, Re-Absorption Effect

Trivalent lanthanide ions (Ln^{III}), due to their large magnetic anisotropies, have been regarded as one of the most promising candidates in designing single molecule magnets (SMMs), which exhibit slow magnetic relaxation in the single-molecule domain. Since the behavior of such nanomagnets strongly depends on temperature, a contactless and accurate temperature measurement is of great importance for the future practical SMM operations. Thanks to the emissive properties of Ln^{III}, numerous research interest has been focused on the combination of SMMs with luminescent thermometry based on Ln^{III} complexes.[1]

In these regards, we reported a series of cyanido-bridged dinuclear molecules, $\{[Ho^{III}(4\text{-pyridone})_4(H_2O)_2][M^{III}(CN)_6]\}\cdot nH_2O$ (M = Co, **1**; Rh, **2**; Ir, **3**) and their respective magnetically diluted samples by yttrium(III), **1@Y-3@Y**.[2] These compounds exhibit rare slow magnetic relaxation centered at the non-Kramer Ho^{III} ion, and their SMM behaviors were elucidated by *ab initio* calculations. Photoluminescence study on **1@Y-3@Y** revealed an intense blue emission band from the 4-pyridone ligand, together with a series of re-absorption lines ascribed to the f-f transitions of Ho^{III} ion. Additionally, the re-absorption peaks show variable temperature dependences, giving rise to an innovative approach in constructing ratiometric optical thermometry with high sensitivities.

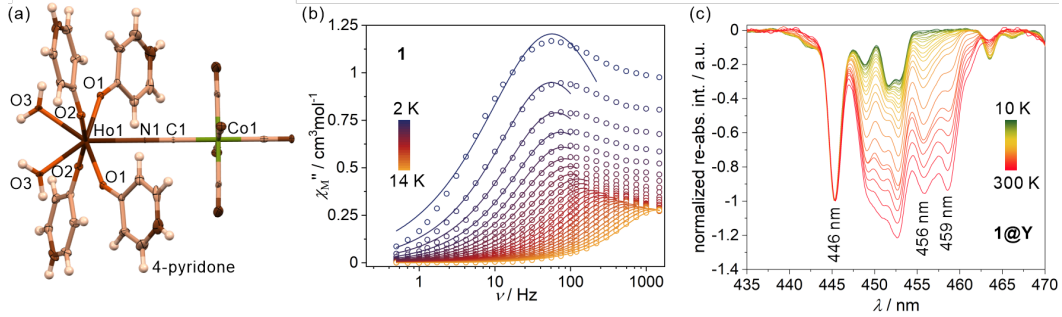


Fig. 1. Structure of dinulcear molecule of **1** (a), SMM characterization of **1** under zero *dc* field (b), and normalized *T*-dependent luminescent re-absorption f-f transitions of **1@Y** used for constructing optical thermometry (c).

1) J. Wang, J. J. Zakrzewski, M. Heczko, M. Zychowicz, K. Nakagawa, K. Nakabayashi, B. Sieklucka, S. Chorazy, S. Ohkoshi, ***J. Am. Chem. Soc.*** 2020, *142*, 3970-3979. 2) J. Wang, J. J. Zakrzewski, M. Zychowicz, V. Vieru, L. F. Chibotaru, K. Nakabayashi, S. Chorazy, S. Ohkoshi, ***Chem. Sci.***, 2021, DOI: 10.1039/D0SC04871B.

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外部磁場印加によるイリジウムおよび白金錯体からの磁気円偏光発光(MCPL)

(近畿大[1]・大阪府立大[2]・阪大院理[3]・日本分光株式会社[4]・奈良先端科学技術大学院大[5]) ○松平 華奈[1]・布袋 純一[2]・山下 健一[3]・近藤 喜郎[4]・鈴木 仁子[4]・八木 繁幸[2]・藤木 道也[5]・今井 喜胤[1]

Magnetic circularly polarized luminescence (MCPL) from iridium (Ir) and platinum (Pt) complexes by applying an external magnetic field ([1]*Kindai University,* [2]*Osaka Prefecture University,* [3]*Osaka University,* [4]*JASCO,* [5]*NAIST*) ○Kana Matsudaira,[1] Junichi Hotei,[2] Kenichi Yamashita,[3] Yoshirou Kondou,[4] Satoko Suzuki,[4] Shigeyuki Yagi,[2] Michiya Fujiki,[5] Yoshitane Imai,[1]

We investigated the magnetic circularly polarized luminescence (MCPL) properties from racemic iridium (Ir) and achiral platinum (Pt) complexes under magnetic field. As a result, racemic Ir and achiral Pt luminophores could emit MCPL under 1.6T magnetic field in both solution and PMMA-film states.

Keywords : Magnetic circularly polarized luminescence (MCPL); iridiumu (Ir); platinum (Pt); non-classical circularly polarized luminescence (NC-CPL); phosphorescence

近年、発光効率が高く、分子設計により特異的な機能を付与できる機能性有機発光体や円偏光発光(CPL)特性を有する光学特性有機-無機ハイブリッド発光体が注目されている。

当研究室では、ラセミ体の Eu(III)(hfa)$_3$ および Tb(III)(hfa)$_3$ などのランタノイドハイブリッド発光体に対して、外部磁場を印加することにより、Eu(III), Tb(III)由来のシャープな磁気円偏光発光(MCPL)の発現に成功している。[1)]

本研究では、ラセミ体のイリジウム(Ir) およびアキラルな白金(Pt)含有有機-無機ハイブリッド発光体に対して、外部磁場を印加することにより MCPL 特性の発現について検討した。イリジウム(**Ir-1**)発光体を CH_2Cl_2(Deoxidized)溶液中で、MCPL を測定したところ、ラセミ体であるにもかかわらず、濃度 1.0×10^{-3} M において極大 MCPL 波長(λ_{MCPL}) 539 nm、異方性因子($|g_{MCPL}|$) 1.68×10^{-3} で観測することに成功した (Fig. 1)。当日は、**Pt-1** の MCPL 特性についても発表する。

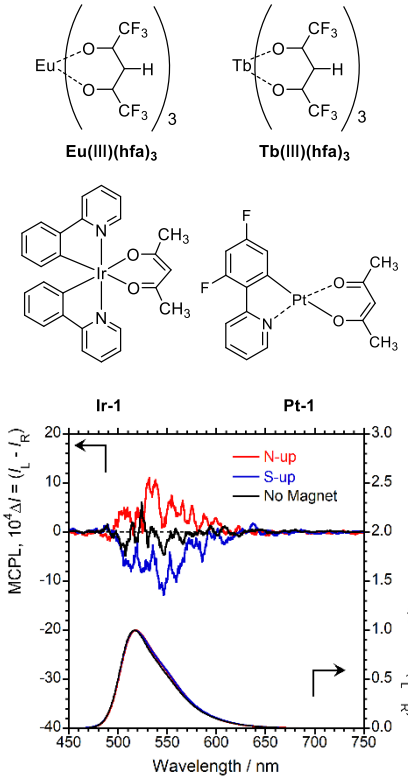


Fig. 1 MCPL (upper) and PL (lower) spectra of **Ir-1** at N-up (red), at S-up (blue) and at No Magnet (black) in 1.0×10^{-3} M CH_2Cl_2(Deoxidized).

1) *Dalton Transactions*, **2020**, *49*, 9588-9594.

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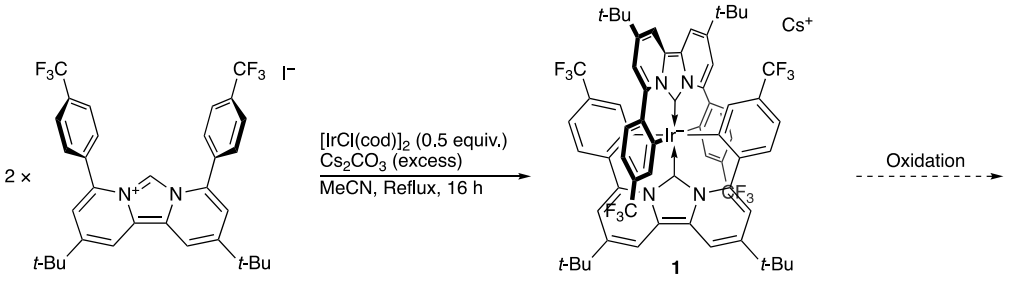
Toward Iridium Complexes with High Oxidation States through All-carbon Ligated Pincer Ligand-type Aryl-substituted Dipyrido-annulated Carbenes

([1]Graduate School of Advanced Science and Engineering, Hiroshima University, [2]Division of Natural and Exact Sciences, University of Guanajuato),○Kazuki Nakanishi[1], Rong Shang[1], Masaaki Nakamoto[1], Yohsuke Yamamoto[1], Hiroto Yoshida[1], J. Oscar C Jimenez-Halla[2]

Keywords: Iridium complexes, High-oxidation state, C–H activation, Pincer ligand, Dipyrido-annulated carbene

Iridium complexes favor the oxidation state of I and III in the view of d-orbital splitting. At an oxidation state of IV, Ir is a 17-electron radical spices, which is readily reduced to an 18-electron Ir(III) center. Thus, isolation of iridium complexes with oxidation state of IV remains challenging and usually required π-donating ligands such as amino/imino, alkoxide, and halide[1]. However, structural characterization of Ir(IV) complexes bearing carbon-based ligands has not been achieved yet.

Previously, our group established the introduction method of various substituents such as aryl groups at 4,8-positions of dipyrido-annulated carbenes which have high π donating properties[2]. Herein, we will present the complexation of our carbene as a pincer ligand toward an iridium, which afforded all-carbon ligated anionic Ir(III) complex (**1**) via quadrable C–H activation. The cyclic voltammetry indicated that complex **1** was readily oxidized in air, which afforded the NMR-silent Ir(IV) complex. The redox behaviors by chemical oxidants were investigated.



(1) Sharninghausen, L. S.; Sinha, S. B.; Shopov, D. Y.; Mercado, B. Q.; Balcells, D.; Brudvig, G. W.; Crabtree, R. H., *Angew. Chem. Int. Ed.* **2017**, *56* (42), 13047–13051.

(2) Maeta, N.; Yamamoto, J.; Fuku-En, S. I.; Shang, R.; Yamamoto, Y., *Zeitschrift fur Anorg. und Allg. Chemie* **2015**, *641* (12–13), 2199–2203.

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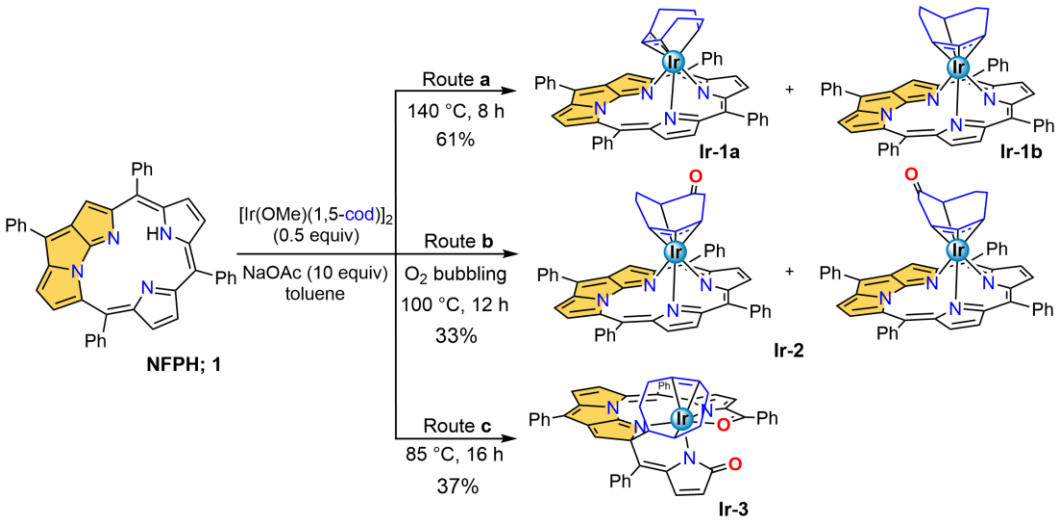
Synthesis and Characterization of N-Fused Porphyrin Iridium Complexes

(*Graduate School Engineering, Kyushu University*) ○Jibin Alex Abraham, Masatoshi Ishida, Hiroyuki Furuta

Keywords: N-Fused Porphyrin, Iridium Complex, Rotational Isomerism, Oxidative Cleavage

N-fused porphyrin (NFpH) is a class of porphyrin analogs containing an inner fused tri-pentacyclic pyrrole unit, which serves as a unique monovalent N3 tridentate ligand (Scheme 1).[1] To date, several sitting atop metal complexes of NFp with ruthenium(II), manganese(I), iron(II), ruthenium(II), and tungsten(VI) ions at the inner core have been reported.[2] In this work, we have investigated the iridium(I) (1,5-cyclooctadiene: cod) complexation of NFp to understand the metal effect on the coordination mode, reactivity, and optical properties.

Complexation with an $[Ir(I)(cod)(OMe)]_2$ afforded a sitting atop iridium complex (**Ir-1**) supported by a transformed η^3-allylic and σ-bonded cod ligand (Scheme 1). The resulting complex has two independent ancillary cod rotational isomers (i.e., **Ir-1a** and **Ir-1b**), and under aerobic conditions, a methylene-oxygenated cod analog (**Ir-2**) was formed. During the study, a unique octahedral Ir complex possessing a cod-fused and ring-broken dioxo-analog of NFp (**Ir-3**) was obtain. We have further studied their optical and electrochemical properties of these Ir complexes.



Scheme 1. Synthesis of N-Fused Porphyrin Iridium Complexes

1) H. Furuta, T. Ishizuka, A. Osuka, T. Ogawa, *J. Am. Chem. Soc*. **1999**, *121*, 2945–2946.
2) M. Toganoh, H. Furuta, *Chem. Lett*. **2019**, *48*, 615–622.

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[A15-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair:Takuya Kochi, Tomohiro Iwai

Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 15 (Online Meeting)

[A15-3pm-01] Iron-Catalyzed Cross-Coupling of Organoboron Reagents with Propargyl Electrophiles

○Siming Lu[1], Ryosuke Agata[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto University)

1:00 PM - 1:20 PM

[A15-3pm-02] Iron-Catalyzed ortho C– H Homoallylation of Aromatic Ketones Using Methylenecyclopropanes

○Naoki Kimura[1], Shiori Katta[1], Yoichi Kitazawa[1], Takuya Kochi[1], Fumitoshi Kakiuchi[1] (1. Keio University)

1:20 PM - 1:40 PM

[A15-3pm-03] Highly Active Cross-Metathesis of Tetrafluoroethylene with a Seven-membered NHC-Ruthenium Catalyst

○Midori Akiyama[1], Kenta Mori[1], Ko Inada[2], Yutaka Imamura[2], Yuichiro Ishibashi[2], Yusuke Takahira[2], Kyoko Nozaki[1], Takashi Okazoe[1,2] (1. The University of Tokyo, 2. AGC Inc.)

1:40 PM - 2:00 PM

[A15-3pm-04] Ruthenium-Catalyzed Enantioselective Propargylic Reduction of Propargylic Alcohols with Hantzsch Esters

○Haowei Ding[1], Shogo Kuriyama[1], Ken Sakata[2], Yoshiaki Nishibayashi[1] (1. University of Tokyo, 2. Toho University)

2:00 PM - 2:20 PM

[A15-3pm-05] Asymmetric Remote C– H Bond Borylation with a Modular Iridium Catalyst

○Ronald Lazo Reyes[1,2], Miyu Sato[2], Tomohiro Iwai[2], Kimichi Suzuki[1], Satoshi Maeda[1,2], Masaya Sawamura[1,2] (1. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, 2. Chemistry Department, Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

[A15-3pm-06] Imidazole-Directed Ir(III)-catalyzed Direct Intermolecular α-Amidation of Masked Aliphatic Acids: A Facile Route to α-Amino Acids

○Sanjit Kumar Mahato[1], Nozomi OHARA[1], Naoto CHATANI[1] (1. Faculty of Engineering, Osaka University)

2:40 PM - 3:00 PM

[A15-3pm-07] Reaction of H_2 with mitochondria-relevant metabolites using a single-metal-site (PNNP)iridium complex

○Shota Yoshioka[1], Sota Nimura[1], Masayuki Naruto[1], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

3:00 PM - 3:20 PM

[A15-3pm-08] Iridium(III)-Catalyzed Regioselective Branch Alkenylation of Aniline with Alkenes

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○Shrikant Manmathappa Khake[1], Naoto Chatani[1] （1. Faculty of Engineering, Osaka University）

3:20 PM - 3:40 PM

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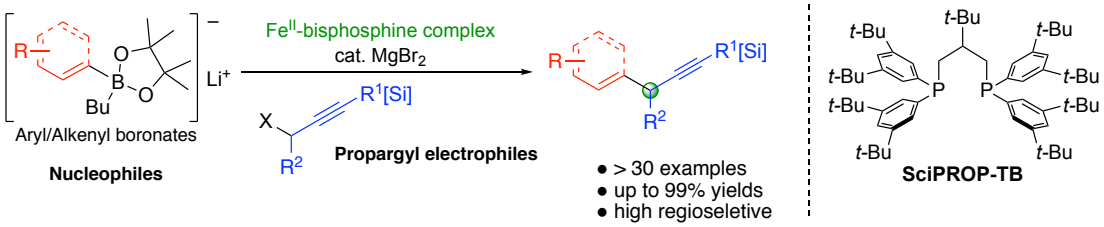
Iron-Catalyzed Cross Coupling of Organoboron Reagents with Propargyl Electrophiles

(*Institute for Chemical Research, and Graduate School of Engineering, Kyoto University*)
○Siming Lu, Ryosuke Agata, Katsuhiro Isozaki, Masaharu Nakamura
Keywords: Cross-Coupling Reaction; Iron-bisphosphine complex catalyst; Regioselective reaction; Propargyl electrophiles; Organoboron reagent

Cross-coupling reactions of propargyl electrophiles with various nucleophiles have been extensively investigated over the last few decades because of their synthetic potential to access various alkynes and allenes, the fundamental functional groups in organic chemistry. Early researchers focused on second and third-row transition metals, such as rhodium and palladium, to catalyze the cross-coupling reactions to produce allene products in a highly regioselective manner.[1] On the other hand, catalytic reactions using first-row transition metals, such as nickel and iron, have been proved a new strategy to afford alkyne products with the opposite regioselectivity.[2] Recently, we reported an iron-catalyzed cross-coupling reaction of primary propargyl halides under ligand-free conditions. Secondary substrates resulted in low yield.[2b] Herein, we present the ligand-controlled iron-catalyzed regioselective cross coupling of a broader range of propargyl electrophiles with organoboron reagents.

The organoboron reagents activated by BuLi cross-coupled with propargyl electrophiles smoothly in the presence of a catalytic amount of iron-bisphosphine complex and $MgBr_2$ (Scheme 1). The combination of a bulky bisphosphine ligand SciPROP-TB and $FeCl_2$ was found to show a high catalytic activity by screening ligands and iron pre-catalysts, providing the final alkyne compounds regioselectively in good to excellent yields. This reaction shows excellent functional and heterocycle group tolerance, exhibiting a broad scope of substrates, including more than 30 examples. This presentation will report the scope of organoboron reagents and secondary propargyl electrophiles. In addition, the mechanistic investigation, which shows the intermediacy of propargyl radicals, will be discussed.

Scheme 1



1) (a) Ma, S.; Zhang, A. *J. Org. Chem.* **2002**, *67*, 2287–2294. (b) Ma, S. *Eur. J. Org. Chem.* **2004**, 1175–1183. (c) Ruchti, J.; Carreira, E. M. *Org. Lett.* **2016**, *18*, 2174–2176.
2) (a) Sean, W.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 12645–12647. (b) Agata, R.; Lu, S.; Matsuda, H.; Isozaki, K.; Nakamura, M. *Org. Biomol. Chem.* **2020**, *18*, 3022–3026.

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鉄触媒によるメチレンシクロプロパンを用いた芳香族ケトンのオルト位 C–H 結合切断を経るホモアリル化反応

（慶大理工）○木村 直貴・勝田 史織・北澤 瑶一・河内 卓彌・垣内 史敏

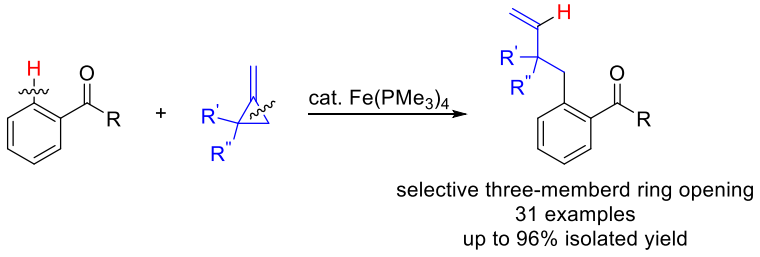
Iron-Catalyzed ortho C–H Homoallylation of Aromatic Ketones Using Methylenecyclopropanes (*Faculty of Science and Technology, Keio University*)

○Naoki Kimura, Shiori Katta, Yoichi Kitazawa, Takuya Kochi, Fumitoshi Kakiuchi

C–H functionalizations using iron catalysts have been widely studied, but expansion of its scope is still desired. We recently found that iron(0) complex catalyzes ortho-selective C–H/olefin coupling of aromatic ketones. Here we report an iron(0)-catalyzed ortho homoallylation of aromatic ketones with methylenecyclopropanes via selective opening of the three-membered ring. For example, when *p*-trifluoromethylpivalophenone was reacted with 2-phenyl-1-methylenecyclopropane in the presence of 5 mol % of $Fe(PMe_3)_4$ in cyclohexane at 40 °C for 20 h, the *ortho*-selective homoallylation proceeded in 93% isolated yield. A variety of aromatic ketones and methylenecyclopropanes were applicable to this reaction. The homoallylated products were amenable to further elaborations and mechanistic studies were also investigated.

Keywords : Iron Catalyst; C–H Bond Cleavage; C–C Bond Cleavage; Aromatic Ketones; Homoallylation

鉄触媒を用いた C–H 結合の官能基化は精力的に研究されているが、その種類および基質適用範囲は未だ限られている [1]。最近我々は、鉄(0)錯体を触媒とした芳香族ケトンのオルト位選択的な C–H/オレフィンカップリング反応を報告している [2]。今回我々は、メチレンシクロプロパンを反応剤として用いたところ、選択的な三員環の開環によるホモアリル化反応が進行することを見出した。例えば、5 mol %の $Fe(PMe_3)_4$ 存在下、*p*-トリフルオロメチルピバロフェノンを 2-フェニル-1-メチレンシクロプロパンとシクロヘキサン溶媒中、40 °C で 20 時間反応させると、オルト位選択的にホモアリル基が導入されたカップリング生成物が単離収率 93%で得られた。本反応には様々な芳香族ケトン、メチレンシクロプロパンが適用可能であった。また、ホモアリル化体のさらなる変換や反応機構に関する知見も併せて報告する。



1) R. Shang, L. Ilies, E. Nakamura, *Chem. Rev.* **2017**, *117*, 9086.
2) (a) N. Kimura, T. Kochi, F. Kakiuchi, *J. Am. Chem. Soc*. **2017**, *139*, 14849. (b) N. Kimura, T. Kochi, F. Kakiuchi, *Asian J. Org. Chem*. **2019**, *8*, 1115.

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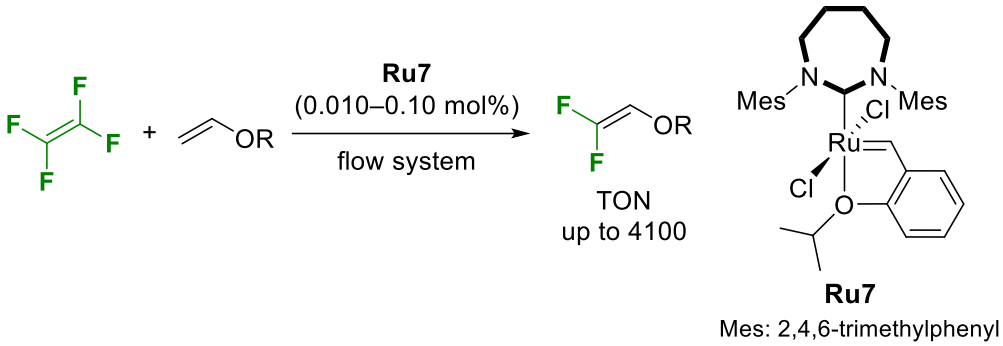
Highly Active Cross-Metathesis of Tetrafluoroethylene with a Seven-membered NHC-Ruthenium Catalyst

([1]*Graduate School of Engineering, The University of Tokyo* [2]*AGC Inc.*) ○ Midori Akiyama,[1] Kenta Mori,[1] Ko Inada,[2] Yutaka Imamura,[2] Yuichiro Ishibashi,[2] Yusuke Takahira,[2] Kyoko Nozaki,[1] Takashi Okazoe[1,2]

Keywords: olefin metathesis, fluoroalkene, ruthenium catalyst, NHC ligand

Tetrafluoroethylene (TFE) is an economical feedstock for the industrial production of poly(tetrafluoroethylene) and copolymers with other olefins.[1] If TFE could be employed as a substrate for olefin metathesis, it would serve as a promising difluoromethylene source for the production of 1,1-difluoroalk-1-enes, which are important structural motifs used in fine chemicals, pharmaceuticals, and agrochemicals, as well as in materials science.[2–4]

In 2015, one of the authors (Takahira) and his co-worker achieved the first and so far only cross-metathesis of TFE by employing an alkyl vinyl ether as the counter-substrate;[5] unfortunately, the efficiency of this reaction was very low (TON ≈ 13.4). Here, we report a discontinuous improvement in this catalytic reaction, wherein (i) a continuous-flow system is provided to shift the equilibrium to the desired product, and (ii) a catalyst with a seven-membered NHC ligand (**Ru7**) presents exceptionally high efficiency (Scheme 1). Using the optimized conditions, the TON reaches 4100, which is two orders of magnitude higher than the highest hitherto reported TON. Computational studies suggest that the seven-membered NHC ligand destabilizes the most stable difluromethylidene intermediate more effectively than the conventional five-membered NHC ligand, reducing the relative energy of the highest transition state and thus promoting the reaction.



Scheme 1. Cross metathesis of tetrafluoroethylene and vinyl ethers catalyzed by a seven-membered NHC-Ruthenium catalyst

(1) Okazoe, T. *Proc. Jpn. Acad., Ser. B* **2009**, *85*, 276–289. (2) Zhang, X.; Cao, S. *Tetrahedron Lett.* **2017**, *58*, 375–392. (3) Decostanzi, M.; Campagne, J. M.; Leclerc, E. *Org. Biomol. Chem.* **2015**, *13*, 7351–7380. (4) Ichikawa, J. *J. Fluorine Chem.* **2000**, *105*, 257–263. (5) Takahira, Y.; Morizawa, Y. *J. Am. Chem. Soc.* **2015**, *137*, 7031–7034.

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Ruthenium-Catalyzed Enantioselective Propargylic Reduction of Propargylic Alcohols with Hantzsch Esters

(*School of Engineering, The University of Tokyo*) ○Haowei Ding, Shogo Kuriyama, Ken Sakata, Yoshiaki Nishibayashi

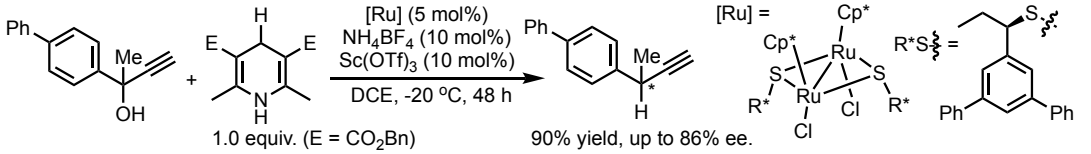
Keywords: Hantzsch ester; Diruthenium complex; Propargylic substitution

Deoxygenation reactions, removal of oxygen functional groups from organic skeletons, are attractive molecular transformations because of their broad utility. As one of the most useful protocols, transition metal-catalyzed enantioselective allylic reduction of allylic alcohol derivatives with reductant has been extensively studied to date since the first successful example of the enantioselective allylic reduction of allylic alcohol derivatives with formic acid reported by Hayashi and co-workers in 1994.[1] In sharp contrast to the allylic reduction, the enantioselective propargylic reduction of propargylic alcohols has been severely limited. To our knowledge, only one protocol was reported by Sun and co-workers in 2017 by applying optically active phosphoric acids as chiral catalysts and Hantzsch esters as reductants.[2]

Previously, our group reported non-enantioselective propargylic reduction of propargylic alcohols with some hydride sources such as triethylsiliane,[3] isopropyl alcohol[4] and Hantzsch ester[5] by using thiolate-bridged diruthenium complexes as catalysts. As an extensive study, we have now investigated the ruthenium-catalyzed enantioselective propargylic reduction of propargylic alcohols with Hantzsch esters as formal hydride donors.

Reactions of tertiary propargylic alcohols with Hantzsch ester in the presence of catalytic amounts of a chiral thiolate-bridged diruthenium complex, ammonium tetrafluoroborate and a Lewis acid gave the corresponding propargylic reduction products in good yields with a high enantioselectivity (up to 86% ee) (Scheme 1). Details of the present reaction system will be shown in this presentation.

Scheme 1.



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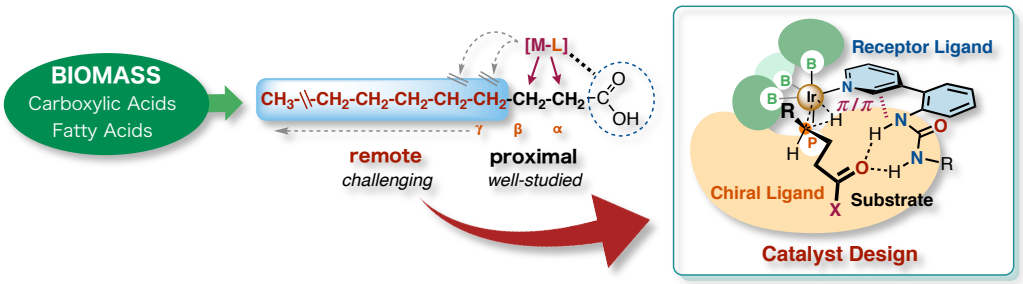
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Asymmetric Remote C–H Bond Borylation with a Modular Iridium Catalyst

(*[1]Department of Chemistry, Faculty of Science, Hokkaido University, [2]Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Japan)*
○ Ronald L. Reyes,[1,2] Miyu Sato,[1] Tomohiro Iwai,[1] Kimichi Suzuki,[2] Satoshi Maeda,[1,2] Masaya Sawamura[1,2]
Keywords: C–H Activation, Borylation, Asymmetric Synthesis, Iridium Catalyst, Carboxylic acids

The direct functionalization of C–H bonds has emerged as an attractive and powerful tool to introduce molecular complexity.[1] In particular, the prevalence of aliphatic carboxylic acids and their derivatives as common feedstock chemicals has resulted to the upsurge of methodologies for the direct activation of C–H bonds within their hydrocarbon framework. However, compared to the functionalization of proximal C–H bonds, remote C(sp^3)–H bonds in these compounds is far less developed.

Here we report a highly enantio- and site-selective catalytic borylation of remote C(sp^3)–H bonds γ to the carbonyl group in aliphatic carboxylic acid derivatives.[2] A high-performing chiral C–H activation catalyst was modularly assembled from an iridium center, a chiral monophosphite ligand, an achiral urea-pyridine receptor ligand, and pinacolatoboryl groups. Quantum chemical calculations support an enzyme-like structural cavity formed by the catalyst components, which bind the substrate through multiple noncovalent interactions. Versatile synthetic utility of the enantioenriched γ-borylcarboxylic acid derivatives was demonstrated paving the opportunity for developing strategic synthetic tools for building structural diversity from readily available raw materials.



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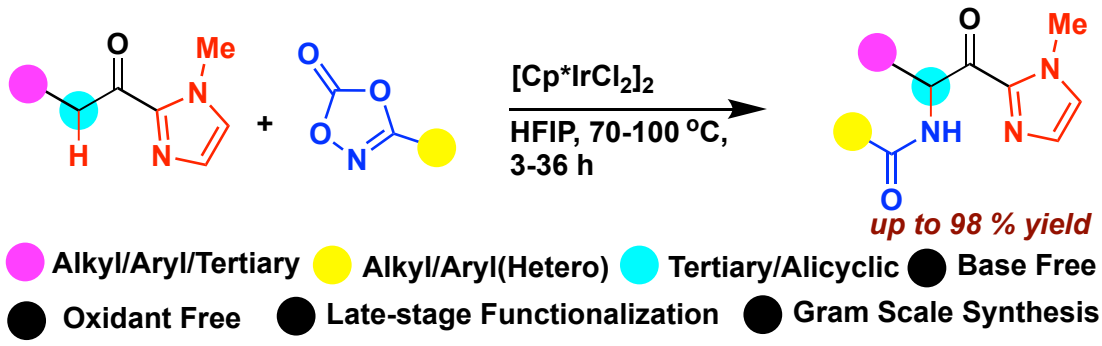
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Imidazole-Directed Ir(III)-catalyzed Direct Intermolecular α-Amidation of Masked Aliphatic Acids: A Facile Route to α-Amino Acids

(*Faculty of Engineering, Osaka University*) ○Sanjit Kumar Mahato, Nozomi Ohara, Naoto Chatani

Keywords: Iridium Catalyst; Carbon-Hydrogen Bond Cleavage; α-Amidation; Nitrene Intermediate; α-Amino Acids

C-N bond forming reaction through nitrene insertion strategies was made attractive for last few decades after the seminal worked by Breslow.[1] α-Amidation of carboxylic acid derivatives would be the best tactics to access α-amino acids although it has remained less explored and has a lack of generality.[2] Here, we report a direct Ir(III)-catalyzed intermolecular α-C(sp^3)-H amidation of imidazole-masked aliphatic acids with dioxazolones. This is a straight forward method to access unnatural α-amino acid derivatives after the removal of an imidazole moiety.[3] A broad substrate scope for various carboxylic acids including tertiary group being highly tolerated. The 'gram' scale synthesis and late-stage functionalization imply the pragmatism of this methodology. The perceptiveness of reaction mechanism has been accomplished by deuterium-labeling experiments, Hammett plots, NMR and/or FAB-MS, and suggested an intermediacy of the iridium-nitrene intermediate.



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Reaction of H_2 with mitochondria-relevant metabolites using a single-metal-site (PNNP)iridium complex

([1]*Graduate School of Science,* [2]*Research Center for Material Science, Nagoya University*)
○Shota Yoshioka,[1] Sota Nimura,[1] Masayuki Naruto,[1] Susumu Saito[1,2]

Keywords: Polycarboxylic acids; Polyols; Hydrogenation; (PNNP)Iridium complex; Krebs cycle

The Krebs cycle occurs in mitochondrial matrix in cells to produce and transfer electrons to generate energy-rich NADH, GTP and $FADH_2$, and conversely to produce not only C_4-dicarboxylic acids (succinic acid (SucA), fumaric acid (FumA), malic acid (MliA), oxaloacetic acid (OacA)), but also C_5- (2-oxoglutaric acid (OglA)) and C_6-polycarboxylic acid (aconitic acid (AcoA) and citric acid (CitA)) as metabolites. Those polycarboxylic acids are in highly oxidized or oxygenated states and thus energy-poor molecules, which are potential candidates as bio-renewable carbon feedstock if hydrogen atoms and electrons could be back into these molecules (Figure 1).

We report herein that those C_4, C_5, and C_6 resources, in addition to mitochondria-relevant metabolites (aspartic acid (AspA), tartaric acid (TarA), itaconic acid (ItaA)), sugar-derived artificial feedstock (levulinic acid (LevA)), and petrochemical product (phthalic acid (PhtA)) are convergently reduced and dehydrated to corresponding diols or triols upon reaction with H_2 catalyzed by iridium (Ir) complex (**IrPCY2**, Figure 2) comprising sterically confined Ir-bipyridyl frameworks.[1]

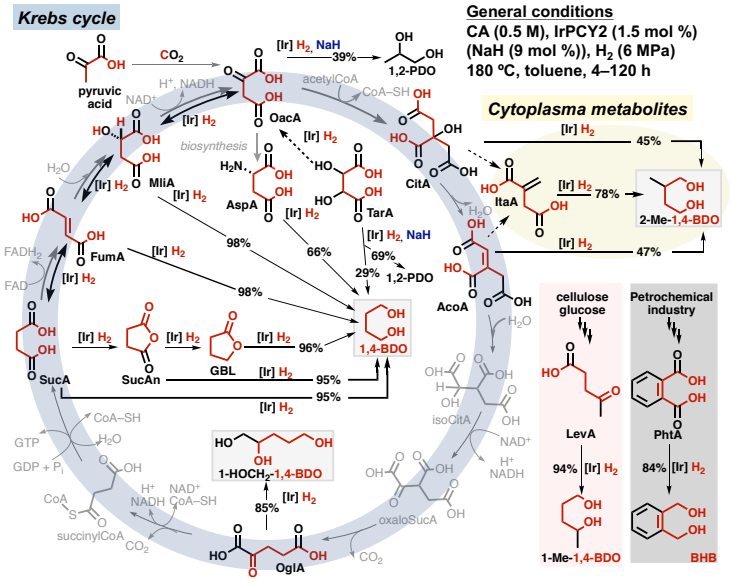


Figure 1. Summary of this work

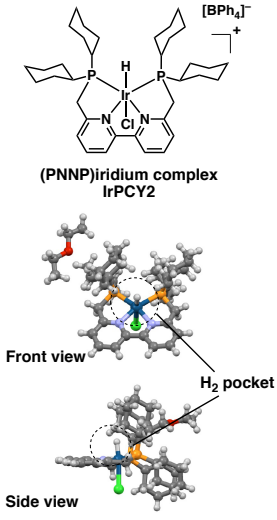


Figure 2. IrPCY2

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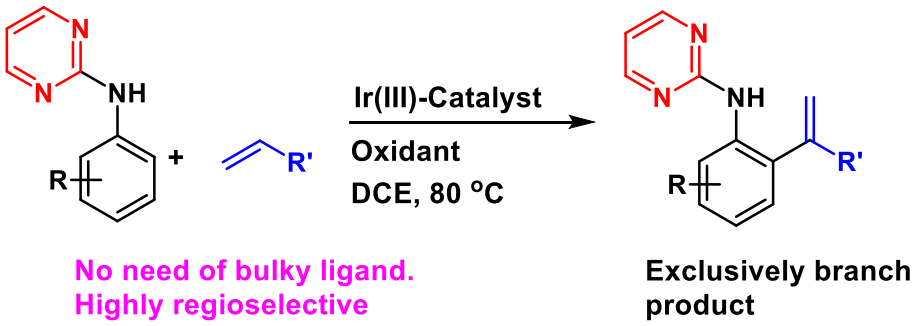
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Iridium(III)-Catalyzed Regioselective Branch Alkenylation of Anilines with Alkenes

(*Faculty of Engineering, Osaka University*) ○Shrikant M. Khake, Naoto Chatani

Keywords: Iridium Catalyst; Carbon–Hydrogen Bond Cleavage; Branch Alkenylation; Iridacycle; Alkene Coordination.

The transition metal catalyzed direct C–H bond functionalization via chelation assistance is one of the most attractive fields in organic chemistry because of it's step economical applications in synthetic field.[1] In this context, transition metal catalyzed direct C–H alkenylation reaction has emerged as a powerful tool to access various pharmaceutical precursors, complex organic molecules and drug compounds in step and atom economical manner.[2] Transition metals, such Pd, Rh, Ru and Ir have shown great advancement in the C–H bond alkenylation using directing group strategy.[3] Among all these reports, reaction provides linear alkenylated products, which is highly common. However, few examples are available for direct C–H branch-selective alkenyaltion of aniline derivatives.[4] Herein, we present the Ir(III)-catalyzed regioselective C–H branch alkenylation of aniline derivatives with alkenes using a pyrimidinyl group as a directing group. This reaction provides broad substrate scope for aniline derivatives. In addition, the reaction tolerates various important functional groups. This protocol provides regioselective branch products without using bulky phosphine ligands and branch selectivity was governed by a pyrimidinyl directing group.



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[A16-3pm] 10. Organic Chemistry -Organometallic Compounds-

Chair:Koji Hirano, Kei Murakami

Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 16 (Online Meeting)

[A16-3pm-01] Solid-State Cross-Coupling Reactions of Insoluble Aryl Halides Using Mechanochemistry

○Tamae Seo[1], Naoki Toyoshima[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

[A16-3pm-02] Palladium-Catalyzed Regioselective C-H Alkenylation and Alkynylation of Allylic Alcohols by Phenanthroline-Type Bidentate Auxiliary

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

1:20 PM - 1:40 PM

[A16-3pm-03] The Intermolecular 1,2-Alkylborylation of Unactivated Olefins through Copper(I)-Catalyzed Radical Relay Reation

○Sota Akiyama[1], Natsuki Oyama[1], Tsubura Endo[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)

1:40 PM - 2:00 PM

[A16-3pm-04] Cross-Couplings of Acyl Halides with Potassium Perfluorobenzoates via Decarboxylation and Decarbonylation

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

2:00 PM - 2:20 PM

[A16-3pm-05] Palladium-Catalyzed Addition of Acylsilanes to Olefins via the Cleavage of a Carbon-Silicon Bond

○Shun Sakurai[1], Tetsuya Inagaki[1], Takuya Kodama[1], Mamoru Tobisu[1] (1. The Univ. of Osaka)

2:20 PM - 2:40 PM

[A16-3pm-06] Synthesis of alpha-Amino Acid Derivatives by Copper-Catalyzed Electrophilic Amination

○Soshi Nishino[1], Toshimichi Kobayashi[2], Koji Hirano[1], Masahiro Miura[1] (1. Graduate School of Engineering, Osaka University, 2. Osaka University)

2:40 PM - 3:00 PM

[A16-3pm-07] Base-free Suzuki– Miyaura cross-coupling reaction

○Takashi Niwa[1], Yuta Uetake[2], Miki Nakaoka[1], Tadashi Takimoto[1], Hidehiro Sakurai[2,3], Takamitsu Hosoya[1,4] (1. RIKEN BDR, 2. Grad. Sch. Eng., Osaka Univ., 3. OTRI, Osaka Univ., 4. IBB, Tokyo Med. &Dent. Univ.)

3:00 PM - 3:20 PM

[A16-3pm-08] Mechanistic study on base-free Suzuki– Miyaura cross-coupling reaction

○Yuta Uetake[1], Takashi Niwa[2], Takamitsu Hosoya[2,3], Hidehiro Sakurai[1,4] (1. Grad. Sch.

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Eng., Osaka Univ., 2. RIKEN BDR, 3. IIB, Tokyo Med. &Dent. Univ., 4. OTRI, Osaka Univ.)
3:20 PM - 3:40 PM

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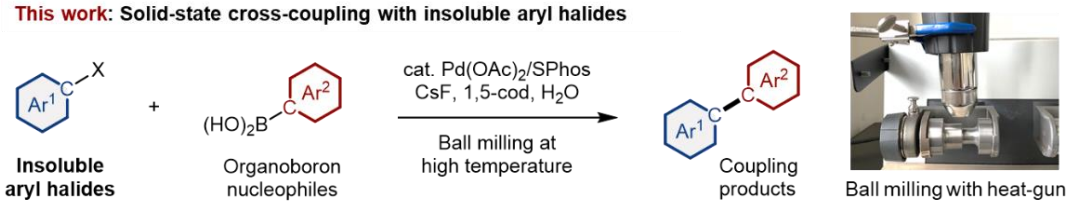
日本化学会 第101春季年会 (2021)

メカノケミストリーによる不溶性アリールハライドの固体クロスカップリング反応

(北海道大学大学院工学研究院応用化学部門[1]・北海道大学反応創成研究拠点[2])
○瀬尾 珠恵[1]・豊島 直喜[1]・久保田 浩司[1,2]・伊藤 肇[1,2]
Solid-State Cross-Coupling Reactions of Insoluble Aryl Halides Using Mechanochemistry
([1]*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University,* [2]*WPI-ICReDD, Hokkaido University*)
○Tamae Seo,[1] Naoki Toyoshima,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Conventional solution-based organic synthesis generally relies on the use of liquid organic solvents to dissolve the reactants.[1,2] Therefore, reactions of sparingly soluble or insoluble substrates are challenging and often ineffective. The development of solid-state approach that overcomes this solubility issue would provide innovative synthetic solutions. In this study, we show the use of a high temperature ball milling technique using a heat-gun enables extremely fast and highly efficient palladium-catalyzed Suzuki‐Miyaura cross-coupling reactions in solid-state. [3] In addition, this solid-state approach allows for efficient cross-coupling with insoluble dyes and pigments as suitable coupling partners that barely react under the corresponding solution conditions. This study provides a practical method for accessing unexplored areas of chemical space through molecular transformations of insoluble organic compounds that cannot be carried out by any other approach.
Keywords : Mechanochemistry; Suzuki-Miyaura Cross-Coupling; Palladium; Ball Mill; Solid-State Reaction

従来の有機溶媒を用いた有機合成は、化合物の溶解性に依存しているため、有機溶媒に溶けにくい基質に対して反応を行うことは困難である。[1,2] したがって、基質の溶解性に左右されない固体反応を開発することができれば、溶解性問題を克服する有用な手法になると考えられる。本研究では外部からヒートガンで加熱しながらボールミルを行う加熱メカノケミカル合成を、パラジウム触媒を用いた固体鈴木-宮浦クロスカップリング反応に適用することで、反応が劇的に加速することを明らかにした。[3] 本手法は、従来の溶液系の合成法では実施困難な不溶性化合物の変換反応を可能にし、未踏のケミカルスペースを切り開く実用的な方法になると考えられる。



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3) Seo, T.; Toyoshima, N.; Kubota, K.; Ito, H. *submitted.*

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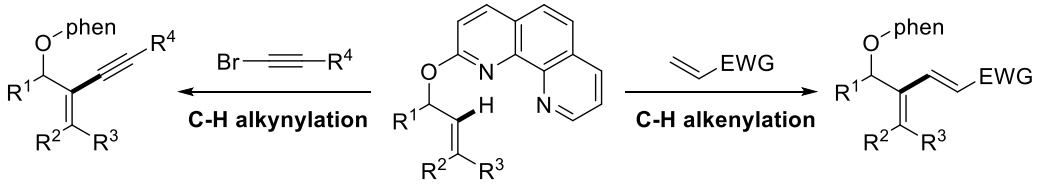
Palladium-Catalyzed Regioselective C-H Alkenylation and Alkynylation of Allylic Alcohols by Phenanthroline-Type Bidentate Auxiliary

(Graduate School of Engineering, Osaka University) ○XU, Shibo; HIRANO, Koji; MIURA, Masahiro

Keywords: Palladium Catalysts; Phenanthroline-Type Bidentate Auxiliary; Allylic Alcohols; C-H Alkenylation; C-H Alkynylation

Allylic alcohols are important structural motifs and frequently occurring in natural products and bioactive molecules. Accordingly, the development of efficient and general access to multiply substituted allylic alcohol derivatives is of great meaning. As an attractive strategy, manipulation of relatively simple allylic alcohols *via* metal-mediated alkenyl C-H functionalizations has recently received much attentions from synthetic chemists. However, despite certain advances,[1] a significant limitation in scope should be noticed: only terminal or *cis*-allylic alcohols could be employed.

