Fri. Mar 19, 2021

Area 1

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

[P01-1am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

9:40 AM - 11:10 AM Area 1 (Online Meeting)

[P01-1am-01] Theoretical Study of Thermal Neutron Scattering by Light and Heavy Water with Molecular Dynamics Simulation

○Akira Ichihara[1], Yutaka Abe[2] (1. Japan Atomic Energy Agency, 2. Kyoto University)

[P01-1am-02] Prediction of Gas Phase Acidity for *in Silico* Design of Super Acids with High Precision Quantum Chemical Calculations and Machine Learning

○Rima Suzuki[1], Nahoko Kuroki[1], Hirotoshi Mori[1,2] (1. Chuo University, 2. Institute for Molecular Science)

[P01-1am-03] Theoretical Design of Blended Amine Solution for CO_2 Chemical Absorption Method

○Iori Shimizu[1], Sumika Nagato[1], Mikito Fujinami[1], Hiromi Nakai[1,2,3] (1. School of Advanced Science and Engineering, Waseda University, 2. Waseda Research Institute for Science and Engineering, Waseda University, 3. Elements Strategy Initiative for Catalysts and Batteries, Kyoto University)

[P01-1am-04] Effect of solvent permittivity and heteroatoms properties on the formation pathways of Keggin-type polyoxometalates ($[XW_{12}O_{40}]^{n-}$)

○Masahiko Akune[1], Kazuo Eda[1], Toshiyuki Osakai[1], Takahito Nakajima[2] (1. Kobe Univercity, 2. Institute of Physical and Chemical)

[P01-1am-05] Development and application of FMO-based analysis of the electrostatic complementarity of protein-protein interaction toward rational antibody design

○Hiroki Ozono[1], Takeshi Ishikawa[1] (1. kagoshima university)

[P01-1am-06] Computational Study of Azobenzene-based dye Covalently Attached to the Silane Coupling Agentes

○tatsuya takeshita[1] (1. Fukui Univ. of Tech.)

[P01-1am-07] Elucidation of Conduction Behaviors for Heteroatom-Containing π-Conjugated Single-Molecular Junctions by Using the Graph Theory

○Kazuki Okazawa[1], Yuta Tsuji[1], Kazunari Yoshizawa[1] (1. IMCE, Kyushu Univ.)

[P01-1am-08] Theoretical study of the methane activation on the surface of binary alloys with the combination of DFT calculation and chemoinformatics

○Masataka Yoshida[1], Masashi Saito[1], Yuta Tsuji[1], Takashi Kamachi[2], Kazunari Yoshizawa[1] (1. Kyushu University, 2. Fukuoka Institute of Technology)

[P01-1am-09] Elucidation of factors for the enhanced oxygen reduction activity of carbon-free connected Pt catalysts using first-principle calculation

○Mizuki Kamata[1], Hidenori Kuroki[1,2], Yuuki Sugawara[1], Hiroshi Ushiyama[3], Takeo Yamaguchi[1] (1. Tokyo Institute of Technology, 2. Kanagawa Institute of Industrial Science and Technology, 3. Research Organization for Information Science and Technology)

Area 2

Academic Program [Poster] | 03. Physical Chemistry -Structure- | Poster

[P02-1am] 03. Physical Chemistry -Structure-

9:40 AM - 11:10 AM Area 2 (Online Meeting)

[P02-1am-01] Diffusion process of chlorobenzophenones probed by transient grating method

○Wataru Kashihara[1], Sotaro Hiramoto[1], Tadashi Suzuki[1] (1. Grad. Sch. Sci., Eng., Aoyama Gakuin Univ.)

9:40 AM - 11:10 AM

[P02-1am-02] Electronic structures of weakly exchange coupled systems with trityl and nitroxide radicals as studied by cw/pulsed ESR spcetroscopy

○Kazunobu Sato[1], Rei Hirao[1], Kenji Sugisaki[1], Hideto Matsuoka[1], Kazuo Toyota[1], Daisuke Shiomi[1], Elena Zaytseva[2], Victor M. Tormyshev[2],

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Elena Bagryanskaya[2], Takeji Takui[1] (1. Osaka City University, 2. Nobosibirsk Institute of Organic Chemistry)

9:40 AM - 11:10 AM

[P02-1am-03] Structures of Terephthalamide Networks on Graphite (0001)

○Takeshi Okamatsu[1], Toshihide Kaneko[1], Takato Suzuki[1], Hiroto Sato[1], Koki Imahayashi[1], Hayato Sanada[1], Osamu Endo[1], Hiroyuki Ozaki[1] (1. Tokyo University of Agriculture and Technology)

9:40 AM - 11:10 AM

Area 3

Academic Program [Poster] | 04. Physical Chemistry -Properties- | Poster

[P03-1am] 04. Physical Chemistry -Properties-

9:40 AM - 11:10 AM Area 3 (Online Meeting)

[P03-1am-01] Study of magnetic property on a surface of magnetic thin film of iron hexacyanochromate

○Shuntaro Nagashima[1], Yuji Yahagi[1], Kosuke Nakagawa[2], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. The Univ. of Tokyo)

[P03-1am-02] Mode order dependence of the Rabi splitting in molecular vibrational polaritons

○Garrek Stemo[1], Jonas Paletscheck[2], Hiroyuki Katsuki[1], Hisao Yanagi[1] (1. Nara Institute of Science and Technology, 2. University of Regensburg)

[P03-1am-03] Preparation and property of Azulene-1-$CONHCH_2SO_3^-$ and its charge-transfer salt

○Taiki Oyama[1], Hiroki Akutsu[2], Yasuhiro Nakazawa[2] (1. Osaka University, 2. Osaka Univ.)

[P03-1am-04] Electronic states of unsymmetrical platinum complexes with square planar coordination of 2,2’-bipyridine derivatives and dithiolene ligands and their application to conducting materials

○Mizuki Yumino[1], Yuna Kim[2], Tomofumi Kadoya[1], Jun-ichi Yamada[1], Kazuya Kubo[1] (1. Graduate School of Material Science, University of Hyogo, 2. Research Institute for Electronic Science, Hokkaido University)

[P03-1am-05] Synthesis and Femtosecond Spectroscopic Study of CdSe/CdTe Core/crown Nanoplatelets

○Haruka Nagasawa[1], Naoto Tamai[1], Daichi Eguchi[1] (1. Kwanseigakuin University Graguate School)

[P03-1am-06] Synthesis and properties of supramolecular organic conductors based on the novel iodine-containing π-donor IETSe

○Chihiro Yamabe[1], Tatsuro Imakubo[1] (1. Nagaoka Univ. of Tech.)

[P03-1am-07] The structure of the excited states and relaxation dynamics of an organic luminescence material showing dual emission

○Tomohiro Ryu[1], Yuushi Shimoda[1], Masaki Saigo[1], Ryota Fukuda[1], Kiyoshi Miyata[1], Youichi Tsuchiya[2], Hajime Nakanotani[2], Chihaya Adachi[2], Ken Onda[1] (1. Kyushu University, 2. OPERA, Kyushu University)

[P03-1am-08] Elementary exciton dynamics of cadmium-free blue-emitting InGaP quantum dots.

○hiroki kitajima[1], Yurina Yamaguchi[1], Ayana Fujitaka[1], Daichi Eguchi[1], Naoto Tamai[1] (1. Kwanseigakuin University Graguate School)

[P03-1am-09] Structures and physical properties of radical anion salts of TCNQ derivatives with *N*-alkylated DABCO as a counter cation

○Ogawa Ryohei[1], Kohdai Ishida[1], Manabu Ishikawa[1], Shota Okamato[1], Yoshiaki Nakano[1], Akihiro Otsuka[1], Hideki Yamochi[1] (1. Kyoto University)

[P03-1am-10] Synthesis and Photostability of New Pentacene Derivatives with Radical Substituent controlled the Excited Spin-State by π-Topology

○Nishiki Minami[1], Keijiro Maeguchi[1], Ken Kato[1], Kohei Yoshida[1], Akihiro Shimizu[1], Genta Kashima[2], Yoshio Teki[1] (1. Osaka City Univ., Grad. School of Sci., 2. Osaka City Univ., Sci.)

[P03-1am-11] Development of Novel Organic Conductors Using Iodine-bonded π-Donor IDMe-TSeF

○VERT E[1], Tatsuro Imakubo[1] (1. Nagaoka Univ. of Tech.)

[P03-1am-12] Cell culture and preparation of molecular nanocoil scaffolds composed of TTF

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derivatives with chiral units

○Tamaki Nishimura[1], Yuka kanno[1], Sadafumi Nishihara[2], Tomoyuki Akutagawa[3], Takayoshi Nakamura[4], Yoko Tatewaki[1] (1. Tokyo University of Agriculture and Technology, 2. Hiroshima University, 3. Tohoku University, 4. Hokkaido University)

[P03-1am-13] Crystal structure and physical properties of radical cation salts of triptycene derivatives annulated with thianthrene skeletons

○Takuma YOSHIYUKI[1], Yoshiaki SHUKU[1], Kunio AWAGA[1] (1. Nagoya Univ.)

[P03-1am-14] Proton conductivity of imidazole containing phosphonic acid-modified mesoporous silica

○Ryoka Asano[1], Yasuhiro Shigeta[3], Takuya Kurihara[2], Shogo Amamori[3], Tomonori Ida[2], Motohiro Mizuno[2,3] (1. School of Chemistry, College of Science and Engineering, Kanazawa University, 2. Graduate School of Natural Science and Technology, Kanazawa University, 3. Nanomaterials Research Institute, Kanazawa University)

[P03-1am-15] Analysis of Proton Conduction Mechanism in Alginic Acid-Polyacrylic Acid-Triazole Composites

○Ryota Watanabe[1], Takuya Kurihara[1], Yasuhiro Shigeta[2], Shogo Amemori[2], Tomonori Ida[1], Motohiro Mizuno[1,2] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nanomaterials Research Institute, Kanazawa University)

[P03-1am-16] Proton Conductivity of Phosphonic Acid Group-Modified MCM-41 / Imidazole Composites

○yuta arai[1], Takuya Kurihara[3], Yasuhiro Shigeta[2], Shogo Amemori[2], Tomonori Ida[3], Motohiro Mizuno[1,2,3] (1. Graduate School of Frontier Science Initiative, Kanazawa University, 2. NanoMaterials Research Institute, 3. Graduate School of Natural Science and Technology, Kanazawa University)

Area 4

[P04-1am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

9:40 AM - 11:10 AM Area 4 (Online Meeting)

[P04-1am-01] Elucidation of Energy Transfer in a Single Perovskite Nanocrystal-Dye Molecules Hybrid System

○Kaho Matsunaga[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. The Univ. of Kwansei Gakuin)

9:40 AM - 11:10 AM

[P04-1am-03] Synthesis of Perovskite Nanoplatelets and Evaluation of Emission Behavior at a Single Dot Level

○Yuka Arimoto[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-04] Carrier dynamics of a CH_3NH_3PbBr3 crystal by utilizing transient absorption microscopy

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

9:40 AM - 11:10 AM

[P04-1am-05] Size-Dependent Emission Behavior of Cesium Lead Halide Perovskite Nanocrystals

○Hina Igarashi[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-06] Passivation of Halide Vacancies in Lead Halide Perovskite Quantum Dots for Photoluminescence Blinking Suppression

○Lata CHOUHAN[1], Vasudevanpillai BIJU[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

9:40 AM - 11:10 AM

[P04-1am-07] Energy transfer in a single perovskite nanocrystal-dye molecules
-Nanocrystal size dependence-

○Haruki Horibe[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-08] Interfacial Transport and Collection of Photogenerated Charge Carriers

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in Bandgap Engineered Lead Halide Perovskite Heterostructures

○MD SHAHJAHAN[1], Lata Chouhan[1], Vasudevanpillai Biju[1,2] （1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University）

9:40 AM - 11:10 AM

[P04-1am-09] Kinetic analysis of halide exchange reaction of an inorganic perovskite nanocrystal

○Yuki Tajika[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University）

9:40 AM - 11:10 AM

[P04-1am-10] Control of the Emission Behavior of a Single Quantum Dot by a One-Dimensional Metal Periodic Structure

○Hiroto Takase[1], Hinako Chida[1], Mitsuaki Yamauchi[1], Keiko Tawa[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University ）

9:40 AM - 11:10 AM

[P04-1am-11] The n-π interactions and electron correlations in intramolecular rotation of chalcogenoanisole

○Kotai Ka[1], Yoshihiro Yamakita[1] （1. The Univ. of Electro-Communications）

9:40 AM - 11:10 AM

[P04-1am-12] Photoexcited dynamics of microcrystals of dimethylhexatriene

○yusuke chichi[1], takuya Nakamura[1], tomoaki yago[1], masanobu wakasa[1] （1. Saitama University）

9:40 AM - 11:10 AM

[P04-1am-13] Methanol photoaddition reaction of (*R*)-(+)-limonene in a microreactor

○Riku Suzuki[1], Wataru Kashihara[1], Tadashi Suzuki[1] （1. Aoyama Gakuin Univ）

9:40 AM - 11:10 AM

[P04-1am-14] Direct observation of ultrafast electron ejection from higher excited state in solution phase

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

9:40 AM - 11:10 AM

[P04-1am-15] Examination of Low Magnetic Field Effect of Photochemical Reaction in Micelles

○Atsuya Hosoda[1], Tomoaki Yago[1], Kiminori Maeda[1], Masanobu Wakasa[1] （1. Graduate School of Science and Engineering, Saitama University ）

9:40 AM - 11:10 AM

Area 1

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

[P01-1vn] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

4:10 PM - 5:40 PM Area 1 (Online Meeting)

[P01-1vn-01] photodimerization of 1-aryl-6-pyridylhexatriene

○Haruka Ito[1], Shinji Yamada[1] （1. Ochanomizu University, department of chemistry）

[P01-1vn-02] Effect of intramolecular cation-π interaction on the fluorescence properties of nicotinamide derivatives

○Miori Sasaki[1], Shinji Yamada[1] （1. department of chemistry, Ochanomizu University）

[P01-1vn-03] Stereoselective Norrish-Yang Reactions of Imidazolidinone Derivatives Using an Ammonium-π interaction

○Hanako Nakajima[1], Shinji Yamada[1] （1. Ochanomizu University）

[P01-1vn-04] Development of chromophoric materials towards highly efficient visible-to-UV photon upconversion

○Tae Tamemoto[1], Kana Orihashi[1], Nobuhiro Yanai[1,2,3], Nobuo Kimizuka[1,2] （1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. PRESTO, JST）

[P01-1vn-05] Copper-Catalyzed Enantioselective Intramolecular [2+2]Photocycloaddition of 1,4-Naphthoquinone-Alkene System

○Daiki Asanuma[1], Hajime Shigemitsu[1], Tadashi Mori[1], Toshiyuki Kida[1] （1. Osaka University）

[P01-1vn-06] Fabrication and Characterization of Expanded Perylene Diimide Derivatives Insoluble Thin Films by Photo-Induced Scholl Reactions

○Yamato Manjome[1], Tomoya Ogawa[1], Daiki Kuzuhara[1] （1. Iwate University）

[P01-1vn-07] The photoreaction of coumaryl-4-methyl

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derivative bearing electron donating group at 7-position

○Ma-aya Takano[1], Abe Manabu[1] (1. The Univ. of Hiroshima)

[P01-1vn-08] Photon Upconversion of Dyads Linked with Nonconjugated Units

○Masaya Kanoh[1], Kiyomasa Honda[1], Takuya Ogaki[1], Yasunori Matsui[1], Eisuke Ohta[1], Hiroshi Ikeda[1] (1. Osaka Pref. Univ.)

[P01-1vn-09] Photoredox 1,4-addition onto α,β-unsaturated carboxylic acid and development of photocatalyst

○Misaki Umezawa[1], Toshiya Hirahama[1], Mitsuru shoji[1] (1. Yokohama Univ. of Pharmacy)

[P01-1vn-10] Multi-photon Excitable Imidazo[1,2-*a*]pyridinium Salts for Mitochondria-targeted Image-guided Photodynamic Therapy

Fumitoshi Yagishita[1,2], ○Shota Kunimi[1], Keita Hoshi[1], Masaki Okamoto[1], Atsushi Tabata[3], Hideaki Nagamune[3], Eiji Hase[2], Keiji Minagawa[1], Yasushi Imada[1] (1. Department of Applied Chemistry, Tokushima University, 2. Institute of Post-LED Photonics, Tokushima University, 3. Faculty of Bioscience and Bioindustry, Tokushima University)

[P01-1vn-11] Research on ITO/PEN electrodes modified by organic dyes and their photoelectrochemical properties

○Thi Thu Trang Tran[1], Kentaro Suzuki[1], Toshi Nagata[1] (1. Meijo University)

[P01-1vn-12] Photoreaction of quinones with an amphiphilic porphyrin sensitizer

○Yui Tanaka[1], Toshi Nagata[1] (1. Graduate School of Science and Technology, Meijo University)

[P01-1vn-13] Development of Environmentally Benign Julia Olefination by Reductive Desulfonylation Utilizing Pyrene Photocatalyst

○Hikaru Watanabe[1], Kazuki Nakajima, Ryota Edagawa, Yasuhiro Okuda[1], Akihiro Orita[1] (1. Okayama University of Science)

[P01-1vn-14] Synthesis and Aggregate Properties of Pentacene Derivatives Bearing Quadruple Hydrogen Bonding Units

○Naoki Koike[1], Shunta Nakamura[1], Hayato Sakai[1], Taku Hasobe[1] (1. Keio University)

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

[P01-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

1:20 PM - 2:50 PM Area 1 (Online Meeting)

[P01-1pm-01] Activated charcoal as an effective additive for alkaline hydrolysis of esters in water

○Kiyoshi TANEMURA[1], Taoufik Rohand[2] (1. Nippon Dental University, 2. Cadi Ayyad University)

[P01-1pm-02] Synthesis of Jasmonic Acid Derivatives Using Intramolecular C-H Insertion Reaction

○Mayuko Morita[1], Yoshiharu Okada[1] (1. Kindai University)

[P01-1pm-03] Simple Synthesis and Physiological Activities of Acerogenins

○Ikumi Ohata[1], Mina Nagarede[1], Yoshiharu Okada[1] (1. Kindai University)

[P01-1pm-04] Asymmetric hydrosilylation of imines catalyzed by a chiral pyridine N-oxide derivative

○Yusuke Fukushima[1], Gakushi Morita[1], Hinoki Sakamura[1], Michimasa Hayashi[1], Akane Yoshino[1], Tetsuya Fujimoto[1] (1. Shinshu university)

[P01-1pm-05] $AgNO_3/TiO_2$-photocatalyzed N-Methylation of Amino Acids with Methanol

○I WEN HUANG[1], Yuna Morioka[1], Hiroshi Naka[2,3], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ., 3. Grad. Sch. Pharm. Sci., Kyoto Univ.)

[P01-1pm-06] 13C NMR and IR Spectroscopic and Computational Studies of Intra- and Intermolecular Interactions of Amino Acid Derivatives in Solutions

○Yoshikazu HIRAGA[1], Satomi NIWAYAMA[2], Ryosuke HOSHIDE[1] (1. Graduate School of Science and Technology, Hiroshima Institute of Technology, 2. Graduate School of Technology, Muroran Institute of Technology)

[P01-1pm-08] Stereoselective Synthesis of Tetrahydropyranones using β-Silyl-

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γ-Alkylidene-γ-Butyrolactones with Aldehydes and Ketones

○Shoma Ariyoshi[1], Kazuhiko Sakaguchi[1], Takahiro Nishimura[1] (1. Osaka City University)

[P01-1pm-09] Lipase-catalyzed Desymmetrization by Mono-Hydrolysis of Symmetric 1,5-Diacetyl-3-*O*-silyl Protected Pentanetriol

○Yusuke Uchida[1], Yoshikazu HIRAGA[1] (1. Graduate School of Science and Technology, Hiroshima Institute of Technology)

[P01-1pm-10] Syntheses of specific tricyclopropane compounds by cyclopropane-shift type transformation of diaryl(2-halocyclopropyl)methanols

○Shotaro Morimoto[1], Kento Moriguchi[1], Yoo Tanabe[1] (1. Kwansei Gakuin University)

[P01-1pm-11] Ir-catalyzed transformation of bio-renewable carboxylic acids toward C– C bond formation

○Kazuki Teramoto[1], Shota Yoshioka[1], Susumu Saito[1,2] (1. Grad. Sch. Sci. Nagoya Univ., 2. RCMS, Nagoya Univ.)

[P01-1pm-12] Synthesis of fatty acids having a trifluoromethyl group at the end

○Kazuki Naito[1], Tsuyuka Sugiishi[1], Masashi Sonoyama[1], Hideki Amii[1] (1. Gunma University)

[P01-1pm-13] Chiral synthesis of cyano-substituted cyclopropane-type pyrethroid with two asymmetric centers and its insecticidal stereostructure-activity relationship

○Yusa Aoyagi[1], Mizuki Moriyama[1], Noritada Matsuo[1], Yoo Tanabe[1] (1. Kwansei Gakuin Univ)

[P01-1pm-14] Regioselective Difluorocyclopropanation of Dienes

○Hiroto Mukai[1], Tsuyuka Sugiishi[1], Hideki Amii[1] (1. Gunma university)

[P01-1pm-15] α-Formylation of α,β-unsaturated thioesters utilizing Ti-Claisen condensation

○Soma Fukunaga[1], Sachiyo Yamaguchi[1], Mizuki Moriyama[1], Tanabe Yoo[1] (1. Kwansei Gakuin University)

[P01-1pm-16] Radical reactions of α-(thio)difluoromethyl arenes

○Azuma Iizuka[1], Kohei Ueyama[1], Tuyuka Sugiishi[1], Hideki Amii[1] (1. The Univ. of Gunma)

[P01-1pm-17] The synthetic application of (aryl)fluoromethylsilane

○Manami Sato[1], Yuto Haga[1], Tsuyuka Sugiishi[1], Hideki Amii[1] (1. Gunma Univ.)

[P01-1pm-18] Regioselective umpolung alkylation reactions of α-iminoesters

○Mayu Kukita[1], Yasushi Yoshida[1], Takashi Mino[1], Masami Sakamoto[1] (1. Graduate School of Engineering, Chiba University)

[P01-1pm-19] Regioselective Diels-Alder reaction using hydrogen bonding of amides

○Wangbin Ni[1] (1. Kanagawa University)

Area 2

Academic Program [Poster] | 19. Colloid and Interface Chemistry | Poster

[P02-1pm] 19. Colloid and Interface Chemistry

1:20 PM - 2:50 PM Area 2 (Online Meeting)

[P02-1pm-01] Preparation of water soluble quantum dots and elucidation of their emission behaviors at a single dot level

○Natsumi Nagasaki[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

[P02-1pm-02] Preparation of Non-spherical Polyimide Particles

○Akiko Nakahashi[1] (1. Osaka Research Institute of Industrial Science and Technology)

[P02-1pm-03] Chemical Synthesis and Local Structure Analysis of Tungsten Oxide Nanoparticles

○Yuki Kitazaki[1], Mari Takahashi[1], Masafumi Harada[2], Shinya Maenosono[1] (1. JAIST, 2. Nara Women's Univ.)

[P02-1pm-04] pH-dependent Orientational Changes of Gold Nanorods on a DNA polymer brush

○Yu Sekizawa[1], Hideyuki Mitomo[2,3], Satoshi Nakamura[4], 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, 4. National Institute of Advanced Industrial Science and Technology (AIST)))

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[P02-1pm-05] Synthesis and properties of Au_{25} cluster protected by semi-fluorinated ligand.
○duhong sun[1], Yuki Saito[1], Yukatsu Shichibu[1,2], Hideyuki Mitomo[3], Kuniharu Ijiro[3], Katsuaki Konishi[1,2] （1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University, 3. Research Institute for Electronic Science, Hokkaido University）

[P02-1pm-06] Regulating Photocatalytic Activity by Self-Assembly of Fluorescein Derivatives
○Masakazu Kobayashi[1], Tomoe Tamemoto[1], Youhei Tani[1], Hajime Shigemitsu[1], Kida Toshiyuki[1] （1. Osaka University）

[P02-1pm-07] Control over One-Dimensional Arrangements of Perovskite Nanocrystals
○Kanako Nakatsukasa[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University）

[P02-1pm-08] Construction of Hybrid Supramolecular Structures Using a Perylene Bisimide Derivative and a Perovskite Nanocrystal
○Naoki Kubo[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University）

[P02-1pm-09] Photocontrol of crystallization-induced emission in azobenzene derivatives
○Miho Okaji[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. kwansei Gakuin univ.）

[P02-1pm-10] Metastabilization of cis-azobenzene using hydrogen bonds
○Erika Kida[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University）

[P02-1pm-11] What key parameter for determing shape of taurocholic acid-based mixed micelle ?
○Hideki Aizawa[1] （1. Setsunan University）

[P02-1pm-12] Micellization of tetradecylquinolinium and tetradecylisoquinolinium bromides
Reina Sakota[1], ○Katsuhiko Fujio[1] （1. School of Science, Tokai University）

[P02-1pm-13] Micelle Formation and Photo-Responsive Behavior of an Amphiphilic Azotolane Liquid Crystal
○Anna Tamai[1], Ayumi Kobayashi[1], Kohei Iritani[1], Yamashi Takashi[1] （1. Tokyo University of Technology.）

[P02-1pm-14] Molecular Orientation Analysis in a Thin Film of a p-Gelator Forming a Unique Aggregate at Air– Water Interface
○Yuta Yamaguchi[1], Takafumi Shimoaka[1], Nobutaka Shioya[1], Ayyappanpillai AJayaghosh[2], Taizo Mori[3,5], Katsuhiko Ariga[4,5], Takeshi Hasegawa[1] （1. ICR, Kyoto Univ., 2. CSIR-NIIST, 3. ISSP, The Univ. of Tokyo, 4. Grad. Sch. of Front. Sci., The Univ. of Tokyo, 5. NIMS）

[P02-1pm-16] Guest-responsive supramolecular hydrogel expressing selective sol-gel transition for sulfated glycosaminoglycans
○Naofumi Kuroda[1], Shun-ichi Tamaru[1], Seiji Shinkai[2] （1. Graduate School of Engineering, Sojo University, 2. Institute of Systems, Information Technologies and Nanotechnologies）

[P02-1pm-17] Preparation and properties of supramolecular hydrogels for the development of self-healing soft materials.
○Yuki Edamoto[1], Naofumi Kuroda[2], Shun-ichi Tamaru[1,2], seiji Shinkai[3] （1. Department of Engineering Sojo University , 2. Graduate School of Engineering Sojo University, 3. Institute of Systems, Information Technologies and Nanotechnologies）

[P02-1pm-18] Supramolecular hydrogel showing gelation and color change in response to metal cations
Ryo Taniguchi[1], Masayuki Izumi[1], Tomoyuki Akutagawa[2], Takayoshi Nakamura[3], ○Rika Ochi[1] （1. Kochi Univ., 2. Tohoku Univ., 3. Hokkaido Univ.）

[P02-1pm-19] Evaluation of Magnetic Ionic Liquid Gel Properties Formed by Fluorine-Containing Low Molecular Weight Gelators Having Linear Alkyl Group at Terminal Position
○Tatsuya Tomarino[1], Miura Masahiro[1], Morita Yuki[2], Okamoto Hiroaki[1] （1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University）

[P02-1pm-20] Electrochemical Properties of Ionic Liquid Gel Formed by Semi-perfluoroalkyl Benzoate Derivatives
○Kenta Matsumoto[1], Yuki Morita[2], Hiroaki Okamoto[1] （1. Graduate School of Sciences and

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Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University)

[P02-1pm-21] Gel strength of ionic liquid gels by low molecule weight gelator with fluoro-substituent at both ends of molecules

○Koohei Nakamura[1], Yuta Kanesigte[1], Yuki Morita[2], Hiroaki Okamoto[1] (1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University)

[P02-1pm-22] Gel Properties Formed by Dimer Type 4-Mercaptobenzoic Acid Derivatives Having Perfluoroalkyl Group at Both Terminal Position

○Sota Kanemitsu[1], Ryoichiro Yoshihara[2], Kotaro Kanetada[2], Yuki Morita[1], Hiroaki Okamoto[2] (1. Faculty of Engineering, Yamaguchi University, 2. Graduate School of Sciences and Technology for Innovation)

[P02-1pm-23] Electrochemical Properties of Gel Electrolyte for Li-ion Battery Formed by Fluorine-Containing Gemini-Type Low Molecular Gelators

○Yui Endo[1], Tomohiro Yoshida[2], Morita Yuki[1], Hiroaki Okamoto[2] (1. Faculty of Engineering, Yamaguchi University, 2. Graduate School of Sciences and Technology for Innovation, Yamaguchi University)

[P02-1pm-24] Microscopic observation on the effect of non-equilibrium flow on Aβ-lipid membrane interaction

○Mitsuhiro Abe[1], Akane Iida[1], Hideki Nabika[2] (1. Graduate School of Sci. and Eng. Yamagata Univ., 2. Faculty of science Yamagata Univ.)

[P02-1pm-25] Elucidation of Aβ aggregation behavior in liposome dispersion under non-equilibrium stirring

○Fumiya Sato[1], Akane iida[2], Mitsuhiro Abe[2], Hideki Nabika[1] (1. Faculty of Science of Yamagata Univ., 2. Graduate School of Sci. and Eng. Yamagata Univ.)

[P02-1pm-26] Preparation of Lipid Vesicle Supported by Micro-Honeycomb Porous Film

○Keisuke Kimura[1], Ruria Yano[1], Kazunari Matsumura[1] (1. Shibaura Institute of Technology)

[P02-1pm-27] Multiple droplets formation by a simple mixing method with maicrofabricated channel and their mass-transport mechanism

○Kyoka Nakanishi[1], Kenta Goto[1], Fumito Tani[1] (1. The Univ. of Kyushu)

Academic Program [Poster] | 23. CIP Poster | Poster

[P02-1vn] 23. CIP Poster

4:10 PM - 5:40 PM Area 2 (Online Meeting)

[P02-1vn-01] Wavelength dependence of photocapacitnce of layered MnO2 with metal complexes using lipid confinement effect

○Makoto Itakura[1], Riku Okiguti[1], Ituou Ou[1], Kei Hsegawa[1], Motoyuki Kamata[1], Kazuaki Tomono[1] (1. Kantogakuin University)

[P02-1vn-02] Photocatalytic function induced by self-assembly of organic dyes

○Hajime Shigemitsu[1], Youhei Tani[1], Tomoe Tamemoto[1], Toshiyuki Kida[1] (1. Osaka Univ.)

[P02-1vn-03] Electrochemical CO_2 reduction to C_2 products utilizing cuprous coordination polymer electrode

○Naonari Sakamoto[1], Yusaku F Nishimura[1], Takamasa Nonaka[1], Masataka Ohashi[1], Nobuhiro Ishida[1], Kosuke Kitazumi[1], Yuichi Kato[1], Keita Sekizawa[1], Takeshi Morikawa[1], Takeo Arai[1] (1. TOYOTA CENTRAL R&D LABS., INC.)

[P02-1vn-04] Development of alkali-resistant reversed phase HPLC column based on eggshell

○Tomoka Yoshii[1], Mai Mochida[1], Kogi Kaizu[1], Hiroaki Imai[1], Daniel Citterio[1], Yuki Hiruta[1] (1. Fac. Sci. Tech., Keio Univ.)

[P02-1vn-05] Subcritical Water Decomposition of Polychlorotrifluoroethylene (PCTFE) under Alkaline Conditions

○Kazuma Igarashi[1], Hisao Hori[1] (1. Kanagawa Univ.)

[P02-1vn-06] Efficient Decomposition of Fluoropolymer ETFE in Subcritical Water under Alkaline Conditions

○Jin Hamaura[1], Hisao Hori[1] (1. Kanagawa Univ.)

[P02-1vn-07] Iridium Catalyzed C-C Bond Formation of

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Methyl Groups of N-Heterocyclic Compounds with Alcohols
○Mitsuki Onoda[1], Ken-ichi Fujita[1] (1. Graduate School of Human and Environmental Studies, Kyoto University)

[P02-1vn-08] An Efficient Dimethylamination of Alcohols Using Iridium Catalyst Bearing an N-Heterocyclic Carbene Ligand
○Jaeyoung Jeong[1], Ken-ichi Fujita[1] (1. Graduate School of Human and Environmental Studies, Kyoto University)

[P02-1vn-09] Nanoporous Metal Complex Covered on Metal Oxide Nanowires for Molecular Recognition by Molecular Sieving
○Akira Yonezu[1], Junya Kubo[2], Shinpei Kusaka[1,2], Takao Yasui[1,2], Yoshinobu Baba[1,2], Ryotaro Matsuda[1,2] (1. Grad. Sch. Eng., Nagoya University, 2. Sch. Eng., Nagoya University)

[P02-1vn-10] Development of tough biomass mechanical material by hybridization of plant-derived polysaccharides and hydroxyapatite
○Kohei Okuda[1], Tadashi Mizutani[1] (1. The Univ. of Doshisha)

[P02-1vn-11] Organogels formed from a starch-derived 1,5-anhydro-D-glucitol glycolipid and their properties
○Rika Iwaura[1], Shiro Komba[1], Takahito Kajiki[2] (1. National Agriculture and Food Research Organization, 2. SUNUS Co., Ltd.)

[P02-1vn-12] Research on Adsorption of Boron using Hydrogels
○Daiki Matsumura[1], Kazunori Nakano[1] (1. Nagoya Municipal Industrial Research Institute)

[P02-1vn-13] Development of high-strength cellulose nanofiber hydrogels by freeze-crosslinking
○Yurina Sekine[1], Takuya Nankawa[1], Daisuke Miura[2], Shunji Yunoki[3], Tsuyoshi Sugita[1], Hiroshi Nakagawa[1], Teppei Yamada[4] (1. Japan Atomic Energy Agency, 2. Yamagata University, 3. Tokyo Metropolitan Industrial Technology Research Institute, 4. The University of Tokyo)

[P02-1vn-14] Emission Properties of Hybrid Films of Benzylideneaniline-based Amorphous Molecular Materials with Organic Acids
○Takuma Tsukada[1], Yuya Kitamura[1], Hideyuki Nakano[1] (1. Muroran Inst. Tech.)

[P02-1vn-15] Emission and Photochemical Reaction of Cyanostilbene-based Amorphous Molecular Materials
○Hiroya Fukushima[1], Kensuke Mori[1], Yoshimitsu Sagara[2], Kenta Kokado[3], Takayoshi Nakamura[3], Nobuyuki Tamaoki[3], Hideyuki Nakano[1] (1. Muroran Inst. Tech., 2. TITEC, 3. RIES, Hokkaido Univ.)

[P02-1vn-16] Emission and Photochemical Reaction of a Novel Amorphous Molecular Material Possessing Diphenylanthracene Moiety
○Ryoma Matsui[1], Hiroki Asanuma[1], Hideyuki Nakano[1] (1. Muroran Inst. Tech.)

[P02-1vn-17] Photoinduced Helical Structure Formation of Azobenzene-based Molecular Glass Particles
○Motona Matsubara[1], Hiroyasu Ukai[1], Masahiro Kuragano[1], Kiyotaka Tokuraku[1], Hideyuki Nakano[1] (1. Muroran Inst. Tech.)

[P02-1vn-18] Development of linear silicones with unique mechanical properties
○Mitsuo Hara[1], Yuta Iijima[1], Shusaku Nagano[2], Takahiro Seki[1] (1. Nagoya University, 2. Rikkyo University)

[P02-1vn-19] Transmission Electron Microscope (TEM) Measurement of the PLGA Nanocapsules
○Kazutaka Arai[1], Kensuke Osada[1], Hong Taefun[1,2], Jun-ichiro Jo[3], Ichio Aoki[1] (1. National Institute of Radiological Science (NIRS), QST, 2. School of Engineering, The Tokyo Univ., 3. Inst. Frontier Med. Sci., Kyoto Univ.)

[P02-1vn-20] A study of the preparation of gold nanoparticles using the electric current application in electrolyte solution
○Shinichirou Ozawa[1], Yuichiro Iwasaki[1], Masaya Nishio[1], Ryo Saito[1], Hisashi Miyazaki[1], Yoichi Okamoto[1] (1. National Defense Academy)

[P02-1vn-21] Fabrication of Carbon Nanotube Thin Films for Flexible Transistor Applications using a Cross-linked Amine Polymer
Kaisei Matsumoto[1], Kazuki Ueno[1], Jun Hirotani[2], Yutaka Ohno[2,3], ○Haruka Omachi[1,4] (1. Grad. Sch. of Sci., Nagoya Univ., 2. Grad. Sch. of Eng., Nagoya Univ., 3. IMaSS, Nagoya Univ., 4. RCMS, Nagoya Univ.)

[P02-1vn-22] Identification of orthogonal RNA-RNA-

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binding protein pairs through library-versus-library in vitro selection

○Keisuke Fukunaga[1], Yohei Yokobayashi[1] （1. OIST）

[P02-1vn-23] Immobilization of Biomolecules by Photoinduced Oxygenation of Graphene Surface with Chlorine Dioxide

○Haruyasu Asahara[1,2], Shota Kumano[1], Junso Fujita[3], Kei Ohkubo[2,4], Tsuyoshi Inoue[1,2] （1. Graduate School of Pharmaceutical Sciences, Osaka University, 2. Institute for Open and Transdisciplinary Research Initiatives, Osaka University, 3. Graduate School of Frontier Biosciences, Osaka University, 4. Institute for Advances Co-Creation Studies, Osaka University）

[P02-1vn-24] The Development of Furimazine Derivatives for Long-Term and High-Sensitive Bioluminescence Imaging

○Mariko Orioka[1], Yuki Mizui[1], Masatoshi Eguchi[2], Yuma Ikeda[1], Hideaki Yoshimura[2], Takeaki Ozawa[2], Daniel Citterio[1], Yuki Hiruta[1] （1. Fac. Sci. Tech., Keio Univ., 2. Dept. Chem., The Univ. of Tokyo）

[P02-1vn-25] Practical Synthesis of 2-Oxazolidinones Using a Triethylamine Hydroiodide Catalyst

○Ken Okuno[1], Ryuichi Nishiyori[1], Seiji Shirakawa[1] （1. Graduate School of Fisheries and Environmental Sciences, Nagasaki University）

[P02-1vn-26] Development of New Catalytic Synthetic Methods of N-Unprotected Ketimines and its Applications to One-Pot Synthesis of N-Unprotected Amines and Amino Acid Derivatives

○Hiroyuki Morimoto[1], Yuta Kondo[1], Tetsuya Kadota[1], Yoshinobu Hirazawa[1], Kazuhiro Morisaki[1], Takashi Ohshima[1] （1. Graduate School of Pharmaceutical Sciences, Kyushu University）

[P02-1vn-27] New umpolung strategy of aromatic carbonyl compounds to α-hydoroxybenzyl anion equivalents: carboxylation with carbon dioxide

○Shintaro Okumura[1], Yasuhiro Uozumi[1] （1. Institute for Molecular Science）

[P02-1vn-28] Biotransformation of molecular nanocarbon by *Spodoptera litura* larvae

○Atsushi Usami[1], Amaike Kazuma[1], Itami Kenichiro[1,2] （1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University）

[P02-1vn-29] Synthesis and transistor applications of robust and high-mobility n-type organic semiconductors having phenylalkyl side chains

○Shohei Kumagai[1], Hiroyuki Ishii[2], Go Watanabe[3], Eiji Fukuzaki[4], Tatsuro Annaka[1], Yukio Tani[4], Hiroki Sugiura[4], Tetsuya Watanabe[4], Tadanori Kurosawa[1], Shun Watanabe[1,5], Jun Takeya[1,5,6], Toshihiro Okamoto[1,5,7] （1. The Univ. of Tokyo, 2. The Univ. of Tsukuba, 3. Kitasato Univ., 4. FUJIFILM Corp., 5. AIST-UTokyo OPERANDO-OIL, 6. NIMS WPI-MANA, 7. JST-PRESTO）

[P02-1vn-30] Synthesis of natural product-connected molecules by the Ugi reaction using medicinal plant extracts as substrates

○Keisuke Tomohara[1], Nao Ohashi[2], Takeru Nose[1,2] （1. Faculty of Arts and Science, Kyushu University, 2. Graduate School of Science, Kyushu University）

[P02-1vn-31] Solid-state DNP-NMR spectroscopy for polymer-supported organocatalysts

○Shinji Tanaka[1], Yumiko Nakajima[1], Kazuhiko Sato[1] （1. National Institute of Advanced Industrial Science and Technology）

[P02-1vn-32] Deep Learning Analysis of SARS-CoV-2 Using the Codification Techniques of Conformations

○Hiroshi Izumi[1] （1. National Institute of Advanced Industrial Science and Technology (AIST)）

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

[P01-1am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Fri. Mar 19, 2021 9:40 AM - 11:10 AM Area 1 (Online Meeting)

[P01-1am-01] Theoretical Study of Thermal Neutron Scattering by Light and Heavy Water with Molecular Dynamics Simulation

○Akira Ichihara[1], Yutaka Abe[2] (1. Japan Atomic Energy Agency, 2. Kyoto University)

[P01-1am-02] Prediction of Gas Phase Acidity for *in Silico* Design of Super Acids with High Precision Quantum Chemical Calculations and Machine Learning

○Rima Suzuki[1], Nahoko Kuroki[1], Hirotoshi Mori[1,2] (1. Chuo University, 2. Institute for Molecular Science)

[P01-1am-03] Theoretical Design of Blended Amine Solution for CO_2 Chemical Absorption Method

○Iori Shimizu[1], Sumika Nagato[1], Mikito Fujinami[1], Hiromi Nakai[1,2,3] (1. School of Advanced Science and Engineering, Waseda University, 2. Waseda Research Institute for Science and Engineering, Waseda University, 3. Elements Strategy Initiative for Catalysts and Batteries, Kyoto University)

[P01-1am-04] Effect of solvent permittivity and heteroatoms properties on the formation pathways of Keggin-type polyoxometalates ($[XW_{12}O_{40}]^{n-}$)

○Masahiko Akune[1], Kazuo Eda[1], Toshiyuki Osakai[1], Takahito Nakajima[2] (1. Kobe Univercity, 2. Institute of Physical and Chemical)

[P01-1am-05] Development and application of FMO-based analysis of the electrostatic complementarity of protein-protein interaction toward rational antibody design

○Hiroki Ozono[1], Takeshi Ishikawa[1] (1. kagoshima university)

[P01-1am-06] Computational Study of Azobenzene-based dye Covalently Attached to the Silane Coupling Agentes

○tatsuya takeshita[1] (1. Fukui Univ. of Tech.)

[P01-1am-07] Elucidation of Conduction Behaviors for Heteroatom-Containing π-Conjugated Single-Molecular Junctions by Using the Graph Theory

○Kazuki Okazawa[1], Yuta Tsuji[1], Kazunari Yoshizawa[1] (1. IMCE, Kyushu Univ.)

[P01-1am-08] Theoretical study of the methane activation on the surface of binary alloys with the combination of DFT calculation and chemoinformatics

○Masataka Yoshida[1], Masashi Saito[1], Yuta Tsuji[1], Takashi Kamachi[2], Kazunari Yoshizawa[1] (1. Kyushu University, 2. Fukuoka Institute of Technology)

[P01-1am-09] Elucidation of factors for the enhanced oxygen reduction activity of carbon-free connected Pt catalysts using first-principle calculation

○Mizuki Kamata[1], Hidenori Kuroki[1,2], Yuuki Sugawara[1], Hiroshi Ushiyama[3], Takeo Yamaguchi[1] (1. Tokyo Institute of Technology, 2. Kanagawa Institute of Industrial Science and Technology, 3. Research Organization for Information Science and Technology)

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分子動力学シミュレーションに基づく軽水及び重水に対する熱中性子散乱の理論研究

(原子力機構[1]・京大院工[2])○市原 晃[1]・安部 豊[2]

Theoretical Study of Thermal Neutron Scattering by Light and Heavy Water with Molecular Dynamics Simulation

([1]Nuclear Data Center, Japan Atomic Energy Agency, [2]Department of Nuclear Engineering, Kyoto University) ○Akira Ichihara,[1] Yutaka Abe[2]

Light and heavy water are used as moderators in fission reactors. Reliable information of thermal neutron scattering in these materials is fundamental to the analysis of reactor cores, where thermal neutrons may be defined as neutrons with kinetic energy around 0.025 eV. In this study we tried to compute angular distribution and energy spectrum of emitted neutrons theoretically. We evaluated them employing the data obtained from molecular dynamics simulations[1)], excluding normalization factors such as neutron scattering length. The simulations have been performed for light and heavy water. The thermal neutron scattering has been evaluated by using the fluctuation-dissipation theorem of statistical mechanics, where the trajectory data for hydrogen, deuterium and oxygen atoms were utilized. In calculation, incoherent scattering was assumed to be dominant in light water, while both the coherent and incoherent scattering contributions were considered in heavy water.

Keywords : molecular dynamics simulation; light water; heavy water; thermal neutron scattering

原子炉の減速材として、軽水及び重水が使用されている。これらに対する熱中性子散乱の信頼できるデータは、炉心解析にとって重要である。熱中性子は 0.025eV 程度の運動エネルギーを持つ中性子として特徴づけられる。本研究では、軽水や重水中で散乱される中性子の角度分布とエネルギースペクトルを理論的に計算することを試みた。これらは、熱中性子の散乱長といった規格化因子を除いて、分子動力学シミュレーションから得られる情報を利用して計算することができる[1)]。分子動力学シミュレーションを、軽水及び重水に対して実施した。統計力学の揺動散逸定理に基づき、軽水では非コヒーレント散乱、重水ではコヒーレント散乱と非コヒーレント散乱の両者の寄与を考慮し、シミュレーションで得た水素、重水素及び酸素原子のトラジェクトリーデータを利用して散乱データを求めた。

1)A. Ichihara, JAEA-Review 2019-046 (2020).

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超強酸 *in silico* 設計に向けた高精度量子化学計算と機械学習による気相酸性度予測

（中央大理工[1]・JST ACT-X[2]・分子研[3]）○鈴木 里麻[1]・黒木 菜保子[1,2]・森 寛敏[1,3]

Prediction of Gas Phase Acidity for *in Silico* Design of Super Acids with High Precision Quantum Chemical Calculations and Machine Learning ([1]*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*, [2]*JST ACT-X*, [3]*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science*) ○Rima Suzuki,[1] Nahoko Kuroki,[1,2] Hirotoshi Mori[1,3]

In semiconductor processing, it is necessary to design super acids having desired physicochemical properties according to the situation where they will be applied. In the engineering fields, there is a growing momentum breaking away from the traditional experiment-driven molecular design in which whole candidates are synthesized in brute force. We have performed a set of ab initio molecular orbital calculations to predict the gas phase acidities of various organic substances, which is the basis of superacid design. In this presentation, we will report on the possibility of "whether the gas phase acidity can be predicted quickly by the approach of electronic state informatics".

Keywords : Superacid; Gas Phase Acidity; Quantum Chemical Calculation; Machine Learning; Materials Informatics

半導体分野では、場面に応じ、所望の物性をもつ超強酸を設計せねばならない。当該分野では、「電子吸引性置換基を導入すると性能が向上する」という実験的経験則に基づき、候補物質を手当たり次第に合成する実験主導型分子設計が行われてきた。設計された超強酸の骨格は限定されており[1)]、大規模な探査によってより強い超強酸を発見することが可能であると考えられる。だが、超強酸分子を合成する際には、危険な作業を伴う。実験に先立ち、安全・高速・精密に目的の超強酸分子を設計するための、新たな理論分子設計指針が求められている。酸の pK_a 値は諸手法により、実測値と約 1 pK_a 程度の誤差により算出されているが、予め経験的な化合物種ごとの分類を必要とする[2)]。

我々は、超強酸設計の基礎となる気相酸性度制御法について、実測値が存在する約 1,000 化合物の高精度分子軌道法による系統調査を実施し、その精度評価を実施してきた。関連して、「電子状態インフォマティクスのアプローチにより気相酸性度を迅速予測できるか」を併せて検討したので、その可能性まで含めて報告する。

1)Equilibrium Acidities of Superadids. A. Kütt, et.al., *J. Org. Chem.* **2011**, *76*, 391.
2)プロトンの水和自由エネルギー:酸解離定数および標準水素電極電位の高精度計算 松井 亨, 喜屋武 茜, 庄司 光男, 重田 育照, *J. Comput. Chem. Jpn,* **2016**, *15*, 184.

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CO_2 化学吸収法に対するアミン混合溶液の理論設計

（早大先進理工[1]・早大理工総研[2]・京大 ESICB[3]）○清水 伊織[1]・長門 澄香[1]・藤波 美起登[1]・中井 浩巳[123]

Theoretical Design of Blended Amine Solution for CO_2 Chemical Absorption Method ([1]*School of Advanced Science and Engineering, Waseda University*, [2]*Waseda Research Institute for Science and Engineering, Waseda University*, [3]*Elements Strategy Initiative for Catalysts and Batteries, Kyoto University*) ○Iori Shimizu,[1] Sumika Nagato,[1] Mikito Fujinami,[1] Hiromi Nakai[123]

Chemical absorption method, which is one of the practical techniques to reduce CO_2 emission, uses amine solution to separate CO_2 from the exhaust gas. The discovery of efficient blended amine solution is desired to decrease thermal costs in the CO_2 regeneration process. The present theoretical study evaluates the thermal energies for 34 amines and their pairs, by estimating the enthalpy changes by the density functional tight-binding molecular dynamics (DFTB-MD) simulations and changes in amount of substance by the equilibrium model analysis, respectively.
Keywords : quantum mechanical molecular dynamics; carbon dioxide capture and storage; chemical absorption method

化学吸収法はアミン-CO_2 反応を利用した CO_2 排出量削減手法である。化学吸収法に用いられるアミン溶液には、CO_2 の吸収速度が速く、かつ、CO_2 再生過程の熱コストが小さいことが求められる。それを達成するために、2 成分混合アミン溶液がしばしば用いられる[1]。本研究では、34 種のアミンについて、2 成分混合アミン溶液におけるアミン-CO_2 反応の熱コストを評価し、化学吸収法に適したアミンの組を探索することを目指した。化学吸収法では、次式に示すように CO_2 はカルバメート（$RR'NCOO^-$）および重炭酸イオン（HCO_3^-）としてアミン溶液に吸収される。

$$R^1R^2R^3N + R^4R^5NH + CO_2 \rightleftarrows R^1R^2R^3NH^+ + R^4R^5NCOO^- \quad (1)$$

$$R^1R^2R^3N + CO_2 + H_2O \rightleftarrows R^1R^2R^3NH^+ + HCO_3^- \quad (2)$$

本研究では、混合アミン溶液における熱コストを次式の反応エンタルピーで評価した。

$$Q = \Delta H_{car}\Delta n_{car} + \Delta H_{bic}\Delta n_{bic} + Q_{rest} \quad (3)$$

ここで、$\{\Delta H_{car}, \Delta H_{bic}\}$は(1),(2)式の反応エンタルピーであり、密度汎関数強束縛分子動力学 (DFTB-MD) 法を用いて算出した。$\{\Delta n_{car}, \Delta n_{bic}\}$はカルバメートおよび重炭酸イオンの物質量変化であり、化学平衡を仮定したモデルにより見積った。

Table 1 に、Piperazine (PZ) および *N*-Methyldiethanol-amine (MDEA) の、ΔH_{car}, ΔH_{bic} を示す。Figure 1 に、混合系における CO_2 濃度に依存したカルバメートおよび重炭酸イオンの物質量変化を示す。横軸はアミン全量に対する CO_2 の吸収割合 (ローディング) を、縦軸は物質量を表す。ローディング幅 0.3〜0.6 での Q は −5.13 kJ/mol と求まった。

Table 1. ΔH of each amine [kJ/mol].

	ΔH_{car}	ΔH_{bic}
PZ	-89.1	-67.5
MDEA	-	-65.8

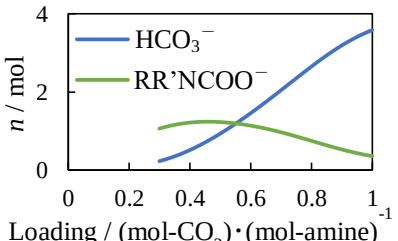

Figure 1. Loading curve of PZ + MDEA.

[1]S.Bishnoi and G. T. Rochelle, *AlChE J*, **48**, 2788(2002).

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日本化学会 第101春季年会 (2021)

ケギン型ポリオキソメタレート（$[XW_{12}O_{40}]^{n-}$）の形成反応経路に及ぼす溶媒の誘電率およびヘテロ原子の影響

（神戸大学[1]・国立研究開発法人理化学研究所[2]）○阿久根 昌彦[1]・枝 和男[1]・大堺 利行[1]・中嶋 隆人[2]

Effect of solvent permittivity and heteroatoms properties on the formation pathways of Keggin-type polyoxometalates ($[XW_{12}O_{40}]^{n-}$) ([1] *Kobe University*, [2] *RIKEN*) ○Masahiko Akune,[1] Kazuo Eda,[1] Toshiyuki Osakai,[1] Takahito Nakajima [2]

Polyoxometalates (POMs) are expected to be catalysts for multi-electron transfer reactions. Our previous studies have shown that Keggin-type POMs (K-POMs, $[XM_{12}O_{40}]^{n-}$) having a large and lower charged cation as a heteroatom X^{m+} may exhibit multi-electron transfer [1]. However, we predict it is difficult to synthesize such K-POMs, and have thus investigated the synthetic reaction by using quantum chemical calculations to obtain the information about synthetic conditions suitable for the synthesis. The calculations were performed for the hydrolysis of Anderson-type POMs（A-POMs, $[XW_6O_{24}H_6]^{n-}$）[2], which is the initial step of the formation processes of K-POMs. The calculation level used was ωB97XD/Def2-SVP, and the effective core potential was used for W^{6+} and Cd^{2+}. The effects of solvent permittivity were also examined by using COSMO.

According to the calculation results, the solvent permittivity suitable for stabilizing Keggin type precursor varied depending on the kind of heteroatoms. The reaction barrier was about 200 kJ mol^{-1} for the system of $X^{m+} = Cd^{2+}$ (a large and lower charged atom). This value was high, but comparable to that for $X^{m+} = Si^{4+}$ (an usual heteroatom of K-POMs). These findings have suggested that K-POM with $X^{m+} = Cd^{2+}$ may be synthesized.