In this study, we developed a phenanthroline-directed,[2] Pd-catalyzed regioselective C-H alkenylation of allylic alcohols: a bidentate coordinating nature of phenanthroline auxiliary enables the C-H activation selectively at the proximal position over the conceivable allylic C-O activation.[3] The Pd catalysis accommodates *cis*-, *trans*-, and even more challenging trisubstituted substrates. Additionally, a related C-H alkynylation of allylic alcohols was also demonstrated under the Pd/phenanthroline catalytic system. Mechanistic studies with the putative 6-membered palladacycle intermediate and further transformations of the products will also be included in this presentation.



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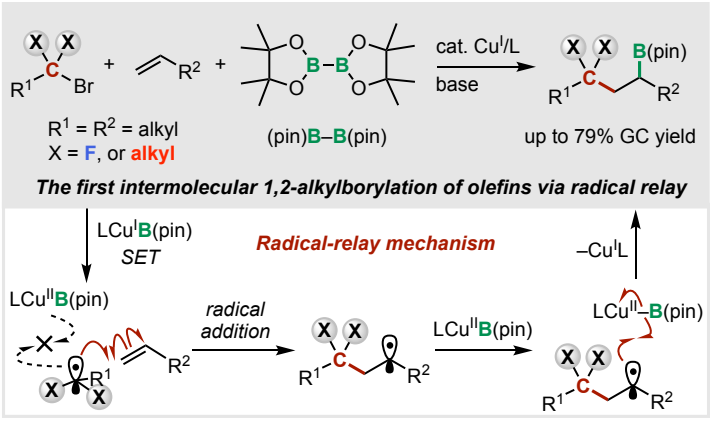
The Intermolecular 1,2-Alkylborylation of Unactivated Olefins through Copper(I)-Catalyzed Radical Relay Reaction

([1]*Divison of Applied Chemistry, Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*) ○Sota Akiyama,[1] Natsuki Oyama,[1] Tsubura Endo,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Keywords: Radical Relay; Copper(I) Catalysis; 1,2-Carboborylation; Fluorine-Containing Compounds

The transition-metal-catalyzed radical-relay strategy for intermolecular 1,2-carbofunctionalization of widely available unactivated olefins is one of the most useful protocols for rapid construction of complex carbon-based structures with a catalytic amount of a radical-generating reagent.[1] One of the main advantages of this protocol is that it tolerates electronically or sterically demanding alkyl electrophiles that cannot be used in catalytic 1,2-carbofunctionalization reactions that involve S_N2-type nucleophilic substitutions. In this context, the intermolecular 1,2-carboborylation of olefins via a radical relay, a transformation that involves the simultaneous installation of a C–C bond and a transformable C–B bond, would undoubtedly be highly attractive. Despite the significant progress that has been made in radical-relay chemistry, the intermolecular 1,2-carboborylation of olefins via a radical relay remains elusive so far.

Herein, we report the first example of an intermolecular 1,2-alkylborylation of unactivated olefins via a radical-relay strategy. The key to the success of this protocol is the use of electronically or sterically demanding alkyl electrophiles such as α,α-difluoro alkyl bromides or tertiary alkyl bromides to suppress undesired boryl-substitution reactions. Notably, the products of these reactions are difficult to access via any other hitherto reported carboborylation strategies.[2]



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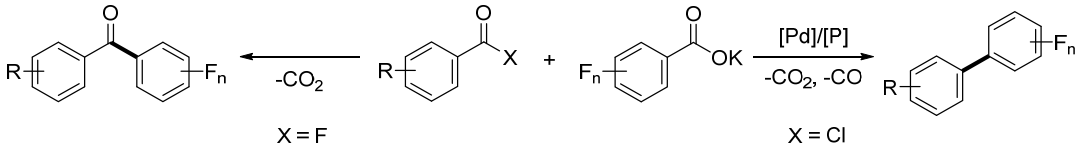
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Cross-Couplings of Acyl Halides with Potassium Perfluorobenzoates via Decarboxylation and Decarbonylation

([1]Graduate School of Natural Science and Technology, Okayama University, [2]Research Institute of Interdisciplinary Science, Okayama University)
○Liyan Fu,[1] Qiang Chen,[1] Jingwen You,[1] Yasushi Nishihara[2]
Keywords: Decarboxylation; Decarbonylation; Potassium Perfluorobenzoate; Acyl Fluoride; Acyl Chloride

Over the past few decades, carboxylic acids and their derivatives have attracted great interest in the field of organic synthesis due to their ready availability, abundance, and environmental friendliness. For this reason, benzoic acids and their derivatives have been developed as convenient surrogates for conventional coupling partners by decarbonylative[1] and decarboxylative[2] couplings via loss of CO or CO_2. These methods avoid the use of either toxic organic halides or expensive organometallic reagents, but the employment of either is still necessary. As a result, the development of synthetic protocols for unsymmetrical ketones and biaryls that use both reagents could be synthesized from benzoic acid is of great interest.

Acyl halides are among the simplest carboxylic acid derivatives and can be readily prepared from related carboxylic acids and other carboxylic acid derivatives.[3] On the other hand, synthetic approaches to perfluorinated arenes have attracted much attention in the field of material and pharmaceutical sciences due to their attractive properties. Previously, we developed a transition-metal-free decarboxylative cross-coupling reaction of acyl fluorides with potassium perfluorobenzoates.[4] Along this line, we herein report the palladium-catalyzed decarbonylative and decarboxylative cross-coupling reactions of acyl chlorides with potassium perfluorobenzoates affording unsymmetrical biaryls. This transformation is a unique reaction in which the decarbonylation and decarboxylation proceeded simultaneously under redox-neutral conditions. In comparison to conventional cross-coupling protocols for the synthesis of unsymmetrical ketones and biaryls, in these synthetic strategies, all reactants can be readily prepared from abundant and inexpensive aromatic carboxylic acids. These methods also allowed for two efficient and highly selective approaches for the installation of perfluorophenyl groups.



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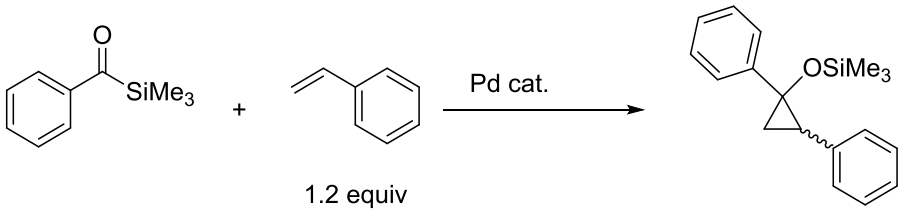
Palladium-Catalyzed Addition of Acylsilanes to Olefins via the Cleavage of a Carbon-Silicon Bond

([1]*Graduate School of Engineering, Osaka University*) ○Shun Sakurai,[1] Tetsuya Inagaki,[1] Takuya Kodama,[1] Mamoru Tobisu[1]

Keywords: Palladium Catalyst; Acylsilane; Cyclopropanation

Among the unique reactivities exhibited by acylsilanes,[1] a 1,2-shift of the silyl group with the generation of siloxycarbenes, which occurs either thermally (>250 °C) or photochemically, has attracted the interest of synthetic chemists. In fact, the siloxycarbenes that are generated from acylsilanes have been used in insertion reactions with compounds bearing H-X bonds[2] and organoboronic esters.[2f,3] Siloxycarbenes are also known to participate in the cyclopropanation of alkenes[4] and alkynes,[5] although the substrates are limited to electron-deficient derivatives presumably due to a nucleophilic character of siloxycarbene derivatives.

We found that cyclopropane derivatives can be produced by the palladium-catalyzed reaction of acylsilanes with various electronically neutral alkenes. This reaction proceeds in the dark, excluding the photo-mediated generation of siloxycarbenes.



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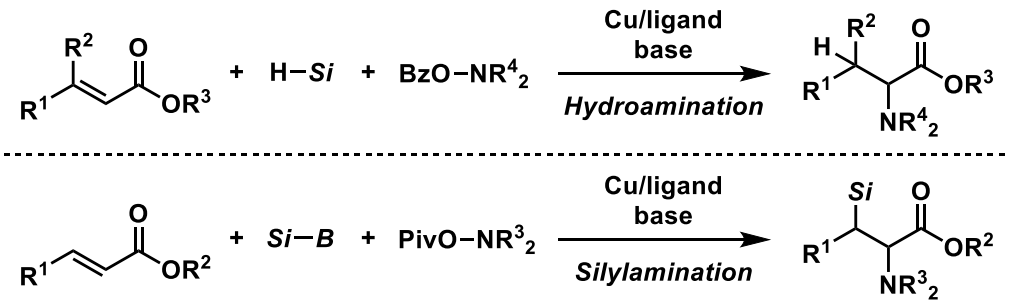
Synthesis of α-Amino Acid Derivatives by Copper-Catalyzed Electrophilic Amination

(*Graduate School of Engineering, Osaka University*) ○Soshi Nishino, Toshimichi Kobayashi, Koji Hirano, Masahiro Miura

Keywords: Copper Catalysts; Electrophilic Amination; α-Amino Acids; Hydroamination; Silylamination

Conjugate additions of nucleophiles to *α,β*-unsaturated carbonyl compounds have been intensely investigated. In particular, copper hydride [1] or silylcopper [2] complexes have been utilized for the chemoselective conjugate reduction or hydrosilylation of *α,β*-unsaturated carbonyl compounds. On the other hand, the functionalizations at the *α* position of *α,β*-unsaturated carbonyl compounds in the transition-metal-catalyzed conjugate addition are quite rare and challenging because of the predominant protonation at the *α* position. To the best of our knowledge, there is no report of the hydroaminations and silylaminations of *α,β*-unsaturated carbonyl compounds for the synthesis of *α*-amino acids derivatives.

Herein, we report the copper-catalyzed hydroamination of *α,β*-unsaturated esters with hydrosilanes and hydroxylamines giving the corresponding *α*-amino acids derivatives. Additionally, asymmetric induction is also possible by using the chiral bisphosphine ligand, and optically active *α*-amino acids derivatives are obtained with high enantioselectivity.[3] Moreover, with silylboranes instead of hydrosilanes, the silylaminations of *α,β*-unsaturated esters proceed to form the corresponding *β*-silyl-*α*-amino acids derivatives, which are known to show unique biological activity.



1) a) Mori, A.; Fujita, A.; Nishihara, Y.; Hiyama, T. *Chem. Commun.* **1997**, 2159. b) Ito, H.; Ishizuka, T.; Arimoto, K.; Miura, K.; Hosomi, A. *Tetrahedron Lett.* **1997**, *38*, 8887. 2) a) Ito, H.; Ishizuka, T.; Tateiwa, J.-i.; Sonoda, M.; Hosomi, A. *J. Am. Chem. Soc.* **1998**, *120*, 11196. b) Lee, K. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 2898. 3) a) Appella, D. H.; Moritani, Y.; Shintani, R.; Ferreira, E. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9473. b) Lipshutz, B. H.; Papa, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 4580.

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塩基を用いない鈴木・宮浦クロスカップリング反応の開発

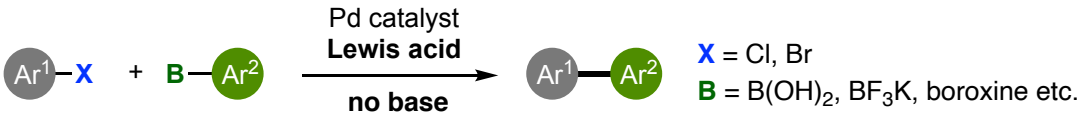
(理研 BDR[1]・阪大院工[2]・阪大先導研[3]・医科歯科大生材研[4])
○丹羽 節[1]・植竹 裕太[2]・中岡 光妃[1]・瀧本 正[1]・櫻井 英博[2,3]・細谷 孝充[1,4]
Base-Free Suzuki–Miyaura Cross-Coupling Reaction ([1]RIKEN BDR, [2]*Grad. Sch. Eng., Osaka Univ.*, [3]*OTRI, Osaka Univ.*, [4]*IBB, Tokyo Med. & Dent. Univ.*) ○Takashi Niwa,[1] Yuta Uetake,[2] Miki Nakaoka,[1] Tadashi Takimoto,[1] Hidehiro Sakurai,[2,3] Takamitsu Hosoya[1,4]

Suzuki–Miyaura cross-coupling reaction is one of the reliable methods for C–C bond formation. This reaction requires addition of a base to enhance the nucleophilicity of organoborons and to facilitate the transmetalation process. However, the base also induces competitive protodeborylation reducing the efficiency of the transformation. We have found that the addition of a Lewis acid instead of base efficiently promotes the cross-coupling reaction with excellent tolerance to various functional groups. In this presentation are discussed the detailed reaction conditions and the synthetic utility of this reaction.
Keywords : Suzuki–Miyaura Cross-Coupling Reaction; Palladium Catalyst; Lewis Acid; Carbon–Carbon Bond Formation; Transmetalation

鈴木・宮浦クロスカップリング反応は、信頼性の高い炭素–炭素結合形成法の一つである。この反応では有機ホウ素化合物の求核性を向上させ金属交換を進行させるために、塩基の添加が必須である。一方、塩基性条件で競争的に進行する有機ホウ素化合物の脱ホウ素プロトン化による効率低下が課題として知られている。

この抜本的な解決策として、触媒中心の求電子性の向上による金属交換の促進により、塩基非添加条件で本反応を進行させられないかと着想した。実際に、アリールジアゾニウム塩を求電子剤として用いた場合、塩基非添加条件で金属交換が進行することが知られている[1)]。しかし、中間体として生じるパラジウムカチオン性錯体が熱的に不安定であるためか[1c)]、酸化的付加に加熱条件が必要な臭化アリールなどを求電子剤として用いる例は報告されていない。

これに対し我々は、塩基の代わりにルイス酸を添加することによって、ハロゲン化アリールと有機ホウ素化合物のカップリング反応が進行することを明らかにした。本条件は塩基性条件下で脱ホウ素プロトン化が進行しやすい有機ホウ素化合物のほか、生物活性化合物など多数の極性官能基を有する基質にも適用できるなど、際立って高い基質適用範囲を示した。本発表では本反応の設計戦略、詳細な反応条件、ならびに有機合成化学における有用性を中心に議論する。



1) a) S. Darses, T. Jeffery, J.-P. Genet, *Tetrahedron. Lett.* **1996**, *37*, 3857; b) S. Darses, J.-P. Genet, J.-L. Brayer, J.-P. Demoute, *Tetrahedron Lett.* **1997**, *38*, 4394; c) L. Chen, D. R. Sanchez, B. Zhang, B. P. Carrow, *J. Am. Chem. Soc.* **2017**, *139*, 12418.

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塩基を用いない鈴木・宮浦クロスカップリング反応における反応機構研究

(阪大院工[1]・理研 BDR[2]・医科歯科大生材研[3]・阪大先導研[4])
○植竹裕太[1]・丹羽 節[2]・細谷孝充[2,3]・櫻井英博[1,4]

Mechanistic study on base-free Suzuki–Miyaura cross-coupling reaction

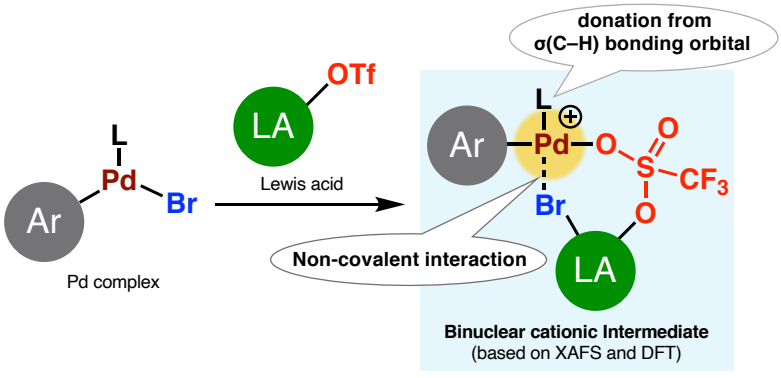
([1]*Grad. Sch. Eng., Osaka Univ.*, [2]RIKEN BDR, [3]*IBB, Tokyo Med. & Dent. Univ.*, [4]*OTRI, Osaka Univ.*) ○Yuta Uetake,[1] Takashi Niwa,[2] Takamitsu Hosoya,[2,3] Hidehiro Sakurai[1,4]

To gain further insight into the reaction mechanism on the base-free Suzuki-Miyaura cross-coupling reaction, synchrotron radiation XAFS measurements were performed. Analysis of XAFS spectra at Pd-K and Br-K absorption edges revealed the formation of a binuclear cationic Pd complex connected with Lewis acid through triflate. DFT calculation and electron density analysis indicated that the cationic Pd complex was stabilized by the electron donation from the bonding C–H σ-orbital of the ligand, and the bromine atom through non-covalent interaction.

Keywords :X-ray absorption fine structure (XAFS), density functional theory (DFT) calculation, electron density analysis, Suzuki–Miyaura cross-coupling

我々は、塩基の代わりにルイス酸を添加することによって、ハロゲン化アリールと有機ホウ素化合物のカップリング反応が進行することを見出している。本研究では、本触媒反応の機構を明らかにするため、放射光 XAFS と理論化学計算を取り入れた反応解析を行った。

大型放射光施設 SPring-8 BL14B2 にて、Pd-K および Br-K 吸収端 XAFS 測定を透過法で行った。得られた EXAFS 振動を解析した結果、反応系中ではカチオン性パラジウム錯体が生成しており、添加したルイス酸とパラジウムがトリフラートで架橋された二核構造となっていることが示唆された。XAFS から得られた局所構造をもとに DFT 計算を用いて最安定構造を導出し、それに対して電子密度解析を行った。その結果、中間体のパラジウム中心は、配位子の σ(C–H)軌道からの電子供与と近傍に存在する臭素原子との非結合性相互作用により速度論的・熱力学的な安定化を受けていることが示唆され、既報のカチオン性パラジウム錯体[1]と比較して高い安定性をもつ理由を明らかにすることができた。本発表では、XAFS 実験および電子密度解析の詳細を中心に議論する。



1) L. Chen, D. R. Sanchez, B. Zhang, B. P. Carrow, *J. Am. Chem. Soc.* **2017**, *139*, 12418.

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[A17-3pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair:Shinji Toyota, Takeshi Kawase

Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 17 (Online Meeting)

[A17-3pm-01] Synthesis of Unsubstituted Polyarylenes

○Shusei Fujiki[1], Akiko Yagi[1], Kenichiro Itami[1] （1. Graduate School of Science, Nagoya University）

1:00 PM - 1:20 PM

[A17-3pm-02] Synthesis and properties of twisted alkene-inserted cycloparaphenylenes

○Tomoaki Terabayashi[1], Eiichi Kayahara[1], Tatsuhisa Kato[1], Shigeru Yamago[1] （1. Institute for Chemical Research, Kyoto University）

1:20 PM - 1:40 PM

[A17-3pm-03] A new synthetic method for cycloparaphenylenes via a macrocyclic gold(I) complex: from mechanism to application

○Yoshitaka Tsuchido[1], Naoki Narita[1], Yohei Tanji[1], Tomohito Ide[3], Kohtaro Osakada[2], Hidetoshi Kawai[1] （1. Tokyo University of Science, 2. Tokyo Institute of Technology, 3. National Institute of Technology, Tokyo College）

1:40 PM - 2:00 PM

[A17-3pm-04] Synthesis of π-Extended [2n+1]Helicenes: Helically Twisted Wire Molecules with Large Effective Conjugation Length

○Yusuke Nakakuki[1], Takashi Hirose[2], Hikaru Sotome[3], Hiroshi Miyasaka[3], Kenji Matsuda[1] （1. Grad. Sch. of Eng. Kyoto Univ. , 2. ICR, Kyoto Univ., 3. Grad. Sch. of Eng. Sci. Osaka Univ. ）

2:00 PM - 2:20 PM

[A17-3pm-05] Synthesis, Structure, and Reactivity of Thiophene-fused 1,4-Diazapentalene

○Junichi Usuba[1], Aiko Fukazawa[2] （1. Graduate School of Science, Nagoya University, 2. Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University）

2:20 PM - 2:40 PM

[A17-3pm-06] Development of Benzo[*de*]isoquinolino[1,8-*gh*]quinoline Diimide n-Type Organic Semiconductors with Asymmetric Substituents

○Craig Yu[1], Shohei Kumagai[1], Hiroyuki Ishii[2], Go Watanabe[3], Hiroki Sugiura[4], Yukio Tani[4], Tetsuya Watanabe[4], Jun Takeya[1,5,6], Toshihiro Okamoto[1,5,7] （1. The University of Tokyo, 2. University of Tsukuba, 3. Kitasato Univeresity, 4. FujiFilm Corp., 5. OPERANDO-OIL, AIST-UTokyo, 6. WPI-MANA, NIMS, 7. PRESTO, JST）

2:40 PM - 3:00 PM

[A17-3pm-07] π-Electronic Ion Pairs: Ordered Arrangement Based on Noncovalent Interaction

○Hiroki Tanaka[1], Yohei Haketa[1], Hiromitsu Maeda[1] （1. Ritsumeikan Univ.）

3:00 PM - 3:20 PM

[A17-3pm-08] Synthesis of Thiophene-Based Twisted Bistricyclic Aromatic Ene with Tricoordinate Boron

○Yohei Adachi[1], Takanori Nomura[1], Shion Tazuhara[2], Hiroyoshi Naito[2], Joji Ohshita[1] （1.

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Hiroshima University, 2. Osaka Prefecture University)
3:20 PM - 3:40 PM

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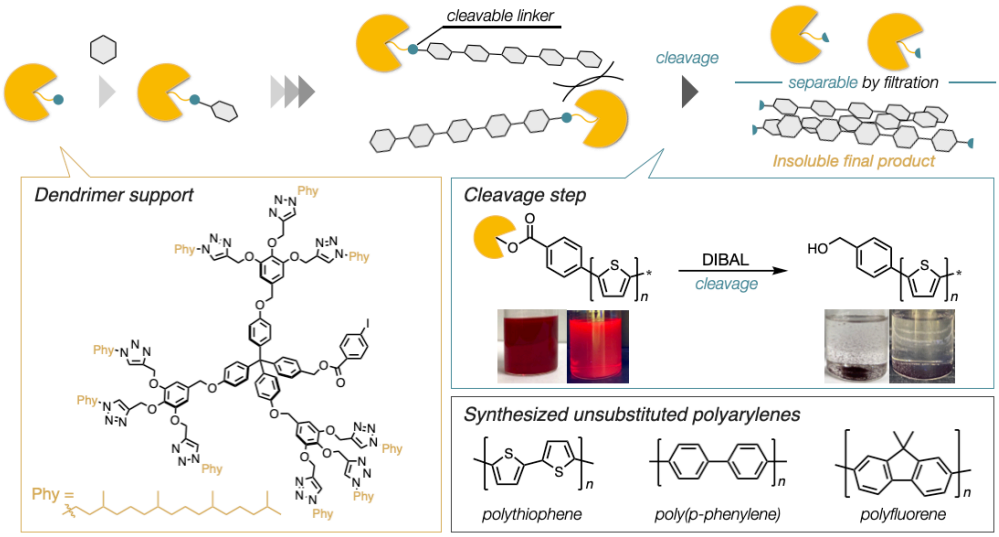
無修飾芳香族系高分子の合成

（名大院理[1]・名大 WPI-ITbM[2]）○藤木 秀成[1]・八木 亜樹子[1,2]・伊丹 健一郎[1,2]
Synthesis of Unsubstituted Polyarylenes ([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*) ○Shusei Fujiki[1], Akiko Yagi[1,2], Kenichiro Itami[1,2]

Polyarylenes are promising candidate for materials in electronic devices. Because of their strong intermolecular interactions, polyarylenes easily form aggregates. In order to suppress the aggregation, long alkyl or alkoxy chains are often installed as substituents in the synthesis of polyarylenes. Since the substituents cause the undesired change of physical properties, a synthetic method for unsubstituted polyarylenes is highly demanded. Herein, we report a new synthetic methodology circumventing this long-standing problem. In this synthetic method, huge dendrimer which have long alkyl chain in its periphery was used as the “solubilizing group”. Unsubstituted polyarylenes were successfully synthesized with the aid of sterically demanding dendrimer molecule. This result implies that strong aggregation of polyarylenes are effectively hampered by the developed strategy.

Keywords：Molecular Nanocarbon, Insoluble Compound, Polyarylene, Solubility

芳香族系高分子は優れた電子的性質をもち、多くの電子デバイスへの応用が期待される物質群である。これらは強い分子間相互作用によって凝集して難溶性となるため、多くの長鎖アルキル基などを修飾基として導入することで凝集を防ぎながら合成される。しかし、修飾基の導入は熱安定性の低下や発光の短波長化などの物性変化を引き起こすことが知られている。そこで、本研究では無修飾の芳香族系高分子を合成する新たな手法の開発を行った。末端に多数の長鎖アルキル基が導入されたデンドリマー構造をもつ担体を新たに設計し、その上で重合反応を行うことにより、デンドリマー担体により可溶化された芳香族系高分子を得た。最終的にデンドリマー担体と芳香族系高分子を切断することによって、最大で 20 個の芳香環からなる無修飾ポリチオフェン等の芳香族系高分子を合成することに成功した。



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ねじれ構造を持つアルケン挿入環状パラフェニレンの合成と物性

（京大化研）○寺林 智昭・茅原 栄一・加藤 立久・山子 茂
Synthesis and properties of twisted alkene-inserted cycloparaphenylenes (*Institute for Chemical Research, Kyoto University*) ○Tomoaki Terabayashi, Eiichi Kayahara, Tatsuhisa Kato, Shigeru Yamago

We report here a new and simple strategy for the synthesis of twisted CPP derivatives (**1**, **2**), and their physical properties. Single crystal X-ray analysis revealed that **1** and **2** have Möbius and Hückel topology. Molecular orbital analysis revealed that the HOMO and LUMO of **1a** are delocalized over the whole molecular, indicating the presence of fully conjugation.
Keywords : Cycloparaphenylene; Twist; Alkene; Conjugation; Radical cation.

環状π共役分子におけるトポロジーの変化は、新たな物性発現の可能性から注目されている。[1] 我々は、曲面環状π共役分子であるシクロパラフェニレン（CPP)の大量合成と物性を報告してきた。[2] しかし、これまでにメビウスあるいは二重ねじれ構造を持つ CPP 誘導体の合成は 3 例に限られている [3]。そこで今回、CPP 骨格にアルケンを挿入することで、ねじれ構造を持つ CPP 誘導体 **1**、**2**（Figure 1）の合成に成功したので報告する。

まず、ジブロモ-*cis*-スチルベン **3**[4] のハロゲン-リチウム交換反応と、続くケトン **4** との反応により、鎖状ユニット **5** を得た(Scheme 1)。続く、分子内環化反応と H_2SnCl_4[2] を用いた還元的芳香族化により、**1a** を合成した。さらに、ホウ素体 **6** と三環性ユニット **7** のカップリング反応から出発し、環サイズを拡大した **1b-c** を合成した。**1a** の単結晶 X 線構造解析(Figure 2a)から、アルケンとパラフェニレン間の二面角は-54°であり、パラフェニレン単位は互いにジグザク構造で配列していた。従って、結晶状態では **1a** はメビウス構造を持つことを確認した。さらに、理論計算により HOMO と LUMO が分子全体に広がっていることから(Figure 2b)、**1a** は共役していることが示唆された。本発表では、**1** と **2** のねじれ構造が与える、光、酸化特性への効果を解明したので併せて報告する。

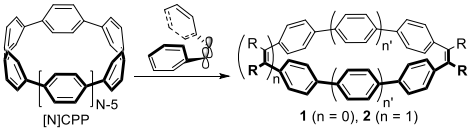


Figure 1. Structures of [N]CPP, **1**, and **2**

Scheme 1. Synthesis of **1**

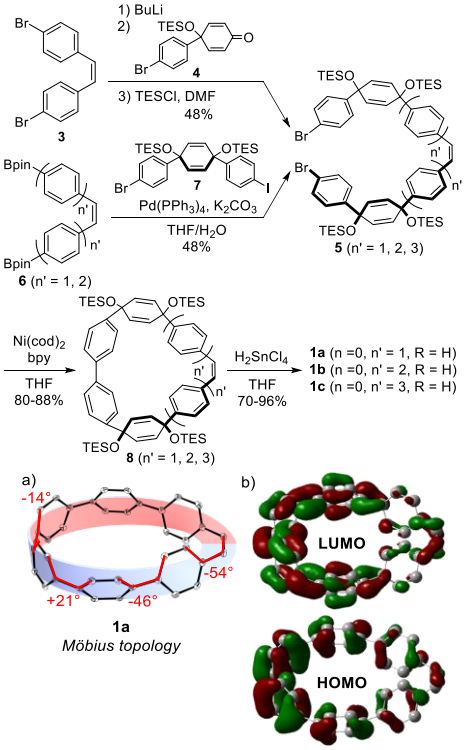


Figure 2. a) Crystal structure of **1a**, **b)** HOMO and LUMO calculated by B3LYP/6-31G*

References:
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4. Miao, Q. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 9003.

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大環状金(I)錯体を鍵中間体としたシクロパラフェニレン類の新規合成法：メカニズムから応用まで

（東理大理[1]・東工大化生研[2]・東京高専物質工[3]）○土戸良高[1]・成田直生[1]・丹治洋平[1]・井手智仁[3]・小坂田耕太郎[2]・河合英敏[1]

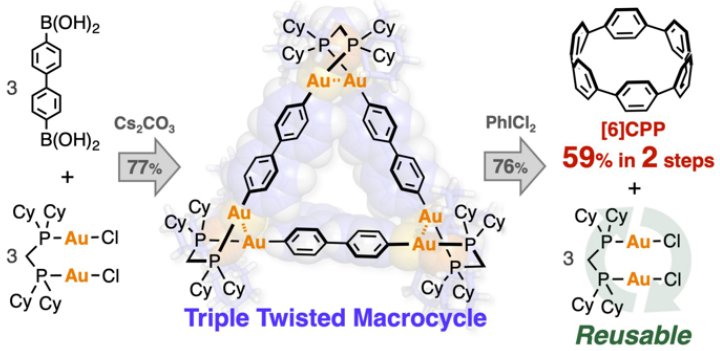
A New Synthetic Method for Cycloparaphenylenes via a Macrocyclic Gold(I) Complex: from Mechanism to Application ([1]*Tokyo University of Science*, [2]*Tokyo Institute of Technology*, [3]*National Institute of Technology, Tokyo College*) ○Yoshitaka Tsuchido,[1] Naoki Narita,[1] Yohei Tanji,[1] Tomohito Ide,[3] Kohtaro Osakada,[2] Hidetoshi Kawai[1]

The reaction of 4,4'-diphenylene diboronic acid with $[Au_2Cl_2(Cy_2PCH_2PCy_2)]$ produced the triangular hexagold(I) complex, $[Au_2(C_6H_4)_2(Cy_2PCH_2PCy_2)]_3$, which was isolated in 77% yield. The oxidative chlorination of Au complex occurs upon the addition of $PhICl_2$, which afforded [6]CPP in 76% isolated yield (total 59% yield). Detailed procedure, reaction mechanism, and substrate applicability will be mentioned in the presentation.

Keywords: Cycloparaphneylnene, Gold(I) complex, Aurophilicity, Transmetallation.

n 個のベンゼン環がパラ位で連結した大環状有機化合物である[n]シクロパラフェニレン（[n]CPP）は，歪んだπ共役系に基づく特異な光物性・電気化学的性質を有していることから注目を集めている化合物群である．これまでに歪みの少ない多角形状の環状分子を経由することで，5 から 18 個のベンゼン環から成る CPP の合成が達成されている[1]．一方，最近我々は三角形状の構造を有する大環状六核金(I)-ビフェニレン錯体を経由した[6]CPP の新規合成法の開発に成功した[2]．具体的には，4,4'-ビフェニレンビスボロン酸と二核金錯体$[Au_2Cl_2(Cy_2PCH_2PCy_2)]$を塩基性条件下，1:1 のモル比で反応させたところ，大環状六核金錯体$[Au_2(C_6H_4)_2(Cy_2PCH_2PCy_2)]_3$が選択的に生成した．この錯体に対して 3 倍モル量の $PhICl_2$ を作用させたところ，アリール配位子の C-C 結合形成を伴う還元的脱離が進行し，[6]CPP が生成した（2 段階の総収率 59%）．

本手法は，従来の合成手法と比較して短工程かつ高収率で[6]CPP を得ることができ，さらに二核金錯体はリサイクルすることが出来るため，コスト・環境面でも有用な合成法である．



発表では，本手法の詳細な合成手順，反応メカニズム，さらに基質適用性に関して包括的に述べる．

[1] Review: a) Y. Segawa, K. Itami *et al. Angew. Chem. Int. Ed.* **2016**, *55*, 5136-5158; b) R. Jasti *et al. Chem. Soc. Rev.* **2015**, *44*, 6401-6410; c) S. Yamago *et al J. Synth. Org. Chem., Jpn.* **2019**, *77*, 1147-1158.

[2] Y. Tsuchido, K. Osakada *et al. Angew. Chem. Int. Ed.* **2020**, *59*, 22928-22932.

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Synthesis of π-Extended [2*n* + 1]Helicenes: Helically Twisted Wire Molecules with Large Effective Conjugation Length

([1]*Graduate School of Engineering, Kyoto University,* [2]*Institute for Chemical Research (ICR), Kyoto University,* [3]*Graduate School of Engineering Science, Osaka University*) ○Yusuke Nakakuki,[1] Takashi Hirose,[2] Hikaru Sotome,[3] Hiroshi Miyasaka,[3] Kenji Matsuda[1]

Keywords: Helical Structures; Polycyclic Aromatic Hydrocarbons; Chiroptical Properties; Quantum Calculations; Transient Absorption Spectroscopy

π-Conjugated aromatic molecules with helically twisted geometry are fascinating materials with potential applications in inductors, springs, and pressure sensors working on the nanometer scale. In this work, we synthesized π-extended [5], [7], and [9]helicene derivatives **1**–**3** (Figure 1a).

The homogeneously π-extended helicenes showed the lowest-energy absorption bands at 500−1100 nm (i.e., $\lambda_{max,abs}$ = 529, 675, 809 nm for **1**, **2**, and **3**, respectively), which were attributed to the HOMO→LUMO transitions by DFT calculations. Given that the excitation energy of the original [*n*]helicenes is largely independent of the length of the helical structure, the prominent red shift of **1**–**3** in the absorption bands is likely attributed to significant orbital interactions between phenanthrene subunits in the π-extended helicene framework. Enantiomers of **1**–**3**, isolated by HPLC with a chiral column, exhibited Cotton effects with dissymmetry factors of g_{CD} = 0.2–3.0 × 10^{-2} (Figure 1b). Interestingly, π-extended helicenes **1**–**3** were not emissive due to their ultrafast nonradiative decay dynamics in the $S_1 \rightarrow S_0$ transition with time constants of about 1 ps, which is marked contrast to emissive planar molecules such as rylenes[1] and carbon-bridged oligo(phenylene vinylene) molecules[2].

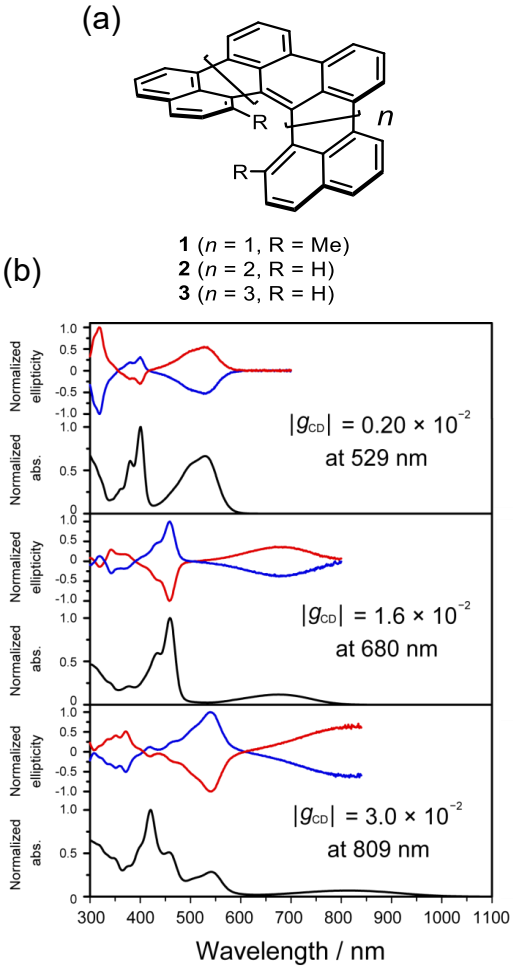


Figure 1. (a) Molecular structures of π-extended helicenes **1**–**3** (b) Absorption and circular dichroism (CD) spectra of **1** (top), **2** (middle), **3** (bottom). Red and blue lines denote the (*P*)- and (*M*)-isomers.

[1] A. Bohnen *et al*., *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 525.
[2] M. Morales-Vidal *et al*., *Nat. Commun.* **2015**, *6*, 8458.

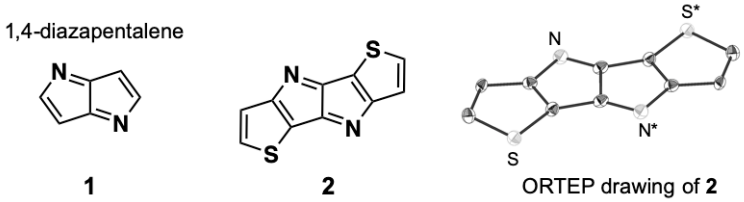
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チオフェン縮環 1,4-ジアザペンタレンの合成，構造および反応性

（名大院理[1]・京大 iCeMS[2]）◯薄葉 純一[1]・深澤 愛子[2]
Synthesis, Structure, and Reactivity of Thiophene-fused 1,4-Diazapentalene ([1]*Graduate School of Science, Nagoya University,* [2]*Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University*) ◯Junichi Usuba,[1] Aiko Fukazawa[2]

Replacement of C=C bonds in π-conjugated systems with C=N bonds has long been recognized as a promising approach for the modulation of the electronic structure and thus properties. However, the studies on the effect of such replacement in the cyclic 4nπ-electron systems with pronounced antiaromaticity still remain unexplored because of their inherent instability. In this context, we have recently demonstrated that annulation of thiophene moiety to pentalene is effective for the stabilization without bulky substituents while retaining strong antiaromaticity.[1] Based on this strategy, we here succeed the synthesis and characterization of thiophene-fused diazapentalene **2**, a C=N-containing 8π-electron system bearing fused thiophene moieties. Notably, **2** thus obtained was stable under ambient conditions in the solid state despite of higher antiaromaticity compared to the pristine 1,4-diazapentalene **1**. In addition, **2** exhibited high electron affinity owing to the electronic effect of the C=N bonds. The effects of partial replacement of C=C with C=N bonds in a 4nπ electron system will be discussed from both experimental and theoretical viewpoints.
Keywords : Nitrogen-containing π electron system, Thiophene, Antiaromaticity, π Conjugation, Reactivity

π 共役化合物の C=C 結合の一部を C=N 結合に置き換えるとその性質は大きく変化する．環状 4nπ 電子系についてこのような元素置換の効果を調べるためには，その不安定性の克服が課題となる．最近我々は 8π 電子系ペンタレンにチオフェンを縮環させることで，強力な反芳香族性を維持しながらかさ高い置換基を用いなくとも安定化できることを明らかにした[1]．本研究ではこの安定化法を C=N 結合をもつ 8π 電子系 1,4-ジアザペンタレン **1** に適用することで，チオフェン縮環ジアザペンタレン **2** の合成および構造解析に成功したので報告する．**2** は固体状態では室温大気中で安定である一方，無縮環のモデル化合物 **1** よりも強い反芳香族性をもつことがわかった．また，**2** は C=N 結合の電子構造を反映し高い電子受容性をもつことが確認された．本発表では **2** の構造や反応性に基づき，実験と理論の両面から 4nπ 電子系の一部を C=N 結合に置換した効果について論じる．



1 **2** ORTEP drawing of **2**

1. J. Usuba, A. Fukazawa *et al.*, *Chem. Eur. J.* DOI: 10.1002/chem.202004244.

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Development of Benzo[*de*]isoquinolino[1,8-*gh*]quinoline Diimide n-Type Organic Semiconductors with Asymmetric Substituents

([1]*Graduate School of Frontier Sciences, The University of Tokyo*, [2]*University of Tsukuba,* [3]*Kitasato University,* [4]*FujiFilm Corp.,* [5]*OPERANDO-OIL, AIST-UTokyo,* [6]*WPI-MANA, NIMS,* [7] *PRESTO, JST*)
○Craig P. Yu,[1] Shohei Kumagai,[1] Hiroyuki Ishii,[2] Go Watanabe,[3] Hiroki Sugiura,[4] Yukio Tani,[4] Tetsuya Watanabe,[4] Jun Takeya,[1,5,6] Toshihiro Okamoto[1,5,7]
Keywords: Organic semiconductors; n-Type; Asymmetric substituents; Molecular assemblies; Charge transport

The molecular assembly of organic semiconductors (OSCs) is arguably the most essential factor to achieve band-like charge-transport[1], suppression of molecular flucuations[2], and high charge-carrier mobility (μ). In contrast to the high-performance hole-transporting p-type OSCs (μ > 10 cm^2 V^{-1} s^{-1})[3], the electron-transporting n-type OSCs exhibit much lower μ that are inadequate for the construction of all-organic logic circuits. It shows that our current understanding of molecular assemblies needs to be improved in order to effectively develop high-performance n-type OSCs. Recently, our group developed a robust synthetic method to decorate the nitrogen-containing benzo[*de*]isoquinolino[1,8-*gh*]quinoline diimide (**BQQDI**)[4] π-electron core with asymmetric substituents (**Figure**). We have demonstrated that the interlayer interactions of asymmetric **BQQDI** can be effectively tuned by varying the length of alkyl sidechains, and we also discovered an intriguing *gauche* alkyl conformation as a result of molecular mimicry to achieve favorable molecular assemblies and suppressed molecular fluctuations. To further examine the molecular assembly-performance relation of **BQQDI**, we investigated the effect of different heterocyclic substituents in asymmetric **BQQDI**. Owing to the labile nature of some heterocycles, a new synthetic strategy with mild reaction conditions was developed, and the asymmetric **BQQDI** derivatives were extensively investigated in terms of molecular assemblies, charge-transport properties, and device performances to advance our understanding of high-performance n-type OSCs.

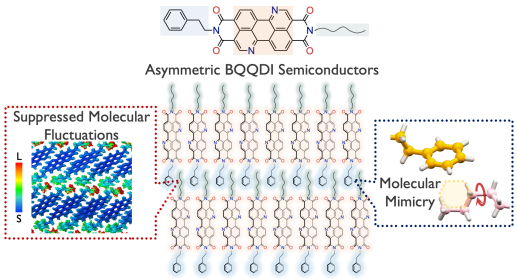


Figure. Molecular design of asymmetric **BQQDI**.

1) V. Podzorov *et al*., *Phys. Rev. Lett.* **2005**, *95*, 226601. 2) S. Illig *et al*., *Nat. Commun.* **2016**, *7*, 10736. 3) T. Okamoto *et al*., *J. Am. Chem. Soc.* **2020**, *142,* 9089. 4) T. Okamoto *et al*., *Sci. Adv.* **2020**, *6*, eaaz0632.

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π-Electronic Ion Pairs：Ordered Arrangement Based on Noncovalent Interactions

(*College of Life Sciences, Ritsumeikan University*) ○Hiroki Tanaka, Yohei Haketa, Hiromitsu Maeda

Keywords: Ion-Pairing Assemblies; π-Electronic Systems; Porphyrin Ions; Noncovalent Interaction

π-Electronic ion pairs are of interest for the fabrication of electronic materials with potential ferroelectric and electric conductive properties. Because of their appropriate sizes, geometries, and electronic states, π-electronic ions can achieve ordered ion-pair arrangements as dimension-controlled assemblies, including supramolecular gels and liquid crystals.[1] Despite numerous studies on assembling modes, the interactions between π-electronic ions are not well understood. This study focuses on the characteristic interactions operative in ion-pairing assemblies comprising porphyrin ions, which delocalize the charge in the core units. π-Electronic anions produced upon deprotonation of *meso*-hydroxy-substituted porphyrins (MHPs)[2] can form various π-electronic ion pairs in combination with π-electronic cations such as porphyrin–Au^{III} complexes[3] and triazatriangulenium cations ($TATA^+$). π-Electronic ion pairs were formed by mixing Na^+ salts of porphyrin anions, prepared from the CH_2Cl_2 solutions of MHPs with aqueous NaOH, and 1 equiv of chloride salts of desired countercations, followed by the removal of NaCl by washing with water (Fig. 1). The π-electronic ion pairs exhibited characteristic ^{1}H NMR signal shifts due to ion-pairing stacking in solution (Fig. 2). Furthermore, the energy decomposed analysis of single-crystal packing structures revealed that electrostatic and dispersion interactions were important for stabilizing the stacking π-electronic ions.

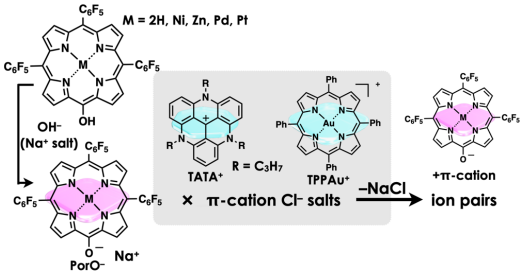


Fig. 1 Method for preparing π-electronic ion pairs.

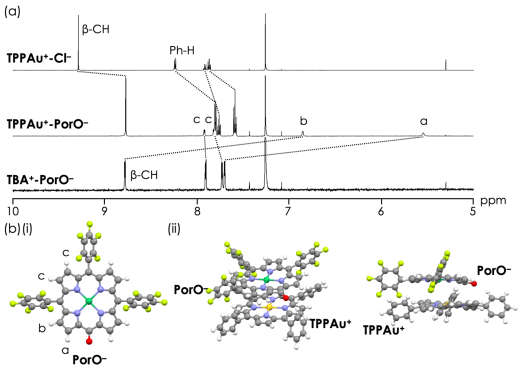


Fig. 2 (a) ^{1}H NMR spectra of $TPPAu^+$-Cl^-, $TPPAu^+$-$PorO^-$, and TBA^+-$PorO^-$ in $CDCl_3$ (1.0×10^{-3} M) and (b) optimized structures of (i) $PorO^-$ and (ii) $TPPAu^+$-$PorO^-$.

1) A recent review: Haketa, Y. et al., *Mol. Syst. Des. Eng.* **2020**, *5*, 757. 2) (a) Sasano, Y. et al., *Dalton Trans.* **2017**, *46*, 8924; (b) Sasano, Y. et al., *Chem. Eur. J.* **2019**, *25*, 6712. 3) (a) Haketa, Y. et al., *iScience* **2019**, *14*, 241; (b) Tanaka, H. et al., *Chem. Asian J.* **2019**, *14*, 2129.

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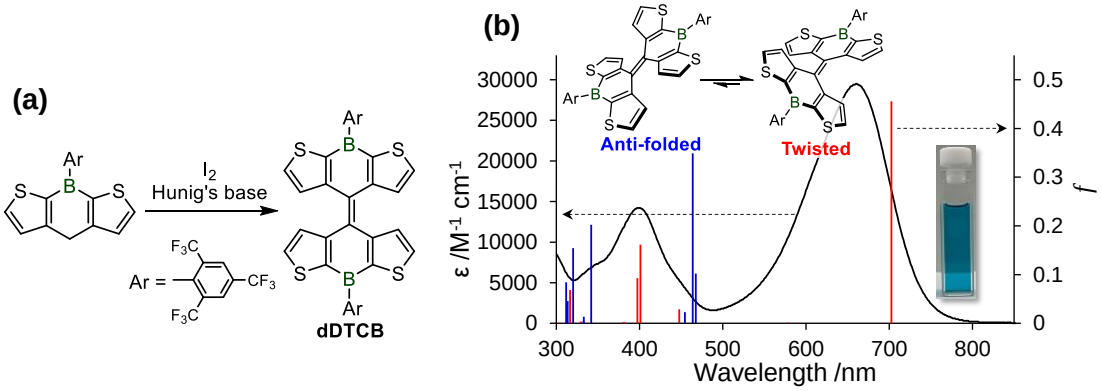
Synthesis of Thiophene-Based Twisted Bistricyclic Aromatic Ene with Tricoordinate Boron

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University,* [2]*Graduate School of Engineering, Osaka Prefecture University*) ○Yohei Adachi,[1] Takanori Nomura,[1] Shion Tazuhara,[2] Hiroyoshi Naito,[2] Joji Ohshita[1]

Keywords: Boron; Thiophene; Conjugated Material; OFET

Overcrowded bistricyclic aromatic enes (BAEs) are known as stimulus-responsive materials according to conformational change, e.g., between twisted and anti-folded ones.[1] The twisted conformers of BAEs generally have low-energy absorption relative to the folded one, which is due to the highly twisted central C=C double bond. However, the easy isomerization makes it difficult to apply the twisted conformers to photo absorption/conversion materials. On the other and, the incorporation of tricoordinate boron into conjugated systems is of current interest in the field of materials chemistry as it induces Lewis acidity and specific orbital interactions (p-π* interactions).[2] In this work, we synthesized a tricoordinate boron-embedded and thiophene-based BAE (**dDTCB**) as a new boron-containing conjugated system. The robust sp^2 structure of tricoordinate boron and the relatively low aromaticity of thiophene were expected to impose the twisted conformer.

The predominant population of the twisted conformer of **dDTCB** was confirmed by NMR, absorption, and single-crystal XRD analysis. Electrochemical measurements suggested the electron-deficient character of **dDTCB** (E_{red} = −0.81 V vs $Fc^{0/+}$). Indeed, preliminary studies on the application of **dDTCB** to organic field-effect transistors (OFETs) revealed its moderately high electron mobility of 1.9×10^{-3} cm^2 V^{-1} s^{-1}.[3]



(a) Synthetic scheme of **dDTCB**. (b) Experimental absorption spectrum in toluene (black line) and calculated TD-DFT results of twisted (red) and folded (blue) conformers.

1) P. Ulrich Biedermann, J. J. Stezowski, I. Agranat, *Eur. J. Org. Chem.* **2001**, 15234; 2) L. Ji, S. Griesbeck, T. B. Marder, *Chem. Sci.*, **2017**, *8*, 846–863; 3) Y. Adachi, T. Nomura, S. Tazuhara, H. Naito, J. Ohshita, *Chem. Commun.*, **2021**, doi:10.1039/D0CC07952A.

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[A09-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair:Masayuki Takeuchi, Tomoki Ogoshi
Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 9 (Online Meeting)

[A09-3pm-01] Synthesis and Cooperative Molecular Recognition of Homoditopic Host Molecule with Rebek’ s Cavitands

○Haruna Fujimoto[1], Daisuke Shimoyama, Takehiro Hirao[1], Takeharu Haino[1] （1. Hiroshima University）

1:00 PM - 1:20 PM

[A09-3pm-02] Triaxially Woven Hydrogen-Bonded Network of Tetrakis(carboxybiphenyl)ethene: Structure and Mechanochromic Behavior

○Yuto Suzuki[1], Norimitsu Tohnai[2], Ichiro Hisaki[1] （1. Graduate School of Engineering Science, Osaka University, 2. Graduate School of Engineering, Osaka University）

1:20 PM - 1:40 PM

[A09-3pm-03] Host– guest chemistry and optical properties of porous molecular crystals

○Hiroshi Yamagishi[1] （1. Univ. of Tsukuba）

1:40 PM - 2:00 PM

[A09-3pm-04] Base-/Acid-Induced Multi-Step Fluorescence of Trefoil Azine

○Noriho Taniguchi[1], Masaya Naito[1], Shinobu Miyagawa[1], Yuji Tokunaga[1] （1. University of Fukui）

2:00 PM - 2:20 PM

[A09-3pm-05] ^{129}Xe NMR structural analysis of continuous porosity of columnar liquid crystal composed of stacked macrocycles

○Shin-ichiro Kawano[1], Takahiro Taki[1], Hiroaki Yoshimizu[2], Kentaro Tanaka[1] （1. Nagoya University, 2. Nagoya Institute of Technology）

2:20 PM - 2:40 PM

[A09-3pm-06] Conformational Control of Aliphatic Oligoketones by Pillar[5]arene and its Application

○Yumehiro Manabe[1], Keisuke Wada[2], Yudai Baba[2], Tomoki Yoneda[1], Tomoki Ogoshi[3,4], Yasuhide Inokuma[1,5] （1. Grad. Sch. Eng., Hokkaido Univ., 2. Grad. Sch. Eng. Sci. Tech., Kanazawa Univ., 3. Grad. Sch. Eng., Kyoto Univ., 4. WPI-NanoLSI, Kanazawa Univ., 5. WPI-ICReDD, Hokkaido Univ.）

2:40 PM - 3:00 PM

[A09-3pm-07] Building Heterodimer Porphyrin Capsules Bearing Different Number of Hydrogen bond Function and Application to Aromatic Multi-Layer Structure

○Masahiro Ueda[1], Ban Hayato[1], Kimura Masaki[1], Miyagawa Shinobu[1], Naito Masaya[1], Tokunaga Yuji[1] （1. University of Fukui）

3:00 PM - 3:20 PM

[A09-3pm-08] Selective inclusion of regioisomers of disubstituted aromatic compounds with crystals of *p-tert*-butylcalix[4]arene: Mechanistic

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consideration for guest selectivity and application for separation

○Tomoaki Matsumoto[1], Atsuya Sakamoto[1], Takuro Sasaki, Naoya Morohashi[1], Tetsutaro Hattori[1] （1. The University of Tohoku）

3:20 PM - 3:40 PM

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Synthesis and Cooperative Molecular Recognition of Homoditopic Host Molecule with Rebek's Cavitands

(*Graduate School of Hiroshima University*) ○ Haruna Fujimoto, Daisuke Shimoyama, Takehiro Hirao, Takeharu Haino

Keywords: supramolecurar chemistry, molecular recognition, cooperativity

A resorcinarene-based cavitand possesses a deepened vase-like structure, showing unique molecular recognitions and catalytic properties. We developed ditopic bisresorcinarene **2**, which is composed of two resorcinarenes connected with four aliphatic chains.[1] Here, we synthesized biscavitand **1** possessing two Rebek's deepened cavitand units (Figure 1a).

In the crystal structure of **1**, two stereoisomerisms were found: one is the clockwise/anticlockwise interconversion of the interannular hydrogen bonding of the amide groups, and the other is the (P)/(M) helical interconversion of the bisresorcinarene unit. The kinetic analysis using EXSY technique revealed that the interconversion of the interannular hydrogen bonds and the helix-helix interconversion occurred independently. To reveal the guest binding behavior of the biscavitand **1**, NMR and ITC experiment were conducted in toluene. The guest binding of biscavitand **1** with **G1** showed strong negative cooperativity with association constants (Ka_1 and Ka_2) of 440,000 and 10,000 L mol^{-1}, respectively, in toluene (Figure 1b).

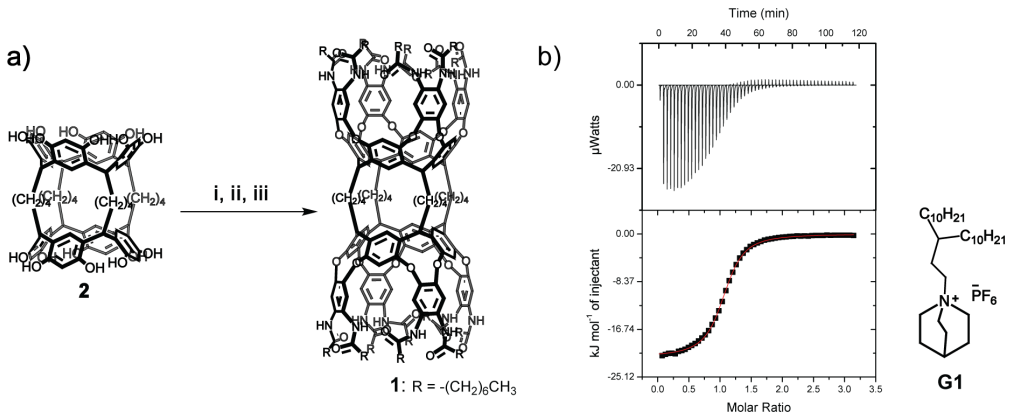


Figure 1. a) Synthesis of biscavitand **1**. Reagents: (i) 1,2-difluoro-4,5-dinitrobenzene, DIPEA, DMF; (ii) Raney-Ni, H_2, DMF/MeOH; (iii) octanoyl chloride, DMAP, pyridine. b) ITC titration experiment of **1** with **G1** in toluene and chemical structure of **G1**.

[1] H. Yamada, T. Ikeda, T. Mizuta, T. Haino, *Org. Lett.*, **2012**, *14*, 4510–4513.; D. Shimoyama, T. Ikeda, R. Sekiya, T. Haino, *J. Org. Chem.,* **2017**, *82*, 13220-13230.; D. Shimoyama, H. Yamada, T. Ikeda, R. Sekiya, T. Haino, *Eur. J. Org. Chem.,* **2016**, 3300-3303.

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テトラフェニルエテン誘導体が形成する水素結合性二次元ネットワークの編み込み集積構造とその蛍光挙動

(阪大院基工[1]・阪大院工[2]) ○鈴木　悠斗[1]・藤内　謙光[2]・久木　一朗[1]
Triaxially Woven Hydrogen-Bonded network of Tetrakis(carboxybiphenyl)ethane: Structure and Mechanochromic Behavior. ([1]*Graduate School of Engineering science, Osaka University*, [2] *Graduate School of Engineering, Osaka University*) ○Yuto Suzuki,[1] Norimitsu Tohnai,[2] Ichiro Hisaki [1]

Many porous organic materials such as hydrogen-bonded organic frameworks (HOFs), are constructed via assembling of low-dimensional network motifs. Their assembly manner is an important factor for designing whole porous structure. In this work, we found that tetrakis(carboxybiphenyl)ethene (**CBPE**) provides a porous HOF **CBPE-1** with an exotic structure. **CBPE** forms a 2D chicken wire via H-bonding, followed by interpenetrating into a triaxially woven porous framework. This **CBPE-1** has a 1D channel pore with 9.3 Å aperture and shows permanent porosity after solvent removal. The activated framework shows fluorescence changes induced by mechanical force. Here, we report the porous structure, molecular inclusion, and mechanochromic behavior of the framework.

Keywords : Hydrogen-bonded organic framework; Porous structure; Carboxylic acid; Tetraphenylethene; Woven structure.

水素結合性有機フレームワークなどの有機分子を用いた多孔質構造体を構築する際、低次元の分子集合モチーフの設計のみならず、そのモチーフがどのように集積して高次構造を与えるのか、例えばその集積様式や相互貫入数など、を考慮する必要がある。本研究では、テトラカルボキシビフェニルエテン誘導体 **CBPE** が分子間水素結合によって 2 次元ネットワーク(Fig. 1a)を形成し、さらにそのネットワークが 3 方向より相互貫入した多孔質構造 **CBPE-1** (Fig. 1b)を与えることを見出した。興味深いことに、本構造は類縁体のテトラカルボキシフェニルエテン **CPE** が形成する 2 次元ネットワークの非相互貫入積層構造[1]とは大きく異なる。**CBPE-1** は *a* 軸方向に 1 次元チャネル空孔を有しており、その空孔径は最大 9.3 Å、最小 3.6 Å であった。脱ゲストや 220 °C の加熱に対して構造を維持する永続的多孔性を有し、その BET 比表面積は 555 m^2g^{-1} であった[2]。また本構造は、外部刺激による蛍光変化を示した。本発表では結晶構造とそのメカノクロミック挙動について述べる。

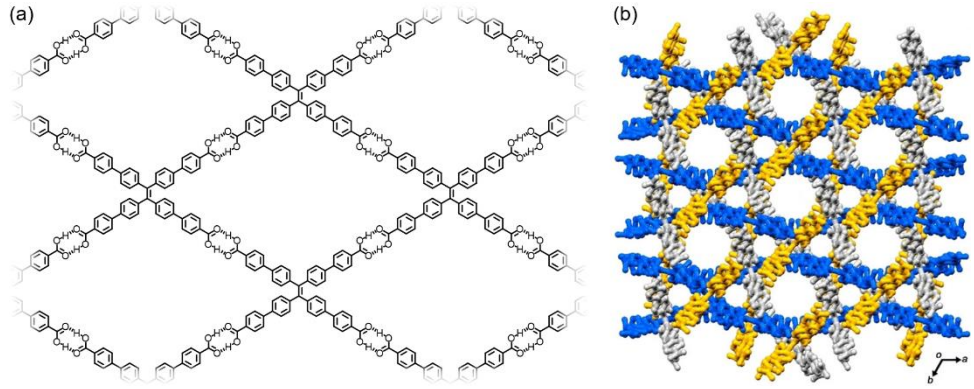


Figure 1. (a) A H-bonded 2D chicken wire of **CBPE** and (b) a crystal structure of woven **CBPE-1**.

1) N. B. Shustova, B. D. McCarthy, and M. Dincă, *J. Am. Chem. Soc.* **2011**, *133*, 20126–20129.
2) Y. Suzuki, N. Tohnai, and I. Hisaki, *Chem. Eur. J.* **2020**, *26,* 17056–17062.

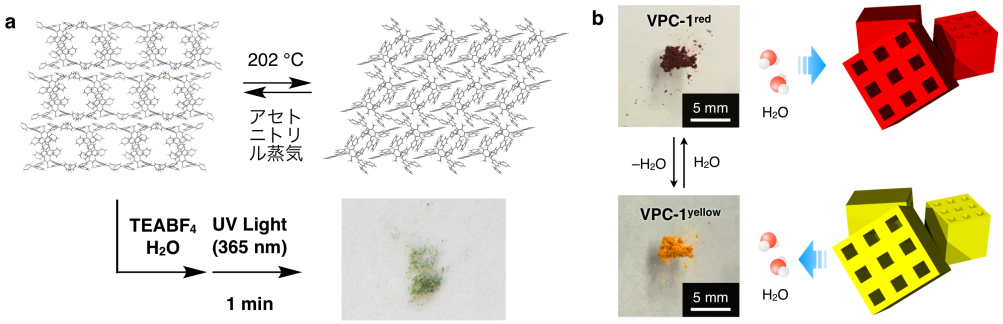
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多孔質分子性結晶に発現する吸着特性と光物性

（筑波大数理[1]）○山岸 洋[1]
Host–guest chemistry and optical properties of porous molecular crystals ([1] *Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba*) ○Hiroshi Yamagishi[1]

Porous molecular crystals, whose constituent organic molecules are bound together via weak intermolecular interactions such as van der Walls forces, exhibit distinct structural flexibility and stimuli responsivity. However, the study about the porous crystals has yet to be established due to the difficulty in designing and synthesizing a thermally stable porous framework. Here, I introduce a series of novel porous molecular crystals that feature excellent thermal stability as well as unique chemical and physical functionalities. These crystals consist of aromatic dendrimers that spontaneously assemble into porous framework just upon simple re-crystallization in an appropriate organic solvent. Resultant porous crystals not only work as typical microporous adsorbate but exhibit self-healing ability, photo-chemical activity, and humidity-dependent chromism.
Keywords : Porous crystals; Molecular crystals; Self-healing; Photo-chemical reaction; Hydrochromism

ファンデルワールス力などの極めて弱い分子間力で構成分子が結び付けられている多孔質分子性結晶（VDW 多孔質結晶）には、堅牢な多孔質結晶とは一線を画した構造柔軟性や刺激応答性が発現する。ただし、構成有機分子間に働く引力相互作用が弱いために戦略的な設計・合成が困難であり、これまでは偶然から見いだされてきた僅かな例が知られているのみであった。本発表では発表者が見出してきた VDW 多孔質結晶をいくつか紹介するとともに、結晶化プロセスと結晶構造との相関について新たに見出した知見について紹介する。また、これらの VDW 多孔質結晶に発現する特徴的な吸着能や光反応特性、湿度依存的なクロミズム特性などを紹介する。



1) Yamagishi, H. *et al*., Self-assembly of lattices with high structural complexity from a geometrically simple molecule. *Science* **2018**, *361*, 1242–1246.
2) Nakayama, A. *et al*., Facile light-initiated radical generation from 4-substituted pyridine under ambient conditions. *Chem. Commun.* **2020**, *56*, 6937–6940.
3) Yamagishi, H. *et al*., Sigmoidally hydrochromic molecular porous crystal with rotatable dendrons. *Communications Chemistry* **2020**, *3*.

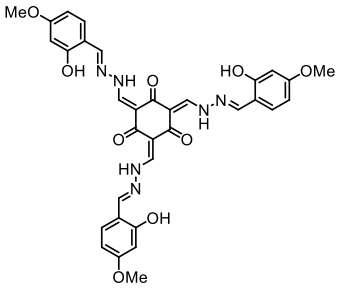
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三つ葉型アジンの塩基/酸による発光特性制御

（福井大院工）○谷口 典穂・内藤 順也・宮川 しのぶ・徳永 雄次
Base-/Acid-Induced Multi-Step Fluorescence of Trefoil Azine (*Graduate School of Engineering, University of Fukui*) ○Noriho Taniguchi, Masaya Naito, Shinobu Miyagawa, Yuji Tokunaga

Base-/acid-induced multi-step luminescence was demonstrated by using a trefoil-shaped salicylaldehyde azine derivative bearing multiple acidic protons. ^{1}H NMR analysis revealed that the azine exists as an equilibrium mixture of two geometric isomers at room temperature in solution. Base-induced three-step deprotonation of the azine in solution was confirmed by ^{1}H NMR, UV-vis absorption, and emission spectroscopy.
Keywords : Salicylaldehyde Azine; Fluorescence; Multi-Step Switching; Protonation/Deprotonation

酸/塩基に応答する発光性化合物は非接触的な pH センサーへの応用が可能なため、生物学や環境化学の分野で近年注目されている。酸や塩基の添加により 2 状態の色調変化を示す蛍光物質は数多く報告されているが、多状態で色調変化する例は少ない。本研究で我々は、複数のプロトン供与性部位を有する三つ葉型のサリチルアルデヒドアジン誘導体 **1** が、塩基添加による段階的な脱プロトン化と、それに伴う 4 状態の発光特性変化を示すことを見出した。



1

1,3,5-トリホルミルフロログルシノールと 4-メトキシサリチルアルデヒドヒドラゾンとを 1:3 の物質量比で反応させることで目的の三つ葉型サリチルアルデヒドアジン誘導体 **1** を合成した。**1** は DMSO 溶液中において NaOH 水溶液を添加することで、塩基の当量に従った段階的な脱プロトン化が進行することを、^{1}H NMR、UV-Vis 吸収および発光スペクトル解析により明らかにした。**1** の発光特性は、NaOH の当量を 0、1、6 および 20 eq と増加させることで、黄色、弱黄色、強黄色および青緑色と 4 状態に変化した (Figures 1 and 2)。塩基添加後の溶液に対してトリフルオロ酢酸を添加すると、わずかに分解生成物を伴いながら元の ^{1}H NMR スペクトルに回復した。酸添加による本可逆性は発光スペクトルにおいては観測されなかったが、これは微量の発光性分解物によるものと考えられる。

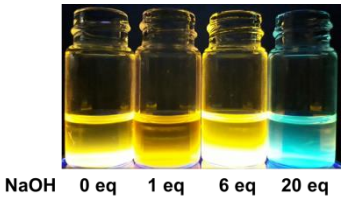


Figure 1. **1** の NaOH 存在下での発光の写真 [0.10 mM in DMSO/H_2O = 20:1 (v/v), λ_{ex} = 365 nm]。

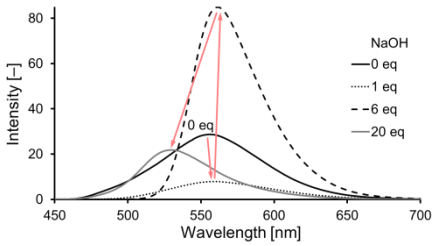


Figure 2. **1** の NaOH 存在下での発光スペクトル [0.10 mM in DMSO/H_2O = 20:1 (v/v), λ_{ex} = 440 nm]。

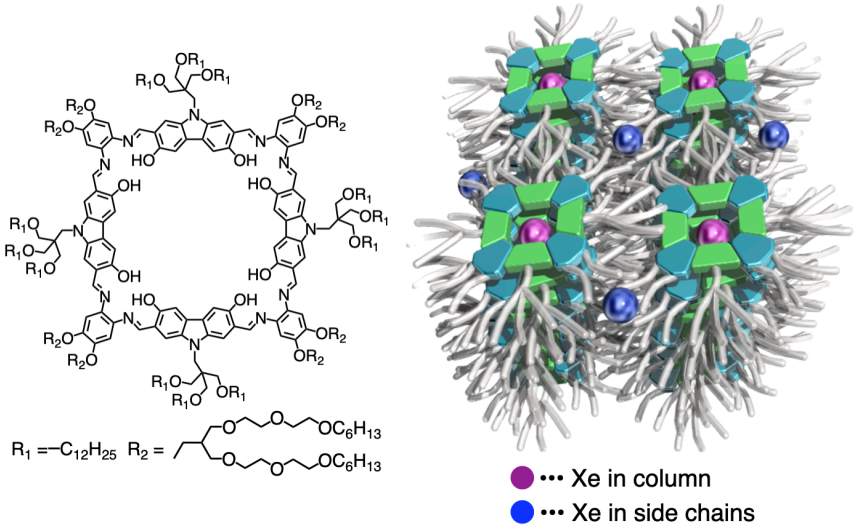
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^{129}Xe NMR Structural Analysis of Continuous Porosity of Columnar Liquid Crystal Composed of Stacked Macrocycles

([1]*Department of Chemistry, Graduate School of Science, Nagoya University*, [2]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Shin-ichiro Kawano,[1] Takahiro Taki,[1] Hiroaki Yoshimizu,[2] Kentaro Tanaka[1]

Keywords: Liquid Crystals; Xenon; Macrocycles; Nanospace; Supramolecular Chemistry

Columnar assembly of macrocyclic molecules in liquid crystals are promising system for fluid nanoporous materials. Recently, we reported the columnar liquid-crystalline (LC) macrocycle composed of carbazoles and salphens that can accommodate tetraalkylammonium ions as the guest molecules inside the nanospace of the columnar liquid crystal through electrostatic interaction.[1] In this paper, we will discuss the first experimental analyses of void in the columnar liquid crystal of the macrocyclic mesogens by means of ^{129}Xe NMR spectroscopy. The chemical shift of ^{129}Xe in the nanospace inside the middle of the column are significantly affected by Xe pressure, temperature, and transitions of LC phases. Pulse-field gradient technique of ^{129}Xe NMR suggests that the xenon diffuses with a similar diffusion coefficient to those in the microspace of zeolites.[2] The substantial size of the nanospace is estimated to be 4.9 Å according to the ^{129}Xe NMR experimental results.



1) S. Kawano, Y. Ishida, K. Tanaka, *J. Am. Chem. Soc.* **2015**, *137*, 2295. 2) J.-L. Bonarded, A. Gédéon, M.-A. Springuel-Huet, J. Fraissard, *Mol. Sieves.* **2007**, 5, 155.

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Conformational Control of Aliphatic Oligoketones by Pillar[5]arene and its Application

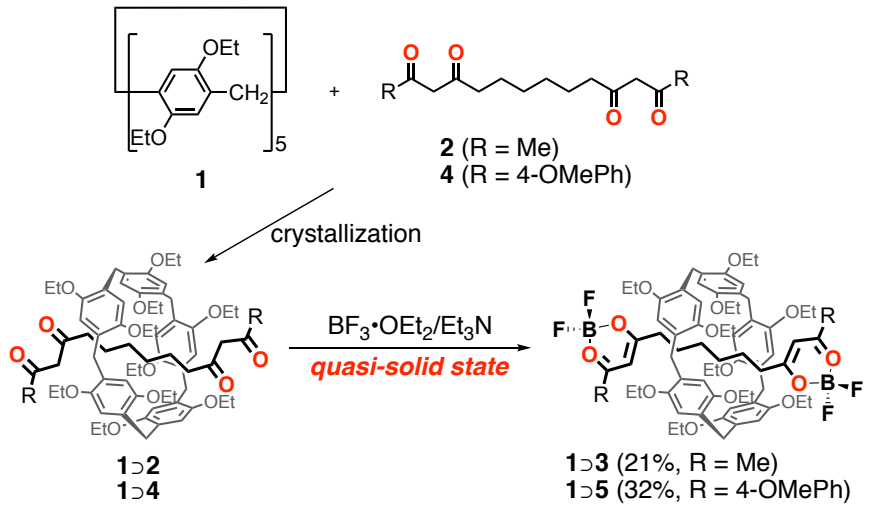
([1]*Grad. School of Eng., Hokkaido Univ.*, [2]*Grad. School of Nat. Sci. Tech., Kanazawa Univ.*, [3]*Grad. School of Eng., Kyoto Univ.*, [4]*WPI-Nano LSI, Kanazawa Univ.*, [5]*WPI-ICReDD, Hokkaido Univ.*) ○ Yumehiro Manabe,[1] Keisuke Wada,[2] Yudai Baba,[2] Tomoki Yoneda,[1] Tomoki Ogoshi,[3,4] Yasuhide Inokuma[1,5]

Keywords: Aliphatic Oligoketones; Conformational Control; Pillar[5]arene; Rotaxane

Control of specific conformations in flexible chain molecules is a key for controlling their reactivities and properties. Herein, we show induction and fixation of linear conformation of aliphatic oligoketones, which combine structural flexibility of aliphatic chains and reactivities of carbonyl groups, by host-guest complexation with pillar[5]arene **1**.[1]

Conformationally flexible tetraketone **2** was reversibly incorporated into pillar[5]arene **1** with an association constant of $K = 14\ M^{-1}$ in chloroform. The linear conformation of **2** induced by host-guest complexation was locked by BF_2-complexiation at the 1,3-diketone sites; when pseudo-rotaxane **1**⊃**2** was treated with BF_3•OEt_2 and Et_3N in quasi-solid state reaction conditions, rotaxane **1**⊃**3** was obtained in 21% yield (Scheme 1). Single crystal X-ray structure of rotaxane **1**⊃**3** revealed the linear conformation of axis molecule **3** was retained after BF_2-complexiation, and both ends of axis molecule **3** was 12.4 Å apart from each other.

Similar conformational control was applied to alkyl-linked flexible chromophore dyad **5**. Rotaxane **1**⊃**5** was similarly obtained in 32% yield from pseudo-rotaxane **1**⊃**4** (Scheme 1). The UV-vis spectra of conformationally flexible dyad **5** showed solvatochromic behavior in CH_2Cl_2, THF and 1,4-dioxane while the solvatochromism was not observed in rotaxane **1**⊃**5** due to the conformational restriction of intramolecular aggregation of axis molecule **5**.



Scheme 1. Synthesis of rotaxane **1**⊃**3** and **1**⊃**5** under quasi-solid state reaction conditions.

[1] Y. Manabe, K. Wada, Y. Baba, T. Yoneda, T. Ogoshi, Y. Inokuma, *Org. Lett.*, **2020**, *22*, 3224–3228.

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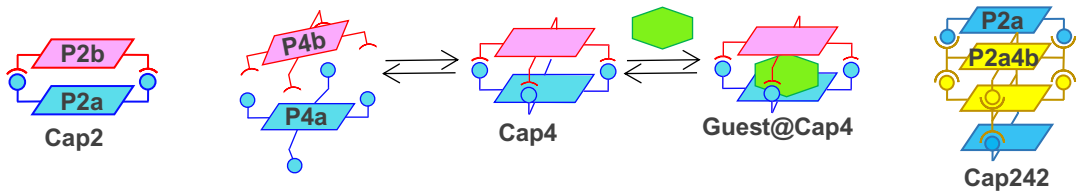
Building Heterodimer Porphyrin Capsules Bearing Different Number of Hydrogen Bond Function and Application to Aromatic Multi-Layer Structure

(*Graduate School of Engineering, University of Fukui*) ○Masahiro Ueda, Hayato Ban, Masaki Kimura, Shinobu Miyagawa, Masaya Naito, Yuji Tokunaga
Keywords: Porphyrin; Self-Assembled Capsule; Molecular Recognition; Hydrogen Bond; Thermodynamics

We have achieved construction of self-assembled porphyrin dimer and trimer capsules.[1,2] The capsules consisted of a pair of porphyrins bearing two or four benzoic acid or aminoquinoline units as H-bonding moieties at meso position, respectively, and could bind π-aromatic compounds, forming multi-layer π-aromatic structures. Here, we report kinetic and thermodynamic stabilities of two- and four- armed porphyrin dimers and their molecular recognition behaviors. Taking the results into account, we present construction of a higher order structure by using porphyrins featuring different numbers of the complementary H-bonding donor and acceptor pair.

Stabilities of porphyrin dimers: Two- and four- armed porphyrin dimers **Cap2** and **Cap4** quantitatively formed from the corresponding pairs of porphyrins in $CDCl_3$. In ^{1}H NMR spectra of an equimolar mixture of the pairs in a mixture of $CDCl_3$ and DMSO-d_6, the dimers and monomeric species were observed, respectively. **Cap4** is kinetically and thermodynamically more stable than **Cap2**. ^{1}H NMR titration experiments of the capsules and electron-deficient mono- and bicyclic aromatic guests revealed that recognition abilities of **Cap2** were ca. 10 times higher than those of **Cap4**.

Formation of porphyrin tetramer: We designed and synthesized porphyrin **P2a4b**, bearing two terephthalic acid and two aminoquinoline, for construction of porphyrin tetramer **Cap242**. Although **P2a4b** was not soluble in $CDCl_3$, the addition of an equimolar amount of the two-armed aminoquinolylporphyrin **P2a** and DMSO-d_6 solution of aromatic guest resulted in homogeneous solution. The ^{1}H NMR spectrum of the mixture featured complexes formed from **Cap242** and the guest molecule(s).



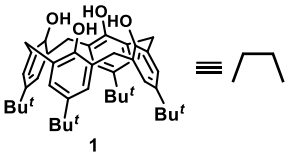
1) M. Kimura, J. Miyashita, S. Miyagawa, T. Kawasaki, H. Takaya, Y. Tokunaga, *Asian J. Org. Chem.* **2018**, *7*, 2087－2093. 2) M. Ueda, M. Kimura, S. Miyagawa, H. Takaya, M. Naito, Y. Tokunaga, *Chem. Asian J.* **2020**, *15*, 2212－2217.

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Selective inclusion of regioisomers of disubstituted aromatic compounds with crystals of *p-tert*-butylcalix[4]arene: Mechanistic consideration for guest selectivity and application for separation

(*Graduate School of Engineering, Tohoku University*) ○ Tomoaki Matsumoto, Atsuya Sakamoto, Takuro Sasaki, Naoya Morohashi, Tetsutaro Hattori

Keywords: Calixarene; Inclusion; Aromatic compounds; Molecular crystals



1

The development of solid materials that can strictly discriminate the size and shape of organic molecules and selectively collect them is important in the separation and purification processes. We have been studying the selective inclusion of organic compounds with crystals of calixarenes. Although crystals of *p-tert*-butylcalix[4]arene (**1**) exhibit almost no inclusion selectivity toward chain alcohols and alkanes with flexible structures, the crystals included rigid regioisomers of disubstituted benzenes with high selectivities.[1] However, the discussions about quantitativity are not enough. In this study, we investigated the quantitativity of the inclusion with the intention of developing a practical method for the separation of regioisomeric disubstituted benzenes.

Inclusion experiments were performed by suspending crystals of **1** in decane solutions containing three regioisomers of disubstituted benzenes (1 or 0.5 molar equiv each to **1**). The resulting crystals were collected by filtration, dried in vacuo, and analyzed by ^{1}H NMR. Several disubstituted benzenes gave inclusion crystals with high selectivity and quantitativity. For example, the crystals of **1** included *p*-nitrotoluene and *p*-xylene, giving inclusion crystals formulated as **1**·*p*-nitrotoluene and **1**$_2$·*p*-xylene, respectively (Fig. 1). The guests could be recovered from the crystals by guest exchange. For example, suspending **1**·*p*-nitrotoluene in hexane gave crystals including only hexane. Isomerically pure *p*-Nitrotoluene was recovered from the filtrate in 84% yield. Mechanisms to realize the guest selectivities are also reported.

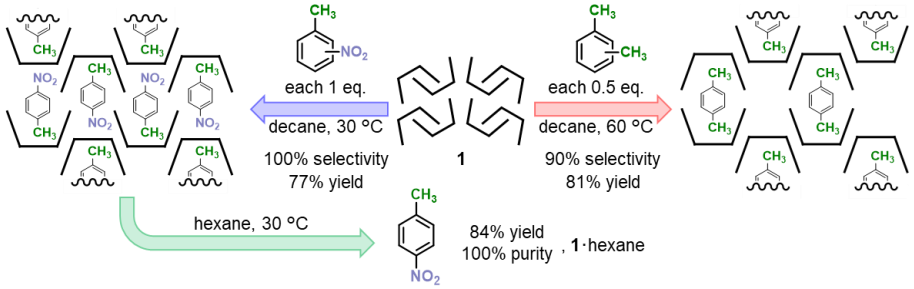


Figure 1. Selective inclusion of disubstituted benzenes with the crystals of **1**.

1) Morohashi, N.; Tonosaki, A.; Kitagawa, T.; Sasaki, T.; Ebata, K.; Hattori, T. *Cryst. Growth Des.* **2017**, *17*, 5038.

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[A21-3am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair:Hiroshi Ikeda, Yoichi Kobayashi

Sun. Mar 21, 2021 9:00 AM - 11:40 AM Room 21 (Online Meeting)

[A21-3am-01] A Mechanism for Opening an Unusual Reaction Pathway in the Mechanochemical Synthesis of Dibenzophenazine

○Naoki Haruta[1,2,3], Paulo Filho Marques de Oliveira[4,5], Alain Chamayou[4], Tohru Sato[1,2,3], Kazuyoshi Tanaka[1,2], Michel Baron[4] (1. FIFC, Kyoto Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. ESICB, Kyoto Univ., 4. IMT Mines Albi, 5. Univ. of São Paulo)

9:00 AM - 9:20 AM

[A21-3am-02] Development of Radical Difunctionalization of Ethylene Gas Predicted by Quantum Chemical Calculations

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

9:20 AM - 9:40 AM

[A21-3am-03] Development of Diversity-Oriented Synthesis Methodologies for Lactones via Activation of Molecular Iodine by Visible Light

○Saki Maejima[1], Eiji Yamaguchi[1], Akichika Itoh[1] (1. Gifu Pharmaceutical University)

9:40 AM - 10:00 AM

[A21-3am-04] Ratiometric fluorescent force probe that works in gels

○Takuya Yamakado[1], Shohei Saito[1] (1. Grad. Sch. of Sci., Kyoto Univ.)

10:00 AM - 10:20 AM

[A21-3am-05] Non-classical control of magnetic circularly polarized luminescence (MCPL) of pyrene and phenanthrene luminophores by electron donor and acceptor effects

○Nobuyuki Hara[1], Maho Kitahara[1], Takaharu Sugimura[1], Hayato Toda[1], Motohiro Shizuma[2], Akari Itou[3], Makoto Miyasaka[3], Michiya Fujiki[4], Yoshitane Imai[1] (1. Kindai University, 2. Osaka Research Institute of Industrial Science and Technology, 3. Tokyo Denki University;, 4. Nara Institute of Science and Technology)

10:20 AM - 10:40 AM

[A21-3am-06] Singlet Fission in Tetracene Dimers and Oligomers

○Shunta Nakamura[1], Hayato Sakai[1], Masaaki Fuki[2], Yasuhiro Kobori[2], Nikolai V. Tkachenko[3], Taku Hasobe[1] (1. Faculty of Science and Technology, Keio University, 2. Molecular Photoscience Reserch Center, Kobe University, 3. Tampere University)

10:40 AM - 11:00 AM

[A21-3am-07] Preparation and Application of Novel Pt Nanoparticles Supported on TiO_2 Photocatalyst

○Yuki Wada[1], Toshiki Akiyama[1], Kazuo Harada[1], Tetsuo Honma[2], Hiroshi Naka[3], Susumu Saito[3], Mitsuhiro Arisawa[1] (1. Graduate School of Pharmaceutical Sciences, Osaka University, 2. Japan Synchrotron Radiation Research Institute, SPring-8, 3. Graduate School of Science, Nagoya University)

11:00 AM - 11:20 AM

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[A21-3am-08] Mg-Promoted Reductive CO_2 Fixation of Propenyl Ketones

○Suhua ZHENG[1], Tianyuan ZHANG[1], Hirofumi MAEKAWA[1] （1. Nagaoka Univ. of Tech.）

11:20 AM - 11:40 AM

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ジベンゾフェナジンのメカノケミカル合成における特異な反応経路の発現メカニズム

（京大福井セ[1]・京大院工[2]・京大 ESICB[3]・アルビ国立高等鉱業学校[4]・サンパウロ大学[5]）○春田 直毅[1,2,3]、Paulo Filho Marques de Oliveira[4,5]、Alain Chamayou[4]、佐藤 徹[1,2,3]、田中 一義[1,2,3]、Michel Baron[4]

A Mechanism for Opening an Unusual Reaction Pathway in the Mechanochemical Synthesis of Dibenzophenazine ([1]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*, [3]*Unit of Elements Strategy Initiative for Catalysts & Batteries, Kyoto University,* [4]*IMT Mines Albi, Université de Toulouse,* [5]*University of São Paulo*)○Naoki Haruta,[1,2,3] Paulo Filho Marques de Oliveira,[4,5] Alain Chamayou,[4] Tohru Sato,[1,2,3] Kazuyoshi Tanaka,[1,2] Michel Baron[4]

Dibenzophenazine was recently synthesized in a ball-milling way at a high yield[1)]. This synthesis has been expected to involve two types of reactions[2-3)]. In this study, the reaction paths were determined by using density functional theory[4)]. A stepwise path was the lowest-energy path and a concerted path was also found with a higher barrier. The highest energy point along the latter path is not a transition state but a higher-order saddle point, and therefore the concerted path is not accepted as a reaction path. However, we found that only small mechanical force dissolves imaginary frequencies so that the higher-order saddle point is changed into a transition state. This shows how mechanical action opens a new reaction path.

Keywords： Mechanochemistry; Ball Mill; Dibenzophenazine; Quantum Chemistry; Transition State

最近、ジベンゾフェナジンがボールミリングによって、溶媒も触媒も用いることなく、高い収率（> 99%）で合成された[1)]。速度論実験や熱量測定の結果から、この高効率合成には二種類の反応が関与していると考えられているが[2-3)]、反応経路や力学的作用の影響について、量子化学的な観点からは明らかにされてこなかった。

本研究では、密度汎関数理論に基づき、ジベンゾフェナジン合成経路を決定した[4)]。外力のない通常条件下では、段階的反応が最もエネルギーの低い経路として、協奏的反応がエネルギーの高い経路として見つかった。しかし、後者の経路では、最もエネルギーの高い点が 1 次鞍点ではなく、高次鞍点になっており、遷移状態としては認められない。そこで、この系にわずかな外力を加えてみたところ、余分な虚数振動数が解消され、高次鞍点が遷移状態に変化することが分かった。ボールミリング中にはこのようにして、段階的反応に加えて、協奏的反応がオンとなる。今回の結果は、力学的作用が新たな反応経路を開くメカニズムを示すものである。

1) L. Carlier, M. Baron, A. Chamayou, G. Couarraze, *Tetrahedron Lett.* **2011**, *52*, 4686.
2) L. Carlier, M. Baron, A. Chamayou, G. Couarraze, *Powder Technol.* **2013**, *240*, 41.
3) P. F. M. de Oliveira, N. Haruta, A. Chamayou, B. Guidetti, M. Baltas, K. Tanaka, T. Sato, M. Baron, *Tetrahedron* **2017**, *73*, 2305.
4) N. Haruta, P. F. M. de Oliveira, T. Sato, K. Tanaka, M. Baron, *J. Phys. Chem. C* **2019**, *123*, 21581.

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量子化学計算に基づくエチレンガスのラジカルダブル官能基化反応の開発

（北大 WPI-ICReDD[1]・JST-ERATO[2]・北大院理 [3]）○髙野 秀明 [1,2]・美多 剛 [1,2]・原渕 祐 [1,2,3]・前田 理 [1,2,3]

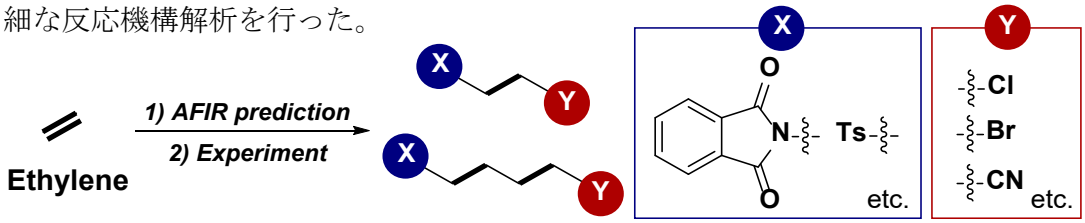
Development of Radical Difunctionalization of Ethylene Gas Predicted by Quantum Chemical Calculations

([1]*WPI-ICReDD, Hokkaido Univ.,* [2]*JST-ERATO,* [3]*Fac. of Sci., Hokkaido Univ.*)
○Hideaki Takano,[1,2] Tsuyoshi Mita,[1,2] Yu Harabuchi,[1,2,3] Satoshi Maeda[1,2,3]

Ethylene is a fundamental molecule produced about 170 million tons annually in the world, which is widely used on an industrial scale such as polyethylene synthesis. Compared with other alkenes, however, ethylene has been rarely utilized for fine chemical synthesis because it is a simple gaseous compound.[1] Herein we predict new transformations of ethylene by the artificial force induced reaction (AFIR) method.[2] The AFIR calculations suggested that 1,2-double functionalization via radical mechanism could proceed to introduce various functional groups onto both sides of ethylene. As a result of experimental demonstration, we achieved ethylene functionalization by carbon, nitrogen, sulfur and halogen atoms in the presence of a photoredox catalyst under irradiation of blue LED. Since two molecules of ethylenes were incorporated under some reaction conditions, further mechanistic studies were actively conducted.

Keywords : Ethylene, Quantum Chemical Calculation, Radical Reaction, Double Functionalization, Reaction Prediction

エチレンは世界で年間約 1.7 億トン生産されており、ポリエチレンなどの原料として工業的に広く利用されている。しかし単純な構造のガス状分子であるため、他のアルケンと比べ低分子ファインケミカルの化学合成などにはあまり用いられていない。そこで我々は量子化学計算に基づく人工力誘起反応（AFIR）法を用いた反応経路予測を行い、エチレンの新規合成変換のゼロからの探索を行った。その結果、ラジカル機構を経由する付加反応により 2 つの官能基をエチレンの両端に同時に導入する 1,2-ダブル官能基化反応が進行することが示唆された。得られた計算結果に基づき合成化学実験を行ったところ、光触媒存在下青色 LED を照射することにより、エチレンの 1 位と 2 位それぞれに炭素、窒素、硫黄、ハロゲンなどを導入することに成功した。また条件検討によりエチレンが 2 分子関与する反応が見いだされたことから、更なる詳細な反応機構解析を行った。



1) Saini, V.; Stokes, B. J.; Sigman, M. S. *Angew. Chem. Int. Ed*. **2013**, *52*, 11206–11220.
2) Maeda, S.; Harabuchi, Y.; Takagi, M.; Taketsugu, T.; Morokuma, K. *Chem. Rec*. **2016**, *16*, 2232.

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可視光と分子状ヨウ素の活性化を基軸とした高反応性活性種の創出およびラクトン類の多様性指向型合成法の開発

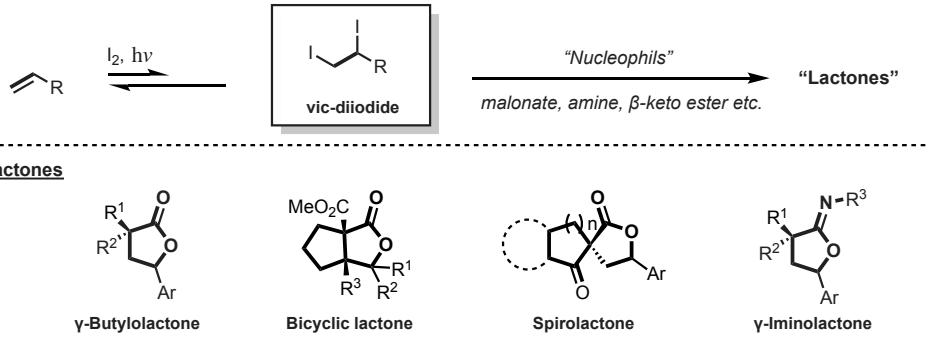
（岐阜薬大院[1]）○前島　咲[1]・山口　英士[1]・伊藤　彰近[1]

Development of Diversity-Oriented Synthesis Methodologies for Lactones via Activation of Molecular Iodine by Visible Light ([1]*Gifu Pharmaceutical University*)○Saki Maejima,[1] Eiji Yamaguchi,[1] Akichika Itoh[1]

In this study, we found that the creation of highly reactive haloalkyl species based on the photochemical activation of molecular iodine, and its used diversity-oriented synthesis methodologies for the complex heterocyclic compounds. That is to say, we developed some methodologies leading to various lactone derivatives such as γ-butyrolactones, bicyclic lactones, spirolactones, and iminolactones by forming C-C/C-O bond in the intra or intermolecular reaction. In the reaction, some lactones were synthesized by the reaction of olefins with nucleophilic reagents in the presence of molecular iodine under visible light irradiation. The reaction mechanism and the diastereo-selective mechanism of the lactones are comprehensively reported.