Keywords : Polyoxometalates, Quantum chemistry calculations, Reaction Path Search

ポリオキソメタレート (POM) は多電子移動反応の触媒として期待されており、先行研究によりイオン半径が大きく、電荷の小さなヘテロ原子 X^{n+}を構造中に持つ Keggin 型 POM(K-POM, $[XM_{12}O_{40}]^{n-}$) は多電子移動を起こしやすいことが明らかにされている[1]。しかし、そのような K-POM を合成するのは難しいことが予想されるため、どのような条件が合成に適するのかを、量子化学計算を用いて調べた。計算対象は、K-POM の生成初期過程にあたる Anderson 型 POM（A-POM, $[XW_6O_{24}H_6]^{n-}$）の加水分解反応[2]とし、$X^{n+} = Al^{3+}, Si^{4+}, P^{5+}, S^{6+}, Cd^{2+}$ とした。計算レベルはωB97XD/Def2-SVP で W^{6+}と Cd^{2+}に有効内核ポテンシャルを使用し、溶媒からの誘電率の効果は COSMO 法を用いて取り入れた。

計算の結果、溶媒の誘電率による Keggin 型前駆体の安定化の程度はヘテロ原子によって異なることがわかった。また、Cd^{2+} の場合、反応障壁は約 200 kJ mol^{-1} と高かったが、K-POM の一般的なヘテロ原子として知られている Si^{4+} の場合と同程度の活性化エネルギーを有することが明らかとなり、$X^{n+} = Cd^{2+}$ とする K-POM が合成されうることが示唆された。

1) K. Nakajima, K. Eda, S. Himeno, *Inorg. Chem*., **49**, 5212 (2010)

2) S. Himeno, S. Murata, K. Eda, *J. Chem. Soc., Dalton Trans.*, 6114 (2009)

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抗体医薬品開発を目指したFMO法に基づくタンパク質間相互作用解析法の開発と応用

（鹿大院理工[1]）○大園 紘貴[1]・石川 岳志[1]

Development and application of FMO-based analysis of the electrostatic complementarity of protein-protein interaction toward rational antibody design ([1] *Graduate School of Science and Engineering, Kagoshima University*) ○Hiroki Ozono,[1]Takeshi Ishikawa,[1]

Analysis of protein-protein interactions (PPI) is an important issue for development of antibody drugs. Here, we have developed a new method for analyzing PPIs using fragment molecular orbital (FMO) method. In our method, the PPI interface is defined by using the electron density obtained from the FMO calculations, and electrostatic complementarity of the PPI is analyzed by the FMO-based electrostatic potential. As an illustrative example, we analyzed the immune checkpoint molecules (PD-1/PD-L1) and their inhibitors (Nivolumab and Pembrolizumab), by which high affinity and target specificity of inhibitors were clearly shown.

Keywords: fragment molecular orbital method; protein-protein interaction; immune checkpoint; electrostatic potential; electrostatic complementarity

抗体医薬品開発において抗体と標的のタンパク間相互作用(PPI)を詳細に理解することは重要である。しかし、抗体と標的タンパクの接触面は広く、複雑に相互作用をしているため、従来の計算化学の手法で解析するのは困難である。そこで我々は、フラグメント分子軌道(FMO)法[1]を利用した新たな PPI 解析法[2]を開発している。我々の解析法では、まず、複合体を形成する 2 つのタンパク質の電子密度が互いに等しくなる面を接触面とする。次に、接触面における各タンパク質の静電ポテンシャルを可視化する。最後に、可視化された静電ポテンシャルの相補性を定量化することで、接触面における複雑な相互作用を解析する。

本研究では、この解析方法を免疫チェックポイントの PD-1/PD-L1 複合体、及び PD-1 を標的とする抗体医薬品ニボルマブとペンブロリズマブの複合体に応用した。得られた静電ポテンシャルを Fig.1 に示す。これらに対して静電的相補性を定量化した結果、すべての複合体において接触面の約 90%が引力相互作用であり、親和性の高さを反映していると考えられる。又、複雑な静電ポテンシャルが相補的に一致する様は、特異性の高さを反映してると考えられる。

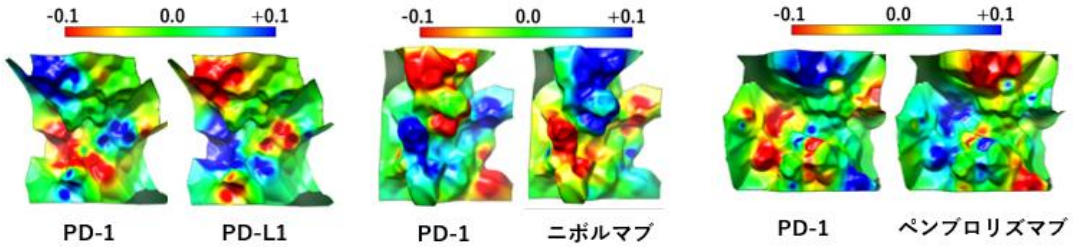

Fig.1　FMO 計算によって得られた接触面における静電ポテンシャル

[1] K. Kitaura, et al., Chem. Phys. Lett., 313 (1999) 701.

[2] T. Ishikawa, Chem. Phys. Lett., 761 (2020) 138103.

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量子化学計算によるアゾベンゼン色素－シランカップリング剤の物性予測

（福井工大）○竹下 達哉
Computational Study of Azobenzene-based dye Covalently Attached to the Silane Coupling Agents (Faculty of *Environmental and Information Sciences, Fukui University of Technology*)
○Tatsuya Takeshita

In this study, computational investigation was carried out on azobenzene-based dye covalently attached to silane coupling agents (SCAs). The potential of azobenzene-based dye covalently attached to SCAs (Azo-SCAs) to act as a photosensitizing dye was analyzed. Time-dependent density functional theory and frontier molecular orbital calculations revealed that Azo-SCAs has excellent optical properties and electron injection ability. These findings enhance the understanding of the covalent attachment strategy using SCAs and contribute to improving photocatalytic activity of titanium dioxide-based photocatalysts and photovoltaic conversion efficiency of dye-sensitized solar cells.
Keywords : Azobenzene; Silane Coupling Agents; Titanium Dioxide; Dye-Sensitized Solar Cell; DFT calculation

シランカップリング剤(SCAs)は異種材料間の接着や表面改質などに使用される材料であり、酸化チタン(TiO_2)の光触媒活性や色素増感太陽電池(DSSC)の耐久性の向上などにも用いられている[1)]。本研究では、オキシラン基を有する SCAs (OTES)と共有結合した 4-[(*E*)-(4-methoxyphenyl)diazenyl]-1-naphthalenamine (*E*-MPDNA-OTES)が TiO_2 や DSSC の光増感色素として機能する可能性を明らかにするために、量子化学計算による物性予測を実行した。

TiO_2 クラスター上における *E*-MPDNA-OTES の HOMO および LUMO を Fig. 1 に示す。HOMO は *E*-MPDNA 全体と第二級アミン部位に分布していた。一方で、LUMO はシリルアンカーと結合した Ti 原子周辺に分布していることが確認された。この結果より、*E*-MPDNA から TiO_2 への電子注入が生じることが明らかとなった。すなわち、*E*-MPDNA-OTES が TiO_2 や DSSC の光増感色素として機能することが明らかとなった。

当日は、*E*-MPDNA-OTES のコンフォマー、紫外可視吸収スペクトル、分子軌道、*Z*-MPDNA-OTES の物性などにつても合わせて報告する。

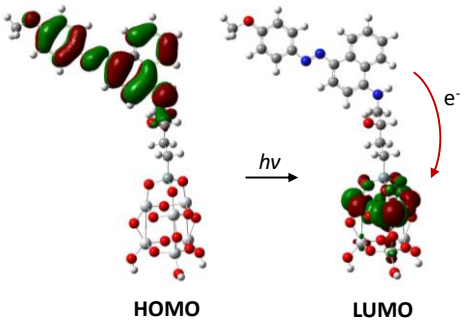

Fig. 1 HOMO and LUMO of *E*-MPDNA-OTES adsorbed on the TiO_2 cluster using CPCM in EtOH. Calculations were carried out at the B3LYP/6-31G*/LanL2DZ level of theory. Surface isovalue: 0.02 e/bohr^3.

1) Luitel, T.; Zamborini, F.P. Covalent Modification of Photoanodes for Stable Dye-Sensitized Solar Cells. *Langmuir* **2013**, *29*, 13582-13594.

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グラフ理論を用いたヘテロ原子含π共役単分子接合における伝導挙動の解明

（九大先導研）○岡澤 一樹・辻 雄太・吉澤 一成

Elucidation of Conduction Behaviors for Heteroatom-Containing π-Conjugated Single-Molecular Junctions by Using the Graph Theory (*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Kazuki Okazawa, Yuta Tsuji, Kazunari Yoshizawa

One of the unique electron transport properties in single-molecule junctions is the interference between transport electrons, called quantum interference (QI), which is caused by the wave-particle duality of electrons. There are two types of QI: one is the constructive QI, which occurs when the electron phases are the same, and the other one is the destructive QI, which occurs when the electron phases are opposite. Whether the constructive or the destructive QI occurs depends on which atoms in the molecule are connected with the electrodes on the junction. To predict whether the destructive QI occurs or not for a specific connection mode in the junction, graph-theoretic path-counting approaches have been proposed. However, this method cannot be applied to molecules containing heteroatoms. In this study, we have extended the theory based on the Hückel method and the Sachs formula.

Keywords : Graph Theory; Single-Molecular Junction; Quantum Interference

π共役分子を用いた単分子接合では，電子の波動性に由来する量子論的な影響が非常に顕著であり，特異な伝導特性が観測される。単分子接合における特異な伝導特性は，フロンティア軌道論やグラフ理論に基づいたアプローチによって予測可能である[1]。辻らは交互炭化水素からなる単分子接合において，２つの電極が接続された炭素原子間の経路の歩数を数えることで伝導特性を予測する方法をグラフ理論に基づいて示した[2]。しかし，この方法はヘテロ原子を含んだ分子には適用することができない。そこで我々は，交互炭化水素中の１つの炭素原子をヘテロ原子に置換した単分子接合における伝導特性の解明をグラフ理論に基づいて行った。また，グラフ理論に基づく予測の妥当性を検証するため，非平衡 Green 関数法を用いていくつかの分子について実際に伝導度の計算を行った。これらの詳細については当日発表する。

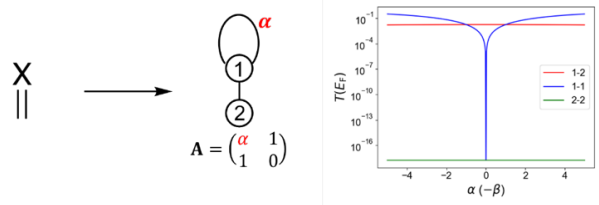

Figure 1. Hetero-containing ethylene derivative with its molecular graph representation and adjacency matrix (left); Transmission probabilities for the three connection modes are plotted as a function of the Coulomb integral of the hetero atom X (right).

参考文献

[1] K. Yoshizawa, T. Tada, A. Staykov, *J. Am. Chem. Soc.* **2008**, *130*, 9406–9413.
[2] Y. Tsuji, E. Estrada, R. Movassagh, R. Hoffmann, *Chem. Rev.* **2018**, *118*, 4887–4911.

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Informatics study on Methane Activation on binary alloy

([1]*Institute for Materials Chemistry and Engineering, Kyushu University*, [2]*Department of Life, Environment and Materials Science, Fukuoka Institute of Technology*) ○Masataka Yoshida,[1] Masashi Saitou,[1] Takashi Kamachi,[2] Yuta Tsuji,[1] Kazunari Yoshizawa[1]

Keywords: Machine learning; Methane activation; Binary alloy; DFT calculation;

In the current steam reforming process, the surface of nickel is mainly used as a catalyst due to its high reactivity and low cost. As shown in figure 1, Blaylock et al. used DFT calculations to examine the C-H bond cleavage of methane on the Ni(111) surface.[1] The nickel surface can cleave the strong C-H bond of methane, and further cleaving the C-H bonds produces CH*, the most energetically stable adsorbate of CH_n* (n=1-4). By using heterogeneous catalyst that stabilize CH_3* rather than CH*, it is expected that the intermediate CH_3* will have a longer lifetime and coking will be suppressed. Based on this idea, we explored various binary alloys that enables the direct conversion of methane by a combination of DFT computation[2] and catalyst informatics.

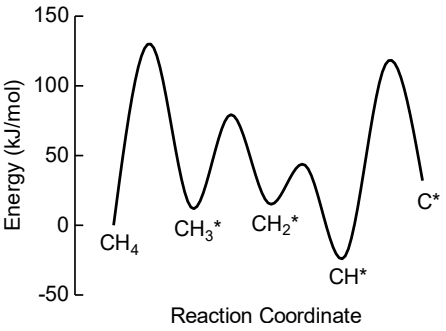

Figure 1. Energy diagram for the C–H bond cleavage of methane on the Ni(111) surface. Data were taken from ref. 1.

The structure of each alloy was obtained from AFLOW[3], the calculation database based on the Vienna ab initio simulation package (VASP). The surface energies of the low index planes of all alloys in the database were calculated by using CASTEP, and the lowest-energy surface was used for subsequent calculations. VASP was used for geometrical optimization of adsorption structures of CH_3* and CH*. We calculated the adsorption energy of CH_3* and CH* on each alloy surface, and evaluated the stability of CH_3* versus CH*. The genetic algorithm-based partial least squares (GA-PLS) regression is used to search effective catalyst.

310 alloys were retrieved from the AFLOW database. The stability of CH_3* against CH* for 88 alloys was calculated. The GA-PLS regression model which predicts the reaction enthalpy ($CH_4 \rightarrow CH_3$*+H*) and the stability of CH_3* versus CH *, was built with 88 training data. The coefficient of determination obtained by LOO-CV was 0.625 for the former and 0.622 for the latter. The model predicted that 26 of the 222 alloys not included in the training dataset would satisfy both conditions. (shown in Figure 2)

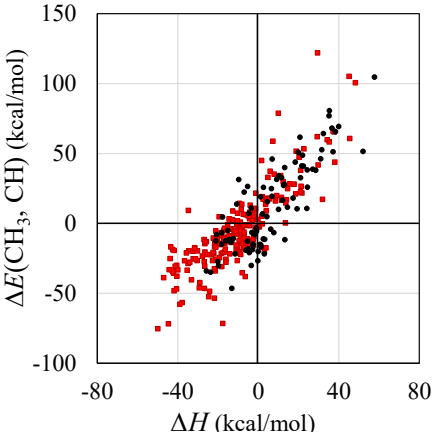

Figure 2: Predicted values of ΔE(CH_3, CH) and ΔH by PLS regression. ● means predicted values and ■ means data values contained in the training dataset.

1) D. W. Blaylock, T. Ogura, W. H. Green, G. J. O. Beran, *J. Phys. Chem. C,* **113**, 4898 (2009). 2) T. Kamachi, et al. *J. Comput. Chem. Jpn.*, **16**, 147 (2017). 3) Automatic FLOW for Materials Discovery Home Page. http://aflowlib.org/

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第一原理計算を用いたカーボンフリーPt ナノ粒子連結触媒の酸素還元活性向上要因の解明

(東京工業大学[1]・神奈川県立産業技術総合研究所[2]・高度情報科学技術研究機構[3])
○蒲田瑞季[1]・黒木秀記[1,2]・菅原勇貴[1]・牛山浩[3]・山口猛央[1]

Elucidation of factors for the enhanced oxygen reduction activity of carbon-free connected Pt catalysts using first-principles calculation

([1]*Tokyo Institute of Technology*, [2]*Kanagawa Institute of Industrial Science and Technology (KISTEC)*, [3]*Research Organization for Information Science and Technology (RIST)*) ○Mizuki Kamata,[1] Hidenori Kuroki,[1,2] Yuuki Sugawara,[1] Hiroshi Ushiyama,[3] Takeo Yamaguchi[1]

The development of highly active oxygen-reduction-reaction (ORR) catalysts is required to spread the use of polymer electrolyte fuel cells. We have developed carbon-free connected Pt-based catalysts (Pt capsule) comprising of nanonetworks formed by the connection of Pt-based nanoparticles (Fig. 1a).[1)] The connected Pt catalyst shows four times higher ORR specific activity than a conventional carbon-supported Pt nanoparticle catalyst (Pt/C); however, the factors in the enhanced activity are not yet clarified (Fig. 1b). In this study, we constructed various models that simulated the structures of a carbon-free connected Pt catalyst and Pt/C to evaluate the adsorption energies of ORR intermediates (oxygen and water) on Pt atoms using first-principles calculation. As a result, we found out that the presence of carbon support would affect the adsorption of oxygen on the Pt atoms, indicating that a carbon-free structure is an important factor for an enhanced ORR activity.

Keywords : First-principles Calculation; Oxygen Reduction Reaction; Fuel Cells

固体高分子形燃料電池の普及拡大のため、酸素還元反応(ORR)触媒の高活性化が求められている。本グループは、Pt 系ナノ粒子が連結したナノネットワークで構成されるカーボンフリーPt 系ナノ粒子連結触媒(Pt capsule)を開発している(図 1a)[1)]。Pt ナノ粒子連結触媒は、従来の Pt ナノ粒子担持カーボン(Pt/C)より 4 倍高い ORR 表面比活性を示すが、その要因は明らかとなっていない(図 1b)。そこで、本研究ではカーボンフリーPt ナノ粒子連結触媒と Pt/C の触媒構造を模擬した様々なモデルを構築し、Pt 上での ORR 中間体(酸素や水)の吸着エネルギーを第一原理計算により評価した。その結果、カーボン担体の存在が Pt 上への酸素種吸着エネルギーに影響することが分かり、カーボンフリー構造は ORR 高活性化に重要であることが示唆された。

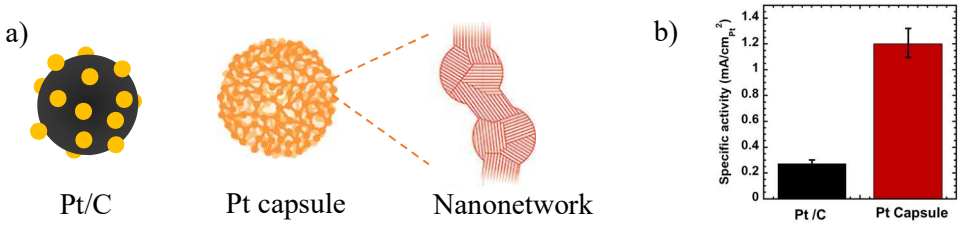

図 1 a) Schematics of Pt/C and Pt capsule catalysts, and b) ORR activity of the catalysts

[Acknowledgment] Part of this presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

1) T. Yamaguchi, *et al.*, *Energy Environ. Sci.*, 2015, **8**, 3545–3549.

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Academic Program [Poster] | 03. Physical Chemistry -Structure- | Poster

[P02-1am] 03. Physical Chemistry -Structure-

Fri. Mar 19, 2021 9:40 AM - 11:10 AM Area 2 (Online Meeting)

[P02-1am-01] Diffusion process of chlorobenzophenones probed by transient grating method

○Wataru Kashihara[1], Sotaro Hiramoto[1], Tadashi Suzuki[1] (1. Grad. Sch. Sci., Eng., Aoyama Gakuin Univ.)

9:40 AM - 11:10 AM

[P02-1am-02] Electronic structures of weakly exchange coupled systems with trityl and nitroxide radicals as studied by cw/pulsed ESR spcetroscopy

○Kazunobu Sato[1], Rei Hirao[1], Kenji Sugisaki[1], Hideto Matsuoka[1], Kazuo Toyota[1], Daisuke Shiomi[1], Elena Zaytseva[2], Victor M. Tormyshev[2], Elena Bagryanskaya[2], Takeji Takui[1] (1. Osaka City University, 2. Nobosibirsk Institute of Organic Chemistry)

9:40 AM - 11:10 AM

[P02-1am-03] Structures of Terephthalamide Networks on Graphite (0001)

○Takeshi Okamatsu[1], Toshihide Kaneko[1], Takato Suzuki[1], Hiroto Sato[1], Koki Imahayashi[1], Hayato Sanada[1], Osamu Endo[1], Hiroyuki Ozaki[1] (1. Tokyo University of Agriculture and Technology)

9:40 AM - 11:10 AM

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過渡回折格子法によるクロロベンゾフェノンの拡散過程

（青山学院大院理工）○柏原航・平本宗太郎・鈴木正
Diffusion process of chlorobenzophenones probed by transient grating method (*Grad. Sch. Sci., Eng., Aoyama Gakuin Univ.*) ○Wataru Kashihara, Sotaro Hiramoto, Tadashi Suzuki

Molecular diffusion in solution provides important information of reactivity in various chemical reactions. The Stokes-Einstein equation shows that there is a correlation between the diffusion coefficient and the molecular radius. However, the molecular diffusion depending on the structure of the molecule is still not understood in detail.

In this study, we investigated the molecular diffusion process of chlorobenzophenone using the transient grating method. It was found that the diffusion coefficient of translational diffusion by 2-chlorobenzophenone becomes smaller than that of other isomers. In addition, 2-chlorobenzophenone had a significantly larger torsion of the two phenyl rings were found by the quantum chemical calculation. These results indicate that the decrease in planarity leads to a decrease in the diffusion coefficient. This study would show the molecular diffusion is greatly influenced by the difference in molecular structure.

Keywords : Benzophenone; Transient grating method; Diffusion coefficient; Molecular structure

溶液中での分子拡散は、種々の化学反応における反応性を議論するうえで重要な知見を与える。ストークス・アインシュタインの式では、分子拡散の大きさを表す拡散係数と、分子の大きさ（分子半径）に相関があることを示している[1]。しかしながら、分子の構造がどのように分子拡散に影響を及ぼすかについては、現在でも詳しく理解されていない。

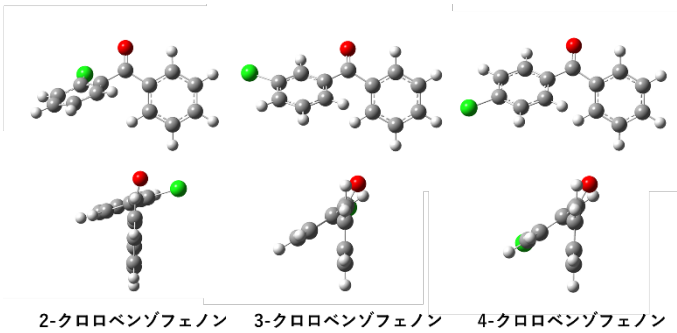

図 1. クロロベンゾフェノンの分子構造

本研究では過渡回折格子法を用いて、クロロベンゾフェノンの分子拡散過程を調べた。ベンゾフェノンの 2 位にクロロ基の置換したとき、並進拡散の拡散係数が他の異性体(3 位と 4 位にクロロ基を置換したもの)と比べて小さくなることが分かった。また、量子化学計算の結果から、2 位にクロロ基を置換したベンゾフェノンのみ、2 つのフェニル環のねじれが顕著に大きくなり平面性が低下した。以上より、平面性が低下することにより、拡散係数が小さくなることが考えられる。この結果は、分子拡散の大きさは分子構造の違いに大きく影響していることを指摘するものである。

1) John T. Edward, *J. Chem. Educ.* **1970**, *47*, 261

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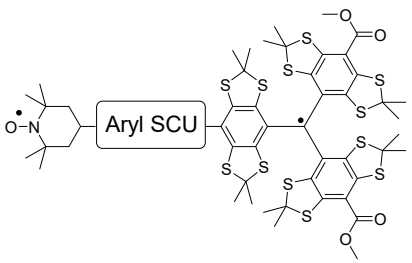
cw 及びパルス ESR 法によるトリチルラジカルとニトロキシドラジカルが連結した弱交換相互作用ビラジカルの電子状態

(阪市大院理[1]・ノボシビルスク有機化学研[2]) ○佐藤和信[1]・平生怜[1]・杉崎研司[1]・松岡秀人[1]・豊田和男[1]・塩見大輔[1]・Elena Zaytseva[2]・Victor M. Tormyshev[2]・Elena Bagryanskaya[2]・工位武治[1]
Electronic structures of weakly exchange coupled systems with trityl and nitroxide radicals as studied by cw/pulsed ESR spcetroscopy ([1]*Graduate School of Science, Osaka City University*, [2]*Nobosibirsk Institute of Organic Chemistry SB RAS*) ○Kazunobu Sato[1]・Rei Hirao[1]・Kenji Sugisaki[1]・Hideto Matsuoka[1]・Kazuo Toyota[1]・Daisuke Shiomi[1]・Elena Zaytseva[2]・Victor M. Tormyshev[2]・Elena Bagryanskaya[2]・Takeji Takui[1]

Trityl and nitroxide radicals that are connected by π-topologically controlled aryl linkers have been studied by cw and pulsed ESR spectroscopy. ESR spectra of the radicals showed spectral pattern separated by exchange interaction between two electron spin moieties. The splitting by the exchange interaction was confirmed by using multifrequency ESR spectroscopy. They serve as typical models for biradicals in which the exchange (*J*) and hyperfine interactions compete with the *g*-difference electronic Zeeman interactions. The *g*-engineered biradicals have been also tested as a prototype for AWG (Arbitrary Wave Generator) based spin manipulation techniques, which enable GRAPE (GRAdient Pulse Engineering) microwave control of spins in molecular magnetic resonance spectroscopy for use in molecular spin quantum computers, demonstrating efficient signal enhancement of specific weakened hyperfine signals.
Keywords : Arbitrary waveform pulsed ESR; Weakly exchange coupled biradical; Trityl radical; Nitroxide radical; Multifrequency ESR

分子スピン系における電子・核スピンは, 代表的な量子情報リソースの一つである。分子内のスピンを量子ビットとする量子情報処理を目的として、新しい量子アルゴリズムの開発と共に実装研究を進めている。近年のマイクロ波技術の発展により様々な任意波形パルスを用いた量子状態制御が実現可能となっている。本研究では、多電子スピン系への拡張と精密制御を実現するため、弱く交換相互作用する 2 電子スピン系 **1**, **2** を合成し、任意波形マイクロ波技術による量子スピン制御を行った[1)]。

ニトロキシドラジカルとトリチルラジカルがアリール基で架橋された分子 **1**、**2** は、溶液中でそれぞれ各々の ESR 遷移が 6.4、3.7 MHz の大きさで分裂するスペクトルを示した。多周波 ESR 法を適用することにより、この分裂が磁場の大きさに依存しないことを示し、2 電子スピン間の交換相互作用によるものであることを明らかにした。また、任意波形マイクロ波パルスを用いて、2 電子スピン系 **1**、**2** の ESR スペクトルが制御できることを実証した。発表では、多周波 ESR スペクトルの解析による **1**、**2** の電子状態の考察とともに、パルス波形によるスピン応答について報告する。



Aryl SCU = *p*-Phenylene (**1**)
or 2,7-naphthenylene (**2**)

1) K. Sato, E. Bagryanskaya, T. Takui et al. *J. Phys. Chem. A*, **2019**, *123*, 7507-7517 (2019).

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グラファイト (0001) 面上のテレフタルアミドネットワークの構造

(東京農工大院工[1]・工[2]) ○岡松傑[1]・兼子俊英[1]・鈴木敬人[1]・佐藤拓人[2]・今林光輝[1]・真田隼登[1]・遠藤理[1]・尾﨑弘行[1]

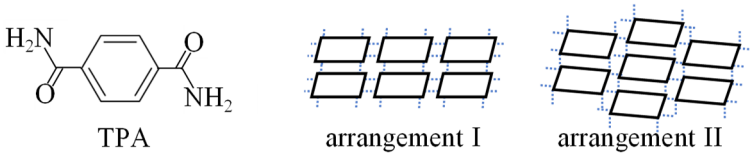
Structures of Terephthalamide Networks on Graphite (0001)

([1]*Graduate School of Engineering and* [2]*Faculty of Engineering, Tokyo University of Agriculture and Technology*) ○Takeshi Okamatsu[1], Toshihide Kaneko[1], Takato Suzuki[1], Hiroto Sato[2], Koki Imahayashi[1], Hayato Sanada[1], Osamu Endo[1], Hiroyuki Ozaki[1]

Upon deposition onto a graphite cleavage plane under ultrahigh vacuum, most planar molecules belonging to the D_{3h} or C_{3h} point group and having plural groups capable of hydrogen bonding (HB) are laid flat and gathered to form various isotropic networks (NWs)[1,2]. However, 1,3,5-benzenetricarboxamide are slightly tilted and partially overlapped with one another to make a complicated anisotropic NW.[3] We examine here the NWs of terephthalamide (TPA) containing fewer carbamoyl groups. Scanning tunneling microscopy reveals two molecular arrangements I and II: HB along the molecular long axis (HB^L) forms tapelike aggregates and HB along the short axis (HB^S) pastes the tapes in the former; HB^L and HB^S bridge a molecule to four and two neighbors, respectively, in the latter. Though angle between the unit vectors differs for arrangements I and II, the lengths are almost the same and the benzene rings must be twisted from the carbamoyl NW. Arrangement I is in agreement with a structure optimized by the first-principles calculations under periodic boundary conditions.
Keywords : Terephthalamide network; Vapor-deposited monolayer; Graphite; Hydrogen bonding; Scanning tunneling microscopy

超高真空下でグラファイトの劈開面に水素結合 (HB) 性基を複数持つ平面有機物を蒸着すると、横たわった分子間に HB が導入されてネットワーク (NW) 構造が生成する。D_{3h}・C_{3h} 分子は通常等方的な 2 次元 NW を与えるが [1]、1,3,5-ベンゼントリカルボキサミドは傾いて異方的で複雑な NW を生ずる [2]。本研究ではカルバモイル基が少ないテレフタルアミド (TPA) がつくる NW の構造を検討した。

STM 観察により 2 種類の配列 I と II が見出された。配列 I では分子の長軸方向の HB (HB^L) によりテープ状会合体が生じ、短軸方向の HB (HB^S) でテープが貼り合わされるのに対して、配列 II では各分子を HB^L が 4 つ、HB^S が 2 つの隣接分子と結ぶ。両配列の格子ベクトルは成す角が異なるが長さはほぼ同じであり、ベンゼン環はカルバモイル NW から捻れる。配列 I は 2 次元周期的境界条件を課した第 1 原理計算による最適化構造と良く対応する。NW 化による TPA の電子構造の改変を検討中である。



1) K. Kannappan et al., *J. Phys. Chem. B* **2007**, 111, 6634−6642. 2) S. Griessl et al., *Single Mol.* **2002**, 3, 25−31. 3) S. Yamazaki et al., *J. Phys. Chem. C* **2013**, 117, 9652−9662.

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Academic Program [Poster] | 04. Physical Chemistry -Properties- | Poster

[P03-1am] 04. Physical Chemistry -Properties-

Fri. Mar 19, 2021 9:40 AM - 11:10 AM Area 3 (Online Meeting)

[P03-1am-01] Study of magnetic property on a surface of magnetic thin film of iron hexacyanochromate

○Shuntaro Nagashima[1], Yuji Yahagi[1], Kosuke Nakagawa[2], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. The Univ. of Tokyo)

[P03-1am-02] Mode order dependence of the Rabi splitting in molecular vibrational polaritons

○Garrek Stemo[1], Jonas Paletscheck[2], Hiroyuki Katsuki[1], Hisao Yanagi[1] (1. Nara Institute of Science and Technology, 2. University of Regensburg)

[P03-1am-03] Preparation and property of Azulene-1-CONHCH$_2$SO$_3^-$ and its charge-transfer salt

○Taiki Oyama[1], Hiroki Akutsu[2], Yasuhiro Nakazawa[2] (1. Osaka University, 2. Osaka Univ.)

[P03-1am-04] Electronic states of unsymmetrical platinum complexes with square planar coordination of 2,2’-bipyridine derivatives and dithiolene ligands and their application to conducting materials

○Mizuki Yumino[1], Yuna Kim[2], Tomofumi Kadoya[1], Jun-ichi Yamada[1], Kazuya Kubo[1] (1. Graduate School of Material Science, University of Hyogo, 2. Research Institute for Electronic Science, Hokkaido University)

[P03-1am-05] Synthesis and Femtosecond Spectroscopic Study of CdSe/CdTe Core/crown Nanoplatelets

○Haruka Nagasawa[1], Naoto Tamai[1], Daichi Eguchi[1] (1. Kwanseigakuin University Graguate School)

[P03-1am-06] Synthesis and properties of supramolecular organic conductors based on the novel iodine-containing π-donor IETSe

○Chihiro Yamabe[1], Tatsuro Imakubo[1] (1. Nagaoka Univ. of Tech.)

[P03-1am-07] The structure of the excited states and relaxation dynamics of an organic luminescence material showing dual emission

○Tomohiro Ryu[1], Yuushi Shimoda[1], Masaki Saigo[1], Ryota Fukuda[1], Kiyoshi Miyata[1], Youichi Tsuchiya[2], Hajime Nakanotani[2], Chihaya Adachi[2], Ken Onda[1] (1. Kyushu University, 2. OPERA, Kyushu University)

[P03-1am-08] Elementary exciton dynamics of cadmium-free blue-emitting InGaP quantum dots.

○hiroki kitajima[1], Yurina Yamaguchi[1], Ayana Fujitaka[1], Daichi Eguchi[1], Naoto Tamai[1] (1. Kwanseigakuin University Graguate School)

[P03-1am-09] Structures and physical properties of radical anion salts of TCNQ derivatives with *N*-alkylated DABCO as a counter cation

○Ogawa Ryohei[1], Kohdai Ishida[1], Manabu Ishikawa[1], Shota Okamato[1], Yoshiaki Nakano[1], Akihiro Otsuka[1], Hideki Yamochi[1] (1. Kyoto University)

[P03-1am-10] Synthesis and Photostability of New Pentacene Derivatives with Radical Substituent controlled the Excited Spin-State by π-Topology

○Nishiki Minami[1], Keijiro Maeguchi[1], Ken Kato[1], Kohei Yoshida[1], Akihiro Shimizu[1], Genta

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Kashima[2], Yoshio Teki[1] （1. Osaka City Univ., Grad. School of Sci., 2. Osaka City Univ., Sci.）

[P03-1am-11] Development of Novel Organic Conductors Using Iodine-bonded π-Donor IDMe-TSeF

○VERT E[1], Tatsuro Imakubo[1] （1. Nagaoka Univ. of Tech.）

[P03-1am-12] Cell culture and preparation of molecular nanocoil scaffolds composed of TTF derivatives with chiral units

○Tamaki Nishimura[1], Yuka kanno[1], Sadafumi Nishihara[2], Tomoyuki Akutagawa[3], Takayoshi Nakamura[4], Yoko Tatewaki[1] （1. Tokyo University of Agriculture and Technology, 2. Hiroshima University, 3. Tohoku University, 4. Hokkaido University）

[P03-1am-13] Crystal structure and physical properties of radical cation salts of triptycene
derivatives annulated with thianthrene skeletons

○Takuma YOSHIYUKI[1], Yoshiaki SHUKU[1], Kunio AWAGA[1] （1. Nagoya Univ.）

[P03-1am-14] Proton conductivity of imidazole containing phosphonic acid-modified mesoporous silica

○Ryoka Asano[1], Yasuhiro Shigeta[3], Takuya Kurihara[2], Shogo Amamori[3], Tomonori Ida[2], Motohiro Mizuno[2,3] （1. School of Chemistry, College of Science and Engineering, Kanazawa University, 2. Graduate School of Natural Science and Technology, Kanazawa University, 3. Nanomaterials Research Institute, Kanazawa University）

[P03-1am-15] Analysis of Proton Conduction Mechanism in Alginic Acid-Polyacrylic Acid-Triazole Composites

○Ryota Watanabe[1], Takuya Kurihara[1], Yasuhiro Shigeta[2], Shogo Amemori[2], Tomonori Ida[1], Motohiro Mizuno[1,2] （1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nanomaterials Research Institute, Kanazawa University）

[P03-1am-16] Proton Conductivity of Phosphonic Acid Group-Modified MCM-41 / Imidazole Composites

○yuta arai[1], Takuya Kurihara[3], Yasuhiro Shigeta[2], Shogo Amemori[2], Tomonori Ida[3], Motohiro Mizuno[1,2,3] （1. Graduate School of Frontier Science Initiative, Kanazawa University, 2. NanoMaterials Research Institute, 3. Graduate School of Natural Science and Technology, Kanazawa University）

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Study of magnetic property on a surface of magnetic thin film of iron hexacyanochromate

([1]*Depatment of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba,* [2]*Department of Chemistry, School of Science, The University of Tokyo*)
○S. Nagahima[1], Y. Yahagi[1], K. Nakagawa[2], S. Ohkoshi[2], H. Tokoro[1]
Keywords: Cyano-bridged bimetal assemblies, molecular-based magnets

Introduction: Magnetic domain is one of the most important property of magnetic materials. Up to now, molecular-based magnets have been studied vigorously since they can exhibit various magnetic functionalities.[1)] However, magnetic domain of molecular-based magnets has not been studied. In this work, we synthesized an iron chromate hexacyanochromate as a magnetic thin film.[2)] The surface morphology, the magnetic properties, and the magnetic domain of the film are reported.

Experiment: The target films composed of $(Fe^{II}_{x}Cr^{II}_{1-x})[Cr^{III}(CN)_6]_{2/3}\cdot zH_2O$ were prepared by reducing aqueous solutions containing Fe^{III}, Cr^{III}, and $K_3[Cr^{III}(CN)_6]$. When the reduction potential was kept at -800 mV (vs. Ag/AgCl) and electrical capacity of 600 mC was loaded, metal cyanides was deposited on an electrode surface as a film. Sample characterization and magnetic property was measured by IR spectrum, and SEM images, AFM images, and SQUID magnetometer. In addition, surface magnetic domain is observed by MFM.

Result: For the sample of $x = 0.175$, a strong IR peak was observed at 2180 cm^{-1}. This peak can be assigned to the CN stretching mode due to the mixture of Fe^{II}-NC-Cr^{III} and Cr^{II}-NC-Cr^{III}. SEM images of the obtained film exhibited a smooth surface, and the average crystalline size was about 0.52 μm ± 0.14 μm (Fig.1 (a), (b)). The images were consistent with the AFM images (Fig.1 (c)). The magnetization vs temperature curves exhibited the T_C at 222 K, and compensation temperature, T_{comp}, at 134 K. The MFM image at 175 K showed the ferromagnetism, i.e., N and S magnetic poles were observed as light and dark contrast.

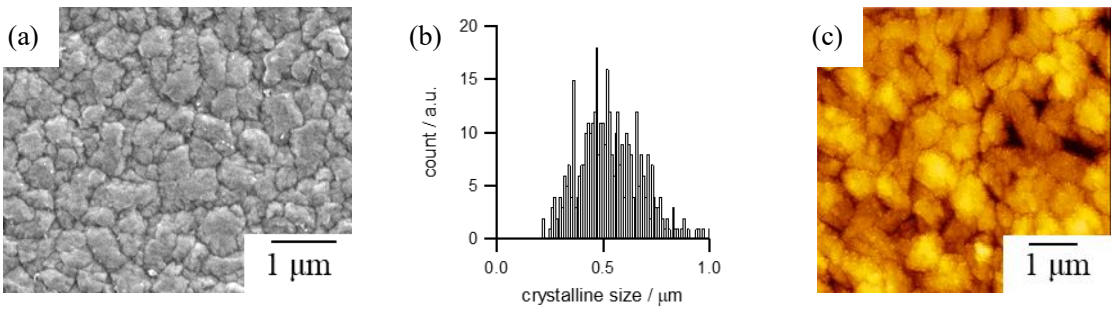

Fig.1 (a) SEM image (b) crystalline size count (c) AFM image for $x = 0.175$.

References 1) H. Tokoro, S. Ohkoshi, Bull. Chem. Soc. Jpn., **88**, *227* (2015). 2) S. Ohkoshi, A. Fujishima, and K. Hashimoto, J. Am. Chem. Soc., **120**, *5349* (1998).

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Mode dependence of Rabi splitting in molecular vibrational polaritons

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Keywords: strong coupling; vibrational polariton; molecular polariton

Coupling between resonant molecular vibrational transitions and optical modes in microcavities offers exciting prospects for applications such as all-optical switches, sensing mechanisms, and coherent light sources. Among them, perhaps the most exciting is the application of light-matter strong coupling for precision control of chemical reactions. Light-matter coupling manifests as a mode splitting in spectroscopic measurements, with each new eigenmode having both light and matter characteristics. Collections of molecules and a cavity mode become strongly coupled when their energy exchange rate is faster than the decay of either the bare molecular transition or the cavity photon [1]. The two eigenmodes constitute a quasiparticle, called a molecular vibrational polariton, and the energy difference between them is called the Rabi splitting, depicted in Figure 1. In general, a stronger coupling results in a larger splitting.

Here, we examine how the Rabi splitting changes when the vibrational mode is coupled to different orders of cavity mode, with an eye towards future ultrafast pump-probe measurements of the polariton dynamics. Previous studies have demonstrated that coupling strength depends on the molecular distribution within the cavity arising from the spatial variance of the electric field profile [2]. By varying the mode order, we change the cavity field profile and affect the Rabi splitting. For the pump-probe experiment, the laser beam volume overlaps with the full cavity length, so the optimum cavity length should be chosen carefully and take into account the Rabi splitting energy, overall signal intensity, and the availability of the flow-cell sample circulation setup.

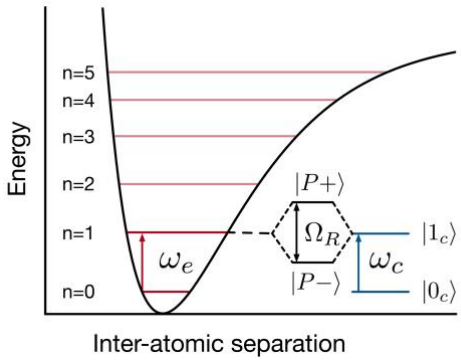

Figure 1. Energy level diagram showing polariton mode splitting when cavity mode and molecular absorption are resonant. The energy separation between the hybridized modes is called the Rabi splitting.

We choose the N=N=N stretching vibration of diphenyl phosphoryl azide (DPPA) [3] in toluene and inject the solution into a Fabry-Pérot microcavity of lengths ~3 – 25 μm and consisting of two CaF_2 windows, each coated with a 14 nm-thin, highly reflective Au layer. The chosen lengths correspond to mode orders between 3 and 14. As the cavity is angle-tuned, the cavity mode sweeps through the vibrational absorption at 2170 cm^{-1}. Performing a global fit on the angle-dependent dispersion response of the upper and lower polariton branches yields the experimental Rabi splitting values, which do indeed decrease as mode order increases. The results of this study will have implications for cavity and flow cell design, as well as implementations for future studies using Fabry-Pérot cavity coupling for reaction control.

[1] F. Herrera and J. Owrutsky, J. Chem. Phys. **152**, 100902 (2020).
[2] W. Ahn *et al.*, ACS Photonics **5**, 158 (2018).
[3] J. George *et al.*, J. Phys. Chem. Lett. **6**, 1027 (2015).

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Azulene-1-CONHCH$_2$SO$_3^-$とその電荷移動塩の開発

（阪大院理）○尾山 泰聖・圷 広樹・中澤 康浩
Preparation and property of Azulene-1-CONHCH$_2$SO$_3^-$ and its charge-transfer salt (*Graduate School of Science, Osaka University*) Taiki Oyama, Hiroki Akutsu, Yasuhiro Nakazawa

According to Little's model for excitonic superconductivity, we have attempted to introduce oscillating dipole into organic conductors. We focused on Azulene as an oscillating dipole. Azulene consists of condensed 5-membered and 7-membered rings, has dipole moment, and can be used as a source of an oscillating dipole. We have synthesized the title anion as a use of a counterion of organic conductors. We have prepared the PPh$_4$ salt. There are two types of crystals, purple and blue, in the latter of which each azulene ring forms a face-to-face dimer.
Keywords: Organic Conductors; Little Model; Superconductivity; Oscillating Dipole; Azulene

本研究では、Little 型超伝導の実現を目指し、振動分極を有する Azulene に着目した。今までにドナー・アニオン型有機伝導体のドナー側に Azulene を導入した研究は行われている [1] が、アニオン側に導入した研究は行われていない。今回、スルホ基(-SO$_3^-$)を Azulene に導入した表題アニオン(**A1**, 図 1)の合成を行ったので報告する。

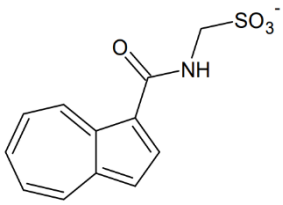

図 1.Azulene-1-CONHCH$_2$SO$_3^-$ (**A1**)

Azulene-1-CHO を Na$_2$CO$_3$、KMnO$_4$ 存在下、アセトン:H$_2$O = 5:1 中で約 4 時間撹拌し、Azulene-1-COOH を得た [2](収率 77%)。得られた Azulene-1-COOH を DCC、DMAP 存在下、CH$_2$Cl$_2$ 中で数日間撹拌し、続いて PPh$_4$Br と塩交換することにより **A1** を PPh$_4$ 塩として得た(収率 29%)。CH$_2$Cl$_2$ とエーテルを用いた溶液拡散法により、紫色[(PPh$_4$)**A1**・H$_2$O]と青色[(PPh$_4$)**A1**]の二種類の単結晶が得られた。それぞれの単結晶について X 線構造解析を行った結果、前者では Azulene 環が PPh$_4^+$に囲まれていたが、後者では Azulene 環同士の接触が見られ(図 2)、このため結晶の色が異なったと考えられる。現在、TTF や BEDT-TTF との塩の作成を行っているところである。その結果については、当日発表する。

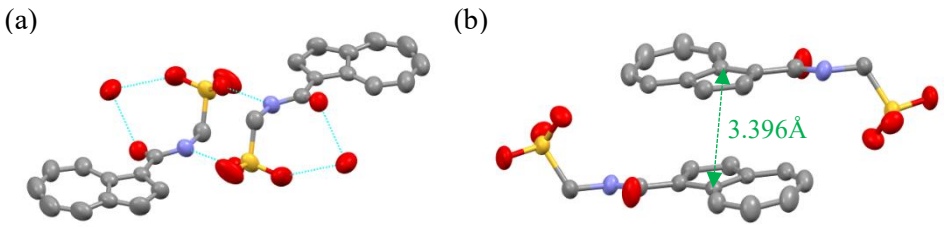

図 2.二種類[(a)紫 (b)青]の結晶中のアニオン配列 (水色点線は水素結合を示す)

1) H. M. Yamamoto, J. Yamaura and R. Kato, *J. Mater. Chem.*, 1998, **8**(2), 289–294.
2) C. Maeng, J. Y. Son, S. C. Lee, Y. Baek, K. Um, S. H. Han, G. H. Ko, G. U. Han, K. Lee, K. Lee, and P. H. Lee, *J. Org. Chem.*, 2020, **85**, 3824−3837.

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2,2'-ビピリジン誘導体とジチオレン配位子をもつ平面四配位型非対称白金錯体の電子状態と伝導材料への応用

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Electronic states of unsymmetrical platinum complexes with square planar coordination of 2,2'-bipyridine derivatives and dithiolene ligands and their application to conducting materials

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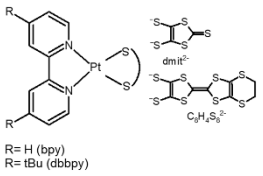
We have developed molecular conductors based on unsymmetrical metal dithiolene complexes such as [(bpy)Pt($C_8H_4S_8$)] with intramolecular polarization [1]. In this study, [(dbbpy)Pt(dmit)] (**1**) and [(dbbpy)Pt($C_8H_4S_8$)] (**2**) with two *tert*-butyl groups introduced to the bipyridine moiety and their radical cation crystals were synthesized. Electrochemical measurements in chloroform showed a one-electron redox wave corresponding to $[\mathbf{1}]^0/[\mathbf{1}]^+$ at +0.32 V (*vs.* Ag/AgCl) for **1**, and two-electron redox waves corresponding to $[\mathbf{2}]^0/[\mathbf{2}]^+$ and $[\mathbf{2}]^+/[\mathbf{2}]^{2+}$ at -0.15 and +0.44 V (*vs.* Ag/AgCl) for **2**, respectively. The radical cation crystals of $[\mathbf{1}]_2$(TCNQ) and [**2**](X) (X = BF_4^-, ClO_4^-, PF_6^-) were obtained by using chemical and electrochemical oxidation methods. In the crystal of $[\mathbf{1}]_2$(TCNQ), a donor-donor-acceptor type columnar arrangement containing head-to-tail dimers of **1** was observed along the *b*-axis direction. A columnar structure composed of a head-to-head molecular arrangement of **2** was constructed in [**2**](PF_6) (Fig. 1). The shortest sulfur-sulfur distances in the crystals were 4.068 Å for $[\mathbf{1}]_2$(TCNQ) and 3.710 Å for [**2**](PF_6). In this presentation, the relationship between crystal structures and physical properties will be discussed.

Keywords : Molecular conductor; Unsymmetrical metal complex; Platinum complex

我々は、[(bpy)Pt($C_8H_4S_8$)]などの分子内分極をもつ非対称型金属錯体を構成分子とする分子性導体を開発してきた [1]。本研究では、ビピリジン骨格に *tert*-ブチル基を導入した[(dbbpy)Pt(dmit)] (**1**)および[(dbbpy)Pt($C_8H_4S_8$)] (**2**)を合成した。クロロホルム中における電気化学測定の結果、**1** では$[\mathbf{1}]^0/[\mathbf{1}]^+$に対応する一電子の酸化還元波が +0.32 V (*vs.* Ag/AgCl)に、**2** では$[\mathbf{2}]^0/[\mathbf{2}]^+$と$[\mathbf{2}]^+/[\mathbf{2}]^{2+}$に対応する二電子の酸化還元波が-0.15 および +0.44 V (*vs.* Ag/AgCl)に見られた。化学的酸化および電解酸化により **1** と **2** のラジカルカチオン塩$[\mathbf{1}]_2$(TCNQ)と[**2**](X) (X = BF_4^-, ClO_4^-, PF_6^-)の単結晶を得た(図 1)。結晶$[\mathbf{1}]_2$(TCNQ)内では、錯体 **1** が head-to-tail で二量体を形成し、*b* 軸方向にドナー・ドナー・アクセプター型のカラムを形成していた。結晶[**2**](PF_6)内の錯体 **2** は、head-to-head で配列してカラム構造を形成していた。結晶$[\mathbf{1}]_2$(TCNQ)と[**2**](PF_6)における最近接硫黄原子間距離は、それぞれ 4.068 Å および 3.710 Å であった。発表では、得られたラジカルカチオン塩の物性について結晶構造を基に議論する。



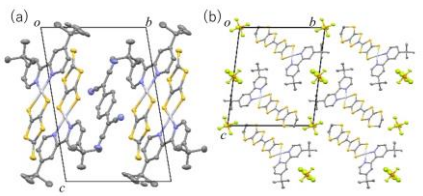


図 1 (a) $[\mathbf{1}]_2$(TCNQ)および(b) [**2**](PF_6)の結晶構造

[1] K. Kubo, R. Kato, *Top. Organomet. Chem.* **2009**, *27*, 35-53.

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CdSe/CdTe core/crown 型ナノプレートの合成とキャリア移動・再結合素過程の研究

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Synthesis and Femtosecond Spectroscopic Study of CdSe/CdTe Core/crown Nanoplatelets

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○Haruka Nagasawa, Daichi Eguchi, Naoto Tamai

CdSe/CdTe core/crown nanoplatelets (NPLs) have a Type-II electronic structure with a two-dimensional CdSe core platelet and crown layer of CdTe grown epitaxially in the planar direction. Auger recombination of core/crown NPLs may be reduced due to the carrier separation into CdSe core and CdTe crown layers. However, interfacial currier separation and recombination dynamics of core/crown NPLs in multiple exciton states have not been well understood. In the present study, we synthesized CdSe/CdTe core/crown NPLs and analyzed elementary carrier transfer and Auger recombination processes by picosecond luminescence and femtosecond transient absorption spectroscopy.

Keywords : CdSe/CdTe core/crown Nanoplatelet; Femtosecond Transient Absorption Spectroscopy, Carrier Transfer

近年, コロイド合成法の発展によって励起子が一次元方向に閉じ込めを受けた量子井戸構造に対応する半導体ナノプレート (NPLs) の合成が報告されたが，CdTe NPLs の合成は難しく，不安定である事が知られている。一方，CdSe NPLs を core として CdTe を周りに接合した Type-II の電子構造をもつ core/crown (c/c) を合成すると, 表面欠陥を抑制したり, キャリアを core 層と crown 層に分離することができる。しかし，その電荷分離の初期過程や界面構造など未解明な点が多い。本研究では，4 層の厚みを持つ 4 ML CdSe/CdTe c/c NPLs を合成すると共に, 励起されたキャリアの振る舞いをフェムト秒～ピコ秒時間分解レーザー分光を用いて解析を行った。発光寿命の測定を行ったところ, c/c NPLs に見られる CT 由来の発光寿命は約 130 ns で, 4ML CdSe NPLs の約 5 ns と比較して 30 倍近く長くなった。また，過渡吸収測定を高エネルギーの 400 nm 励起だけでなく，CdSe や CdTe 由来の HH 吸収，CT 吸収を励起すると共に，23 ～ 50℃での測定も行った。その結果，理論的には励起された電子は CdTe crown 側から CdSe core 側へ移動すると考えられるが，電子の移動が完全には出来ておらず crown 側に留まっていることが分かった。TEM 測定による構造の解析結果と電荷移動の関係についても議論する予定である。

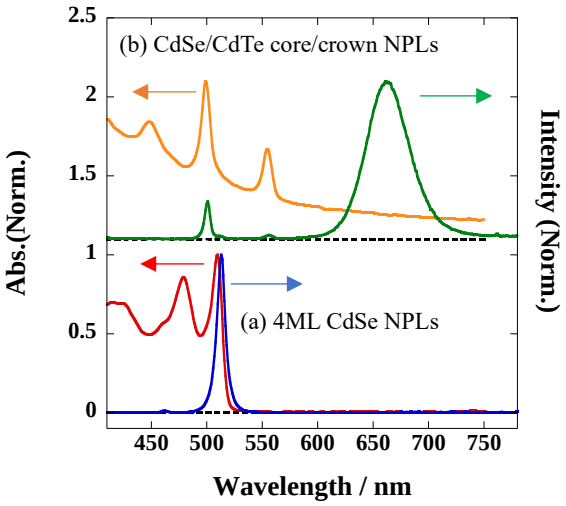

図 1. (a) 4ML CdSe NPLs および (b) CdSe/CdTe core/crown NPLs の吸収・発光スペクトル

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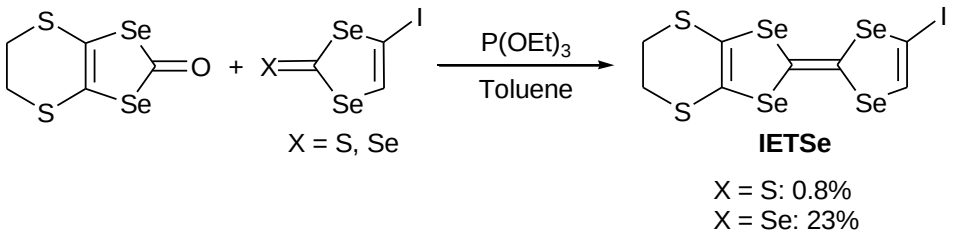
新規含ヨウ素ドナー分子 IETSe を用いた超分子有機伝導体の合成と性質

（長岡技科大院工）○山部 知浩・今久保 達郎
Synthesis and properties of supramolecular organic conductors based on the novel iodine-containing π-donor IETSe derivatives (*Graduate School of Engineering, Nagaoka University of Technology*) ○Chihiro Yamabe, Tatsuro Imakubo

IEDT was employed for introducing the iodine bond into organic conductors for the first time. On the other hand, DIETSe gave the first ambient-pressure organic superconductor based on the iodinated TTFs. In this paper, we will report on the synthesized IETSe (iodo(ethylenedithio)tetraselenafulvalene), which is the hybrid of IEDT and DIETSe. IETSe was obtained by a $P(OEt)_3$ mediated cross-coupling reaction of 4,5-ethylenedithio[1,3]diselenole-2-one and 4-iodo[1,3]diselenole-2-thione or 4-iodo[1,3]diselenole-2-selone. When the iodo thione unit was used for the coupling reaction, the yield of IETSe was extremely low (0.8%). Therefore, we used the corresponding selone instead of the thione and the yield increased up to 23%. Preparations of cation radical salts of IETSe together with their crystal structure and electrical conductivity will be also reported.
Keywords : Tetraselenafulvalene; Iodine bond; Supramolecule; Organic Conductor

有機伝導体にヨウ素結合を初めて導入することに成功した含ヨウ素ドナー分子 IEDT と、含ヨウ素系で初めての常圧超伝導体を与えたドナー分子 DIETSe の二つの特徴を併せ持つ、新規含ヨウ素ドナー分子 IETSe（iodo(ethylenedithio)tetraselenafulvalene）の合成を行った。IETSe は、4,5-ethylenedithio[1,3]diselenole-2-one と 4-iodo-[1,3]diselenole-2-thione あるいは 4-iodo[1,3]diselenole-2-selone を原料として、$P(OEt)_3$ を用いたクロスカップリング反応により得ることが出来た。ヨウ素側のユニットとしてチオン体を用いてカップリング反応を行った場合には、収率が 0.8%と著しく低くなってしまった。そこでチオン体に代えてセロン体を用いて反応を行ったところ、収率を 23%まで向上させることに成功した。当日は、IETSe を用いたカチオンラジカル塩の合成と構造、および電気伝導性についても併せて報告する。



1) T. Imakubo, H. Sawa and R. Kato, *Synth. Met.*, 1995, **73**, 117-122.
2) T. Imakubo and T. Shirahata, *Chem. Commun.*, 2003, 1940-1941.