Keywords : Iodine Radical; Visible Light; One-Pot Synthesis of Lactones; Bi-Functionalization of Olefin

演者らは、可視光による典型元素の活性化を基盤とした環境負荷低減型―新規分子変換反応の開発を行なっている。近年、オレフィン類に対し分子状ヨウ素存在下、可視光を外部照射することで高反応性ハロアルキル種が生成し、種々の反応剤と新規結合形成が可能であることを見出した。すなわち、反応系中で生成した高反応性ハロアルキル種に対し求核剤としてカルボニル反応剤やアミン等を用いることで、多置換γ―ブチロラクトン[1)]、二環式ラクトン[2)]、スピロラクトン[3)]、γ―イミノラクトン[4)]など、オレフィンの二重官能基化を介した多様なラクトン誘導体合成法の開発および体系化を達成した。さらに、精細な反応条件の検討よりラクトン誘導体の立体制御法[5,6)]についても明らかにした為、その詳細について網羅的に報告する。



1) S. Maejima, E. Yamaguchi, A. Itoh, *Adv. Synth. Catal.*, **2017**, *359*, 3883-3887. 2) S. Maejima, M, Osuka, E. Yamaguchi, A. Itoh, *Tetrahedron*, **2018**, *74*, 2985-2990. 3) S. Maejima, E. Yamaguchi, A. Itoh, *J. Org. Chem.*, **2019**, *84*, 9519-9531. 4) S. Maejima, E. Yamaguchi, A. Itoh, *J. Org. Chem.*, **2020**, *85*, 10709-10718. 5) S. Maejima, E. Yamaguchi, A. Itoh, *ACS Omega*, **2019**, *4*, 4856-4870. 6) K. Oe, M. Goto, S. Maejima, E. Yamaguchi, A. Ito, *Asian J. Org. Chem.*, **2020**, *9*, 571-574.

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Ratiometric fluorescent force probe that works in gels

(*Graduate School of Science, Kyoto University*) ○Takuya Yamakado, Shohei Saito
Keywords: Force Probe; Fluorescent Molecules; Pyrene; Dual Fluorescence; Gel

Flapping molecule (FLAP) has a force-probing function by a reversible fluorescence spectral change (Figure 1). This function of FLAP is based on a ground-state conformational change rather than covalent bond cleavage, and the mechanical response has been studied in crystalline[1] and polymeric[2] environments. However, conventional anthracene-based FLAP (**FLAP1**) cannot probe local force in the presence of solvent molecules (namely, in solution or gel) due to spontaneous planarization in the excited state.[3] In this study, we synthesized a new FLAP force probe bearing two pyrene units (**FLAP2**) that showed a dual fluorescence even in solution, emitted from both the V-shaped and planar species.

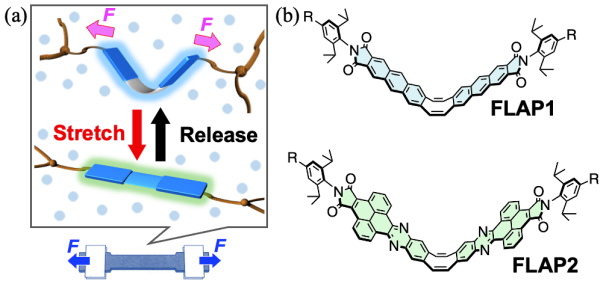


Figure 1. (a) Flapping force probes incorporated into a polymer chain. (b) Chemical structures of anthracene-based FLAP (**FLAP1**) and pyrene-based FLAP (**FLAP2**).

First, sensitive force response of **FLAP2** was confirmed in a polymeric environment (without solvent). **FLAP2** was chemically incorporated into main chains of polyurethane elastomers, and the force-probing performance was compared with **FLAP1** based on ratiometric FL analysis (Figure 2). Then, the corresponding gels were prepared by swelling the film with toluene, but FL response was not observed by stretching. Since the local stress should be more concentrated at crosslinking points of the polymer network than main chains[2], chemical location of **FLAP2** was changed into crosslinking points. Ratiometric FL analysis of the deformed gels will be reported.

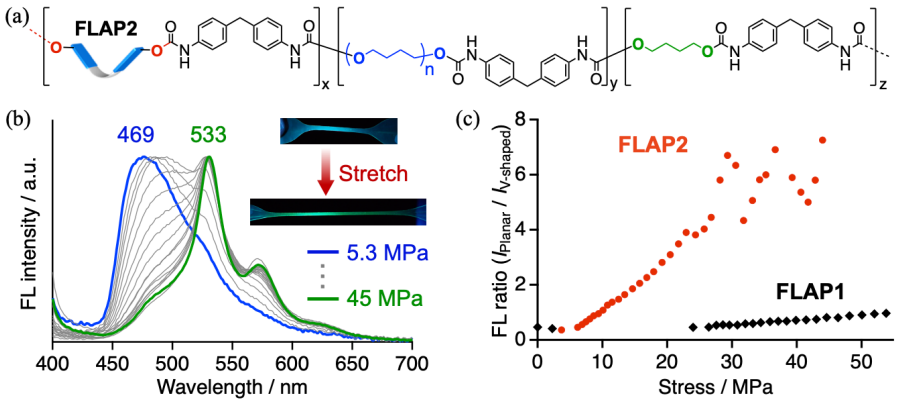


Figure 2. (a) Chemical structure of FLAP-incorporated polyurethane. (b) Fluorescence (FL) response of **FLAP2** during stretching the film. (c) Ratiometric FL analysis of FLAP-incorporated films (without solvent molecule).

1) **T. Yamakado**, S. Saito *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 6245. 2) R. Kotani, H. Yabu, S. Saito *et al.*, arXiv:2011.00202v2. 3) **T. Yamakado**, K. Watanabe, S. Saito *et al.*, *Angew. Chem. Int. Ed.* **2018**, 57, 5438.

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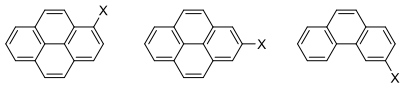
Non-classical Control of Magnetic Circularly Polarized Luminescence (MCPL) of Pyrene and Phenanthrene Luminophores by Electron Donor and Acceptor Effects

([1]*Graduate School of Science and Engineering, Kindai University*, [2]*Department of Biochemistry, Osaka Research Institute of Industrial Science and Technology,* [3]*Department of Applied Chemistry, Tokyo Denki University,* [4]*Graduate School of Materials Science, Nara Institute of Science and Technology*)

○ Nobuyuki Hara,[1] Maho Kitahara,[1] Takaharu Sugimura,[1] Hayato Toda,[1] Motohiro Shizuma,[2] Akari Ito,[3] Makoto Miyasaka,[3] Michiya Fujiki, [4] and Yoshitane Imai[1]

Keywords: Chiral; Magnetic circularly polarized luminescence (MCPL); Non-classical circularly polarized luminescence (NC-CPL); Phenanthrene; Pyrene

Recently, we have reported that achiral pyrene luminophore exhibited magnetic circularly polarized luminescence (MCPL) derived from pyrene monomer by Faraday and Zeeman-split effect in photoexcited state under a 1.6 T magnetic field and their MCPL sign could be also controlled both by the N-up and S-up geometry and by positioning effect using hydroxyl group on pyrene moieties even in one side ((N)-up or (S)-up) magnetic field.[1]



1a, X = OH
1b, X = OMe
1c, X = COOH

2a, X = OH
2b, X = OMe
2c, X = COOH

3a, X = OH
3b, X = OMe
3c, X = COOH

In this work, we demonstrate that the sign of MCPL spectra can be controled by donor/acceptor substituent effect in addition to the N-up and S-up Faraday geometry on pyrene and phenanthrene moieties as simple achiral luminophore with electron donor (ED) units (hydroxyl and methoxy groups) (**1a**, **1b**, **2a, 2b, 3a** and **3b**) or with electron accepter (EAC) units (carboxylic acid groups) (**1c**, **2c** and **3c**). The MCPL sign inverts by changing from the ED to EAC groups on pyrenes (Figs. 1 and 2) and phenanthrenes (Fig. 3) at same Faraday geometry. Furthermore, the MCPL signs are invert by changing the substituent positions (1-position or 2-position) for ED and EDA groups on pyrene (Figs. 1 and 2). Regardless of the substituent positions, the absolute MCPL magnitudes of **1** and **2** bearing ED substituents are slightly larger than those of the **3** bearing EWD groups.

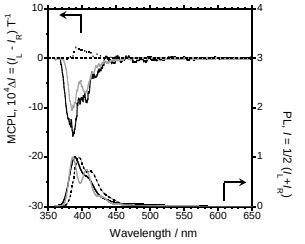


Fig. 1. MCPL and PL spectra of **1a** (black), **1b** (gray) and **1c** (dotted black) in $CHCl_3$

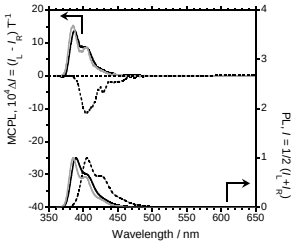


Fig. 2. MCPL and PL spectra of **2a** (black), **2b** (gray) and **2c** (dotted black) in $CHCl_3$

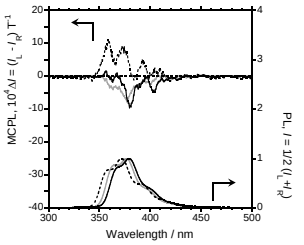


Fig. 3. MCPL and PL spectra of **3a** (black), **3b** (gray) and **3c** (dotted black) in $CHCl_3$

1) *Chem. Lett.*, **2020**, *49*, 674-676. *RSC Adv.,* **2021**, 11, 1581-1585. *PCCP*., **2020**, *22*, 13862-13866.

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Singlet Fission in Tetracene Dimers and Oligomers

([1]*Faculty of Science and Technology*, *Keio University*, [2]*Molecular Photoscience Reserch Center*, *Kobe University*, [3]*Tampere University*) ○Shunta Nakamura,[1] Hayato Sakai,[1] Masaaki Fuki,[2] Yasuhiro Kobori,[2] Nikolai V. Tkachenko,[3] Taku Hasobe[1]

Keywords: Singlet Fission; Tetracene; Covalent Bond; Dimer; Oligomer

Singlet fission (SF) is a photophysical phenomenon that is able to generate two individual triplet states (T_1) from one photon absorption in two nearby molecules.[1] The mechanism of SF process is well-studied in intramolecular SF (ISF) using covalently-linked dimers. The advantageous point of covalently-linked dimers for ISF is strict control of distance and orientation between two nearby chromophores. Our previous report of covalently-linked pentacene dimers demonstrated electronic coupling between two chromophores is an important parameter for controlling rate constant of ISF process.[2] On the other hand, tetracene (Tet) is a good candidate for SF material considering the high energy of triplet excited state: $E(T_1)$ = ~1.3 eV and long-lived triplet excited state (τ_T = 0.64 ms). We previously reported the high-yield and long-lived individual T_1 states by ISF using a 2,2'-biphenyl-bridged Tet dimer.[3] Electronic coupling between two chromophores is well-known as a key parameter and is dependent on the distance and orientation. However, the design strategy of these dimers for quantitative and long-lived individual T_1 states through ISF remains still unclear.

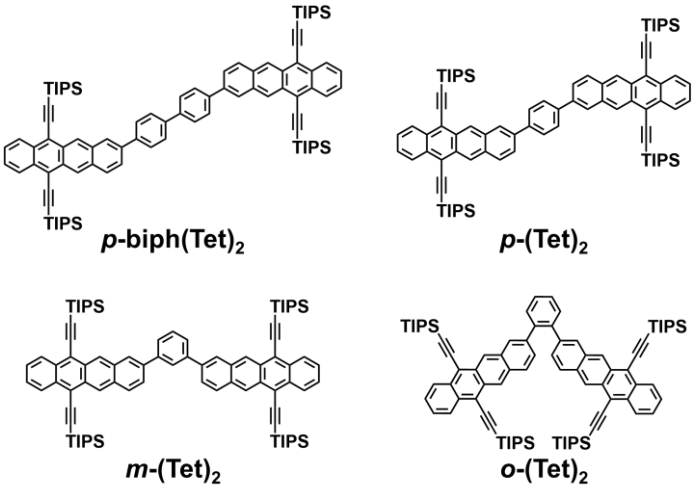


Figure 1. Tet dimers used in this study.

In this work, we newly synthesized Tet dimers bridged by different phenylene-based linkers, focusing on the conformational flexibility between two Tet units (Figure 1). As a result, the complementary combination of electronic coupling and conformational flexibility plays an important role for quantitative and long-lived individual T_1 state through ISF. In particular, *p*-biph$(Tet)_2$ with weak electronic coupling and large conformational flexibility exhibited the quantitative individual triplet yield. Moreover, we successfully observed an efficient exciton transport process through ISF by using a Tet hexamer.

1) Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891-6936. 2) Sakai, H.; Nakamura, S.; Kobori, Y.; Hasobe, T. et al. *J. Phys. Chem. Lett.* **2018**, *9*, 3354-3360. 3) Nakamura, S.; Sakai, H.; Kobori, Y.; Hasobe, T. et al. *ACS Energy Lett.* **2019**, *4*, 26-31.

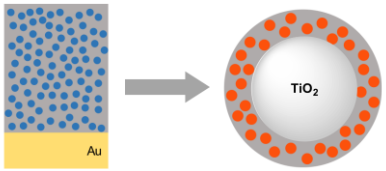
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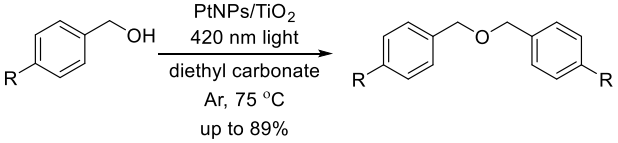
新規白金ナノ粒子担持型酸化チタン光触媒の開発とその応用

（阪大院薬[1]・JASRI, Spring-8[2]・名大理[3]）○和田 祐希[1]・秋山 敏毅[1]・原田 和生[1]・本間 徹夫[2]・中 寛史[3]・斎藤 進[3]・有澤 光弘[1]
Preparation and Application of Novel Pt Nanoparticles Supported on TiO2 Photocatalyst ([1]*Graduate School of Pharmaceutical Sciences, Osaka University*, [2]*Japan Synchrotron Radiation Research Institute, Spring-8,* [3]*Graduate School of Science, Nagoya University*)
○Yuki Wada[1], Toshiki Akiyama[1], Kazuo Harada[1], Tetsuo Honma[2], Hiroshi Naka[3], Susumu Saito[3], Mitsuhiro Arisawa[1]

We aimed to explore the preparation and chemical reactivity of novel catalyst, PtNPs/TiO_2, which is self-assembled multilayered PtNPs supported on the surface of semiconductor photocatalyst TiO_2. The catalyst was prepared by heating a solution of piranha-treated TiO_2, $Pt(acac)_2$, and 4-methoxybenzyl alcohol in *p*-xylene. We investigated the state of Pt supported on the surface of PtNPs/TiO_2 with X-ray absorption near edge structure (XANES) analysis, and it was found that the Pt supported on PtNPs/TiO_2 was Pt(0). This catalyst is effective for the conversion of benzyl alcohol derivatives to the corresponding dibenzyl ether derivatives in diethyl carbonate under 75 ℃ with 420 nm light.
Keywords : Platinum; Titanium dioxide; Etherification

本研究では半導体光触媒である酸化チタン（TiO_2）を担持固体とし、その表面へ白金ナノ粒子（PtNPs）を自己組織的多層状に担持させることで、これまでに報告例のない触媒 PtNPs/TiO_2 を創製すると共に、本触媒が有する半導体光触媒と金属ナノ粒子の双方の特徴を引き出すことを目的とした。ピラニア溶液によって処理した TiO_2 を $Pt(acac)_2$ と 4-メトキシベンジルアルコールの *p*-キシレン溶液中で加熱すると、所望の触媒 PtNPs/TiO_2 が得られた。PtNPs/TiO_2 の Pt-L 殻を X 線吸収微細構造解析に付した結果、担持された Pt は 0 価 Pt ナノ粒子であることが確認された。続いて、ベンジルアルコール誘導体と PtNPs/TiO_2 の炭酸ジエチル溶液を 420 nm の光照射下、75 ℃で加熱すると、ジベンジルエーテル誘導体が得られることを見出した。種々検討した結果、この反応では PtNPs と TiO_2、最適な波長、温度というすべての要素が必要であることが分かった。本発表では基質適用範囲についても紹介する





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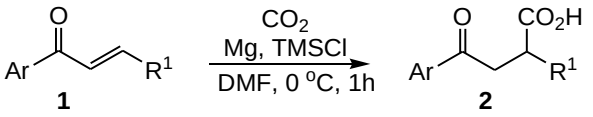
Mg-Promoted Reductive CO_2 Fixation of Propenyl Ketones

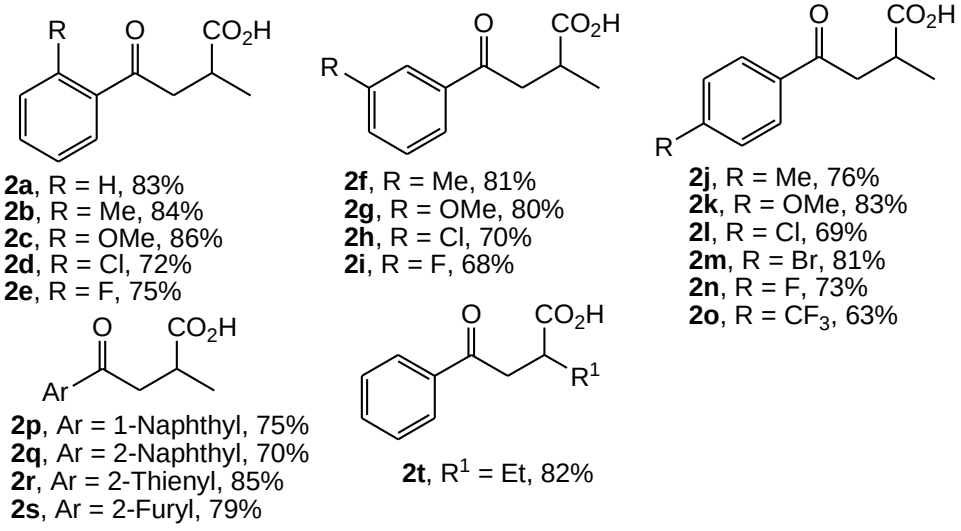
(*Graduate School of Engineering, Nagaoka University of Technology*) ○Suhua Zheng, Tianyuan Zhang, Hirofumi Maekawa

Keywords: Electron transfer reaction; Magnesium; Reductive carboxylation; Carbon dioxide; Propenyl ketones

The effective fixation of carbon dioxide has been one of the important themes in organic synthesis for a long time, many reactions of carbon dioxide as a reagent have been reported. We previously reported Mg-promoted reduction of ethyl cinnamates in the presence of carbon dioxide followed by esterification to give a mixture of β-carboxylated compound and α,β-dicarboxylated compound.[1)]

In this research, Mg-promoted reductive carboxylation of phenyl propenyl ketone **1a** in the presence of chlorotrimethylsilane and carbon dioxide in DMF, afforded a γ-keto carboxylic acid **2a** as the main product in 83% yield. The optimized reaction conditions were applied to diverse propenyl ketones **1b**-**1t** to give the corresponding carboxylic acids **2b**-**2t** in 63-86% yields. The study on the effects of various substituents under the optimized reaction conditions indicated that the present reaction has a wide substrate scope and good reaction efficiency. The reaction mechanism and the related reactions will be also presented in detail.





Reaction Conditions: **1** (1.0 mmol), TMSCl (4 eq.), Mg (4 eq.), DMF (7 mL), 0 °C, 1 h, CO_2 (1 atm).

1) H. Maekawa, T. Murakami, T. Miyazaki, I. Nishiguchi, *Chem. Lett.* **2011**, *40*, 368-369.

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[A10-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair:Mao Minoura, Takeshi Fujita
Sun. Mar 21, 2021 1:00 PM - 3:20 PM Room 10 (Online Meeting)

[A10-3pm-01] Photocatalytic redox-neutral hydroxyalkylation of *N*-heteroaromatics with aldehydes

○Hiromu Fuse[1], Hiroyasu Nakao[1], Yutaka Saga[2], Arisa Fukatsu[3], Mio Kondo[2], Shigeyuki Masaoka[2], Harunobu Mitsunuma[1], Motomu Kanai[1] (1. The Univ. of Tokyo, 2. Osaka Univ., 3. Inst. for Molecular Science)

1:00 PM - 1:20 PM

[A10-3pm-02] Phosphorus-Based Organocatalysis for Dehydrative Cyclization of *N*-(2-Hydroxyethyl)amides into 2-Oxazolines

○Farzaneh Soleymani-Movahed[1], Siong Wan Foo[1], Saeko Ogawa[1], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

1:20 PM - 1:40 PM

[A10-3pm-03] Acid-Mediated C– F/C– H Coupling of Fluorobenzofurans with Arenes

○Ryutaro Morioka[1], Takuya Fukuda[1], Takeshi Fujita[1], Junji Ichikawa[1] (1. University of Tsukuba)

1:40 PM - 2:00 PM

[A10-3pm-04] Design, Synthesis, and Properties of TEtraQuinoline (TEQ)

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

2:00 PM - 2:20 PM

[A10-3pm-05] Synthesis of Water-Soluble 3-Acyl-2-alkoxyindolizines for Red Light-Induced Release of Bioactive Carboxylic Acids

○Kenji Watanabe[1], Nodoka Terao[1], Takashi Niwa[1], Takamitsu Hosoya[1,2] (1. RIKEN, 2. TMDU IBB)

2:20 PM - 2:40 PM

[A10-3pm-06] Mild Hydrogenation of Arenes/Heteroarenes

○Nao Tanaka[1], Toyonobu Usuki[1] (1. Sophia University)

2:40 PM - 3:00 PM

[A10-3pm-07] Synthesis and Reaction of Dipotassiodisilene and -digermene Bearing Extended Triptycyl Groups

○Ryohei Nishino[1], Mao Minoura[1] (1. College of Science, Rikkyo Univ.)

3:00 PM - 3:20 PM

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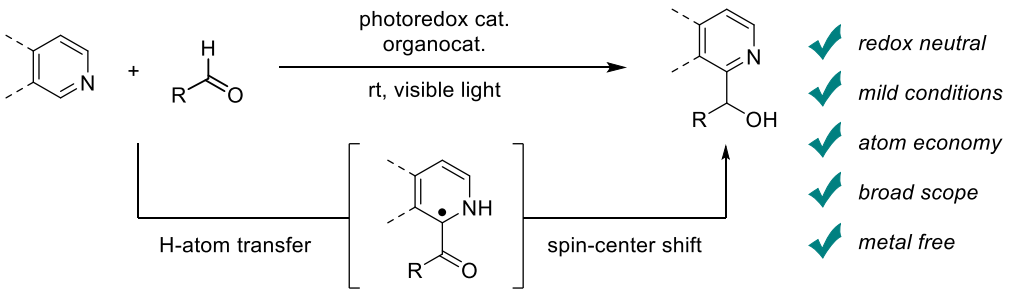
Photocatalytic redox-neutral hydroxyalkylation of *N*-heteroaromatics with aldehydes

([1]*Graduate School of Pharmaceutical Sciences, The University of Tokyo*, [2]*Graduate School of Engineering, Osaka University,* [3]*Institute for Molecular Science*) ○Hiromu Fuse,[1] Hiroyasu Nakao,[1] Yutaka Saga,[2] Arisa Fukatsu,[3] Mio Kondo,[2] Shigeyuki Masaoka,[2] Harunobu Mitsunuma,[1] Motomu Kanai[1]

Keywords: Radical chemistry; Minisci reaction; C-H activation; Photoredox catalyst; *N*-heteroaromatics

N-Heteroarylation of aldehydes affords hydroxyalkylated *N*-heteroaromatics as important intermediates for the synthesis of pharmaceuticals and agrochemicals. In conventional methods, however, strong base was required for deprotonation of less acidic C(sp^2)-H bond in *N*-heteroaromatics. Recently, several C-H hydroxyalkylation reactions utilizing radical reactions were developed, but they suffered from unsatisfactory atom economy or substrate generality.[1,2] Therefore, we envisioned the development of *N*-heteroarylation of aldehydes which proceeded under mild conditions with excellent atom economy.

As a result, we developed hybrid catalysis comprising an acridinium photoredox catalyst and a thiophosphoric acid organocatalyst to activate the formyl C-H bonds in aldehydes and achieved the desired *N*-heteroarylation of aldehydes. The key steps in proposed catalytic cycle are 1) hydrogen atom transfer from formyl C-H bonds, 2) Minisci-type radical addition to *N*-heteroaromatics, 3) a subsequent spin-center shift process and 4) single-electron reduction and protonation of the benzylic anion. This reaction proceeded under mild conditions of visible light irradiation at room temperature without metal species. This method was applicable to various *N*-heteroaromatics including isoquinolines, quinolines and pyridines. Moreover, due to the high functional group compatibility, late-stage modification of drugs and their leads was achieved.[3]



1) C. A. Correia, L. Yang, C.-J. Li, *Org. Lett.* **2011**, *13*, 4581. 2) B. Bieszczad, L. A. Perego, P. Melchiorre, *Angew. Chem., Int. Ed.* **2019**, *58*, 16878. 3) H. Fuse, H. Nakao, Y. Saga, A. Fukatsu, M. Kondo, S. Masaoka, H. Mitusnuma, M. Kanai, *Chem. Sci.* **2020**, *11*, 12206.

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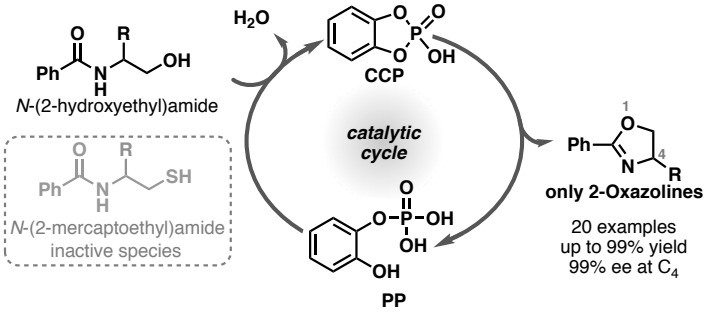
Phosphorus-Based Organocatalysis for Dehydrative Cyclization of *N*-(2-Hydroxyethyl)amides into 2-Oxazolines

([1]*Graduate School of Science, Nagoya University*, [2]*Research Center for Materials Science, Nagoya University*) ○Farzaneh Soleymani Movahed,[1] Siong Wan Foo,[1] Saeko Ogawa,[1] Susumu Saito[1,2]

Keywords: *organophosphorus catalysis; phosphate catalysis; oxazoline; biomimetic cyclization; dehydrative catalysis*

2-Oxazolines possess an extensive range of applications as significant naturally occurring pharmacophores,[1] building blocks for functional copolymers,[2] and optically active ligands.[3] Due to the vital potential of the heterocyclic units in natural products and pharmaceuticals, practical and cost-efficient synthesis of oxazolines that meets the economic and environmental demands has yet to be developed. Modern chemistry strives to establish approaches with high atom economy, for this subject has become a crucial concept in green chemistry.[4] To this end, catalytic synthesis of oxazolines by dehydrative cyclization of *N*-(2-hydroxyethyl)amides is an attractive method that only produces water as the by-product.

In this work, a metal-free, biomimetic catalytic protocol for the cyclization of *N*-(2-hydroxyethyl)amides was promoted by a 1,3,5-triazo-2,4,6-triphosphorine (TAP)-derived organocatalyst. This system features the minimum employment of the precatalyst and a broad substrate scope (up to 99% yield), which provides the relative 2-oxazolines with full retention of configuration at C_4. The mechanism of the reaction was vigorously studied, and the ^{31}P NMR, HRMS, HPLC analyses, and *^{18}O*-labeling experiment gave valuable insights into the proposed mechanism. This organophosphorus catalytic protocol has proved to be highly chemoselective toward 2-oxazolines; furthermore, it can be utilized as a gram-scale (4 g) synthetic pathway with high efficiency.



1) A. R. Tyler, H. Mosaei, S. Morton, P. G. Waddell, C. Wills, W. McFarlane, J. Gray, M. Goodfellow, J. Errington, N. Allenby, N. Zenkin, M. J. Hall, *J. Nat. Prod*. **2017**, *80*, 1558. 2) P. H. M. Van Steenberge, O. Sedlacek, J. C. Hernandez-Ortiz, B. Verbraeken, M.-F. Reyniers, R. Hoogenboom, D. R. D'hooge, *Nat. Commun.* **2019**, *10*, 3641. 3) G. Yang, W. Zhang, *Chem. Soc. Rev*. **2018**, *47*, 1783. 4) P. Anastas, N. Eghbali, *Chem. Soc. Rev*. **2010**, *39*, 301.

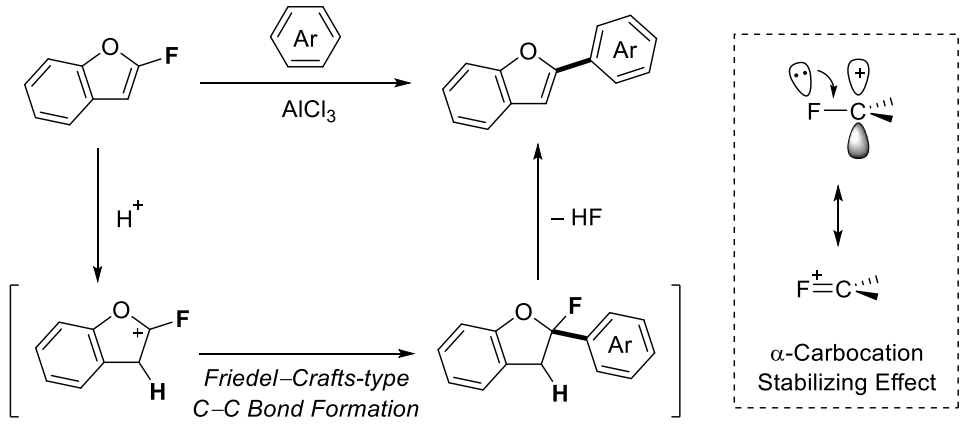
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Acid-Mediated C–F/C–H Coupling of Fluorobenzofurans with Arenes

(*Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba*)
○Ryutaro Morioka, Takuya Fukuda, Takeshi Fujita, Junji Ichikawa
Keywords: *C–F Bond Activation*; *Coupling; Acid; Benzofuran; Carbocation*

Although transition-metal-catalyzed intermolecular cross-coupling is one of the most notable achievements in the past half century, metal-free cross-coupling has been attracting much attention over the last decade. For example, aryl iodides and bromides undergo cross-coupling with arenes under appropriate conditions via the corresponding aryl radicals. In contrast, such a cross-coupling of aryl fluorides has been difficult so far. However, we have developed acid-mediated intramolecular cross-coupling of aryl fluorides via aromatic C–F bond activation, which is promoted by the α-carbocation stabilizing effect of a fluorine substituent. Herein, we report acid-mediated intermolecular C–F/C–H cross-coupling of 2-fluorobenzofurans with arenes, leading to the synthesis of 2-arylbenzofurans.

In the presence of $AlCl_3$, defluorinative cross-coupling of 2-fluorobenzofurans, readily prepared via 5-*endo-trig* cyclization of β,β-difluoro-*o*-hydroxystyrenes,[1] effectively proceeded with arenes to afford 2-arylbenzofurans. In this reaction, fluorine-stabilized cationic intermediates underwent Friedel–Crafts-type C–C bond formation with arenes, followed by HF elimination. 2-Fluorobenzofurans bearing a wide variety of substituents and several electron-rich arenes were applicable to the cross-coupling. Furthermore, we succeeded in a short-step synthesis of bioactive arylbenzofurans by using this protocol starting from readily available β,β-difluoro-*o*-hydroxystyrenes.



1) Morioka, R.; Fujita, T.; Ichikawa, J. *Helv. Chim. Acta* **2020**, *103*, e2000159.

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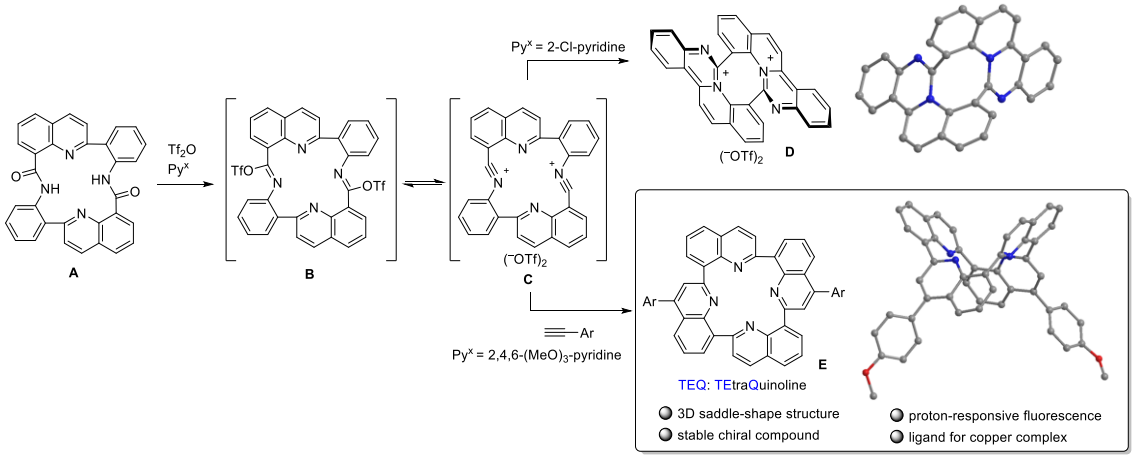
Design, Synthesis, and Properties of TEtraQuinoline (TEQ)

(*Institute of Microbial Chemistry*) ○Wei Xu, Naoya Kumagai

Keywords: Heterocyclic compounds

Quinoline is a nitrogen-embedded 10π aromatic planar unit which can be potentially used to build higher order functional molecular architectures. Recently, our group synthesized a novel quasi-flat head-to-tail quinoline trimer TriQuinoline (TQ), which displays unexpected unusual physical and chemical properties. Herein, we endeavored to construct a new and non-flat chiral quinoline tetramer, TEtraQuinoline (TEQ), which was indeed synthesized from the dimer of quinoline-amide **A** and an alkyne in the presence of Tf_2O and 2,4,6-$(MeO)_3$-pyridine. In addition, dimeric DiazaChrysene (dDC) **D** was also obtained when 2-Cl-pyridine was employed as base. DFT calculations are in line with the differential reaction outcomes depending on the conditions employed.

TEtraQuinoline (TEQ) has a unique saddle-shape structure and the calculated flipping energy barrier was very high (53.8 kcal/mol), which was experimentally supported by no erosion of enantiomeric integrity even at 240 °C in 20 h. It also displays intriguing chemical and physical properties e.g. proton-responsive fluorescence. The synthesis of TEQ/metal complexes and their catalytic properties will be also discussed.



1) S. Adachi, M. Shibasaki, N. Kumagai, *Nat. Commun.* **2019**, *10*, 3820.

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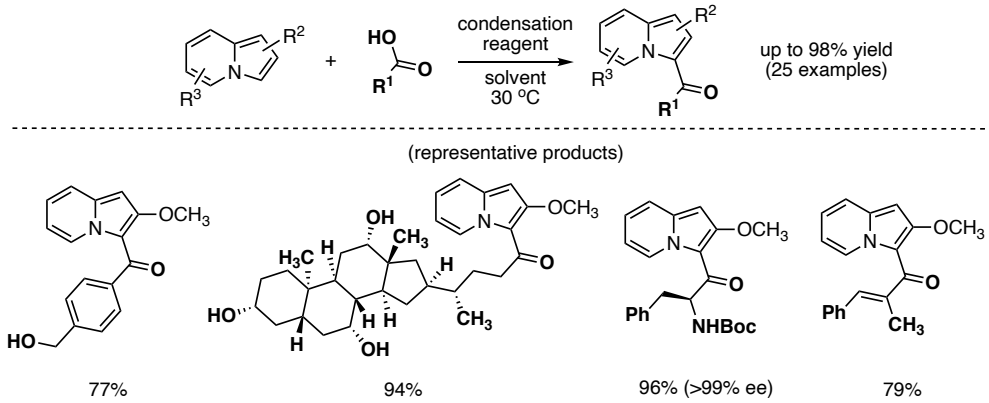
生物活性カルボン酸の赤色光誘導放出のための水溶性 3-アシル-2-アルコキシインドリジンの合成

（理研 BDR[1]・医科歯科大生材研 [2]）○渡邊賢司 [1]・寺尾和花 [1]・丹羽 節 [1]・細谷孝充 [1,2]

Synthesis of Water-Soluble 3-Acyl-2-alkoxyindolizines for Red Light-Induced Release of Bioactive Carboxylic Acids ([1]*RIKEN Center for Biosystems Dynamics Research* (*BDR*), [2]*Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University*)
○Kenji Watanabe,[1] Nodoka Terao,[1] Takashi Niwa,[1] Takamitsu Hosoya[1,2]

We recently reported an efficient method for uncaging of carboxylic acids from 3-acyl-2-methoxyindolizines by irradiation of biopermeable red light.[1] To enhance the utility of this method, we have developed a synthetic method for 3-acylindolidines from carboxylic acids using a widely-used condensation reagent. The desired reaction proceeded efficiently under mild conditions with a broad substrate scope. This method allowed for the synthesis of caged compounds of an anticancer natural product and a peptide via 3-acylation of indolizine to afford water-soluble photoreactive precursors having an intramolecular photosensitizer. Efficient release of carboxylic acids from the precursors upon red light-irradiation was achieved in a neutral aqueous buffered solution containing human serum albumin.
Keywords : Indolizine; Carboxylic Acid; Photoreaction; Caged Compound; Water-Solubility

我々は最近、生体透過性の高い赤色光の照射により、3-アシル-2-メトキシインドリジンからカルボン酸が効率的に放出される事を報告した [1)]。今回、本反応の有用性を高めるために、広く使用されている縮合試薬を用いて、カルボン酸から 3-アシルインドリジンを合成する手法を開発した。目的のアシル化反応が温和な条件で進行し、多様な生物活性カルボン酸のインドリジニル化を行える事が分かった。本法を用いて、生物活性天然物およびペプチドのインドリジニル化に成功するとともに、分子内に光増感部位を持つ水溶性光反応性前駆体の合成にも成功した。また、赤色光照射により、ヒト血清アルブミンを含む中性の緩衝水溶液中において、前駆体からのカルボン酸の放出を効率的に行なえることを実証した。



1) K. Watanabe, N. Terao, I. Kii, R. Nakagawa, T. Niwa, T. Hosoya, *Org. Lett.* **2020**, *22*, 5434.

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芳香族化合物の温和な接触水素化反応の開発

（上智大理工）○田中 尚・臼杵 豊展
Mild Hydrogenation of Arenes/Heteroarenes (*Faculty of Science and Technology, Sophia University*) ○Nao Tanaka, Toyonobu Usuki

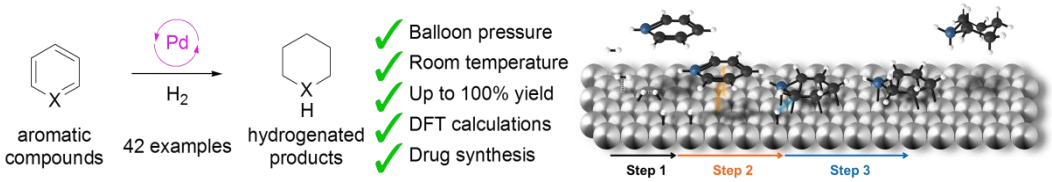
Hydrogenation of aromatic compounds is a powerful tool used in organic synthesis laboratories and the chemical industry for constructing alicyclic skeletons. Hydrogenation of aromatic rings was first achieved more than a century ago,[1] and since then, additional approaches to dearomatic hydrogenation have been reported. However, the reactions generally require harsh conditions and expensive metals, which hampers the practical use of these procedures in synthetic chemistry at both laboratory and industrial scales.

Herein, hydrogenation of over dozen aromatic compounds, including both heteroarenes and arenes, over palladium on carbon (Pd/C, 1-100 mol%) with H_2-balloon pressure at room temperature is reported. Reaction using pyridine as a model substrate revealed that acetic acid was the best solvent, as use of only 1 mol% Pd/C provided piperidine quantitatively. Substrate scope analysis and density functional theory calculations indicated that reaction rates are highly dependent on frontier molecular orbital characteristics and the steric bulkiness of substituents. Moreover, the established method was used for concise synthesis of the anti-Alzheimer drug donepezil (Aricept®).[2]

Keywords : Heterogeneous hydrogenation; Heteroarenes; Arenes; Pd/C; Donepezil

芳香族化合物接触水素化反応は、有機合成における脂環構造形成の手段の一つとして有用である。芳香環の水素化は、一世紀以上前に達成され以来[1]、多くの反応例が報告されている。しかしながら、本反応は一般に高温・高圧などの厳しい条件を要する。さらに、利用される Rh、Ru などの金属種は比較的高価であり、実験室と産業のいずれの規模においても汎用性に乏しい。

本研究では、パラジウム炭素（Pd/C, 1-100 mol%）存在下、室温・風船圧における種々の芳香族化合物の水素化反応を検討した。ピリジンを基質とした条件検討の結果、酢酸中、1 mol%の Pd/C によってピペリジンが定量的に得られた。基質検討および DFT 計算によって、反応性がフロンティア分子軌道と立体的嵩高さに依存することが示唆された。さらに、開発した本反応を、抗アルツハイマー薬ドネペジル（Aricept®）の合成に適応し、その有用性を示した[2]。



1) Willstätter, R.; Hatt, D. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1471.
2) Tanaka, N.; Usuki, T. *Eur. J. Org. Chem.* **2020**, *34*, 5514 [Highlighted in *Synfacts* **2020**, *16*, 1462].

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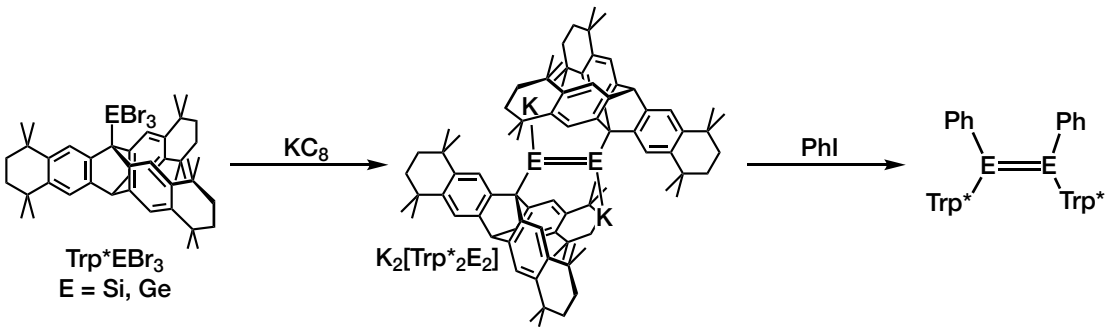
Synthesis, Reaction of the Dipotassiodisilene and -digermene Bearing Extended Triptycyl Groups

(*College of Science, Rikkyo University*) ○Ryohei Nishino, Mao Minoura
Keywords: *Triptycene, Digermene, Disilene, Dianionic Species, Crystallogtraphic Analysis*

Heavier analogues of vinyllithium, dimetallenides[1] (dimetallene monoanions) can be utilized as building blocks for E=E bonds. Dimetallene dianions which are assumed to have a potential role of introducing two functional groups into the E=E bond. However, synthetic examples[2] are so limited due to their high reactivity and lack of suitable stynthetic route.

We have succeeded in the synthesis of the dipotassiodisilene and -digermene ($K_2[Trp^*_2E_2]$, E = Si, Ge) as the stable red crystals by taking advantage of a novel aliphatic steric protection group having rigid triptycyl framework (Trp* group). In this presentation, we report the synthesis, structure, and reaction of the dimetallenedianions bearing Trp* groups.

Treatment of the 6 equivalents of KC_8 to Trp^*SiBr_3 or Trp^*GeBr_3 in THF gave $K_2[Trp^*_2E_2]$ as the thermally stable red crystals, respectively. Each structure was determined by X-ray crystallographic analysis and revealed the effective steric protection of Trp* groups around E=E double bond moiety. Reaction of dimetallene dianions with iodobenzene gave the corresponding disilene or digermene derivatives. The detailed structure and other reactivities will also be discussed.



1) D. Scheschkewitz, *Angew. Chem. Int. Ed.*, **2004**, *43*, 2965-2967, M. Ichinohe, K. Sanuki, S. Inoue, A. Sekiguchi, *Organometallics*, **2004**, *23*, 3088-3090. 2) K. Haga, M. Ichinohe, A. Sekiguchi, 93rd CSJ annual meeting, C. Cui, *J. Am. Chem. Soc.*, **2020**, *142*, 4131-4135, L. Pu, M. O. Senge, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.,* **1998**, *120*, 12682-12683, A. Rit, J. Campos, H. Niu, S. Aldridge, *Nat. Chem.,* **2016**, *8*, 1022-1026.

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[A19-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair:Yoshiaki Tanabe, Tatsuhiko Yoshino
Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 19 (Online Meeting)

[A19-3pm-01] Silane- and peroxide-free hydrogen atom transfer hydrogenation using ascorbic acid and cobalt-photoredox dual catalysis

○Masahiro Kojima[1], Yuji Kamei[1], Yusuke Seino[2], Yuto Yamaguchi[2], Tatsuhiko Yoshino[1], Satoshi Maeda[3,4,5], Shigeki Matsunaga[1,6] (1. Graduate School of Pharmaceutical Sciences, Hokkaido University, 2. Faculty of Pharmaceutical Sciences, Hokkaido University, 3. WPI-ICReDD, 4. Department of Chemistry, Graduate School of Science, Hokkaido University, 5. JST-ERATO, 6. GI-CoRE)

1:00 PM - 1:20 PM

[A19-3pm-02] Enantioselective Radical Cation-induced [4+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Effect of Photoirradiation

○Shuhei Ohmura[1], Takahiro Horibe[1], Kazuaki Ishihara[1] (1. Nagoya Univ.)

1:20 PM - 1:40 PM

[A19-3pm-03] Palladium- and Photoredox-Catalyzed Alkylation-Cyclization Reactions of Iodoalkenes with 4-Alkyl-1,4-dihydropyridines and Mechanistic studies

○Yulin Zhang[1], Yoshiaki Tanabe[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo)

1:40 PM - 2:00 PM

[A19-3pm-04] Addition of C(sp^3)– H Bonds to Styrenes via Hydrogen Atom Transfer to Aqueous Hydroxyl Radical under Photocatalysis

○Shogo Mori[1], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

2:00 PM - 2:20 PM

[A19-3pm-05] Switching from Biaryl Formation to Amidation with Convoluted Polymeric Nickel Catalysis

○Abhijit Sen[1], Raghu, N Dhital[1], Takuma Sato[1], Aya Ohno[1], Yoichi M. A. YAMADA[1] (1. RIKEN)

2:20 PM - 2:40 PM

[A19-3pm-06] Pot-Economical Synthesis of Prostaglandins

○Nariyoshi Umekubo[1], Yujiro Hayashi[1] (1. Univ. of Tohoku)

2:40 PM - 3:00 PM

[A19-3pm-07] Development of Nitrogen-doped Carbon Incarcerated Rhodium Nanoparticles for Asymmetric Insertion of Carbenoids and Application for Efficient Continuous Synthesis of Chiral Amino Acids

○Ryusuke Masuda[1], Tomohiro Yasukawa[1], Shū Kobayashi[1] (1. The University of Tokyo)

3:00 PM - 3:20 PM

[A19-3pm-08] Zinc-Catalyzed Phosphonylation of Alcohols with Alkyl Phosphites

○Soomin Cho[1], Luca Alessandro Danieli[1], Akira Matsunaga[1], Yuki Saito[1], Shū Kobayashi[1]

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（1. University of Tokyo）
3:20 PM - 3:40 PM

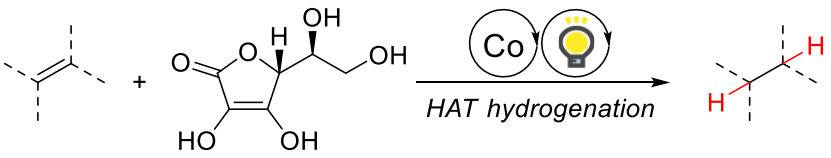
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Silane- and Peroxide-Free Hydrogen Atom Transfer Hydrogenation Using Ascorbic Acid and Cobalt-Photoredox Dual Catalysis

([1]*Graduate School of Pharmaceutical Sciences, Hokkaido University*, [2]*Faculty of Pharmaceutical Sciences, Hokkaido University,* [3]*WPI-ICReDD,* [4]*Department of Chemistry, Graduate School of Science, Hokkaido University,* [5]*JST-ERATO,* [6]*GI-CoRE*)
○Masahiro Kojima,[1] Yuji Kamei,[1] Yusuke Seino,[2] Yuto Yamaguchi,[2] Tatsuhiko Yoshino,[1] Satoshi Maeda,[3,4,5] Shigeki Matsunaga[1,6]
Keywords: Hydrogenation; Cobalt Catalysis; Photoredox Catalysis; Ascorbic Acid; Chemoselectivity

Hydrogen atom transfer (HAT) hydrogenation of alkenes developed by Shenvi[1] and Herzon[2] provides a complementary method for conventional noble metal-catalyzed hydrogenation and is increasingly appreciated in natural-product synthesis. However, reported catalytic HAT hydrogenation generally requires stoichiometric silane and peroxide in order to achieve a wide substrate scope.[3] This limitation has posed challenges regarding sustainability and safety concerns.

Herein we report a dual cobalt-photoredox catalytic system which enables silane- and peroxide-free HAT hydrogenation using ascorbic acid (also known as vitamin C) as a sole stoichiometric reactant.[4] The cobalt complex with a planar tetradentate ligand is identified as the optimal cocatalyst and realizes HAT hydrogenation with a broad substrate scope including amino acid derivatives, terpenes and drug molecules. Notably, the developed method is uniquely effective for hydrogenation of unprotected sugar derivatives compared to the established HAT hydrogenation protocols. The proposed dual catalytic mechanism is supported by experimental and theoretical studies.



Unique FG tolerance
Silane- and peroxide-free
Suitable for hydrophilic compounds

1) K. Iwasaki, K. K. Wan, A. Oppedisano, S. W. M. Crossley, R. A. Shenvi, *J. Am. Chem. Soc.* **2014**, *136*, 1300. 2) S. M. King, X. Ma, S. B. Herzon, *J. Am. Chem. Soc.* **2014**, *136*, 6884. 3) P. V. Kattamuri, J. G. West, *J. Am. Chem. Soc.* **2020**, *142*, 19316. 4) Y. Kamei, Y. Seino, Y. Yamaguchi, T. Yoshino, S. Maeda, M. Kojima, S. Matsunaga, *Nat. Commun.* **2021**, DOI: 10.1038/s41467-020-20872-z.

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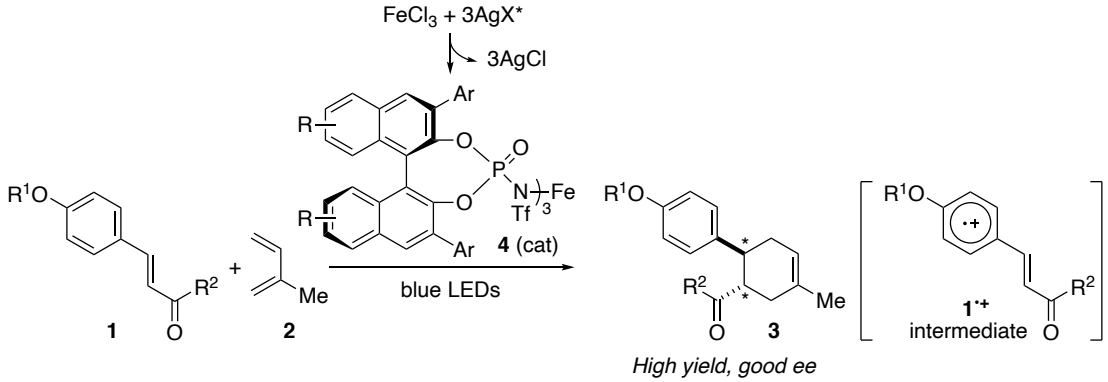
Enantioselective Radical Cation-induced [4+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Effect of Photoirradiation

([1]*Graduate School of Engineering, Nagoya University*) ○Shuhei Ohmura,[1] Takahiro Horibe,[1] Kazuaki Ishihara[1]

Keywords: Radical Cation; [4+2] Cycloaddition; Chiral Iron(III) Salt; Chiral Counter Anion; Photoirradiation

Radical cation-induced [4+2] cycloaddition has received much attention over the past decade because of its unique regioselectivity and reactivity complementary to those of thermal [4+2] cycloaddition.[1] These unconventional characteristics are attributed to radical cation intermediates $\mathbf{1}^{\bullet+}$ generated by one-electron oxidation of electron-rich alkenes such as *trans*-anethole derivatives **1**. To generate the key radical cation intermediates, more than 10 methods have been developed so far. However, despite these tremendous effort in this area, highly enantioselective method is unprecedented. It is still challenging to control such a labile radical cation species in an asymmetric manner.[2]

Previously, we reported environmentally benign and abundant cationic iron(III) salts, such as $FeCl_3$ and $Fe(OTf)_3$, as active one-electron oxidants for generation of $\mathbf{1}^{\bullet+}$.[3] Here, we developed chiral iron(III) salts for enantioselective radical cation-induced [4+2] cycloaddition. With the use of catalytic amounts of chiral iron(III) *N*-triflyl phosphoramide **4**, which is prepared *in situ* from $FeCl_3$ and chiral silver salts, [4+2] cycloaddition of anetholes **1** with isoprene **2** proceeded smoothly. Interestingly, irradiation with blue LEDs dramatically improved the yield. As a result, [4+2] cycloadducts **3** were obtained in high yield with good enantioselectivity. To elucidate the reaction mechanism, several control experiments were conducted.



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Palladium- and Photoredox-Catalyzed Alkylation-Cyclization Reactions of Iodoalkenes with 4-Alkyl-1,4-Dihydropyridines and Mechanistic Studies

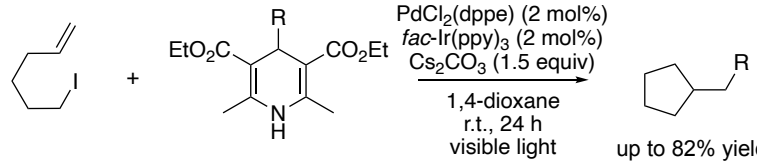
([1]*School of Engineering, The University of Tokyo*) ○Yulin Zhang, Yoshiaki Tanabe, Yoshiaki Nishibayashi

Keywords: Alkylation; Cyclization; Dihydropyridines; Palladium; Photoredox catalyst

Molecular transformation based on unstrained C(sp^3)–C(sp^3) bond cleavage is one of the most challenging research topics in organic chemistry. In order to develop a new method to achieve the target molecular transformation, our group has recently succeeded in photoredox-catalyzed utilization of 4-alkyl-1,4-dihydropyridines as alkylation reagents for aromatic substitution reactions of cyanoarenes, where generation of alkyl radicals via C–C bond cleavage is a key step.[1] Furthermore, combination of nickel and photoredox catalysts promoted novel cross-coupling reactions of aryl and alkenyl halides with dihydropyridines,[2,3] providing novel synthetic methods to control the stereochemistry around the produced alkenes.[3] To date, various types of reactions using dihydropyridines as alkylation reagents in the presence of transition metals and photoredox catalysts have been reported,[4] although alkylative functionalization of unactivated alkenes has been rather limited. As an extensive study, we have focused on the use of iodoalkenes as substrates to react with dihydropyridines as alkylating reagents to obtain the corresponding alkylative functionalized products.

Treatment of 6-iodo-1-hexene with 4-alkyl-1,4-dihydropyridines and Cs_2CO_3 in the presence of catalytic amounts of $PdCl_2$(dppe) and *fac*-[Ir(ppy)$_3$] in 1,4-dioxane at room temperature under the irradiation of visible light gave the alkylative and cyclic products such as cyclopentanes in high yields (Scheme1). We consider that this transformation provides a novel palladium- and photoredox-catalyzed reaction system of iodoalkenes with dihydropyridines. Details of the present reaction system and mechanistic studies are also examined.

Scheme 1



1) K. Nakajima, S. Nojima, K. Sakata. Y. Nishibayashi, *ChemCatChem* **2016**, *8*, 1028. 2) K. Nakajima, S. Nojima, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2016**, *55*, 14106. 3) K. Nakajima, X. Guo, Y. Nishibayashi, *Chem. Asian J.* **2018**, *13*, 3653. 4) a) J. A. Milligan, J. P. Phelan, S. O. Badir, G. A. Molander, *Angew. Chem. Int. Ed.* **2019**, *58*, 6152. b) A. Hossain, A. Bhattacharyya, O. Reiser, *Science* **2019**, *364*, 450.

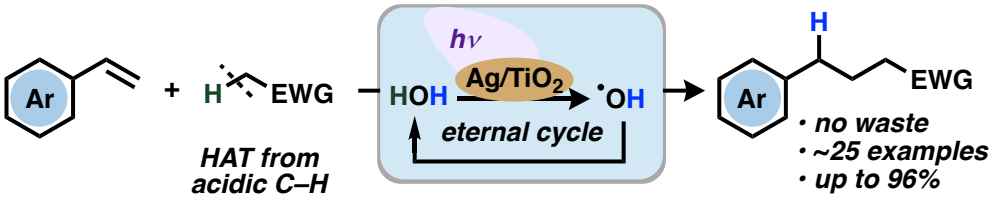
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Addition of C(sp^3)–H Bonds to Styrenes via Hydrogen Atom Transfer to Aqueous Hydroxyl Radical under Photocatalysis

([1]*Grad. Sch. Sci., Nagoya Univ.*, [2]*RCMS, Nagoya Univ.*) ○Shogo Mori,[1] Susumu Saito[1,2]
Keywords: Semiconductor photocatalyst, photoreaction, water oxidation, hydroxyl radical, hydrogen atom transfer

To date, the development of photocatalytic hydrogen atom transfer (HAT) methodologies has enabled the functionalization of hydridic to neutral C(sp^3)–H bonds under mild conditions. In contrast, photocatalytic HAT strategies for relatively acidic C(sp^3)–H bonds remain elusive. Recently, the HAT was demonstrated to occur from acidic C(sp^3)–H bonds to aryl radicals (Ar$^\bullet$)[1] or *O*-centered carboxyl radicals (RCOO$^\bullet$)[2] generated under photocatalytic conditions, where these radicals were used as sacrificial agents.

Herein, we report addition reactions of the α-C–H bonds of acetonitrile and acetone to styrenes (olefin insertion to C–H bonds) at ambient temperature.[3] The HAT from relatively acidic C(sp^3)–H bonds was enabled by aqueous hydroxyl radicals generated eternally via the oxidation of water by silver-nanoparticle-loaded titania (Ag/TiO_2) under photocatalytic conditions without using any stoichiometric oxidation agents. This mild, environmentally friendly, and redox-neutral protocol accommodates the transformation of a wide variety of styrenes into the corresponding longer-chain nitriles and ketones in good to excellent yield with very high atom efficiency.



(1) (a) Anselmo, M.; Basso, A.; Protti, S.; Ravelli, D. *ACS Catal.* **2019**, *9*, 2493–2500. (b) Zhang, J.-L.; Liu, Y.; Song, R.-J.; Jiang, G.-F.; Li, J.-H. *Synlett* **2014**, *25*, 1031–1035. (c) Kang, J.; Hwang, H. S.; Soni, V. K.; Cho, E. J. *Org. Lett.* **2020**, *22*, 6112–6116.
(2) Fang, J.; Dong, W.-L.; Xu, G.-Q.; Xu, P.-F. *Org. Lett.* **2019**, *21*, 4480–4485.
(3) Mori, S.; Saito, S. manuscript submitted.

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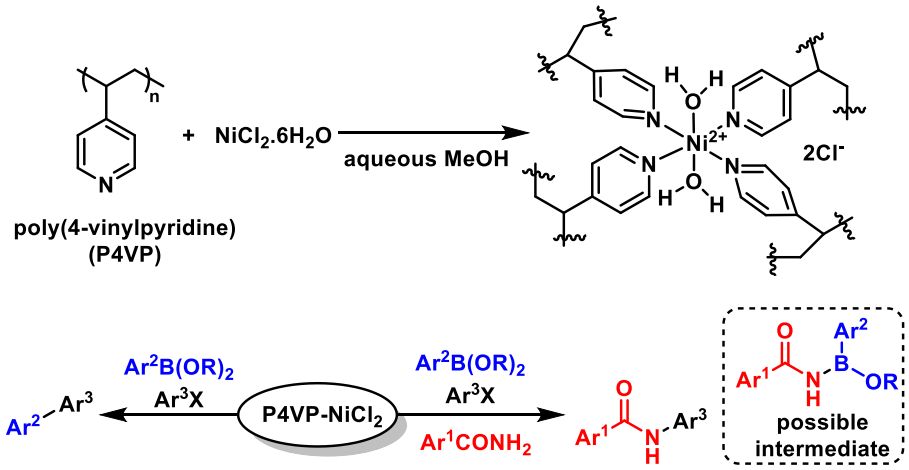
Switching from Biaryl Formation to Amidation with Convoluted Polymeric Nickel Catalysis

(*[1]RIKEN CSRS)* ○Abhijit Sen[1], Raghu, N. Dhital[1], Aya Ohno,[1] Takuma, Sato[1], Yoichi M. A. Yamada[1]

Keywords: Poly(4-vinylpyridine); Nickel catalysis; Heterogeneous catalysis; Switchable selectivity; Cross coupling

Amide linkage is very important for pharmaceuticals, natural products, and synthetic intermediates. Recently, we showed unique nickel-catalyzed halogen-dependent reactivity switch between Buchwald-Hartwig type C-N bond forming reaction and Suzuki-Miyaura type C-C bond forming reaction in the presence of phenylboronic acid/ester and anilines, respectively.[1] Anilines in Suzuki-Miyaura type coupling and phenylboronic acid/esters in Buchwald-Hartwig type coupling acted as activators.

This time, we developed a reusable and insoluble poly(4-vinylpyridine)-supported nickel catalyst P4VP-$NiCl_2$ for switching Suzuki-Miyaura type coupling and amidation.[2] Thus, P4VP-$NiCl_2$ (0.1 mol% Ni) promoted the Suzuki-Miyaura-type coupling of aryl halides and arylboronic esters to afford the corresponding biaryl compounds in up to 94% yield. Unpredictably, the reaction of aryl halides and arylboronic acid/ester was carried out in the presence of amides, providing the corresponding arylamides exclusively in up to 99% yield. In contrast, the same reaction in the absence of arylboronic acid/ester did not proceed. The amidation took place via a boron-amide ate complex formation. The catalyst was reusable five times without significant loss of reactivity. The kinetic and mechanistic studies also will be presented.



1) Dhital, R. N.; Sen, A.; Sato, T.; Hu, H.; Ishii, R.; Hashizume, D.; Takaya, H.; Uozumi, Y.; Yamada, Y. M. A. *Org. Lett.* **2020**, *22*, 4797. 2) Sen, A.; Dhital, R. N.; Sato, T.; Ohno, A.; Yamada, Y. M. A. *ACS Catal.* **2020**, *10*, 14410.

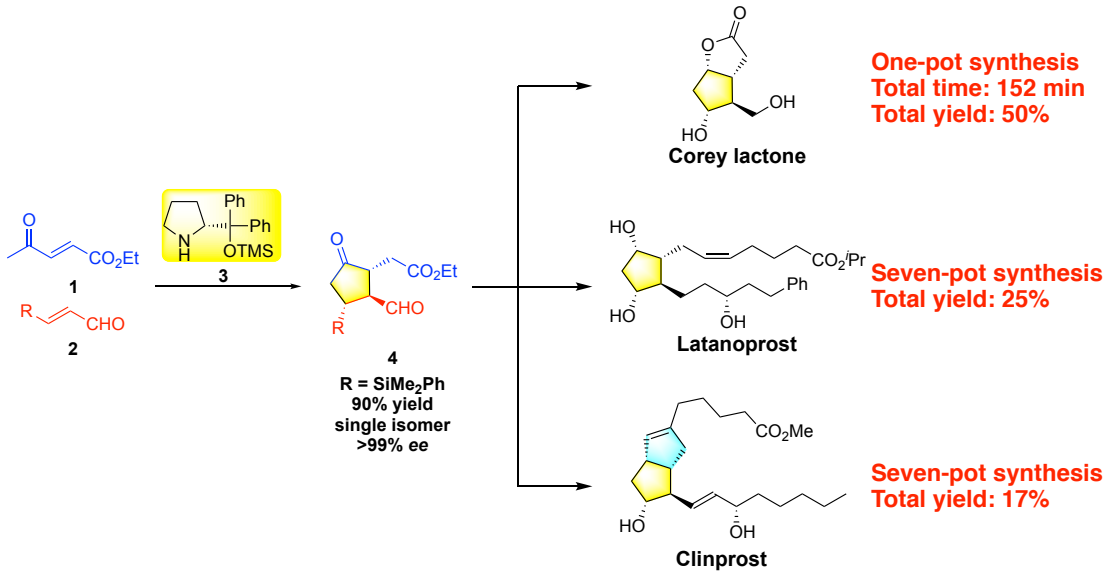
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Pot-Economical Synthesis of Prostaglandins

(*Graduate School of Science, Tohoku University*) ○Nariyoshi Umekubo, Yujiro Hayashi
Keywords: Organocatalyst; Domino reaction; Asymmetric synthesis; Michael reaction; Prostaglandins

Prostaglandins (PGs) are known to act as local hormones with the ability to control a multitude of important physiological properties. Some of their derivatives serve as useful medicines. For instance, latanoprost is a medication used in the treatment of glaucoma. Clinprost, the methyl ester of isocarbacyclin, was also found to be a potent neuroprotective compound in animal studies and efficiently crossed the blood- brain barrier. Given the biological importance of PGs, the scientific community has invested a great deal of effort and ingenuity into their efficient synthesis. Corey's synthesis[1] via the Corey lactone is a landmark achievement, which greatly facilitated the science of PGs.

Herein, we developed the Hayashi-Jørgensen catalyst[2] mediated asymmetric domino Michael/Michael reaction[3] between α,β-unsaturated ketone **1** and α,β-unsaturated aldehyde **2** to afford cyclopentanone **4** in 90% yield as a single isomer with >99 % *ee*. Using this reaction as a key reaction, a pot- and time-economical enantioselective total synthesis of the Corey lactone was accomplished[3] in a single reaction vessel within 152 minutes from commercially available reagents. In addition, we achieved the 7-pot syntheses of latanoprost[4] in 25% overall yield and clinprost[5] in 17 % overall yield.



1) E. J. Corey, et al, *J. Am. Chem. Soc.* **1969**, *91*, 5675. 2) Y. Hayashi, et al, *Angew. Chem. Int. Ed.* **2005**, *44*, 4212. 3) N. Umekubo, Y. Suga, Y. Hayashi, *Chem. Sci.* **2020**, 11, 1205. 4) N. Umekubo, Y. Hayashi, *Eur. J. Org. Chem.* **2020**, 6221. 5) N. Umekubo, Y. Hayashi, *Org. Lett.* **2020**, *22*, 9365.

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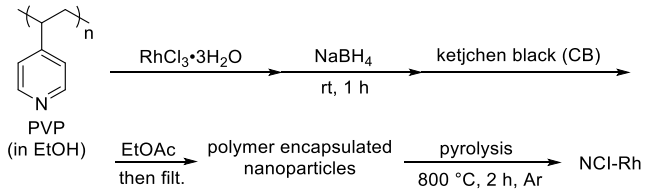
Development of Nitrogen-Doped Carbon Incarcerated Rhodium Nanoparticles for Asymmetric Insertion of Carbenoids and Application for Efficient Continuous Synthesis of Chiral Amino Acids

(School of Science, The Univ. of Tokyo) ○Ryusuke MASUDA, Tomohiro YASUKAWA, Shū KOBAYASHI

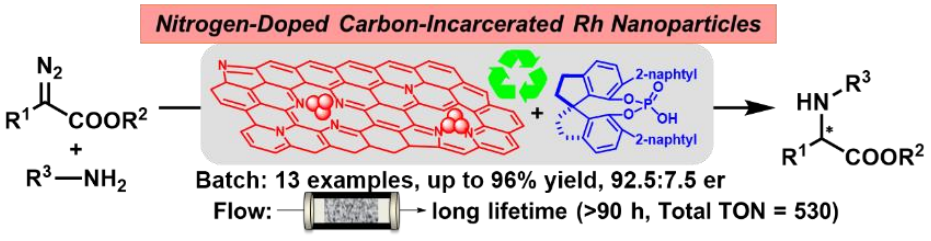
Keywords: Heterogeneous catalyst, Nitrogen-doped carbon, Asymmetric reaction, Chiral amino acid, Flow reaction

Heterogeneous catalysts have great advantages due to their reusability and applicability to continuous-flow synthesis; therefore, the development of stable heterogeneous catalyst systems is crucial for sustainable society. Though metal nanoparticles are robust species, the study of their asymmetric catalysis has been restricted because there is few method to activate metal nanoparticles without metal leaching.[1] Chiral amino acids are essential building blocks of many bioactive compounds such as peptides. Although asymmetric insertion of carbenoids into N—H bonds is one of the most efficient synthetic methods,[2] effective heterogeneous catalyst systems have not been developed.

We developed Rh nanoparticle catalysts (NCI-Rh) supported on nitrogen-doped carbon as a solid ligand to strongly interact with metals for asymmetric insertion of α-diazoesters into N—H bonds in the presence of chiral phosphoric acids. Nitrogen dopants played a crucial role in both catalytic activity and enantioselectivity. Various chiral α-amino acid derivatives were synthesized in high yields with high enantioselectivities, and NCI-Rh could be reused in seven runs without Rh leaching under batch reactions.



The corresponding continuous-flow reactions using a column packed with NCI-Rh were also successfully demonstrated. The desired product was obtained efficiently over 90 h through the reactivation of NCI-Rh. The chiral phosphoric acid could be recovered by trapping with a basic resin. Furthermore, it was found that the reaction proceeded in a heterogeneous manner and that Rh carbenoid was formed on the solid-state.



1) S. Kobayashi, *et al. ACS Catal.* **2016**, *6*, 7979. 2) Q.-L. Zhou, *et al. Angew. Chem. Int. Ed.* **2011**, *50*, 11483.

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Zinc-Catalyzed Phosphonylation of Alcohols with Alkyl Phosphites

(School of Science, The University of Tokyo) ○ Soo Min CHO; Luca Alessandro DANIELI; Akira MATSUNAGA; Yuki SAITO; Shū KOBAYASHI

Keywords: Phosphonylation, H-Phosphonate, Lewis Acid Catalyst, Transesterification

Organophosphonate molecules are important functional groups that are found in various kinds of natural products and pharmaceutical agents. They also play a key role in synthesizing oligonucleotides that are short DNA/RNA molecules, which consist of 2'-deoxyrivonucleosides or ribonucleosides joined via phosphodiester linkages. Phosphorylation of alcohols is the most straightforward way to gain organophosphate molecules, but conventional methods have some drawbacks such as requiring stoichiometric amounts of activation reagents that are incompatible with some substrates.[1] Some catalytic phosphorylation reactions have also been reported, but they all require harsh reaction conditions and substrate scopes are rather limited. Most importantly, there has been no effort made to introduce second alcohol to obtain di-substituted phosphates.[2] Therefore, we decided to focus on the phosphonylation of alcohols using a catalytic amount of Lewis acid under mild reaction conditions to access various kinds of phosphates/phosphites/phosphonates and further that allows second introduction of alcohols.

After screening various Lewis acid catalysts, zinc(II) complexes with diketonate units that have square-planar structures were found to be the best catalysts for the reaction, and more sterically hindered Zn complexes showed better activity. Molecular sieves were employed to capture the leaving methanol, and therefore efficiency of the transesterification reaction was increased. The desired reactions proceeded smoothly to afford the products in high yields with wide substrate scope. We also confirmed that a second alcohol could be successfully introduced to obtain a di-substituted phosphite. In this presentation, we will discuss details of the project, focusing on the development of the catalytic systems and reaction mechanism.[3]



1) Miller, S. J. *et al. J. Am. Chem. Soc.* **2001**, *123*, 10125−10126.
2) Ishihara, K. *et al. Angew. Chem., Int. Ed.* **2007**, *46*, 1423−1426.
3) Kobayashi, S. *et al. Org. Lett.* **2020**, *22*, 3171-3175.

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[A22-3am] 16. Natural Products Chemistry, Chemical Biology

Chair:Gosuke Hayashi, Kiichiro Totani

Sun. Mar 21, 2021 9:00 AM - 11:40 AM Room 22 (Online Meeting)

[A22-3am-01] Total Synthesis of Antibiotic Cyclic Peptide Hytramycin V

○Tetsuya Inaba[1], Yoshimasa Ishizaki[2], Masayuki Igarashi[2], Masahito Yoshida[1], Hideo Kigoshi[1] (1. Graduate School of Pure and Applied Sciences, University of Tsukuba, 2. Institute of Microbial Chemistry)

9:00 AM - 9:20 AM

[A22-3am-02] Peptide ligation between α-amidonitrile and N-terminal cysteine

○Xiaoling Wang[1], Jing Li[1], Yujiro Hayashi[1] (1. Tohoku University, Graduate School of Science)

9:20 AM - 9:40 AM

[A22-3am-03] Structure and biological activity of iezoside, a novel peptide-polyketide hybrid compound from marine cyanobacteria

○Naoaki Kurisawa[1], Arihiro Iwasaki[1], Kiyotake Suenaga[1] (1. Keio university)

9:40 AM - 10:00 AM

[A22-3am-04] New spumigin analogues from a cyanobacterium *Dolichospermum* sp.

○Chin-Soon Phan[1], Andrea Roxanne J. Anas[1], Jakia Jerin Mehjabin[1], Tatsufumi Okino[1] (1. Hokkaido University)

10:00 AM - 10:20 AM

[A22-3am-05] Synthetic study of *N*-glycan from hyperthermophilic archaeon *Thermococcus kodakarensis*

○Kohtaro Hirao[1], Yoshiyuki Manabe[1], Immacolata Speciale[2], Haruyuki Atomi[3], Antonio Molinaro[2], Cristina De Castro[2], Koichi Fukase[1] (1. Graduate School of Science, Osaka University, 2. University of Napoli Federico II, 3. Graduate School of Engineering, Kyoto University)

10:20 AM - 10:40 AM

[A22-3am-06] Opened-Fmoc group: protecting group activated by gold-catalyst

○Tomoya Yamamoto[1], Katsunori Tanaka[1,2,3] (1. RIKEN CPR, 2. Sch. Mater. &Chem. Tech., Tokyo Tech., 3. A. Butlerov Inst. of Chem., KFU)

10:40 AM - 11:00 AM

[A22-3am-07] Development of receptor subtype selective ligands via focused library screening composed of stereoisomers of coronatine

○Kengo Hayashi[1], Nobuki Kato[1], Haruna Nomoto[1], Misuzu Nakayama[1], Takuya Kaji[1], Raku Watanabe[2], Rina Saito[2], Yousuke Takaoka[1], Koji Miyamoto[3], Hideo Inagaki[3], Kazunori Okada[4], Minoru Ueda[1,2] (1. Graduate School of Science, Tohoku University, 2. Graduate School of Life Science, Tohoku University, 3. Graduate School of Science and Engineering, Teikyo University, 4. Biotechnology Research Center, The University of Tokyo)

11:00 AM - 11:20 AM

[A22-3am-08] Creation of H_2O_2-Activatable Photosensitizer based on Hypocrellin B

○Takashi Kitamura[1], Hirotaka Nakata[1], Daisuke Takahashi[1], Kazunobu Toshima[1] (1. Fac. Sci. Tech., Keio Univ.)

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11:20 AM - 11:40 AM

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抗菌活性環状ペプチド Hytramycin V の全合成

(筑波大院数理物質[1]・微生物化学研究所[2]) ○稲葉哲也[1]・石﨑仁將[2]・五十嵐雅之[2]・吉田将人[1]・木越英夫[1]

Total Synthesis of Antibiotic Cyclic Peptide Hytramycin V ([1]*Grad. Sch. of Pure & Appl. Sci., Univ. of Tsukuba,* [2]*Institute of Microbial Chemistry*) ○Tetsuya Inaba,[1] Yoshimasa Ishizaki,[2] Masayuki Igarashi,[2] Masahito Yoshida,[1] Hideo Kigoshi[1]

Hytramycin V (**1**), isolated from *Streptomyces hygroscopius* stain ECUM14046, is an 18-membered cyclic peptide consisting of three non-proteinogenic piperazic acids[1]. The natural product exhibits antibacterial activity against *Mycobacterium tuberculosis*, however, the mechanism of action has not been elucidated. Therefore, we planned total synthesis and biological evaluation of hytramycin V (**1**) and its analogs. According to the following synthetic strategy including the macrolactamization of cyclization precursor **2**, we have achieved the total synthesis of hytramycin V (**1**). In this presentation, we will report the details of the total synthesis and biological evaluation of natural product **1** and its analogs.

Keywords : Natural product; Cyclic peptide; Piperazic acid; Antibacterial activity; Macrolactamization

Hytramycin V (**1**)は、放線菌 ECUM14046 から単離・構造決定された 18 員環の抗菌活性環状ペプチドであり、非タンパク質性アミノ酸であるピペラジン酸を 3 つ含む[1]。天然物は結核菌に対して抗菌活性を示すが、詳細な活性発現機構は分かっていない。そこで、天然物およびその誘導体の合成と活性評価により、活性発現機構を明らかにすることとした。今回我々は、液相合成による環化前駆体 **2** の合成と、高希釈条件下でのマクロラクタム化により、所望の hytramycin V (**1**)の全合成を達成した（図１）。本発表では、**1** および誘導体の合成と抗菌活性試験の詳細について報告する。

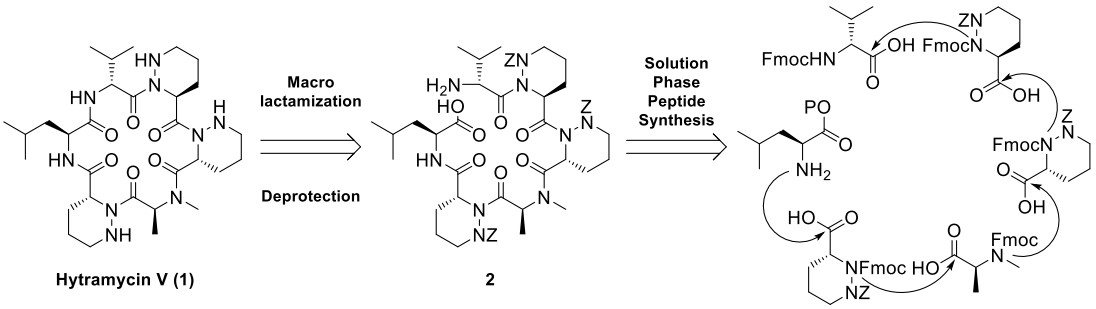


図 1 Hytramycin V (**1**)の逆合成

Reference

1) Cai, G.; Napolitano, J. G.; McAlphine, J. B.; Wang, Y.; Jaki, B. U.; Suh, J.-W.; Yang, S. H.; Lee, I.-A.; Franzblau, S. G.; Pauli, G. F.; Cho, S. *J. Nat. Prod.* **2013**, *76*, 2009.

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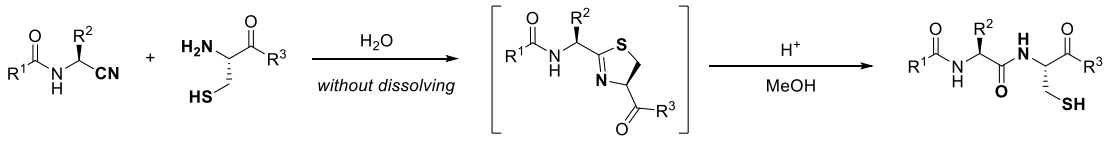
Peptide Ligation between α-Amidonitrile and N-terminal Cysteine

([1]*Graduate School of Science, Tohoku University*) ○Xiaoling Wang,[1] Jing Li,[1] Yujiro Hayashi[1]

Keywords: Peptide Ligation; α-Amidonitrile; Cysteine

Peptides and proteins are essential components in living organisms and play unparalleled central functions. Chemical synthesis represents one of the most reliable access to obtain the desired peptides and proteins with respect to quality and quantity. Native chemical ligation originated by Kent's group in 1994 is one of the most widely used synthetic methods.[1] It leads to a native cysteine amide bond by reacting one peptide bearing a carboxylic end with the other having a cysteine terminal. Even though this method requires a N-terminal cysteine and additional thiol to form thiol ester first from the carboxy end, native chemical ligation still holds its practically useful position. As continued interests of oxidative amide synthesis using dicyano compounds,[2] we recently extended this method to an efficient synthesis of tripeptides and tetrapeptides with formation of glycine amino amide bond at the ligation site in aqueous media. During this investigation, we found a rapid and selective reaction of cyano group and cysteine methyl ester. We then focused on a more general peptide ligation method inspired by this discovery.

α-Amidonitrile was found to react efficiently with cysteine-terminated peptide using water as the only dispersing media, even though the two substrates do not dissolve completely. This organic solvent-free coupling reaction affords thiazoline as an intermediate and it can be further hydrolyzed to give a cysteine amide linked peptide. Gratifyingly, the two-step sequence can be conducted in one pot. As like the native chemical ligation, a cysteine residue is necessary to achieve the ligation. However, this method realizes a much simpler reaction system by exempting additional thiol additive, which is a green and atom-economical synthetic method and provides an alternative to native chemical ligation.



1) a) P. Dawson, T. Muir, I. Clark-Lewis, S. Kent, *Science* **1994**, *266*, 776. b) V. Agouridas, O. El. Mahdi, V. Diemer, M. Cargoet, J. C. M. Monbaliu, O. Melnyk, *Chem. Rev.* **2019**, *119*, 7328. 2) J. Li, M. Lear, Y. Hayashi, *Angew. Chem. Int. Ed.* **2016**, *55*, 9060.

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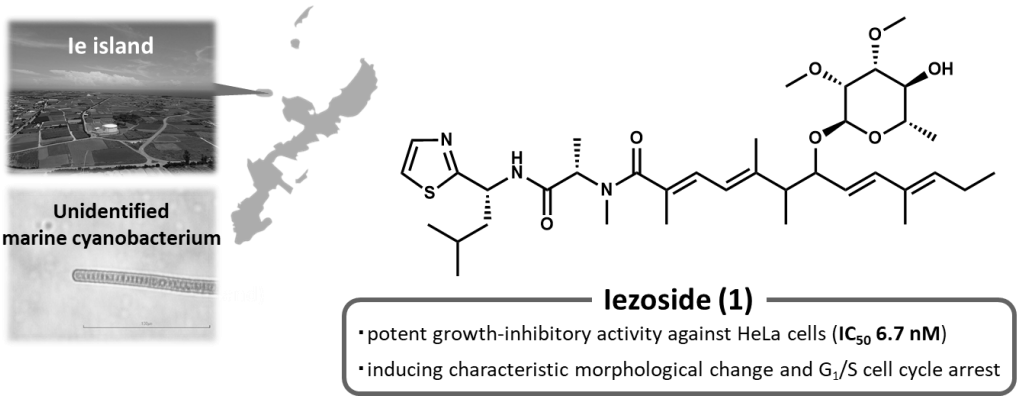
Structure and Biological Activity of Iezoside, a Novel Peptide-Polyketide Hybrid Compound from Marine Cyanobacteria

([1] Faculty of Science and Technology, Keio University)
○Naoaki Kurisawa,[1] Arihiro Iwasaki,[1] Kiyotake Suenaga[1]
Keywords: peptide; polyketide; natural products; marine cyanobacteria

Marine cyanobacteria are prosperous sources of structurally novel secondary metabolites possessing a wide range of biological activities. In a series of investigations, we isolated a novel peptide-polyketide hybrid, iezoside (**1**), from unidentified marine cyanobacterium collected at Ie island.

The gross structure of **1** was determined based on the analyses of several spectral data. As a result, it was clarified that iezoside (**1**) has an unprecedented peptide-polyketide hybrid structure which contains an *O*, *O*-diMe-rhamnose residue between an α, β, γ, δ-unsaturated amide group and a conjugated diene group. The absolute configuration of a peptide moiety of **1** was determined by acid hydrolysis followed by chiral phased HPLC analyses and Marfey's method, revealing the presence of L-leucine and *N*-Me- D-alanine. The stereochemistry of *O*, *O*-diMe-rhamnose was determined to be L-form based on the analyses of proton coupling constants and NOESY correlations, and modified Mosher's method. Now, we are trying to determine the absolute configuration of the fatty acid moiety by comparing the HPLC retention times between a degradation product of **1** and synthetic standards.

Iezoside (**1**) showed a potent growth-inhibitory activity (IC_{50} 6.7 nM) against HeLa cells and induced the characteristic morphological change. In addition, we clarified that **1** arrested cell cycle at the G_1/S stage. In order to analyze the mode of action of **1**, we examined its growth-inhibitory profile against 39 human cancer cell lines (JFCR39)[1)]. The results clarified that compound **1** showed potent and differential growth-inhibitory activities (average GI_{50} 87 nM) against various cancer cell lines. To reveal the potential of **1** as an anticancer drug with a novel mode of action, we are carrying out detailed evaluations of its bioactivity.



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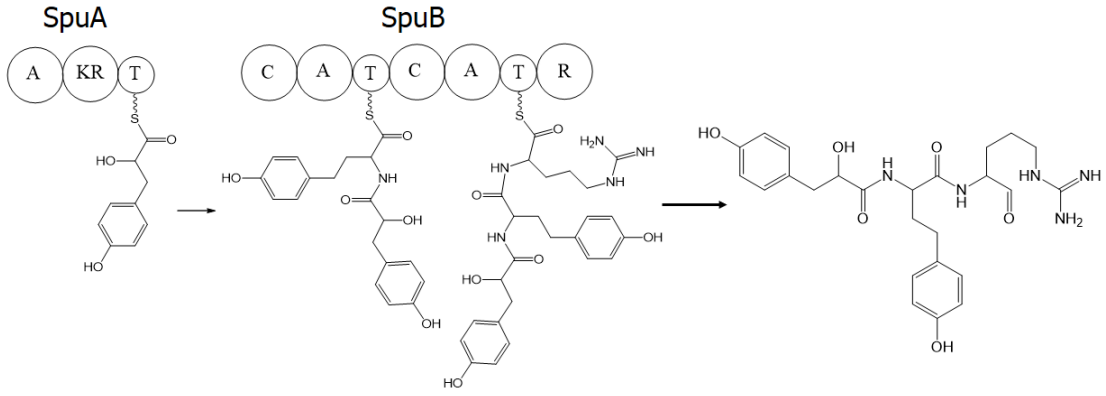
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New Spumigin Analogues from a Cyanobacterium *Dolichospermum* sp.

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Chin-Soon Phan,[1] Andrea Roxanne J. Anas,[1] Jakia Jerin Mehjabin,[1] Tatsufumi Okino[1,2]

Keywords: Cyanobacterium; *Dolichospermum*; Natural products; Spumigins; Biosynthetic gene cluster

Cyanobacteria produce lots of biological active secondary metabolites such as antibacterial, antiviral, antifungal, anticancer, immunosuppressive, and protease inhibitory activities.[1-4] Spumigins are characterized as linear peptide of four units.[5] Our previous study showed spumigins A and J possessed thrombin and cathepsin B inhibitory activities.[5] Our present study of a cyanobacterium *Dolichospermum* sp. has led to the isolation of two new spumigin analogues. The $NaBH_4$ reduction enabled the purification of reduced spumigins by HPLC. Surprisingly, these spumigins have a rare feature of three units compared to known spumigins with four units.



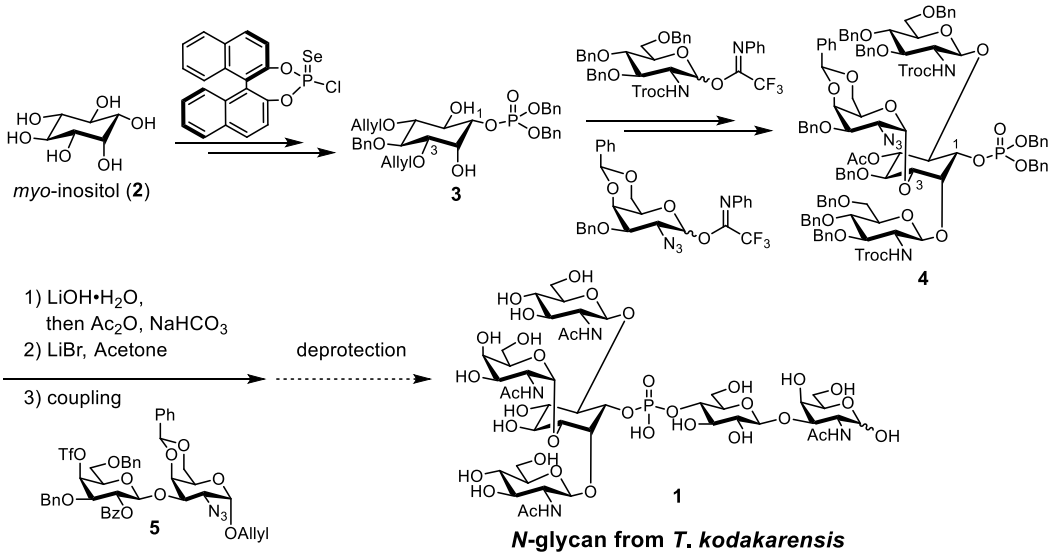
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Synthetic study of *N*-glycan from hyperthermophilic archaeon *Thermococcus kodakarensis*

([1]*Graduate School of Science, Osaka University*, [2]*Project Research Center for Fundamental Sciences, Osaka University*, [3] *University of Napoli Federico II,* [4]*Graduate School of Engineering, Kyoto University*) ○ Kohtaro Hirao,[1] Yoshiyuki Manabe,[1,2] Immacolata Speciale,[3] Haruyuki Atomi,[4] Antonio Molinaro,[3] Cristine De Castro,[3] Koichi Fukase[1, 2]
Keywords: Thermophilic Archaea; *N*-Glycan; Glycosylation; Inositol; Phosphorylation

Archaea membrane proteins are glycosylated with asparagine linked oligosaccharides (*N*-glycans), like eukaryote's. However, their functions have not been elucidated. To address this issue, we first isolated *N*-glycan from the hyperthermophilic archaeon, *Thermococcus kodakarensis*, and determined the structure. *N*-Glycan **1** possesses quite unique structure consisting in highly glycosylated inositol linked with the disaccharide via phosphate. We next investigated the synthesis of **1** (Scheme 1). Compound **3** was synthesized via regioselective phosphorylation using an asymmetric phosphorylation reagent from *myo*-inositol (**2**) according to our previous report.[1] Introduction of two glucosamines followed by galactosamination afforded **4**. After the conversion of Troc to Ac, benzyl ester at the phosphate was cleaved using LiBr. Coupling between the resulting inositol phosphate and the disaccharide was then investigated. Conjugation reaction using various reagents, including CDI, DCC, and PyBOP, did not proceed due to the steric hinderance of both substrates. After the thorough investigation, S_N2 type reaction between the phosphoric acid salt and triflate **5** successfully gave the desired coupling product. In this reaction, formation of cesium salt and addition of 24-crown-8 ether were essential. Deprotection for the synthesis of **1** is under investigation.



Scheme 1. Synthesis of *N*-glycan **1**

1) Aiba, T. et al. *Chem. Eur. J.* **2017**, *23*, 8304.

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Opened-Fmoc group: protecting group activated by gold catalyst

(*[1]RIKEN CPR, [2]Sch. Mater. & Chem. Tech., Tokyo Tech., [3]A. Butlerov Inst. of Chem., KFU*)
○Tomoya Yamamoto,[1] Katsunori Tanaka[1,2,3]

Keywords: *Gold catalysis, Protecting group, Peptide synthesis, In vivo reaction*

Orthogonal protecting groups, which are chemoselectively removable with specific reagents, are essential for the synthesis of complex natural products, branched peptides, and oligosaccharides. Previously, palladium-labile (such as allyl and allyloxycarbonyl group), hydrazine-labile (such as levulinoyl group), and oxidant-labile (such as *p*-methoxybenzyl group) protecting groups have been developed as orthogonal protecting groups and applied for the synthesis of complex compounds. Although various orthogonal protecting groups have already been developed, there are still limitations in its application such as the stability of protecting groups and the harshness of the deprotection condition. Furthermore, the number of choices for protecting groups is the key to the efficient synthesis of complex molecules. Therefore, it is important to develop a protecting group with novel deprotection conditions.

In this study, we have developed a novel protecting group chemoselectively removable with a gold-catalyzed transformation and a subsequent reaction with piperidine (**Figure 1**). This protecting group is stable under acidic and basic conditions which are generally used for the deprotection of general protecting groups. On the other hand, the gold catalysis transforms this structure quickly (less than 10 minutes), and the resulting structure is labile to mild basic conditions using piperidine. We have applied this protecting group to various functional groups such as amine and alcohols of peptide and sugar derivatives. In addition, the transformation and removal of this protecting group proceed quickly even on resins. Thus, this protecting group is applicable to the solid-phase synthesis of branched and cyclic peptides.

We have also found that the gold-catalyzed transformation of this protecting group proceeds under aqueous conditions, and thus is promising for biocompatible reactions. We will report the application of this protecting group for masking and uncaging of bioactive molecules *in vivo*.