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二重発光性有機発光材料の励起状態構造と緩和ダイナミクス

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The structure of the excited states and relaxation dynamics of an organic luminescence material showing dual emission ([1]*Graduate School of Science, Kyushu University*, [2]*OPERA, Kyushu University*) ○Tomohiro Ryu[1], Yuushi Shimoda[1], Masaki Saigo[1], Ryota Fukuda[1], Kiyoshi Miyata[1], Youichi Tsuchiya[2], Hajime Nakanotani[2], Chihaya Adachi[2], Ken Onda[1]

Dual emission is a phenomenon in which one material exhibits two types of luminescence. Phenothiazine triphenyltriazine (PTZ-TRZ, Fig. 1a) is one of the molecules exhibiting dual emission. PTZ-TRZ has two emissive geometries in the excited states (Fig. 1b).[1] However, the detailed mechanism such as unique solvent dependence of the dual emission has not been elucidated. In this study, we investigated the excited-state structural dynamics of PTZ-TRZ using time-resolved infrared spectroscopy (TR-IR).

From the comparison between the TR-IR spectra of the lowest singlet and triplet excited state (S_1 and T_1) and quantum chemical calculations (Fig. 1c, d), we concluded that the equatorial structure is the major conformation in both the S_1 and T_1 states in a toluene solution. We also found that the equatorial structure is the major conformer in the S_1 states in a THF solution. We will discuss the relation between geometries and photophysical properties.

Keywords : Dual Emission, Time-Resolved Infrared Spectroscopy, Time-Resolved Photoluminescence

二重発光とは一つの物質が二種類の発光を示す現象である。二重発光性材料の一種であるフェノチアジントリフェニルトリアジン(PTZ-TRZ, Fig. 1a)は、励起状態で二つの構造を取り(Fig. 1b)、それぞれの構造から発光することが示唆されている[1]。しかし詳細なメカニズムは未だ解明されていない。本研究では、時間分解赤外分光法(TR-IR)と量子化学計算を用いて、PTZ-TRZ の励起状態構造を検討した。

最低一重項励起状態(S_1)と三重項励起状態 (T_1)での TR-IR スペクトルと量子化学計算との比較から(Fig. 1c,d)、トルエン溶液中では S_1 状態と T_1 状態の両方で equatorial 構造を取ることがわかった。また THF 溶液中でも、S_1 状態で equatorial 構造を取ることが示唆された。ポスターでは励起状態での立体構造と光物理特性について議論する。

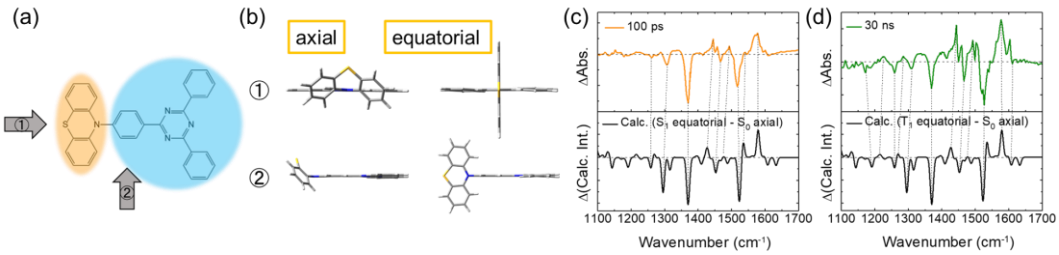

Fig. 1. (a) PTZ-TRZ の構造、(b) PTZ-TRZ の二つの励起状態構造、(c, d) 各励起状態構造の TR-IR スペクトルと量子化学計算との比較：(c) S_1 状態(100 ps)、(d) T_1 状態(30 ns)

1). Tanaka, H., Shizu, K., Nakanotani, H. & Adachi, C. *J. Phys. Chem. C* **118**, 15985–15994 (2014).

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カドミウムフリー青色発光量子ドット InGaP QDs の合成と励起子素過程の解明

(関西学院大・理工)○北島弘貴・山口優里奈・藤高綾那・江口大地・玉井尚登

Elementary Exciton Dynamics of Cadmium-Free Blue-Emitting InGaP Quantum Dots

(*Department of Chemistry, School of Science and Technology, Kwansei Gakuin University*)
○Hiroki Kitajima, Yurina Yamaguchi, Ayana Fujitaka, Daichi Eguchi, Naoto Tamai

InGaP quantum dots (QDs) are one of the few blue emitting quantum dots, and expected to be applied to LEDs because of cadmium free, highly nontoxic materials. For this application, it is essential to understand Auger recombination leading to reduced efficiency. However, many unclear points are remaining for InGaP QDs. In the present study, we synthesized InGaP QDs, and their elementary exciton processes were examined by femtosecond transient absorption spectroscopy and picosecond single-photon timing.
Keywords; InGaP QD, Blue Emission, Auger Recombination, Femtosecond Spectroscopy

InGaP 量子ドット (QDs) は，数少ない青色発光量子ドットの一つである。また，カドミウムなどの毒性の高い金属を含まないため LED などへの応用に期待されている。量子ドットでは，バルク半導体と比べ励起された電子（正孔）同士が相互作用し片方の電子（正孔）がエネルギーを渡して無輻射的に緩和し，もう片方がより高い状態に遷移するオージェ再結合が起きやすいことが知られている。LED への応用のためには効率の低下につながるオージェ再結合の理解が必要不可欠だが，InGaP QDs についてはまだ未解明な部分が多い。本研究では青色発光を示す InGaP/ZnS を合成し，その励起子素過程を明らかにした。InGaP QDs は臭化インジウム，トリスジメチルアミノホスフィンを用いて InP QDs を合成した後，ヨウ化ガリウムを用いて In (III) を Ga (III) へと陽イオン交換を行い合成した。更に，InGaP QDs をコアとし ZnS シェルを形成した [1]。合成した試料は透過型電子顕微鏡，XRD，蛍光 X 線測定で同定した。合成した QDs の発光スペクトルを Fig. 1 に示す。シェルを形成することで発光スペクトルが約 10 nm 長波長にシフトし，発光量子収率が 1%から 11%まで向上したが，スペクトル形状は Gauss 型ではない。これは ZnS シェルを形成することで表面欠陥が抑えられると共に，コアに閉じ込められていた波動関数がシェルまで染み出したが，サイズ分布の影響を受けているものと考えられる。発表では，フェムト秒過渡吸収分光により InGaP および InGaP/ZnS QDs の励起子素過程を解明した結果も含めて報告する。

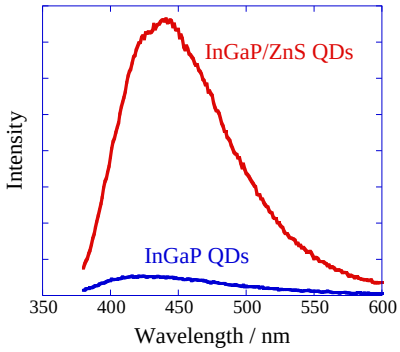

Fig. 1 Luminescence spectra of InGaP QDs (blue), InGaP/ZnS QDs (red). Samples were excited at 370 nm.

1) Kyung-Hye Kim *et al.*, *Chem. Mater.* **2020**, 32, 8, 3537–3544.

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N-アルキル化 DABCO を対カチオンとする TCNQ 誘導体のラジカルアニオン塩の構造と物性

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Structures and physical properties of radical anion salts of TCNQ derivatives with *N*-alkylated DABCO as a counter cation

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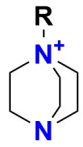
The control of molecular arrangement in organic conductors enables the regulation of physical properties. We have focused on the supramolecular interactions such as hydrogen and halogen bonds to constrain molecular arrangement. TCNQ and F_4TCNQ afforded 7 kinds of salts with (RDABCO)I (R = Me, Et), including polymorphs. Among them, $(MeDABCO)_2(TCNQ)_3$ (**1**), (MeDABCO)(TCNQ)I (**2**), (EtDABCO)(F_4TCNQ) (**3**), and $(EtDABCO)_2(F_4TCNQ)_3$ (**4**) contained one-dimensional (F_4)TCNQ columns and showed a variety types of hydrogen bonds with RDABCO. The salts **1**−**4** were semiconducting with room-temperature electrical conductivities (activation energies) of 6.0×10^{-3} (0.31 eV), 1.05×10^{-4}, 1.1×10^{-8}, 2.4×10^{-7} S cm^{-1} (0.60 eV), respectively.



RDABCO
(R = Me, Et)

Keywords *: Organic Conductor, Tetracyanoquinodimethane Derivative, N-Alkylated DABCO Cation*

有機導電体において、構成分子の配列を制御することにより所望の物性を発現させることが可能である。我々は、分子配列の制御のため、水素結合やハロゲン結合等の超分子相互作用に着目してきた。今回、TCNQ、またはF_4TCNQと(RDABCO)I (R = Me, Et)を混合することにより、多形を含め、7種類の塩を得た。その中で特に、$(MeDABCO)_2(TCNQ)_3$ (**1**)、(MeDABCO)(TCNQ)I (**2**)、(EtDABCO)(F_4TCNQ) (**3**)、$(EtDABCO)_2(F_4TCNQ)_3$ (**4**)では、TCNQまたはF_4TCNQ分子が1次元積層カラムを形成し、RDABCOと水素結合を形成していた。例えば**1**では、TCNQ分子の3量体から成る積層カラムがMeDABCOの1次元鎖と水素結合を形成し、TCNQの結合長から電荷秩序状態にあることが分かった（Fig. 1(a)）。一方、**2**では、中性のTCNQ分子から成る均一な積層カラムが、MeDABCOとヨウ化物イオンから成る1次元鎖と水素結合を形成していた（Fig. 1(b)）。また、**1-4**は、それぞれ室温電気伝導度（活性化エネルギー）が、6.0×10^{-3} (0.31 eV)、1.05×10^{-4}、1.1×10^{-8}、2.4×10^{-7} S cm^{-1} (0.60 eV)の半導体的挙動を示した。当日は、得られた他の塩を含め、結晶構造、導電性の詳細について紹介する。

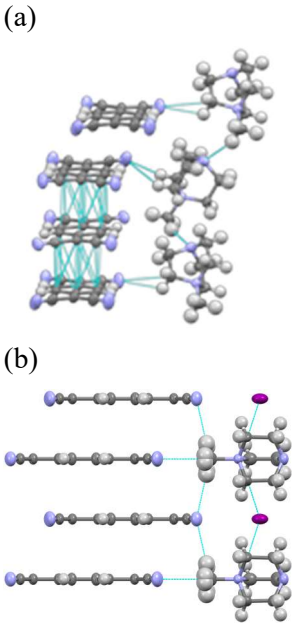


Fig. 1 (a) **1**、(b) **2** における、TCNQ の積層カラムと MeDABCO の短距離接触。

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π トポロジーを考慮して励起スピン状態を制御した新規ペンタセンーラジカル連結系の合成とその光耐久性

(阪市大院理[1]・阪市大理[2]) ○南 錦[1]・前口 慶治郎[1]・加藤 賢[1]・吉田 考平[1]・清水 章皓[1]・加島 源太[2]・手木 芳男[1]

Synthesis and Photostability of New Pentacene Derivatives with Radical Substituent controlled the Excited Spin-State by π-Topology ([1]*Graduate School of Science, Osaka City University*, [2]*Faculty of Science, Osaka City University*) ○Nishiki Minami,[1] Keijiro Maeguchi,[1] Ken Kato,[1] Kohei Yoshida,[1] Akihiro Shimizu,[1] Genta Kashima,[2] Yoshio Teki[1]

Pentacene is a promising organic semiconductor, but it has a disadvantage that it reacts easily with oxygen in the presence of ambient light. In our laboratory, we have achieved a remarkable enhancement of photostability by utilizing enhanced intersystem crossing due to the addition of stable radical substituents. In this study, in order to achieve further photostability and solubility enhancement, we synthesized new pentacene derivatives (**1** and **2**) with oxoverdazyl (OV) and isopropylsilyl (TIPS) substituents and with different π topology. The lowest excited states of **1** and **2** are expected to be quartet and doublet spin states, respectively. For photostability measurements, we examined the decay of the characteristic absorption band of pentacene moiety of **1** and **2** under light irradiation in the air-saturated dichloromethane solutions. Their decomposition lifetimes was determined to be 430 h for **1** and 587 h for **2**. This lifetime deference can be understood due to the characteristics of the deactivation pathway to the ground state via the lowest excited state, that is spin-allowed in **2**, but spin-forbidden in **1**.
Keywords : Pentacene; Photostability; Enhanced intersystem crossing; π topology

ペンタセン(Pn) は有望な有機半導体材料であるが、可視光存在下で酸素と反応することが欠点である。当研究室では、安定ラジカルの付加により引き起こされる増強系間交差を利用して光耐久性の著しい向上を達成した[1]。本研究では、さらなる光耐久性の向上を目指して、oxoverdazyl(OV) と isopropylsilyl(TIPS) 基を付加した **1** 及びそれと π トポロジーの異なる **2** (図 1) を設計・合成した。それぞれの最低励起状態は **1** では四重項、**2** では二重項状態となると考えられる。

光照射に伴い **1** 及び **2** が溶存酸素と反応してペンタセン骨格を消失することによる、ペンタセン部位の ππ* 吸収遷移の吸光度の時間変化を追跡することにより光耐久性を評価した。結果として、**1** のペンタセン骨格の分解寿命は 430 時間であり、**2** の分解寿命は 587 時間であった (図 1) 。最低励起状態を経由する基底状態への失活経路が、**1** ではスピン禁制で、近接して存在する励起二重項を介して基底状態へ失活していると期待されるが、**2** ではスピン許容であるため **2** は **1** よりも励起状態の寿命が短くなり、光耐久性が向上したと考えられる。

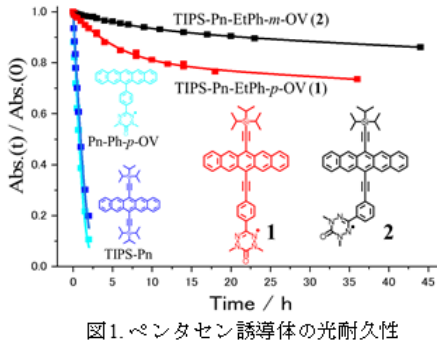

図1. ペンタセン誘導体の光耐久性

1) Y. Kawanaka, A. Shimizu, T. Shinada, R. Tanaka, and Y. Teki, *Angew.Chem. Int. Ed.*, **2013**, *52*, 6643.

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含ヨウ素ドナー分子 IDMe-TSeF を用いた新規有機伝導体の開発

（長岡技科大院工）○イバート・今久保 達郎

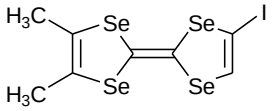
Development of Novel Organic Conductors Using Iodine-bonded π-Donor IDMe-TSeF

(*Graduate School of Engineering, Nagaoka University of Technology*) ○Evert, Tatsuro Imakubo

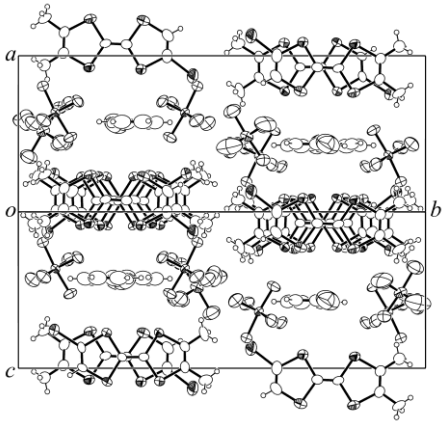
Most reported iodine-bonded π-donors are composed of an iodine-bonded half unit and another half unit containing a heterocycle. On the other hand, there are few reports on the iodine-bonded π-donors containing simple alkyl substituents. In this paper, we will report on the synthesis of a novel asymmetric iodine-bonded TSeF derivative IDMe-TSeF, together with the preparations of its cation radical salts with various counter anions. IDMe-TSeF was obtained by a cross-coupling reaction of the corresponding 1,3-diselenole units, and its cation radical salts were prepared by the galvanostatic oxidation. In the crystal of the SbF_6 salt, one-dimensional column is constructed by the π-π stacking of the donor molecules and the donor : anion : chlorobenzene (solvent of the crystallization) ratio is 2 : 2 : 1. Crystal structure and electrical conductivity of the other cation radical salts will be also reported.

Keywords : Tetraselenafulvalene; Iodine Bond; Organic Conductor

既報の含ヨウ素ドナー分子の多くは含ヨウ素ユニットにヘテロ環を含むユニットを組み合わせているが、単純なアルキル置換ユニットを用いた報告は少ない。そこで本研究では、モノヨードユニットとジメチルユニットを組み合わせた非対称 TSeF 誘導体である IDMe-TSeF を新たに合成し、様々なカウンターアニオンとの組み合わせによるカチオンラジカル塩の作成を行った。IDMe-TSeF の合成は、対応する 1,3-diselenole ユニットのクロスカップリング反応により行った。定電流電気分解法によるカチオンラジカル塩の作成では、四面体型および八面体型のアニオンを用いた場合に比較的良好な単結晶を得ることが出来た。SbF_6 塩の結晶中ではドナー分子は一次元カラムを形成しており、ドナー：アニオン：クロロベンゼン（結晶溶媒）比が 2 : 2 : 1 の組成であることがわかった。当日は、その他の塩の構造と物性についても併せて報告する。



IDMe-TSeF



Molecular structure of IDMe-TSeF (top) and crystal structure of the SbF_6 salt (bottom).

1) 今久保達郎、白旗崇、水津理恵、「ヨウ素と有機伝導体」（ヨウ素化合物の機能とその応用、6.1 章、pp.193–206）、横山正孝監修、シーエムシー出版 (2005).

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キラル側鎖を有する TTF 誘導体を用いた分子性ナノコイルスキャホールドの作成と細胞培養

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Cell Culture and Preparation of Molecular Nanocoil Scaffolds Composed of TTF Derivatives with Chiral Units ([1] *Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology,* [2] *Graduate School of Advanced Science and Engineering, Hiroshima University,* [3] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,* [4]*Research Institute for Electronic Science, Hokkaido University*) ○ Tamaki Nishimura,[1] Yuka kanno,[1] Sadafumi Nishihara,[2] Tomoyuki Akutagawa,[3] Takayoshi Nakamura,[4] Yoko Tatewaki[1]

In the field of regenerative medicine, there is need to develop scaffolds that cells to function effectively for regeneration. Molecular nanocoils have a large surface area and porosity that are fit for scaffolds. In addition, they showed the induced electromotive force that can activate cells by magnetic field.

In this study, we prepared molecular nanocoil scaffolds composed of TTF derivatives (***R*-, *S*-TTF-4UM**) having chiral and hydrogen-bonding side chains (Fig.1) and F_4TCNQ. Cytotoxicity test in L6 rat fibroblasts showed the molecular nanocoil scaffolds on glass substrates had low cytotoxicity because of these cells adapted to the scaffolds after 3 days.

Keywords : Charge Transfer Complexes; Scaffolds; Nanocoils; Self-organization

再生医工学の現場では、再生に必要な細胞を効果的に機能させるスキャホールドの開発が渇望されている。導電性･磁性を有する分子性ナノコイルは、大表面積や多孔質性といったスキャホールドに適した形状を有している。さらに、電場･磁場印加により細胞を活性化できる起電力を誘起する可能性があることから、自己発電型メディカルデバイスとして注目されている。

本研究では、側鎖に光学活性部位と水素結合鎖を有する TTF 誘導体(***R*-, *S*-TTF-4UM**)(Fig.1)と F_4TCNQ を混合し、分子性ナノコイルからなるスキャホールドを作成した。作成した分子性ナノコイルスキャホールドに対して電磁特性評価を行ったところ、交流磁場下で 1.43 mV の誘導起電力を生じることが明らかとなった。次に、細胞毒性を確認した。ガラス基板上に分子性ナノコイルスキャホールドを作成し、その上にラット骨格筋 L6 細胞を播種したところ､3 日後には細胞が安定したことから、細胞毒性の低い系であると明らかとなった。当日は、スキャホールドが細胞に与える効果や機能についても併せて報告する。

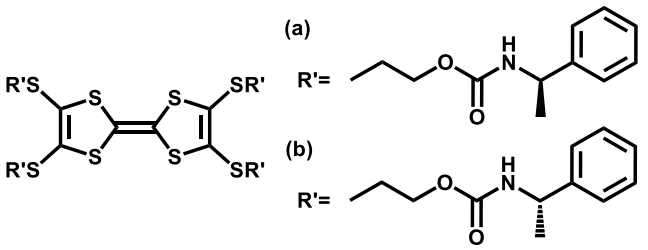

Fig.1 Chemical structures of (a) ***R*-TTF-4UM** and (b) ***S*-TTF-4UM**

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チアントレン骨格を有するトリプチセン誘導体のカチオンラジカル塩の結晶構造および物性

（名大院理[1]）吉行 琢馬[1]・珠玖 良昭[1]・阿波賀 邦夫[1]
Crystal structure and physical properties of radical cation salts of triptycene derivatives annulated with thianthrene skeletons ([1]*Graduate School of Science, Nagoya University*) Takuma Yoshiyuki,[1] Yoshiaki Shuku,[1] Kunio Awaga[1]

Graphene, in which sp^2 carbon forms a honeycomb structure, is in the spotlight due to its unique physical properties derived from the band structure called Dirac cone. To construct the honeycomb structure with molecules, we focused on paddle-wheel shaped triptycene derivatives having a three-fold rotational symmetry axis. Previously, we have reported that the radical anion species of a triptycene derivative with a *p*-benzoquinone skeleton (*p*-TT) form a honeycomb structure by strong π-π interactions, and theoretical calculation based on tight-binding approximation predicts that the band structure has not only Dirac cone but also flat band.[1)] To realize the physical properties based on these band structures, achievement of continuous band filling control is an urgent issue. However, the size of pores in the crystal structure of anionic *p*-TT was too small to insert ions on the band filling control. Therefore, we focused on the thianthrene skeleton as an extended and electron donating π conjugated system which is expected to form a redox active honeycomb structure with larger pore size. It is known that the thianthrene molecule exhibits good electron donor properties, and its radical cation becomes a dimer by strong π-π interaction [2)]. In this study, we designed and synthesized a triptycene derivative having thianthrene moieties and prepared radical cation salts by chemical oxidation. The details of the crystal structures and physical properties will be discussed.

Keywords : Triptycene; Honeycomb Structure; Radical Cation Salt; Crystal Structure; Physical Property

sp^2 炭素がハニカム構造を形成したグラフェンは、ディラックコーンというバンド構造に由来する特殊な物性によって注目を集めている。このハニカム構造を分子で構築するにあたり、我々は三回回転対称軸をもつ paddle wheel 型分子のトリプチセン誘導体に着目した。実際、*p*-ベンゾキノン骨格を有するトリプチセン誘導体のラジカルアニオン種は、強いπ-π相互作用によってハニカム構造を形成することが報告されており、そのバンド構造はディラックコーンだけでなくフラットバンドまでも兼備した特異なものであることが、強束縛近似に基づく理論計算によって予想されている [1)]。しかし、その結晶中の空孔は小さく、バンドフィリング制御にともなうイオン挿入が困難だったため、バンド構造由来の物性の発現は実現できなかった。そこで、*p*-ベンゾキノンよりπ共役系が大きく、かつ電子授受能も示す骨格として、我々はチアントレン骨格に注目した。チアントレン分子は良好な電子ドナー性を示し、そのラジカルカチオンは強いπ-π相互作用によって二量体となることが知られている [2)]。本研究では、チアントレン骨格を有するトリプチセン誘導体の設計・合成と、その酸化によるラジカルカチオン塩の作成を行った。当日はこれらの結晶構造解析および物性測定の結果について発表する。

1) Y. Shuku, *et al. Chem. commun.* 2018, 54, 3815-3818
2) J. Beck, T. Bredow and R. T. Tjahjanto. *Z. Naturforschung*. 2009, 64b, 145-152

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イミダゾールを導入したホスホン酸修飾メソポーラスシリカのプロトン伝導性

（金沢大理工[1]・金沢大院自然[2]・金沢大ナノマリ[3]）○朝野 綾香[1]・重田 泰宏[3]・栗原拓也[2]・雨森 翔悟[3]・井田 朋智[2]・水野 元博[2,3]

Proton conductivity of imidazole containing phosphonic acid-modified mesoporous silica

([1]*School of Chemistry, College of Science and Engineering, Kanazawa University,* [2] *Graduate School of Natural Science and Technology, Kanazawa University,* [3]*Nanomaterials Research Institute, Kanazawa University*) ○Ryoka Asano,[1] Yasuhiro Shigeta,[3] Takuya Kurihara,[2] Shogo Amemori[3], Tomonori Ida[2], Motohiro Mizuno[2,3]

Recently, proton conductors as a solid electrolyte in fuel cells has attracted much attention. Especially, it is expected that composite exhibit high proton conductivity under dehydration conditions. In this study, we have newly prepared imidazole containing phosphonic acid-modified mesoporous silica (SBA-15) and investigated its proton conductivity. We prepared composite with different amount of imidazole relative to the amount of phosphonic acid and measured the proton conductivity. Obtained composite exhibited a maximum proton conductivity of 5.7×10^{-4} S/cm at 413 K.

Keywords : Mesoporous Silica; Proton Conductivity; Imidazole; Solid State NMR

近年、燃料電池における固体電解質としてプロトン伝導体の研究が盛んに行われている。特に脱水条件においても機能するプロトン伝導体の開発が期待されている。本研究ではホスホン酸で化学修飾されたメソポーラスシリカ(SBA-15)[1]にイミダゾールを導入した新規複合体を調製し、プロトン伝導性を調べた。ホスホン酸量に対するイミダゾール量を変えた試料についてプロトン伝導度の温度変化を測定した。Fig. 1 に各試料の伝導度の最大値を示す。伝導度の最大値はイミダゾール量が増えるにしたがって上昇した。ホスホン酸量に対するイミダゾール量（Im/P）が 300 mol%の複合体では 413 K において最大値 5.7×10^{-4} S/cm のプロトン伝導度を示した。

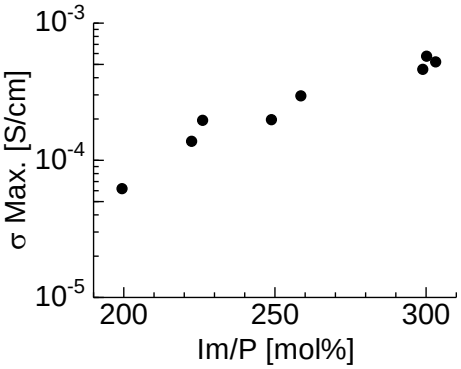

Fig. 1 ホスホン酸量に対するイミダゾール量とプロトン伝導度の相関

1) Robert J. P. Corriu, Lucien Datas, Yannick Guari, Ahmad Mehdi, Catherine Reye and Chloe Thieuleux, *Chem. Commun.*, **2001**, *763-764*

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アルギン酸-ポリアクリル酸-トリアゾール複合体のプロトン伝導メカニズムの解析

(金沢大学大学院自然科学研究科[1]・金沢大学ナノマテリアル研究所[2])
○渡邉 陵太[1]・栗原 拓也[1]・重田 泰宏[2]・雨森 翔悟[2]・井田 朋智[1]・水野 元博[1,2]

Analysis of Proton Conduction Mechanism in Alginic Acid-Polyacrylic Acid-Triazole Composites

([1]*Graduate School of Natural Science and Technology, Kanazawa University*, [2]*Nanomaterials Research Institute, Kanazawa University*)
○Ryota Watanabe,[1] Takuya Kurihara,[1] Yasuhiro Shigeta ,[2] Shogo Amemori ,[2] Tomonori Ida ,[1] Motohiro Mizuno[1,2]

Composites of polymer and triazole (Tz) are known to exhibit high proton conductivity at high temperatures. High proton conductivity of these composites is considered to originate from the continuous proton transfer (Grotthuss Mechanism) induced by the reorientational motion of Tz molecules in polymer. However, to our best knowledge, the detailed motion of Tz has not been clarified yet. Therefore, in this study, we prepared polymer-Tz compounds and investigated the mobility of Tz by solid-state NMR measurement. Then, we aimed to clarify the proton conduction mechanism from the relationship between the mobility of Tz and the proton conductivity.

Keywords : Solid-State NMR; Proton Conductivity; Solid Electrolyte

高温で高いプロトン伝導性を示す固体電解質としてポリマーとトリアゾール（Tz）の複合体が期待されている。これらの複合体はポリマーに取り込まれた Tz の再配向運動に伴うプロトンホッピング（グロータス機構）によって、プロトン伝導が生じていると考えられている。しかし Tz の詳細な運動状態は未だ明らかになっていない。本研究では、ポリアクリル酸（PAA）、アルギン酸（AA）の 2 種類のポリマーを用いて、Tz との複合体を作製し、プロトン伝導率を調べた。また、重水素化した Tz を用いた複合体を調製し、固体 ^{2}H NMR 測定により、Tz の運動性を解析した。そして、Tz の運動性とプロトン伝導性との関係からプロトン伝導メカニズムを考察した。図 1 にプロトン伝導率の温度変化を示す。温度上昇に伴い、伝導率は向上し、413 K で最大値 1.0×10^{-3} S/cm を示した。固体 ^{2}H NMR スペクトルの温度変化を図 2 に示す。スペクトルは 303 K ではリジッドな線形であったが高温になるにつれ、Tz の等方回転運動による 0 kHz 付近のシャープな成分が支配的となった。これらの結果から、高温では Tz の等方回転運動が関与したグロータス機構により、プロトン伝導性が向上したと予想される。

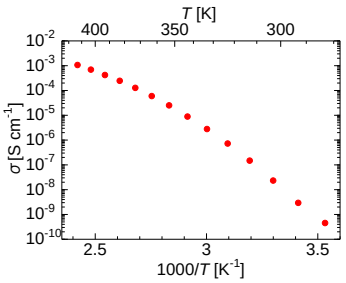

図 1 0.1AA-0.9PAA-0.75Tz のプロトン伝導率の温度変化

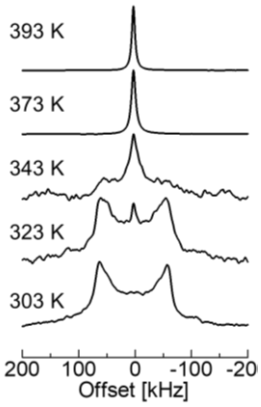

図 2 0.1AA-0.9PAA-0.75Tz の固体 ^{2}H NMR スペクトルの温度変化

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ホスホン酸基修飾 MCM-41/イミダゾール複合体のプロトン伝導性

（金沢大院新学術,[1] 金沢大ナノマリ,[2] 金沢大院自然 [3]）○ 荒井 佑太 [1]・栗原 拓也 [3]・重田 泰宏 [2]・雨森 翔悟 [2]・井田 朋智 [3]・水野 元博 [1,2,3]

Proton Conductivity of Phosphonic Acid Group-Modified MCM-41/Imidazole Composites ([1] *Graduate School of Frontier Science Initiative, Kanazawa University,* [2] *NanoMaterials Research Institute,* [3] *Graduate School of Natural Science and Technology, Kanazawa University*) ○Yuta Arai,[1] Takuya Kurihara,[3] Yasuhiro Shigeta,[2] Shogo Amemori,[2] Tomonori Ida,[3] Motohiro Mizuno[1,2,3]

Recently, solid electrolytes have attracted attention due to their high proton conductivity and stability. However, the proton conductivity decreases at high temperature because of losing proton carrier water molecules. In this research, we have introduced imidazole into phosphonic acid modified MCM-41 mesoporous silica, in order to retain proton conductivity under anhydrous condition. Imidazole was incorporated into MCM-41 under various amounts. All the obtained samples retained their proton conductivity under anhydrous condition above 373 K. Moreover, the proton conductivity of MCM-41 increased with increasing amount of imidazole. Temperature change in line width of solid state ^{2}H NMR spectrum revealed that the activation energy of rotational motion tended to be lower and the mobility tended to be higher as the amount of imidazole was larger.

Keyword: Proton Conductivity; Porous Material

近年、固体燃料電池における電解質としてプロトン伝導体の研究が行われているが、高温では脱水によってプロトン伝導性が低下する問題がある。本研究ではホスホン酸で多孔質材料であるメソポーラスシリカ (MCM-41)を修飾して(Fig. 1)、プロトン伝導媒体としてイミダゾールを導入した。

ホスホン酸基修飾 MCM-41 にイミダゾールを異なる量で反応させ、導入量の異なる複数の試料を得た。これらの試料のプロトン伝導度を測定した結果、373 K 以上でもプロトン伝導性は低下せず、イミダゾールの導入量が増加するほど上昇する傾向が見られた(Fig. 2)。固体 ^{2}H NMR のスペクトルの線幅の温度変化からイミダゾールの回転運動の活性化エネルギーを見積もったところ、イミダゾール導入量が多いほど活性化エネルギーは低くなり、運動性が高い傾向が見られた。

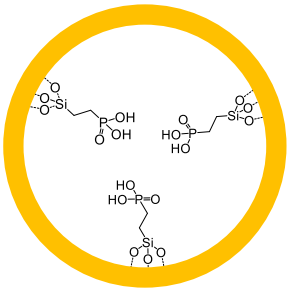

Fig. 1 ホスホン酸基修飾 MCM-41 のイメージ

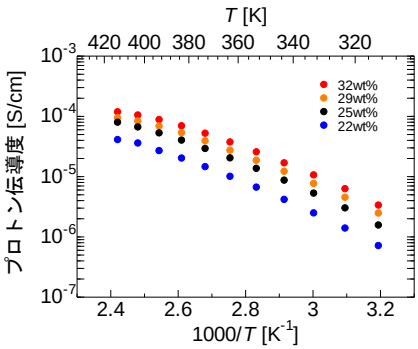

Fig. 2 プロトン伝導度の温度変化 (全重量とイミダゾールの重量比)

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

[P04-1am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Fri. Mar 19, 2021 9:40 AM - 11:10 AM Area 4 (Online Meeting)

[P04-1am-01] Elucidation of Energy Transfer in a Single Perovskite Nanocrystal-Dye Molecules Hybrid System

○Kaho Matsunaga[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. The Univ. of Kwansei Gakuin)

9:40 AM - 11:10 AM

[P04-1am-03] Synthesis of Perovskite Nanoplatelets and Evaluation of Emission Behavior at a Single Dot Level

○Yuka Arimoto[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-04] Carrier dynamics of a CH_3NH_3PbBr3 crystal by utilizing transient absorption microscopy

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

9:40 AM - 11:10 AM

[P04-1am-05] Size-Dependent Emission Behavior of Cesium Lead Halide Perovskite Nanocrystals

○Hina Igarashi[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-06] Passivation of Halide Vacancies in Lead Halide Perovskite Quantum Dots for Photoluminescence Blinking Suppression

○Lata CHOUHAN[1], Vasudevanpillai BIJU[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

9:40 AM - 11:10 AM

[P04-1am-07] Energy transfer in a single perovskite nanocrystal-dye molecules -Nanocrystal size dependence-

○Haruki Horibe[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-08] Interfacial Transport and Collection of Photogenerated Charge Carriers in Bandgap Engineered Lead Halide Perovskite Heterostructures

○MD SHAHJAHAN[1], Lata Chouhan[1], Vasudevanpillai Biju[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

9:40 AM - 11:10 AM

[P04-1am-09] Kinetic analysis of halide exchange reaction of an inorganic perovskite nanocrystal

○Yuki Tajika[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

9:40 AM - 11:10 AM

[P04-1am-10] Control of the Emission Behavior of a Single Quantum Dot by a One-Dimensional Metal Periodic Structure

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○Hiroto Takase[1], Hinako Chida[1], Mitsuaki Yamauchi[1], Keiko Tawa[1], Sadahiro Masuo[1] （1. Kwansei Gakuin University ）

9:40 AM - 11:10 AM

[P04-1am-11] The n-π interactions and electron correlations in intramolecular rotation of chalcogenoanisole

○Kotai Ka[1], Yoshihiro Yamakita[1] （1. The Univ. of Electro-Communications）

9:40 AM - 11:10 AM

[P04-1am-12] Photoexcited dynamics of microcrystals of dimethylhexatriene

○yusuke chichi[1], takuya Nakamura[1], tomoaki yago[1], masanobu wakasa[1] （1. Saitama University）

9:40 AM - 11:10 AM

[P04-1am-13] Methanol photoaddition reaction of (*R*)-(+)-limonene in a microreactor

○Riku Suzuki[1], Wataru Kashihara[1], Tadashi Suzuki[1] （1. Aoyama Gakuin Univ）

9:40 AM - 11:10 AM

[P04-1am-14] Direct observation of ultrafast electron ejection from higher excited state in solution phase

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

9:40 AM - 11:10 AM

[P04-1am-15] Examination of Low Magnetic Field Effect of Photochemical Reaction in Micelles

○Atsuya Hosoda[1], Tomoaki Yago[1], Kiminori Maeda[1], Masanobu Wakasa[1] （1. Graduate School of Science and Engineering, Saitama University ）

9:40 AM - 11:10 AM

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単一ペロブスカイトナノ結晶－有機色素間におけるエネルギー移動解明

（関西学院大院理工）○松永 花穂・山内 光陽・増尾 貞弘
Elucidation of Energy Transfer in a Single Perovskite Nanocrystal-Dye Molecules Hybrid System (*Kwansei Gakuin University*) ○Kaho Matsunaga, Mitsuaki Yamauchi, Sadahiro Masuo

Perovskite nanocrystals (PNCs) are focused on great attention as photofunctional materials. By combining them with dyes, new optoelectronic properties can be expected based on the energy transfer (FRET). In this study, we aimed to elucidate the FRET mechanism from PNC to dyes (Cy3 and Cy5) by preparing a PNC-dyes system and observing FRET in solution and at the single PNC level.

Upon mixing Cy3 with carboxyl group and PNC in toluene, Cy3 was adsorbed on PNCs. When single PNC-Cy3 was measured, Cy3 emitted fluorescence at the initial part of the measurement as shown in Fig.1(a). After Cy3 was photobleached, PNC emission emerged (Fig.1a). In the emission decay curves, the shortening of the PNC lifetime and the rise of the Cy3 were observed, which indicated the FRET from PNC to Cy3 (Fig.1b). We discuss the FRET in the details based on the experimental results.

Keywords : Perovskite; Nanocrystal; Quantum Dot; Single Molecule Detection; Energy Transfer

ペロブスカイトナノ結晶（PNC）は，優れた発光特性を持つ光機能性材料である。しかし，PNC からのエネルギー移動（FRET）については不明な点が多い。そこで本研究では，PNC-色素（Cy3, Cy5）間の FRET について，溶液中，および単一レベルで詳細に検討した。

まず，カルボキシ基を有する Cy3 と PNC をトルエン中で混合し，PNC-Cy3 溶液を作製した。その発光スペクトルを測定すると，Cy3 の濃度が増大するとともに PNC の発光強度が減少し，それに伴い，Cy3 の発光が観測された。これより，PNC から Cy3 への FRET が起こることがわかった。次に，単一 PNC-Cy3 を測定すると，測定開始時には Cy3 が発光しており，Cy3 光退色後は PNC の発光増加が見られた（Fig.1a）。発光減衰曲線（Fig.1b）においては，PNC の短寿命化と Cy3 の発光に立ち上がり成分が見られたことから，FRET を単一レベルで観測できたといえる。さらに，スペクトルの重なりが異なる Cy5 についても同様に実験を行ったので，詳細を報告する。

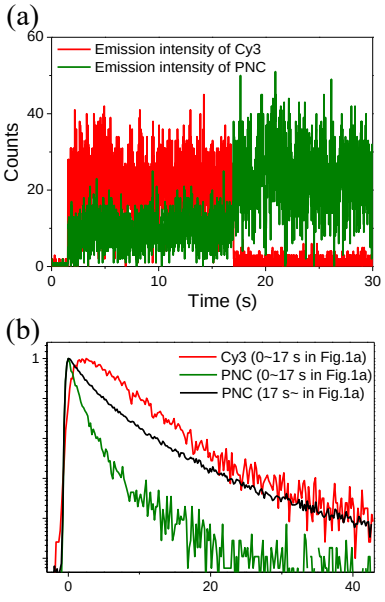

Fig.1 (a) Time trace of emission intensity of a single PNC-Cy3 system.
(b) Emission decay curves of PNC and Cy3 constructed at each time.

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ペロブスカイトナノプレートレットの合成および単一レベルでの発光挙動評価

（関西学院大理工）○在本 有伽・山内 光陽・増尾 貞弘

Synthesis of Perovskite Nanoplatelets and Evaluation of Emission Behavior at the Single Dot Level

(*Kwansei Gakuin University*) ○Yuka Arimoto, Mitsuaki Yamauchi, Sadahiro Masuo

Recently, perovskite nanocrystals have been intensively studied. However, optical properties of platelet-shaped perovskite nanocrystals (NPLs) have not been fully understood. By using ultrafast spectroscopy technique, it was reported that the Auger recombination rate of the NPLs decreases due to the one-dimensional quantum confinement effect. In this work, we aimed to elucidate the emission behavior of $CsPbBr_3$ NPL at the single dot level. Emission spectra of synthesized NPL showed PL peak at 472nm. This result indicated that 5 units cell NPLs were synthesized. Furthermore, it was confirmed that halide exchange reaction is possible by adding PbI_2 into NPL solution. We investigated the emission properties of the NPLs at the single level.

Keywords : Perovskite; Nanoplatelet; Single Photon; Quantum Dot; Photon Antibunching

近年，ペロブスカイトナノ結晶は盛んに研究されているが，プレートレット形状(NPLs)の研究例は少ない。NPLs は厚さ方向の量子閉じ込め効果により Auger 再結合速度がナノ結晶より遅くなることが報告されている [1]。そこで本研究では，$CsPbBr_3$ NPL の発光挙動, 特に単一光子発生挙動を単一レベルで解明することを目的とした。

合成した NPL は，ピーク波長 472nm の発光スペクトルを示し、5 層の NPL が作製されていることがわかった (Fig.1a)。さらに，NPL のヘキサン溶液にヨウ化鉛(II)を加えることで，ハロゲン交換反応が可能なことを確認した (Fig.1b)。これらの NPL について，単一レベルの測定を行い，発光挙動を評価したので詳細を発表する。

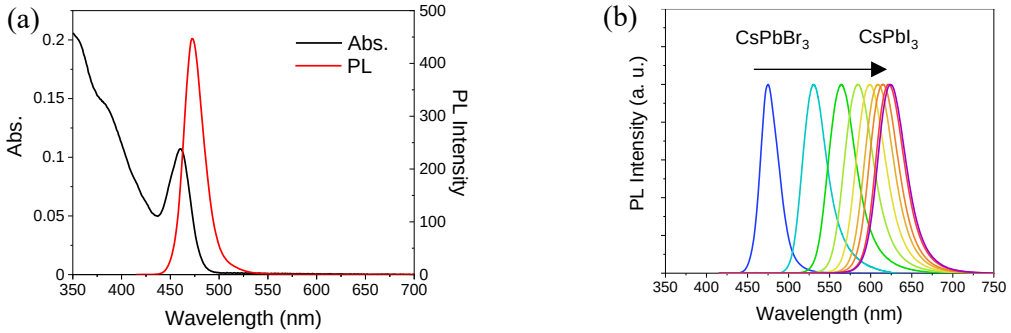

Fig. 1(a) Absorption and emission spectra of $CsPbBr_3$NPL in hexane.
(b) Emission spectra of the NPL with halogen exchange reaction.

1) Q. Li, Y. Yang, W. Que, and T. Lian, *Nano Lett*. **2019**, *19*, 5620−5627

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日本化学会 第101春季年会 (2021)

フェムト秒顕微過渡吸収スペクトル測定装置を用いた $CH_3NH_3PbBr_3$ 微結晶のキャリアダイナミクス

（徳大理工）○藤田 優真・赤木 裕一郎・片山 哲郎・古部 昭広

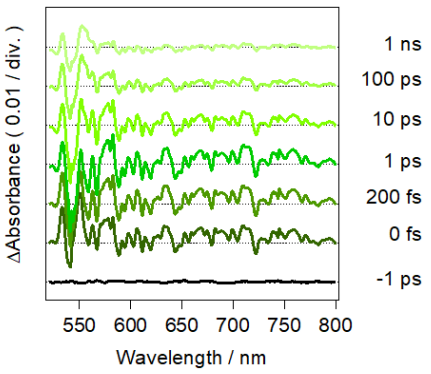
Carrier dynamics of a $CH_3NH_3PbBr_3$ crystal by utilizing transient absorption microscopy

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

Lead halide perovskites have attracted much attention for their applications for solar cells and light-emitting devices, and have been reported to exhibit nonlinear emission at low threshold. In order 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. This interference signal can be seen even at a delay time of 1 ns. We discuss the origin of the interference signal along with the density-dependent carrier dynamics.

Keywords : Femtosecond transient absorption spectra, Lead halide perovskite

ハロゲン化鉛ペロブスカイトは太陽電池・発光デバイ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、レージングのような非線形発光を示すことが報告されているが、未だこの低閾値発振機構について明らかでない点が多い。この非線形ダイナミクスを理解するため本研究では、励起光を単一微結晶よりも十分に大きなサイズに広げ、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装置でおこなった。Fig.1(a)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。この干渉信号は 1 ns の遅延時間でも見られる。Fig.1(b)に示すように過渡吸光度の時間変化には非線形発光の閾値以下(4.2 μJcm^{-2})と比較すると、閾値以上(11.4 μJcm^{-2})では初期のキャリア再結合過程に数ピコ程度の減衰が観測された。発表では、過渡吸収スペクトルに観測された干渉信号の起源についても議論する。



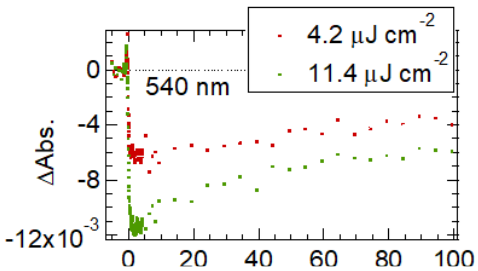


Fig.1 (a) Femtosecond transient absorption spectra of a $CH_3NH_3PbBr_3$ microcrystal (Ex. 400 nm, 11.4 μJcm^{-2}), (b) time profiles of transient absorbance (Mon. 540 nm).

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$CsPbBr_3$ ペロブスカイトナノ結晶における発光挙動のサイズ依存性

（関西学院大理工）○五十嵐 比菜・山内 光陽・増尾 貞弘
Size-Dependent Emission Behavior of Cesium Lead Halide Perovskite Nanocrystals
(*Kwansei Gakuin University*) ○Hina Igarashi, Mitsuaki Yamauchi, Sadahiro Masuo

Several nm sized-perovskite nanocrystals (PNCs) have been known to act as quantum dots (QDs) and exhibit single-photon emission behavior by quantum confinement effect. However, the single-photon emission behavior has not been fully revealed in larger PNCs up to 20 nm at weak quantum confinement region. In this work, we discussed the relationship between single-photon emission behavior and the size of $CsPbBr_3$ PNC by using single crystal spectroscopy technique combined with an atomic force microscope at the same time.

Photon-correlation histograms from the single PNCs with several nm showed low central peak at 0 ns in the photon-correlation histograms (Fig. 1a), indicating single-photon emission behavior. On the other hand, about 20 nm sized PNCs showed multiphoton emission behavior confirmed by the high central peak (Fig. 1c). We discuss the single-photon emission behavior depending on the PNC size.

Keywords : Perovskite; Quantum Dots; Sigle-Photon; Single Molecule Detection; Nanocrystal

数 nm サイズのペロブスカイトナノ結晶 (PNC) は量子閉じ込め効果により，一般的な量子ドットと同様にブリンキング挙動や単一光子発光挙動を示すことが知られている [1]。しかしながら，弱い量子閉じ込め領域である 20 nm 程度までの PNC については発光挙動が十分にわかっていない。本研究では，$CsPbBr_3$ PNC を合成し，単一粒子分光と AFM 測定を同時に行うことでサイズと発光挙動の相関を検討した。

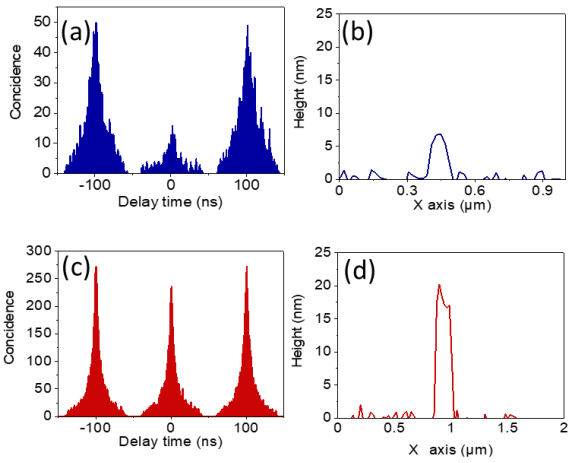

Fig. 1 Photon-correlation histograms (a, c), and AFM cross-sections (b, d) obtained from single $CsPbBr_3$ PNCs.

Fig. 1 に PNC の単一粒子分光から得られた光子相関ヒストグラム (a, c) と AFM 測定から得られた PNC の断面図 (b, d) を示す。数 nm の PNC では，光子相関ヒストグラムの中央のピークが低いことから，単一光子発生挙動が観測された。一方，20 nm 程度の PNC では中央のピークが高いため，多光子発生挙動が観測されることがわかった (Fig. 1c, d)。これらのサイズに依存した単一光子発生挙動について詳細を報告する。

1) Y. Park, S. Guo, N. Makarov, V. Klimov, *ACS Nano,* **2015**, *9*, 10386-10393.

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Passivation of Halide Vacancies in Lead Halide Perovskite Quantum Dots for Photoluminescence Blinking Suppression

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Research Institute for Electronic Science, Hokkaido University*) ○Lata Chouhan,[1] Vasudevanpillai Biju,[1,2]
Keywords: Halide Perovskite, Quantum Dots, Blinking Suppression, Halide Vacancy, Single-Particle Studies

Halide perovskites are promising for applications to the light-harvesting and light-emitting technologies owing to their brilliant optical and electronic properties.[1] However, these perovskites are susceptible to moisture, water, oxygen, and light.[2] Further, the photoluminescence (PL) of these perovskites fluctuates or blinks due to undesired nonradiative recombination of the photogenerated excitons/charge carriers through the halide vacancies.[1,2] In this work, we fill the halide vacancies in methylammonium lead halide ($MAPbX_3$, X= Br, I) perovskite at the ensemble and single quantum dot (QD) levels by treating with the corresponding methylammonium halide (MABr or MAI) to suppresses the halide vacancy-assisted nonradiative recombination and PL blinking.[3]

We recorded the single-particle PL intensity trajectories before [Figure 1a(i), b(i)] and after [Figure 1a(ii), b(ii)] the treatment of the QDs with a solution of MABr/MAI. Before the treatment, the QDs show intense blinking with short ON- and OFF-times. In contrast, after the treatment, the blinking is suppressed. Thus, the PL quantum efficiencies of the QDs are increased after the treatment.

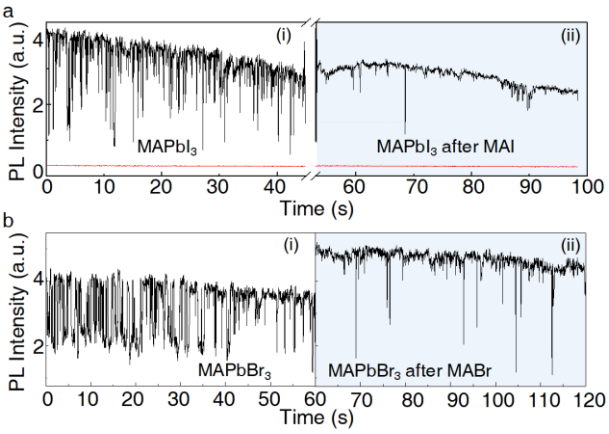

Figure 1. (a,b) Single-particle PL intensity trajectories of (a) $MAPbI_3$ QD and (b) $MAPbBr_3$ QD, (i) before and (ii) after the treatment with MAI and MABr. $MAPbI_3$ QDs were excited with a 532 nm cw laser (2 W cm^{-2}) and $MAPbBr_3$ QDs with a 405 nm cw laser (8.6 W cm^{-2}).

1) L. Chouhan, et al. *Chem. Soc. Rev.* **2020**, 49, 2869. 2) L. Chouhan, et al. *Angew. Chem. Int. Ed.* **2019**, 58, 4875. 3) L. Chouhan, et al. *ACS Nano* **2021**, 15, (*In press*).

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単一ペロブスカイトナノ結晶-有機色素間エネルギー移動 ーナノ結晶のサイズ依存性ー

（関西学院大理工）○堀部 春希・山内 光陽・増尾 貞弘

Energy Transfer in a Single Perovskite Nanocrystal-Dye Molecules -Nanocrystal Size Dependence-

(*Kwansei Gakuin University*) ○Haruki Horibe, Mitsuaki Yamauchi, Sadahiro Masuo

To realize the efficient use of generated excitons in various systems, we have been investigated the energy transfer (ET) between multiple excitons in a perovskite nanocrystal (PNC) and dye molecules (Cy3) adsorbed on the PNC. However, multiple excitons are decayed nonradiatively by the Auger recombination (AR) before the ET. In this work, we have investigated the ET between large-sized PNCs (~20 nm) which exhibit slower AR rate and multiple Cy3 on the PNC in solution and at the single nanocrystal level.

Cy3 was adsorbed on the PNCs by mixing PNCs and Cy3 with carboxyl group in toluene. By measuring PNC-Cy3 in the single level, we observed Cy3 emission at the initial part of the measurement. Then, the emission intensity of the PNC increased after photobleaching of the Cy3. We also observed the shortened lifetime of the PNC and the rise of Cy3 in the emission decay curves. From these results, we confirmed the ET between the large sized PNCs and Cy3. We discuss the ET from multiple excitons in PNCs to multiple Cy3 depending on the PNC size.