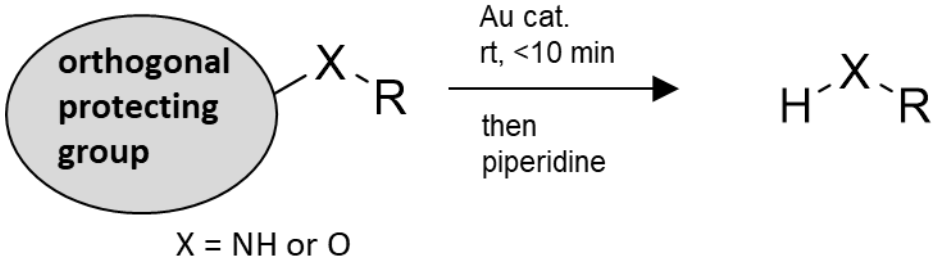


Figure 1. Novel protecting group activated by gold catalysis

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コロナチン立体異性体ライブラリースクリーニングによる植物ホルモン受容体サブタイプ選択的リガンドの開発

（東北大院理[1]・東北大院生命[2]・帝京大院理工[3]・東京大生物工学セ[4]）○林 謙吾[1]、加藤 信樹[1]、野本 春菜[1]、中山 美涼[1]、加治 拓哉[1]、渡部 楽[2]、齊藤 里菜[2]、高岡 洋輔[1]、宮本 皓司[3]、稲垣 秀生[3]、岡田 憲典[4]、上田 実[1,2]

Development of receptor subtype selective ligands via focused library screening composed of stereoisomers of coronatine ([1]*Graduate School of Science, Tohoku University*, [2]*Graduate School of Life Sciences, Tohoku University*, [3]*Graduate School of Science and Engineering, Teikyo University*, [4]*Biotechnology Research Center, The University of Tokyo*) ○Kengo Hayashi[1], Nobuki Kato[1], Haruna Nomoto[1], Misuzu Nakayama[1], Takuya Kaji[1], Raku Watanabe[2], Rina Saito[2], Yousuke Takaoka[1], Koji Miyamoto[3], Hideo Inagaki[3], Kazunori Okada[4], Minoru Ueda[1,2]

Plant hormone, jasmonoyl-L-isoleucine (JA-Ile), causes various physiological events such as growth inhibition, defense responses, and secondary metabolite production in plants. These diverse bioactivities are attributed to plural subtypes of the co-receptor, COI1-JAZ. Functional analysis of each subtype of COI1-JAZ is limited in genetic approach due to genetical and functional redundancy of COI1-JAZ. In contrast, chemical genetics approach using subtype selective ligands would enable to reveal the function of each COI1-JAZ subtype.

In this report, we constructed focused chemical library of 16 stereochemical isomers of coronatine which is structural mimic of JA-Ile. By using this library, we successfully found several subtype-selective ligands for the COI1-JAZ co-receptors in the typical model plant species Arabidopsis, tomato, and rice.

Keywords: Focused-chemical library; Plant hormone; Protein-protein interaction

植物ホルモンのジャスモン酸イソロイシン（JA-Ile）は、植物体内に存在する COI1-JAZ 共受容体に結合することで、生長阻害や病虫害防御応答など、多様な生物応答を引き起こす。しかし、COI1-JAZ 共受容体には複数のサブタイプが存在し、その遺伝的冗長性により、各受容体サブタイプの機能を遺伝学的手法で解明することは困難であった。一方、サブタイプ選択的リガンドを用いる化学遺伝学的手法は、このような遺伝的冗長性の高い受容体それぞれの機能を解析するうえで有効であると期待され、開発が望まれている。

今回我々は、JA-Ile の構造を模倣した天然物 コロナチン（COR）の、三次元的な構造がわずかに異なる立体異性体のフォーカスドケミカルライブラリー（全 16 種）が、COI1-JAZ 共受容体サブタイプ選択的リガンドの開発に有用であることを見出した。**2** の立体異性体ライブラリーの各受容体サブタイプに対する親和性を網羅的に評価した結果、複数の立体異性体が、シロイヌナズナ、トマト、イネに対して、高い選択性を示した。さらに、生物活性評価及び作用機序解析の結果、高いサブタイプ選択性を持つ立体異性体は、シロイヌナズナに対して、生長阻害という副作用を伴わずに病原菌感染防御応答を選択的に活性化することを見出した。

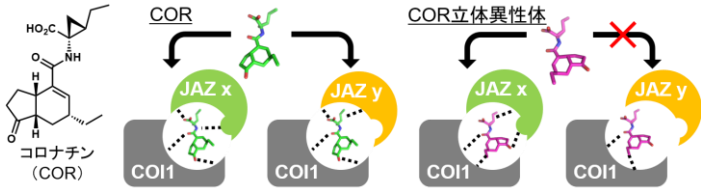


Figure: Chemical structure of COR. A stereoisomer of COR has selective affinity with a COI1-JAZ co-receptor.

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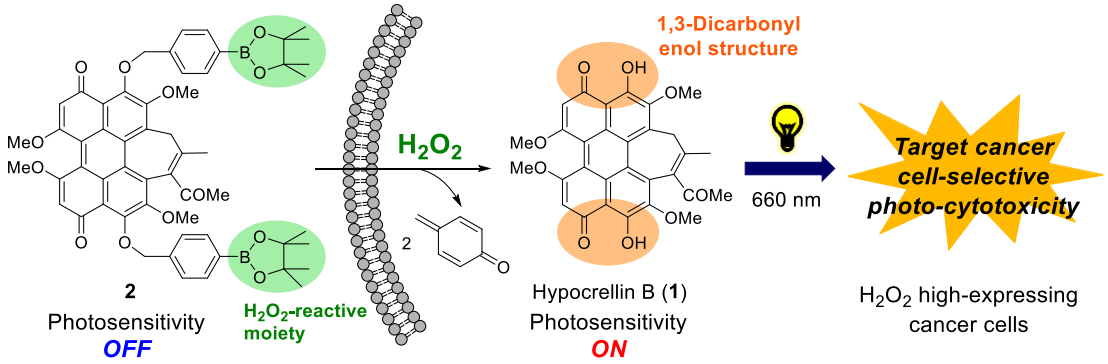
Creation of H_2O_2-Activatable Photosensitizer based on Hypocrellin B

(*Faculty of Science and Technology, Keio University*) ○Takashi Kitamura, Hirotaka Nakata, Daisuke Takahashi, Kazunobu Toshima

Keywords: Stimuli Activatable Photosensitizer; Hypocrellin B; Hydrogen Peroxide; Boronic Acid; Photocytotoxicity

Stimuli activatable photosensitizers, which can turn on their photosensitizing ability by reacting with a specific biomarker expressed in the target tissues, have great potential for minimizing non-specific photodamage to healthy tissues during and after photodynamic therapy (PDT). In this context, we focused on a natural perylenequinone dye hypocrellin B (**1**) as a core structure of an activatable photosensitizer, because **1** is a potent PDT agent with absorption at long-wavelength visible region,[1] and has a 1,3-dicarbonyl enol structure, which we recently found as a responsive substructure of photosensitizer to control its photosensitivity.[2] Herein, we report a molecular design, chemical synthesis, and biological evaluation of a tumor-related biomarker, H_2O_2-activatable photosensitizer based on **1**.

Firstly, H_2O_2-activatable photosensitizer **2** consisting of **1** and H_2O_2-reactive boronic ester moieties conjugated to the hydroxyl group of **1** through a benzyl ether link, was designed. After chemical synthesis of **2**, its singlet oxygen ($^1O_2$) generating ability was evaluated under 660 nm light irradiation. The results showed that the $^1O_2$ generating ability of **2** significantly decreased in comparison with that of **1**. Next, the reactivity of **2** against H_2O_2 was evaluated, indicating that **2** reacted with H_2O_2, and released **1**. Finally, the cytotoxicity of **2** against normal human-lung fibroblast WI-38 cells and mouse melanoma B16F10 cells, which express H_2O_2 at a higher concentration, was examined with or without photo-irradiation. As the results, it was found that **2** showed significant and selective cytotoxicity against targeted B16F10 cells only with photo-irradiation.



1) G. G. Miller, K. Brown, Å. M. Ballangrud, O. Barajas, Z. Xiao, J. Tulip, J. W. Lown, J. M. Leithoff, M. J. Allalunis-Turner, R. D. Mehta, R. B. Moore, *Photochem. Photobiol.* **1997**, *65*, 714.
2) T. Kitamura, S. Shiroshita, D. Takahashi, K. Toshima, *Chem. Eur. J.* **2020**, *26*, 14351.

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

[A26-3am] 17. Biofunctional Chemistry, Biotechnology

Chair:Atsushi Shimoyama, Katsunori Tanaka

Sun. Mar 21, 2021 9:00 AM - 11:40 AM Room 26 (Online Meeting)

[A26-3am-01] Development of highly functionalized lipid A for self-adjuvanting vaccines.

○Yusuke Yamanaka[1], Atsushi Shimoyama[1], Koichi Fukase[1] (1. Graduate School of Science, Osaka University)

9:00 AM - 9:20 AM

[A26-3am-02] Preparation of Bone-like Hydroxyapatite and its application for cell culture

○Hiroki Miyajima[1], Hiroki Touji[1], Yuanyi Chen[1], Taichi Furukawa[1], Shoji Maruo[1], Kazutoshi Iijima[1] (1. Yokohama National University)

9:20 AM - 9:40 AM

[A26-3am-03] Molecular Dynamics Simulation of Interaction between Polysaccharides and Fabrication of Cell Scaffolds

○Kazutoshi Iijima[1], Makoto Yamazaki[1], Makoto Yabe[2] (1. Yokohama Natl. Univ., 2. Mol Processing)

9:40 AM - 10:00 AM

[A26-3am-04] Spatial and Temporal Regulation of Cellular Morphology using a Photo-Responsive Mechanical DNA Polymer

○Soumya Sethi[1], Tomoko Emura[1], Kumi Hidaka[1], Masayuki Endo[1,2], Hiroshi Sugiyama[1,2] (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Sciences ,Kyoto University)

10:00 AM - 10:20 AM

[A26-3am-05] Structural basis for membrane receptor activity of ganglioside GM3 regulated by lipid-lipid interactions

○Katsuaki Sasaki[1], Shinya Hanashima[1], Yuuichi Umegawa[1], Michio Murata[1] (1. Osaka University)

10:20 AM - 10:40 AM

[A26-3am-06] *In situ* Detection of Penicillin and Avermectin in Microbes by Raman Microspectroscopy and Multivariate Analysis

○Shumpei Horii[1,2], Masahiro Ando[3], Takuji Nakashima[1], Ashok Zachariah Samuel[3], Yoko Takahashi[1], Haruko Takeyama[1,2,3,4] (1. The Univ. of Waseda, 2. CBBD-OIL, AIST-Waseda Univ., 3. Res. Org. Nano Life Innov., The Univ. of Waseda, 4. Inst. Adv. Res. Biosyst. Dynam., Waseda Res. Inst. Sci. Eng., The Univ. of Waseda)

10:40 AM - 11:00 AM

[A26-3am-07] Development of a Drug Encapsulated Micelle Loaded Photoresponsive Platform for the Treatment of Coronary Stenosis

○Hayato Laurence Mizuno[1], Yasutaka Anraku[1], Ichiro Sakuma[1], Yuki Akagi[1] (1. The Univ. of Tokyo)

11:00 AM - 11:20 AM

[A26-3am-08] Lysosome-targeting magnetic-plasmonic hybrid nanoparticles for the imaging and isolation of intact lysosomes

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○The Son Le[1], Mari Takahashi[1], Yuichi Hiratsuka [1], Kazuaki Matsumura [1], Tomohiko Taguchi[2], Shinya Maenosono[1] （1. Japan Advanced Institute of Science and Technology, 2. Tohoku University）

11:20 AM - 11:40 AM

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Development of highly functionalized lipid A for self-adjuvanting vaccines.

(*Graduate School of Science, Osaka University*)
○Yusuke Yamanaka, Atsushi Shimoyama, Koichi Fukase
Keywords: Adjuvant, Self-adjuvanting Vaccine, Lipopolysaccharide, Lipid A, Immunity

Lipopolysaccharide (LPS), the outer membrane component of Gram-negative bacteria, has been known as a potent immunostimulator. Its terminal glycolipid moiety "lipid A" is an active principal of the LPS. Monophosphoryl lipid A derivative 3D-MPL (GlaxoSmithKline) has been practically used as a vaccine adjuvant.[1)] It has also been reported that a self-adjuvant vaccine composed of an antigen and an adjuvant can promote efficient antibody production.[2)] Meanwhile, the lipid A conjugation strategy maintaining its innate immunological function is still under developing. In this study, we investigated the lipid A conjugation method that enables highly functionalized lipid A for self-adjuvanting vaccines.

We developed self-adjuvanting vaccine **5** based on MPL504, attenuated lipid A developed by our group (Figure 1). We planned to introduce antigen moiety using hydrophilic (sugar mimic) linker at 6'-position of lipid A via an amide bond considering increased stability *in vivo* and linking of the polysaccharide moiety to 6'-position of lipid A in natural LPS. We previously found that the linker influenced the activity of lipid A, *i.e.*, polyethylene glycol linker significantly decreased the lipid A activity, whereas the more hydrophilic linkers maintained the activity.[3)] In this study, we designed and synthesized a novel hydrophilic sugar mimic linker **2** from D-mannitol. The disaccharide intermediate **1** was synthesized according to our previous report.[4)] Introduction of fatty acids and 6'-amination **3** afforded **3**. Coupling of **3** with the linker **2** afforded **4**. After the introduction of antigen moiety, all protecting groups were removed to afforded **5**.

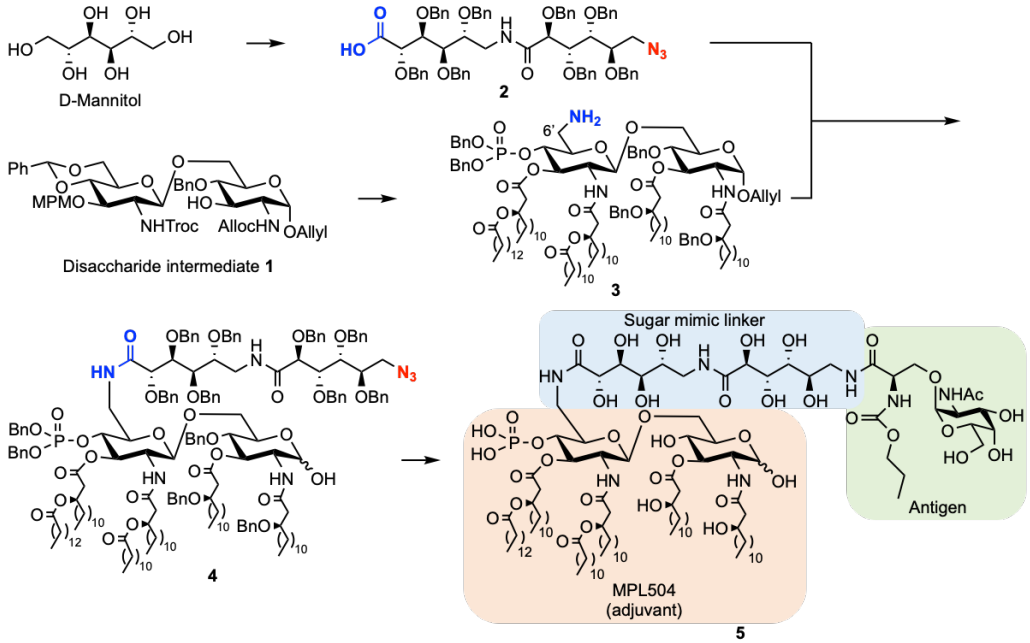


Figure 1. Synthesis of self-adjuvanting vaccine **5** based on MPL504

1) Mata-Haro *et al.*, *Science*, **2007**, *316*, 1628. 2) S. Ingale, *et al.*, *Nat Chem Biol.*, **2007**, *3*, 663. 3) Y. Fujimoto, *et al.*, *TL.* **2006**, *47*, 539. 4) A. Shimoyama *et al.*, *Chem. Eur. J.*, **2011**, *17*, 14464.

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骨類似ヒドロキシアパタイトの作製と細胞培養への応用

（横国大院工[1]・横国大理工[2]）○宮島 浩樹[1]・田路 弘樹[2]・陳 元依[1]・丸尾 昭二[1]・飯島 一智[1]

Preparation of Bone-like Hydroxyapatite and its Application for Cell Culture

([1]*Faculty of Engineering, Yokohama National University*, [2]*College of Engineering Science, Yokohama National University*) ○Hiroki Miyajima,[1] Hiroki Touji,[2] Yuanyi Chen,[1] Taichi Furukawa,[1] Shoji Maruo,[1] Kazutoshi Iijima[1]

A simulated body fluid (SBF) is a solution mimicking inorganic ion concentrations in body fluid. Preparation of hydroxyapatite (HAp) by using SBF is a biomimetic synthesis inspiring biomineralization process. HAp obtained from SBF has been known as bone-like HAp because the HAp has the similar composition to natural bone. In this study, preparation of HAp was conducted by using SBF whose ion concentrations and pH were controlled. To investigate the solution pH on formation of HAp, calcium ion concentrations in SBF were measured. Furthermore, a three-dimensional model was fabricated to apply HAp to cell scaffold. As a result, by using 1.5SBF having 1.5-fold ion concentrations than ordinal SBF, microparticles and nanoparticles were obtained from pH 7.4 and pH 8.4, respectively. The obtained particles showed different morphologies and properties. A three-dimensional model was fabricated by microsteleolithgraphy and cells seeded on the model showed high viability.

Keywords : Hydroxyapatite; Cell Scaffold; Three Dimensional Fabrication

[緒言] 擬似体液（simulated body fluid, SBF）は、ヒト血漿の無機イオン組成を模倣した溶液である。SBF を用いたヒドロキシアパタイト（HAp）作製は、バイオミネラリゼーションを模倣した作製法であり、得られる HAp は生体骨に近い組成を示すことから、骨類似 HAp と呼ばれている [1)]。本研究では、SBF の組成を調整することで得られる粒子の物性・性質の制御を行い、粒子形成メカニズムについても検討した。また、粒子を細胞足場として応用するため、三次元細胞足場の構築を目指した。

[手順] SBF の無機イオン濃度を 1.5 倍に調整した 1.5SBF の pH を変化させ、その溶液中に析出した粒子を回収した。粒子形成過程での溶液中の Ca^{2+}濃度を測定し、粒子形成における pH の影響とその形成メカニズムを調査した。また、光ファイバーマイクロ光造形法により粒子を用いた三次元造形物を作製し、細胞足場として応用した。

[結果と考察] pH 調整した 1.5SBF において、pH 7.4 からは結晶性の高いマイクロ粒子（Fig. 1）、pH 8.4 からは結晶性の低いナノ粒子を得た。1.5SBF 中の Ca^{2+}濃度測定では、pH 7.4 の場合のみ Ca^{2+}濃度の段階的な減少が確認でき、粒子の成長に伴うカルシウムの析出が示唆された。得られたマイクロ粒子について三次元造形物を作製し、造形物にヒト間葉系幹細胞 UE7T-13 を播種し、細胞の生存を確認した。

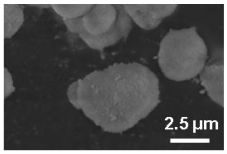


Figure 1. SEM image of microparticles obtained from 1.5SBF (pH 7.4).

1) (a) H.-M. Kim, *et al*., *J. R. Soc. Interface* 1, 17–22 (**2004**).
(b) M. Hashizume, *et al*., *Colloids Surf. B* 84, 545–549 (**2011**).

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多糖間相互作用の分子動力学シミュレーションと細胞足場の作製

（横浜国大[1]・モルプロセッシング[2]）○飯島 一智[1]・山崎 誠[1]・矢部 誠[2]
Molecular Dynamics Simulation of Interaction between Polysaccharides and Fabrication of Cell Scaffolds ([1]*Yokohama National University*, [2]*Mol Processing*) ○ Kazutoshi Iijima,[1] Makoto Yamazaki,[1] Makoto Yabe[2]

By forming a polyion complex, a water-insoluble material can be prepared from a highly water-soluble polysaccharide. In this study, molecular dynamics simulations on the process of formation of polysaccharide complexes from cationic polysaccharides and anionic polysaccharides were performed in order to elucidate the effects of the chemical structure of polysaccharides on the formation of polysaccharide complexes. The molecular dynamics simulation was performed using GROMACS ver. 2020.2. The 12 mer polysaccharides such as chitosan (CHI), heparin (HEP), chondroitin sulfate (CS), hyaluronic acid (HYA), and carboxymethyl cellulose (CMC) were used. As a result, it was shown that CHI and each anionic polysaccharide interacted and associated with each other. Interactions between polysaccharides were evaluated based on indexes such as the number of hydrogen bonds, radial distribution function, and exposed surface area of solvent. We will also introduce the fabrication of cell scaffolds of films and hydrogels from polysaccharide polyion complex nanoparticles.
Keywords : Polysaccharide; Polyion Complex; Molecular Dynamics Simulation; Cell Scaffold

カチオン性多糖とアニオン性多糖との間で形成されるポリイオンコンプレックスを用いることで、水溶性の高い多糖から水不溶性の材料を得ることができる。本研究では、カチオン性多糖とアニオン性多糖より多糖複合体が形成される過程について分子動力学シミュレーションを行い、各多糖の化学構造が複合体形成に与える影響について解析を行なった。分子動力学シミュレーションは GROMACS ver. 2020.2 を用いて行った。多糖はいずれも 12 mer とし、カチオン性多糖としてキトサン（CHI）、アニオン性多糖としてヘパリン（HEP）、コンドロイチン硫酸（CS）、ヒアルロン酸（HYA）、カルボキシメチルセルロース（CMC）を用いた。分子動力学シミュレーションの結果、CHI と各アニオン性多糖が相互作用し、会合する様子が確認された。水素結合数、動径分布関数、溶媒露出表面積などの指標をもとに詳細な解析を行なった。

多糖複合ナノ粒子を用いたフィルムおよびハイドロゲル型の細胞足場の作製と細胞培養についても紹介する。

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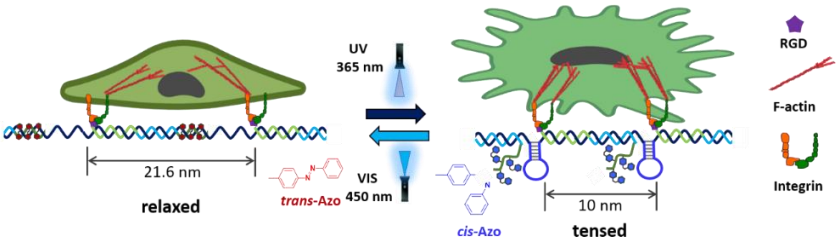
Spatial and Temporal Regulation of Cellular Morphology using a Photo-Responsive Mechanical DNA Polymer

*Soumya Sethi[1], Tomoko Emura[1], Kumi Hidaka[1], Masayuki Endo[1,2], Hiroshi Sugiyama[1,2] (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Sciences ,Kyoto University)

Extracellular matrix is the non-cellular component in which the cells are present in tissues and organs. The extracellular matrix, residing the cells provides a dynamic and reversible environment for the cells. These spatial and temporal cues are essential for the cells especially when they are undergoing morphogenesis, repair, and differentiation. [1,2] Recapitulation of such an intricate system with reversible presentation of nanoscale cues can help us better to understand important cellular processes and can help us precisely manipulate cell function in vitro. Previously researchers have tried to develop such systems but they are either static[3] or involve strand displacement reactions which limits their usage over several cycles and can be laborious. [4]

Herein, using principles of DNA Nanotechnology we designed a light powered DNA nanostructure containing azobenzene moieties[5] that can dynamically and reversibly cause the change in the spatial orientation of the cell adhesion peptides (RGD). The changes in the nanoscale distance of the adhesion peptides can significantly affect the morphology of the cells from a well spread state (when nanostructure is in the contracted form i.e. when RGD are closer to each other) to a less spread state (when nanostructure is in extended form i.e when RGD are farther apart) and allow us to study cell- matrix adhesion, organization of cell surface receptors etc and thus provide us a tool to decipher the language of the extracellular matrix better.

Keywords: azobenzene, cellular morphology, nanoscale cues, DNA Nanotechnology



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Structural Basis for Membrane Receptor Activity of Ganglioside GM3 Regulated by Lipid-Lipid Interactions

(*Graduate School of Science, Osaka University*) ○Katsuaki Sasaki, Shinya Hanashima, Yuichi Umegawa, Michio Murata

Keywords: Lipid Rafts; Ganglioside; Binding Assay; Solid State NMR; Orientational Analysis

Ganglioside is one of the key components in the bio-functional membrane domains, so called lipid rafts. As the structural feature, ganglioside consists of hydrophobic ceramide and hydrophilic glycan moieties (Fig.1). This amphiphilic molecule is involved in various biological functions, one of which is binding activity for exogenous proteins, such as viral spike-proteins and bacterial toxins. Cholesterol-ganglioside interaction occurring in the lipid rafts has been thought to regulate the protein-ganglioside interplay by altering orientation of the ganglioside head group.[1] However, there are few reports on the experimental evidence supporting this orientation change.[2]

To elucidate the mechanism in regulating affinity between glycan-binding proteins and ganglioside GM, we here examined their interactions with the focus on the three-dimensional structure of the glycan moiety. The binding event of membrane GM3 with a fluorescence-labeled lectin was evaluated with the lipid bilayer models mimicking the rafts or the non-rafts. As a result, the binding affinity of them was found to be affected by membrane ordering with cholesterol. For the orientational analysis, ^{2}H-labeled GM3 probes were synthesized and incorporated in the lipid bilayer models mimicking the rafts and the non-rafts. We observed the orientational difference of the sialic acid moiety of GM3 in the different membrane conditionsby solid state NMR. The solid-state ^{2}H NMR results suggested that the orientation of the sialic acid moiety of GM3 was different depending on the membrane environment.

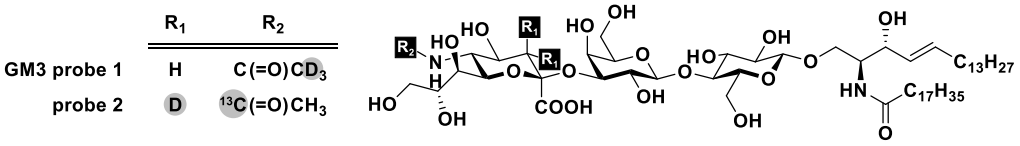


Fig.1 Design of Isotopic-labeled Ganglioside GM3

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顕微ラマン多変量スペクトル分解法を用いた生物活性物質 penicillin 及び avermectin の菌体内検出

(1. 早稲田大学、2. 産総研 CBBD-OIL、3. 早大　ナノ・ライフ創新研、4. 早大先進生命動態研)○堀井俊平[1,2]、安藤 正浩[3]、中島 琢自[1]、Ashok Samuel[3]、高橋 洋子[1]、竹山 春子[1,2,3,4]

In situ Detection of Penicillin and Avermectin in Microbes by Raman Microspectroscopy and Multivariate Analysis

(1. The Univ. of Waseda, 2. CBBD-OIL, AIST-Waseda Univ., 3. Res. Org. Nano Life Innov., Waseda Univ., 4. Inst. Adv. Res. Biosyst. Dynam., Waseda Res. Inst. Sci. Eng., Waseda Univ.) ○Shumpei Horii[1,2], Masahiro Ando[3], Nakashima Takuji[1], Ashok Zachariah Samuel[3], Yoko Takahashi[1], Haruko Takeyama[1,2,3,4]

In this study, we report the application of Raman microspectroscopy to *in situ* detection of bioactive compounds. Raman spectroscopy provides characteristic information on the molecular structure of metabolites and does not require any sample pretreatment such as dye labeling or genetic manipulation, thus allowing for rapid and low-invasive observations. Moreover, for the spectral analysis, we used multivariate curve resolution-alternating least squares (MCR-ALS) method which can extract meaningful “pure” spectral components from the overlapped and complicated spectra arising from several molecular compositions. By using MCR-ALS analysis, the Raman spectrum of bioactive compounds can be distinguished from other cellular components and the accumulation was visualized.

Keywords : Raman microspectroscopy; MCR-ALS; Secondary metabolites; Screening

環境微生物が産生する二次代謝産物は多様な生物活性を示すため、医薬品をはじめ幅広い分野で利用されている。しかし、現行の二次代謝産物の生産能評価は、培養・分離精製などの煩雑な工程を含み、微生物内の二次代謝産物を直接検出する手法はない。そこで、本研究では、非標識・低侵襲に物質の分子構造を明らかにできる顕微ラマン分光法を用いて、微生物内で産生される二次代謝産物の *in situ* 検出を行い、生体内物質の生産能評価と菌体内分布の可視化を試みた。Penicillin の生産菌である糸状菌 *Penicillium chrysogenum* NBRC-4626 及び avermectin の生産菌である放線菌 *Streptomyces avermectinius* MA4680^T を研究対象とし、培養後の各菌体のラマンスペクトル測定を行った。スペクトル解析手法として多変量スペクトル分解法(MCR-ALS)を用い、複雑な生体由来のラマンスペクトルから単一の生体成分に由来するスペクトル成分及び各成分の強度分布情報の抽出を行った。MCR-ALS 解析の結果、複雑なマッピングデータから各生体成分及び二次代謝産物に由来するラマンスペクトルをそれぞれ抽出することができ、penicillin および avermectin の菌体内検出及び局在の可視化に成功した。また、*S. avermectinius* MA-4680^T を寒天培養した際に生じる形態変化における avermectin の生体内動態を経日的にモニタリングしたところ、avermectin が胞子鎖に局在することが明らかとなった。以上より、本手法が、微生物内の二次代謝産物の産生を迅速に評価できるだけでなく、二次代謝産物の菌体内分布情報から生物学的に新たな知見を得ることを示した。

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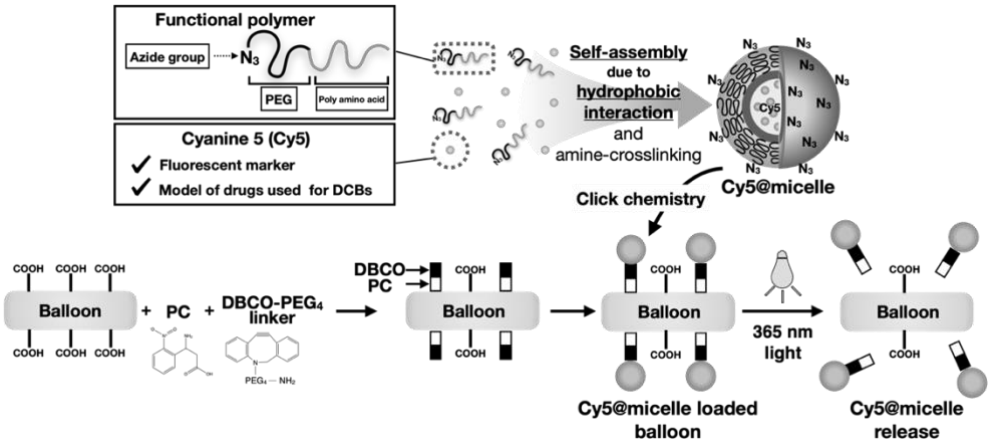
Development of a Drug Encapsulated Micelle Loaded Photoresponsive Platform for the Treatment of Coronary Stenosis

([1]*Graduate School of Engineering, The University of Tokyo*) ○Hayato Laurence Mizuno,[1] Yasutaka Anraku,[1] Ichiro Sakuma,[1] Yuki Akagi[1]

Keywords : Photoresponsivity; Polymeric micelle; Topical drug delivery; Drug coated balloon; Hemocompatibility

Drug coated balloon (DCB) has been attracting attention as a medical device for the treatment of coronary stenosis. However, with conventional DCBs, a large portion of the initially loaded drug were washed off from the balloon due to blood stream and another large portion remained on the balloon after delivery, which resulted in only about 1.4% of the initially loaded drug to reach the stenosis.[1] Past work has been conducted to enhance drug delivery efficiency by incorporating a photocleavable (PC) linker to covalently bond drugs onto balloon surface then initiate release through light irradiation.[2] However, because this platform required drug to be covalently conjugated onto the PC linker, drug denaturation could decrease its medicinal effect. To prevent this problem, we proposed to encapsulate drugs into micelles and load them onto balloons while preserving their photoresponsivity.

We fabricated a photocleavable linker, Azadibenzylcyclooctyne-PEG_4-3-amino-3-(2-nitrophenyl) propanoic acid (DBCO-PEG_4-ANP) and conjugated this onto the carboxyl group on the surface of medical balloons. Note here that ANP is a photocleavable group that cleaves in reaction to 365 nm light. We then fabricated azide (N_3) functionalized Cy5-micelle and conjugated this onto the linker. For initial evaluation, micelle load and photoresponsivity of the platform were validated via wettability measurement and fluorescent microscopy, respectively. The results of wettability and fluorescent microscopy showed that Cy5-micelles were successfully loaded onto the balloons at approximately 3.8×10^{-2} ug/mm^2 and also showed 80% release in event of light irradiation (365 nm, 360 mW/cm^2, 1 min.). Thus, we concluded that the proposed photocleavable platform has the potential to realize topical drug delivery with unprecedented efficiency.



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Lysosome-Targeting Magnetic-Plasmonic Hybrid Nanoparticles for the Imaging and Isolation of Intact Lysosomes

([1]*School of Materials Science, JAIST*, [2]*Graduate School of Life Science, Tohoku University*)
○The Son Le,[1] Mari Takahashi,[1] Yuichi Hiratsuka,[1] Kazuaki Matsumura,[1] Tomohiko Taguchi,[2] Shinya Maenosono[1]

Keywords: Nanoparticles, Lysosome, Isolation, Bioimaging, Magnetic Separation

The proteomic analyses of lysosomal protein defects are crucial tasks to understand the role of lysosomal dysfunction in pathological conditions.[1] The key factor for generating comprehensive lysosomal proteome datasets requires a novel isolation technique with high yield and purity. Commonly used methods for lysosome fractionation are density-gradient centrifugation and antibody-based pulldown assay, which often result limited yield and low purity.[2] In addition, long isolation times are needed, and thus the functional loss of lysosomal proteins during separation would be caused. Recently, superparamagnetic nanoparticles-based isolation has emerged as an approach to separate 'intact' lysosomes.[3] In this technique, nanoparticles are required to be delivered into the lumen of lysosomes through a endocytic pathway. The intracellular fate of nanoparticles strongly affects to the yield and purity of lysosome fractionation.

Herein, we synthesized dextran (Dxt) modified magnetic-plasmonic Ag@FeCo@Ag core@shell@shell nanoparticles (MPNPs) with the hydrodynamic size of around 50 nm in PBS buffer (Fig. 1a) and demonstrated a magnetic separation of lysosomes in COS-1 cells using the Dxt-modified MPNPs which are targeted to the lumen of lysosomes through the endocytic machinery. Unlike other existing magnetic fractionation techniques, the plasmonic scattering from MPNPs enables us to trace the localization of MPNPs in the endocytic pathway by confocal laser scanning microscopy (CLSM) (Fig. 1b). In this talk, we will show the results of plasmonic imaging and magnetic separation of lysosomes using Dxt-modified MPNPs.

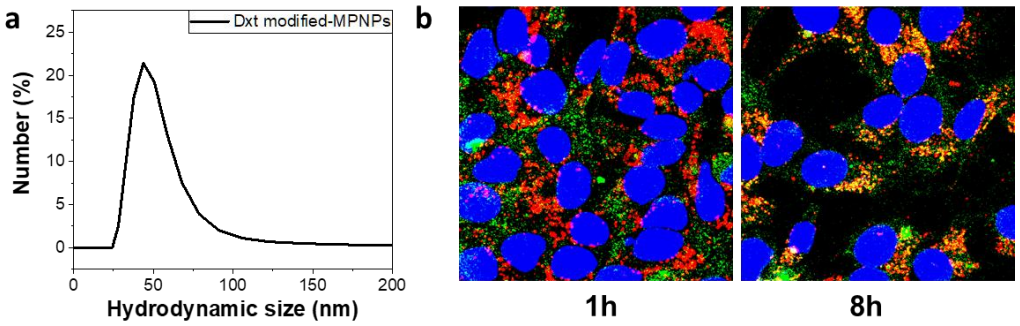


Fig. 1. (a) Hydrodynamic size distribution of Dxt-modified MPNPs dispersed in a PBS buffer. (b) CLSM images of Dxt-modified MPNPs in COS-1 cell after 1 (left) and 8 (right) hours incubation (blue: nuclei, green: MPNPs, red: lysosomes).

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

[A27-3pm] 18. Polymer

Chair:Takahiro Kakuta, Michio Matsumoto

Sun. Mar 21, 2021 1:00 PM - 3:20 PM Room 27 (Online Meeting)

[A27-3pm-01] Synthesis of π-conjugated two-dimensional polymers and their electronic properties

○Michio Matsumoto[1] (1. National Institute for Materials Sceince)

1:00 PM - 1:20 PM

[A27-3pm-02] Design of temperature-responsive polymer-gold nanoparticle hybrids using novel gold nanoparticle monomers and regulation of reduction activity

○Takashi Miyata[1], Yoshiko Oota[1], Atsushi Saka[1], Akifumi Kawamura[1] (1. Kansai Univ.)

1:20 PM - 1:40 PM

[A27-3pm-03] Preparation and properties of polysilsesquioxane membrane with proton conductivity

○Hiroshi Fujioka[1] (1. Tokyo University of Science)

1:40 PM - 2:00 PM

[A27-3pm-04] Development of Two-Dimensional Nanostructured Virus Filtration Membranes Based on Gemini Smectic Liquid Crystals

○Kazuma Hamaguchi[1], Rino Ichikawa[1], Satoshi Kajiyama[1], Shotaro Torii[1], Yusuke Hayashi[1], Hiroyuki Katayama[1], Takashi Kato[1] (1. Sch. Eng., The Univ. of Tokyo)

2:00 PM - 2:20 PM

[A27-3pm-05] Development of Halogen-Sensitive Solvatochromism Materials Using Phenolic Polymers

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

2:20 PM - 2:40 PM

[A27-3pm-06] Polarization-Responsive Behavior in Nonlinear Optical Effect of Polymer-Stabilized Dye-Doped Liquid Crystals

○Kohsuke Matsumoto[1], Koji Usui[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

[A27-3pm-07] Metallo-supramolecular polymers: electrochromic and supercapattery device application

○Masayoshi Higuchi[1], Sanjoy Mondal[1], Manas Kumar Bera[1] (1. National Institute for Materials Science)

3:00 PM - 3:20 PM

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Synthesis of π-conjugated two-dimensional polymers and their electronic properties

(*International Center for Materials Nanoarchitectonics, National Institute for Materials Science*) ○Michio Matsumoto

Keywords: Covalent Organic Frameworks (COFs); Multidimensional Polymers; Ullmann-coupling reaction, π-conjugated macromolecules

Two-dimensional covalent organic frameworks (2D COFs) are crystalline 2D polymer networks whose monomers are organized predictably using directional bonding principles. Although various examples have been reported so far in this class of materials, their electronic conductivities are very limited, which is unlike their natural 2D polymer counterparts, such as graphene/graphite. Here we studied 2D polymers consisting of benzotrithiophene (BTT) derivative monomers. BTT has two structural isomers depending on the direction of three thiophenes in their fused structures: **BTT**$_{C3sym}$ has the same direction for three thiophenes in it, while **BTT**$_{Asym}$ has one thiophene directing oppositely from the other two (Fig. 1). By employing with DFT calculation methods, we found the 2D polymers made from those two different BTTs exhibit very different band structures and **BTT**$_{Asym}$ can construct a 2D polymer with a highly distorted band structure.[1]

For synthesizing the 2D polymer structure composed of **BTT**$_{Asym}$, tribrominated **BTT**$_{Asym}$ monomer, **BTT**$_{Asym}$**Br**$_3$, was synthesized and heated on metal surfaces to conduct Ullmann coupling reaction, affording π-conjugated 2D polymers under ultra-high vacuum conditions. By carefully selecting metal surfaces to use, we successfully obtained a 2D polymer composed of **BTT**$_{Asym}$, which is visualized by STM imaging (Fig 2).[2] The detailed synthetic conditions and features of obtained 2D polymer structures will be discussed in this talk.

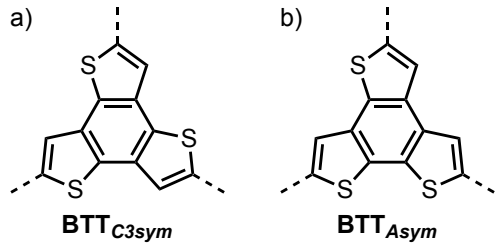


Fig. 1 Chemical structures of (a) **BTT**$_{C3sym}$ and (b) **BTT**$_{Asym}$

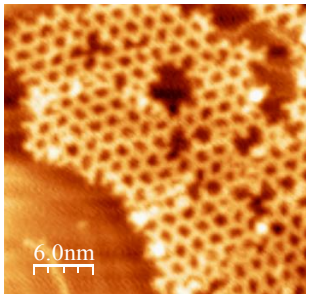


Fig. 2 STM topography of **BTT**$_{Asym}$**Br**$_3$ polymerized on Au(111).

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新規な金ナノ粒子モノマーを用いた温度応答性高分子－金ナノ粒子ハイブリッドの設計とその還元活性制御

(関西大化学生命工[1]・関西大 ORDIST[2]) ○宮田 隆志[1,2]・太田 慶子[1]・坂 篤[1]・河村 暁文[1,2]
Design of Temperature-responsive Polymer-gold Nanoparticle Hybrids Using Novel Gold Nanoparticle Monomers and Regulation of Reduction Activity ([1]*Faculty of Chemistry, Materials and Bioengineering, Kansai University*, [2]*ORDIST, Kansai University*) ○Takashi Miyata,[1,2] Yoshiko Oota,[1] Atsushi Saka,[1] Akifumi Kawamura[1,2]

Stimuli-responsive polymers that undergo a drastic change in the solubility in water have many potential applications in designing smart device and systems. In this study, we designed a gold nanoparticle (AuNP) monomer well-dispersed in water by introducing both polymerizable and carboxy groups onto the surface of AuNP. Temperature-responsive polymer-AuNP hybrids were prepared by copolymerization of the resulting AuNP monomer and *N*-isopropylacrylamide. Transmittance measurements of an aqueous solution with the resulting poly(*N*-isopropylacrylamide)(PNIPAAm)-AuNP hybrids revealed that they have a low critical solution temperature (LCST) at 34 ºC. The NIPAAm-AuNP hybrids catalyzed the reduction of *p*-nitrophenol to *p*-aminophenol below their LCST, but did not do above their LCST. Thus, we achieved temperature-responsive regulation of the reduction activity of the PNIPAAm-AuNP hybrids for *p*-nitrophenol.
Keywords : Temperature-responsive Polymers; Gold Nanoparticles; Hybrid; Responsiveness; Reduction Activity

刺激応答性高分子は，外部刺激に応答して溶媒に対する溶解性が急激に変化し，センサーや DDS，細胞制御など幅広い分野への応用が展開されている。一方，金ナノ粒子（AuNP）は，局在表面プラズモン共鳴による色彩変化や安定した触媒活性などのバルク材料には無いユニークな特性を示す。本研究では，重合性官能基とカルボキシ基を導入した AuNP モノマーを調製し，*N*-isopropylacrylamide（NIPAAm）と共重合させることによって温度応答性を示す PNIPAAm-AuNP ハイブリッドを合成した。さらに，基質として *p*-ニトロフェノール（PNP），還元剤としてホウ素化水素ナトリウム，触媒として PNIPAAm-AuNP を用いて温度変化に応答した PNP の還元反応制御を試みた。

まず，濁度測定の結果，水中で PNIPAAm-AuNP は 34 ºC に下限臨界溶液温度（LCST）をもつことが明らかとなった。次に，PNIPAAm-AuNP を用いて PNP の還元反応を行うと，LCST 以下の温度では還元反応が進行したが，LCST 以上になると還元反応を示さなかった。したがって，PNIPAAm-AuNP は PNP の還元で触媒活性を示し，その活性を温度によって ON-OFF 制御できることが明らかとなった。

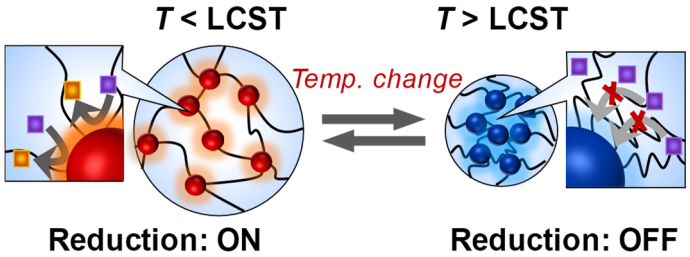


Fig. 1. Schematic illustration for the regulation of the reduction by volume phase transition of PNIPAAm-AuNP hybrids.

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プロトン伝導性を有するポリシルセスキオキサン膜の調製と特性

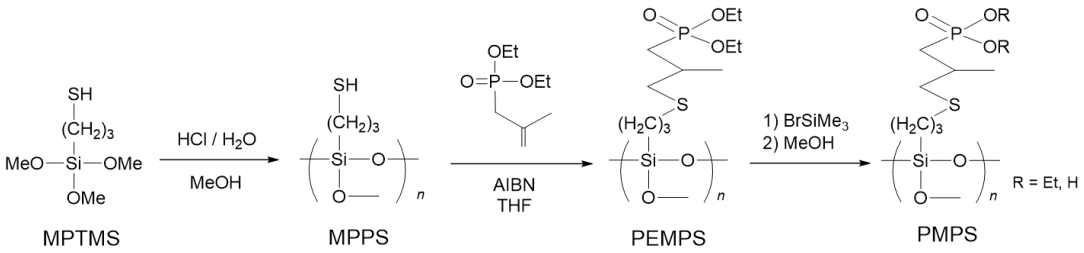
（東理大理工）○藤岡　洋・山本　一樹・郡司　天博
Preparation and properties of polysilsesquioxane membrane with proton conductivity (*Faculty of Science and Technology, Tokyo University of Science*) ○ Hiroshi Fujioka, Kazuki Yamamoto, Takahiro Gunji

Polymer electrolyte fuel cell (PEFC), whose electrolyte is solid, has the advantages of small size, light weight, and quick startup. Nafion® membranes, which are currently the mainstream of electrolyte membranes, have the problem that proton-conductivity decreases at high temperatures. We previously prepared polysilsesquioxane free-standing film having sulfonic acid as a proton conducting path, but there has been a problem that the siloxane bond becomes unstable due to the strong acidity. In this study, we synthesized a proton-conductive polymer PMPS having phosphonic acid instead of sulfonic acid, and prepared a free-standing film and evaluated its properties. The PMPS film showed proton conductive values of 6×10^{-6} S / cm at r.t. & R.H. 90%, and 4×10^{-4} S / cm at 120 ° C. & r.R.H.

Keywords : Organic-inorganic hybrid materials; Fuel cell; Solid electrolyte film; Polysilsesquioxane; Sol-gel method

固体高分子型燃料電池（PEFC）は、電解質が固体であり、小型で軽量、起動が早いといったメリットを持つ。現在、Nafion®膜が電解質膜の主流であるが、高温下でプロトン伝導度が低下するという問題があり、機能の改善が求められている。当研究室では、高温下でも作動が可能な膜の作製を目的として、主鎖に熱に強いポリシルセスキオキサンを持ち、プロトン伝導パスとしてスルホン酸を有するプロトン伝導膜を調製したが、スルホン酸の強い酸性によりシロキサン結合が不安定化する問題が生じた。そこで本研究では、スルホン酸よりも酸性が弱いホスホン酸をプロトンの伝導パスとして導入したプロトン伝導性ポリマーPMPS を合成し、自立膜の調製および物性評価を行った。

PMPS を下記のスキームに従い合成し、それによる自立膜のプロトン伝導度の評価を行った。その結果、室温・相対湿度 90%の条件では 6×10^{-6} S / cm、120℃・室湿度の条件では 4×10^{-4} S / cm、の伝導度を示した。



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Development of Two-Dimensional Nanostructured Virus Filtration Membranes Based on Gemini Smectic Liquid Crystals

([1]*School of Engineering, The University of Tokyo*) ○Kazuma Hamaguchi,[1] Rino Ichikawa,[1] Satoshi Kajiyama,[1] Shotaro Torii,[1] Yusuke Hayashi,[1] Hiroyuki Katayama,[1] Takashi Kato[1]

Keywords: Liquid Crystal; Gemini Amphiphile; 2D Nanostructure; Water Treatment; Virus Removal

Nanostructured liquid crystals have attracted wide attention because of their ability to form ordered functional nanostructures by self-organization processes. In general, conversion of fluidic liquid-crystalline (LC) materials to solid ordered materials can be achieved by introducing polymerizable moieties into molecules and subsequent in situ polymerization of LC phases. We have developed self-organized nanostructured water treatment membranes based on ionic liquid crystals.[1–4] Uniform size of water channels in the range from sub-nanometer to nanometer scale is achieved by self-assembly of 1D columnar, 2D smectic, and 3D bicontinuous cubic LC monomers, which are preserved by in situ polymerization. The LC nanostructured membranes show selective ion permeation[1,4] and high virus rejection.[2,3]

We here report a new strategy employing gemini smectic liquid crystals exhibiting 2D nanostructures for virus filtration membranes.[5] We synthesized polymerizable gemini ionic amphiphiles, where two monomeric amphiphiles were laterally linked with each other (Figure 1). These gemini amphiphiles showed thermotropic smectic A (SmA) phases with layered nanostructures. The in situ photopolymerization of the SmA liquid crystals allowed for fixation of the LC nanostructures, resulting in the formation of 2D nanostructured crosslinked polymer membranes. The 2D nanostructured membranes removed small viruses in water (>99.99997%) by filtration. Furthermore, the membranes achieved higher water permeation compared to other types of LC nanostructured membranes.

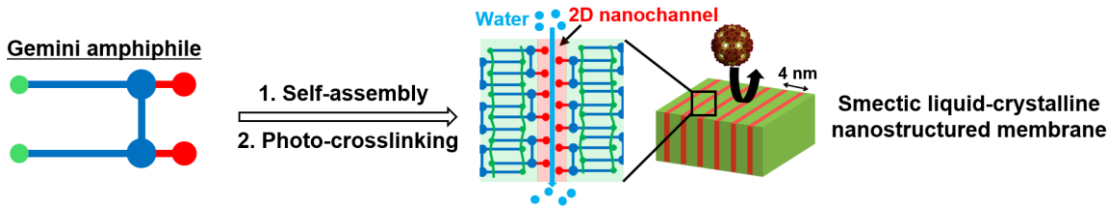


Figure 1. 2D nanostructured membranes based on gemini smectic liquid crystals.

1) T. Sakamoto, M. Henmi, T. Kato et al., *Adv. Sci.*, **2017**, *5*, 1700405. 2) N. Marets, H. Katayama, T. Kato et al., *Adv. Healthcare Mater.*, **2017**, *6*, 1700252. 3) D. Kuo, T. Sakamoto, H. Katayama, T. Kato et al., *Small*, **2020**, *16*, 202001721. 4) R. Watanabe, T. Kato, H. Harada et al., *Angew. Chem. Int. Ed.*, **2020**, *59*, 23461. 5) K. Hamaguchi, T. Kato et al., in revision.

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フェノールポリマーを利用したハロゲン応答性ソルバトクロミズム材料の開発

（金沢大院自然[1]）○角田 貴洋[1]・林 祐衣[1]・中西 良太[1]・山岸 忠明[1]
Development of Halogen-Sensitive Solvatochromism Materials Using Phenolic Polymers ([1]*Graduate School of Natural Science of Technology, Kanazawa University*[1]) ○Takahiro Kakuta,[1] Yui Hayashi,[1] Ryota Nakanishi,[1] Tada-aki Yamagishi[1]

Phenolic polymers, which has high heat resistance and insulation properties, are crosslinking phenol derivatives with methylene bonding. Previously, we have successfully synthesized phenol polymers (TPE-P) using tetraphenylethane (TPE) as the basic skeleton.[1] In this study, we investigated to change structures of the binding unit of TPE-P (Fig. 1). Furthermore, polymers were characterized optical properties depending on binding units. As a result, high molecular weight TPE-P was obtained by reacting with formaldehyde solution. The high molecular weight TPE-P showed solvatochromism with new absorption at 510 nm for halogen solvents. In addition, the absorption peak intensity was changed over time in response to halogenated solvents. The solution color was appeared according to the modification position and the number of halogen groups.

Keywords : Solvatochromism; Phenolic Polymers; Tetraphenylethene; Halogenated compounds

メチレンでフェノール誘導体が結合したフェノールポリマーは、高い耐熱性や電気絶縁性を有するため広く利用されている。原料であるフェノール誘導体は、様々な構造をもち、機能に応じて選択可能である。当研究室では、テトラフェニルエテン (TPE) を基本骨格として、メチレンで結合したフェノールポリマー (TPE-P) の合成に成功している。[1] 本研究では、TPE-P のメチレン結合部位の構造変化を試みた (Fig. 1)。さらに、得られた高分子の物性をメチレン結合部位の違いにより評価した。その中で、ホルムアルデヒド溶液を利用することで、分子量の大幅な増加とハロゲン種による特殊なソルバトクロミズムがみられたため報告する。

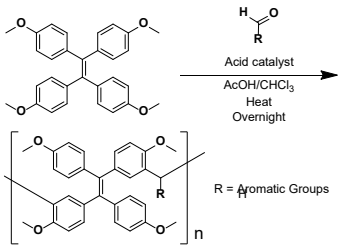


Figure 1. Synthesis scheme of phenolic polymers based on tetraphenylethene.

分子量の大きな TPE-P は、ハロゲン溶媒に対して 510 nm の新たな吸収が表れるソルバトクロミズムを示した。吸収ピーク強度の時間による変化を検討した結果、ハロゲン化合物のハロゲン基の修飾位置および個数に応じて、溶液色の濃淡や色調変化の速度が変化した (Fig. 2)。修飾位置を見分ける材料として期待される。

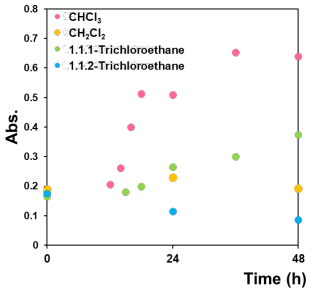


Figure 2. Absorbance value at 510 nm for TPE-P depending on halogenated solvents.

1. Kakuta, T.; Nakanishi, R.; Ogoshi, T.; Yamagishi, T. *RSC Adv.* **2020**, *10*, 12695.

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Polarization-Responsive Behavior in Nonlinear Optical Effect of Polymer-Stabilized Dye-Doped Liquid Crystals

(*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○Kohsuke Matsumoto, Koji Usui, Atsushi Shishido
Keywords: Nonlinear Optical Effect; Liquid Crystal; Diffraction

Liquid crystals (LCs) exhibit functional optical properties for hologram and light modulator based on their molecular orientation. The orientation can change by application of external stimuli such as electric field and light to the LCs. In particular, dye-doped LCs undergo their molecular reorientation by irradiation with linearly polarized light [1]. Such molecular reorientation occurs in accordance with an incident light intensity, which is recognized as a typical nonlinear optical effect. Recently, we found that the nonlinear optical response of oligothiophene dye-doped LCs could be successfully sensitized by adding low-concentration polymers [2-4]. In a series of experiments, we revealed that an elliptical diffraction beam appeared on the screen despite the irradiation of the polymer-containing LCs with a circular beam. In this study, we investigated the formation behavior of the diffraction rings in response to the polarization direction of the incident light to explore the mechanism of the deformed diffraction.

A host LC (5CB), acrylate monomer (A4CB), guest dye (TR5), and photopolymerization initiator (Irgacure 651) was mixed and injected into a 100-μm-thick glass cell treated with octadecyl trimethoxy silane to obtain homeotropic alignment of LCs. The glass cell was irradiated with ultraviolet (UV) light at a wavelength of 365 nm to perform photopolymerization. Polarized optical microscopy and polarized UV-visible absorption spectroscopy revealed that the LC and dye molecule in the cell were homeotropically aligned. We investigated the photoinduced molecular reorientation behavior of the LC by irradiation with a circular-shaped DPSS laser beam at a wavelength with 488 nm. As a result, an elliptical diffraction beam was observed by irradiation of the sample with the laser beam. Moreover, the elliptical pattern of diffraction rings reflected the polarization direction of the incident beam.

1) I. C. Khoo, J. H. Park, J. Liou, *Appl. Phys. Lett.*, **2007**, *90*, 151107.
2) Y. Aihara, M. Kinoshita, J. Wang, J. Mamiya, A. Priimagi, and A. Shishido, *Adv. Opt. Mater.*, **2013**, *1*, 787.
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4) K. Usui, E. Katayama, J. Wang, K. Hisano, N. Akamatsu, and A. Shishido, *Polym. J.*, **2017**, *49*, 209.

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Metallo-Supramolecular Polymers: Electrochromic and Supercapattery Device Application

(*National Institute for Materials Science*) ○Masayoshi Higuchi, Sanjoy Mondal, Manas Kumar Bera

Keywords: Metallo-Supramolecular Polymer; Electrochromic; Supercapattery; Redox

Metallo-supramolecular polymers (MSPs) are synthesized by the complexation of metal ions and multi-topic ligands. One- and two-dimensional structures of MSPs, the control of two metal species in MSP, and the electrochromic and supercapattery (= supercapacitor + battery) devices with MSPs are reported in this presentation.

Two-dimensional (2D) nanosheets of MSP (Figure 1a) was synthesized by the complexation of tris-phenanthroline ligand (**L1**) and Fe(II) salt at the interface of a water layer and an organic layer.[1] The polymer film showed red-to-colorless electrochromism. As to the one-dimensional (1D) linear MSP, a new stepwise synthetic method to introduce Fe(II) and Os(II) ions alternately was developed (Figure 1b).[2] The polymer showed multi-color electrochromism. The visible-to-near IR electrochromism was achieved in a zigzag structure of MSP with a redox-active ligand (**L3**) (Figure 1c).[3] The EC devices with MSPs was revealed to have energy storage functions.[4-6]

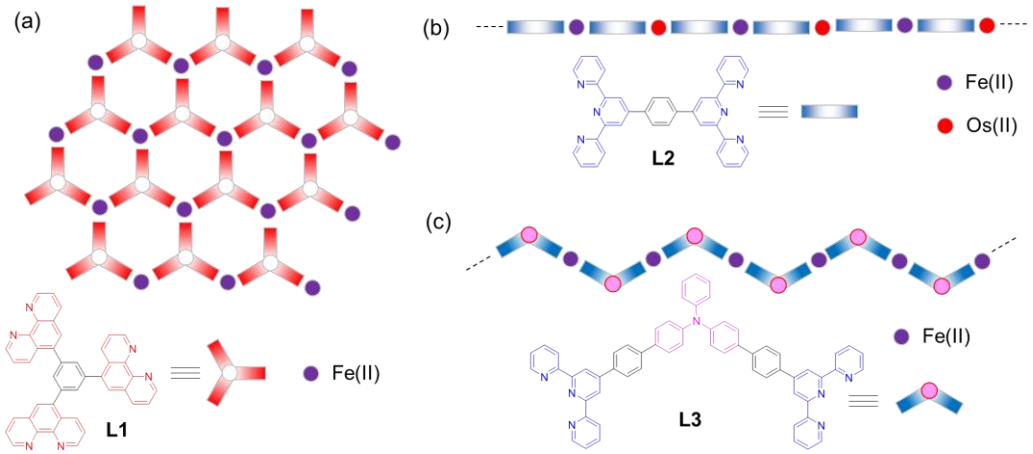


Figure 1. (a) 2D nanosheets of MSP, (b) the control of two metals in MSPs, (c) a zigzag structure of MSP.

1) S. Mondal, M. Higuchi *et al.*, *ACS Appl. Mater. Interfaces* **2020**, *12*, 31896. 2) M. K. Bera, Y. Ninomiya, M. Higuchi, *ACS Appl. Mater. Interfaces* **2020**, *12*, 14376. 3) S. Mondal, D. C. Santra, Y. Ninomiya, T. Yoshida, M. Higuchi, *ACS Appl. Mater. Interfaces* **2020**, *12*, 58277. 4) S. Mondal, T. Yoshida, S. Maji, K. Ariga, M. Higuchi, *ACS Appl. Mater. Interfaces* **2020**, *12*, 16342. 5) G. Cai, J. Chen, J. Xiong, A. L.-S. Eh, J. Wang, M. Higuchi, P. S. Lee, *ACS Energy Lett.* **2020**, *5*, 1159. 6) S. Mondal, Y. Ninomiya, M. Higuchi, *ACS Appl. Energy Mater.* **2020**, *3*, 10653.

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[A01-3pm] 19. Colloid and Interface Chemistry

Chair:Atsuhiro Fujimori, Takuya Nakashima

Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 1 (Online Meeting)

[A01-3pm-01] Prediction of surface energy and surface wettability assisted by machine learning

○Yuki Tokura[1], Yasuhiko Igarashi[2,3], Hiroaki Imai[1], Yuya Oaki[1,3] （1. Keio Univ., 2. Univ. of Tsukuba, 3. JST PRESTO）

1:00 PM - 1:20 PM

[A01-3pm-02] Control Factor of the Molecular Optical Trapping at Solid-Liquid Interface

○Nobuaki Oyamada[1], Hiro Minamimoto[2], Kei Murakoshi[2] （1. Grad. Sch. of Chem. Sci. and Eng. Hokkaido Univ., 2. Fac. of Sci. Hokkaido Univ.）

1:20 PM - 1:40 PM

[A01-3pm-03] Switchable surface properties induced by photo/thermal responsive molecular layer consisted with anthracene moieties

○Miho Aizawa[1], Haruhisa Akiyama[1], Yoko Matsuzawa[1] （1. National Institute of Advanced Industrial Science and Technology (AIST)）

1:40 PM - 2:00 PM

[A01-3pm-04] Monolayer of polyethoxylated alkyl amine functionalized gold nanoparticles

○Md. Abdullah Al Nahid[1], Ken-ichi Iimura[1] （1. Utsunomiya University）

2:00 PM - 2:20 PM

[A01-3pm-05] Fabrication of photocathode using modal coupling between plasmon and Fabry– Pé rot nanocavity

○Tomoya Oshikiri[1], Xu Shi[1], Hiroaki Misawa[1,2] （1. Hokkaido University, 2. National Chiao Tung University）

2:20 PM - 2:40 PM

[A01-3pm-06] Self-organization of organic-inorganic hybrid dendrimer with a magnetic Fe_3O_4 nanocore

○Takehiro Yachi[1], Masaki Matsubara[2,1], Atsushi Muramatsu[1], Kiyoshi Kanie[1] （1. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, 2. National Institute of Technology, Sendai College）

2:40 PM - 3:00 PM

[A01-3pm-07] Development of highly functional oriental lacquer for suppression of rash and improvement of light resistance

○Masaki MATSUBARA[1,2], Tetsuo SATO[1], Akiko TOKUTAKE[1], Atsushi MURAMATSU[2], Kiyoshi KANIE[2] （1. National Institute of Technology, Sendai College, 2. IMRAM, Tohoku University）

3:00 PM - 3:20 PM

[A01-3pm-08] Magnetically Controllable Phage Assembly with Centimeter Sizescale

○shuxu wang[1,2], Yasuhiro Ishida[2], Noriyuki Uchida[2], Takuzo Aida[1,2] （1. the Univ. of Tokyo, 2. CEMS, Riken）

3:20 PM - 3:40 PM

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機械学習を活用した表面エネルギーおよび濡れ性予測の検討

(慶大理工[1]・筑波大システム情報工[2]・JST さきがけ[3]) ○都倉 勇貴[1]・五十嵐 康彦[2,3]・今井 宏明[1]・緒明 佑哉[1,3]
Prediction of surface energy and surface wettability assisted by machine learning ([1]*Keio University*, [2]*The University of Tsukuba,* [3]*JST PRESTO*) ○Yuki Tokura,[1] Yasuhiko Igarashi,[2,3] Hiroaki Imai,[1] Yuya Oaki[1,3]

Surface energy is an essential physical factor to control the solubility, wettability, and adhesiveness of a variety of materials and coatings. However, it is challenging to calculate the surface energy because this value is attributed to the complicated intermolecular forces. Currently, a large number of these values are obtained by huge amounts of experiments and calculation based on wettability theory. On the other hand, the empirical models and the models using values obtained from time-consuming quantum calculation for predicting the surface energy were reported.[1,2)] However, it is difficult to predict the surface energy of unknown materials. Our group has focused on predicting performances of materials from a small amount of data using sparse modeling.[3)] In the present work, we studied the construction of the models predicting the surface energy of a variety of liquid using essential physicochemical parameters by sparse modeling, a method of machine learning (Figure 1). Moreover, we constructed the models for predicting the contact angle between a variety of substrates and liquids.

Keywords : surface energy; wettability; sparse modeling

物質の表面エネルギーは、材料の溶解性や薄膜の濡れ性・接着性を制御するために必要不可欠な物性値である。これは物質内部の複雑な分子間力に起因するため、簡便な計算手法は確立されていない。そのため、現状の表面エネルギー値を得る方法としては、膨大な実験と濡れ性理論を用いた計算が主流である。一方、経験則から構築されたモデルや量子計算から求めた因子を使ったモデルを用いて、表面エネルギーを予測する研究が報告されているが、未知物質の予測が困難である[1,2)]。我々のグループでは、スパースモデリングを用い、少ないデータから目的性能を予測することを試みてきた[3)]。本研究では、文献値や実験値をもとに、比較的入手しやすい物性値や計算値から、液体の表面エネルギーを予測するモデルを構築した(Figure 1)。さらに、表面濡れ性の指標の 1 つである基材に対する液体の接触角を、液体や基材の種類問わず予測可能なモデルの構築を検討した。

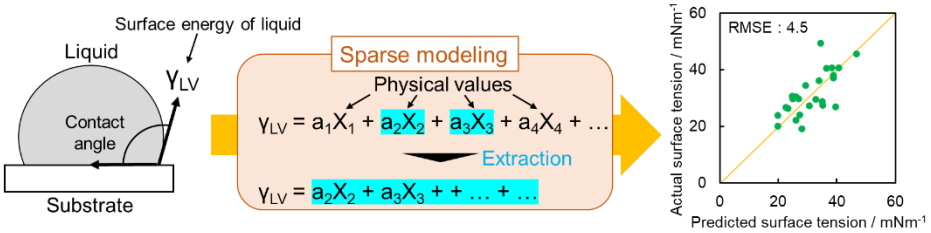


Figure 1 Overview and relationship between the predicted and actual surface energy.

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Control Factor of the Molecular Optical Trapping at Solid-Liquid Interface

([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Faculty of Science, Hokkaido University*) ○Nobuaki Oyamada,[1] Hiro Minamimoto,[2] Kei Murakoshi,[2]
Keywords: Surface-Enhanced Raman Scattering (SERS), Optical Force, Localized Surface Plasmon Resonance

Localized surface plasmon resonance excited on metal nanostructures under visible light illumination would have the possibility for the control of the molecular diffusion process at the nanoscale region due to the strong gradient force within the electric field.[1] In our previous study, we have demonstrated the single molecular manipulation through surface-enhanced Raman scattering (SERS) measurements.[2] For further understanding, in this study, we have tried to figure out the detail information on the control factors of optical manipulation at solid-liquid interface.

As the platform for the molecular manipulation, Au gold dimer nanostructures were prepared. At the present experiment, 4,4'-bipyridine (44bpy) was the target molecule and SERS measurements were performed under the room-temperature condition. Figure (a) shows 2D plot of time series SERS spectra obtained in aqueous solution containing 1 mM 44bpy. As can be found from figure, SERS scattering intensities were increased with increasing laser illumination time. The time-series intensity changes at 1608 cm^{-1} demonstrated the obvious increment behavior (Figure (b)). This phenomenon indicated that 44bpy molecules were highly aggregated at Au nano structures interface. On the other hands, when we changed the solvents, almost no increment behavior was observed as shown in Figure (b). In addition, through the verification of the trapping behavior depending on the electrolyte concentration, the control factors such as the molecular orientation, solvation property, and activity were successfully elucidated for the molecular manipulation under the ambient condition.

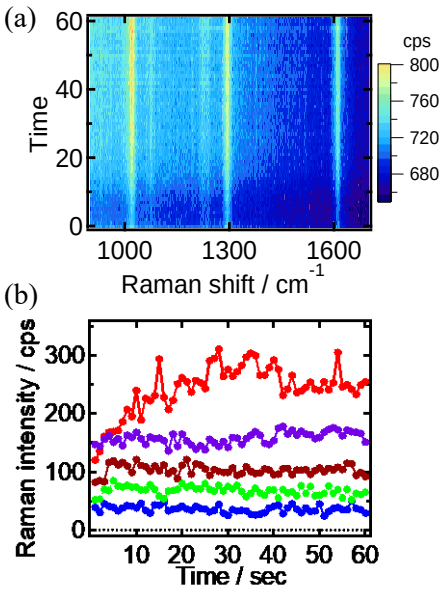


Figure. (a) 2D-plot of time series SERS spectra of 1 mM 44bpy solved in water under 785nm laser illumination with 140 $\mu W/\mu m^2$. (b) Time dependent Raman intensity changes at 1608 cm^{-1} obtained from 1 mM 44bpy in (red) H_2O, (purple) *N, N*-dimethylformamide, (brown) acetonitrile, (blue) *n*-hexane, and (green) 2-propanol, respectively.

1) H. Xu and M. Käll, *Phys. Rev. Lett.*, **2002**, 89, 246802.
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アントラセンを有する光／熱応答性分子層による表面物性変化

（産総研機能化学[1]・産総研ナノ材料[2]）○相沢 美帆[1]・秋山 陽久[2]・松澤 洋子[1]

Switchable surface properties induced by photo/thermal responsive molecular layer consisted with anthracene moieties

([1]*Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology,* [2]*Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology*) ○ Miho Aizawa,[1] Haruhisa Akiyama,[2] Yoko Matsuzawa[1]

Immobilization of functional molecules as a molecular layer on a substrate surface can provide a strong pathway to develop desired surface functions. In addition, utilizing stimulus-responsive molecules enables to realize switchable surface properties. Among these functional molecules, we focused on the stimuli-responsive chemical bond change of anthracene moieties, which is known as photodimerization and thermal/photo-cleavage reactions. This reversible chemical bond change of anthracene has a potential to use for exhibiting the desired surface properties by controlling the composition of the molecular layer. However, the reproducible generation/cleavage reaction of covalent bonds between the laminated molecular layers has not been realized. In this study, we fabricated photo/thermal responsive molecular layer consisted with anthracene moieties and investigated the surface properties by contact angle measurements and atomic force microscopy.

Keywords : Molecular Layer; Stimulus- Responsive Surface; Anthracene; Photodimerization

機能性分子を分子層として基材表面に固定化することは，目的とする表面物性を得る上で効果的な方法である。さらに，刺激応答性分子を利用することで，刺激印加によりその特性を切り替え可能な表面とすることができる。数ある刺激応答性分子の中で，今回われわれは，アントラセンが示す刺激応答性の化学結合変化に着目した。アントラセンは光照射により二量体を形成し，加熱やより短波長の光照射を行うと共有結合が開裂して単量体に戻ることが知られている[1)]。この熱／光応答性の化学結合変化を積層した分子層間で繰り返し引き起こすことができれば，分子層の構成をより緻密に制御することが容易となり，表面物性のコントロールに利用できると考えた。本研究では，アントラセンを含む分子層を作製し，加熱や光照射に応じた化学結合変化の解析を行った。刺激印加に伴う表面物性の変化について，接触角測定および原子間力顕微鏡観察により評価した。

分子層は，シリル基を有する合成したアントラセン分子を用いて石英基板上に形成した。この分子層上にアントラセン単量体を積層させて波長 405 nm の光照射を行うと，二量体が形成することを紫外可視吸収スペクトル測定により調べた。さらに加熱や波長 254 nm の光照射により単量体へと復元する様子を観測し，この結合変化が繰り返し誘起できることを明らかにした。これらの刺激印加に伴い，接触角や分子層の凹凸形状が繰り返し変化することがわかった。この結果は，アントラセンの化学結合変化が表面物性制御に利用できることを示している。

1) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.* **2000**, *29*, 43.

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Monolayer of Polyethoxylated Alkyl Amine Functionalized Gold Nanoparticles

(*Graduate School of Engineering, Utsunomiya University*) ○ Md. Abdullah Al Nahid, Ken-ichi Iimura

Keywords: Gold nanoparticles, Atomic Force Microscopy, Silicon Wafer, Monolayer Film, Polyethoxylated alkyl amine

Formation of gold nanoparticles at the air-water interface and its deposition on solid substrate remains challenging. In preliminary experiments, we have synthesized polyethoxylated alkyl amine functionalized gold nanoparticles (AMIET-AuNPs) and transferred to organic solvents. Afterwards, the organic dispersed AMIET-AuNPs were used for the formation of monolayer films and the deposition on silicon wafer using Langmuir-Blodget (LB) technique. It is found that the immobilization of AuNPs is maximum when the substrate is dipped shortly in dilute HF aqueous solution prior to film deposition. This is due to the HF last step has hydrolyzed silicon native oxide and the final surface is left hydrophobic[1] as shown in Fig. 1.However, in this work, two main strategies including the dispersion of AMIET-AuNPs in an appropriate solvent[2] sufficient to form a film on the water surface and treating the substrate to achieve maximum adhesion for the desired AuNPs have been optimized. The surface morphology of the monolayer film was investigated by atomic force microscopy. The developed process is likely to predict the effectiveness of gold nanoparticles deposition[3] onto Si substrate using LB technique.

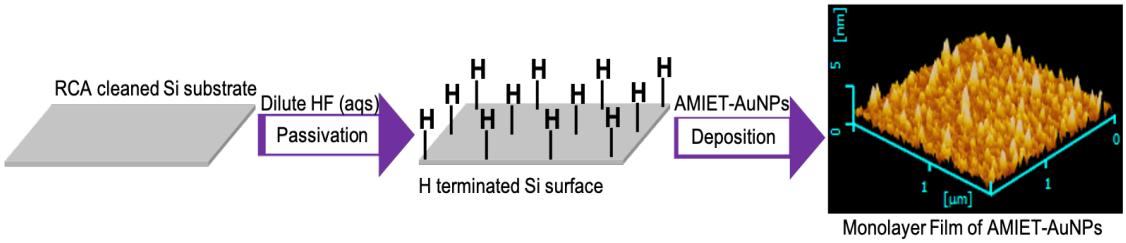


Fig. 1 Schematic presentation of the deposition of AMIET-AuNPs onto Si wafer.

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Fabrication of photocathode using modal coupling between plasmon and Fabry–Pérot nanocavity

([1]*Research Institute for Electronic Science, Hokkaido University*, [2]*Center for Emergent Functional Matter Science, National Chiao Tung University, Taiwan*) ○Oshikiri Tomoya[1]; Shi Xu[1]; Misawa Hiroaki[1,2]

Keywords: Localized surface plasmon; Modal coupling; Artificial photosynthesis; Photocathode

Plasmon-assisted photoreactions are promising candidates for a novel way to utilize the visible region of the solar spectrum because of their light-harvesting effects.[1-4] Recently, we found that a photoanode under the strong coupling condition between the localized surface plasmon resonance (LSPR) and Fabry–Pérot (FP) nanocavity dramatically enhances the absorption and photoelectrochemical oxidation efficiency.[5,6] The hot-electron is injected into the n-type semiconductor, and the residual hole participates in the reaction on the photoanode. Therefore, to directly utilize the hot-electron for the reduction, the development of an efficient photocathode is indispensable. In this study, we fabricated a novel photocathode composed of gold nanoparticles (Au-NPs), nickel oxide (NiO), and platinum film (Pt-film) (Au-NPs/NiO/Pt-film, ANP).

The absorption spectrum of the ANP structure showed broad absorption from 500 to 800 nm because the coupling between LSPR and FP nanocavity forms two-hybrid states. The photoelectrochemical measurement was performed in an aqueous solution of $KClO_4$ 0.1 mol L^{-1} using ANP as a working electrode, Ag/AgCl as a reference electrode, Pt as a reference electrode. The action spectrum of the incident photon-to-current efficiency (IPCE) based on the cathodic current with an applied potential of -0.2 V vs. Ag/AgCl showed good correspondence with the absorption spectrum, and the maximum IPCE reached 0.2% under the irradiation of 650 nm light, which is three-order larger than that of the conventional plasmonic photocathode[7] without coupling to the Fabry–Pérot nanocavity. This result suggests that the hot-electron ejected from Au-NPs of the ANP cathode efficiently reduces the water because the sacrificial electron acceptor was not added in the reaction system.

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2) T. Oshikiri, K. Ueno, H. Misawa, *Angew. Chem. Int. Ed.* **2014**, *53*, 9802.
3) T. Oshikiri, K. Ueno, H. Misawa, *Angew. Chem. Int. Ed.* **2016**, *55*, 3942.
4) T. Oshikiri, K. Ueno, H. Misawa, *Green Chem.* 2019, **21**, 4443.
5) X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki, H. Misawa, *Nat. Nanotechnol.* **2018**, *13*, 953.
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Self-organization of organic-inorganic hybrid dendrimer with a magnetic Fe_3O_4 nanocore

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Graduate School of Engineering, National Institute of Technology, Sendai College*)
○Takehiro Yachi,[1] Masaki Matsubara,[1,2] Atsushi Muramatsu,[1] Kiyoshi Kanie[1]
Keywords: Self-assembly; Magnetic nanoparticles; Organic-inorganic hybrid materials; Liquid-crystalline dendrons

Magnetic nanoparticles (NPs) show interparticle distance-dependent magnetic properties because of their strong magnetic interactions. Therefore, the control of magnetic NPs-based array structures is one of the promising techniques not only to control the magnetic properties but also to provide novel functions. However, the regulation to the structures seems difficult due to their strong magnetic attraction only to induce uncontrollable aggregation. Our previous studies have been shown that the introduction of liquid crystallinity derived from organic dendrons into the inorganic NPs by surface modification is a powerful tool for the dynamic control of NPs array[1, 2].

In this study, the dendron-modified self-assembling Fe_3O_4 magnetic NPs have been developed. **Figure 1** shows the TEM images of Fe_3O_4 NPs before and after the dendron modification. TEM observation revealed that a 2D hexagonal array with the interparticle distance of 12.9 nm was formed after dendron modification, while a random texture was formed before dendron modification. Namely, the self-assembling property was introduced into the Fe_3O_4 NPs by dendron modification. **Figure 2** shows grazing-incidence small angle X-ray scattering (GI-SAXS) patterns of the dendron-modified Fe_3O_4 NPs on a hydrophobic silicon substrate at 130 and 170 °C. The isotropic ring-like scattering pattern was observed at 130 °C and it changed to the anisotropic pattern with the vertical arrangement to the substrate at 170 °C, which was seemed to be derived from formation of a cubic liquid crystalline structure. These results demonstrated that the magnetic Fe_3O_4 NPs-based array structure could be thermally controlled by the surface modification with liquid-crystalline dendron. The self-assembling behavior of the resulting hybrid dendrimers will be discussed.

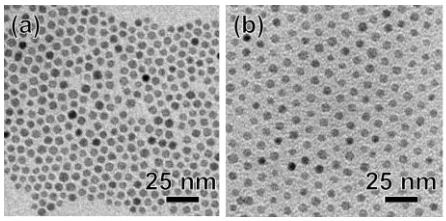


Figure 1. TEM images of Fe_3O_4 NPs (a) before and (b) after the dendron modification.

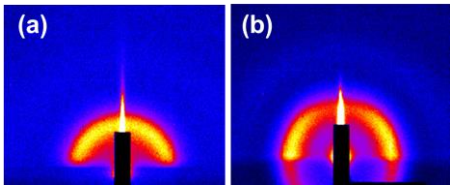


Figure 2. Temperature-dependent GI-SAXS pattern of dendron-modified Fe_3O_4 NPs at (a) 130 °C and (b) 170 °C.

1) K. Kanie, M. Matsubara, X. Zheng, F. Liu, G. Ungar, H. Nakamura, A. Muramatsu, *J. Am. Chem. Soc.*, **2012**, 134, 808. 2) M. Matsubara, W. Stevenson, J. Yabuki, X. Zeng, H. Dong, A. Muramatsu, G. Ungar, K. Kanie, *Chem*, **2017**, 2, 86.

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かぶれの低減と耐光性の向上を目的とした新規高機能性漆の開発

(仙台高専[1]・東北大多元研[2]) ○松原 正樹[1,2]・佐藤 徹雄[1]・徳竹 亜希子[1]・村松 淳司[2]・蟹江 澄志[2]

Development of highly functional oriental lacquer for suppression of rash and improvement of light resistance ([1]*National Institute of Technology, Sendai College*, [2]*IMRAM, Tohoku University*)
○Masaki Matsubara,[1,2] Tetsuo Sato,[1] Akiko Tokutake,[1] Atsushi Muramatsu,[2] Kiyoshi Kanie[2]

Oriental lacquer is one of the traditional Japanese paint, showing excellent design properties and high strength. However, it is problem that the oriental lacquer has a low light resistance and causes rashes. TiO_2 has excellent ultraviolet (UV) absorbing property, so that if we could suppress the photocatalytic activity of TiO_2 by surface coating, it will lead to the development of new UV absorbers. Here, TiO_2 nanoparticles coated with inner SiO_2 and outer alkyl layers were synthesized for improvement of light resistance. The resulting surface modified TiO_2 nanoparticles showed low photocatalytic activity. Direct modification of urushiol molecules for suppression of rash also carried out.
Keywords : Oriental Lacquer; Ultraviolet absorber; Photocatalysis; Urushiol

日本の伝統的塗料である漆は高意匠性に優れ，高い強度から接合剤にも利用されるが，耐光性が低く，かぶれの原因となる．かぶれは主成分であるウルシオールのカテコール基および側鎖の二重結合部位に皮膚のたんぱく質が結合することが原因である (Figure 1)．一方で，耐光性の低さは紫外線照射時に発生するラジカルにより光劣化することに由来する．本研究では，耐光性を向上させた高機能性漆の開発を目的として，優れた紫外線吸収能をもつ光触媒 TiO_2 ナノ粒子に着目し，光吸収特性を活用した新規紫外線吸収剤を合成した．さらに，かぶれの低減を視野に，ウルシオール分子の直接改質についても検討した．TiO_2 は紫外線吸収により励起電子およびホールが生成し，ナノ粒子表面でヒドロキシラジカルなどの活性酸素種を生成するため高分子材料の分解を招く．そのため，紫外線吸収能を維持しつつナノ粒子表面で起こる光触媒反応を抑制することができれば，新規紫外線吸収剤としての活路が広がる．そこで，Figure 2 に示すように TiO_2 ナノ粒子表面に，内部で生成した励起電子の表面への拡散を抑制する内側の SiO_2 層および周囲からの水分子や酸素分子の表面への拡散を抑制する外側のアルキル鎖層からなる二重層を形成させ，TiO_2 の光触媒活性の抑制をおこなった．講演では，ウルシオール分子の直接改質についても議論する．

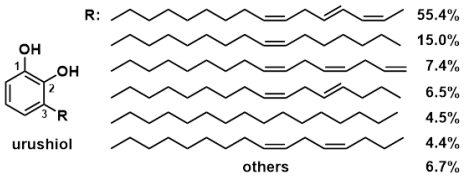


Figure 1. Molecular structure of urushiol.

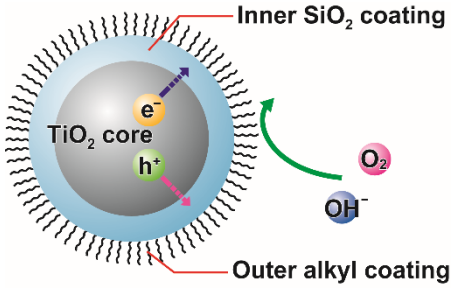


Figure 2. Schematic of surface modified TiO_2 nanoparticles.

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Magnetically Controllable Phage Assembly with Centimeter Sizescale

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Ordered colloidal assemblies have multiple potential applications on optical, optoelectronic and material fields[1]. Many methods have been developed to achieve beautiful colloidal assemblies[1-3]. However, it is still challenging to modulate the assembly to achieve the exchange of different ordered structure.

In this study, we developed a novel colloidal assembly with centimeter sizescale which could be modulated by a magnetic field and undergo an intriguing structure change from ordered structure to another ordered structure. We utilized filamentous phage M13KO7, a mutant of M13 bacteriophage with 1.2 μm in length and 6.6 μm in diameter, as a model system (**Figure 1**). When M13KO7 was mixed with dextran (400 K Da), the phage rods self-assembled into smectic assemblies due to depletion effect[4]. By applying a magnetic field (10T) to incubate the mixture, the phage rods were aligned along the magnetic field and therefore formed uniform and larger size of lamellar assemblies facing the same direction. The maximum size of assembly could reach to centimeter scale. Furthermore, after removing the magnetic field, the large lamellar assemblies gradually changed their structure into helical fibers due to intrinsic chirality of M13KO7 bacteriophage in order to achieve a new thermodynamically stable state. These fibers could even go back to the lamellar structure by applying a magnetic field again, which revealed the creation of an intriguing dynamic system that could transform between two completely different ordered structures.

This work gives a promising solution on how to modulate between different ordered colloidal assemblies by the balance of intrinsic chirality and an external field.

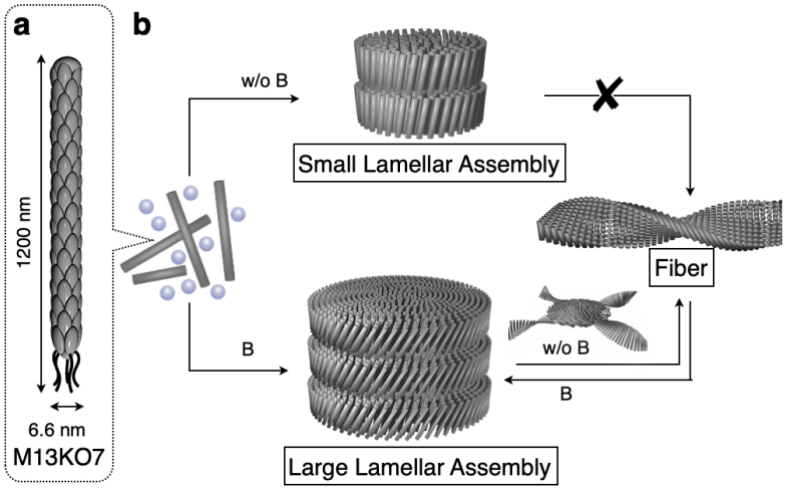


Figure 1. (a) Structure of M13KO7 bacteriophage. (b) Schematic representation for three assembled structures (small lamellar, large lamellar, and fiber) and for pathways of transformation between them.

Reference:

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[2] Mirkin C A, et al. *Nature* **382**, 607-609 (1996).
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Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B

[A02-3pm] 19. Colloid and Interface Chemistry

Chair:Tsuyoshi Asahi, Makoto Tanabe

Sun. Mar 21, 2021 1:00 PM - 3:40 PM Room 2 (Online Meeting)

[A02-3pm-01] Spontaneous formation and dynamic structural evolution of nanoparticle superstructure during the growth process of copper sulfide nanoparticles

○Masaki Saruyama[1], Fumiko Nakagawa[1], Ryo Takahata[1], Ryota Sato[1], Toshiharu Teranishi[1] （1. Institute for Chemical Research, Kyoto Univeristy）

1:00 PM - 1:20 PM

[A02-3pm-02] Control over the regioselectivity in ligand exchange reaction of a Au_{25} cluster

○Wataru Suzuki[1], Ryo Takahata[1], Toshiharu Teranishi[1] （1. Institute of Chemical Research, Kyoto University）

1:20 PM - 1:40 PM

[A02-3pm-03] Synthesis and Optical Properties of *C*1-$PtIn_2$ Plasmonic Nanoalloys

○Haruka Takekuma[1], Ryota Sato[1], Kenji Iida[2], Tokuhisa Kawawaki[3], Mitsutaka Haruta[1], Hiroki Kurata[1], Toshiharu Teranishi[1] （1. Kyoto Univ., 2. Hokkaido Univ., 3. TUS）

1:40 PM - 2:00 PM

[A02-3pm-04] Mixed oleic acid and oleylamine as the matrix for synthesizing metal nanoparticles by sputter deposition

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

2:00 PM - 2:20 PM

[A02-3pm-05] Tuning of the responsive temperature of gold nanoparticle assembly by surface modification with oligo(ethylene glycol)-based molecules

○KUN XIONG[1], Hideyuki Mitomo[2,3], Yier Shi, Yusuke Yonamine[2,3], Kuniharu Ijiro[2,3] （1. Graduate School of Life Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University, 3. Global Institution for Collaborative Research and Education, Hokkaido University）

2:20 PM - 2:40 PM

[A02-3pm-06] Copper-Metal Oxide Hybrid Subnanoparticles for Catalytic Selective Oxidations

○Hiromu Koizumi[1], Tetsuya Kambe[1,2], Makoto Tanabe[2], Kimihisa Yamamoto[1,2] （1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-ERATO）

2:40 PM - 3:00 PM

[A02-3pm-07] Dependence of Plasmon-Induced Charge Separation on the Resonance Mode of Silver Nanocubes

○Hiroyasu Nishi[1], Tetsu Tatsuma[1] （1. The University of Tokyo）

3:00 PM - 3:20 PM

[A02-3pm-08] Structural analysis of AOT/water/organic solvent mixed emulsion systems containing silver nanoparticles by SAXS/SANS

○Masafumi Harada[1], Miho Yamamoto[1] （1. Nara Women's University）

3:20 PM - 3:40 PM

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硫化銅ナノ粒子成長過程におけるナノ粒子超構造体の自発形成と配列構造の動的変化

（京大化研 [1]・京大院理 [2]）○猿山 雅亮 [1]・中川 芙美子 [2]・高畑 遼 [1]・佐藤 良太 [1]・寺西 利治 [1]

Spontaneous formation and dynamic structural evolution of nanoparticle superstructure during the growth process of copper sulfide nanoparticles ([1]*Institute for Chemical Research, Kyoto University*, [2]*Graduate School of Science, Kyoto University*) ○Masaki Saruyama,[1] Fumiko Nakagawa,[2] Ryo Takahata,[1] Ryota Sato,[1] Toshiharu Teranishi[1]

Development of methodology to control assembly manner of nanoparticles (NPs) into superlattice is desirable because the assembly manner strongly affects the concerted properties of superlattice. Here we show the spontaneous formation of 3-dimensional superlattice of djurleite $Cu_{31}S_{16}$ NPs in liquid phase and the dynamic evolution of NPs' arrangement within the superlattice. In the synthesis of $Cu_{31}S_{16}$ NPs, monodisperse spherical $Cu_{31}S_{16}$ NPs were spontaneously assembled into highly-ordered polyhedral superlattice. The regularly ordered array was transformed into random aggregate of discotic $Cu_{31}S_{16}$ NPs as the reaction proceeded. *In-situ* small-angle X-ray scattering measurements revealed the overall process of the reaction.
Keywords : Copper sulfide; Nanoparticle; Superlattice; Self-assembly; In-situ SAXS

無機ナノ粒子の集合体がもつ協奏的物理特性は、ナノ粒子の配列に大きく影響を受けるため、その配列様式や規則化度を制御する方法の開発は重要である。本発表では、化学的液相合成法による硫化銅ナノ粒子の形成過程において、自己集合による三次元超構造体の形成、および、それらのランダム凝集体への転移現象をはじめて発見したので報告する。銅ドデカンチオール錯体の熱分解による単分散な球状 $Cu_{31}S_{16}$ ナノ粒子の形成後、ファンデルワールス引力による凝集が発生し、多面体形状のナノ粒子規則超構造体が形成することを見出した（Fig. 1a）。反応を継続すると超構造体中でも $Cu_{31}S_{16}$ ナノ粒子は成長を続け、球状の $Cu_{31}S_{16}$ ナノ粒子がディスク形状に異方成長することで超構造体内の最密充填が解消され、規則配列に大きな乱れを生じた（Fig. 1b）。これらの一連の過程におけるナノ粒子および超構造体の形成と構造変化について、放射光を用いた *in-situ* での小角X線散乱測定によりリアルタイムでとらえることに成功し、より詳細な機構の推定を行ったので、合わせて報告する。

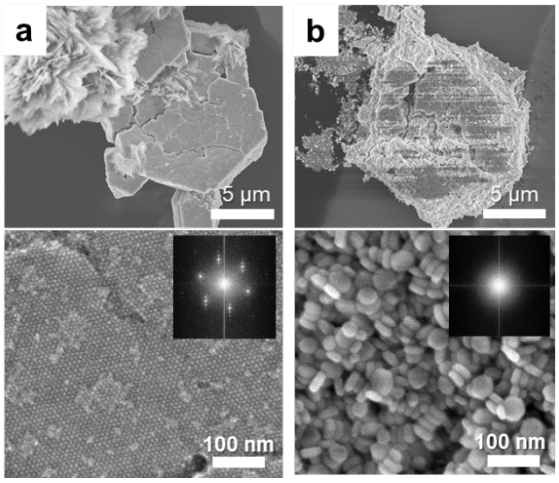


Figure 1. SEM images of (a) ordered superlattice of spherical $Cu_{31}S_{16}$ NPs and (b) disordered aggregate of discotic $Cu_{31}S_{16}$ NPs.