Keywords : Perovskite; Nanocrystal; Quantum Dot; Energy Transfer; Single Molecule

我々は励起子の有効活用を目的とし，ペロブスカイトナノ結晶(PNC)に生成する複数の励起子から複数の有機色素(Cy3)へのエネルギー移動(ET)を検討してきている。しかしながら，ETより速く，複数励起子間でオージェ再結合(AR)が起こり，励起子が失活してしまう。そこで本研究では，弱い量子閉じ込め効果により AR 速度が遅いと期待される(~20 nm)程度の PNC を合成し，溶液中，および単一レベルで測定することで複数の励起子から複数の Cy3 への ET を詳細に検討した。

カルボキシ基をもつ Cy3 と PNC をトルエン中で混合し吸着させた。これを単一レベルで測定すると，Fig.1(a)のように測定開始時は Cy3 の発光が観測され，Cy3 の光退色後は PNC の発光強度の増加が観測された。さらに，発光減衰曲線(Fig.1b)では PNC の短寿命化と Cy3 の立ち上がりが見られたことから，サイズの大きい PNC について ET が起こることを確認した。PNC のサイズに依存した多励起子からの ET 挙動について詳細を報告する。

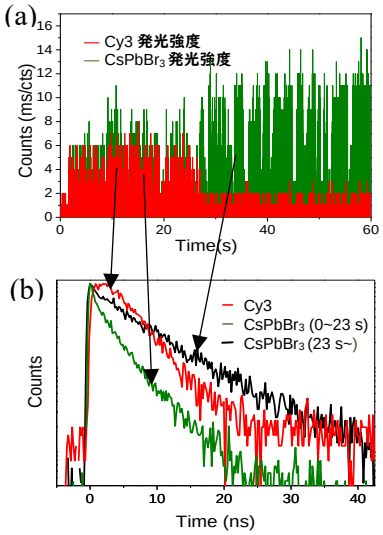

Fig.1(a) Time traces of PL intensity of a single PNC-Cy3.
(b) Emission decay curves of the PNC and Cy3 at different time domains.

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Interfacial Transport and Collection of Photogenerated Charge Carriers in Bandgap Engineered Lead Halide Perovskite Heterostructures

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Halide perovskites have emerged into a class of promising semiconductor materials for next-generation optoelectronic devices due to their unique excitonic and charge carrier properties. Also, architecting perovskite heterostructures with distinct halide compositions become promising for the generation and transport of charge carriers in solar cells. A facile way to prepare such perovskite heterostructure is halide exchange reactions by partly replacing the halide ions in a parent crystal. Here, we utilize a tightly focused near-infrared (NIR) laser beam to prepare bandgap engineered perovskite heterojunctions as well as control the transport and accumulation of charge carriers across the heterojunctions in methylammonium lead bromide ($MAPbBr_3$) microcrystals.

$MAPbBr_3$ microcrystals (micro-plates and micro-rods) are prepared by the evaporation of the solvent from the precursor solution of $MAPbBr_3$ placed on a glass coverslip in a reaction chamber. To prepare heterojunctions in a $MAPbBr_3$ crystal, a reaction solution of MAI was added into the chamber, and a 1064-nm laser beam was focused onto the surface of the crystals (Figure 1a). Before the NIR laser irradiation, the whole $MAPbBr_3$ crystal shows green emission due to its intrinsic property, which gradually changes into the red at the focal spot. (Figure 1b). The red-shifted photoluminescence (PL) spectrum (Figure 1c) of the laser irradiated area confirms the formation of $MAPb(Br.I)_3$. Furthermore, we investigate the dynamics of photogenerated charge carriers in the heterojunction structures by recording the PL lifetimes of the crystals at different distances starting from the halide exchanged part. We discuss the possible mechanism of charge carrier dynamics in such heterojunction structures from the viewpoint of valence and conduction band continuities.

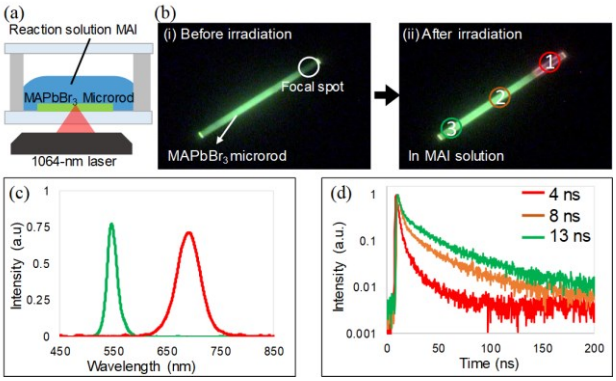

Figure 1. (a) A scheme of the laser irradiation to a $MAPbBr_3$ microrod, (b) the PL images of a $MAPbBr_3$ microrod crystal (i) before and (ii) after the exchange reaction, , (c) the PL spectra collected from a part of the crystal (green) before and (red) after the halide exchange reaction, and (d) the PL decay profiles of the crystal from the irradiated and non-irradiated parts marked in 'b(ii)'.

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ペロブスカイトナノ結晶におけるハロゲン交換反応の速度論的解明

（関西学院大院理工）○多鹿 祐貴・山内 光陽・増尾 貞弘
Kinetic Analysis of Halide Exchange Reaction of Inorganic Perovskite Nanocrystals
(*Kwansei Gakuin University*) ○Yuki Tajika, Mitsuaki Yamauchi, Sadahiro Masuo

Inorganic perovskite nanocrystals (PNCs) exhibit the photoluminescence (PL) with a high color purity. Furthermore, their wavelength can be tuned over the whole visible region by the halide-exchange reaction. However, the reaction mechanism has not been fully understood. Here, we attempted to reveal the mechanism kinetically by conducting the halide-exchange in toluene with observing the PL spectral changes. The redshift of PL from 508 nm to 614 nm was observed for 120 s after adding I^-. The redshift indicates that Br^- in PNCs was replaced by I^-. Notably, the PL spectrum then blueshifted by 17 nm for 25 h. The unexpected blueshift indicates that the ratio of Br^- in PNC increased. Generally, binding energy of Br^- with Pb is stronger than that of I^-. Therefore, the second shift occurred to be more stable.

Keywords : Perovskite; Nanocrystal ; Halide Exchange Reaction; Quantum Dot

ペロブスカイトナノ結晶 (PNCs)は色純度の高い発光を示し，ハロゲン部位の交換により発光波長を全可視光域で制御可能なことから盛んに研究されている [1]。本研究では，ハロゲン交換反応の詳細なメカニズム解明を目的とし，$CsPbBr_3$ PNCs トルエン溶液のハロゲン交換反応に伴う発光スペクトルの時間変化を追跡した。

図 1 に示すように、I^-を添加すると，発光ピーク波長が 120 秒間で 508 nm から 614 nm に長波長シフトし，その後，25 時間で 17 nm 短波長シフトした。I^-を PNCs に添加すると，PNC 内外で濃度勾配が生じるため，Br^- → I^-交換が起き，長波長シフトを伴いながら速度論的安定状態に至ったと考えられる。しかし，Pb との結合力は $Br^- > I^-$であるため，その後 I^- → Br^- 交換が起き，熱力学的な安定状態に至るため，短波長シフトが観測されたと考えられる。

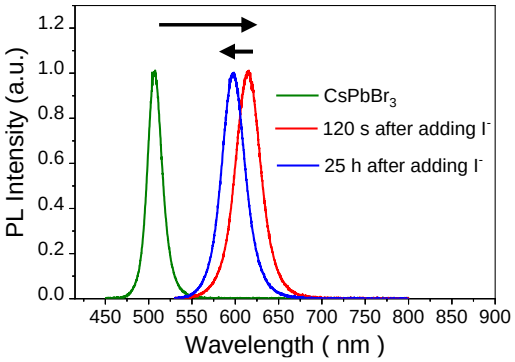

Figure 1. Time dependent PL spectra after adding I^- to $CsPbBr_3$ PNC in toluene.

1) L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R.X. Yang, A. Walsh, and M.V. Kovalenko., *Nano Lett*. **2015**, 15, 3692-3696

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一次元金属周期構造による単一量子ドットの発光挙動制御

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Control of the Emission Behavior of Single Quantum Dots by a One-Dimensional Metal Periodic Structure (*Kwansei Gakuin University*) Hiroto Takase, Hinako Chida, Mitsuaki Yamauchi, Keiko Tawa, Sadahiro Masuo

Surface plasmon generated in plasmonic nanostructures (PNSs) can enhance the excitation, the radiative and non-radiative rates of the adjacent emitters. The purpose of this study is to control the emission behavior, i.e., emission photon statistics such as single-photon emission and multiphoton emission, of quantum dots (QDs) using PNSs. In this work, CdSe/ZnS QDs dispersed on a periodic structure of silver were measured at the single QD level. We found that the emission intensity of the single QDs was enhanced, but the control of the emission photon statistics was difficult. These results indicated that the periodic structure mainly enhanced the excitation rate of the QDs.

keywords: CdSe/ZnS quantum dot, Single-photon, Plasmon, Plasmonic nanostructure, Photon antibunching

量子ドット(QD)に生成した多励起子が発光すると，QDは多光子発光を示すが，高効率にオージェ再結合が起こり，励起子が消滅するため，単一光子発光を示す。我々はこれまで，プラズモンによる増強効果を用いることにより，単一量子ドット(QD)の発光光子数を制御してきた[1, 2)]。本研究では，波長サイズの銀周期構造を持つプラズモニックナノ構造（PNS、Fig.1a）を用い，単一CdSe/ZnS QDの発光光子数制御を検討した。

PNS 上と PNS 外(銀上)について，単一 QD を測定したところ，PNS 上で発光強度が増強された（Fig.1b）。しかし，発光寿命，および発光光子数は変化が見られず，QD は単一光子発光を示した。以上の結果から，今回用いた PNS では発光光子数の制御が困難で，発光強度の増強のみが起こることがわかった。今後は，PNS の条件を検討し，輻射速度を増強させることで，発光光子数の制御を可能にしたいと考えている。

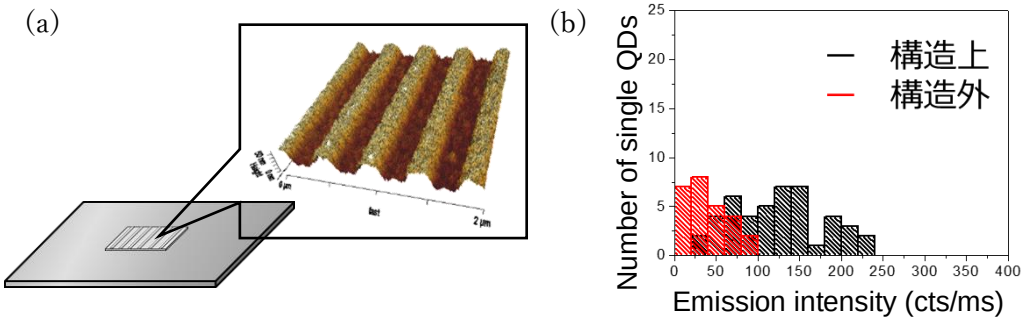

Fig.1 (a). An illustration and AFM image of a PNS with silver periodic structure.
(b). Histogram of the emission intensity obtained from the single QDs (Black: on PNS, Red: on Ag).

1) H. Takata, H. Naiki, L. Wang, H. Fujiwara, K. Sasaki, N. Tamai, and S. Masuo, *Nano Lett*., **2016**, *16*, 5770-5778.
2) S. Masuo, K. Kanetaka, R. Sato, T. Teranishi, *ACS Photonic*s, **2016**, *3*, 109-116.

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カルコゲノアニソールの分子内回転における n-π 相互作用と電子相関

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The n-π interactions and electron correlations in intramolecular rotation of chalcogenoanisole
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〇Kotai Ka, Yoshihiro Yamakita

In this study, we investigated the effect of electron correlation on intramolecular rotation. We calculated the rotational potential barrier ΔE=E(vertical)–E(planar) of chalcogenoanisole $C_6H_5XCH_3$ (X=O, S, Se) around the dihedral angle between C_6H_5 and XCH_3 groups by using the CASSCF and CASPT2 methods. Upon conformational change, the orbital energy of HOMO and HOMO–2 in the planar form change significantly due to the n-π interaction. The CASPT2 calculations involving 5 orbitals and 6 electrons describing n-π interaction predict that ΔE decreases as X = O→S→Se, and that the vertical conformer is the most stable in the case of X=Se. The results are consistent with the previous experimental PIES and calculations.
Keywords: n-π Interaction; Rotational Potential Barrier; Electron Correlation; Chalcogenoanisole; Nonbonding Orbital

カルコゲノアニソール $C_6H_5XCH_3$ (X=O, S, Se) の平面構造と垂直構造は、それぞれ n-π 相互作用とσ-π 相互作用によって安定化していると考えられる。これらの分子内回転の安定性はこれまでに研究されてきたが、いまだ X=Se については明らかになっていない。本研究では、これらのカルコゲノアニソールを対象に分子内回転に対する電子相関の影響を研究した。Fig. 1 は C_6H_5 基と XCH_3 基の二面角 τ を回転させた時の、X=Se の軌道エネルギーの変化である。3 分子とも平面構造における HOMO と HOMO–2 の軌道エネルギーが大きく変化した。X=Se の HOMO（ϕ42）から HOMO–2（ϕ40）は、平面構造で n_{Se}–π_2, π_3, π_2+n_{Se}、垂直構造で n_{Se}, π_3–σ_{SeC}, π_2 の性質があり、n-π相互作用が変化していることがわかる。3 分子の回転ポテンシャル障壁ΔE=E(vertical)–E(planar)を、n-π軌道の関係する HOMO を含めた 5 軌道と 6 電子を active space に取り入れた CASSCF, CASPT2 法を用いて計算した。Table 1 に示すように CASPT2 法では X=O→S→Se となるにつれてΔE は小さくなり、X=O, S は平面構造が安定、X=Se は垂直構造が安定という結果が得られた。これは実測および計算 PIES[1]での結論と一致している。

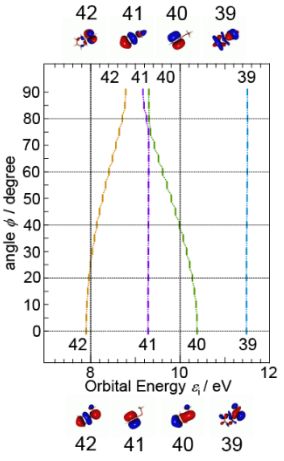

Fig. 1. Changes in Orbital Energy of selenoanisole

Table 1. Rotational Potential ΔE (kJmol^{-1}) of CASPT2, CASSCF/cc-pVTZ and B3LYP/6-31++G(d,p) [1].

	CASPT2	CASSCF	B3LYP
anisole	12.31	10.00	12.45
thioanisole	2.24	1.80	2.09
selenoanisole	-0.53	2.29	-5.13

1）Y. Ishiguro, Y. Yamakita, and N. Hayashi, *Chem. Phys. Lett.* **2020**, 754, 137653.

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ジフェニルヘキサトリエンのマイクロ結晶の光励起ダイナミクス

（埼大院理工[1]）○知々田　優介[1]・中村　拓世[1]・矢後 友暁[1]・若狭　雅信[1]
Photoexcited dynamics of microcrystals of diphenylhexatriene ([1]*Graduate School of Science and Engineering, Saitama University*) ○Yusuke Chichida,[1] Takuya Nakamura,[1] Tomoaki Yago,[1] Masanobu Wakasa[2]

Singlet fission (SF) is a process in which single singlet excition generates a couple of triplet excitions. SF can be one of the options to control the number of excitons and the energy of excitons in organic devices. Diphenyl hexatriene (DPH) crystals have been recognized as an efficient singlet fission material and have been studied with bulk crystals. Though the several important informations on SF such as a SF rate, the structure of a triplet pair, the lifetime of triplet pair were obtained with bulk crystals, the size of the material parts in organic devices are typically on the order of nanometer. In the present study, we intend to clarify the photodynamics of DPH microcrystals whose sizes are on the order of 0.1 μm～1 μm.

We prepared DPH microcrystals with the reprecipitation method. We measured the lifetime of fluorescence and the magnetic field effects on the intensity of fluorescence. It was found that the photodynamics of the DPH crystals depends on the size of crystals.
Keywords : Singlet fission; microcrystals; Fluorescence; Magnetic field effects

シングレットフィッション（SF）とは、一つの励起一重項から、二つの励起三重項が生成する過程であり、有機デバイス中で励起子の数、エネルギーを制御する方法として注目されている。ジフェニルヘキサトリエン（DPH）結晶中においては、結晶の光励起後に効率よく SF が進行することが知られている[1)]。これまでの DPH に関する研究は、主にバルク結晶を用いて行われ、様々な知見が得られてきた[2)]。しかし、実際の有機デバイスにおいては、バルク結晶ではなくナノメートルのサイズの結晶や、ナノメートルオーダーの膜厚を持つ薄膜が利用されることが多い。そこで、本研究では、DPH の微結晶を作成し、その光励起ダイナミクスを蛍光測定により検討した。

DPH の微結晶は再沈法により作成した[3)]。作成された微結晶の粒径は 0.1 μm～1 μm 程度であった。この DPH 微結晶における蛍光寿命を測定したところ、バルク結晶の場合に比べ、遅延蛍光の寿命が大幅に長くなった。また、蛍光強度による磁場効果を測定したところ、磁場効果の大きさは、バルク結晶のときの磁場効果の大きさに比べ顕著に大きくなった。これらのことから、微結晶中においては、SF によって生成した励起三重項が、拡散後に再び出会う（geminate の再結合）確率が増大していることがわかった。これは、生成した励起三重項の拡散が、0.1 μm～1 μm の空間に制限されていることによるものと考えられる。本研究により、SF 後の光励起ダイナミクスは、結晶のサイズに大きく影響されることが明らかになった。

1) Badeen C. J. et al. *J. Am. Chem. Soc.* **2013**, *135*, 17278.
2) Ishikawa, K.; Yago, T.; Wakasa, M. *J. Phys. Chem. C* **2018**, *122*, 22264.
3) Amemori, S.; Sasaki, Y.; Yanai, N.; Kimizuka, N. *J. Am. Chem. Soc.* **2016**, *138*, 8702.

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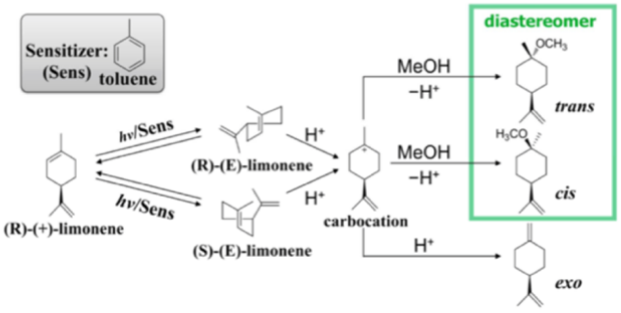
マイクロリアクターによる(*R*)-(+)-リモネンのメタノール光付加反応

（青学大院理工）○鈴木陸・柏原航・鈴木正
Methanol photoaddition reaction of (*R*)-(+)-limonene in a microreactor (*Grad. Sch. Sci. Eng., Aoyama Gakuin Univ.*) ○Riku Suzuki, Wataru Kashihara, Tadashi Suzuki

In the synthesis of fine chemicals, photoasymmetric synthesis is required to produce useful enantiomers without risk, and the synthesis has been performed in the batch system such as flasks and beakers. However, there are some problems such as sequential reaction due to retention and non-uniform reaction temperature in the batch system. Since the microreactor is a flow reaction system and has a large specific surface area and an extremely small volume, these problems will be solved by using the microreactor.

In this study, the methanol photoaddition reaction of limonene in a microreactor was used as a model reaction. It was found that the photoproduct was obtained with high optical purity as compared with the measurement in the batch reaction vessel. In addition, the values of [*trans*]/[*cis*] increased significantly in the low temperature region. The activation parameters of the reaction in the microreactor were calculated using the Eyring equation. The values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ were significantly different from these in the batch system. It is considered that the influence of the side reaction due to retention was minimized and the reaction temperature could be precisely controlled.

Keywords : Limonene; Microreactor; Photoaddition reaction; Optical purity



ファインケミカルにおいて、鏡像異性体を作り分けるための光不斉合成が重要であり、これまでフラスコやビーカーなどの反応容器(バッチ系)が用いられてきた。しかし、バッチ系では「滞留による逐次反応の進行」や「不均一な反応温度」といった問題点がある。マイクロリアクターは、フロー反応系であり、比表面積が大きいことや体積が極めて小さいことから、これらの問題点の解決が期待される。

本研究では、マイクロリアクター中のリモネンのメタノール光付加反応をモデル反応として実験を行った。バッチ系反応容器での測定[1]と比較して、マイクロリアクター中では高い光学純度で生成物を得ることが分かった。また、低温領域では[*trans*]/[*cis*]比は大きく上昇した。そこで、アイリングの式を用いて、マイクロリアクター中における反応の活性化パラメータの差を求めた。得られた$\Delta\Delta H^{\ddagger}$, $\Delta\Delta S^{\ddagger}$の値は、バッチ系と比べて大きく異なることが分かった。これは、マイクロリアクターの特徴から滞留による副反応の影響を最小限に抑え、反応温度を精密に制御できたためだと考えられる。

1) S. C. Shim *et al., J. Org. Chem.*, **2002**, *67*, 5718.

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液相中高位電子励起状態を介した超高速電子放出ダイナミクスの直接観測

（阪大院基礎工）○古賀 雅史・五月女 光・宮坂 博
Direct observation of ultrafast electron ejection from higher excited state in solution phase
(*Graduate School of Engineering Science, Osaka University*)
○Masafumi Koga, Hikaru Sotome, Hiroshi Miyasaka

In solution phase, photoionization takes place with a photon energy lower than that in the gas phase. In the ionization dynamics with low excitation energy, dielectric interactions with surrounding media and solvation was expected to play an important role in charge separation processes. In order to elucidate the specific interaction involved in the ionization dynamics, we applied transient absorption spectroscopy under multiphoton excitation for *N,N-dimethylaniline* (DMA) in polar solutions. The gradual appearances of the signals due to the radical cation of DMA and solvated electron were observed in sub-picosecond to picosecond timescales, which strongly indicates that the electron ejection took place via specific intermediate state.
Keywords : Molecular Dynamics; Femtosecond transient absorption spectroscopy; Electron transfer; Higher excited state; Solvation

液相中において、光イオン化反応は気相に比べ低い励起エネルギーでも進行可能になる。これは溶媒和といった溶質-溶媒間の超高速な分極相互作用の寄与によるためと考えられてきた。一方で、光励起直後に生成する高位電子励起状態(S_n状態)の寿命は一般に溶媒分子の配向緩和速度に比べ高速であるため、溶媒和過程のみを単純にイオン化の駆動力とみなすことはできない。イオン化にかかわるこの特異的な相互作用のメカニズムを明らかにするため、極性溶媒中 *N,N*-dimethylaniline (DMA)を対象に、逐次二光子励起を用いたフェムト秒過渡吸収スペクトル測定(2PE-TA)を行った(Figure 1a)。エタノール溶媒中において、DMA^{+}に由来する信号が約 10 ps の時定数をもって増大する様子が観測された。さらに溶媒和電子に由来する信号は、同様の時間スケールで、スペクトルのシフトを伴いながら増大した。この結果から、光イオン化過程が特異的な中間体を経由して進行し、中間体の溶媒和過程が電子放出の駆動力であることが強く示唆された(Figure 1b)。

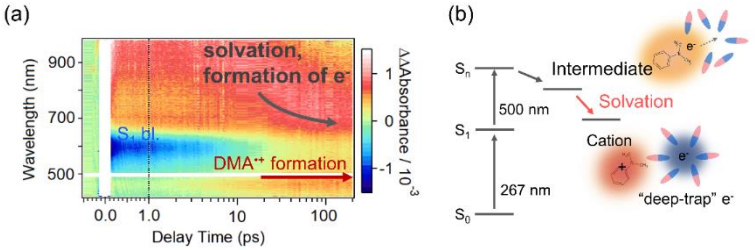

Figure 1. (a) Contour plot of 2PE-TA spectra of DMA in ethanol under stepwise excitation by pump1 (267 nm) and pump2 (500 nm). Pump1 was irradiated 50 ps before the irradiation of pump2.
(b) Photoionization scheme under stepwise two-photon excitation.

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ミセル中の光化学反応の低磁場効果の検討

（埼大院理工[1]）○細田敦也[1]・矢後友暁[1]・前田公憲[1]・若狭雅信[1]

Examination of Low Magnetic Field Effect of Photochemical Reaction in Micelles

([1]*Graduate School of Science and Engineering, Saitama University*) ○Atsuya Hosoda[1], Tomoaki Yago[1], Kiminori Maeda[1], Masanobu Wakasa[1]

It is known that there are organisms that use the geomagnetism for their own navigation, however the mechanism of magnetic sensitivity is not well understood. The sensitivity that radical pairs mechanism is considered to be one of the promising mechanisms on imagine. The magnetic field effect of the radical pairs mechanism in the photochemical reaction in the micelles, the escaped radical yield increases at high magnetic fields, but there are few studies on the low magnetic field effect, and there are many unclear points about the mechanism.

The low magnetic field effect was measured in a system in which a high magnetic field effect was observed by a photochemical reaction in micelles in the past.[1] Specifically, the low magnetic field effect that reduces the escaped radical yield was measured by transient absorption experiment. The magnetic field effect was analyzed, and the mechanism of the low magnetic field effect was examined.

Keywords : spin, magnetic field effect, radical, photochemical

地磁気を自身のナビゲーションに利用する生物がいることが知られている。その磁気感受メカニズムは未だよく分かっていないが、有力視されているものにラジカル対機構がある。ミセル中での光化学反応におけるラジカル対の磁場効果は、高磁場でその散逸ラジカル収量が増加するが、低磁場効果について研究された例は少なく、その機構についても不明な点が多い。

過去にミセル中での光化学反応で高磁場効果が観測された系において、[1] 低磁場効果の測定を行った。具体的には過渡吸収装置を用いて、光化学反応のその散逸ラジカル収量が減少する低磁場効果を測定した。その磁場効果の解析を行い、低磁場効果の機構の検討を行った。

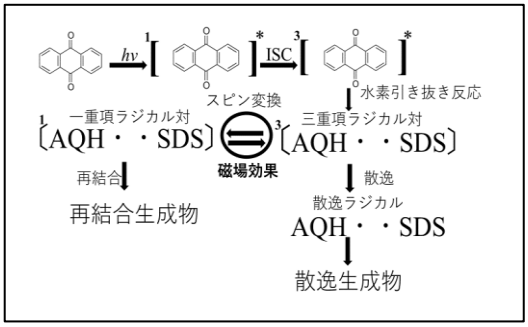

Figure.1 反応系

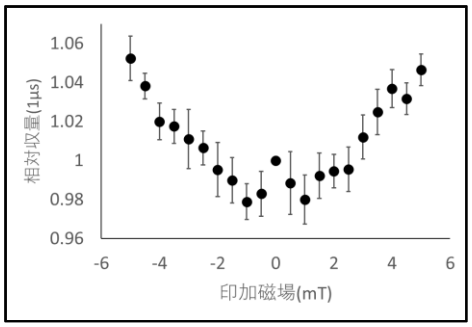

Figure.2 散逸ラジカル収量の低磁場効果

1)Y.Tanimoto,H.Udagawa,M.Itoh,T.*J.Phys.Chem*(1983)

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[P01-1vn] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Fri. Mar 19, 2021 4:10 PM - 5:40 PM Area 1 (Online Meeting)

[P01-1vn-01] photodimerization of 1-aryl-6-pyridylhexatriene
○Haruka Ito[1], Shinji Yamada[1] (1. Ochanomizu University, department of chemistry)

[P01-1vn-02] Effect of intramolecular cation-π interaction on the fluorescence properties of nicotinamide derivatives
○Miori Sasaki[1], Shinji Yamada[1] (1. department of chemistry, Ochanomizu University)

[P01-1vn-03] Stereoselective Norrish-Yang Reactions of Imidazolidinone Derivatives Using an Ammonium-π interaction
○Hanako Nakajima[1], Shinji Yamada[1] (1. Ochanomizu University)

[P01-1vn-04] Development of chromophoric materials towards highly efficient visible-to-UV photon upconversion
○Tae Tamemoto[1], Kana Orihashi[1], Nobuhiro Yanai[1,2,3], Nobuo Kimizuka[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. PRESTO, JST)

[P01-1vn-05] Copper-Catalyzed Enantioselective Intramolecular [2+2]Photocycloaddition of 1,4-Naphthoquinone-Alkene System
○Daiki Asanuma[1], Hajime Shigemitsu[1], Tadashi Mori[1], Toshiyuki Kida[1] (1. Osaka University)

[P01-1vn-06] Fabrication and Characterization of Expanded Perylene Diimide Derivatives Insoluble Thin Films by Photo-Induced Scholl Reactions
○Yamato Manjome[1], Tomoya Ogawa[1], Daiki Kuzuhara[1] (1. Iwate University)

[P01-1vn-07] The photoreaction of coumaryl-4-methyl derivative bearing electron donating group at 7-position
○Ma-aya Takano[1], Abe Manabu[1] (1. The Univ. of Hiroshima)

[P01-1vn-08] Photon Upconversion of Dyads Linked with Nonconjugated Units
○Masaya Kanoh[1], Kiyomasa Honda[1], Takuya Ogaki[1], Yasunori Matsui[1], Eisuke Ohta[1], Hiroshi Ikeda[1] (1. Osaka Pref. Univ.)

[P01-1vn-09] Photoredox 1,4-addition onto α,β-unsaturated carboxylic acid and development of photocatalyst
○Misaki Umezawa[1], Toshiya Hirahama[1], Mitsuru shoji[1] (1. Yokohama Univ. of Pharmacy)

[P01-1vn-10] Multi-photon Excitable Imidazo[1,2-*a*]pyridinium Salts for Mitochondria-targeted Image-guided Photodynamic Therapy
Fumitoshi Yagishita[1,2], ○Shota Kunimi[1], Keita Hoshi[1], Masaki Okamoto[1], Atsushi Tabata[3], Hideaki Nagamune[3], Eiji Hase[2], Keiji Minagawa[1], Yasushi Imada[1] (1. Department of Applied Chemistry, Tokushima University, 2. Institute of Post-LED Photonics, Tokushima University, 3. Faculty of Bioscience and Bioindustry, Tokushima University)

[P01-1vn-11] Research on ITO/PEN electrodes modified by organic dyes and their photoelectrochemical properties
○Thi Thu Trang Tran[1], Kentaro Suzuki[1], Toshi Nagata[1] (1. Meijo University)

[P01-1vn-12] Photoreaction of quinones with an amphiphilic porphyrin sensitizer
○Yui Tanaka[1], Toshi Nagata[1] (1. Graduate School of Science and Technology, Meijo University)

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[P01-1vn-13] Development of Environmentally Benign Julia Olefination by Reductive Desulfonylation Utilizing Pyrene Photocatalyst

○Hikaru Watanabe[1], Kazuki Nakajima, Ryota Edagawa, Yasuhiro Okuda[1], Akihiro Orita[1] （1. Okayama University of Science）

[P01-1vn-14] Synthesis and Aggregate Properties of Pentacene Derivatives Bearing Quadruple Hydrogen Bonding Units

○Naoki Koike[1], Shunta Nakamura[1], Hayato Sakai[1], Taku Hasobe[1] （1. Keio University）

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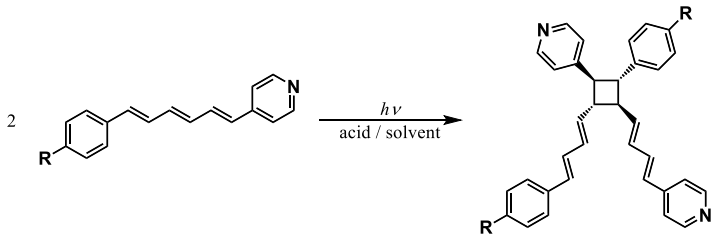
1ーアリールー6ーピリジルヘキサトリエン類の光二量化反応

（お茶女大院人間文化創成科学）○伊藤 陽香・山田 眞二
Photodomerization of 1-Aryl-6-pyridylhexatriene (*Department of Chemistry, Ochanomizu University*) ○Haruka Ito, Shinji Yamada

Cyclobutane is an important structure in organic synthesis because it is found in natural organic compounds and is also used as an intermediate in various bioactive compaunds. While [2+2] photocycloaddition is useful as a general method to obtain cyclobutanes, it has not been studied to control the stereoselectivity of the products. In our laboratory, we have achieved stereoselective [2 + 2] photocycloaddition of styrylpyridines and pyridylbutadienes by controlling molecular arrangement using cation-π interactions [1) 2)]. In this study, we investigated stereoselective photodimerization of 1-aryl-6-pyridylhexatrienes. When the acidic solution of substrates was irradiated with a 400 W high-pressure mercury lamp, *anti*-HT dimers was selectively obtained.
Keywords : cation-π interaction; photodimerization; [2+2] cycloaddition; triene; stereoselectivity

シクロブタン骨格は天然有機化合物等にみられ、生理活性物質の中間体等にも利用されることから、有機合成化学において重要な構造のひとつである。一般的なシクロブタン合成の手法として、[2+2] 光付加環化反応が有用である一方で、課題として生成物の立体選択性の制御が挙げられる。当研究室ではこれまでに、カチオン-π相互作用による分子配列制御を利用し、スチリルピリジン類およびピリジルブタジエン類の立体選択的な [2+2] 光反応を達成している [1), 2)]。本研究では、1-アリール-6-ピリジルヘキサトリエン類を基質として立体選択的な光二量化反応の検討を行った。基質溶液に 400 W の高圧水銀ランプで紫外光を照射すると、酸の非存在下では複雑な混合物が得られたのに対し、酸を添加すると *anti*-HT 型二量体が収率 4~6% で選択的に得られた。



1) S. Yamada, *Chem. Rev.*, **2018**, *118*, 11353-11432.
2) S. Yamada; K. Aya, *Chem. Asian J.*, **2020**, *75*, 581-584.

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ニコチン酸アミド誘導体の蛍光特性に及ぼす分子内カチオン-π相互作用の影響

（お茶女大院　人間文化創成科学）〇佐々木 美織・山田 眞二
Effect of intramolecular cation-π interaction on the fluorescence properties of nicotinamide derivatives (*Department of Chemistry, Ochanomizu University*)〇Miori Sasaki, Shinji Yamada

The phenomenon in which the behavior of fluorescence changes in response to various external stimuli and the light emission can be switched on/off is called a fluorescence switch. As the external stimuli, various intermolecular interactions play a key role to turn these switches on and off. In this study, we investigated the use of cation-pi interactions, which have received much attention in various fields in recent years, for fluorescent switches. We found that the fluorescence of nicotinic amides was enhanced by addition of an acid through the cation-pi interaction between the pyridinium and benzene rings. In fact, in the compounds **1a** and **1b** shown below, fluorescence intensity increased with the addition of an acid (Figure). The results for similar compounds will also be reported.
Keywords : nicotinic amide; fluorescence switch; cation-pi interaction; intramolecular interaction; pyridinium

種々の外部刺激に応答し，蛍光のオン／オフの変化を可能にする現象は蛍光スイッチと呼ばれ，多くの研究に取り入れられている．このスイッチを切り替える仕組みには様々な分子間相互作用が利用されている．本研究ではニコチン酸アミド類の分子内カチオン-π相互作用の蛍光スイッチへの利用を検討した．外部刺激として酸を添加することで，ピリジニウムカチオンが生成し分子内ベンゼン環との相互作用により蛍光スイッチ機能発現を見出した．以下に示す化合物 **1a**, **1b** では，酸の添加に伴う蛍光強度の増加が見られた（Figure）．また，類似化合物の結果についても報告する．

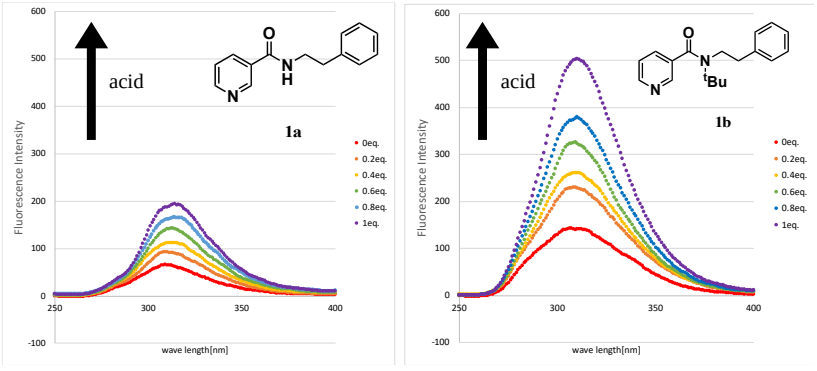

Figure. Fluorescence spectra of **1a** (left) and **1b** (right) with acid

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アンモニウム-π相互作用を利用するイミダゾリジノン類の立体選択的 Norrish-Yang 反応

（お茶女大理）○中島 華子・山田 眞二

Stereoselective Norrish-Yang Reactions of Imidazolidinone Derivatives Using an Ammonium-π interaction (*Department of Chemistry, Faculty of Science, Ochanomizu University*) ○Hanako Nakajima, Shinji Yamada

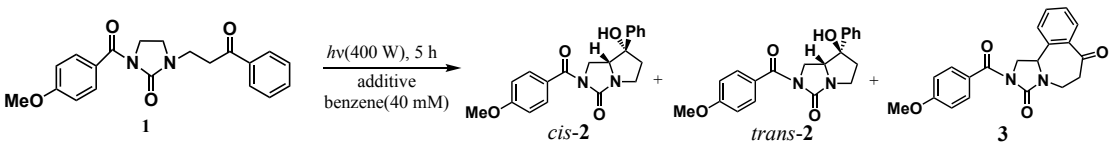
Cation-π interactions are effective in controlling the conformation of substrates and are used in the synthetic chemistry [1].

We present here that Norrish-Yang reaction of an imidazolidinone derivative (1) afforded a cis bicyclic compound (*cis*-2) as a major product. On the other hand, the trans compound (*trans*-2) increased by addiction of a quaternary ammonium salt. This is because an ammonium-π interaction, between a substrate and a quaternary ammonium salt, affects to change conformation and stereoselectivity. Moreover, isomer (3) is also obtained depending on the combination of solvent and quaternary ammonium salts. According to computation, the trans structure and the other isomer are found to be more unstable than the cis structure. Our finding is that addition of a quaternary ammonium salt produced the compounds that are generally unavailable.

Keywords : Norrish-Yang reaction; Ammonium-π interaction; Stereoselectivity; Imidazolidinone derivatives; quaternary ammonium salts

カチオン−π相互作用は有機分子のコンフォメーション制御に利用でき、合成化学において有用であることが報告されている [1]。

本研究では、イミダゾリジノン誘導体(1)の Norrish-Yang 反応において、*cis* 体の二環性化合物(*cis*-2)のが主生成物として得られるのに対し、第四級アンモニウム塩を添加すると、*trans* 体(*trans*-2)の割合が増えることを見出した。これは基質と第四級アンモニウム塩とのアンモニウム−π相互作用により、コンフォメーションが制御されることで立体選択性が変化したものと考えられる。さらに、溶媒と第四級アンモニウム塩の組み合わせにより、立体異性体以外の異性体(3)も生成した。これらの化合物は計算化学により、*cis* 体よりも不安定構造であることがわかった。以上より、アンモニウム塩を添加する事により、通常得られない化合物を得ることができることを明らかにした。



Without Bu_4NOAc	71	:	29	:	0
With Bu_4NOAc	31	:	43	:	36

1) Yamada. S.; *Chem. Rev.* **2018**, *118*, 11353-11432

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結晶性の多孔質材料における可視ー紫外フォトン・アップコンバージョン

（九大院工[1]・九大 CMS[2]・JST さきがけ[3]）○爲本多惠[1]・折橋佳奈[1]・楊井 伸浩[1,2,3]・君塚 信夫[1,2]
Visible-to-UV photon upconversion in crystalline porous materials ([1]*Grad. Sch. Eng., Kyushu Univ.*, [2]*CMS, Kyushu Univ.*, [3]*PRESTO, JST*) ○Tae Tamemoto,[1] Kana Orihashi,[1] Nobuhiro Yanai,[1,2,3] Nobuo Kimizuka[1,2]

Photon upconversion based on triplet-triplet annihilation (TTA-UC) is a methodology that can convert low-energy light into higher-energy light efficiently with low-intensity excitation light. Especially visible-to ultraviolet (UV) TTA-UC is important in its application to photocatalysis and artificial photosynthesis, but it remains challenging to achieve highly efficient TTA-UC in solid systems at low excitation intensity due to the deactivation of triplet excitons by crystal defects and aggregation of sensitizers. In this study, we attempted to achieve highly efficient vis-to-UV TTA-UC with low excitation light intensity by dispersing a sensitizer in porous ionic crystals consisting of acceptor molecules.
Keywords : Photon upconversion; Triplet-triplet annihilation, porous ionic crystals

三重項ー三重項消滅に基づくフォトン・アップコンバージョン（TTA-UC）は、低い励起光強度において低エネルギーの光を高エネルギーの光に高効率に変換できる技術である。特に可視光から紫外光への TTA-UC は光触媒への応用において重要であるが、固体中では結晶欠陥による三重項励起子の失活や増感剤の凝集などにより低励起光強度で高効率な TTA-UC 系は未達成である。本研究では発光分子からなる多孔性結晶中に増感剤を分散させ、低励起光強度で高効率な可視-紫外 TTA-UC の達成を試みた。紫外発光を示す多孔質イオン結晶である HOF-GS-10 を合成し、その細孔中にドナー分子 FIrpic を導入して UC 特性を調べた（Fig. 1）。FIrpic を含んだ HOF-GS-10 を 445 nm のレーザーにより励起したところ、紫外領域において UC 発光が観測され、固体状態における可視-紫外 TTA-UC に成功した（Fig. 2）。講演では新たに設計したアクセプター分子を用いた検討についても報告する予定である。

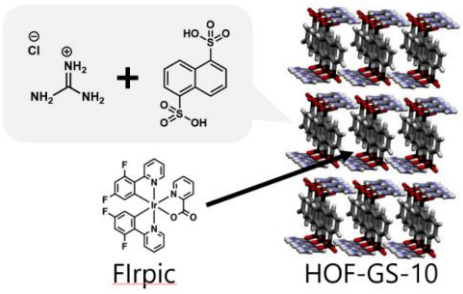

Figure 1. Chemical structures of HOF-GS-10 and FIrpic

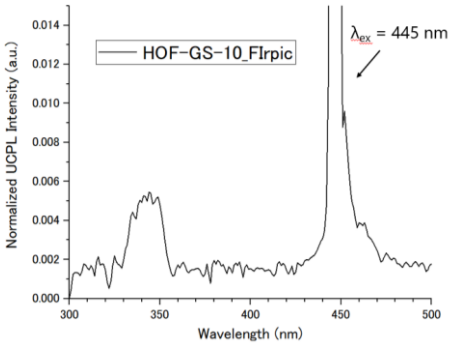

Figure 2. UC emission spectra

[1] Sujit K. Ghosh et al., *Angew. Chem. Int.Ed*, **2016**, 55,10667‐10671

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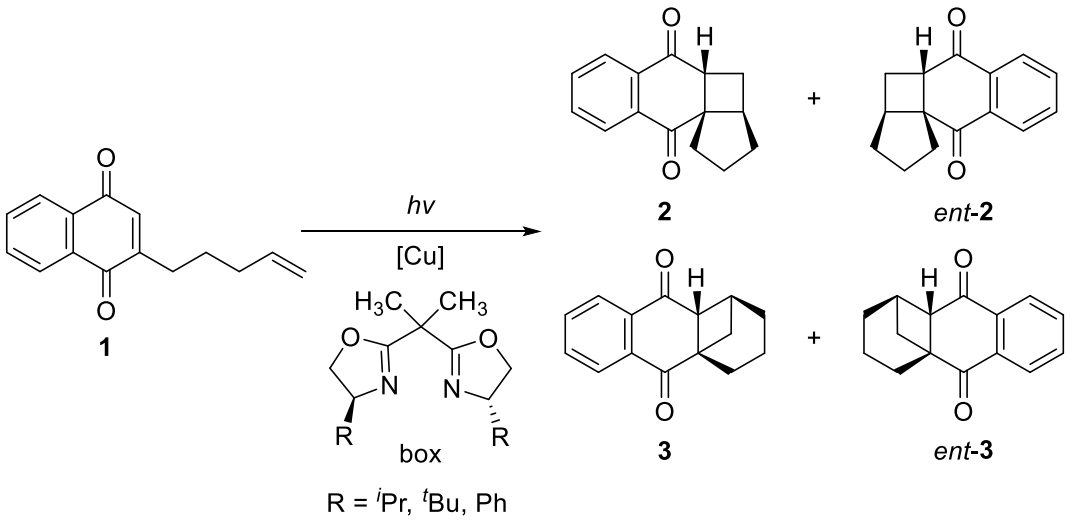
銅触媒による 1,4-ナフトキノン-アルケン連結系のエナンチオ選択的分子内[2+2]光付加環化反応

（阪大工）○浅沼 大輝・清水 菜生・重光 孟・森 直・木田 敏之
Copper-Catalyzed Enantioselective Intramolecular [2+2]Photocycloaddition of 1,4-Naphthoquinone-Alkene System (School of Engineering, Osaka University)
○Daiki Asanuma, Nao Shimizu, Hajime Shigemitsu, Tadashi Mori, Toshiyuki Kida

An enantioselective intramolecular [2+2]photocycloaddition of a 1,4-naphthoquinone tethered alkene (**1**), to afford enantiomeric cyclobutanes (**2**) and (**3**), was investigated in the presence of a copper catalyst and bisoxazoline (box) as a chiral ligand.
Keywords : Photocycloaddition; Intramolecular Cyclization; Asymmetric Reaction

銅触媒を用いる光反応では、一般的な遷移金属よりも比較的安価であることや可視光照射が可能であるなどの利点を有する。しかしながら、銅触媒を用いる不斉有機反応の研究と比較して光不斉反応への適用例は限定的である。例えば、ビスオキサゾリン (box) をキラル配位子とした銅触媒はフォトレドックス反応において不斉ラジカル付加反応等に用いられている。また、アリールオキシエノンの光環化反応にも用いられ、エナンチオ選択的に反応が進行することも知られている。

本研究では、同様のキラル銅触媒存在下、1,4-ナフトキノン-アルケン連結系 (**1**) のエナンチオ選択的分子内[2+2]光付加環化反応を検討した。化合物 (**1**) は直接光照射により典型的な環化生成物 (**2**) に加え、交差型環化生成物 (**3**) を与える。初期的検討において、配位子として置換基 R に *t*-ブチル基を有する box を用い銅触媒存在下、可視光を照射するとエナンチオ選択的に反応が進行した。用いる銅塩や価数及び配位子構造の影響を検討し、他の金属触媒とも比較検討した。また、反応温度や照射光波長の最適化を行い、立体選択性の決定因子に関して考察した。



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光縮環反応を用いた拡張ペリレンジイミド不溶性薄膜の作製と評価

（岩手大理工学）万城目大和・小川倫弥・葛原大軌
Fabrication and Characterization of Expanded Perylene Diimide Derivatives Insoluble Thin Films by Photo-Induced Scholl Reactions (*Faculty of Science and Engineering*, *Iwate University*) ○Yamato Manjome, Tomoya Ogawa, Daiki Kuzuhara

Precursor methods have been developed for device fabrications in solution processes. In this study, we focused on perylene diimide (PDI) with aromatic substitutions at 1,7-positions, which can be converted to coronene diimide (CDI) derivatives by photo-induced cyclization reaction (Fig. 1). As a result of photo-induced cyclization reaction, the solubility of PDI derivatives was drastically decreased because of the expansion of the π-conjugations. We used the changes of solubility of PDI derivatives to fabricate multi-layer thin-films by the solution process.

Upon photoirradiation of a chlorobenzene solution of PDI derivatives, the UV-visible absorption spectrum gradually changed, indicating that the photo-induced cyclization reaction proceeded (Fig. 2). Furthermore, the photo-induced cyclization reaction proceeded in thin films as well. In this presentation, we will report the effects of substituents on PDI and heavy atom effects on the photo-induced cyclization reaction.

Keyword: Perylene Diimide; photo-induced cyclization reaction; multi-layer structure; precursor method; organic semiconductor

溶液プロセスにおけるデバイス作製のため、これまでに前駆体法が開発されてきた[1]。本研究では、1, 7 位に芳香族を置換したペリレンジイミド(PDI) に注目し (Fig. 1)、光縮環反応による PDI 誘導体の溶解度制御および溶液プロセスによる PDI 誘導体積層膜の作製を試みた。

PDI 誘導体 **1** のクロロベンゼン溶液に光照射すると、紫外可視吸収スペクトルが徐々に変化し、光縮環反応が進行してコロネンジイミド誘導体 **2** が生成した(Fig. 2)。さらに薄膜においてもこの光縮環反応が進行した。本発表では、PDI 上の置換基や重原子効果が光縮環反応に与える影響についても併せて報告する。

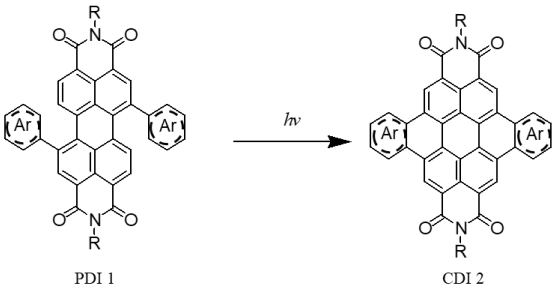

Fig.1 Photo-induced cyclization reaction from PDI 1 to CDI 2

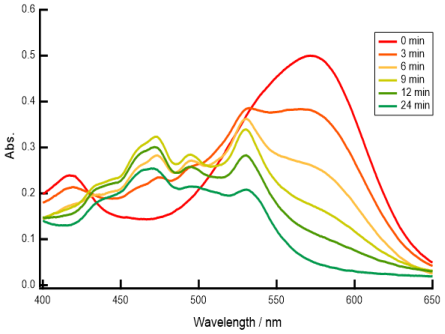

Fig.2 Changes in UV-vis absorption during the conversion of PDI 1 to CDI 2 under photoirradiation

[1] T. Motoyama, T. Kiyota, H. Yamada, K. Nakayama, *Sol. Energy Mater. Sol. Cells* **2013**, *114*, 156.

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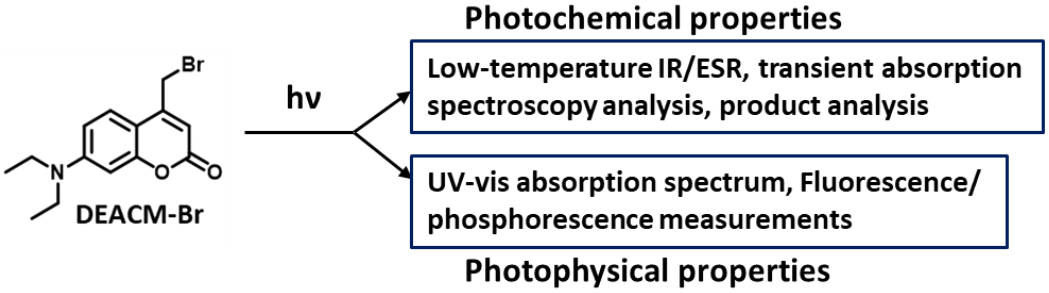
7-位に電子供与性基を有する 4-メチルクマリン誘導体の光反応性

（広大院理）安倍 学・○高野 真綾
The Photoreaction of coumarin-4-yl-methyl derivatives featuring electron donating groups at 7-position (*Graduate School of Science, Hiroshima University*) Manabu Abe,○Ma-aya Takano

4-Methyl-coumarin derivatives have been widely utilized as fluorophores and photolabile protecting groups (PPG). When an amino group is introduced at 7-position, the absorption maximum will be bathochromically shifted. Thus, 7-diethylamino-4-methyl coumarin (DEACM) is often used as PPG. However, that photoreaction mechanism of DEACM caged compound is still unclear. In this study, the photochemistry of DEACM-Br featuring Br at C4-position was studied in detail using low-temperature IR/ESR measurement, transient absorption measurement, product analysis, and spectroscopic measurements were conducted.
Keywords : 7-diethylamino-4-bromomethyl coumarin; photochemical property ; photophysical property

クマリンの 7 位にジエチルアミノ基を導入した DEACM は光解離性保護基(PPG)としてよく用いられてきた [1]. しかしながら, 解離過程がホモリシスかヘテロリシスか, その詳しい反応機構については未だに議論の余地が残っている．これまで，DEACM を PPG として用いた光反応では主生成物がアルコール体であることが確認されており，この反応は励起一重項状態からのヘテロリシスで進行すると考えられている．近年，興味深いことに，Winter らによってこの光反応中間体であるカチオン種が基底三重項状態を取ることが量子化学計算の結果から示唆され [2]，DEACM の光反応の反応機構に対する議論の幅が広がった. そこで, 本研究ではシンプルなモデル分子として, 脱離基に Br を導入した DEACM-Br の光化学的・光物理的性質について低温 IR,ESR, 過渡吸収などの分光学的調査，生成物分析を用いて調査し，DEACM を PPG として用いたときの光反応機構について新たな知見を得た．また，蛍光色素として盛んに用いられるクマリンの励起一重項が酸素によってクエンチされる現象について初めて詳細に議論した.



1) Klán, P.; Šolomek, T.; Bochet, G. C; Blanc, A.; Givens, R.; Rubina, N.; Popik, V.; Kostikov, A.; Wirz, *J. Chem. Rev.* **2013**, *113*, 119-191.
2) Albright, T. R.; Winter, A. H. *J. Am. Chem. Soc*. **2015**, *137* (9), 3402–3410.

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非共役ユニットで連結したダイアドの フォトンアップコンバージョン

（阪府大）○加納雅也・本田清将・大垣拓也・松井康哲・太田英輔・池田 浩

Photon Upconversion of Dyads Linked with Nonconjugated Units

(*Osaka Pref. Univ.*) ○Masaya Kanoh, Kiyomasa Honda, Takuya Ogaki, Yasunori Matsui, Eisuke Ohta, Hiroshi Ikeda

Photon upconversion (UC) is a technique that converts a low-energy light to a higher-energy one by employing triplet–triplet annihilation (TTA). In this work, to improve the UC efficiency, we evaluated UC behaviors of three dyads (DPA–Cn–DPA, Fig. 1) in which two diphenylanthracenes (DPA, Fig. 1) are linked with dimethylmethylene, cage skeleton, or adamantane, respectively.[1] Upon exciting the energy donor platinum(II) octaethylporphyrin (PtOEP) at 520 nm in dichloromethane, DPA–Cn–DPA exhibited UC emission at 435 nm, which is similar to that of DPA. To discuss the TTA-UC performance, the dependence of I_{UC} on excitation intensity (I_{EX}) was investigated (Fig. 2), and the threshold Intensity (I_{TH})[2] of DPA, DPA–C1–DPA, DPA–C2-DPA, and DPA–C3–DPA were determined to be 13, 27, 10, and 28 mW cm^{-2}, respectively.

Keywords: Triplet Energy Transfer; Triplet–Triplet Annihilation; Laser Flash Photolysis; Excited State

フォトンアップコンバージョン（UC）とは，三重項–三重項消滅（TTA）を利用して低エネルギー光を高エネルギー光に変換する技術である．本研究では UC 効率の向上を目的とし，2 つのジフェニルアントラセン（DPA，Fig. 1）が非共役ユニットであるジメチルメチレン，かご型骨格，またはアダマンタンを介して連結した 3 種のダイアド DPA–Cn–DPA（Fig. 1）の UC 挙動の評価を行った[1]．ジクロロメタン中でエネルギードナーである白金（II）オクタエチルポルフィリン（PtOEP）を 520 nm 光で励起すると，DPA–Cn–DPA は DPA と同様に UC 発光を 435 nm に示した．また，TTA-UC 特性を議論するため，UC 発光強度（I_{UC}）の励起光強度（I_{EX}）に対する依存性を調べたところ（Fig. 2），DPA，DPA–C1–DPA，DPA–C2–DPA および DPA–C3–DPA のしきい励起光強度（I_{TH}）[2] は，それぞれ 13，27，10，および 28 mW cm^{-2} と算出された．

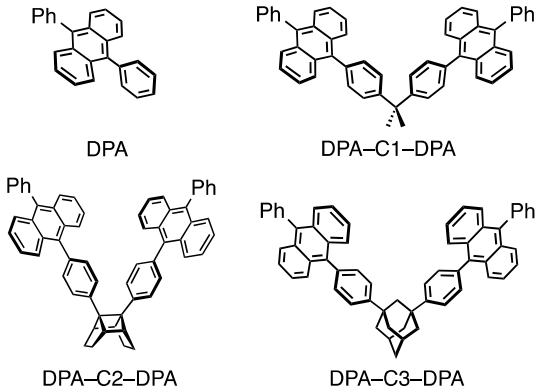

Fig. 1. Structures of DPA and DPA–Cn–DPA (n = 1~3).

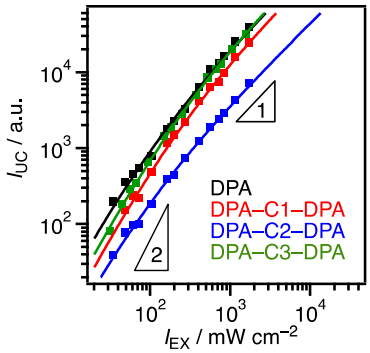

Fig. 2. Double-logarithmic plots and fitted curves of I_{UC} at 435 nm against I_{EX} upon the 520-nm excitation of a degassed CH_2Cl_2 solution of DPA or DPA–Cn–DPA containing PtOEP.

[1] Matsui, Y.; Kanoh, M.; Ogaki, T.; Ohta, E.; Ikeda, H. *J. Photochem. Photobiol. A: Chem.* **2020**, *387*, 112107.
[2] Kamada, K.; Sakagami, Y.; Mizokuro, T.; Fujiwara, Y.; Kobayashi, K.; Narushima, K.; Hirata, S.; Vacha, M. *Mater. Horiz.* **2017**, *4*, 83–87.

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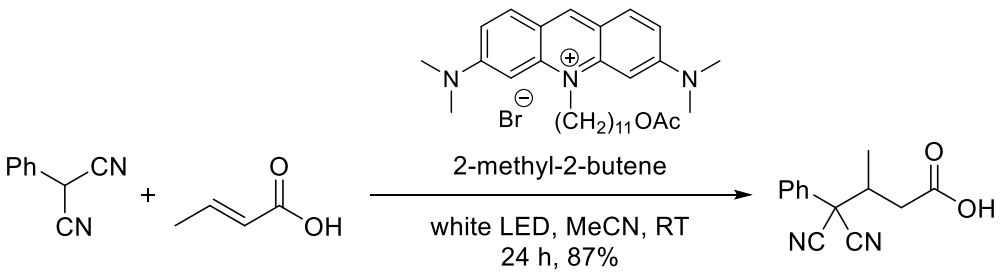
光酸化還元反応を用いるα,β−不飽和カルボン酸への直截的 1, 4−付加および光触媒の開発

（横浜薬大）○梅沢　岬・平濱　俊哉・庄司　満
Direct 1,4-addition onto α,β-unsaturated carboxylic acids using visible-light Photoredox reaction (*Yokohama Univ. of Pharmacy*) ○Misaki Umezawa, Toshiya Hirahama, Mitsuru Shoji

1,4-Adducts derived from α,β-unsaturated carboxylic acid are generally prepared by three following steps: 1) protection of carboxylic acid to the corresponding ester, 2) 1,4-addition of nucleophiles onto the α,β-unsaturated ester, 3) hydrolysis of the ester to generate the β-substituted carboxylic acid. Recently, a lot of radical reactions under visible-light irradiation have been reported. In this study, we discovered a 1,4-addition onto α,β-unsaturated carboxylic acids. A radical species derived from phenylmalononitrile under blue-light irradiation in the presence of acridinium catalyst could connect to the β-carbon of the acid to furnish γ,γ-dicyanocarboxylic acid in good yield.

α,β-不飽和カルボニル化合物の β 位に求核剤が付加し、炭素-炭素結合を形成する 1,4-付加は、有機合成化学において非常に重要な反応であり、生理活性化合物の合成をはじめ幅広く用いられている。ここで、α,β-不飽和カルボニル化合物である α,β-不飽和カルボン酸に 1,4-付加を行う場合、1）α,β-カルボン酸のエステル化、2）生じた α,β-不飽和エステルへの求核試薬の 1,4-付加、3）エステルの加水分解による β-置換カルボン酸の生成、の 3 工程が必要となる。本研究では、アクリジニウム塩を用いた光酸化還元反応により、フェニルマロノニトリルの α,β-不飽和カルボン酸への直截的 1,4-付加を見出した [1)]。さらに、アクリジン骨格を有する種々の触媒の活性と、基質一般性について検討したので報告する。



1)Hirahama T., Umezawa M., and Shoji M., *Tetrahedron Lett*., ***61***, 151824 (2020).

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多光子励起可能なイミダゾ[1,2-*a*]ピリジニウム塩の合成と光細胞傷害性

(徳島大院理工[1]・徳島大ポスト LED フォトニクス研究所[2]・徳島大生物資源[3]) 八木下史敏[1,2]・○國見祥太[1]・星恵太[1]・岡本将輝[1]・田端厚之[3]・長宗秀明[3]・長谷栄治[2]・南川慶二[1]・今田泰嗣[1]

Multi-photon Excitable Imidazo[1,2-*a*]pyridinium Salts for Mitchondria-targeted Image-guided Photodynamic Therapy ([1]Department of Applied Chemistry, Tokushima University, [2]Institute of Post-LED Photonics, Tokushima University, [3]Faculty of Bioscience and Bioindustry, Tokushima University) Fumitoshi Yagishita,[1,2] ○Shota Kunimi,[1] Keita Hoshi,[1] Masaki Okamoto,[1] Atsushi Tabata,[3] Hideaki Nagamune,[3] Eiji Hase,[2] Keiji Minagawa,[1] Yasushi Imada[1]

We have synthesized a series of multi-photon excitable donor-π-acceptor type imidazo[1,2-*a*]pyridinium salts. These compounds accumulated into the mitochondrial inner membrane, and multi-photon fluorescence imaging of mitochondria in HeLa cells was successfully achieved. In this work, we synthesized bromo-substituted derivative to promote intersystem crossing for improving PDT efficiency and evaluated their photocytotoxicity against HeLa cells. When HeLa cells stained by the salt were irradiated using UVA-LED, the cell viabilities were gradually decreased whereas the photocytotoxicity against HeLa cells was not observed in the absence of salt after UVA-LED irradiation for 60 min.

Keywords : Bioimaging; Imidazo[1,2-a]pyridinium salts; Multi-photon excitation; Photodynamic therapy

当研究室ではD-π-A型構造を有する芳香族複素様の合成と光機能性の開拓を行っている。最近イミダゾ[1,2-*a*]ピリジニウム塩が，多光子励起においても蛍光発光性を示すことを見出し，これらの塩はミトコンドリア集積性を示し，多光子励起によるミトコンドリアイメージングを達成した[1]。本研究ではミトコンドリアを標的とした光線力学療法への応用を狙いとし，効率的に一重項酸素を生成させることを目的として，系間交差を促進する置換基を導入した誘導体 **1** を合成し，光細胞傷害性の評価を行った(**Figure 1**)。

その結果，化合物 **1** で染色した HeLa 細胞へ光照射すると，照射時間に伴う細胞生存率の低下が確認された(**Figure 2**)。また，JC-1 アッセイの結果，光照射に伴うミトコンドリア膜電位の脱分極が確認され，光細胞傷害性はミトコンドリア損傷によるものだと示唆された。

1) F. Yagishita *et al. Org. Biomol. Chem*. **2020**, *18*, 7571−7576.

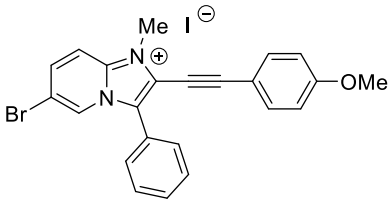

Figure 1. Structure of **1**.

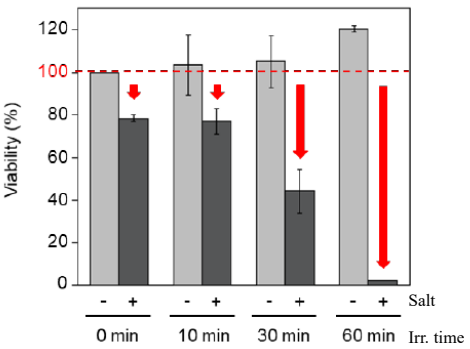

Figure 2. Cell viabilities of HeLa cells after LED irradiation.

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Research on ITO/PEN electrodes modified by organic dyes and their photoelectrochemical properties

(*Graduate School of Science and Technology, Meijo University*) ○Tran Thi Thu Trang, Kentaro Suzuki, Toshi Nagata

Keywords: ITO/PEN electrode, porphyrin carboxylic acid, chemisorption, photoelectrochemistry

Introduction. The ITO/PET and ITO/PEN electrodes have been successfully utilized as the most transparent, light and flexible electrodes since their first report in 1974[1]. By adsorbing organic dyes on these electrodes, oxidation and reduction reactions can be induced by irradiation of light. In order to carry out photoelectrochemical reactions in a flow system, it is necessary to fix the dye firmly on the electrode. In this study, we tried fixation our kinds of porphyrin carboxylic acid derivatives (**1-4**) on the ITO/PEN electrode.

Synthesis. The porphyrin derivatives with one or two carboxy groups (**1**, **2**) were prepared according to the literature procedure.[2] These carboxylic acids were coupled with β-alanine ethyl ester and hydrolyzed, to give the carboxylic acids with β-alanine spacer units (**3**, **4**).

Adsorption Studies. For the pretreatment, the ITO/PEN electrodes were immersed in base-piranha solution (30% H_2O_2 : 30% NH_3 : H_2O = 1:1:5) at room temperature for about 1 hour. Using a stronger solution (H_2O_2:NH_3:H_2O = 1:3:5) resulted in the deterioration at the border of the electrode. There were 3 methods to For modification of the ITO/PEN surface with the porphyrins, three methods (A-C) were examined: (A) direct chemisorption, (B) modification of the ITO/PEN surface with APTMS followed by the formation of ionic bonds, and (C) formation of amide bonds with APTMS. The adsorption density of porphyrin on ITO/PEN electrode was evaluated through the UV-Vis absorption spectrum. As a result, the adsorption density of the porphyrins **2**, **4** was higher than that of the porphyrins **1**, **3**.

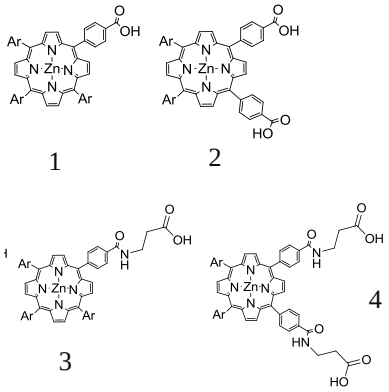

Table 1: The adsorption density of Porphyrin on ITO/PEN electronde

Porphyrin	Adsorption density ($\times10^{-11}$ mol cm^{-2})		
	A	B	C
1	1.5	0.73	0.81
2	3.3	10	11
3	2.1	2.4	4.1
4	19	55	51

1) T. Yatabe, *J. Vac. Soc. Jpn*., **2003**, *46*, 28.

2) H. Tamiaki et al. *Bull. Chem. Soc. Jpn.* **1993,** *66*, 2633.

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Photoreaction of Quinones with an Amphiphilic Porphyrin Sensitizer

(*Graduate School of Science and Technology, Meijo University*) ○Yui Tanaka, Toshi Nagata
Keywords: amphiphilic, porphyrin, quinone, two-phase system, photoreduction

Introduction. Artificial photosynthesis has three components: water oxidation, electron transfer and storage, and carbon dioxide reduction. Yusa et al. reported the photoreduction of quinones in a homogeneous system using a phthalocyanine and a thiol.[1] The reduced product, hydroquinones, can be potentially used as a reusable reductant. For this reaction to be more useful, it is desirable that the reduced product can be isolated in a separate phase. In this context, we attempted to realize this reaction in a two-phase system, by use of amphiphilic photosensitizers (Figure 1). We chose an amphiphilic porphyrin, $[ZnP(C_{12})_1]^{3-}\cdot 3Na^+$, as a photosensitizer in a two-phase system. Dodecyloxy group was used as the hydrophobic group and sulfo group was used as the hydrophilic group.

Synthesis. Porphyrins with trimethylsilyl groups were synthesized from 4-trimethylsilylbenzaldehyde, 4-dodecyloxybenzaldehyde, and pyrrole by the Lindsay method.[2] Me_3SiOSO_2Cl was used to convert the trimethylsilyl groups to sulfo groups.[2] The obtained porphyrin trisulfonic acid was converted to the tris(tetrabutylammonium) salt and extracted with organic solvents to remove water-soluble by-products. Subsequently, zinc was introduced, and the resulting zinc porphyrin was converted to the trisodium salt using Dowex.

Photochemical Properties. The UV and fluorescence spectra of the obtained porphyrin in methanol are shown in Figures 2 and 3, respectively. The results of quenching and photoreaction by quinone will be also reported.

Fig. 1 Photoreduction of quinones with an amphiphilic Porphyrin

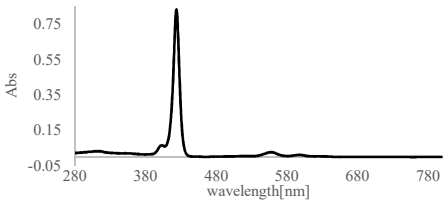

Fig. 2 UV spectrum of $[ZnP(C_{12})_1]^{3-}\cdot 3Na^+$ in CH_3OH

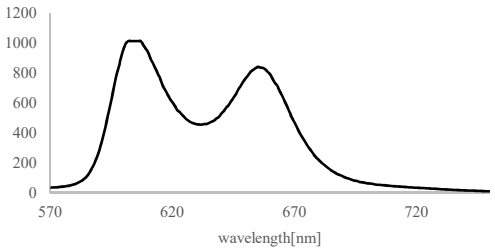

Fig. 3 Fluorescence spectrum of $[ZnP(C_{12})_1]^{3-}\cdot 3Na^+$ in CH_3OH

1) M. Yusa and T. Nagata, *Photochem. Photobiol. Sci.*, **2017**, *16*, 1043-1048.
2) K. Hosomizu, et al., *J. Phys. Chem. B.*, **2008**, *112*, 16517-16524.

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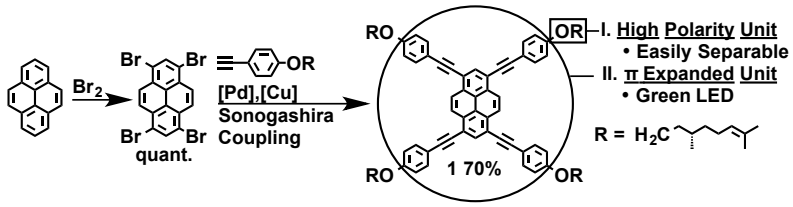
Development of Environmentally Benign Julia Olefination by Reductive Desulfonylation Utilizing Pyrene Photocatalyst

(*Okayama University of Science*) ○Hikaru Watanabe, Kazuki Nakajima, Ryota Edagawa, Yasuhiro Okuda, Akihiro Orita

Keywords: Photochemistry; Pyrene; Desulfonylation; Olefin

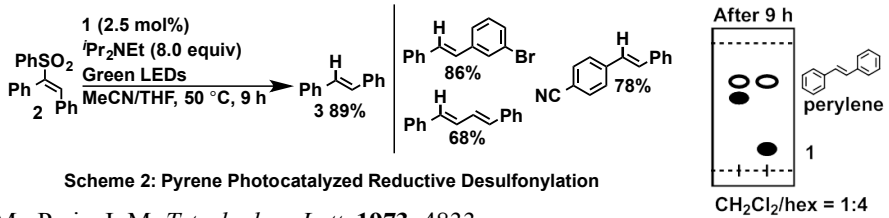
Julia olefination is widely used in synthesis of carbon–carbon double bonds starting from sulfones and aldehydes. Although this protocol is useful due to its mild reaction conditions and high *E*-selectivity, a use of toxic Na(Hg) is required for reductive desulfonylation of *β*-acetoxy sulfone intermediates.[1]

Recently we reported perylene photocatalyst-promoted reductive desulfonylation of ethenyl sulfones which were derived from *β*-acetoxy sulfones. Although this alternative Julia olefination worked well in desulfonylation of various ethenyl sulfones, it was often difficult to separate the perylene photocatalyst from olefinic products due to a small difference of their polarities. To overcome this drawback, we developed easily separable photocatalyst **1** for desulfonylation. The photocatalyst **1** was easily synthesized from pyrene via consecutive tetrabromination and Sonogashira coupling. Pyrene **1** was composed of two components: (I) branched long alkoxy groups and (II) highly expanded π-system. The former could assist high solubility and easy separation of **1** from the desired olefinic products, and the latter could enable lower energy of visible light to promote a catalytic system (Scheme 1).



Scheme 1: Synthesis of Pyrene Photocatalyst

When visible light (green LEDs) was irradiated at an MeCN/THF solution of ethenyl sulfone **2**, **1**, and *i*-Pr_2NEt, the desired reductive desulfonylation proceeded in 9 h, and **3** was successfully purified by column chromatography (Scheme 2). We also synthesized olefins functionalized by bromo, cyano, and dienyl groups.



Scheme 2: Pyrene Photocatalyzed Reductive Desulfonylation

1) Julia, M.; Paris, J. M. *Tetrahedron Lett.* **1973**. 4833.

2) Watanabe, H.; Takemoto, M.; Adachi, K.; Okuda, Y.; Dakegata, A.; Fukuyama, T.; Ryu, I.; Wakamatsu, K.; Orita,A. *Chem. Lett.*, **2020**, *49*, 409.

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四重水素結合部位を有するペンタセン誘導体の合成と会合特性

（慶大理工）○小池 直樹・中村 俊太・酒井 隼人・羽曾部 卓
Synthesis and Aggregate Properties of Pentacene Derivatives Bearing Quadruple Hydrogen Bonding Units (*Fac. Sci. Tech., Keio Univ.*) ○Naoki Koike, Shunta Nakamura, Hayato Sakai, Taku Hasobe

Singlet fission (SF) is a spin-allowed photophysical process where two triplet excitons are generated from one-photon absorption between two nearby molecules. Most SF systems in homogeneous solutions have been observed by utilizing covalently-linked acene dimers, which enable to control the appropriate intermolecular interactions of two chromophores. In this work, we focus on the molecular organization by the non-covalent hydrogen bond and newly synthesized a series of pentacene derivatives with quadruple hydrogen bonding sites. In this presentation, we report the synthesis and spectroscopic properties together with aggregate forms.
Keywords : Singlet Fission; Pentacene; Quadruple Hydrogen Bond

分子集合体の形成において合成的な煩雑さを伴う共有結合に対し、水素結合は自発的に集合化するためメゾ・マクロなスケールへの展開が容易である。水素結合の問題として相対的に弱い結合力が挙げられるが、近年では会合定数が 10^7 M^{-1} を超える強力な四重水素結合が報告されている[1]。一方、一重項分裂 (Singlet Fission : SF) とは、光励起によって生じた 1 つの最低励起一重項状態の分子が近傍に存在する基底状態の分子と相互作用し、2 つの最低励起三重項状態を生成する光物理過程である。均一溶液中での SF の報告例の多くは共有結合による二量体であり[2]、水素結合などの非共有結合を利用した例は限られている。特に、強固な四重水素結合を用いた例はない。そこで本研究では、以下の図 1 に示す四重水素結合部位を持つペンタセン HBUBnPC および異なるリンカー鎖長を有する各種誘導体を合成した。^{1}H NMR の測定から水素結合が確認され、その会合定数が 9.5×10^5 M^{-1} 以上であると算出された。本発表では合成と会合状態における分光特性について報告する。

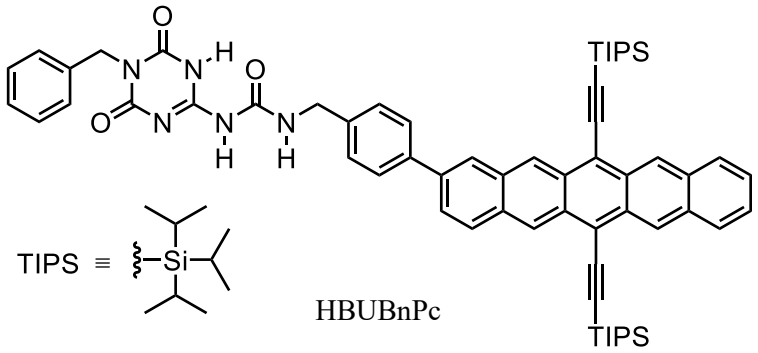

図 1　本研究で用いるペンタセン誘導体の化学構造の一例

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[P01-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Fri. Mar 19, 2021 1:20 PM - 2:50 PM Area 1 (Online Meeting)

[P01-1pm-01] Activated charcoal as an effective additive for alkaline hydrolysis of esters in water

○Kiyoshi TANEMURA[1], Taoufik Rohand[2] (1. Nippon Dental University, 2. Cadi Ayyad University)

[P01-1pm-02] Synthesis of Jasmonic Acid Derivatives Using Intramolecular C-H Insertion Reaction

○Mayuko Morita[1], Yoshiharu Okada[1] (1. Kindai University)

[P01-1pm-03] Simple Synthesis and Physiological Activities of Acerogenins

○Ikumi Ohata[1], Mina Nagarede[1], Yoshiharu Okada[1] (1. Kindai University)

[P01-1pm-04] Asymmetric hydrosilylation of imines catalyzed by a chiral pyridine N-oxide derivative

○Yusuke Fukushima[1], Gakushi Morita[1], Hinoki Sakamura[1], Michimasa Hayashi[1], Akane Yoshino[1], Tetsuya Fujimoto[1] (1. Shinshu university)

[P01-1pm-05] $AgNO_3/TiO_2$-photocatalyzed N-Methylation of Amino Acids with Methanol

○I WEN HUANG[1], Yuna Morioka[1], Hiroshi Naka[2,3], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ., 3. Grad. Sch. Pharm. Sci., Kyoto Univ.)

[P01-1pm-06] 13C NMR and IR Spectroscopic and Computational Studies of Intra- and Intermolecular Interactions of Amino Acid Derivatives in Solutions

○Yoshikazu HIRAGA[1], Satomi NIWAYAMA[2], Ryosuke HOSHIDE[1] (1. Graduate School of Science and Technology, Hiroshima Institute of Technology, 2. Graduate School of Technology, Muroran Institute of Technology)

[P01-1pm-08] Stereoselective Synthesis of Tetrahydropyranones using β-Silyl-γ-Alkylidene-γ-Butyrolactones with Aldehydes and Ketones

○Shoma Ariyoshi[1], Kazuhiko Sakaguchi[1], Takahiro Nishimura[1] (1. Osaka City University)

[P01-1pm-09] Lipase-catalyzed Desymmetrization by Mono-Hydrolysis of Symmetric 1,5-Diacetyl-3-*O*-silyl Protected Pentanetriol

○Yusuke Uchida[1], Yoshikazu HIRAGA[1] (1. Graduate School of Science and Technology, Hiroshima Institute of Technology)

[P01-1pm-10] Syntheses of specific tricyclopropane compounds by cyclopropane-shift type transformation of diaryl(2-halocyclopropyl)methanols

○Shotaro Morimoto[1], Kento Moriguchi[1], Yoo Tanabe[1] (1. Kwansei Gakuin University)

[P01-1pm-11] Ir-catalyzed transformation of bio-renewable carboxylic acids toward C– C bond formation

○Kazuki Teramoto[1], Shota Yoshioka[1], Susumu Saito[1,2] (1. Grad. Sch. Sci. Nagoya Univ., 2. RCMS, Nagoya Univ.)

[P01-1pm-12] Synthesis of fatty acids having a trifluoromethyl group at the end

○Kazuki Naito[1], Tsuyuka Sugiishi[1], Masashi Sonoyama[1], Hideki Amii[1] (1. Gunma

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University)

[P01-1pm-13] Chiral synthesis of cyano-substituted cyclopropane-type pyrethroid with two asymmetric centers and its insecticidal stereostructure-activity relationship

○Yusa Aoyagi[1], Mizuki Moriyama[1], Noritada Matsuo[1], Yoo Tanabe[1] (1. Kwansei Gakuin Univ)

[P01-1pm-14] Regioselective Difluorocyclopropanation of Dienes

○Hiroto Mukai[1], Tsuyuka Sugiishi[1], Hideki Amii[1] (1. Gunma university)

[P01-1pm-15] α-Formylation of α,β-unsaturated thioesters utilizing Ti-Claisen condensation

○Soma Fukunaga[1], Sachiyo Yamaguchi[1], Mizuki Moriyama[1], Tanabe Yoo[1] (1. Kwansei Gakuin University)

[P01-1pm-16] Radical reactions of α-(thio)difluoromethyl arenes

○Azuma Iizuka[1], Kohei Ueyama[1], Tuyuka Sugiishi[1], Hideki Amii[1] (1. The Univ. of Gunma)

[P01-1pm-17] The synthetic application of (aryl)fluoromethylsilane

○Manami Sato[1], Yuto Haga[1], Tsuyuka Sugiishi[1], Hideki Amii[1] (1. Gunma Univ.)

[P01-1pm-18] Regioselective umpolung alkylation reactions of α-iminoesters

○Mayu Kukita[1], Yasushi Yoshida[1], Takashi Mino[1], Masami Sakamoto[1] (1. Graduate School of Engineering, Chiba University)

[P01-1pm-19] Regioselective Diels-Alder reaction using hydrogen bonding of amides

○Wangbin Ni[1] (1. Kanagawa University)

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Activated Charcoal as an Effective Additive for Alkaline Hydrolysis of Esters in Water

([1]*Nippon Dental University*, [2]*Cadi Ayyad University*) ○Kiyoshi Tanemura,[1] Taoufik Rohand[2]

Keywords: Activated Charcoal; Hydrolysis; Esters; Carboxylic Acids; Water

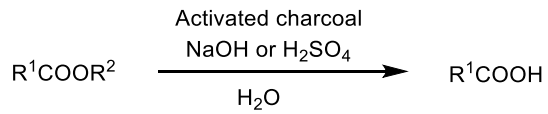
Reactions in water are a challenging investigation in synthetic organic chemistry. In order to dissolve organic substrates in water, surfactants are often used in organic synthesis. As the problem of surfactants, work-up is frequently difficult because of lathering. In addition, surfactants are not environmentally friendly because they polluted the water of rivers and ocean. Activated charcoal is amorphous carbon material possessing large surface area. It has been employed as an adsorbent for the removal of a smell, coloration, and impurities in the reaction mixture. Furthermore, it has been used as a catalyst carrier. During the course of our investigation on solid-mediated organic reactions,[1-3] we found that the alkaline and acidic hydrolysis of esters proceeded smoothly in water in the presence of activated charcoal.[4]

We examined the alkaline hydrolysis of a variety of esters. Esters were treated in aqueous 1.5 M NaOH solution at room temperature for 24 h at 400 rpm in the presence of activated charcoal. The reactions of methyl, ethyl, and *n*-propyl esters gave the corresponding carboxylic acids in excellent yields. When the products were solids, organic solvent-free work-up was possible.

Various esters were treated in aqueous 3M H_2SO_4 solution at 100 °C for 24 h at 400 rpm in the presence of activated charcoal. The reactions of methyl, ethyl, and *n*-propyl esters afforded the corresponding carboxylic acids in good yields.

The recycle experiments for the alkaline and acidic hydrolysis of ester were carried out. Activated charcoal could be recycled five times without the significant loss of the yields.

The reaction mixture consisted of the organic and aqueous phases. Activated charcoal was suspended in the organic phase of esters. It will be caused by the hydrophobic interaction between esters and condensed aromatic rings of activated charcoal. Although the detailed mechanism is not clear now, activated charcoal would adsorb esters on the surface by dispersion forces, and it may increase many ester molecules exposed to where the hydrolysis by aqueous NaOH or H_2SO_4 solution can occur.



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日本化学会 第101春季年会 (2021)

Synthesis of Jasmonic Acid Derivatives Using Intramolecular C-H Insertion Reaction

(*Faculty of Engineering, Kindai University*) ○Mayuko Morita, Yoshiharu Okada

Keywords: Jasmonic Acid Derivatives; C-H Insertion Reaction; β-Keto Phosphonate

Jasmonic acid derivatives such as methyl jasmonate which were recognized as aroma components, have been reported physiological activity of inducing the formation of potato-tuber. In this study, the synthesis of the title compounds using intramolecular C-H insertion reaction as key reaction, of β-keto phosphonate prepared from adipic acid as starting material was investigated.

Reaction of *tert*-butyl ethyl adipate **1** with dimethyl methylphosphonate in the presence of LDA gave the corresponding β-keto phosphonate **2** in 64% yield. The diazo transfer reaction of **2** with TsN_3 gave **3** in 57% yield. Thermal decomposition of **3** in 1,2-dichloroethane containing Rh(II) catalysts were afforded the corresponding α-phosphonocyclopentanone **4** in 4-21% yields (Table 1). The Horner-Wadsworth-Emmons (HWE) reaction of **4** with pentanal gave **5a** in 22% yield. Hydrogenation of **5a** and subsequent treatment of hydrochloric acid in methanol solution gave methyl dihydrojasmonate **6**. The similar reaction of **4** with 5-*tert*-butyldimethylsiloxy-2-pentynal gave the HWE product **5b**.

Scheme 1. Synthesis of Jasmonoide.

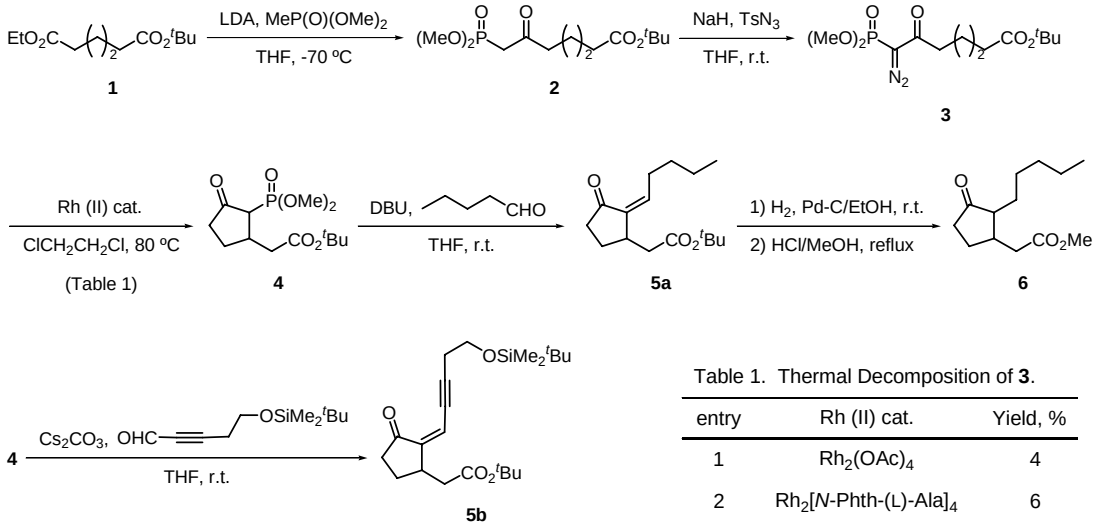

Table 1. Thermal Decomposition of **3**.

entry	Rh (II) cat.	Yield, %
1	$Rh_2(OAc)_4$	4
2	Rh_2[*N*-Phth-(L)-Ala]$_4$	6
3	Rh_2[*N*-Phth-(L)-Phe]$_4$	11
4	Rh_2[*N*-Phth-(L)-PhGly]$_4$	13
5	Rh_2[(S)-mandelate]$_4$	21

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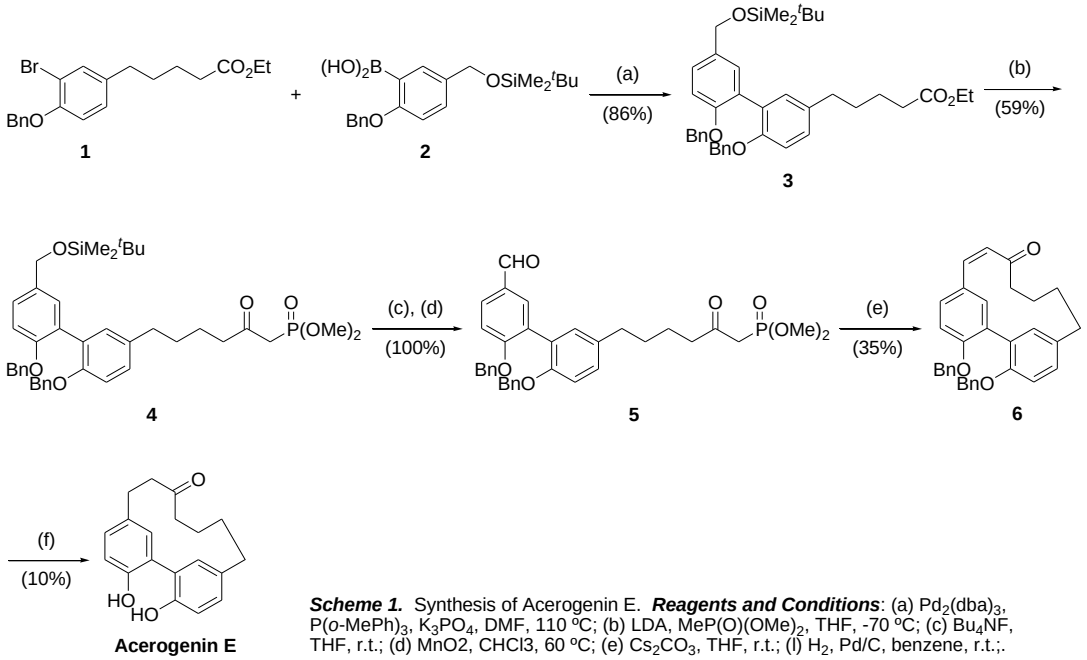
Simple Synthesis and Physiological Activities of Acerogenins

([1]*Graduate School of Systems Engineering, Kindai University*, [2]*Faculty of Engineering, Kindai University*) ○Ikumi Ohata,[1] Mina Nagarede,[2] Yoshiharu Okada,[2]

Keywords: Acerogenins; *Acer nikoense*; Intramolecular Horner-Wadsworth-Emmons reaction; Tyrosinase inhibition activity

Acerogenins bearing 4-(4-hydroxyphenyl)-2-butanol moieties were isolated from bark of *Acer nikoense* M., a maple indigenous in Japan, and assigned chemical structures. It is known that acerogenins have interesting physiological activities such as anti-inflammatory effect, anti-tumor promoting effect, nitric oxide production inhibition activity. In addition, acerogenins have melanogenesis inhibitory activity (whitening effect). We have interested in these natural occurring compounds and investigated the activity of their analogues. So, we report here the simple synthesis of acerogenins and their physiological activities.

Ethyl 5-(4-benzyloxy-3-bromophenyl)pentanoate **1** was prepared from 4-benzyloxy-3-bromobenzaldehyde in five steps. 2-Benzyloxy-5-(*tert*-butyldimethylsiloxymethyl)phenylboronic acid **2** was prepared from similar benzaldehyde in three steps. Suzuki-Miyaura cross-coupling reaction of **1** with **2** gave biphenyl derivative **3** in 86% yield. Reaction of **3** with dimethyl methylphosphonate in the presence of LDA gave β-keto phosphonate **4** in 59% yield. Deprotection of **4** with TBAF and subsequent oxidation with MnO_2 gave aldehyde **5** in quantitative yield. Intramolecular Horner-Wadsworth-Emmons reaction of **5** in the presence of Cs_2CO_3 was succeeded to give acerogenin E precursor **6** in 35% yield. Hydrogenation and hydrogenolysis of **6** in the presence of Pd/C catalyst gave acerogenin E in 10% yield.



Scheme 1. Synthesis of Acerogenin E. ***Reagents and Conditions***: (a) $Pd_2(dba)_3$, P(*o*-MePh)$_3$, K_3PO_4, DMF, 110 ºC; (b) LDA, MeP(O)(OMe)$_2$, THF, -70 ºC; (c) Bu_4NF, THF, r.t.; (d) MnO2, CHCl3, 60 ºC; (e) Cs_2CO_3, THF, r.t.; (l) H_2, Pd/C, benzene, r.t.;.

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キラルピリジン N-オキシド誘導体を触媒とするイミンの不斉ヒドロシリル化反応

(信州大繊維) ○福嶋 雄介・森田 岳志・坂村 ひのき・林 道正・吉野 朱音・藤本 哲也

Asymmetric Hydrosilylation of Imines Catalyzed by a Chiral Pyridine N-Oxide Derivative

(*Faculty of Textile Science and Technology, Shinshu University*) ○Yusuke Fukushima, Gakushi Morita, Hinoki Sakamura, Michimasa Hayashi, Akane Yoshino, Tetsuya Fujimoto

Enantioselective reduction of imines using trichlorosilane ($HSiCl_3$) is one of the essential methods for obtaining chiral amines. Many asymmetric catalysts for the method have been investigated. The catalysts with higher catalytic activity have been investigated in our laboratory. It was obtained that catalyst 1 (cat.1), in which a pyridine N-oxide and a urea functional group were embedded has extremely high catalytic activity (Fig.1). The reaction of imines with $HSiCl_3$ in the presence of a 0.1 mol% cat.1 afforded the corresponding amines with 6–90% yield and 91–98% ee (Scheme 1). Substitution sites and electric properties of R substituents on benzene rings do not affect the stereoselectivity of amines. Thus, this catalyst is effective for the direct asymmetric reductive amination of ketones. The reaction of *p*-bromoacetophenone and *p*-anisidine with $HSiCl_3$ in the presence of a 0.5 mol% cat.1 produced an amine with 81% yield and 97% ee.

Keywords : Imine; Hydrosilylation; Asymmetric reduction; Organocatalyst,

キラルなアミンを合成する上でイミンのトリクロロシランによる不斉還元は有用な方法論の 1 つであり、これまで多くの不斉触媒が報告されている。本研究室においてもより高活性な触媒開発を目的とする研究を行っており、ピリジン N-オキシドとウレア基が共存する cat. 1（Fig.1）が極めて高活性な触媒であることを見出した。本触媒においては 0.1 mol%でも十分反応が進行し、ベンザルアセトンのイミン誘導体の反応において、6~90% 収率、91～98% ee で対応するアミンが得られた（Scheme 1）。ベンザルアセトン誘導体のベンゼン環上の置換基 R の置換位置、また電子的な性質に影響されることなく高選択的にアミンが得られた。

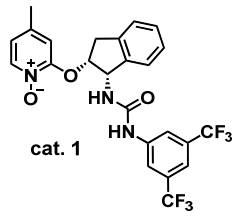
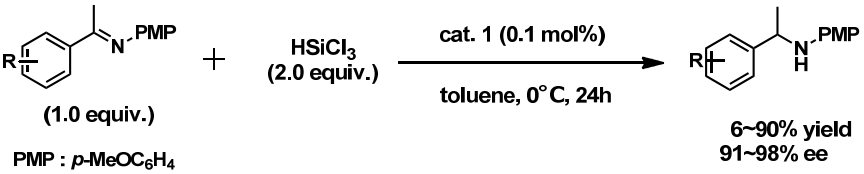


Fig.1



Scheme 1

本触媒は、ケトン、アミンを原料とする直接的な不斉還元アミノ化においても有効な触媒であり、0.5 mol%の触媒存在下、*p*-ブロモアセトフェノン、*p*-アニシジン、トリクロロシランの反応により目的とするアミンが、81% 収率、97% ee で生成した。

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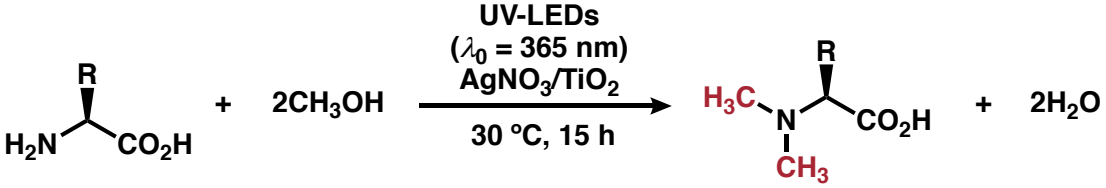
$AgNO_3/TiO_2$-photocatalyzed N-Methylation of Amino Acids with Methanol

([1]*Grad. Sch. Sci. Nagoya Univ.*, [2]*RCMS, Nagoya Univ.*, [3]*Grad. Sch. Pharm. Sci. Kyoto Univ.*)
○I WEN HUANG,[1] Yuna Morioka,[1] Hiroshi Naka,[2,3] Susumu Saito[1,2]
Keywords: Amino Acid; Methylation; Photocatalysis; Silver; Methanol

N-Methylated amino acids are important structural features in peptides. *N,N*-Dimethyl amino acids derived from valine, leucine, and phenylaniane are commonly found in pharmaceuticals, dyes, detergents, synthetic intermediates, and bioactive natural products. Representative examples include cobamide A[1] and dolastatin 10[2], both of which are natural products with potent antitumor activity. Direct N-methylation of primary or secondary amino acids is a very powerful method for producing N-methylated amino acids. Conventional methods include the direct N-methylation of amino acids with alkyl halides[3] and the reductive amination of formaldehyde using stoichiometric amounts of reducing agents[4]. We previously demonstrated that L-proline can be N-methylated with methanol using a silver-loaded titanium dioxide (Ag/TiO_2) photocatalyst under irradiation with near UV-light.[5] This photocatalytic method is advantageous over conventional methods because the Ag/TiO_2 system does not require any hazardous reducing reagents. However, the scope on other amino acids remained unclear.

Herein, we developed a method for the direct N-methylation of various amino acids with methanol at ambient temperature using a silver(I)-loaded TiO_2 photocatalyst. The methylating reagent methanol is cheap and abundant. This method does not require any hazardous stoichiometric reducing reagents, water being the only byproduct. Various N-methylated amino acids were obtained after mixing amino acids with 10.0 mg of the photocatalyst in 10 mL dehydrated methanol, and exposing the stirring reaction mixture for 15 h under the UV-light irradiation.



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^{13}C NMR 分光法，赤外分光法および理論計算によるアミノ酸誘導体の溶液中での分子間および分子内相互作用の評価

（広島工大院工 [1]・室蘭工大院工 [2]）○平賀 良知 [1]・庭山 聡美 [2]・星出 亮佑 [1]

^{13}C NMR and IR Spectroscopic and Computational Studies of Intra- and Intermolecular Interactions of Amino Acid Derivatives in Solutions ([1]*Graduate School of Science and Technology, Hiroshima Institute of Technology*, [2]*Graduate School of Technology, Muroran Institute of Technology*) ○Yoshikazu HIRAGA,[1] Satomi NIWAYAMA,[2] Ryosuke HOSHIDE[2]

Keywords: Amino Acid Derivatives, Intramolecular Forces, ^{13}C NMR spectroscopy, IR spectroscopy, DFT Calculation

Carbonyl compounds are known to form aggregates by intermolecular forces, such as hydrogen bonding and dipole-dipole interaction, etc. in a solution. In this study, ^{13}C NMR chemical shifts were monitored for evaluation of the interaction between amino acid derivatives and various solvents with different polarities.

Figures 1(a) and 1(b) show behaviors of ^{13}C NMR chemical shifts of the carbonyl carbons of the carboxyl groups and those of the Boc groups in *N*-Boc-proline-alanine methyl ester **1a** and *N*-Boc-proline-serine methyl ester **1b,** respectively, in various solvents. As shown in Fig. 1(a) and 1(b), with increase of the solvent polarity, the ^{13}C NMR chemical shifts of the carbonyl group in **1a** (■ , ▲) and **1b** (■) moved downfield, while those of the carbomethoxy group in **1b** (▲) were almost constant. On the other hand, the behaviors of the chemical shifts of the carbonyl carbon in the Boc group of **1a** (●) and **1b** (●) showed a similar tendency and were almost constant regardless of the solvent polarity.

To understand the behavior of the ^{13}C NMR chemical shifts of carbonyl carbons in **1a** and **1b**, the DFT calculations (B3LYP/6-31+G(d) level) were carried out. The most stable structures of **1a** and **1b** are shown in Fig. 1. In the most stable structure of **1a**, it was shown that intramolecular hydrogen bonding was formed between the oxygen atom of the carbonyl group (●) of Boc group and the hydrogen atom in the amide bond. Also, the carbonyl group (●) of the Boc group in **1b** formed intramolecular hydrogen bonding with the hydrogen atom of the amide bond, and the hydrogen atom of hydroxyl group of serine was close to the oxygen atom of the carbonyl carbon (■). These models supported the behaviors of the ^{13}C NMR chemical shifts of the carbonyl carbon in **1a** and **1b**. The behaviors of other amino acid derivatives in various polar solvents are under investigation.

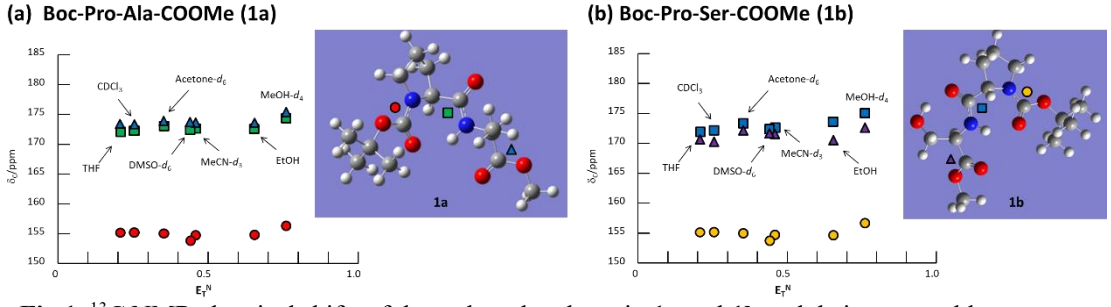

Fig 1. ^{13}C NMR chemical shifts of the carbonyl carbons in **1a** and **1b** and their most stable structures

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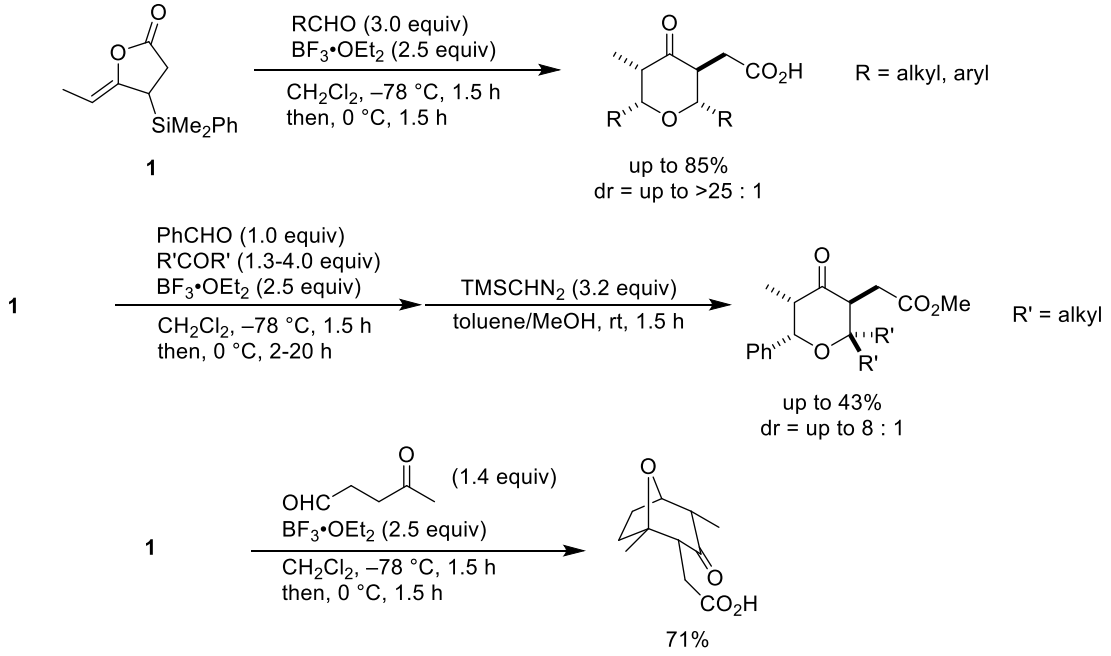
β-シリル-γ-アルキリデン-γ-ブチロラクトンとアルデヒドおよびケトンを用いた四置換テトラヒドロピラノンの立体選択的合成

（阪市大院理）○有吉 将馬・坂口 和彦・西村 貴洋

Stereoselective Synthesis of Tetrahydropyranones Using β-Silyl-γ-Alkylidene-γ-Butyrolactones with Aldehydes and Ketones (*Graduate School of Science, Osaka City University*) ○Shoma Ariyoshi, Kazuhiko Sakaguchi, Takahiro Nishimura

Polysubstituted tetrahydropyranones are found in the skeletons of several pharmaceuticals and bioactive natural products, and the development of methods for constructing them is one of the important issues in the field of organic synthesis. In this study, we found that the reaction of β-silyl-γ-alkylidene-γ-butyrolactones with aldehydes and ketones in the presence of Lewis acids gave the polysubstituted tetrahydropyranones stereoselectively. Various aldehydes and ketones can be applied in this reaction to give the corresponding tetrahydropyranones.
Keywords : Allylsilane; Tetrahydropyranone; γ-Butyrolactones; Lewis acid; Stereoselective

多置換テトラヒドロピラノンは、多くの医薬品化合物や生物活性天然物の骨格に見られ、その構築法の開発は、有機合成分野での重要な課題の 1 つである。本研究では、β－シリル－γ－アルキリデン－γ－ブチロラクトン **1** をルイス酸存在下、アルデヒドおよびケトンと反応させると、多置換テトラヒドロピラノンを立体選択的に与えることを見出した。本法には種々のアルデヒドおよびケトンが適用でき、様々なテトラヒドロピラノンの構築が可能である。



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対称ジアセテートのリパーゼの選択的モノ加水分解による非対称化

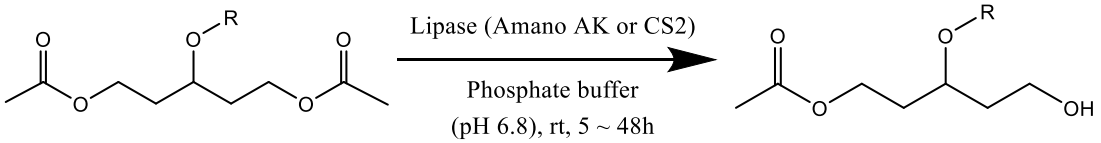
（広島工大院工）○内田裕介・平賀良知
Lipase-catalyzed Desymmetrization by Mono-Hydrolysis of Symmetric 1,5-Diacetyl-3-O-silyl Protected Pentanetriol (*Graduate School of Science and Technology, Hiroshima Institute of Technology*) ○Yusuke UCHIDA, Yoshikazu HIRAGA

Enzyme as biocatalyst has high specificity and high selectivity to substrate and product in comparison with chemical catalyst. The lipase-catalyzed desymmetrization of symmetric 1,5-diacetyl-3-*O*-silyl protected pentanetriol derivatives were studied. The symmetric diacetate having 3-*O*-*tert*-butyl diphenyl silyl (TBDPS) group was converted to the mono-acetate by the lipase-catalyzed hydrolysis with 12% yield (28%ee, Amano AK) and 15% yieid (63%ee, CS2). On the other hand, the symmetric 1,5-diacetate having 3-*O*-*tert*-butyl dimethyl silyl (TBDMS) group was obtained the corresponding mono-acetate with 3.5% yield (Amano AK) and 21% yield (CS2). The enantioselectivities of the mono-acetates having 3-*O*-TBDMS group obtained from the reactions catalyzed by Amano AK and CS2 are under investigation.
Keywords: Desymmetrization, Lipase, Hydrolysis, Diacetate

生体触媒は，化学触媒と比較して，高い基質特異性や立体選択性を有している。これまでに，３位水酸基をシリル基（TBDPS および TBDMS）で保護した対称 1,5-ペンタンジオールのリパーゼによるモノアセチル化による非対称化について調査し，立体選択的にモノアセチル体が得られることを見出した。本研究では，３位水酸基をシリル基で保護した対称ジアセチル体を基質とし，リパーゼの選択的モノ加水分解による非対称化について調査した。

対称ジアセテートは，３位水酸基をシリル基で保護した 1,5-ペンタンジアセテート **1a** (R = TBDPS), **1b** (R = TBDMS）を用いた。リパーゼは，微生物由来のリパーゼ Amano AK (*Pseudomonas fluorescens*)と CS2（*Cryptococcus* sp. S-2）を用いた。加水分解による非対称化反応は，リン酸緩衝液（pH 6.8）中で，5～48 時間行った。

ジアセテート(**1a**)を基質とし，リパーゼ Amano AK を用いたとき，(+)の符号をもつモノアセチル体（収率 12%，28%ee）が得られた。CS2 においても同様に，(+)の符号をもつモノアセチル体（収率 15%，63%ee）が得られた。一方，ジアセテート(**1b**)からは，モノアセチル体がそれぞれ収率 3.5%（Amano AK）および 21%（CS2）で得られた。現在，ジアセテート(**1b**)から Amano AK および CS2 を用いて得られたモノアセチル体の立体選択性は調査中である。



1a: R = TBDPS
1b: R = TBDMS

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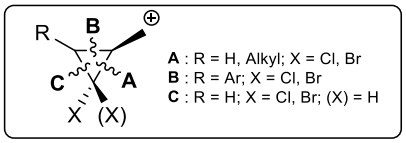
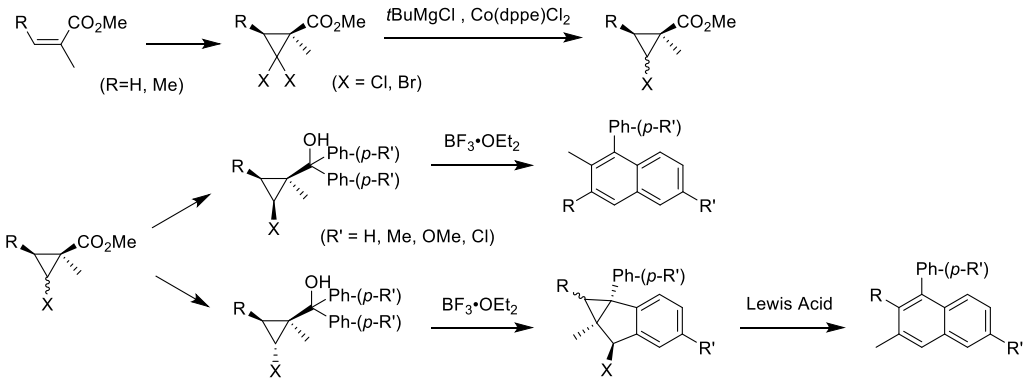
ジアリール(ハロシクロプロピル)メタノールのシクロプロパンシフト型変換反応による特異なトリシクロ化合物の合成

(関学大院理工) ○森本 将太郎・森口 健斗・若杉 和紀・田辺 陽
Syntheses of characteristic tricyclopropane compounds by cyclopropane-shift type transformation of diaryl(2-halocyclopropyl)methanols (*School of Science and Technology*, *Kwansei Gakuin University*)
○Shotaro Morimoto, Kento Moriguchi, Kazunori Wakasugi, Yoo Tanabe

Consistent with our longstanding synthetic studies of *gem*-dihalogenocyclopropanes based on cationic, anionic, and radical approaches, and the relevant chiral cyclopropane-type synthetic pyrethroid chemistry, we present here a unique Lewis acid-promoted cyclopropane-shift transformation using aryl 2-(monohalocyclopropyl)methanols to produce characteristic tricyclic compounds. Notably, the reaction mode is distinctively different from previously reported transformations regarding the cleavage bond position in the cyclopropane framework.
Keywords : cyclopropane; halocyclopropane; cyclopropane-shift

当研究室では，*gem*-ジハロシクロプロパンを基質とする多様なカチオン的・アニオン的・ラジカル的反応群を開発してきた．関連するピレスロイド化学も報告してきた[1)]．今回，カチオン的アプローチとして，掲題基質のカチオン的シクロプロパンシフト型変換反応[2)]による特異なトリシクロ化合物の合成の基質一般性の拡大を計画した．この反応は従来の**結合 A, B の開裂**でなく，異なる三員環の**結合 C での開裂**を伴うユニークな反応である．注目すべきは，Cl, Br の立体配置の違いにより，異なる反応が択一的に進行するという点である．基質の合成には，当研究室の *t*-BuMgCl/cat. $CoCl_2$ 還元反応を利用した[3)]．現在，位置制御型ベンズアヌレーション[4)]の可能性について検討中である．





1) *J. Org. Chem.* **2020**, *85*, 2984-2999. 2) *Tetrahedron Lett.* **2000**, *41*, 5937-5942. 3) *Synlett* **1998**, 67-69. 4) *J. Org. Chem.* **2005**, *70*, 2667-2678.