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Au_{25} クラスターの配位子交換における位置選択性の制御

（京大化研）○鈴木 航・高畑 遼・寺西 利治
Control over the regioselectivity in ligand exchange reaction of a Au_{25} cluster (Institute for Chemical Research, Kyoto University) ○Wataru Suzuki, Ryo Takahata, Toshiharu Teranishi

*A phenylethanethiolate-protected Au_{25} cluster anion (**[Au_{25}(PET)$_{18}$]$^-$**) possesses non-equivalent ligands at the trimeric staple motif (S_1-Au-S_2-Au-S_1), resulting in the formation of regioisomers through the ligand-exchange reaction. However, the controlling factor of this regioselectivity in the exchange reaction of gold clusters has yet to be clarified. We successfully isolated mono-exchanged Au_{25} cluster (**[Au_{25}(PET)$_{17}$(SPor)$_1$]$^-$**) by using porphyrinthiol derivatives (**PorSH**) as an incoming ligand to evaluate the exchanged position and regioselectivity in **[Au_{25}(PET)$_{17}$(SPor)$_1$]$^-$** by ^{1}H NMR spectroscopy. By tuning electronic properties and steric effects of porphyrinthiol, we have revealed that the exchanged position of a porphyrin ligand was mainly controlled by steric effects rather than electronic properties of the incoming ligand.*
Keywords : Gold Cluster; Ligand exchange reaction; Porphyrin; Regioselectivity

フェニルエタンチオラート保護 Au_{25} クラスターアニオン（**[Au_{25}(PET)$_{18}$]$^-$**）は、Staple 構造と呼ばれる-S_1-Au-S_2-Au-S_1-ユニットを有するため[1]、配位子置換反応における置換位置の違いによって位置異性体が生じ得る。しかし、この置換位置選択性の制御要因は明らかになっていない。本研究では、交換配位子としてポルフィリンチオール誘導体（**PorSH**）を用い、ポルフィリンが 1 分子導入された**[Au_{25}(PET)$_{17}$(SPor)$_1$]$^-$**を単離することで配位子交換反応における位置選択性を評価した（Fig. 1）。

まず、**[Au_{25}(PET)$_{18}$]$^-$**とポルフィリンチオール **1** の配位子交換反応によって生成した **[Au_{25}(PET)$_{17}$(1)$_1$]$^-$**における **1** の置換位置を ^{1}H NMR 測定により分析したところ、S_1 : S_2 = 0.4 : 1 の選択性で **1** が導入されることが分かった。次に、交換配位子の立体効果を検討した結果、チオール周りの立体障害がより小さい **2** では S_1 サイトへの導入割合が増加し、立体的に嵩高いチオール **3** を用いると S_2 サイトへの選択性が向上した。以上より、交換配位子の立体効果が位置選択性に大きな影響を与えることが明らかとなった。

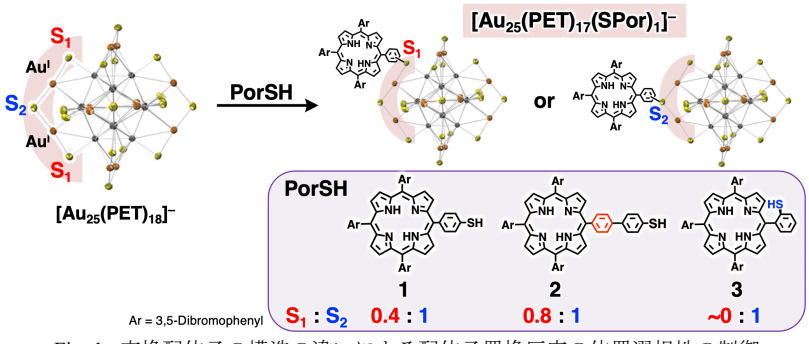


Fig. 1. 交換配位子の構造の違いによる配位子置換反応の位置選択性の制御

[1] R. W. Murray and co-workers, *J. Am. Chem. Soc.* **2008**, *130*, 3754; R. Jin and co-workers, *J. Am. Chem. Soc.* **2008**, *130*, 5883.

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Synthesis and Optical Properties of *C*1-$PtIn_2$ Plasmonic Nanoalloys

([1]*Graduate School of Science, Kyoto University*, [2]*Institute for Chemical Research, Kyoto University*, [3]*Institute for Catalysis, Hokkaido University,* [4]*Faculty of Science, Tokyo University of Science*) ○Haruka Takekuma,[1] Ryota Sato,[2] Kenji Iida,[3] Tokuhisa Kawawaki,[4] Mitsutaka Haruta,[2] Hiroki Kurata,[2] Toshiharu Teranishi[2]

Keywords: Visible Plasmonics; Localized Surface Plasmon Resonance (LSPR); Inorganic Nanoparticles; Intermetallic Compound (Ordered Alloy); Alchemy

Localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs) has attracted much interest. In the case of LSPR in the visible region, the Cu, Ag, Au, and their alloy NPs have been mostly used in various fields, such as sensing and photocatalysis. Although the spherical ordered alloy NPs without group 11 elements which exhibit LSPR in visible region have not been reported, we have recently demonstrated that the spherical PdIn NPs with *B*2 (CsCl-type) structure showed the LSPR in the visible region.[1] We found from the photo-induced electron dynamics that the balance between the free-electrons oscillation in *s-p* band and the bound-electrons oscillation in *d* band, called "screening effect" affects the LSPR absorbance and wavelength. In this work, we synthesized *C*1 (CaF_2-type) structured $PtIn_2$ alloy NPs, which are one of the promising candidates for exhibiting LSPR in the visible region.

The *C*1-$PtIn_2$ NPs were synthesized by reacting Pt seed NPs with In amide complexes in oleylamine under strong basic conditions, following the previous report.[2] TEM and XRD measurements revealed that the 50-nm-sized spherical $PtIn_2$ NPs with *C*1 structure were mainly formed (Fig. 1a and c). Their chloroform dispersion clearly shows a peak at 551 nm in UV-vis-NIR spectrum (Fig. 1b). The electronic structure and excited electron dynamics of *C*1-$PtIn_2$ cluster were also investigated by first-principles calculations, and LSPR features were directly characterized by electron energy loss spectroscopy. This result would contribute to elucidate the LSPR properties of ordered alloy NPs and is useful in the fields from basic science to applications.

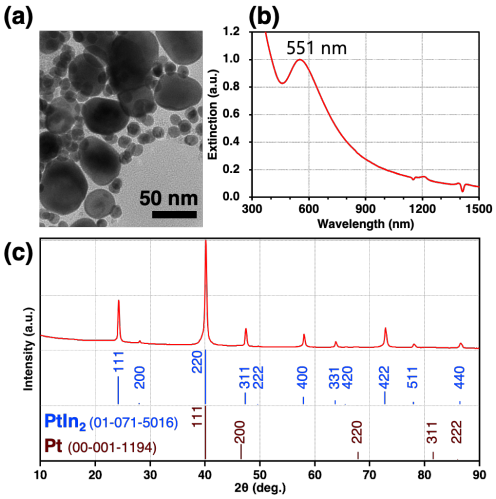


Figure 1. (a) TEM image, (b) UV-vis-NIR spectrum, and (c) XRD pattern of *C*1-$PtIn_2$ NPs

1) R. Sato, H. Takekuma, T. Teranishi, *et al.*, to be submitted. 2) M. He *et al.*, *Chem. Mater*. **2015**, *27*, 635.

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Mixed Oleic Acid and Oleylamine as the Matrix for Synthesizing Metal Nanoparticles by Sputtering Deposition

(*Faculty of Engineering, Hokkaido University*) ○Mai Thanh Nguyen, Tetsu Yonezawa
Keywords: Sputtering onto Liquid; Nanoparticles; Oleic Acid; Oleylamine; Stability

Vacuum sputter deposition onto liquid has been using as a facile synthesis approach for the preparation of nanoparticles dispersed in a liquid.[1] The sputter deposition can produce metal atoms and clusters via inert gas ion bombardment to the bulk metal target. A low volatile liquid matrix is inserted in the vacuum chamber, allows for the sputter deposition proceeding under vacuum. The liquid takes part in regulating nanoparticle formation and growth via trapping the deposited particles, binding to their surface or stabilizing them with high viscosity. So far, most research focus on ionic liquids and low volatile liquid polymer as the liquid matrix.[1]

In the present research,[2] mixtures of oleic acid and oleylamine, which are known as the ligand and solvent in the chemical synthesis of nanoparticles, were used as the liquid matrix. We varied mixing ratios of the oleic acid and oleylamine and investigated their effect in the deposited metal nanoparticles in terms of the particle size, changes of particle size after storage, and the particle agglomeration for Au. The oxidation of sputtered Cu nanoparticles in the liquid matrix with different mixing ratios was also discussed.

Measuring particle size of the deposited Au nanoparticles reveals that an equal volume ratio of oleic acid and oleylamine led to Au nanoparticles of the smallest size, the most uniformity, and colloidal stability during storage.[2] To understand the reason, we conducted viscosity measurement and FT-IR analysis for the liquid and the obtained nanoparticles. The results suggest that the mixed liquids possessed an enhanced viscosity and better protecting effect compared with the single-component liquids via oleic acid-oleylamine interaction. This also accounts for slowing down the oxidation of Cu nanoparticles when they were sputtered onto the mixed liquid of oleic acid and oleylamine at an equal volume.[2]

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オリゴエチレングリコール系分子での表面修飾による金ナノ粒子集合化の温度応答性の制御

（北大院生命 [1]・ 北大電子研 [2]・ 北大 GI-CoRE[3]）○ 熊 坤 [1]・三友秀之 [2,3]・石 軼尓 [1]・与那嶺雄介 [2,3]・居城邦治 [2,3]

Tuning of the responsive temperature of gold nanoparticle assembly by surface modification with oligo(ethylene glycol)-based molecules

([1]Graduate School of Life Science, Hokkaido University, [2]Research Institute for Electronic Science, Hokkaido University, [3]Global Institution for Collaborative Research and Education, Hokkaido University) ○[1]Kun Xiong, [2,3]Hideyuki Mitomo, [1]Yier Shi, [2,3]Yusuke Yonamine, [2,3]Kuniharu Ijiro

Self-assembly of gold nanoparticles (AuNPs) can be used to produce materials with high functionalities. We have previously reported that AuNPs modified with oligo(ethylene glycol)-based ligand molecules self-assemble at assembly temperature (T_A) and their T_A depends on the surface curvature. However, due to the difficulty of exact control of AuNP curvature, we could not tune their T_A precisely. In this study, we investigated the effect of free volume or hydrophobicity at the terminus of ligand molecules on T_A using a mixture of two different ligands. As a result, we found T_A can be controlled by surface modification with ligands having different length, which causes changes in the free volume, or different hydrophobicity.

Keywords : oligo(ethylene glycol), temperature responsiveness, free volume, hydrophobicity, gold nanoparticles

金ナノ粒子の集合化による機能性材料への応用が注目されている。我々はすでに温度応答のオリゴエチレングリコール系リガンドで金ナノ粒子を表面修飾し、加熱によるリガンドの脱水和により粒子を集合させ、その集合温度(T_A)は粒子の曲率に依存することを報告した［1］。しかし、曲率を精密に制御することは難しく、T_A の調整には制限があった。本研究では、リガンドの微小環境に着目し、末端の疎水性の違うリガンドの混合（図 1 - i)）や長さの異なるリガンドの混合による自由体積の調整（図 1 - ii)）による T_A の制御について調べた。

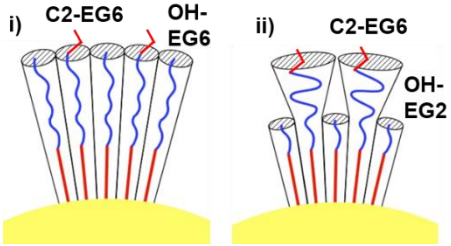


Figure 1. Tuning of surface environment by control of hydrophobicity i) or free volume ii) of ligand

温度応答のリガンド（C2-EG6）と親水性かつ非温度応答のリガンド（OH-EG6）（図 1 - i)）を様々な比率で混合し、金ナノ粒子の表面を修飾し、分光測定によって表面の疎水性の調整による T_A の変化を調べた。その結果、OH-EG6 の比率が少し増加するだけで T_A が大幅に高くなった。一方、C2- EG6 と鎖長の短い非温度応答のリガンド（OH-EG2）（図 1 - ii)）を混合したところ、OH-EG2 の比率を高くすると、T_A が徐々に上昇することがわかった。自由体積の増加が影響していると考えられる。以上より、リガンドの末端の疎水性および自由体積を調整することにより、金ナノ粒子の T_A を制御できることを明らかにした。

1) Iida, R. *et. al J. Phys. Chem. C* **2016**, 120 (29), 15846–15854.

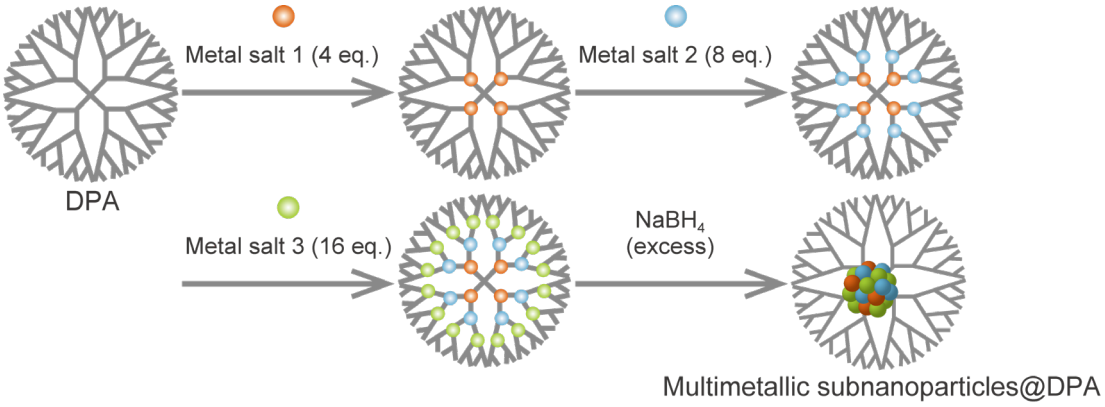
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Copper-Metal Oxide Hybrid Subnanoparticles for Catalytic Selective Oxidations

(*[1]Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, [2]JST-ERATO*)
○Hiromu Koizumi[1], Tetsuya Kambe[1, 2], Makoto Tanabe[2], Kimihisa Yamamoto[1, 2]
Keywords: Subnano; Multimetal; Oxidation; Selective; Dendrimer

Multimetallic subnano particles, consisted of several metal elements with a well-defined total atomicity in the ultrasmall particles (about 1 nm), have attracted a great attention toward the scientific application in the field of catalysis and chemical sensing. The precise controls for the atom numbers and the compositions are the most important issue for tailoring the multimetallic subnano particles. Although conventional synthetic methods have never provided the multimetallic particles with a finely-controlled atomicity and composition, the dendritic phenylazomethine (DPA) as a synthetic template of the ultrasmall particles can define the exact number of metal atoms based on an intramolecular electron density gradient of the imines allowing their stepwise complexations with metal ions. By using stepwise complexations of DPA with metal ions, we have succeeded in synthesizing the multimetallic subnanoparticles (Scheme 1)[1)]. In this study, we employed finely controlled preparation of the copper-based multimetallic particles with main group metals and their catalytic oxidative reactions.

The Cu-M (M = Ga, Bi, *etc.*) hybridized subnanoparticles succeeded to be prepared by chemical reduction of the metal chlorides-DPA complexes. The multimetallic subnanoparticles were used for the alkene oxidation with ^{t}BuOOH. These hybrid subnanoparticles exhibited a catalytic activity in the alkene oxidation greater than those of the corresponding monometallic subnanoparticles.



1) M. Takahashi, H. Koizumi, W. J. Chun, M. Kori, T. Imaoka, K. Yamamoto, *Sci. Adv.* **2017**, *3*, e1700101.

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銀ナノキューブを用いたプラズモン誘起電荷分離の共鳴モード依存性

（東大生研）○西 弘泰・立間 徹
Dependence of Plasmon-Induced Charge Separation on the Resonance Mode of Silver Nanocubes (*Institute of Industrial Science, The University of Tokyo*) ○Hiroyasu Nishi, Tetsu Tatsuma

Our group found plasmon-induced charge separation (PICS) at the interface between a plasmonic nanoparticle and a semiconductor such as TiO_2 and has studied its mechanisms. Because PICS involves injection of hot electrons excited via LSPR into the semiconductor conduction band over the Schottky barrier, its internal quantum efficiency (IQE) often increases with increasing photon energy. In this study, we found that an IQE spectrum of Ag nanocube-modified electrode shows a peak at the wavelength where absorption shows a dip.
Keywords : Plasmon resonance; Plasmon-induced charge separation; Silver nanocubes; Photoelectrochemistry; Higher order plasmon mode

当研究室では、局在表面プラズモン共鳴（LSPR）を示す金属ナノ粒子と酸化チタンなどの半導体の界面で起こるプラズモン誘起電荷分離（PICS）現象を見出し、その機構に関する研究を行っている[1,2]。PICS は LSPR によって励起された熱電子が金属-半導体界面のショットキー障壁を越えて半導体の伝導帯に注入されることで起こるため、波長が短くなり光子のエネルギーが増すにつれ内部量子収率（IQE）は単調に増加し、それゆえ外部量子収率（EQE）スペクトルはナノ粒子の吸収スペクトルに近い形状を示すことが多い（図 1a）[3]。本研究では、2 つ以上の異なる LSPR モードを示す Ag ナノキューブを酸化チタンに担持したところ、IQE スペクトルがピークを示し、しかもその波長では LSPR による吸収は谷を示すことが明らかになった（図 1b）。この特異な結果を、吸収強度の空間分布、正孔放出のエネルギー障壁、各モード間の相互作用（ファノ共鳴）などの観点から考察する。

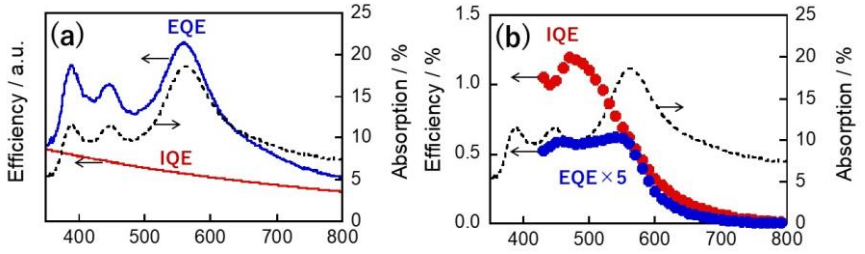


Figure 1. (a) Ag ナノキューブ担持酸化チタン電極の吸収スペクトルから推定される EQE および IQE スペクトルと(b)実際に得られた EQE および IQE スペクトル

1) Y. Tian, T. Tatsuma, *J. Am. Chem. Soc.* **2005**, *127*, 7632. 2) T. Tatsuma, H. Nishi, T. Ishida, *Chem. Sci.* **2017**, *8*, 3325. [3] H. Nishi, T. Tatsuma, *J. Phys. Chem. C* **2018**, *122*, 2330.

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銀ナノ粒子を含有した AOT/水/有機溶媒混合エマルション系の SAXS/SANS による構造解析

（奈良女大生活環境）○原田雅史・山本実穂
Structure analysis of AOT/water/organic solvent mixed emulsion systems containing Ag nanoparticles by SAXS/SANS (*Faculty of Human Life and Environment, Nara Women's University*) ○Masafumi Harada, Miho Yamamoto

Structural change of microemulsions consisting of AOT, water, and organic solvent (such as benzene, octane, and decane) including Ag nanoparticles by photoreduction of $AgClO_4$ was monitored by means of a combination of small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) using the contrast variation (CV) method. From the SANS experiments, the size of water droplets containing Ag nanoparticles as well as the thickness of AOT shell was calculated based on the core-shell model, while the size of Ag nanoparticles and their aggregates was calculated from the SAXS analysis based on the polydisperse sphere model with a Schultz-Zimm distribution.
Keywords : Silver Nanoparticles; Water Droplet; SAXS; SANS; Contrast Variation Method

エマルションは金属ナノ粒子合成の反応場として利用することができる。我々はこれまで、$AgClO_4$ を添加した陰イオン界面活性剤 AOT/水/n-アルカン混合エマルション系中の逆ミセルを反応場とした、紫外線照射による Ag ナノ粒子の合成を試み、小角Ｘ線散乱法(SAXS)と透過型電子顕微鏡(TEM)観察を用いて構造解析を行ってきた[1]。本研究では、SAXS と小角中性子散乱法(SANS)の相補的活用により、ナノ粒子形成前後での AOT/水/有機溶媒混合エマルションの構造変化、ならびに *w* (=[water]/[AOT])、Ag イオン濃度、有機溶媒種が Ag ナノ粒子のサイズおよび逆ミセル構造へ及ぼす影響について検討した。

w 値の異なる AOT/水/ベンゼン混合エマルション系中で Ag ナノ粒子を形成させた試料の SANS と SAXS スペクトルを Fig. 1 に示す。SANS では Ag ナノ粒子の形成前後でスペクトル変化は見られないことから、安定な水滴コア内でナノ粒子が形成・成長することが分かった。CV-SANS から Ag ナノ粒子を含む水滴コアのサイズおよび AOT シェルの厚み等を算出し、SAXS から Ag ナノ粒子および凝集体のサイズを算出することができた。ナノ粒子の形成前後において逆ミセルのサイズはほぼ変化せず(水滴コアの平均直径 3～4 nm, AOT シェルの厚み 0.4～1 nm 程度)、得られた Ag ナノ粒子の平均直径は水滴コアサイズ程度であった。また SAXS/SANS により、有機溶媒または水のコントラスト変調によらず同じ構造の逆ミセルおよび銀ナノ粒子が形成されることも確認できた。

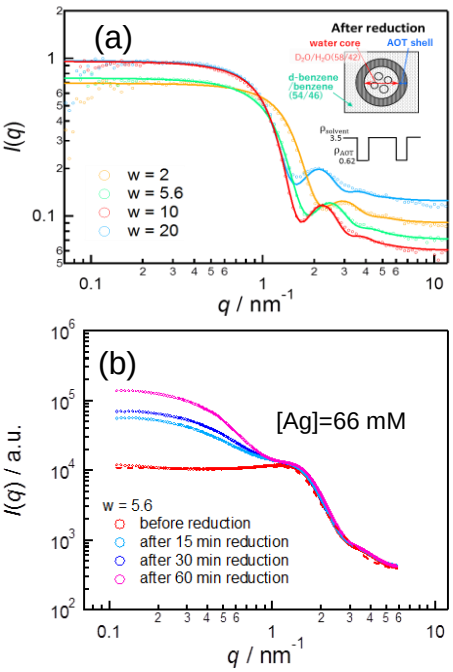


Fig. 1 (a) CV-SANS and (b) SAXS profiles of the AOT/water/benzene microemulsions with different *w* values including Ag nanoparticles.

[1] M. Harada, *Cryst. Growth Des.* **2016**, *16*, 2860-2873.

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

[A22-3pm] 20. Materials Chemistry -Basic and Application-

Chair:Tsuyohiko Fujigaya, Shinya Maenosono

Sun. Mar 21, 2021 1:00 PM - 3:20 PM Room 22 (Online Meeting)

[A22-3pm-01] Thermoelectric Properties of Paracostibite Fabricated using Chemically Synthesized Co– Sb– S Nanoparticles as Building Blocks

○Mari Takahashi[1], Shujie Fei[1], Masanobu Miyata[1], Pratibha Dwivedi[1], Wei Zhou[2], Michihiro Ohta[2], Shinya Maenosono[1] （1. Japan Advanced Institute of Science and Technology, 2. National Institute of Advanced Industrial Science and Technology ）

1:00 PM - 1:20 PM

[A22-3pm-02] Carbonization of polyacrylonitrile chains in coordination nanospaces

○XIYUAN ZHANG[1], Ryoto HONGU[2], Takashi KITAO[1,3], Takashi UEMURA[1,3] （1. Graduate School of Frontier Sciences, the University of Tokyo, 2. Graduate School of Engineering, Kyoto Univiveristy, 3. Graduate School of Engineering, the University of Tokyo）

1:20 PM - 1:40 PM

[A22-3pm-03] Metal-nitrogen co-doped carbon materials with different metal speciation as electrocatalysts for carbon dioxide reduction

○Kazuyuki Iwase[1], Kazuhide Kamiya[2], Juan Herranz[3], Kathrin Ebner[3], Justus Diercks[3], Takashi Harada[2], Itaru Honma[1], Shuji Nakanishi[2] （1. Tohoku Univ., 2. Osaka Univ., 3. Paul Scherrer Institut）

1:40 PM - 2:00 PM

[A22-3pm-04] Near Infrared Photoluminescence Properties of Diarylethene-functionalized Single-walled Carbon Nanotubes

○Tomohiro Shiraki[1,2], Yasuto Nakagawa[1], Takuya Nakashima[3], Tsuyoshi Kawai[3], Tsuyohiko Fujigaya[1,2,4] （1. Kyushu Univ., 2. I2CNER, Kyushu Univ., 3. NAIST, 4. CMS, Kyushu Univ.）

2:00 PM - 2:20 PM

[A22-3pm-05] Non-linear optical properties of magnetic fluoroscent Ytterbium complexes

○KUNAL KUMAR[1], Olaf Stefanczyk[1], Koji Nakabayashi[1], Kosuke Nakagawa[1], Yurie Oki[1], Shin-ichi Ohkoshi[1] （1. University of Tokyo）

2:20 PM - 2:40 PM

[A22-3pm-06] Direct Determination of Optical Isomers for Carbon Nanotubes

○Issei Tomotsuka[1], Nobuya Mamizu[2], Hiromitsu Furukawa[2], Koji Harano[1], Eiichi Nakamura[1] （1. The University of Tokyo, 2. System in Frontier Inc.）

2:40 PM - 3:00 PM

[A22-3pm-07] Solvatochromism of near infrared photoluminescence from molecularly functionalized carbon nanotubes

○Yoshiaki Niidome[1], Tsuyohiko Fujigaya[1,2,3], Tomohiro Shiraki[1,2] （1. Department of Applied Chemistry, Kyushu Univ., 2. WPI-I2CNER, 3. CMS）

3:00 PM - 3:20 PM

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Thermoelectric Properties of Paracostibite Fabricated using Chemically Synthesized Co–Sb–S Nanoparticles as Building Blocks

([1]*School of Materials Science, JAIST*, [2] *Global Zero Emission Research Center, AIST*)
○Mari Takahashi,[1] Shujie Fei,[1] Masanobu Miyata,[1] Pratibha Dwivedi,[1] Wei Zhou,[2] Michihiro Ohta[2] and Shinya Maenosono[1]
Keywords: *Paracostibite*, *Thermoelectric Material, Nanoparticles*

Paracostibite (CoSbS) is regarded as a promising candidate for n-type thermoelectric materials owing to its characteristic band structure. Many researchers have investigated its thermoelectric (TE) properties, however, electrical properties of CoSbS were different and controvertial.[1] For example, different groups reported the existence of either an acceptor level[2] or a donner level.[3] The performance of TE properties is evaluated by dimensionless figure of merit: $ZT = \sigma S^2 T/\kappa$ (σ: electrical conductivity; S: Seebeck coefficient; T: Absolute temperature; κ: thermal conductivity). Doping or substitution for CoSbS was often conducted to increase ZT value.

In this study, we focused on the electrical properties of CoSbS. It is known that different fabrication processes of CoSbS might lead to formation of different defect levels in CoSbS, which would strongly influence the electrical transport properties. In this study we chemically synthesized Co-Sb-S nanoparticles (NPs) and the NPs were pelletized at high temperature to make a CoSbS pellet. The TE properties of the pellet showed that the highest σ and the lowest κ among the existing reports. The detailed analyses of electrical resistivity (Fig. 1a) revealed that the existence of donner levels. It was found that at low temperature (< 170 K) carrier transportation was governed by Mott-variable range hopping (E_a = 30 meV), while band conduction (E_a = 120 meV) became dominant at high temperature (300-661 K) as shown in Fig. 1b. As a result, the ZT value reached 0.05 at 661 K, which was within the reported value range.[1]

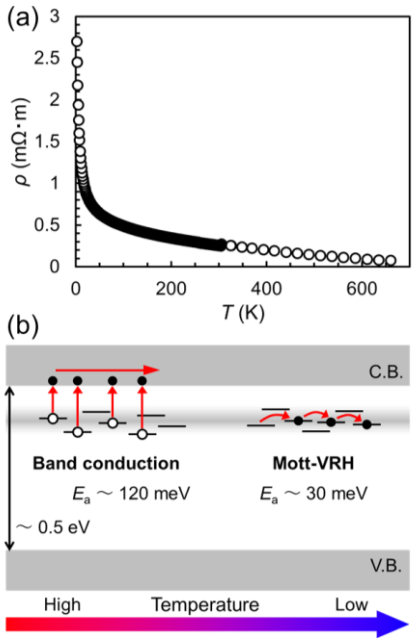


Fig. 1. (a) electrical resistivity of the CoSbS pellet. (b) Schematic illustration of the band structure and electrical transportation process.

1) S. Fei *et al.*, *AIP Adv.* **2020**, *10*, 075021; 2) Q. Du *et al.*, *Phys. Rev. Lett*. **2019**, *123*, 076602; 3) Y. You *et al.*, *RSC Adv*. **2017**, *7*, 34466.

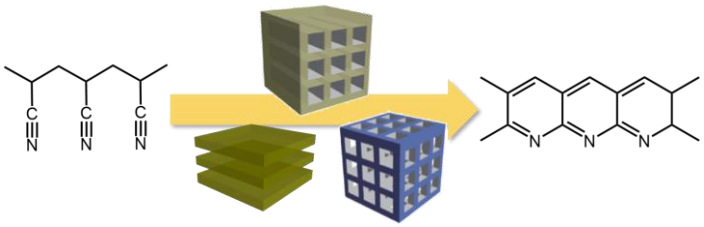
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Carbonization of Polyacrylonitrile Chains in Metal-organic Frameworks

([1]*Graduate School of Frontier Science, The University of Tokyo*, [2]*Graduate School of Engineering, Kyoto University,* [3]*Graduate School of Engineering, The University of Tokyo*)
○Xiyuan Zhang,[1] Ryoto Hongu,[2] Takashi Kitao,[1,3] Takashi Uemura,[1,3]
Keywords: Polyacrylonitrile; Metal-organic Framework; Radical Polymerization; Carbon Materials

Carbon materials have been extensively used in various applications, including catalysts, energy storage, and carbon fibers, because of their outstanding physical properties. Polyacrylonitrile (PAN) is one of the most widely applied precursors to fabricate carbon materials. Although great effort has been paid for decades to control carbonization reaction of PAN, the detailed reaction mechanism still remained unclear due to its random and complex entanglement of the polymer chains in the bulk state.[1] Furthermore, the carbonization reaction is an exothermic process with the rapid evolution of heat, which provokes unfavorable side reactions and scission of the polymer chains; thus the process of carbonization reaction is difficult to control in the bulk state.

Confinement of polymer chains in porous materials is a feasible method to prevent the entanglement and conformational disorder occurring in bulk polymers, allowing regulation of their assembly structures. Carbonization reaction of PAN chains within well-defined nanospaces should provide insight into effect of aggregation structures of PAN on their carbonization reactions. For this purpose, we employed metal−organic frameworks (MOFs) prepared by the self-assembly of metal ions and bridging organic ligands, which offer a wide range of applications, such as gas separation, storage, and catalysts. The regulated and tunable nanopores of MOFs can allow us to achieve precise control of polymer assemblies accommodated in the nanochannels.[2] Here, we encapsulated PAN in MOFs by in-situ polymerization, and subsequently thermal transformation to investigate the confinement effect on the resulting structure of carbon materials.[3]



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異なる金属中心の形態を有する金属窒素共ドープ炭素材料の電気化学的二酸化炭素還元能

（東北大多元研 [1]・阪大太陽エネ研 [2]・ポールシェラー研究所 [3]）○岩瀬 和至 [1]・神谷 和秀 [2]・Juan Herranz[3]・Kathrin Ebner[3]・Justus Diercks[3]・原田 隆史 [2]・本間 格 [1]・中西 周次 [2]

Metal-nitrogen co-doped carbon materials with different metal speciation as electrocatalysts for carbon dioxide reduction ([1]*IMRAM, Tohoku University,* [2]*RCSEC, Osaka University*, [3]*Paul Scherrer Institut*) ○Kazuyuki Iwase[1]・Kazuhide Kamiya[2]・Juan Herranz[3]・Kathrin Ebner[3]・Justus Diercks[3]・Takashi Harada[2]・Itaru Honma[1]・Shuji Nakanishi[2]

Electrochemical carbon dioxide reduction reaction (CO2RR) has attracted keen attention as a conversion reaction of CO_2 to value-added chemicals. In the present study, three kinds of cobalt and nitrogen co-doped carbon materials with different heat treatment conditions are synthesized. The detailed characterizations revealed that Co speciation (i.e., Co agglomerates or singly isolated Co species) can be controlled using different heat treatment temperatures. The results of the evaluation for CO2RR activity revealed that singly isolated Co atoms are active for CO2RR to CO generation and that partial current density of CO increases when single Co species exist in more graphitized carbon layers on agglomerate Co species.
Keywords : Carbon dioxide reduction reaction; Electrocatalysis; Cobalt; Carbon based materials; Heterogeneous catalysts

電気化学的二酸化炭素還元反応(CO2RR)は、二酸化炭素を比較的温和な条件で再資源化しうる手法として期待されている。本研究では、合成温度を変化させコバルト及び窒素を共ドープした炭素材料を CO2RR 触媒として合成した。構造解析の結果、熱処理条件の適切な選択により、単原子状もしくはナノ粒子として凝集した Co の割合が制御できることが示された。第一原理計算及び CO2RR 活性評価の結果から、単原子状の Co が CO2RR による CO 生成を進行させること、及び Co 凝集体上に形成されたより炭素化度の高い炭素層に存在する単原子状 Co が高い CO 生成活性を示すことが示唆された [1]。当日は活性中心の構造解析の詳細や電気化学測定の結果についても議論する。

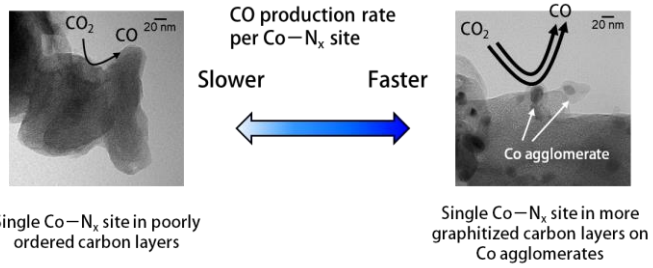


図　本研究の概略図

(1) K. Iwase *et al*., *in revision*.

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Near Infrared Photoluminescence Properties of Diarylethene-functionalized Single-walled Carbon Nanotubes

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Keywords: Carbon Nanotube; Photoluminescence; Near Infrared Light; Chemical Modification; Diarylethene

Local chemical functionalization of single-walled carbon nanotubes (SWCNTs) allows sp^3 carbon defect doping to the crystalline sp^2 carbon networks to enhance their near-infrared (NIR) photoluminescence (PL) properties.[1-3] The locally functionalized SWCNTs (lf-SWCNTs) show new red-shifted PL (E_{11}*) with enhanced quantum yields compared to the original PL (E_{11}). The E_{11}* PL wavelength of lf-SWCNTs have been found to be modulated by using functions of the functionalized molecules on their doped sites. For example, selective molecular binding based on molecular recognition[4] and dynamic covalent bonding[5] on the lf-SWCNTs have induced selective wavelength shifts of E_{11}* PL.

In this study, we synthesize lf-SWCNTs functionalized with diarylethene derivatives (DAE)[6] that show photochromism with high stability and sensitivity. For the synthesis of DAE-functionalized lf-SWCNTs (lf-SWCNTs-DAE), a diazonium salt having a DAE moiety was synthesized and reacted with the solubilized SWCNTs in D_2O. PL spectrum of the lf-SWCNTs-DAE shows peaks at 980 and 1142 nm (Figure 1). The former one is assigned to E_{11} PL and the latter one is assignable to E_{11}* PL of the lf-SWCNTs-DAE. UV light irradiation to the lf-SWCNTs-DAE solution induced red-shifts of E_{11}* PL peak. Moreover, visible light irradiation to the resultant solution induced the E_{11}* PL peak shifts to the initial wavelength position. The reversible wavelength switching was repeatedly observed over 5 cycles. In UV/vis/NIR absorption measurements, photo-isomerization of DAE on the lf-SWCNTs-DAE was confirmed by each light irradiation process. Thus, a photo-induced wavelength switching system for NIR PL has been created by the DAE functionalization.

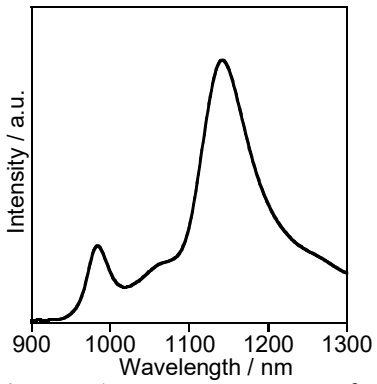


Figure 1. PL spectrum of lf-SWCNTs-DAE**.** λex = 570 nm.

1) T. Shiraki, *Chem. Lett.*, in press, DOI:10.1246/cl.200776. 2) T. Shiraki et al., *Acc. Chem. Res.* **2020**, *53*, 1846. 3) Y. Wang *et al*., *Nat. Rev. Chem*. **2019**, *3*, 375. 4) T. Shiraki *et al*., *Chem. Eur. J.* **2018**, *24*, 9393. 5) T. Shiraki *et al*., *Chem. Eur. J*. **2018**, *24*, 19162. 6) T. Kawai *et al., Eur. J. Org. Chem*. **2017**, *17*, 2451.

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Non-linear optical properties of magnetic fluorescent ytterbium(III) complexes

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Keywords: Lanthanides; Thermometer; Near-infrared; Second Harmonic Generation; Ferroelectricity

Preparing materials with many functionalities have been investigated by the material scientist all over the worlds. We have reported several compounds exhibiting spin-crossover, non-linear optical properties within cyanido-bridged molecular assemblies.[1,2] Learning from these works, we have prepared two complexes $Yb^{III}(NCS)_3(TPPO)_3$ (**Yb-S**) and $Yb^{III}(NCSe)_3(TPPO)_3$ (**Yb-Se**) (Triphenylphosphine oxide = TPPO). They crystallize into *R*3 non-centrosymmetric space group due to the presence of bulkier TPPO organic ligand (**Figure 1a**). Each compound has two right-handed and left-handed phases giving rise to four different crystal structures.

We measured second harmonic generation (SHG) properties for the powdered sample. Both compounds have SHG signal as high as potassium diphosphate (KDP) originating due to the non-centrosymmetric nature of compounds (**Figure 1b**). Apart from non-linear optical behavior these complexes also exhibit a decrease of near-infrared emission intensity upon cooling in the temperature range of 350-85 K acting like a thermometer (**Figure 1c**). In the lower temperature range emission peak around 978 nm splits into five components revealing the constituents of the electronic ground state of Yb(III) ions. Upon substitution by **Se**, the absorption properties of the compound change significantly in the UV-region. Measurement of ac magnetic properties revealed weaker single-molecule magnet behavior originating from the anisotropic Yb(III) ion.

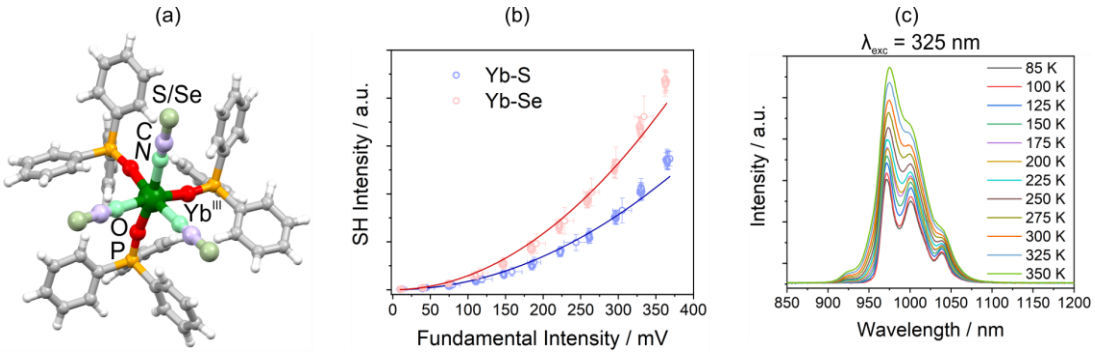


Figure 1. Representative crystal structure of **Yb-S** and **Yb-Se** (a), second-harmonic generation signal (b) and temperature dependent-near infrared properties of **Yb-S** (c).

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nature Photonics*, **2014**, *8*, 65-71. 2) S. Ohkoshi, K. Nakagawa, K. Imoto, H. Tokoro, Y. Shibata, K. Okamoto, Y. Miyamoto, M. Komine, M. Yoshikiyo, and A. Namai, *Nature Chemistry*, **2020**, *12*, 338-344.

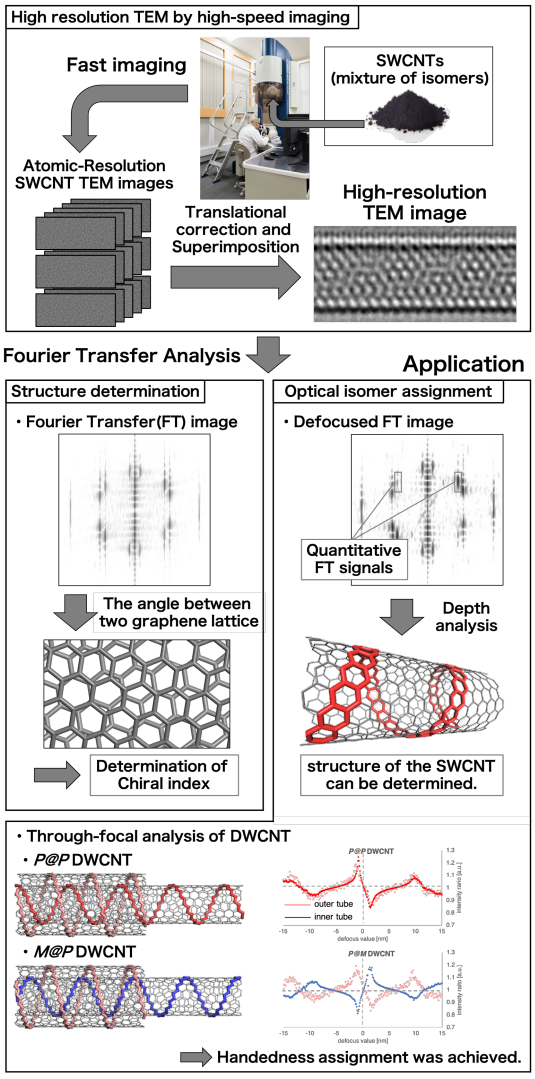
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Direct Determination of Optical Isomers for Carbon Nanotubes

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Keywords: Transmission Electron Microscopy; Carbon Nanotube; Through-focal imaging; Absolute Configuration; Three-dimensional Structure Analysis

Almost all the nanomaterials and molecules have three-dimensional (3D) information, and the structure is closely related to the physical properties. Although atomic resolution microscopy is known as the only method to directly determine the structure, there is no technique with atomic depth resolution. Though the most general method to obtain out of the plane information is rotation, this rotation method has many technical constraints, and the application for the single nanomaterials has not come to the realization yet. There is a need for a new tomography method without any mechanical specimen movement to overcome the problem. In principle, since the information out of the plane is included in the phase contrast of TEM, it is possible to extract the three-dimensional structure. However, since this method involves considerable difficulty, only a few simplified and modeled examples[1,2] were reported.



Herein, we demonstrate a direct determination method for the optical isomer of individual carbon nanotubes (CNTs) without any specimen movement by utilizing fast TEM video imaging and image processing. Improvement of signal intensity originating in graphene lattices[3] by computational motion correction between each frame in the TEM video allows us to determine not only structure (i.e. chiral index) but also relative orientation of top and bottom graphene layers of CNTs and thus optical isomerism.

1) S. Morishita *et al.*, *Appl. Phys. Lett.* **113**, 233101 (2018). 2) K. Hirahara *et al.*, *Nano Lett.* **6**, 1778–1783 (2006). 3) A. Hashimoto *et al., Nature* **430**, 870–873 (2004).

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Solvatochromism of near infrared photoluminescence from molecularly functionalized carbon nanotubes

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Keywords: Carbon Nanotube; Near Infrared Photoluminescence; Chemical Functionalization; Solvatochromism; Exciton

Solvatochromism is a molecularly optical phenomenon, in which absorption or photoluminescence (PL) wavelengths are changed by surrounding solvents. This phenomenon is significant in single-walled carbon nanotubes (SWCNTs).[1] The one-dimensional nanostructures afford quantum confinement and weak dielectric screening to enhance Coulombic interactions, which result in the stable exciton formation and their sensitive solvatochromism.[2] Local chemical functionalization of SWCNTs has been developed for doping defects to the crystalline sp^2 carbon lattices for enhancement of their PL functions.[3] The doped sites have narrower bandgaps and trap mobile excitons to be localized states. The locally functionalized SWCNTs (lf-SWCNTs), therefore, emit red-shifted and brighter E_{11}* PL (~1150 nm) compared to original E_{11} PL (~ 980 nm) observed for non-functionalized SWCNTs.

Here, we investigated the solvatochromism of PL from lf-SWCNTs in terms of structural dependency of the doped site. We used *Mono*-aryl doped (lf-SWCNTs-*m*A, Fig. 1a) and *bis*-aryl doped lf-SWCNTs (lf-SWCNTs-*b*A, Fig. 1b) that were solubilized by sodium dodecylbenzenesulfonate micelles in D_2O. Each of water-immiscible solvents (*e.g. o*-dichlorobenzene) was added to the lf-SWCNTs solutions to make organic solvent atmospheres around the solubilized lf-SWCNTs. E_{11}* PL and E_{11} PL from lf-SWCNTs-*m*A red-shifted according to changes of the orientation polarity parameter of added organic solvents. Importantly, shift values of E_{11}* PL were always greater than those of E_{11} PL by 6 meV.[4] In the case of the lf-SWCNTs-*b*A emitting largely red-shifted $E_{11}{}^2$* PL (~1250 nm),[5] $E_{11}{}^2$* PL shift values were decreased compared to those of E_{11}* PL. The observed difference in the solvatochromic behaviors would be due to the variation of exciton localization degree at the doped sites, which change the strength of interactions with solvents. This result indicates excitonic property modulation for lf-SWCNTs based on molecular structure designs of the doped sites.

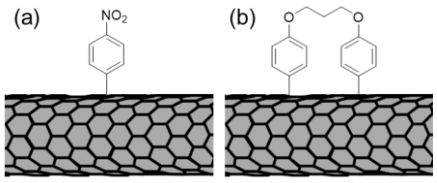


Fig. 1. Structural images of lf-SWCNTs-*m*A (a) and lf-SWCNTs-*b*A (b).

1) Y. Ohno *et al*., *Phys. Status. Solidi. B* **2007**, *244*, 4002. 2) Y. Miyauchi, *J. Mater. Chem. C* **2013**, *1*, 6499. 3) a) R. B. Weisman et al., *Science* **2010**, *330*, 1656. b) Y. Wang *et al*., *Nat. Rev. Chem.* **2019**, *3*, 375. c) T. Shiraki *et al*., *Acc. Res. Chem. Res.* **2020**, *53*, 1846. d) T. Shiraki, *Chem. Lett. in press*. 4) T. Shiraki *et al*., *Chem. Commun.* **2019**, *55*, 3662. 5) T. Shiraki *et al*., *Chem. Lett.* **2019**, *48*, 791.

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