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イリジウム錯体触媒による炭素–炭素結合形成反応に向けたバイオ再生可能なカルボン酸の変換

（名大院理[1]・名大物国セ[2]）寺本 一貴[1]・○吉岡 頌太[1]・斎藤 進[1,2]

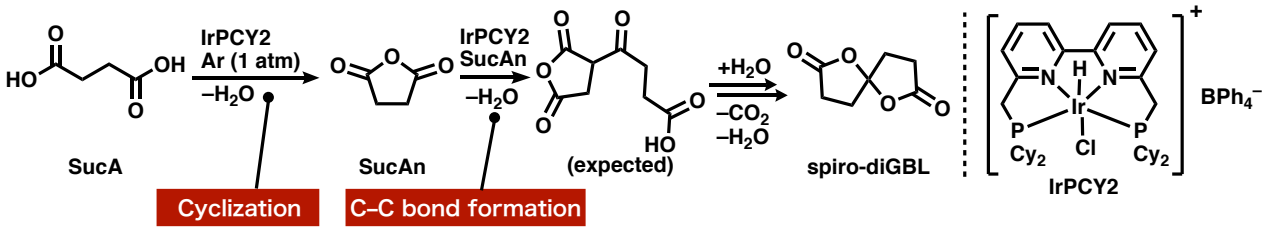
Ir-catalyzed transformation of bio-renewable carboxylic acids toward C–C bond formation

([1]*Graduate School of Science,* [2]*Research Center for Materials Science, Nagoya University*)
○Kazuki Teramoto,[1] Shota Yoshioka,[1] Susumu Saito[1,2]

Development of efficient methods to utilize dicarboxylic acids obtained from bio-renewable resources such as succinic acid (SucA) and fatty acids is an increasingly important subject. Recently, we have developed a multifunctional Iridium pre-catalyst, IrPCY2, for hydrogenation of mitochondria-relevant metabolites such as 1,4-dicarboxylic acids to corresponding diols or triols [1]. In survey of the reaction pathway for hydrogenation, IrPCY2 was found to convert SucA into spiro[4,4]-di-γ-butyrolactone (spiro-diGBL) under Ar atmosphere. In this transformation, it was implied that dehydration of SucA following C–C bond formation between formed succinic anhydrides proceeded. Aiming at the development of novel method to utilize dicarboxylic acids and anhydrides, this transformation was further investigated.

Keywords: Carboxylic Acids; Carboxylic anhydrides; Iridium complex catalyst; C–C bond formation

コハク酸などのジカルボン酸や、パルミチン酸などの長鎖カルボン酸は天然に豊富に存在するバイオマス資源であり、それらを炭素資源として効率的に利用する方法は持続可能な社会の実現に向けて求められている。我々はコハク酸をはじめとするミトコンドリア内代謝物に関連した様々な多価カルボン酸を水素化し、多価アルコールへ変換するイリジウム触媒 IrPCY2 を開発した[1]。その水素化の反応機構を調査する過程において、IrPCY2 がアルゴン雰囲気下では、炭素数 4 のコハク酸を炭素数 7 の spiro[4,4]di-γ-butyrolactone に変換できることを発見した。この変換では、ジカルボン酸から環状酸無水物への変換及び、環状酸無水物同士の炭素－炭素結合形成反応が進行していることが予想される。これらの反応を応用してカルボン酸を炭素資源として有効利用する新しい手法を確立することを目指し、本研究では、今回発見された二つの変換反応について調査を行った。



[1] S. Yoshioka, S. Nimura, M. Naruto, S. Saito. *Sci. Adv.* **2020**, *6*, eabc0274.

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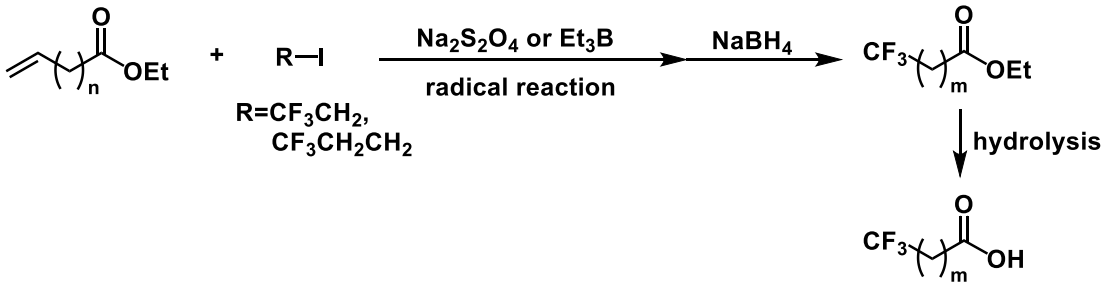
末端にトリフルオロメチル基を有する脂肪酸の合成

（群大院工[1]）○内藤 一樹[1]・杉石 露佳[1]・園山 正史[1]・網井 秀樹[1]
Synthesis of fatty acids having a trifluoromethyl group at the end ([1]*Graduate School of Science and Technology, Gunma University*) ○ Kazuki Naito,[1] Tsuyuka Sugiishi,[1] Masashi Sonoyama,[1] Hideki Amii[1]

Handling of membrane proteins in water using conventional amphipathic molecules is extremely difficult, and experimental data on the three-dimensional structure of membrane proteins is very limited. One of the most promising approaches to overcome this difficulty is to replace some hydrogen atoms in the hydrophobic chain in amphipathic molecules with fluorine atoms. Therefore, in this study, we synthesized the fatty acid with a trifluoromethyl group required for amphipathic molecules. Actually, trifluoromethylated fatty acid esters were obtained by radical reactions using unsaturated esters with CF_3CH_2I or $CF_3CH_2CH_2I$ followed by reduction. Finally, hydrolysis was carried out to obtain the desired CF_3-fatty acids.
Keywords : Fluorine, Radical addition, Trifluoromethyl group, Fatty acid

従来の両親媒性分子を用いた水中での膜タンパク質の取り扱いは非常に困難であり、膜タンパク質の三次元構造の実験データは非常に限られている。この困難を克服するための最も有望なアプローチの 1 つとして、両親媒性分子中の一部の疎水鎖の水素原子をフッ素原子に置換することがあげられる[1]。そこで本研究では、両親媒性分子に必要なトリフルオロメチル化脂肪酸の合成を行った。

実際に、不飽和脂肪酸エステルと CF_3CH_2I, $CF_3CH_2CH_2I$ を用いてラジカル反応を行い、付加生成物のヨード基を還元することでトリフルオロメチル化脂肪酸エステルが得られた。最後に加水分解を行うことで目的物であるトリフルオロメチル化脂肪酸を得た。



1) le. Maire, M.; Champeil, P.; Moller, J. V. *Biochim. Biophys. Acta* **2000**, *1508*, 86-111.

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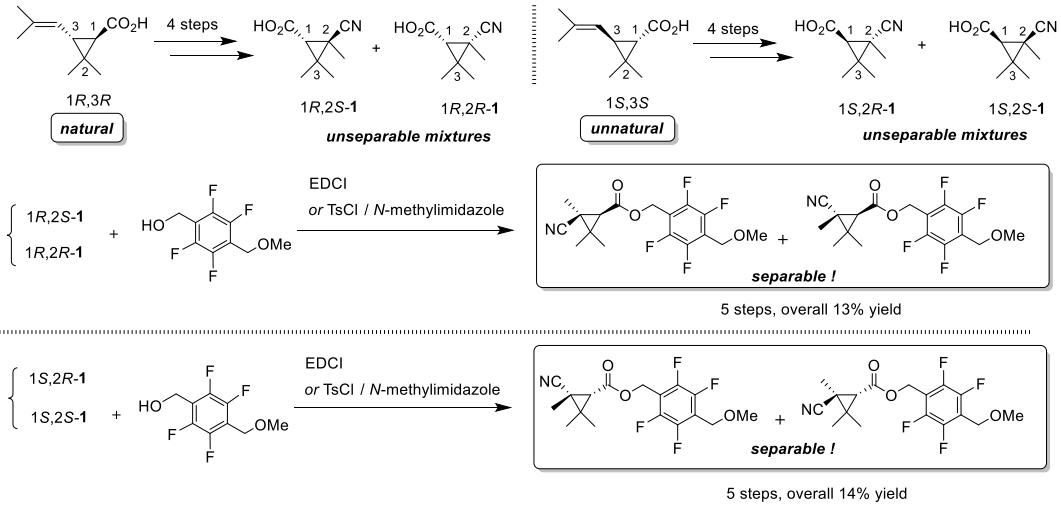
二不斉中心シアノ置換シクロプロパン系ピレスロイド全 4 種のキラル合成および立体構造活性相関

（関学大院理工）○青柳侑沙・森山瑞希・松尾憲忠・田辺 陽

Chiral synthesis of cyano-substituted cyclopropane-type pyrethroid with two asymmetric centers and its insecticidal stereostructure-activity relationship, ○Yusa Aoyagi, Mizuki Moriyama, Noritada Matsuo, Yoo Tanabe

Consistent with our longstanding studies on cyclopropane transformation chemistry, together with cyclopropane pyrethroid chemistry bearing two or three chiral centers, we present here chiral synthesis of a novel cyano-substituted cyclopropane synthetic pyrethroid and its insecticidal stereostructure activity relationship (SAR). Racemates of the present compound were already reported to exhibit high insecticidal activity. Based on the background, we envisage a chiral synthesis of all four enantiomers to investigate the SAR.
Keywords : Pyrethroid., chiral synthesis, stereostructure-activity relationship

当研究室では, シクロプロパンの特性を活かした各種合成研究[1]の一環として, 二・三不斉ピレスロイド殺虫剤の立体構造活性相関の研究を行っている[2]. その展開として, 二不斉中心シアノ置換シクロプロパン系ピレスロイド全 4 種のキラル合成を行った. アルコール側は SumiOne® （虫コナーズの原料）の型である. すでにラセミ体で最高級の殺虫活性を有しているため[3], その立体構造活性相関に興味が持たれる. 合成は既知の光学活性菊酸の両異性体からの誘導化で行った. そのため絶対配置はほぼ確定している. 現在, 殺虫活性試験を行っている. なお, エステル化は当研究室の方法[4]を利用しているが, 常法である EDCI より高速・高収率である.



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2) a) *J. Chem. Soc., Perkin Trans 1* **1996**, *1*, 1243-1249. b) *Bioorg. Med. Chem.* **2001**, *9*, 33-39. c) *Molecules* **2019**, *24*, 1023-1041.
3) Matsuo, N.; Mae, M. *Jpn. Kokai Tokkyo Koho* P2010-24212A, **2010**.
4) *Adv. Synth. Catal.* **2003**, *345*, 1209-1214.

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ジエンの位置選択的ジフルオロシクロプロパン化

（群馬大院理工[1]）○向井 寛人[1]・杉石 露佳[1]・網井 秀樹[1]
Regioselective Difluorocyclopropanation of Dienes ([1]*Graduate School of Science and Technology, Gunma Universtiy*) ○Hiroto Mukai,[1] Tsuyuka Sugiishi,[1] Hideki Amii[1]

Fluorine atoms have properties such as high electronegativity and small atomic radius. Accordingly, organofluorine compounds tend to be characteristic because of the intramolecular and/or intermolecular effects of the fluorine atoms, and are used in pharmaceuticals, agrochemicals, and material science. We have studied the synthesis of *gem*-difluorocyclopropane using sodium bromodifluoroacetate, which is an easy-to-handle difluorocarbene source.[1] During the study of difluorocyclopropanation, it was found that the electronic features of the substituents in the alkenes affect the chemical yield of the procucts. Therefore, we designed the starting 1,3-butadienes (1) endowed with electron-withdrawing and electron-donating groups at 1 and 4-positions, respectively. Herein, we report the regioselective difluorocyclopropanation of dienes 1 containing the two kinds of C-C double bonds using sodium bromodifluoroacetate. Vinyl difluorocyclopropanes 2 and difluorocyclopentenes 3, which would be generated by the ring expansion of 2, were formed from dienes 1 in diglyme with four equivalents of sodium bromodifluoroacetate.
Keywords: Fluorine; Dienes; gem-Difluorocyclopropanation; Regioselective; Sodium difluoroacetate

フッ素原子は、電気陰性度が高く、原子半径が小さいという特性があることから、有機フッ素化合物の分子内または分子間に及ぼす影響が大きい。そのため、有機フッ素化合物は特徴的な性質を持つ傾向があり、医薬品、農薬、材料科学で活用されている。当研究室では、有機フッ素化合物の一つである *gem* -ジフルオロシクロプロパン合成の研究を行っており、これまでにブロモジフルオロ酢酸ナトリウムを用いた合成を報告している[1)]。また、本シクロプロパン化において、出発物質であるアルケン化合物の有する置換基の電子効果が収率を左右することが知られている。そこで、本研究ではその性質を利用し、ジエンの２つの二重結合の片方に対し、選択的にジフルオロカルベンを付加させる反応について研究した。すなわち、両末端に電子供与性および電子求引性置換基をひとつずつ有するジエン 1 を合成し、ジグリム中、ブロモジフルオロ酢酸ナトリウム 4 当量で反応させたところ、ビニルジフルオロシクロプロパン 2 およびジフルオロシクロペンテン 3 が生成した。なお、ジフルオロシクロペンテン 3 はビニルジフルオロシクロプロパン 2 が熱により環拡大を起こして得られたと考えられる。

1 2 3

1) Oshiro, K.; Morimoto, Y.; Amii, H. *Synthesis* **2010**, 2080.

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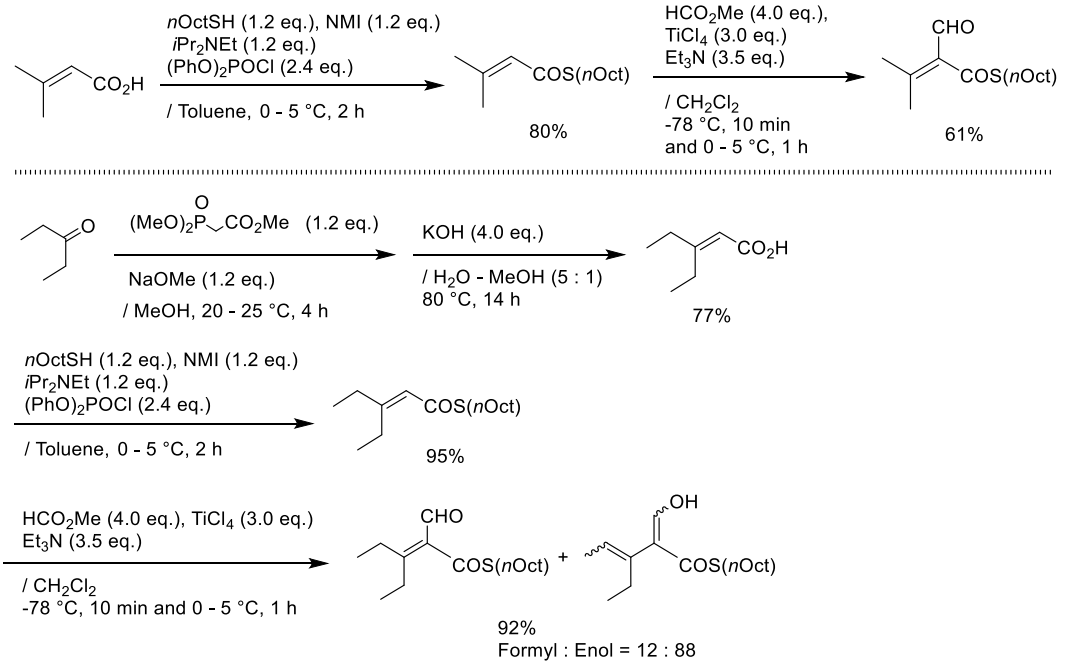
β,β-二置換 α,β-不飽和チオエステルの α-ホルミル化

（関学大院理工）○福永 颯馬・山口 祥代・森山 瑞希・田辺 陽
α-Formylation of α,β-unsaturated thioesters ○Soma Fukunaga, Sachiyo Yamaguchi, Mizuki Moriyama, Yoo Tanabe

Synthesis of α,β-unsaturated α-formyl thioesters bearing three distinctive functional groups (double bond, thioester, aldehyde) have been developed utilizing Ti-Claisen condensation. Compared with the esters, thioesters have severals advantage regarding higher reactivities, flexible functional transformations, etc. The obtained products are promising candidates for key synthetic building blocks. Despite the utility, no report has appeared on the direct α-formylation method of the α,β-unsaturated not only esters but also thioester. Herein, we present Ti-Claisen condensation (α-formylation) of α,β-unsaturated of thioesters using commercially available reagents under accessible conditions.
Keywords : α,β-unsaturated thioester, α-formylation, Ti-Claisen condensation

β,β-二置換 α,β-不飽和チオエステルの直接ホルミル化はこれまで報告されていない．シンプルな化合物に二重結合，チオエステル，アルデヒドと三つの異なる官能基を有しており，またエステルに比べチオエステルは反応性が高く，特異な官能基変換が期待できるため，有機合成上有用と考えられる．今回，当研究室のチオエステル化法[1]を利用して，さらにはエステルを基質とした反応と同様に，Ti-Claisen 縮合（α-ホルミル化）[2]を適用すると簡便に β,β-二置換 α,β-不飽和チオエステルが合成できることを見出した．



1) a) *Adv. Synth. Catal.* **2003**, *345*, 1209-1214. b) *Tetrahedron* **2007**, *63*, 12071-12080.
2) a) *Org. Lett.* **2009**, *11*, 4258 – 4261. b) *Org. Synth.* **2016**, *93*, 286-305.

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チオジフルオロメチル芳香族化合物のラジカル反応の検討

（群馬大院理工[1]） ○飯塚 東[1]・上山 晃平[1]・杉石露佳[1]・網井秀樹[1]

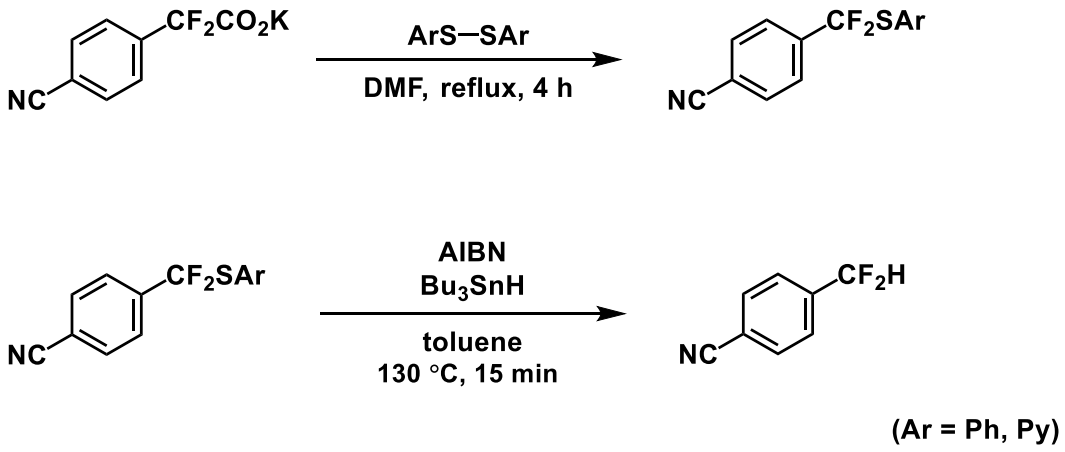
Radical reactions of α-(thio)difluoromethyl arenes

([1]*Graduate School of Science and Technology, Gunma University*) ○Azuma Iizuka,[1] Kohei Ueyama,[1] Tsuyuka Sugiishi,[1] Hideki Amii,[1]

Organofluorine compounds have been paid attention in various fields such as pharmaceuticals, agrochemicals and materials. In our laboratory, decarboxylation reactions based on the formation of α-aryldifluoromethyl anion species ($ArCF_2^-$) have been carried out. The $ArCF_2^-$species react with aryldisulfide. The obtained α-(thioaryl)difluoromethyl arenes underwent radical reduction smoothly in the presence of AIBN and Bu_3SnH in toluene.

Keywords : Fluorine; Radical reaction; Difluoromethyl group; sulfur

含フッ素置換基の一つであるジフルオロメチレン基（$-CF_2-$）を有する化合物は様々な生理活性を持つことが知られており、医薬・農薬・材料など様々な分野で注目されている。当研究室では以前より、α-アリールジフルオロメチルアニオン種($ArCF_2^-$)の生成に基づく脱炭酸反応が行われてきた。その際発生する $ArCF_2^-$種は、求電子種であるジアリールジスルフィドと反応を起こす。得られたα-（チオアリール）ジフルオロメチル化アレーンはトルエン溶媒中、AIBN、Bu_3SnH 存在下で、定量的にラジカル還元された。



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日本化学会 第101春季年会 (2021)

アリールモノフルオロメチルシランの合成化学的応用

（群馬大院理工）○佐藤 愛美・芳賀 悠人・杉石 露佳・網井 秀樹

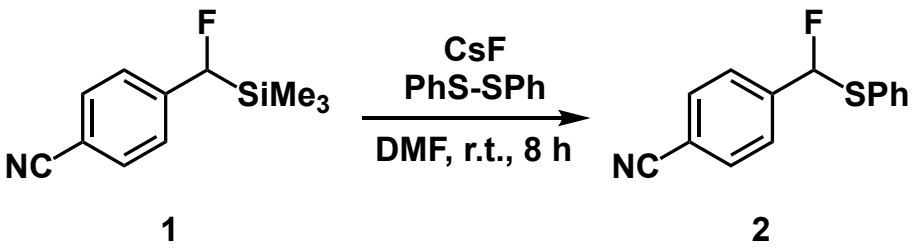
The synthetic application of (aryl)fluoromethylsilane

([1]*Graduate School of Science and Technology, Gunma University*) ○Manami Sato, Yuto Haga,Tsuyuka Sugiishi, Hideki Amii[1]

Organofluorine compounds have been paid attention in various fields such as pharmaceuticals, agrochemicals, and materials. Previously, we synthesized α-(thiophenyl)fluoromethylarenes (ArCFHSPh, **2**) by decarboxylation of (aryl)fluoroacetates ($ArCFHCO_2K$) and applied compounds **2** to radical reactions. As monofluoro building blocks, (aryl)fluoromethylsilanes ($ArCFHSiMe_3$, **1**) were prepared from benzyl fluorides by deprotonation. Arylmonofluoromethyl compounds were synthesized by the reactions of compounds **1** with electrophiles. We succeeded in the synthesis of compound **2** by using diphenyl disulfide as an electrophile for compound **1**.

Keywords : Fluorine; Fluoromethyl group; Silicon; Nucleophile

フッ素は、全元素中で電気陰性度が最大であり、原子半径が水素に次いで小さい。このような特徴から、有機フッ素化合物は医薬・農薬・材料などの様々な分野で注目されている。当研究室では以前、アリールフルオロ酢酸塩($ArCFHCO_2K$)の脱炭酸反応によりα-(チオフェニル)フルオロメチルアレーン($ArCFHSPh$, **2**)を合成し、さらにこれをラジカル還元反応に用いることに成功している。また、フッ化ベンジルを経由してアリールモノフルオロメチルシラン($ArCFHSiMe_3$, **1**)を合成し、これと求電子剤との反応によるアリールモノフルオロメチル化合物の合成を行ってきた。そこで今回、化合物 **1** のさらなる合成化学的応用を検討した。化合物 **1** に対して求電子剤としてジフェニルジスルフィドを用いることで化合物 **2** の合成に成功した。



1 **2**

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α−イミノエステルの位置選択的極性転換アルキル化反応の開発

(千葉大院工）○久木田 茉優・吉田 泰志・三野 孝・坂本 昌巳
Regioselective umpolung alkylation reactions of α-iminoesters (*Graduate School of Engineering, Chiba University*) ○Mayu Kukita, Yasushi Yoshida, Takashi Mino, Masami Sakamoto

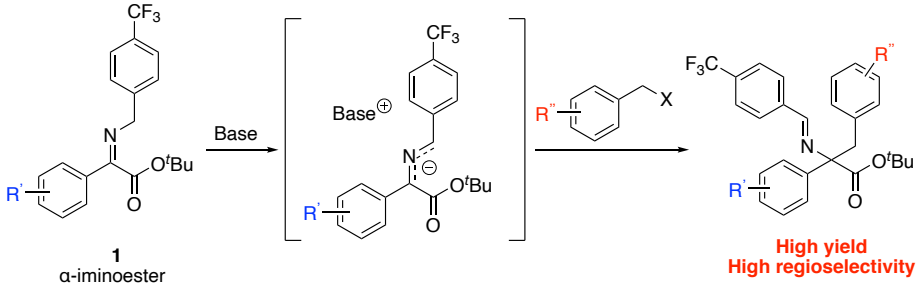
The umpolung reaction have been researched due to their great potential applications for the effective molecular transformations. Recently, we have developed the umpolung alkylation of α-iminoesters with benzyl iodide, however the successful examples were limited because of the product's instabilities. In this presentation, we would like to discuss about the umpolung alkylation reaction of α-iminoesters with higher generality by the stabilization of the products.

When the umpolung alkylation reaction of α-iminoesters **1** with 2 equivalent of benzyl iodide derivatives were carried out in 0.05 M of acetonitrile, the desired alkylation products were obtained in excellent regioselectivities with up to 89% yields. The substrate scope revealed that the present protocol could be applied to the various series of substrates and reactants.

Keywords : Umpolung reaction; Chiral amine; α-Iminoesters; Alkylation; Regioselective reaction

極性転換とは，官能基が本来有する反応性を反転させることであり，シントンの組み合わせを拡大できるため効率的分子変換を可能にする魅力的な合成戦略である。当研究室では近年, α−イミノカルボニル化合物を基質とする極性転換反応に関する研究を行っており，これまでに種々のアミノ酸誘導体の触媒的不斉合成を達成している [1)] 一方で，同反応に用いることができる求電子剤は Michael 受容体に限られていた。最近我々は，求電子剤としてハロアルカンを用いる α−イミノエステルの極性転換アルキル化反応を開発しているものの，適用可能な基質は限られていた。そこで本研究では，生成物を安定化し反応や精製中における分解を抑制することで，同反応の基質適用範囲の拡大を試みた。

極性転換アルキル化反応を 0.05 M のアセトニトリル中，*tert*-ブチルエステル **1** に対し 2 当量のよう化ベンジルを作用させると，目的とするアルキル化反応が位置選択的に進行し，生成物を最高 89%の収率で得た。さらに基質適用範囲を調査したところ，幅広い基質において高収率かつ高位置選択的に生成物を得ることに成功した。



1
α-iminoester

1) Y. Yoshida *et al. J. Org. Chem.*, **2019**, *84*, 7362.

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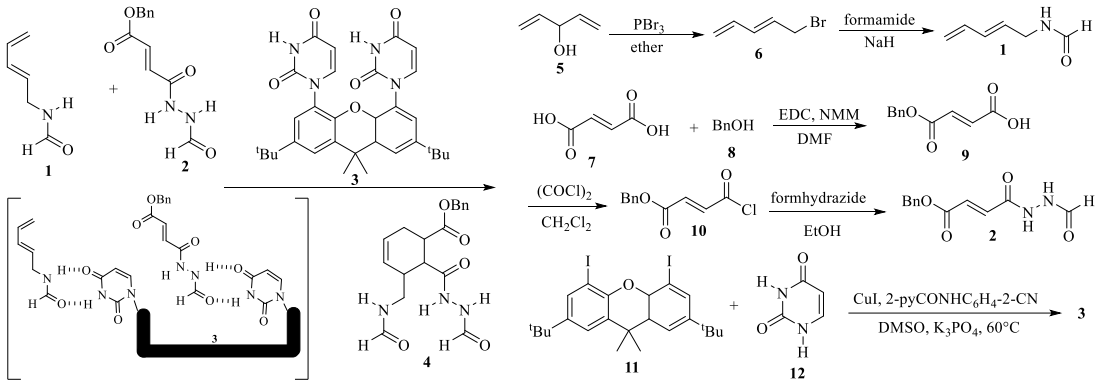
Regioselective Diels-Alder reaction using hydrogen bonding of amides

Graduate School of Science, Kanagawa University, ○NI, Wangbin；KIHARA, Nobuhiro

Keywords: Diels-Alder reaction, hydrogen bonding, amide, regioselectivity

Regioselective Diels-Alder reaction has been carried out by using electronic effect of functional groups. Therefore, when 1,2-di-substituted dienophile has electronically similar functional groups such as ester and amide, Diels-Alder reaction proceeds non-regioselectively. When both the diene and dienophile are aligned by utilizing intermolecular interaction such as hydrogen bonding between amides, regioselective Diels-Alder reaction is expected even with electronically symmetrical dienophile. The diene **1** and dienophile **2** bearing formamide moieties were designed as the substrates. A xanthene derivative **3** with two uracil moieties was also designed as the reaction field. When Diels-Alder reaction of **1** and **2** is carried out in the presence of **3**, the regioselective formation of **4** is expected via the alignment of **1** and **2** on **3** by the hydrogen bonding between amide groups.

Bromination of **5** afforded bromide **6**, by which formamide was alkylated to give **1**. Half ester **9** of fumaric acid **7** was converted to acid chloride to used it for the acylation of formhydrazide to obtain **2**. Cu(I)-catalyzed condensation of **11** and uracil **12** was investigated to prepare **3**.



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[P02-1pm] 19. Colloid and Interface Chemistry

Fri. Mar 19, 2021 1:20 PM - 2:50 PM Area 2 (Online Meeting)

[P02-1pm-01] Preparation of water soluble quantum dots and elucidation of their emission behaviors at a single dot level

○Natsumi Nagasaki[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

[P02-1pm-02] Preparation of Non-spherical Polyimide Particles

○Akiko Nakahashi[1] (1. Osaka Research Institute of Industrial Science and Technology)

[P02-1pm-03] Chemical Synthesis and Local Structure Analysis of Tungsten Oxide Nanoparticles

○Yuki Kitazaki[1], Mari Takahashi[1], Masafumi Harada[2], Shinya Maenosono[1] (1. JAIST, 2. Nara Women's Univ.)

[P02-1pm-04] pH-dependent Orientational Changes of Gold Nanorods on a DNA polymer brush

○Yu Sekizawa[1], Hideyuki Mitomo[2,3], Satoshi Nakamura[4], 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, 4. National Institute of Advanced Industrial Science and Technology (AIST))

[P02-1pm-05] Synthesis and properties of Au_{25} cluster protected by semi-fluorinated ligand.

○duhong sun[1], Yuki Saito[1], Yukatsu Shichibu[1,2], Hideyuki Mitomo[3], Kuniharu Ijiro[3], Katsuaki Konishi[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University, 3. Research Institute for Electronic Science, Hokkaido University)

[P02-1pm-06] Regulating Photocatalytic Activity by Self-Assembly of Fluorescein Derivatives

○Masakazu Kobayashi[1], Tomoe Tamemoto[1], Youhei Tani[1], Hajime Shigemitsu[1], Kida Toshiyuki[1] (1. Osaka University)

[P02-1pm-07] Control over One-Dimensional Arrangements of Perovskite Nanocrystals

○Kanako Nakatsukasa[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

[P02-1pm-08] Construction of Hybrid Supramolecular Structures Using a Perylene Bisimide Derivative and a Perovskite Nanocrystal

○Naoki Kubo[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

[P02-1pm-09] Photocontrol of crystallization-induced emission in azobenzene derivatives

○Miho Okaji[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. kwansei Gakuin univ.)

[P02-1pm-10] Metastabilization of cis-azobenzene using hydrogen bonds

○Erika Kida[1], Mitsuaki Yamauchi[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

[P02-1pm-11] What key parameter for determing shape of taurocholic acid-based mixed micelle ?

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○Hideki Aizawa[1] （1. Setsunan University）

[P02-1pm-12] Micellization of tetradecylquinolinium and tetradecylisoquinolinium bromides

Reina Sakota[1], ○Katsuhiko Fujio[1] （1. School of Science, Tokai University）

[P02-1pm-13] Micelle Formation and Photo-Responsive Behavior of an Amphiphilic Azotolane Liquid Crystal

○Anna Tamai[1], Ayumi Kobayashi[1], Kohei Iritani[1], Yamashi Takashi[1] （1. Tokyo University of Technology.）

[P02-1pm-14] Molecular Orientation Analysis in a Thin Film of a p-Gelator Forming a Unique Aggregate at Air– Water Interface

○Yuta Yamaguchi[1], Takafumi Shimoaka[1], Nobutaka Shioya[1], Ayyappanpillai AJayaghosh[2], Taizo Mori[3,5], Katsuhiko Ariga[4,5], Takeshi Hasegawa[1] （1. ICR, Kyoto Univ., 2. CSIR-NIIST, 3. ISSP, The Univ. of Tokyo, 4. Grad. Sch. of Front. Sci., The Univ. of Tokyo, 5. NIMS）

[P02-1pm-16] Guest-responsive supramolecular hydrogel expressing selective sol-gel transition for sulfated glycosaminoglycans

○Naofumi Kuroda[1], Shun-ichi Tamaru[1], Seiji Shinkai[2] （1. Graduate School of Engineering, Sojo University, 2. Institute of Systems, Information Technologies and Nanotechnologies）

[P02-1pm-17] Preparation and properties of supramolecular hydrogels for the development of self-healing soft materials.

○Yuki Edamoto[1], Naofumi Kuroda[2], Shun-ichi Tamaru[1,2], seiji Shinkai[3] （1. Department of Engineering Sojo University , 2. Graduate School of Engineering Sojo University, 3. Institute of Systems, Information Technologies and Nanotechnologies）

[P02-1pm-18] Supramolecular hydrogel showing gelation and color change in response to metal cations

Ryo Taniguchi[1], Masayuki Izumi[1], Tomoyuki Akutagawa[2], Takayoshi Nakamura[3], ○Rika Ochi[1] （1. Kochi Univ., 2. Tohoku Univ., 3. Hokkaido Univ.）

[P02-1pm-19] Evaluation of Magnetic Ionic Liquid Gel Properties Formed by Fluorine-Containing Low Molecular Weight Gelators Having Linear Alkyl Group at Terminal Position

○Tatsuya Tomarino[1], Miura Masahiro[1], Morita Yuki[2], Okamoto Hiroaki[1] （1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University）

[P02-1pm-20] Electrochemical Properties of Ionic Liquid Gel Formed by Semi-perfluoroalkyl Benzoate Derivatives

○Kenta Matsumoto[1], Yuki Morita[2], Hiroaki Okamoto[1] （1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University）

[P02-1pm-21] Gel strength of ionic liquid gels by low molecule weight gelator with fluoro-substituent at both ends of molecules

○Koohei Nakamura[1], Yuta Kanesigte[1], Yuki Morita[2], Hiroaki Okamoto[1] （1. Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2. Faculty of Engineering, Yamaguchi University）

[P02-1pm-22] Gel Properties Formed by Dimer Type 4-Mercaptobenzoic Acid Derivatives Having Perfluoroalkyl Group at Both Terminal Position

○Sota Kanemitsu[1], Ryoichiro Yoshihara[2], Kotaro Kanetada[2], Yuki Morita[1], Hiroaki Okamoto

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[2] （1. Faculty of Engineering, Yamaguchi University, 2. Graduate School of Sciences and Technology for Innovation）

[P02-1pm-23] Electrochemical Properties of Gel Electrolyte for Li-ion Battery Formed by Fluorine-Containing Gemini-Type Low Molecular Gelators

○Yui Endo[1], Tomohiro Yoshida[2], Morita Yuki[1], Hiroaki Okamoto[2] （1. Faculty of Engineering, Yamaguchi University, 2. Graduate School of Sciences and Technology for Innovation, Yamaguchi University）

[P02-1pm-24] Microscopic observation on the effect of non-equilibrium flow on Aβ-lipid membrane interaction

○Mitsuhiro Abe[1], Akane Iida[1], Hideki Nabika[2] （1. Graduate School of Sci. and Eng. Yamagata Univ., 2. Faculty of science Yamagata Univ.）

[P02-1pm-25] Elucidation of Aβ aggregation behavior in liposome dispersion under non-equilibrium stirring

○Fumiya Sato[1], Akane iida[2], Mitsuhiro Abe[2], Hideki Nabika[1] （1. Faculty of Science of Yamagata Univ., 2. Graduate School of Sci. and Eng. Yamagata Univ.）

[P02-1pm-26] Preparation of Lipid Vesicle Supported by Micro-Honeycomb Porous Film

○Keisuke Kimura[1], Ruria Yano[1], Kazunari Matsumura[1] （1. Shibaura Institute of Technology）

[P02-1pm-27] Multiple droplets formation by a simple mixing method with maicrofabricated channel and their mass-transport mechanism

○Kyoka Nakanishi[1], Kenta Goto[1], Fumito Tani[1] （1. The Univ. of Kyushu）

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水溶性量子ドットの創製および単一レベルでの発光挙動解明

（関西学院大理工）○長崎 夏美・山内 光陽・増尾 貞弘

Preparation of Water Soluble Quantum Dots and Elucidation of their Emission Behaviors at the Single Dot Level

(*Kwansei Gakuin University*) ○Natsumi Nagasaki, Mitsuaki Yamauchi, Sadahiro Masuo

Semiconductor quantum dots (QDs) are expected to be applied to various optoelectronic devices and biomarkers due to their tunable and narrow photoluminescence (PL) spectra, strong durability and high PL quantum yield[1]. However, the typical QD are insoluble in water because the QDs are coated with hydrophobic ligands of alkyl chains. In this work, we prepared the water soluble CdSe/CdS QDs by ligand-exchange reaction on the surface of QDs, and attempted exploring the emission behaviors in solution at the single dot level.

We used L-cysteine as hydrophobic ligands to form water soluble QDs. After the ligand-exchange, the L-cysteine-capped QDs underwent phase-transfer to the aqueous phase. This finding indicates the achievement of preparation of water soluble QD. The PL spectra of the QDs in chloroform and in water showed same PL peak (Fig. 1). Furthermore, we investigated the PL properties of the water soluble QDs at the single QD level.

Keywords : Quantum Dots; Water Soluble; Single-Photon; Nanocrystal; Single Molecule Detection

半導体量子ドット(QD)は，優れた光耐久性や高い発光量子収率を示すことから，様々な光電子デバイスやバイオマーカーなどへの応用が期待されている[1]。しかし，QD の多くは疎水性のアルキル鎖配位子で覆われているため水には分散しない。これまでに，水溶性の配位子への配位子交換法による水溶性 QD の合成が報告されている[2]。本研究では，配位子交換法により水溶性 CdSe/CdS QD を合成し，溶液中および単一レベルで発光挙動の解明を試みた。

水溶性の配位子である L-cysteine を用いて配位子交換を行うと，QD が水層に移動した。配位子交換前後の発光スペクトルを比較すると，発光極大波長は同じであることから (Fig. 1)，水溶性 QD が調製できたと考えられる。さらに，単一粒子分光測定を用いてこれらの QD の発光特性を調べたので，詳細を報告する。

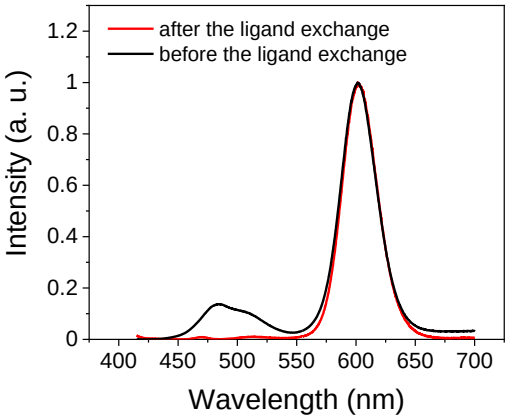

Fig.1. PL spectra of QDs before (black), and after (red) the ligand exchange.

1) D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev*. **2010**, *110*, 389-458.
2) U. Tohgha, K. Varga, M. Balaz, *Chem. Commun.*, **2013**, *49*, 1844-1846.

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非球状ポリイミド微粒子の調製

（阪技術研）○中橋 明子

Preparation of Non-spherical Polyimide Particles (*Osaka Research Institute of Industrial Science and Technology*) ○Akiko Nakahashi

Preparations of polyimide particles have been studied in our laboratory. Polyimides have excellent thermal properties even in the particle form.

Non-spherical particles have larger surface area than spherical particles. Particle shapes affect the properties of the particles and the composites containing the particles. Most of particles prepared by bottom-up methods are spherical, which is thermodynamically stable shape. In this study, non-spherical polyimide particles were prepared by stirring dispersion of spherical polyimide particles in particular organic solvents. Spherical polyimide particles were prepared by precipitation polymerization. Oblate spheroidal polyimide particles were obtained by stirring acetonitrile dispersion. No shape change was observed when particles were stirred in isopropyl alcohol.

Keywords : polyimide, precipitation polymerization, non-spherical particles

これまで、我々の研究所においてポリイミド微粒子（PI 微粒子）の調製および表面修飾を検討してきた。PI 微粒子は微粒子形態であっても高い耐熱性を有し、ジアミンとカルボン酸二無水物との沈殿重合により、球状 PI 微粒子が得られる。

非球状微粒子は、球状微粒子に比べ比表面積が大きい。そのため、非球状微粒子は微粒子単体および複合体の材料物性に形状に由来する特異な効果を与えると考えられる。一般的にボトムアップ法で調製した微粒子は熱力学的に安定な球状となり、非球状微粒子を得るためには粒子調製条件の厳密な制御が必要となる。一方、球状微粒子を変形させて非球状微粒子を得る場合、微粒子に効率よく外力を加える必要があり、操作が煩雑であった。本研究では、球状 PI 微粒子を分散媒中で撹拌することにより、簡便に非球状 PI 微粒子（扁平 PI 微粒子）が調製できることを明らかにした。分散媒にアセトニトリルを用い、1 週間撹拌して扁平 PI 微粒子を得た（Figure 1）。一方、分散媒にイソプロピルアルコールを用いた場合は、変形が見られなかった。

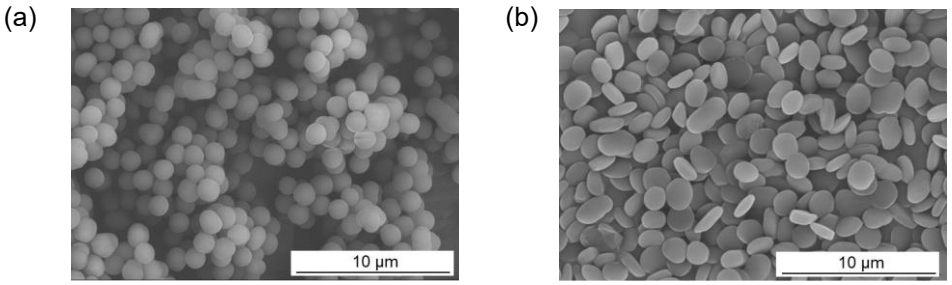

Figure 1. SEM photographs of (a) spherical polyimide particles and (b) non-spherical polyimide particles (stirred in acetonitrile for 1 week).

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酸化タングステンナノ粒子の化学合成と局所構造解析

（北陸先端大[1]・奈良女子大[2]）○北崎裕己[1]・高橋麻里[1]・原田雅史[2]・前之園信也[1]
Chemical Synthesis and Local Structure Analysis of Tungsten Oxide Nanoparticles ([1]*School of Materials Science, JAIST,* [2]*Faculty of Human Life and Environment, Nara Women's University*) ○Yuki Kitazaki,[1] Mari Takahashi,[1] Masafumi Harada,[2] Shinya Maenosono[1]

Tungsten oxide (WO_{3-x}) is used in various applications including catalysts, solar cells, and electrochromic materials.[1)] The various properties in these applications are greatly influenced by the crystal structure of WO_{3-x} and oxidation state of W. In this study, WO_{3-x} nanoparticles were synthesized in organic solvent using different types of precursors and capping ligands in order to control the morphology and the crystal structure. Their structures were analyzed using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS). Fig. 1a shows a TEM image of as-synthesized WO_{3-x} nanoparticles when ammonium metatungstate hydrate was used as a precursor and both oleylamine and oleic acid were used as capping ligands. The rod-shapes WO_{3-x} nanoparticles with a long axis of about 20.8 ± 3.8 nm and a short axis of 1.9 ± 0.4 nm were obtained. From the XRD pattern of the WO_{3-x} nanoparticles (Fig. 1b), it was found that the nanoparticles contained orthorhombic phases of W_3O_8 and W_8O_{21}. Figure 1c shows the radial distribution function of the nanoparticles and the nearest neighbor distance between W and O was determined to be 1.4 Å in agreement with those of W_3O_8 and W_8O_{21}.

Keywords : Tungsten Oxide; Nanoparticles; X-ray Absorption Fine Structure; Local Structure

酸化タングステン（WO_{3-x}）は触媒、太陽電池、エレクトロクロミック材料など様々な分野で利用されている[1)]。これらの用途における種々の特性は WO_{3-x} の結晶構造や W の価数に大きく影響される。本研究では、有機溶媒中で異なる金属前駆体及び表面修飾剤を用いて化学合成した種々の WO_{3-x} ナノ粒子について、TEM、XRD、XPS、XAFS などの分析手法を用いて構造解析を行った。図 1 にメタタングステン酸アンモニウム水和物を前駆体とし、オレイルアミン及びオレイン酸を表面修飾剤として合成した WO_{3-x} ナノ粒子の TEM 像、XRD パターン及び動径分布関数を示す。WO_{3-x} ナノ粒子の形状はロッド状で、W_3O_8 と W_8O_{21} の 2 種の斜方晶相が混在していると考えられる。XAFS スペクトルから、W と O の最近接原子間距離を求めたところ、1.4 Å であり、理論値と一致していることが明らかとなった。

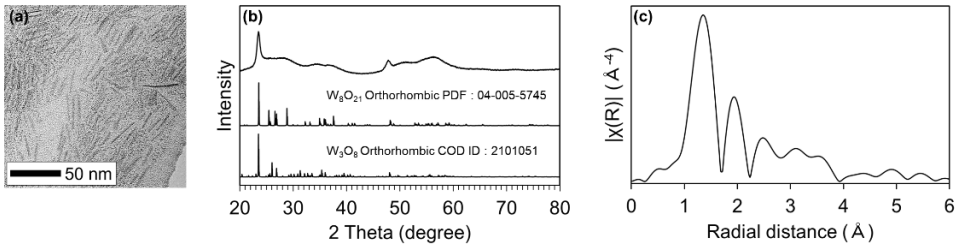

Figure 1. (a) TEM image, (b) XRD pattern and (c) Radial distribution function of WO_{3-x} nanoparticles.

1) H. Zheng *et al*., *Adv. Funct. Mater*. **2011**, *21*, 2175.

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DNA 高分子ブラシを利用した pH 依存的な金ナノロッド配向変化

(北大院生命科学[1]・北大電子研[2]・北大 GI-CoRE[3]・産総研[4])
○関澤 祐侑[1]・三友 秀之[2,3]・中村 聡[4]・与那嶺 雄介[2,3]・居城 邦治[2,3]

pH-dependent gold nanorod orientation change using a DNA polymer brush

([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*, [4]*National Institute of Advanced Industrial Science and Technology (AIST)*) ○Yu Sekizawa[1], Hideyuki Mitomo[2,3], Satoshi Nakamura[4], Yusuke Yonamine[2,3], and Kuniharu Ijiro[2,3]

Gold nanorods (GNRs) have strong plasmonic absorption in the near-infrared region, and this absorption significantly depends on the angle toward incident lights. Therefore, the orientation control of GNRs is important. In our previous work, we have established a method for vertical attachment of cationic GNRs with immobilized DNA on substrates as templates (DNA polymer brushes). In addition, when the surface charge of GNRs was changed by surface modification, the GNR orientation varied depending on the interaction strength between DNA and GNRs [1]. Thus, in this study, we investigated the change in orientation of attached GNRs by pH, which enables to change the amount of GNR surface charge. The orientational state was evaluated with extinction spectra. As a result, we found that the GNRs were vertically oriented in a neutral environment, while the GNRs were notably inclined in an acidic condition. These phenomena occurred reversibly. Moreover, in the pH range from 4.0 to 7.6, the GNR orientation changed gradually in response to the pH [2].

Keywords ：Gold nanorod; DNA; surface plasmon resonance; polymer brush; orientation control

金ナノロッド(GNR) は、表面プラズモン共鳴により近赤外領域に強い光の吸収を持ち、この光の吸収強度は入射光に対する角度に強く依存するため、GNR の配向制御は重要である。我々はこれまでに、基板上に DNA 高分子ブラシを作製し、表面修飾を施して正に帯電させた GNR を DNA 高分子ブラシに沿って垂直に吸着させる方法を確立した[1)]。また、表面修飾により GNR の電荷量を変えると、DNA-GNR 間の相互作用強度が変化し、異なる配向状態で GNR が DNA に吸着することが判明した。

本研究では、GNR 表面を pH 応答性分子で修飾し、DNA-GNR 間の相互作用強度を pH で調整することにより、吸着した GNR の配向を動的に変えることを試みた。基板上の GNR の配向状態は消光スペクトルで評価した。その結果、吸着した GNR は中性環境下(pH 7.6)において垂直に配向した一方で、酸性領域(pH 4.0)においては GNR が大幅に傾斜することが判明した。この現象は可逆的に発生した。また、pH 4.0～7.6 の範囲において、pH の環境変化に応答して GNR の傾斜状態が段階的に変化することが判明した[2)]。

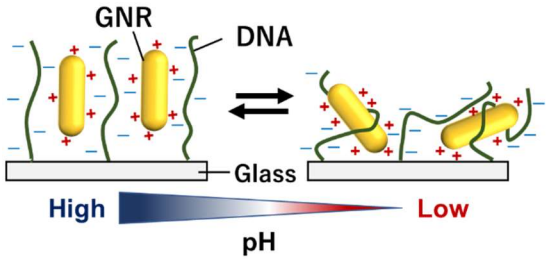

Fig. Schematic illustration of GNR orientational change on a DNA polymer brush

1) S. Nakamura, *et al,* ACS Omega, **2**, 2208 (2017)
2) Y. Sekizawa, *et al,* Nanoscale Adv. **2,** 3798 (2020)

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Synthesis and Properties of Au_{25} cluster protected by semi-fluorinated ligand

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Keywords: Cluster; Amphiphilicity; Self-assembly

Gold clusters are of considerable interests because of their unique structural characteristics and optical properties. However, it is challenging for them to self-assemble into highly ordered structures due to the large surface energy and rather weak interaction between such clusters.[1,2] The use of capping ligands with amphiphilic properties is a promising approach to guide the self-assembly of gold clusters. It has been reported that an introduction of a semi-fluorinated ligand (SFL) to 5 nm gold nanoparticles allows the formation of small vesicles with ~60 nm in diameter,[3] owing to both solvophilic oligo ethylene glycol unit and solvophobic fluorinated tetraethylene glycol segment of SFL (Figure 1a). However, there were few reports on such well-defined nanostructures composed of ~1 nm gold clusters. Thus, in this work, we utilized the SFL as capping agent to promote Au_{25} cluster assembly.

We prepared a Au_{25} cluster protected by the SFL (Figure 1b) in tetrahydrofuran. The cluster was characterized by using ultraviolet-visible (UV-vis) absorption spectroscopy and dynamic light scattering (DLS). The UV-vis spectrum with identical absorption peak at around 675 nm indicated the presence of the SFL-protected Au_{25} cluster. The DLS analysis suggested the formation of a cluster assembly in solution. We also investigated the effect of the ligand's fluorinated unit.

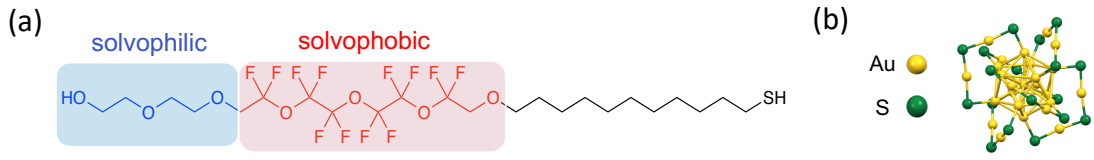

Figure 1. Structures of (a) SFL and (b) $Au_{25}(SR)_{18}$ (Moieties of R segment are omitted).

1) R. Buonsanti *et al*., *Nat. Commun*. **2018**, *9*, 3117. 2) Z.-Y. Lu *et al*., *Angew. Chem., Int. Ed.* **2013**, *52*, 9952. 3) K. Ijiro *et al*., *J. Am. Chem. Soc*. **2012**, *134*, 7632.

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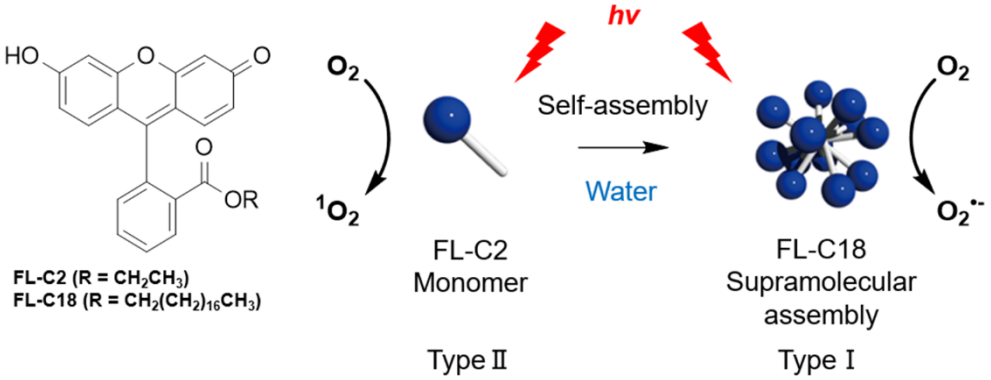
フルオレセイン誘導体の自己集合による光触媒活性制御

（阪大院工）○小林　真和・爲本　智恵・谷　陽平・重光　孟・木田　敏之
Control of Photocatalytic Activity by Self-Assembly of Fluorescein Derivatives (*Graduate School of Engineering, Osaka University*) ○Masakazu Kobayashi, Tomoe Tamemoto, Youhei Tani, Hajime Shigemitsu, Toshiyuki Kida

Reactive oxygen species (ROS) are useful oxidants for organic reactions and photodynamic therapy (PDT). ROSs produced by photocatalysts include free radical species ($O_2^{\cdot -}$) and singlet oxygen ($^1O_2$) via electron transfer (type I) and energy transfer (type II) processes, respectively. In particular, type I photocatalysts have attracted much attention due to the feasibility of non-oxygen-independent PDT. However, most molecular photocatalysts are type II. In this study, we found that a type II fluorescein photocatalyst changes to type I by self-assembly. In this presentation, the self-assembling property and photocatalytic activity of the fluorescein derivatives will be described. In addition, the mechanism of ROS generation by their supramolecular assembly will be discussed.
Keywords : Supramolecular assembly; Self-assembly; Photocatalyst; Fluorescein; Reactive oxygen species

光触媒と酸素の反応によって生成する活性酸素（ROS）は、酸化反応や光線力学療法（PDT）などに有用である。光触媒によって生じる ROS には、電子移動（Type I）によって生じるスーパーオキシド（$O_2^{\cdot -}$）やエネルギー移動（Type II）によって生じる一重項酸素（$^1O_2$）などがある。Type I の光触媒は酸素だけではなく、様々な基質と反応してラジカルを発生させ、酸素濃度に依存しない PDT を実現可能とするために注目を集めている。しかしながら、多くの分子光触媒は Type II であり、Type I の光触媒を創出するための戦略が求められている。本研究では、Type II の光触媒であるフルオレセイン誘導体が、自己集合することで Type I に変化することを見出した。本発表では、それらの自己集合特性、光触媒活性および ROS 発生のメカニズムについて議論する。



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ペロブスカイトナノ結晶の 1 次元配列制御

（関西学院大理工）○中務 加奈子・山内 光陽・増尾 貞弘

Control over One-Dimensional Arrangements of Perovskite Nanocrystals

(*Kwansei Gakuin University*) ○Kanako Nakatsukasa, Mitsuaki Yamauchi, Sadahiro Masuo

Perovskite nanocrystals (PNCs) have been actively researched due to their outstanding emission properties in dispersed conditions. On the other hand, the physical properties derived from their aggregate structures have not been revealed because the formation of PNC aggregates is quite difficult. Recently, we have succeeded in the supramolecular structures consisting of semiconductor nanocrystals and self-assembling organic molecules[1,2]. In this work, we synthesized $CsPbBr_3$ PNCs and a cholesterol derivative (Chol-COOH) which have an adhesion moiety onto the PNC surface and hydrogen bond sites (Fig. 1a). Thereafter, we attempted the one-dimensional arrangements of PNCs by using self-assembly of Chol-COOH. The transmission electron microscopic observation revealed the formation of unique aggregates with arranged PNCs in toluene/cyclohexane (1:9, v/v) (Fig. 1b). This result indicates that PNCs absorb along the one-dimensional aggregates of Chol-COOH.

Keywords : Perovskite Nanocrystals; Nanofiber; One-Dimensional Arrangements; Cholesterol; Self-Assembly

ペロブスカイトナノ結晶(PNC)は，分散状態で優れた発光特性を示すことから近年盛んに研究されている。一方，PNC を溶液中で自己集合させることは難しく，集合構造由来の物性は殆ど明らかになっていない。当研究室では最近，有機分子の自己集合を用いることで半導体ナノ結晶が配列した超分子集合体の構築に成功した [1,2]。本研究では，$CsPbBr_3$ PNC，および PNC への吸着部位と水素結合部位を持つコレステロール誘導体(Chol-COOH, Fig. 1a)を合成し，Chol-COOH の自己集合を用いて PNC の 1 次元配列を試みた。透過電子顕微鏡 (TEM) により，配列した PNC の集合体が観測され，Chol-COOH の 1 次元集合体に沿って PNC が吸着し配列していることが示唆された(Fig. 1b)。

(a) (b)

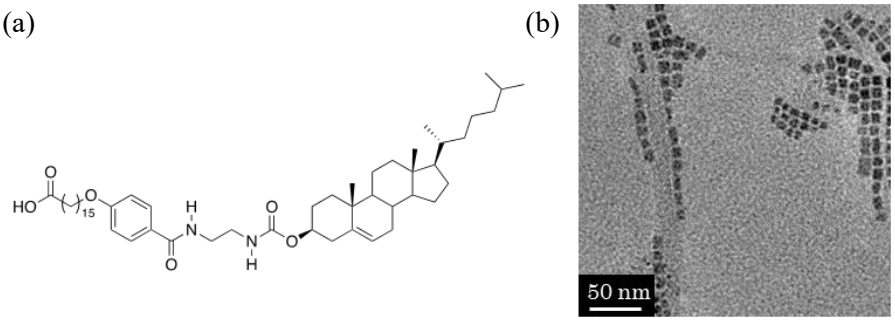

Fig. 1. (a) Chemical structure of Chol-COOH. (b) TEM image of PNCs and Chol-COOH mixture.

1) M. Yamauchi, S. Masuo, *Chem. Eur. J.* **2019**, *25*, 167-172.
2) M. Yamauchi, S. Yamamoto, S. Masuo, *Angew. Chem. Int. Ed.* **2021**, in press.

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ペリレンビスイミドとペロブスカイトナノ結晶からなるハイブリッド超分子構造の構築

（関西学院大院理工）○久保 直輝・山内 光陽・増尾 貞弘

Construction of Hybrid Supramolecular Structures Using a Perylene Bisimide Derivative and a Perovskite Nanocrystal (*Kwansei Gakuin University*) ○Naoki Kubo, Mitsuaki Yamauchi, Sadahiro Masuo

Perovskite nanocrystals (NCs) have been studied widely in dispersed conditions due to their outstanding emission properties, such as high emission quantum yields. However, the photophysical properties of the NCs in aggregated conditions have not been revealed because of their high stability in dispersed condition. Recently, we discovered that supramolecular structures having arranged nanocrystals were formed by mixing self-assembling organic molecules and semiconductor nanocrystals[1,2]. Herein, we attempted constructing organic-inorganic hybrid supramolecular structures having the arranged structure of NCs by mixing the perylene bisimide (PBI) and the NC. In the hybrid structure, the emission intensity of the NC decreased, suggesting the occurrence of energy transfer from the NC to the PBI aggregate. Furthermore, we succeeded in controlling the supramolecular structures by tuning the size of the PBI aggregates.

Keywords : Perovskite Nanocrystal; Perylene Bisimide; Self-assembly; Organic-inorganic Hybrid; Supramolecular Structure

ペロブスカイトナノ結晶（NC）は高い発光量子収率を示す優れた発光材料であり，分散状態で盛んに研究されている。しかし，分散状態での安定性が高いため，集合した NC の光物性は明らかになっていない。当研究室では，自己集合性を持つ有機分子と半導体ナノ結晶を混合することで，ナノ結晶配列構造を有する超分子集合体の構築手法を確立してきた[1,2]。本研究では，ペリレンビスイミドの集合体（PBI, Fig. 1）と NC を混合することで，NC の配列構造をもつ有機-無機ハイブリッド超分子構造の構築を試みた。PBI-NC 混合溶液の発光スペクトルより，NC から PBI 集合体へのエネルギー移動による NC の消光が観測された。さらに，混合する PBI 集合体の大きさを制御することで，得られる超分子構造が変化することを見出した。

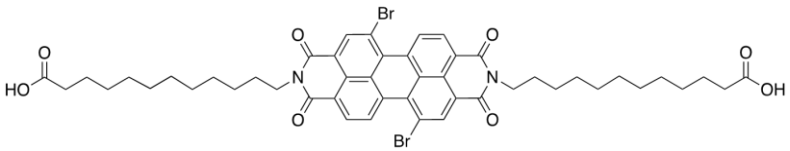

Fig.1 Structure of PBI.

1) M. Yamauchi, S. Masuo, *Chem. Eur. J*. **2019**, *25*, 167-172.
2) M. Yamauchi, S. Yamamoto, S. Masuo, *Angew. Chem. Int. Ed.* **2021**, in press.

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ナフタレン連結アゾベンゼン誘導体における結晶化誘起発光の光制御

（関西学院大院理工）○岡治 美穂・山内 光陽・増尾 貞弘

Photocontrol of Crystallization-Induced Emission in Naphthalene-Functionalized Azobenzene Derivatives (*Kwansei Gakuin University*) ○Miho Okaji, Mitsuaki Yamauchi, Sadahiro Masuo

Azobenzene which possesses light-switchable functions has been widely studied as an important organic molecule to create stimulus responsive materials[1]. On the other hand, excited energy of azobenzene is consumed by photoisomerization, so that azobenzene generally does not show emission. Recently, we found that a pyrene-functionalized azobenzene derivative, in which the pyrene moiety can induce strong assembly, showed crystallization-induced emission (CIE)[2]. In this study, we synthesized a naphthalene-functionalized azobenzene derivative **1**, in which the naphthalene moiety is expected to be relatively weak assembly, and evaluated the photo-responsively in the crystalline state. As a result, the emission spectra indicated that **1** also can show the CIE. In addition, we found that the emission characteristics was changed by photoisomerization of azobenzene moiety.

Keyword: Crystallization-induced Emission; Photoisomerization; Azobenzene; Naphthalene; Stimulus Responsive Materials

光スイッチ機能を備えたアゾベンゼンは, 刺激応答性材料を開発するための重要な有機分子として広く利用されている[1]。一方で，光励起されたエネルギーのほとんどが光異性化反応に消費されるため, 発光しにくいことが知られている。当研究室では, 集合性の高いピレンが連結されたアゾベンゼン誘導体を結晶化させることで, 結晶化誘起発光を示すことを報告した[2]。本研究では, 比較的集合性の低いナフタレンを連結させたアゾベンゼン誘導体 **1**（図 1, a ）を合成し，結晶状態における光応答性を評価した。発光スペクトル測定により，**1** は結晶化誘起発光を示すことが分かり，さらにその結晶に 405 nm レーザー光を照射することで光異性化が生じ，発光波長が短波長シフトすることが明らかになった。（図 1, b ）

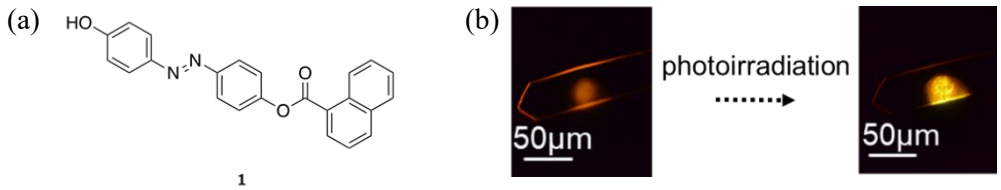

Fig.1 (a) Molecular structure of azobenzene derivatives. (b) PL images of the micro-crystal of **1** under an optical microscopy.

1) H.M. Dhammika Bandara and Shawn C. Burdette. *Chem. Soc. Rev*., **2012**, *41*, 1809-1825.
2) Mitsuaki Yamauchi, Kosuke Yokoyama, Naoki Aratani, Hiroko Yamada, and Sadahiro Masuo. *Angew. Chem. Int. Ed.* **2019**, *58*, 14173-14178.

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水素結合を利用したアゾベンゼンシス体の準安定化

（関西学院大理工）○喜田 恵利花・山内 光陽・増尾 貞弘

Metastabilization of *cis*-Azobenzene Using Hydrogen Bonds

(*Kwansei Gakuin University*)○Erika Kida, Mitsuaki Yamauchi, Sadahiro Masuo

Azobenzene is photoisomerized upon the irradiation of UV and visible light[1]. Generally, *cis*-azobenzene is thermally unstable than *trans*-azobenzene, so that the stabilization of *cis*-azobenzene is quite difficult. In this work, we synthesized an azobenzene derivative **1** with hydrogen bond moieties, and attempted the metastabilization of *cis*-isomers by controlling intramolecular hydrogen bonds.

When **1** in the $CHCl_3$ was irradiated with 365 nm UV lamp, the photoisomerization from *trans*-isomers to *cis*-isomers occurred. After the photoirradiation for 5 seconds, **1** reached the photostationary state. Afterword, we considered the thermal isomerization from *cis*-isomers to *trans*-isomers and investigated the formation of hydrogen bonds by NMR measurements.

Keywords : Azobenzene; Photoisomerization; Metastabilization; Hydrogen Bond

アゾベンゼンは，紫外光・可視光の照射によりトランス体―シス体間で光異性化することが知られている[1]。一般的にシス体は，熱的に不安定であるため自発的にトランス体へ熱異性化することから，シス体を安定化させることは困難である。本研究では，水素結合部位を持つアゾベンゼン誘導体 **1**（Fig. 1）を合成し，分子内水素結合を制御することでシス体の準安定化を試みた。

吸収スペクトル測定により，**1** の $CHCl_3$ 溶液に UV ランプ（365nm）を照射するとトランス体からシス体になり，およそ 5 秒の照射で光定常状態に達することがわかった。その後，暗室でシス体からトランス体への熱異性化について検討した。さらに，NMR 測定により **1** の水素結合の形成を評価したので詳細に報告する。

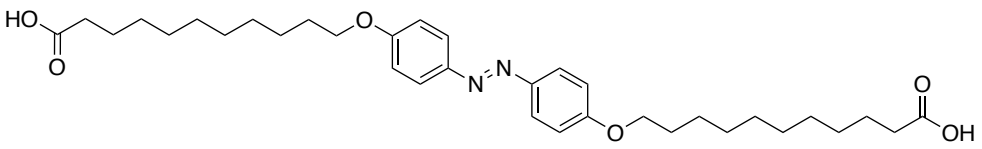

Fig.1 Molecular structure of **1**.

1) S. C. Burdette, H. M. D. Bandara, *Chem. Soc. Rev.* **2012**, *41*, 1809–1825.

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タウルコール酸混合ミセルの形状決定パラメータとは?

（摂南大薬）○相澤 秀樹 [1]

What is suitable parameter to determine shape of taurocholic acid-based mixed micelles, *i.e.*, a bile salt -based mixed micelles? (*Faculty of Pharmaceutical Sciences, Setsunan University*) ○ Hideki Aizawa

In the aqueous environment of the digestive tract, bile salt-based mixed micelles formed by aggregating bile salts, cholesterols, lysophosphatidylcholines, monoacylglycerols, lipophilic components of food and drug. The lipophilic components are absorbed from the inner micelle into the epithelial cells of the small intestine. Because the micelles form different shapes and sizes micelles, for example, spherical, ellipsoidal, cylindrical micelles, the micelle shape should affect the intestinal absorption of the lipophilic component. Combinations of individual components for the micelle are countless. If we find parameter that indicate what shape of the micelle is, the parameter is useful for future studies. We determined shapes of mixed micelles of taurocholic acid (TA, *i.e.*, a bile salt), 1-oleoyl-*rac*-glycerol (MG, *i.e.*, a monoacylglycerol), oleic acid (OLA, *i.e.*, a fatty acid), and either 1-palmitoyl-*sn*-glycero-3-phosphocholine (MPPC; *i.e.*, a lysophospholipid, an LPC) or 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC; *i.e.*, a phospholipid, a PC) (*i.e.*, mixed micelles of bile salt, monoacylglycerol, fatty acid, and either an LPC or a PC) with various molar ratio of the micelle components by small angle X-ray scattering. The micelle shape changed from core-shell spherical micelles to core–shell cylindrical micelles to core–shell cylindrical micelles with increasing sum of the molar ratio of lipophilic components (MG, OLA, and either MPPC or POPC) to the molar ratio of the TA component of 60.1 (SRLtoRT). The finding indicated that SRLtoRT is useful for parameter to determine micelle shape.

Keywords : Taurocholic acid-based mixed micelles; Micelle shape

消化管中で胆汁酸混合ミセル（以降、単に「ミセル」とする。）は、胆汁酸、コレステロール、リン脂質、モノアシルグリセロール、脂溶性の食品・薬成分、その他の成分が会合してできる。脂溶性の食品・薬成分（以降、単に「脂溶性成分」とする。）はミセルの中から小腸へ吸収される。ミセルは、球状、楕円体状、円柱状のミセルになるので、ミセルの形状が脂溶性成分の吸収に影響をあたえるはずである。しかし、ミセル成分の組成の組み合わせが無数にあるので、何の形かを示すパラメータを発見できれば、そのパラメータは今後の研究の展開に役に立つはずである。そこで我々は、タウルコール酸 (TA, *i.e.*,胆汁酸), 1-オレオイル-*rac*-グリセリン (MG, *i.e.*,モノアシルグリセロール), オレイン酸 (OLA, *i.e.*,脂肪酸), そして 1-パルミトイル-*sn*-グリセロ-3-ホスホコリン(MPPC; *i.e.*,リゾリン脂質; an LPC) もしくは 1-パルミトイル-2-オレイル-*sn*-グリセロ-3-ホスホコリン (POPC; *i.e.*, リン脂質; a PC) (*i.e.*, 胆汁酸混合ミセル)の混合モル比率を変化させたミセルの形を小角 X 線散乱で求めた。その結果、タウルコール酸のモル比を 60.1 とした疎水性成分（MG、OLA、そして MPPC もしくは POPC のいずれか）のモル比の総和(SRLtoRT)が増加していくにつれて、二重層球状ミセル、二重層回転楕円体状ミセル、二重層円柱状ミセルに変化していった。この発見は SRLtoRT がミセルの形状を示すパラメータとして役立つことがわかった。

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臭化テトラデシルキノリニウムと臭化テトラデシルイソキノリニウムのミセル形成

（東海大理）迫田 玲奈・○藤尾 克彦
Micellization of tetradecylquinolinium and tetradecylisoquinolinium bromides (*School of Science, Tokai University*) Reina Sakota, ○Katsuhiko Fujio

We synthesized two cationic surfactants having these isomers as head group, tetradecylquinolinium and tetradecylisoquinolinium bromides (TQB and TiQB; **Fig.1**), and compared thermodynamic quantities of micellization calculated from temperature dependences of critical micelle concentration and degree of counterion binding which were obtained from electrical conductivity measurements, in order to investigate an isomer effect on their aggregation behaviors. As a result, it was found that the estimated Gibbs energies ΔG, enthalpies ΔH, and entropies ΔS of micellization of TQB and TiQB were almost same but the temperature at which entropy-driven micellization changes into enthalpy-driven (intersection between $-T\Delta S$ and ΔH lines in **Fig. 2**) of TQB was ca. 5 K higher than TiQB.
Keywords : Isomer Effect; Alkylquinolinium Micelle; Alkylisoquinolinium Micelle; Thermodynamic Quantity of Micellization; Electrical Conductivity

キノリン及びイソキノリンを親水基とする陽イオン性界面活性剤である臭化テトラデシルキノリニウム（TQB）と臭化テトラデシルイソキノリニウム（TiQB）（**Fig. 1**）を合成し、それらのミセル形成に対する異性体効果を調べるために、電気伝導率測定により求めた臨界ミセル濃度と対イオン結合度の温度依存性からミセル形成の熱力学量を見積もり比較した。

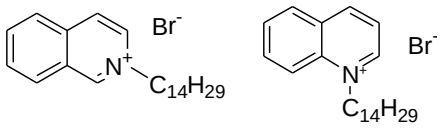

Fig. 1:TQB (left) and TiQB (right).

電気伝導率測定は、電気伝導率計（東亜ディケーケー株式会社 CM-30R）を用い、TQB は 20, 25, 30, 35, 40±0.1℃、TiQB は 25, 30, 35, 40, 45 ±0.1℃において行った。

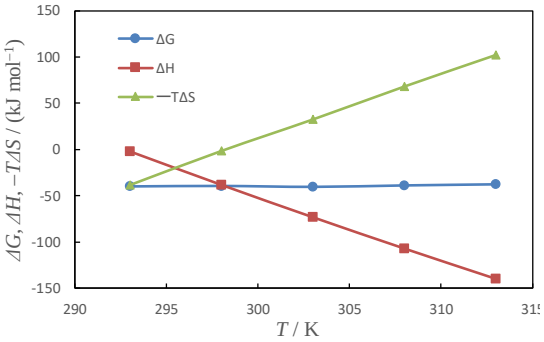

Fig. 2:Thermodynamic quantities of micellization of TQB.

得られた TQB と TiQB のミセル形成のギブズエネルギーΔG、エンタルピーΔH、エントロピーΔS には大きな違いは見られなかったが、ミセル形成がエントロピー駆動からエンタルピー駆動に切り替わる温度（**Fig. 2** における $-T\Delta S$ と ΔH の交点の温度）は TQB のほうが 5 K ほど高いことが分かった。

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両親媒性アゾトラン液晶のミセル形成と光応答挙動

（東京工科大学工）○玉井 杏奈・小林 亜由美・入谷 康平・山下 俊
Micelle Formation and Photo-Responsive Behavior of an Amphiphilic Azotolan Liquid Crystal (*Tokyo University of Technology*)○Anna Tamai, Ayumi Kobayashi, Kohei Iritani, Takashi Yamashita

Previously, we succeeded in macroscopically change of nano-sized phase separation structures by utilizing the photoisomerization of an azobenzene derivative[1]. The purpose of this study is to control fluorescent behavior of micelles formed by an amphipathic molecule having an azobenzene unit due to structural change of micelles by photoirradiation. Therefore, an azotran derivative **1** bearing the azobenzene unit and an ethylene glycol unit as a hydrophilic group was designed and synthesized (Figure 1). Compound **1** was found to exhibit a multiple phase from DSC measurement. Moreover, absorption at 365 nm decreased with photoirradiation, indicating the photoisomerization of trans-form to cis-form of **1** (Figure 2a). In addition, micelles were formed by a Bangham method, and their optical properties were investigated. Figure 2b shows fluorescence spectra of micelles with photoirradiation. It was revealed that emissions at 400 nm decreased probably because of collapse of micelles.
Keywords : Stimulus Responsiveness; Photoisomerization; Micelle; Azotran; Amphiphilic Molecules

本研究室では、アゾベンゼンの光異性化を利用して、ナノサイズの相分離構造を巨視的に変化させる事に成功している[1]。今回我々は、アゾベンゼンを含む両親媒性分子をミセル化し、光照射によるミセルの構造を制御することを研究の目的とした。そのため、光異性化部位と親水基を含むアゾトラン誘導体 **1** を設計し、合成した (Figure 1)。DSC 測定により、化合物 **1** は複数の相をもつ事がわかった。さらに、溶液中において高圧水銀灯を用いて 365 nm の光を照射すると、照射時間に依存して吸収が減少したことから (Figure 2a)、化合物 **1** はトランス体からシス体に光異性化したと考えた。次にクロロホルムを溶媒として用いてバンガム法によりミセル化し、蛍光測定により光物性を測定した (Figure 2b)。高圧水銀灯を用いて光照射すると、照射時間が長くなると 400 nm における発光が低下した。また、光照射前後における粒子径測定により、ミセルが崩壊していることが示された。

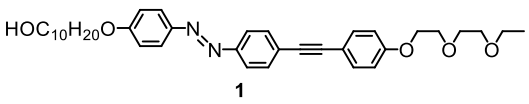

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Figure 1. Chemical structure of **1**.

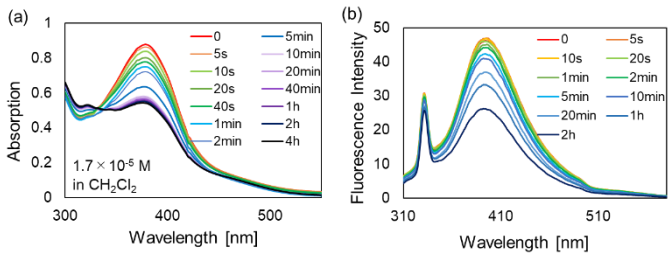

Figure 2. (a) Absorption spectra of **1** and (b) fluorescence spectra excited at 365 nm of micelles formed by **1** with photoirradiation.

[1] K. Okano, Y. Mikami, T. Yamashita, *Adv. Funtut. Mater.* **2009**, *19*, 3804.

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気—水界面において特異な集合構造を形成するπ-ゲル化剤薄膜の分子配向解析

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Molecular Orientation Analysis in a Thin Film of a π-Gelator Forming a Unique Aggregate at Air−Water Interface ([1]*Institute for Chemical Research, Kyoto University*, [2]*CSIR-National Institute for Interdisciplinary Science and Technology,* [3]*The Institute for Solid State Physics, the University of Tokyo,* [4]*Graduate School of Frontier Sciences, the University of Tokyo,* [4]*National Institute for Materials Science*) ○ Yuta Yamaguchi,[1] Takafumi Shimoaka,[1] Nobutaka Shioya,[1] Ayyappanpillai Ajayaghosh,[2] Taizo Mori,[3,5] Katsuhiko Ariga,[4,5] Takeshi Hasegawa[1]

Molecular aggregation and orientation are key parameters for explaining material properties. For example, one of the π-gelators derived from oligo(*p*-phenylene vinylene) OPV-**1** (Figure 1) is known to form two different aggregates: a fiber and a one-dimensional (1-D) nanorod, which show totally different properties in terms of local photo-excited transport. The 1-D rod can be prepared at the air-water interface using the Langmuir-Blodgett technique. Although the formation of the 1-D rod has already been investigated by AFM and fluorescence on a substrate, the aggregation process and molecular orientation change at the air−water interface are not revealed. In the present study, a Langmuir film of OPV-**1** is studied by using infrared external reflection (IR ER) spectroscopy, which reveals that molecules are oriented in a face-on manner at the air−water interface.

Keywords: Langmuir Film; Langmuir-Blodgett Film; External Reflection; pMAIRS

分子集合系が示す性質の理解には、分子配向を含む集合構造の情報が必要である。oligo(*p*-phenylene vinylene)誘導体のひとつであり π-ゲル化剤として知られる OPV-**1**（図 1）は、異なる光励起過程を示すファイバー状と一次元ナノロッド状の 2 種類の集合構造を作り分けることができる。このうち一次元ナノロッドは、気—水界面における分子集合によって作ることができる[1)]。このロッドの形状や分子配向は固体基板に転写した試料の AFM 測定や蛍光測定によって調べられているが、気—水界面における分子論的な集合構造はわかっていない。

本研究では、OPV-**1** が気—水界面で形成する分子薄膜を赤外外部反射（IR ER）分光法によって調べた。得られたスペクトルのピーク強度と ER 法の表面選択律の関係から、OPV-**1** 分子は気—水界面において、共役環と気—水界面とが平行に近い face-on 配向であることがわかった。アルキル鎖は all-trans zigzag 構造が支配的であり、その炭素骨格平面も気—水界面と平行に近い face-on 配向であることがわかった。

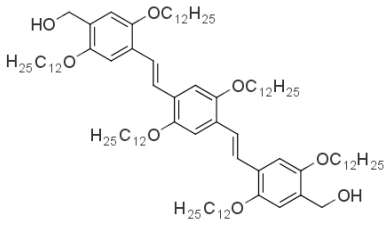

図 1. OPV-**1** の構造式

1) K. Sakakibara et al. *J. Am. Chem. Soc.* **2014**, *136*, 8548.

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ゲスト応答的なゾル-ゲル相転移を利用したグリコサミノグリカンの識別

（崇城大院工[1]・ISIT[2]）○黒田尚史[1]・田丸 俊一[1]・新海征治[2]
Guest-responsive supramolecular hydrogel expressing selective sol–gel transition for sulfated glycosaminoglycans（[1]Graduate School of Engineering, Sojo University, [2]ISIT）○Naofumi Kuroda,[1] Shun-ichi Tamaru,[1] Seiji Shinkai[2]

Here, we discuss about the stimuli-responsive hydrogel constructed by the bola-type amphiphiles composed of two dipeptides containing phenylalanine attached to the ends of a hydrophobic tetrathiophene. The hydrogel formation ability of the amphiphiles was affected by the *N*-terminal amino acid residue, which is an amphiphile possessing phenylalanine-lysine sequence that formed a hydrogel under limited pH conditions. The gel formation occurred because of the phase transition of the gelator assembly from a granular aggregate to a fibrous architecture triggered by the pH control. This stimuli-responsive sol–gel transition was also accomplished by the addition of an anionic polymer, and the discrimination of sulfated glycosaminoglycans was successfully achieved using the hydrogel system.
Keywords：Supramolecular chemistry, hydrogel, molecular recognition, glycosaminoglycans, Phase transition

π 共役系骨格とペプチド構造からなる一連の双頭型界面活性剤を合成し、そのゲル化能を評価した結果、カチオン性ジペプチドを有するテトラチオフェン誘導体が、ヒドロゲルを形成することを見出した。さらに、この超分子ヒドロゲル系において高分子・超分子複合体形成を活用することで、硫酸化グリコサミノグリカン類の識別に成功した。

ジペプチド配列としてフェニルアラニン-リジンを有する **Th4-FK** (**Figure 1**)は、pH 9.5-10.5 という限られた条件でのみ超分子ヒドロゲルを形成した。これは、**Th4-FK** が、この pH 領域で繊維状会合体を形成し 3 次元ネットワーク化できるのに対して、より酸性の pH 条件では顆粒状の会合体を形成し、沈殿するためであった。そこで、**Th4-FK** がゲルを形成しない pH 6.6 の条件で、種々のポリアニオン性高分子を添加したところ、硫酸化された多糖が添加されたときにおいてのみ、顆粒状会合体から繊維状会合体への相転移が発現し、その超分子繊維が 3 次元的ネットワークを構築することでヒドロゲルを形成する事が確認された。この現象を利用する事で、種々のアニオン性の多糖類の中から、硫酸化グリコサミノグルカン類を識別可能である事が示された。本系は、pH 条件とアニオン性多糖の種類の双方が満たされた場合にのみ駆動する and ゲート型の検出系であることから、高い選択性が実現したと考えられる。

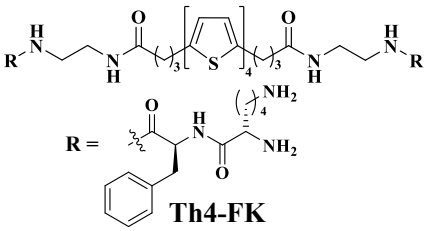

Figure 1. Structure of **Th4-FK**.

Figure 2. Gelation of the **Th4-FK** aqueous upon the addition of the guest polymers.

1) Naofumi Kuroda, Yukie Tounoue, Kouichiro Noguchi, Yutaro Shimasaki, Hitoshi Inokawa, Masayoshi Takano, Seiji Shinkai, Shun-ichi Tamaru, *Polym J.* **2020**, *52*, 939–946.

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自己修復性ソフトマテリアル開発を指向した超分子ヒドロゲルの物性制御

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Preparation and properties of supramolecular hydrogels for the development of self-healing soft materials ([1] *Department of Engineering, Sojo University*, [2] *Graduate School of Engineering, Sojo University,* [3]*ISIT*) ○ Yuki Edamoto,[1] Naofumi Kuroda,[2] Shun-ichi Tamaru,[1,2] Seiji Shinkai[3]

Since the driving force on the formation of supramolecular gel is intermolecular interaction between small molecules, the gelation is reversible and controllable by the external stimulus. On the bases of this reversible gelation properties, many supramolecular gels possessing unique properties were reported so far. In this study, bola-type amphiphiles possessing π-conjugated skeleton and peptide structure were synthesized. Among them, the amphiphiles possessing cationic dipeptide sequence formed hydrogel under the limited pH conditions, and the hydrogels showed the self-healing properties. In addition, it was suggested that the self-healing ability depends on the structure of π-conjugated skeleton.
Keywords : Supramolecular chemistry; Hydrogel; Self-assemble; Stimuli-responsiveness; Self-healing

自己修復能を持つ材料の開発は、持続的な社会の実現を目指す上でも重要な研究課題である。近年、分子間相互作用の可逆性を巧みに利用することで自己修復能を発現する機能材料の開発例が、盛んに報告されている。本研究は、分子間相互作用を駆動力として形成する超分子ヒドロゲルにおいて発現する自己修復能に関する化学の理解を深めるとともに、自己修復能の制御に関する知見を得ることを目標としている。

このために、π 共役系骨格の両末端にジペプチド構造を導入した一連のボラ型界面活性剤（**Figure. 1**）を合成し、これらのヒドロゲル形成能を評価した。その結果、**Th4-FK**, **OPV-FK** および **OPV-FY** が限られた pH 領域においてヒドロゲルを形成することが確認された。よって、本系においては、カチオン性の親水性ジペプチドがヒドロゲル形成能獲得に有利であることが示唆された。**Th4-FY** がヒドロゲル形成能を示さなかったことから、**OPV** 型の中心骨格がより適した構造であると考えられる。一方、これらのヒドロゲルの内、**Th4-FK**, **OPV-FK** ゲルのみが自己修復能を示した。さらに、**OPV-FK** ゲルがより短時間で自己修復することが確認されたことから、自己修復能の獲得においても **OPV** 型の中心骨格がより適した構造であると考えられる。

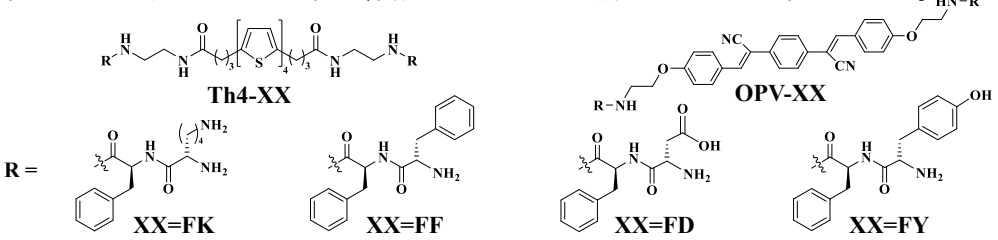

Figure 1. Structure of gelaters.

1) Naofumi Kuroda, Yukie Tounoue, Kouichiro Noguchi, Yutaro Shimasaki, Hitoshi Inokawa, Masayoshi Takano, Seiji Shinkai, Shun-ichi Tamaru, *Polym J.* **2020**, *52*, 939–946.

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金属カチオンに応答してゲル形成ならびに色調変化を示す超分子ヒドロゲルの開発

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Supramolecular hydrogel showing gelation and color change in response to metal cations

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Supramolecular hydrogel constructed through the self-assembly of amphiphiles (hydrogelator) *via* intermolecular interactions shows sharp responses to external stimuli. However, most of stimuli-responsive behaviors of these supramolecular hydrogels were limited to gel–sol transitions. We have succeeded in the development of supramolecular hydrogels exhibiting thermochromism along with a gel–sol transition.[1,2] We already reported that the *N*-alkyl-2-anilino-3-chloromaleimide (AAC) moiety introduced in hydrogelators as a chromophore could act as a probe to readout the self-assembly state through color change. Here, we report the hydrogelators showing gelation associated with color change in response to metal cations such as Mg^{2+} and Ca^{2+} (Fig. 1).

Keywords : Supramolecule; Hydrogel; Metal Cation; Chelation

超分子ヒドロゲルとは、両親媒性分子（ゲル化剤）が自己集合しネットワーク形成することで水を閉じ込めて形成するゲル状物質である。超分子ヒドロゲルは優れた外部刺激応答性を示すため、特定刺激を読み出すためのセンサ材料として有用である。しかしながら、その応答挙動はゲルーゾル相転移にほぼ限られている。そのような背景のなか、我々はゲル化剤分子中に会合状態に依存して吸収波長がシフトする環境応答性色素部位（AAC）を導入することでゲルーゾル相転移のみならず色調変化を示す超分子ヒドロゲルの開発に成功している[1,2]。本研究では、金属カチオン（Mg^{2+}, Ca^{2+}）に応答してゲル形成ならびに色調変化を示す新規ゲル化剤 **1**, **2** の開発に成功したのでその合成ならびに金属カチオン応答性について報告する（Fig. 1）。

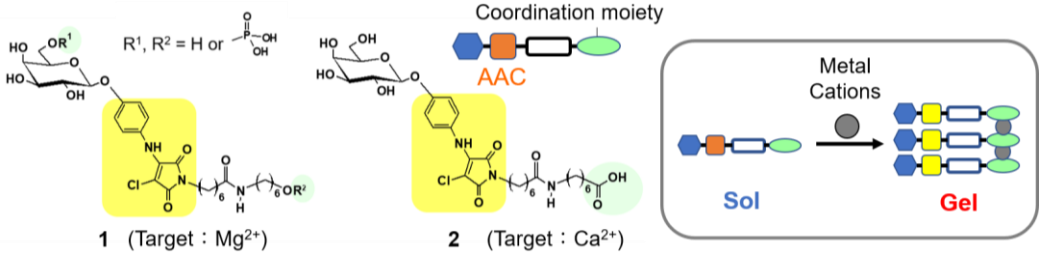

Figure 1. Chemical structures of hydrogelators and schematic representation.

1) R. Ochi, K. Kurotani, M. Ikeda, S. Kiyonaka, and I. Hamachi, *Chem. Commun*. **2013**, *49*, 2115.
2) R. Oosumi, M. Ikeda, A. Ito, M. Izumi, and R. Ochi, *Soft Matter.* **2020**, *16*, 7274.

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Evaluation of Magnetic Ionic Liquid Gel Properties Formed by Fluorine-Containing Low Molecular Weight Gelators Having Linear Alkyl Group at Terminal Position

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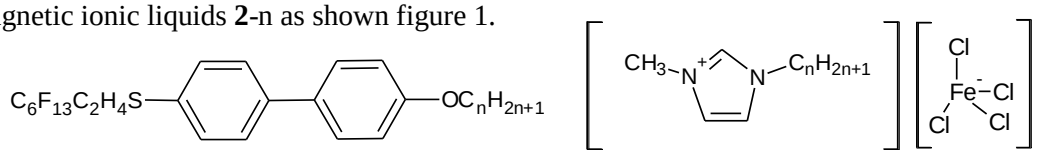
Keywords: Perfluoroalkyl Group; Linear Alkyl Group; Biphenyl Derivatives; Low Molecular Weight Gelators; Magnetic Ionic Liquid

In our previous work, it was found that some low molecular weight compounds having perfluoroalkyl group at terminal position were be able to gelate by dissolved and cooling. In this work, biphenyl derivatives having perfluoroalkyl and linear alkyl group at terminal positions were synthesized (compounds **1**-n) and also examined gelation ability in some magnetic ionic liquids **2**-n as shown figure 1.



Compounds **1**-n (n = 2, 4, 6, 8, 10) Ionic liquids **2**-n (n = 2, 4, 6, 8, 10)

Figure 1 Chemical structures of compounds **1**-n and ionic liquids **2**-n

In table 1, their gelation abilities examined in ionic liquid **2**-n and confirmed that magnetic ionic liquids were able to gelated by compounds **1**-n added in an amount of 1.0wt% or less.

Table 1 Critical gel concentration in ionic liquids **2**-n

Ionic liquids	Compounds (concentration/wt%)				
	1-2	**1**-4	**1**-6	**1**-8	**1**-10
2-2	G (0.6)	G (0.5)	G (0.8)	G (0.6)	G (0.6)
2-4	G (0.3)	G (0.2)	G (0.3)	G (0.4)	G (0.2)
2-6	G (0.3)	G (0.1)	G (0.2)	G (0.4)	G (0.3)
2-8	G (0.2)	G (0.1)	G (0.1)	G (0.6)	G (0.4)
2-10	G (0.6)	G (0.6)	G (0.4)	G (0.8)	G (0.5)

S = Sol, G = Gel, ( ) = wt%

In this presentation, sol-gel transition temperatures of magnetic ionic liquid gels will be reported. In addition, effect of gel properties by elongation of terminal alkyl chain of compounds **1**-n and ionic liquids **2**-n will be discussed.

Reference: M. Miura *et al*., *ECS Transactions*, **50**, 89 (2013)

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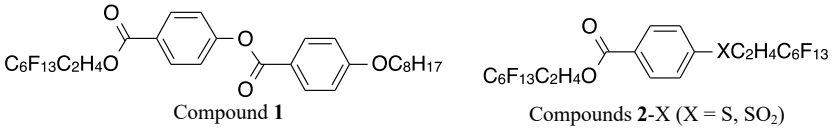
Electrochemical Properties of Ionic Liquid Gel Formed by Semi-perfluoroalkyl Benzoate Derivatives

([1] *Graduate School of Sciences and Technology for Innovation, Yamaguchi University*, [2] *Faculty of Engineering, Yamaguchi University*) ○Kenta Matsumoto[1], Yuki Morita[2], Hiroaki Okamoto[1]

Keywords: Perfluoroalkyl Group; Low Molecular Weight Organic Gelators; Semi-perfluoroalkyl Benzoate Derivatives; Synthesis; Ionic Liquid Gel Electrolyte

In our previous works, it was found that some low molecular weight compounds containing perfluoroalkyl group gelated various organic solvents and ionic liquids. While relationship between gelation mechanism and molecular structures was not elucidated.

In this study, compounds **1** and **2** (Fig. 1) were synthesized and examined gelation abilities in various organic solvents and ionic liquids. Furthermore, electrochemical properties of ionic liquid gels so that electrolyte solutions for Li-ion battery substituted to ionic liquid gel electrolytes formed by compounds **1** and **2**.



Compound **1** Compounds **2**-X (X = S, SO_2)

Fig. 1 Chemical structures of compounds **1** and **2**

Compounds **1** and **2**-SO_2 were able to gelate propylene carbonate (PC) and 1M $LiClO_4$ / PC in an amount of 2wt% or less. Furthermore, compound **2**-SO_2 was also able to gelate [EMIM][FSA] and 1 mol kg^{-1} LiFSA / [EMIM][FSA] in an amount of 3wt%. On the other hand, compound **2**-S was unable to gelate PC and [EMIM][FSA] with or without Li^+.

In addition, sol-gel transition temperature ($T_{gel\text{-}sol}$) of 5wt% gels with Li^+ were 20℃ higher than that of gels without Li^+ so that solubility decreased by solvation to Li^+ (Fig. 2).

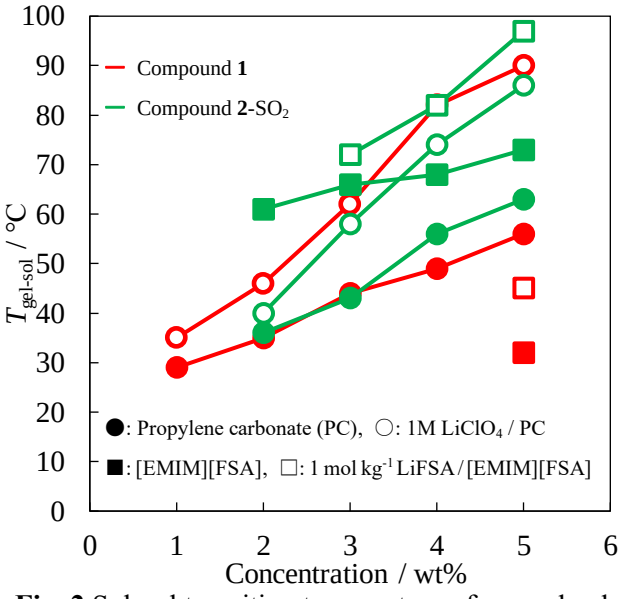


Fig. 2 Sol-gel transition temperature of several gels

In this presentation, electrochemical properties of 1 mol kg^{-1} LiFSA / [EMIM][FSA] gels formed by compounds **1** and **2** will be reported.

Ref: A. Ohashi *et. al.*, *Chem. Lett.*, **47**, 810 (2018), T. Sugimoto *et. al.*, *J .Power Sources*, **183**, 436 (2008).

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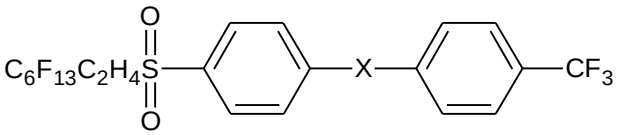
Gel Strength of Ionic Liquid Gels by Low Molecule Weight Gelator with Fluoro-substituent at Both Ends of Molecules

([1]*Graduate School of Sciences and Technology for Innovation, Yamaguchi University*, [2]*Faculty of Engineering, Yamaguchi University*) ○Koohei Nakamura,[1] Yuta Kanesige,[1] Yuki Morita,[2] Hiroaki Okamoto[1]

Keywords: Fluoroalkyl group; Low molecular weight gelator; Gel strength

In our previous works, it was found that low molecular weight compounds having fluoroalkyl group formed fibrous assembly, which formed gel with various organic solvents and ionic liquids[1)]. However, relationship between molecular structures and gelation ability has not been elucidated.

In this work, compounds **1** and **2** (Fig. 1) were synthesized and the gelation abilities and gel strength were examined in some organic solvents and ionic liquids.



Compound **1** X = COO
Compound **2** X = OCO

Fig. 1 Chemical structures of compounds **1** and **2**

Fig. 2 shows sol-gel transition temperatures of [BMIM][TFSA] gels formed by compound **1** or **2**. For compound **1**, the sol-gel transition temperature of 5wt% [BMIM][TFSA] gel was 108°C and that for compound **2** was 58°C.

In this presentation, sol-gel transition temperature and critical gel concentration will be reported. In addition, result of gel strength measurement of ionic liquid gels formed by compounds **1** and **2** will be discussed.

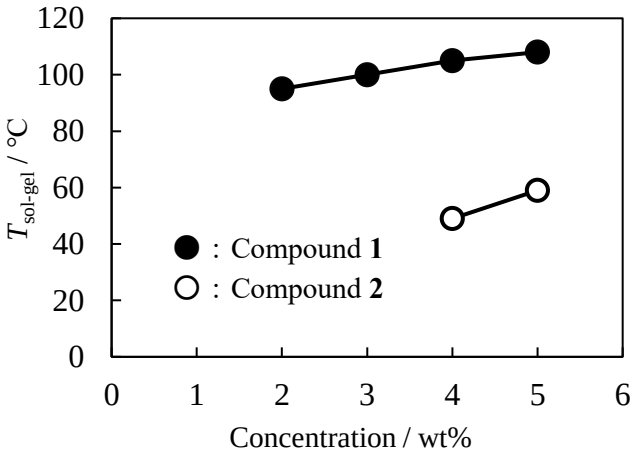


Fig. 2 Sol-gel transition temperatures of [BMIM][TFSA] gels

[Reference]

1) B. Cao, *et. al*., *Journal of Fluorine Chemistry*, ***226***, 109348 (2019).

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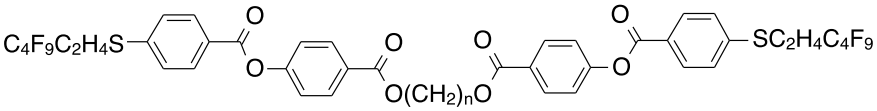
Gel Properties Formed by Dimer Type 4-Mercaptobenzoic acid Derivatives Having Perfluoroalkyl Group at Both Terminal Position

([1]*Faculty of Engineering, Yamaguchi University*, [2]*Graduate School of Sciences and Technology for Innovation, Yamaguchi University*) ○Sota Kanemitsu,[1] Ryoichiro Yoshihara,[2] Kotaro Kanetada,[2] Yuki Morita,[1] Hiroaki Okamoto[2]

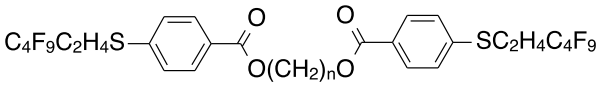
Keywords: Perfluoroalkyl group; Low molecular weight organic gelator; ionic liquid gel; synthesis

In our laboratory, it was found that low molecular weight compounds having a perfluoroalkyl group formed fibrous aggregates and gelate several organic solvents. However, the correlation between molecular structures of gelators and gelation ability has not been clarified.

In this work, dimeric 4-mercaptobenzoic acid derivatives (Fig. 1) were synthesized and evaluation gelation abilities.



Compounds **1**-n (n = 4, 10)



Compounds **2**-n (n = 4, 10)

Fig. 1 Chemical structures of compounds **1**-n and **2**-n

In Table 1, compounds **1**-10 and **2**-4 were able to gelate propylene carbonate (PC). On the other hands, compounds **1**-4 and **2**-10 were unable to gelate PC, acetonitrile, and dimethyl sulfoxide (DMSO).

Compounds **1**-10 was able to gelate 1-Butyl-3-methylimidazorium bis (trifluoromethanesulfonyl) amide ([BMIM][TFSA]). The sol-gel transition temperatures of 5wt% PC gels formed by compound **1**-10 and **2**-4 were 46℃ and 40℃, respectively.

Table 1 Critical gel concentration in each solvent

Solvents	Compounds (Concentration, wt%)			
	1-4	**1**-10	**2**-4	**2**-10
Acetonitrile	S (5.0)	S (5.0)	S (5.0)	S (5.0)
DMSO	S (5.0)	S (5.0)	G (2.0)	S (5.0)
PC	S (5.0)	G (2.0)	G (4.0)	S (5.0)

* S = Sol, G = Gel, ( ) = wt%, PC = Propylene carbonate, DMSO = Dimethyl sulfoxide

In this presentation, critical gel concentration evaluated by ionic liquids will be reported. In addition, thermal properties of gels formed by compounds **1**-n and **2**-n will be discussed.

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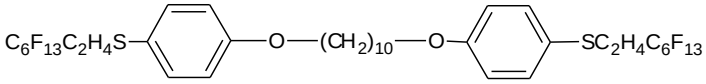
Electrochemical Properties of Gel Electrolyte for Li-ion Battery Formed by Fluorine-Containing Gemini-Type Low Molecular Gelators

([1]*Faculty of Engineering, Yamaguchi University*, [2]*Graduate School of Sciences and Technology of Innovation, Yamaguchi University*) ○Yui Endo[1], Tomohiro Yoshida[2], Morita Yuki[1], Hiroaki Okamoto[2]

Keywords：Perfluoroalkyl group; Gemini-Type Low Molecular Gelators; Li-ion Battery; Gel Electrolyte; Electrochemical Properties

In our previous research, it was found that low molecular compounds with perfluoroalkyl group could gelate several organic solvents.

In this study, gemini-type low molecular gelators having perfluoroalkyl group at both terminal positions were synthesized and evaluated the gelation properties.



Compound **1**

Fig. 1. Chemical structure for compound **1**.

The critical gel concentration and sol-gel transition temperature were measured in electrolyrte solutions **II** (1M LiFSA / EC:PC:DEC (2:1:7)) and **III** (3M LiFSA / EC:PC:DEC (2:1:7)). The sol-gel transition temperatures for the gel **I** 2wt% and gel **II** (2wt%) were 45℃ and 52℃, respectively.

Furthermore, the ionic conductivities of the gel electrolytes which added compound **1** an amount of 2wt% in the electronic solutions were measured by AC impedance measurement (Fig. 2.). In this presentation, comparison of the potential windows between neat electrolyte solutions and gel electrolytes will be reported.

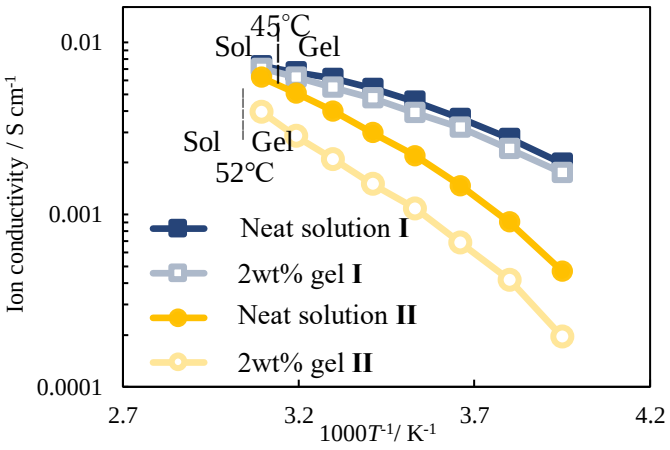


Fig.2. Temperature dependence of ionic conductivity

Ref: Tomohiro Yoshida *et. al*., *Bull. Chem. Soc. Jpn*. **88**, 1447 (2015).

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非平衡流動場が Aβ–脂質膜相互作用におよぼす影響の顕微鏡観察

（山形大院理工[1]・山形大理[2]）○安部 光洋[1]・飯田 茜[1]・並河 英紀[2]
Microscopic observation on the effect of non-equilibrium flow on Aβ-lipid membrane interaction ([1]*Graduate School of Sci. and Eng., Yamagata Univ*, [2]*Faculty of Science, Yamagata Univ.*) ○Mitsuhiro Abe,[1] Akane Iida,[1] Hideki Nabika[2]

Alzheimer's disease is accompanied by aggregation and accumulation of amyloid β (Aβ), whose molecular mechanism is important in the development of treatment and drug discovery. In previous studies, it has been studied in closed systems such as a petri dish where the monomer concentration decreases due to aggregation. However, since the brain is an open system with a continuous production of Aβ from precursor protein, the monomer concentration does not decrease by the aggregation. This inconsistency between in-vivo and in-vitro environments hinders the elucidation of the molecular mechanism. In this study, we conducted experiments in a microchannel where continuous Aβ inflow and outflow are possible. It was confirmed that a non-equilibrium flow played a major role in the formation and growth of Aβ aggregates (Fig. 1). Furthermore, it was suggested that a part of the lipid membrane formed a complex tissue with the aggregate, with thinning the lipid membrane. The results of this study are considered to be due to the combined effects of the open system on suppressing the decrease in monomer concentration, the toxic conformation of Aβ by media flow, and the promotion of nucleation and growth processes.
Keywords : Non-equilibrium Flow; Amyloid beta; Aggregation; Lipid Membrane

アルツハイマー病はアミロイドβタンパク (Aβ) の凝集・蓄積を伴い、その分子機構解明は治療・創薬開発において重要であるため多くの研究が進められている。しかしながら、その多くはシャーレなど閉鎖系にて行われており、反応時間とともに Aβ凝集・蓄積が平衡に達し見かけの反応が停止する。一方、実際の脳内では Aβ前駆体蛋白質から連続的に Aβモノマーが供給され、反応が進行しても Aβモノマー濃度が低下せず Aβ凝集・蓄積が進行し続ける非平衡開放系となっている。この in-vivo と in-vitro の乖離が分子機構解明の障害となっているため、本研究では、in-vivo に近い条件で実験を行うために、連続的な Aβの流入・流出が可能な非平衡開放系マイクロ流路での実験系を駆使し、人工膜上での Aβの凝集・線維化に対する影響を検討した。その結果、平衡閉鎖系では低面積な線維状凝集体のみ形成したのに対し、非平衡開放系では凝集体が大きく高面積化する様子が観察され、非平衡流動が Aβ凝集体の形成・成長を促進することが確認された (Fig. 1) 。さらに、脂質膜の一部が Aβ凝集体と複合的組織体を形成し、脂質膜が薄化する様子も観察された。本結果は、開放系によるモノマー濃度低下抑制効果に加え、媒体流動による Aβの毒性コンホマー化や核形成・成長過程の促進が複合的に影響を及ぼしたものであると考えられる。

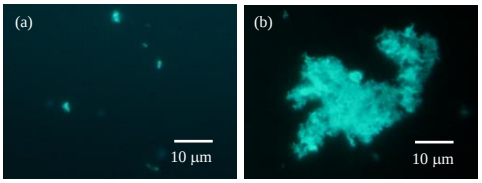

Fig. 1. (a) 平衡閉鎖系と (b) 非平衡開放系で観察された Aβ凝集体の蛍光顕微鏡画像.

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非平衡撹拌下のリポソーム分散液中の Aβ 凝集挙動の解明

（山形大理[1]・山形大院理工[2]）○佐藤 文哉[1]・飯田 茜[2]・安部 光洋[2]・並河 英紀[1]
Elucidation of Aβ aggregation behavior in liposome dispersion under non-equilibrium stirring
([1]*Faculty of Science of Yamagata Univ,* [2]*Graduate School of Sci. and Eng. Yamagata Univ.*)
○Fumiya Sato,[1] Akane Iida,[2] Mitsuhiro Abe,[2] Hideki Nabika[2]

Aggregation and accumulation of amyloid β (Aβ) in brain cells is known for the cause of Alzheimer's disease. In the brain, the interstitial fluid constantly flows to supply and remove Aβ under a non-equilibrium environment. Therefore, it is important to discuss the role of the non-equilibrium environment even for in vitro experiments. The present study provides insight into the molecular or thermodynamic effects of non-equilibrium open system on each elementary process of the Aβ aggregation. Aβ solution containing 5 μM Aβ and 50 μM thioflavin T (ThT) was prepared using 100 mM phosphate buffer and 100 mM sodium chloride solution. The solution was added to the wells and 6 μL of Aβ solution was injected every hour with stirring at 180 rpm. The injection was performed 24 times. As a result, it was confirmed that the increase in fluorescence intensity was faster when Aβ was added than when Aβ was not added. This suggests that the addition of Aβ may affect the Aβ aggregation behavior. In addition, it was observed that liposomes promoted Aβ aggregation by closed system experiments. Based on this result, we will consider the Aβ aggregation behavior in the presence of liposomes.
Keywords : Lipid Bilayer; Amyloid β; Non-equilibrium self-organization

アミロイドβ(Aβ)の脳細胞膜への凝集・蓄積はアルツハイマー病の原因として知られている。脳内では間質液が常に流動しAβが供給・排斥される非平衡場にあるため、*in vitro* においても平衡閉鎖空間ではなく非平衡開放下での議論が重要である。そこで本研究では、非平衡撹拌がAβ凝集の各素過程に及ぼす分子科学的あるいは熱力学的な作用を検証するための実験を行い、非平衡撹拌下でのAβ凝集機構の解明を目指した。100 mM リン酸バッファー (PH 7.4)、100 mM 塩化ナトリウム溶液を用いて、5 μM Aβ、50 μM チオフラビンT (ThT)を含むAβ溶液を調製し、ウェルに96 μL 添加し180 rpm で撹拌しながらAβ溶液を更に1時間おきに6 μL 注入した。注入は24回行った。その結果、Aβを添加した方の蛍光強度が添加していない時よりもAβ凝集が速まる事が確認された (図1)。これにより、Aβの連続的添加がAβ凝集挙動に影響を与える可能性が示唆された。また、閉鎖系の実験によりリポソームがAβの凝集を促進していることも観察された。これらの結果を踏まえて、今後はリポソーム存在下におけるAβ凝集挙動について考察する。

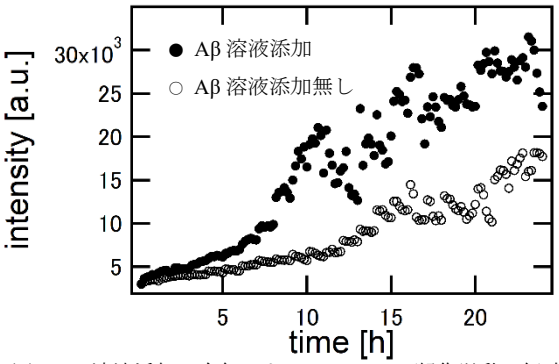

図 1. Aβ 溶液添加の有無による 5 μM Aβ の凝集挙動の経時変化.それぞれの曲線は 3 つのデータの平均値を示す.

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ハニカム状多孔質体に支持された脂質膜小胞構造の調製

（芝浦工大理工院）○木村 圭佑・矢野 瑠理亜・松村 一成

Preparation of Lipid Vesicle Supported by Micro-Honeycomb Porous Film (*Graduate School of Engineering and Science, Shibaura Institute of Technology*) ○Keisuke Kimura, Ruria Yano, Kazunari Matsumura

Although various techniques for immobilizing liposome on solid substrate have been successfully achieved [1], preparation of stable multicellular lipid vesicles such as biological tissue has not yet been reported due to fluidity and fragility of lipid membrane. Herein we demonstrate the preparation of a lipid vesicles array in the micro-honeycomb porous film, whose framework structure prevents the disintegration and fusion of lipid vesicles but not the communication between each compartments. The honeycomb film with a pore size of 2-8 microns was fabricated by self-assemble technique known as the breath-figure method and electroless silver plating. Lipid vesicle in the film was prepared by using w/o lipid emulsion followed by natural swelling. Staining with pH sensitive fluorescent probe pyranine indicates that a prepared membrane separates the interior of vesicle from the outside environment. Our technique must be a key to the development of liposome engineering from artificial cell to tissue.

Keywords : Liposome; Lipid Bilayer Membrane; Honeycomb Film; Supported Bilayer Membrane; Self-Assemble

生体膜の研究･利用のために人工のリン脂質二重膜を基板に支持させる様々な手法が開発されているが [1]、生体組織のような多細胞型の脂質膜を作成するような手法は未だ開発されていない。本研究ではハニカム状多孔質膜を支持体とすることで多細胞型の人工生体膜組織を作成した。 2～8 μ m の孔径をもつハニカム状多孔質体は Breath-Figure 法で自己組織的に作成した後に、無電解銀めっきを施して金属構造とした。w/o 乳液を用いてハニカム孔内に脂質を導入した後に自然膨潤させ脂質膜を展開した。pH 指示蛍光試薬を用いた蛍光顕微鏡観察結果は展開した膜が小胞内部を外部環境から区画していることを示している。ハニカム状多孔質体の骨格は脂質膜の崩壊や融合を防ぐ一方、各孔間の物質移動は妨げないので多細胞的な脂質膜組織を作る上で理想的である。

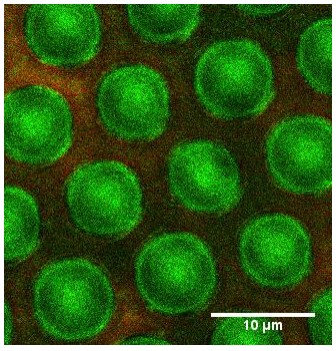

Fig. Confocal fluorescence microscopy image of lipid vesicle structure in honeycomb-film. The vesicles encapsulate 100 μ M pyranine (green).

1) a) Y. Kasuya, K. Tsukamoto, D. Yamada, K. Matsumura, *Chem. Lett*. **2012**, *41*, 1191. b) Y. Kasuya, M. Ohtaka, K. Tsukamoto, Y. Ikeda, K. Matsumura, *Chem. Lett*. **2008**, *37*, 588.

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マイクロ流路を用いた簡便な多重液滴の形成方法とその機構

（九大院理・九大先導研[1]）○中西 京香[1]・五島 健太[1]・谷 文都[1]
Multiple Droplets Formation by a Simple Mixing Method with Maicrofabricated Channel and Their Mass-Transport Mechanism ([1]Graduate School of Sciences and Institute for Materials Chemistry and Engineering, Kyushu University) ○Kyoka Nakanishi,[1] Kenta Goto,[1] Fumito Tani[1]

Multiple droplets and/or emulsions are defined as dispersed droplets including tiny droplets in immiscible liquid phases. A couple of methods are present for formation of multiple droplets. Among them, multiple droplets obtained from phase separation show an attractive phenomena including pattern dynamics and mass-transport. On the other hand, fabricated micro channel is a promising candidate for droplet formation. We developed multiple droplets formation by a simple mixing method with maicrofabricated channel in the diethyl phthalate (DEP)-ethanol-water system in the presence of a polymer surfactant, Pluronic F-127. Formation and mass-transport mechanism on phased-separated multiple droplets will be discussed.
Keywords : emulsion, multiple droplets, microchannel

エマルションの分散相が他の液滴を内包したものは，多重エマルションと呼ばれる．その対称性の高い構造を活かした機能の発現を目的としている．まず，フタル酸ジエチル (DEP)–エタノール–水の三成分系での，相分離による簡便な多重液滴形成方法の開発に取り組んだ．具体的には，油分を主とする A 液とエタノール–水を主とする B 液を界面活性剤 Pluronic F-127 と共に混合することにより，多重液滴が形成されることを見出した (図 1)．これは流路内での混合により，調整した系の組成が共存曲線近傍に移動することで発現されると考えられる (図 2)．最も多重液滴が形成されやすい条件を表 1 に示した．液滴を構成する成分は絶えず流入・流出していることがわかった．その物質移動のバランスをとることによって多重構造が形成されると考えられる．

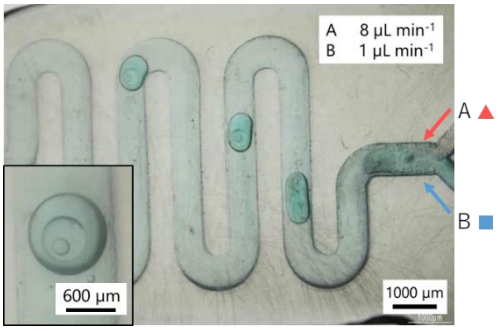

図 1. 流路内での混合の様子（挿入図：多重液滴）

表 1. 混合液の組成

	Volume ratio (v/v%)		
	DEP	EtOH	H_2O*
A	63	27	10
B	26	47	27

* Pluronic F-127 solution (0.05 w/w%)

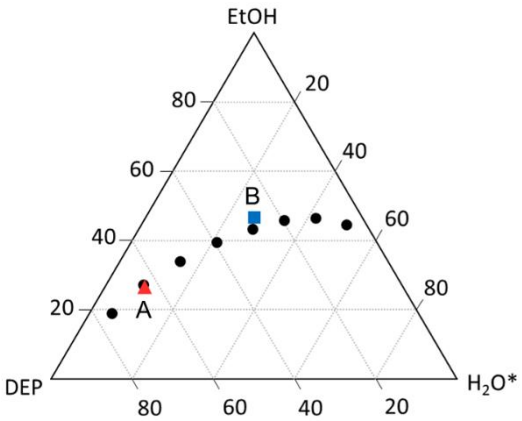

図 2. フタル酸ジエチル(DEP)–エタノール–水の三成分系の相図．共存曲線の各点(●)は濁度法により決定した．

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Academic Program [Poster] | 23. CIP Poster | Poster

[P02-1vn] 23. CIP Poster

Fri. Mar 19, 2021 4:10 PM - 5:40 PM Area 2 (Online Meeting)

[P02-1vn-01] Wavelength dependence of photocapacitnce of layered MnO2 with metal complexes using lipid confinement effect

○Makoto Itakura[1], Riku Okiguti[1], Ituou Ou[1], Kei Hsegawa[1], Motoyuki Kamata[1], Kazuaki Tomono[1] (1. Kantogakuin University)

[P02-1vn-02] Photocatalytic function induced by self-assembly of organic dyes

○Hajime Shigemitsu[1], Youhei Tani[1], Tomoe Tamemoto[1], Toshiyuki Kida[1] (1. Osaka Univ.)

[P02-1vn-03] Electrochemical CO_2 reduction to C_2 products utilizing cuprous coordination polymer electrode

○Naonari Sakamoto[1], Yusaku F Nishimura[1], Takamasa Nonaka[1], Masataka Ohashi[1], Nobuhiro Ishida[1], Kosuke Kitazumi[1], Yuichi Kato[1], Keita Sekizawa[1], Takeshi Morikawa[1], Takeo Arai[1] (1. TOYOTA CENTRAL R&D LABS., INC.)

[P02-1vn-04] Development of alkali-resistant reversed phase HPLC column based on eggshell

○Tomoka Yoshii[1], Mai Mochida[1], Kogi Kaizu[1], Hiroaki Imai[1], Daniel Citterio[1], Yuki Hiruta[1] (1. Fac. Sci. Tech., Keio Univ.)

[P02-1vn-05] Subcritical Water Decomposition of Polychlorotrifluoroethylene (PCTFE) under Alkaline Conditions

○Kazuma Igarashi[1], Hisao Hori[1] (1. Kanagawa Univ.)

[P02-1vn-06] Efficient Decomposition of Fluoropolymer ETFE in Subcritical Water under Alkaline Conditions

○Jin Hamaura[1], Hisao Hori[1] (1. Kanagawa Univ.)

[P02-1vn-07] Iridium Catalyzed C-C Bond Formation of Methyl Groups of N-Heterocyclic Compounds with Alcohols

○Mitsuki Onoda[1], Ken-ichi Fujita[1] (1. Graduate School of Human and Environmental Studies, Kyoto University)

[P02-1vn-08] An Efficient Dimethylamination of Alcohols Using Iridium Catalyst Bearing an N-Heterocyclic Carbene Ligand

○Jaeyoung Jeong[1], Ken-ichi Fujita[1] (1. Graduate School of Human and Environmental Studies, Kyoto University)

[P02-1vn-09] Nanoporous Metal Complex Covered on Metal Oxide Nanowires for Molecular Recognition by Molecular Sieving

○Akira Yonezu[1], Junya Kubo[2], Shinpei Kusaka[1,2], Takao Yasui[1,2], Yoshinobu Baba[1,2], Ryotaro Matsuda[1,2] (1. Grad. Sch. Eng., Nagoya University, 2. Sch. Eng., Nagoya University)

[P02-1vn-10] Development of tough biomass mechanical material by hybridization of plant-derived polysaccharides and hydroxyapatite

○Kohei Okuda[1], Tadashi Mizutani[1] (1. The Univ. of Doshisha)

[P02-1vn-11] Organogels formed from a starch-derived 1,5-anhydro-D-glucitol glycolipid and their properties

○Rika Iwaura[1], Shiro Komba[1], Takahito Kajiki[2] (1. National Agriculture and Food Research Organization, 2. SUNUS Co., Ltd.)

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[P02-1vn-12] Research on Adsorption of Boron using Hydrogels

○Daiki Matsumura[1], Kazunori Nakano[1] （1. Nagoya Municipal Industrial Research Institute）

[P02-1vn-13] Development of high-strength cellulose nanofiber hydrogels by freeze-crosslinking

○Yurina Sekine[1], Takuya Nankawa[1], Daisuke Miura[2], Shunji Yunoki[3], Tsuyoshi Sugita[1], Hiroshi Nakagawa[1], Teppei Yamada[4] （1. Japan Atomic Energy Agency, 2. Yamagata University, 3. Tokyo Metropolitan Industrial Technology Research Institute, 4. The University of Tokyo）

[P02-1vn-14] Emission Properties of Hybrid Films of Benzylideneaniline-based Amorphous Molecular Materials with Organic Acids

○Takuma Tsukada[1], Yuya Kitamura[1], Hideyuki Nakano[1] （1. Muroran Inst. Tech.）

[P02-1vn-15] Emission and Photochemical Reaction of Cyanostilbene-based Amorphous Molecular Materials

○Hiroya Fukushima[1], Kensuke Mori[1], Yoshimitsu Sagara[2], Kenta Kokado[3], Takayoshi Nakamura[3], Nobuyuki Tamaoki[3], Hideyuki Nakano[1] （1. Muroran Inst. Tech., 2. TITEC, 3. RIES, Hokkaido Univ.）

[P02-1vn-16] Emission and Photochemical Reaction of a Novel Amorphous Molecular Material Possessing Diphenylanthracene Moiety

○Ryoma Matsui[1], Hiroki Asanuma[1], Hideyuki Nakano[1] （1. Muroran Inst. Tech.）

[P02-1vn-17] Photoinduced Helical Structure Formation of Azobenzene-based Molecular Glass Particles

○Motona Matsubara[1], Hiroyasu Ukai[1], Masahiro Kuragano[1], Kiyotaka Tokuraku[1], Hideyuki Nakano[1] （1. Muroran Inst. Tech.）

[P02-1vn-18] Development of linear silicones with unique mechanical properties

○Mitsuo Hara[1], Yuta Iijima[1], Shusaku Nagano[2], Takahiro Seki[1] （1. Nagoya University, 2. Rikkyo University）

[P02-1vn-19] Transmission Electron Microscope (TEM) Measurement of the PLGA Nanocapsules

○Kazutaka Arai[1], Kensuke Osada[1], Hong Taefun[1,2], Jun-ichiro Jo[3], Ichio Aoki[1] （1. National Institute of Radiological Science (NIRS), QST, 2. School of Engineering, The Tokyo Univ., 3. Inst. Frontier Med. Sci., Kyoto Univ.）

[P02-1vn-20] A study of the preparation of gold nanoparticles using the electric current application in electrolyte solution

○Shinichirou Ozawa[1], Yuichiro Iwasaki[1], Masaya Nishio[1], Ryo Saito[1], Hisashi Miyazaki[1], Yoichi Okamoto[1] （1. National Defense Academy）

[P02-1vn-21] Fabrication of Carbon Nanotube Thin Films for Flexible Transistor Applications using a Cross-linked Amine Polymer

Kaisei Matsumoto[1], Kazuki Ueno[1], Jun Hirotani[2], Yutaka Ohno[2,3], ○Haruka Omachi[1,4] （1. Grad. Sch. of Sci., Nagoya Univ., 2. Grad. Sch. of Eng., Nagoya Univ., 3. IMaSS, Nagoya Univ., 4. RCMS, Nagoya Univ.）

[P02-1vn-22] Identification of orthogonal RNA-RNA-binding protein pairs through library-versus-library in vitro selection

○Keisuke Fukunaga[1], Yohei Yokobayashi[1] （1. OIST）

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[P02-1vn-23] Immobilization of Biomolecules by Photoinduced Oxygenation of Graphene Surface with Chlorine Dioxide

○Haruyasu Asahara[1,2], Shota Kumano[1], Junso Fujita[3], Kei Ohkubo[2,4], Tsuyoshi Inoue[1,2] (1. Graduate School of Pharmaceutical Sciences, Osaka University, 2. Institute for Open and Transdisciplinary Research Initiatives, Osaka University, 3. Graduate School of Frontier Biosciences, Osaka University, 4. Institute for Advances Co-Creation Studies, Osaka University)

[P02-1vn-24] The Development of Furimazine Derivatives for Long-Term and High-Sensitive Bioluminescence Imaging

○Mariko Orioka[1], Yuki Mizui[1], Masatoshi Eguchi[2], Yuma Ikeda[1], Hideaki Yoshimura[2], Takeaki Ozawa[2], Daniel Citterio[1], Yuki Hiruta[1] (1. Fac. Sci. Tech., Keio Univ., 2. Dept. Chem., The Univ. of Tokyo)

[P02-1vn-25] Practical Synthesis of 2-Oxazolidinones Using a Triethylamine Hydroiodide Catalyst

○Ken Okuno[1], Ryuichi Nishiyori[1], Seiji Shirakawa[1] (1. Graduate School of Fisheries and Environmental Sciences, Nagasaki University)

[P02-1vn-26] Development of New Catalytic Synthetic Methods of N-Unprotected Ketimines and its Applications to One-Pot Synthesis of N-Unprotected Amines and Amino Acid Derivatives

○Hiroyuki Morimoto[1], Yuta Kondo[1], Tetsuya Kadota[1], Yoshinobu Hirazawa[1], Kazuhiro Morisaki[1], Takashi Ohshima[1] (1. Graduate School of Pharmaceutical Sciences, Kyushu University)

[P02-1vn-27] New umpolung strategy of aromatic carbonyl compounds to α-hydoroxybenzyl anion equivalents: carboxylation with carbon dioxide

○Shintaro Okumura[1], Yasuhiro Uozumi[1] (1. Institute for Molecular Science)

[P02-1vn-28] Biotransformation of molecular nanocarbon by *Spodoptera litura* larvae

○Atsushi Usami[1], Amaike Kazuma[1], Itami Kenichiro[1,2] (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University)

[P02-1vn-29] Synthesis and transistor applications of robust and high-mobility n-type organic semiconductors having phenylalkyl side chains

○Shohei Kumagai[1], Hiroyuki Ishii[2], Go Watanabe[3], Eiji Fukuzaki[4], Tatsuro Annaka[1], Yukio Tani[4], Hiroki Sugiura[4], Tetsuya Watanabe[4], Tadanori Kurosawa[1], Shun Watanabe[1,5], Jun Takeya[1,5,6], Toshihiro Okamoto[1,5,7] (1. The Univ. of Tokyo, 2. The Univ. of Tsukuba, 3. Kitasato Univ., 4. FUJIFILM Corp., 5. AIST-UTokyo OPERANDO-OIL, 6. NIMS WPI-MANA, 7. JST-PRESTO)

[P02-1vn-30] Synthesis of natural product-connected molecules by the Ugi reaction using medicinal plant extracts as substrates

○Keisuke Tomohara[1], Nao Ohashi[2], Takeru Nose[1,2] (1. Faculty of Arts and Science, Kyushu University, 2. Graduate School of Science, Kyushu University)

[P02-1vn-31] Solid-state DNP-NMR spectroscopy for polymer-supported organocatalysts

○Shinji Tanaka[1], Yumiko Nakajima[1], Kazuhiko Sato[1] (1. National Institute of Advanced Industrial Science and Technology)

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[P02-1vn-32] Deep Learning Analysis of SARS-CoV-2 Using the Codification Techniques of Conformations

○Hiroshi Izumi[1] （1. National Institute of Advanced Industrial Science and Technology (AIST)）

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脂質閉じ込め効果を利用した金属錯体を有する層状マンガン酸化物の光キャパシタの波長依存性

（関東学院理工）○板倉 誠・欧 逸生・長谷川 慧・鎌田 素之・友野 和哲

Electrochemical Evaluation of the Layered MnO_2 Intercalated with Metal Complexes and Ionic Lipid (*College of Science and Engineering, Kanto-Gakuin University*) ○Makoto Itakura, Ituou Ou, Kei Hasegawa, Motoyuki Kamata, Kazuaki Tomono

Birnessite-type layered manganese oxides (MnO_2) were electrodeposited in $MnSO_4$ solution containing the metal complex or the ionic lipid. The deposited films were characterized using XRD, SEM-EDS, FTIR techniques. These analyses indicated that the obtained MnO_2 films were alternately intercalated with those cations. The specific capacitances of the films with and without the light irradiation were investigated.

Keywords : Layered MnO_2, Metal complex, Ionic lipid, Electrodeposition, Light Irradiation

当研究室では, 層状構造であるマンガン酸化物(MnO_2)の層間に金属錯体を導入した薄膜をワンステップで作製する手法を見出し, キャパシタンスが向上することを明らかにした[(1)(2)]。層間内の金属錯体は，光照射による光電効果によって更なるキャパシタンスの向上が考えられるが, 金属錯体の層間からの脱離によって機能性が消失する。本研究では、疎水性な脂質イオンを層間にもつ MnO_2 薄膜を被膜し，金属錯体の脱離抑制の検討を行い，光照射による波長依存性を調べた。

Figには脂質@MnO_2/Co2@MnO_2薄膜の光照射と脂質層のふたつの有無におけるサイクル数に対するキャパシタンス値を示す。脂質層と光照射がある条件(a)は，初期キャパシタンス値が765.1F/g，50 サイクル目は 678.4F/g になり，脂質層が無い条件(b)と比較すると高い被容量と安定性を示し，脂質層を被膜することで金属錯体の脱離抑制が可能だとわかった。また, 光照射がない条件(c)と比較するとキャパシタンス値は約4倍に向上することがわかった。光照射の有無によって高容量化したと示唆される。

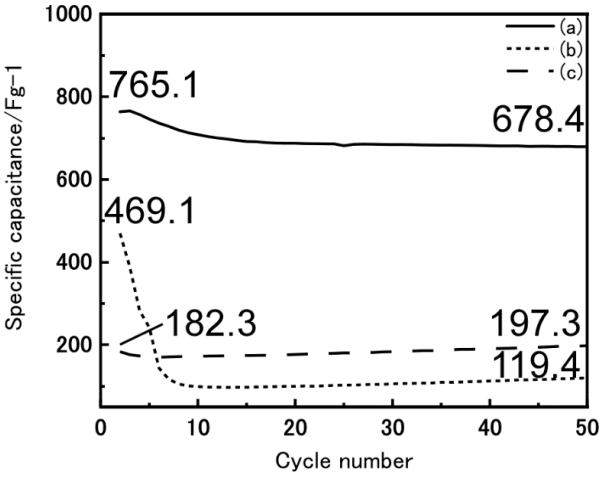

Fig. Plots of the specific capacitance of the Lipid@MnO_2/Co2@MnO_2 films as a function of the cycle number;
(a) Light ON; lipid@MnO_2/Co2@MnO_2 and (b) Light OFF; Lipid@MnO_2/Co2@MnO_2, (c) Light ON: Co2@MnO_2.

(1) K. Tomono, *et al., ECS trans*., 50(52), pp. 135-142 (2013). (2) K. Tomono, *et al., Bull, Institu, Sci. Tech.,* 46, pp. 33-38 (2018).

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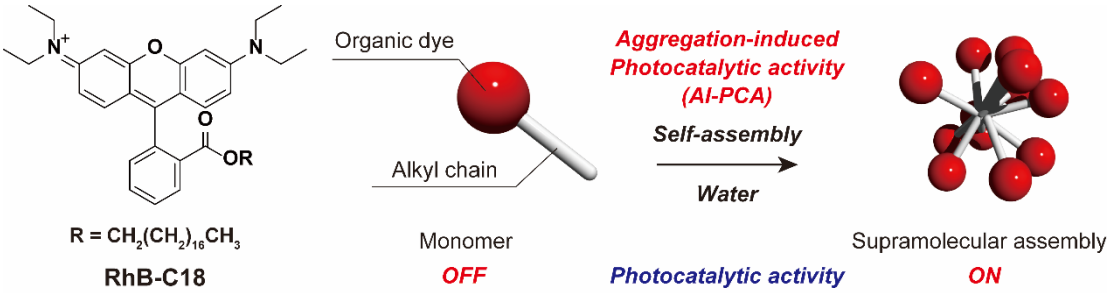
有機色素分子の自己集合による光触媒機能の発現

（阪大院工）○重光 孟・谷 陽平・為本 智恵・木田 敏之
Photocatalytic function induced by self-assembly of organic dyes (*Graduate School of Engineering, Osaka University*) ○Hajime Shigemitsu, Youhei Tani, Tomoe Tamemoto, Toshiyuki Kida

Development of highly efficient photocatalysts is an essential task for sustainable society. Herein, we developed new type photocatalysts which are self-assembled supramolecular photocatalysts (SA-SPCs) consisting of amphiphilic xanthene and cyanine dyes. The SA-SPCs exhibited good hydrogen generation yields and photocatalytic oxidation of water-insoluble organic molecules in water.
Keywords : Supramolecular assembly; Self-assembly; Photocatalyst; Rhodamine; Hydrogen evolution

光触媒は光を駆動力として様々な化学反応を進行させるため、エネルギー・環境・医療などの多岐に渡る分野での応用が期待されている。例えば、水の光分解反応で得られる水素は、次世代クリーンエネルギーの重要な候補である。これまでに無機光触媒を中心とした研究が活発に行われてきたが、利用可能な光波長領域や反応効率などに課題を残している。また、近年では有機光触媒が様々な有機反応を進行させることが明らかとなり、注目を集めている。しかしながら、無機光触媒と同様に量子収率や耐久性に課題であるため、これらを克服する新たな戦略が必要である。

本研究では、従来の光触媒とは異なる『超分子（分子集合体）』を利用した光触媒の創出に成功した。[1] 単分子状態では光触媒活性を有していない水溶性有機色素が、自己集合によって光触媒活性を獲得することを見出した。超分子光触媒においては、一般的な分子光触媒で利用される貴金属やハロゲン原子が不要である。また、分子集合体であるために複数種の機能性分子を容易に複合することができる。これらの特徴は、有機光触媒の多様性を大きく拡張する可能性を秘め、光触媒が抱える課題の解決に繋がると考えている。本発表では、キサンテンおよびシアニン色素を基盤とする超分子光触媒の水素発生反応や有機化合物の酸化反応について発表する。



1) Hajime Shigemitsu, Youhei Tani, Tomoe Tamemoto, Tadashi Mori, Xinxi Li, Yasuko Osakada, Mamoru Fujitsuka, Toshiyuki Kida, *Chem. Sci.* **2020**, *11*, 11843.

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Cu(I)2 核配位高分子電極を用いた CO_2 還元による C_2 化合物生成

（豊田中研 [1]）○坂本 直柔 [1]・西村 友作 [1]・野中 敬正 [1]・大橋 雅卓 [1]・石田 亘広 [1]・北住 幸介 [1]・加藤 雄一 [1]・関澤 佳太 [1]・森川 健志 [1]・荒井 健男 [1]

Electrochemical CO_2 reduction to C_2 products utilizing cuprous coordination polymer electrode

([1]*Toyota Central R&D Labs., Inc.*,) ○Naonari Sakamoto,[1] Yusaku F. Nishimura,[1] Takamasa Nonaka,[1] Masataka Ohashi,[1] Nobuhiro Ishida,[1] Kosuke Kitazumi,[1] Yuichi Kato,[1] Keita Sekizawa,[1] Takeshi Morikawa,[1] Takeo Arai[1]

Metal complex molecules have a superior structure for electron transfer and are suitable for the production of two-electron reductants such as carbon monoxide and formic acid. However, there were few reports of multi-electron products, especially all the reports on C_2 production (ethanol and ethylene) requiring C-C coupling reactions involve the conversion of metal complex to metal particles. We synthesized self-assembled nanoparticles of cuprous coordination polymer (Cu-SCP), which is known as an emitting material with poor solubility to organic solvent and water and utilize it as at metal complex electrocatalyst for CO_2 reduction.(1) Cu-SCP can generate C_2 products with maintaining the metal complex structure and the oxidation state of Cu(I). This is the first example of C_2 production from CO_2 utilizing metal complex catalyst without decomposing into Cu metal aggregates. The Cu-SCP also exhibits activity for C_2 production that is superior to that of a Cu metal electrode, without the flow of the electrolyte and mixing of the carbon materials, which will simplify the fabrication of a CO_2 electrolyzer.

Keywords: *CO_2 reduction, Electrochemical catalyst, Coordination polymer, Copper complex*

CO_2 電解還元において金属錯体触媒は、高選択的に CO や HCOOH などの 2 電子還元物を生成できることが知られている一方で、多電子還元物生成の報告はほとんどなく、特に C-C カップリング反応が必要な C_2 化合物(エタノールやエチレン)を生成する報告はいずれも錯体触媒としての構造は崩壊し金属 Cu に変換したものであった。本研究では、有機溶媒や水に対して難溶性発光材料で知られる Cu(I)2 核配位高分子(Cu-SCP)電極を CO_2 電解還元反応に用いることで金属錯体構造を維持しつつ C_2 化合物の生成を達成した(1)。Cu-SCP 電極は、配位子を変えることで CO_2 還元生成物の選択性を容易に変化させる金属錯体触媒の性質を有し、10 時間の反応にわたって金属 Cu に還元されることなく Cu(I)を安定に保持した。また、金属 Cu 電極で報告されている強アルカリ性電解液のフローや炭素材料との複合化なしで高い C_2 化合物生成を達成した。

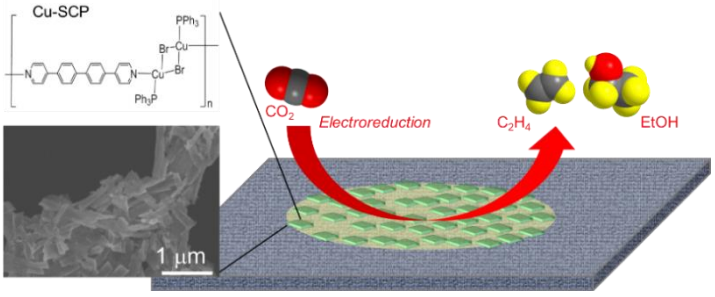

Figure 1 CO_2 electroreduction scheme via Cu-SCP

1) N. Sakamoto *et al., ACS Catal.* **2020**, 10, 10412–10419.

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卵殻を母体とした高アルカリ耐性逆相 HPLC カラムの開発

（慶大理工）○吉井 智夏・持田 麻衣・海津 光儀・今井 宏明・Daniel Citterio・蛭田 勇樹

Development of alkali-resistant reversed phase HPLC column based on eggshell (*Faculty of Science and Technology, Keio University*) ○Tomoka Yoshii, Mai Mochida, Kogi Kaizu, Hiroaki Imai, Daniel Citterio, Yuki Hiruta

In recent years, the need for new sustainable materials has increased. For example, eggshells are discarded in large quantities every year by egg-processing companies, so further effective utilization of eggshells would be advantageous. Therefore, we have established a method for applying eggshells as a column packing material for HPLC.

Previously, we developed alkali-resistant reversed phase column packing material ($CaCO_3$-PMAcO) based on synthesized porous calcium carbonate modified with poly(maleic acid-*alt*-1-octadecene). In this work, eggshell powder, which is a biomineral mainly composed of $CaCO_3$, has been applied instead of synthesized $CaCO_3$. Nanocrystals and biopolymers present on as-received eggshell powder were removed by surface treatment, followed by the modification with PMAcO. The prepared packing material was referred to as Eggshell-PMAcO. Retention capacity of Eggshell-PMAcO was evaluated, and complete separation of two basic drugs was achieved under alkaline condition using Eggshell-PMAcO.

Keywords: Eggshell; Calcium carbonate; Biomineral; Amphiphilic polymer; Reversed phase liquid chromatography

近年、持続可能な新たなマテリアルの必要性が高まっている。例えば、卵殻は卵加工会社等から毎年大量に廃棄されており、さらなる有効活用法が求められている。そこで本研究では、卵殻を HPLC 用カラム充填剤に応用する方法を確立した。

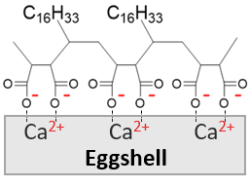

Fig. 1　Eggshell-PMAcO の構造

当研究室では、合成した多孔質炭酸カルシウム粒子に両親媒性ポリマーであるポリマレイン酸オクタデセン（PMAcO）を吸着させた逆相充填剤 $CaCO_3$-PMAcO を開発し、一般的な逆相充填剤であるオクタデシル基修飾シリカゲル ODS では使用不可能な高アルカリ性移動相中での安定性と分離性能を確認している [1]。本研究では、合成した炭酸カルシウムに代わり、炭酸カルシウムを主成分としたバイオミネラルである卵殻を担体として用いた。まず、卵殻粉末に表面処理を施すことで、卵殻表面のナノ結晶および生体高分子を除去し、均一な多孔質構造を露出させた。そして、表面処理後の卵殻粉末に PMAcO を吸着させ、逆相充填剤 Eggshell-PMAcO（Fig.1）を作製した。Eggshell-PMAcO をセミ分取用カラム(150×10 mm I.D.)に充填して疎水性化合物の分析を行った結果、逆相の保持挙動が示された。さらに、アルカリ性移動相中で、最大で 5 mg ずつの塩基性薬物の完全分離が達成され、ODS と同程度の保持容量を有することが確認されたことから、卵殻を塩基性薬物の分取へ有効活用できる可能性が示唆された。

1) M, Mochida; Y, Nagai; H, Kumagai; H, Imai; D, Citterio; Y, Hiruta. A biomimetic hybrid material consisting of $CaCO_3$ mesoporous micro spheres and an alternating co polymer for reversed-phase HPLC. *J. Mater. Chem. B*. **2019**, *7*, 4771-4777

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Subcritical Water Decomposition of Polychlorotrifluoroethylene (PCTFE) under Alkaline Conditions

(*Graduate School of Science, Kanagawa University*)○Kazuma Igarashi, Hisao Hori

Keywords: Fluoropolymer; Subcritical Water; Decomposition; Waste Treatment

Fluoropolymers consist of strong carbon-fluorine bonds so that they show high resistances to heat, chemical, and weather. However, owing to their high stabilities, waste treatment method has not been fully established. In addition, the mine production of fluorite (mineral of CaF_2), the raw material of all organofluorine compounds, is almost limited by few countries. If the wastes of fluoropolymers are converted into fluoride ions (F^-) (i.e., mineralization) by means of an environmentally benign technique, the F^- ions can react with $Ca(OH)_2$ to form CaF_2. Thus, the development of an efficient mineralization technique of fluoropolymers would contribute to closing the loop of fluorine.[1–3] In this study, we tried to mineralize a typical fluoropolymer, polychlorotrifluoroethylene (PCTFE), by a combination of sodium hydroxide and subcritical water.

Figure 1 shows the temperature dependence of the F^- and Cl^- formations in the aqueous phase, where PCTFE (30 mg) was reacted with an aqueous NaOH solution (1.0 M) for 6 hours. When the reaction temperature was elevated to 340 ℃, the yields of F^- and Cl^- formed in the aqueous phase reached both 97%. That is, the F and Cl atoms in initial PCTFE were almost completely mineralized. Rising temperature also increased the total organic carbon (TOC) content in the aqueous phase, indicating that PCTFE generated organic compounds soluble in water. When the reaction was carried out at 340 ℃ or 350 ℃, the resulting aqueous phase became a brown turbid liquid, suggesting the formation of fine carbon-containing residue.

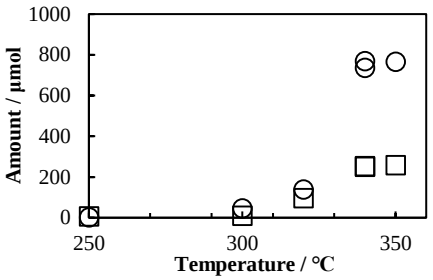

Fig. 1. Temperature dependence of the formed amounts of F^- (○) and Cl^- (□) in the reaction solution.

1)H. Hori, H. Tanaka, K. Watanabe, T. Tsuge, T. Sakamoto, A. Manseri, B. Ameduri, *Ind. Eng. Chem. Res.,* **2015**, *54*, 8650-8658; 2) H. Hori, H. Tanaka, T. Tsuge, R. Honma, S. Banerjee, B. Ameduri, *Eur. Polym. J.*, **2017**, *94*, 322-331; 3) R. Honma, H. Hori, F. Reis da Cunha, N. Horiike, L. Steinbach, B. Ameduri, *Ind. Eng. Chem. Res*., **2019**, *58*, 13030-13040.

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Efficient Decomposition of Fluoropolymer ETFE in Subcritical Water under Alkaline Conditions

(*Graduate School of Science, Kanagawa University*) ○Jin Hamaura, Hisao Hori

Keywords: Subcritical water; Fluoropolymer; Decomposition

Fluoropolymers have unique characteristics such as heat resistance, chemical resistance, and weather resistance. Owing to these characteristics, they have many industrial uses. However, the waste treatment techniques for these polymers have not yet been well established. Incineration is an option. However, it needs high temperatures to destruct the strong carbon-fluorine bonds. Furthermore, during the treatment, gaseous hydrogen fluoride (HF) generates, which seriously degrades the firebricks of incinerators. If these wastes can be decomposed into fluoride ions (F^-) under mild conditions, then conventional technology can be used to treat F^-, by adding calcium-ion source to aqueous F^- to form harmless CaF_2. CaF_2 is a raw material for hydrofluoric acid, which is a raw material for all organofluorine compounds. Thus, the development of a methodology to decompose these polymers could contribute to closing the loops of fluorine element.[1)]

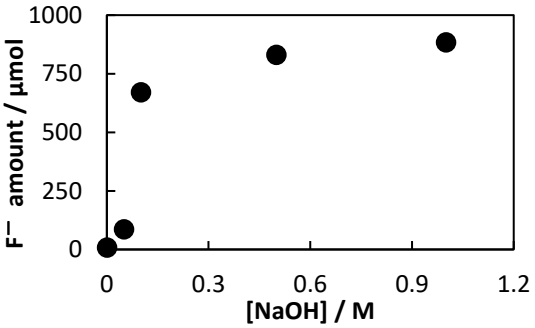

Fig. 1. Effect of NaOH concentration on the F^- formation. ETFE (30 mg; the F and C atom amounts were 925 and 952 μmol, respectively) was reacted at 260 ºC for 6 h.

Poly(ethylene-*co*-tetrafluoroethylene) (ETFE) is a melt-processable fluoropolymer and used in various applications such as piping/valves for chemical plants, wire insulation, protective films, and other purposes in harsh conditions.

In this study, we investigated the sub-critical water reaction of ETFE with addition of alkaline reagents. **Figure 1** shows the effect of NaOH concentration on the F^- amount in the reaction solution, where the reaction was performed at 260 ºC for 6 h under Ar. The F^- amount increased as the initial NaOH concentration increased. When the NaOH concentration was 1.0 M, the F^- yield reached 94%. That is, almost all fluorine atoms in ETFE were mineralized. Details of the reaction mechanism and recycle use of the alkaline reagent will be discussed at the presentation.

1) R. Honma, H. Hori, et al., *Ind. Eng. Chem. Res*. **2019**, *58*, 13030-13040.

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イリジウム錯体触媒による含窒素複素環上のメチル基のアルコールによる C-C 結合形成反応

（京大院人環 [1]）○小野田 光貴 [1]・藤田 健一 [1]

Iridium Catalyzed C-C Bond Formation of Methyl Groups of N-Heterocyclic Compounds with Alcohols ([1]*Graduate School of Human and Environmental Studies, Kyoto University*)

○Mitsuki Onoda[1], Ken-ichi Fjita[1]

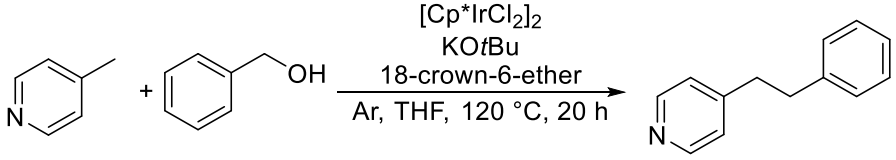
N-Hetero cyclic compounds have been widely used in the fields of medicine, fragrance, and functional materials. The method of extending alkyl chain using a methyl group is useful but difficult, and the reaction of methyl groups of N-heterocyclic compounds with *n*-BuLi followed by reaction with an alkyl halide is the traditional method. However, this method suffers from formation of undesired stoichiometric amounts of wasteful byproducts. We present here, catalytic performance of iridium complexes for the C-C bond formation of methyl groups of heterocyclic compounds with alcohols was investigated.

For example, the reaction of 4-methylpyridine with benzyl alcohol in the presence of base and a catalytic amount of an Ir complex at 120 deg. in THF gave 4-phenethylpyridine in high yield. This catalytic system was applicable for the synthesis of various alkylated heterocyclic compounds from alcohols.

Keywords : Coordination Chemistry; Iridium; Alcohol; N-Heterocyclic Compounds; C-C Bond Formation

ピリジン、ピラジンを始めとした、含窒素複素環式化合物及び、それらの誘導体は、薬剤や天然物など、広範に使用されている。含窒素複素環式化合物の環上にアルキル鎖を導入する反応は有用性が高い一方で難易度が高い。古典的な手法においては、メチル基を有する芳香族含窒素複素環式化合物に対して、*n*-BuLi とアルキルハライドを作用させる手法が使われてきたが、原子効率に難があり、近年では、原子効率のよい、アルコールを反応剤として用いた、錯体触媒による C-C 結合形成反応に注目が集まっている。本研究では、アルキル化剤として第一級アルコールを用いることにより、原子効率の良いイリジウム錯体触媒による含窒素複素環化合物上のメチル基の C-C 結合形成反応について調査した。

例えば、触媒量のイリジウム錯体と塩基存在下、4-メチルピリジンとベンジルアルコールの反応を THF 溶媒中、120 ℃で行ったところ、4-フェネチルピリジンが高収率で得られた。本触媒系は、メチル基を有する含窒素複素環化合物とアルコールから様々なアルキル化体を得る手法として有用である。



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含窒素複素環カルベン配位子を有するイリジウム触媒を用いたアルコールの高効率的ジメチルアミノ化反応

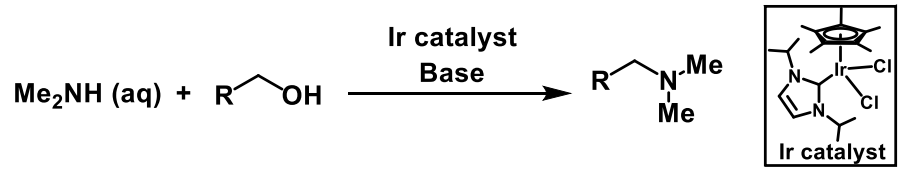
（京大院人環）丁　在瑛・藤田　健一
An Efficient Dimethylamination of Alcohols Using Iridium Catalyst Bearing an *N*-Heterocyclic Carbene Ligand (*Graduate School of Human and Environmental Studies, Kyoto University*) ○Jaeyoung Jeong, Ken-ichi Fujita

Dimethylamine derivatives are the fundamental building block of bioactive compounds and natural products. These compounds have been applied in various fields such as agrochemicals, materials, and pharmaceuticals. The nucleophilic substitution using methyl iodide and Eschweiler-Clarke reaction through *N*-methylation using formic acid and formaldehyde has been reported as conventional methods. However, these reactions have significant disadvantages such as low selectivity, use of toxic reagents and generation of a large amount of waste. Recently, much attention has been focused on environmentally benign and economical *N*-methylation using methanol. On the contrary, in the absence of organic solvent, homogeneous catalytic *N,N*-dimethylamination using inexpensive and commercially available aqueous dimethylamine has so far remained a challenge. In this study, we investigated an synthetic method for NHC iridium complex-catalyzed *N,N*-dimethylamination of alcohol with aqueous solution of dimethylamine.
Keywords : Dimethylamination; Dimethylamine derivatives; Hydrogen transfer; Iridium complex catalyst; N-Heterocyclic carbene ligand

ジメチルアミン誘導体は天然物や生理活性物質によく見出される構造であり、農薬、材料、医薬に至る様々な分野で応用されている。従来の合成法としてはヨウ化メチルを用いた求核置換反応やホルムアルデヒドとギ酸を原料とする還元的アミノ化の一種である Eschweiler-Clarke 反応がある。しかし、これらの反応は選択性が低く、毒性試薬の使用と多量の廃棄物が発生する。

近年では遷移金属触媒を用いたメタノールとアミンを原料とする *N*-メチル化反応のような環境調和型合成反応が多くの注目を集めてきた[1,2]。その一方、入手と取り扱いが簡単であり、経済面で優れたジメチルアミン水溶液を原料とする均一触媒系のジメチルアミノ化反応は今まで報告例が少なく、有機溶媒中の反応にとどまっている。

本研究では含窒素複素環カルベン（NHC）配位子を持つイリジウム錯体触媒を用いて各種のアルコールとジメチルアミン水溶液を原料とする高効率的なジメチルアミノ化反応の検討を行った。



1) T. Irrgang, R. Kempe, *Chem. Rev.* **2019**, *119*, 2524.
2) G. Toyooka, A. Tuji, K. Fujita, *Synthesis* **2018**, *50*, 4617.

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金属酸化物ナノワイヤに被覆したナノポーラス金属錯体の分子ふるい効果を用いた分子認識

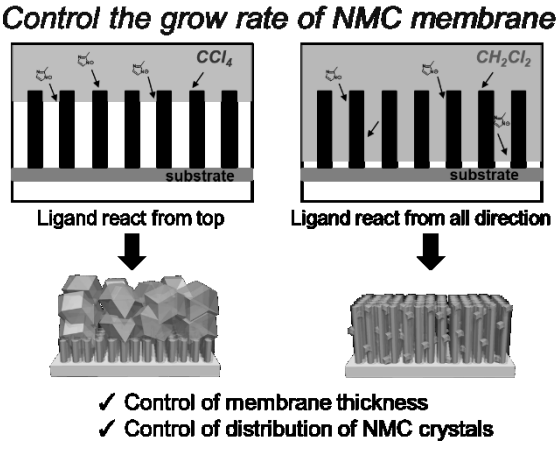
(名大院工[1]・名大工[2]) ○米津 章[1]・久保 淳弥[2]・日下 心平[1,2]・安井 隆雄[1,2]・馬場 嘉信[1,2]・松田 亮太郎[1,2]

Nanoporous Metal Complex Covered on Metal Oxide Nanowires for Molecular Recognition by Molecular Sieving ([1]*Graduate School of Engineering, Nagoya University*, [2]*School of Engineering, Nagoya University*) ○Akira Yonezu,[1] Junya Kubo,[2] Shinpei Kusaka,[1,2] Takao Yasui,[1,2] Yoshinobu Baba,[1,2] Ryotaro Matsuda[1,2]

Nanoporous metal complexes (NMCs) have been widely studied as gas separation membrane materials using molecular sieving effect due to their high designability of pore sizes. However, it is difficult to form a uniform film and control the membrane thickness using conventional membrane synthesis methods. In this study, we used zinc oxide nanowires as a template and controlled the growth rate of NMCs at the nanowire interface by using solvents to synthesize NMCs membrane with the desired crystal shape and thickness. When the imidazole-based ligand solution was added to the zinc oxide nanowires arrayed on the substrate, the nanowires were transformed into NMCs. When dichloromethane was used as the polar solvent, the NMCs membrane was formed to cover the entire nanowires with a thickness corresponding to the height of the nanowire. On the other hand, when carbon tetrachloride, a less polar solvent, was used, the NMCs membrane was gradually formed from the reaction interface depending on the reaction time.

Keywords : Nanoporous Metal Complexes; Metal Oxide Nanowires; Membrane Separation

ナノポーラス金属錯体 (NMC) はその高い設計性から、分子サイズに合わせた細孔による、分子ふるい効果を利用したガス分離膜材料として幅広く研究されている。しかしながら従来の膜合成法では、均一な膜の形成や膜厚の制御が困難であるという課題があった。そこで我々は、酸化亜鉛ナノワイヤを鋳型とし、ナノワイヤ界面での NMC の成長速度を溶媒によって制御することで、目的の結晶形状および膜厚を有する NMC 膜が合成できると考えた。実際に基板に整列させた酸化亜鉛ナノワイヤに対してイミダゾール系配位子溶液を作用させたところ、ナノワイヤが NMC へと変換された。溶媒として極性の高いジクロロメタンを用いた場合、NMC 膜がナノワイヤ全体を被覆するように、ナノワイヤの高さに応じた膜厚で形成され、一方で、極性の低い四塩化炭素を用いた場合は、反応時間によって NMC 膜が反応界面から徐々に形成されていくことが明らかになった。



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植物由来多糖類とヒドロキシアパタイトの複合化による高靭性バイオマス機械材料の開発

（同志社院理工）○奥田 耕平・水谷 義

Development of tough biomass mechanical material by hybridization of plant-derived polysaccharides and hydroxyapatite (*Graduate School of Science and Engineering, Doshisha University*) ○Kohei Okuda, Tadashi Mizutani

We synthesized composites of plant-derived polysaccharides and hydroxyapatite (HAP) by co-precipitation process with the aim of developing tough biomass mechanical materials. The composites of HAP and linear polysaccharide having carboxyl groups such as sodium alginate and TEMPO oxidized cellulose nanofibers had the bending strength of 60-90 MPa. These results indicate that the interaction between the organic-inorganic interface and linear structure of the polysaccharide improve the mechanical properties. Despite its low load on people and environment, these composites have a bending strength comparable to that of petroleum-derived plastic ABS copolymer resin, polycarbonate, polyacetal, and polybutylene terephthalate, so it can be expected to be used in new biomass materials.

Keywords : Biomass material; Hydroxyapatite ; Polysaccharide ; Cellulose nanofiber ; Composite

高靭性バイオマス機械材料の開発を目指し、トウモロコシデンプン（CS）、タピオカデンプン（TS）、グルコマンナン（GM）、アルギン酸ナトリウム（Alg）、TEMPO 酸化セルロースナノファイバー（TCNF）等の植物由来多糖類をそれぞれ $CaCl_2$ 水溶液中で溶解・分散させながら Na_2HPO_4・NaOH 水溶液を加え、骨の無機主成分ヒドロキシアパタイト $Ca_{10}(PO_4)_6(OH)_2$（HAP）と共沈[1]させ無機重量分率 60-70 wt%の複合体を得た。Fig. 1 のとおり共沈温度 70-90 °C で曲げ強度は大きくなり、その中でもカルボキシ基を持つ直鎖状の Alg は最も高い値を示した。さらに、この共沈手順（Protocol 1）を逆にし、Alg、また TCNF をそれぞれ Na_2HPO_4・NaOH 水溶液中で分散させながら $CaCl_2$ 水溶液を加え HAP と複合化（Protocol 2）すると、Fig. 2 のとおり曲げ強度がさらに向上した。これらの結果から、有機-無機界面の結合を形成できるカルボキシ基、多糖類の直鎖構造、十分な HAP の結晶成長、多糖類の構造を制限することなく HAP と共沈させることで複合体の機械的性質が向上することがわかった[2]。人や環境に低負荷であるにも関わらず、石油由来プラスチックの ABS 共重合樹脂やポリカーボネート、ポリオキシメチレン、ポリブチレンテレフタレートなどに匹敵する曲げ強度[3]を示すことから、新規のバイオマス機械材料への利用が期待できる。

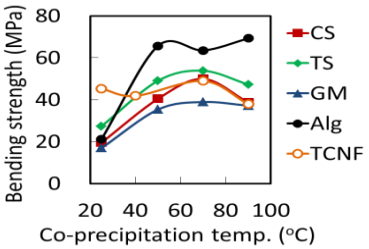

Fig. 1. Effects of co-precipitation temperature and type of polysaccharide on the bending strengths of the composites

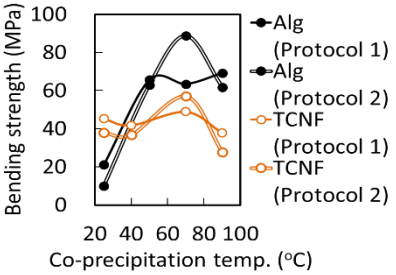

Fig. 2 Effects of co-precipitation temperature and protocols on bending strengths of the composites

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2) K. Okuda *et al. ACS Sustainable Chem. Eng.* 9, pp. 158-167 (2021)
3) プラスチック読本第 22 版（株式会社プラスチックス・エージ）（2019 年発行）

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デンプン由来の 1,5-アンヒドロ-D-グルシトール系糖脂質が形成するオルガノゲルとその特性

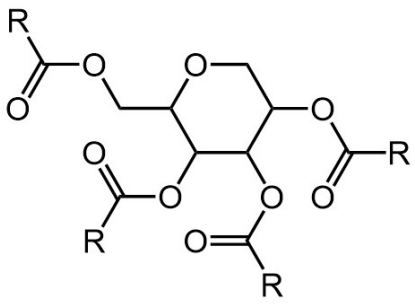
（農研機構[1]・サナス[2]）○岩浦 里愛[1]・今場 司朗[1]・加治木 隆仁[2]

Organogels formed from a starch-derived 1,5-anhydro-D-glucitol glycolipid and their properties ([1]*National Agriculture and Food Research Organization*, [2]*SUNUS Co., Ltd.*)
○Rika Iwaura,[1] Shiro Komba,[1] Takahito Kajiki[2]

We synthesized an alicyclic compound 16AG from the palmitoylated 1,5-anhydro-D-glucitol and found that the 16AG molecules gelatinize various kinds of organic solvents. The sol-to-gel phase transition temperatures of the organogels exhibited different depending on the solvents and could be controlled by the mixed use of the solvents. The organogels consisted of fibrous networks formed from the self-assembly of 16AG molecules via solvophobic interaction and weak hydrogen bondings between CH···OC moieties. DSC measurement of the paraffin gel containing 16AG which possesses a gel-to-sol phase transition temperature at 45 °C, showed exothermic and endothermic peaks at 8 and 32 °C while gel state kept remained. The paraffin gel containing 16AG produced by slow cooling showed only a peak corresponded to the gel-to-sol phase transition. Therefore, we suggest that the multiple exothermic and endothermic peaks were explainable by the phase transition from the metastable phase of the paraffin gel. It can be expected that it is applicable as a heat storage material utilizing the metastable state of the gel.

Keywords : 1,5-Anhydro-D-glucitol; Glycolipids; Organogel; Renewable materials; Self-Assembly

我々はデンプンから酵素合成により得られる 1,5-アンヒドロ-D-グルシトール（AG）の 2、3、4、6 位の水酸基をパルミトイル鎖で置換した脂環式化合物 16AG を合成しその機能を検討した結果、低極性から高極性まで広く有機溶媒をゲル化することを見出した。[1)]ゾル-ゲル相転移温度は溶媒に依存して 35 ℃～55 ℃を示し、溶媒を混合することによりゾル-ゲル相転移温度を制御することも可能であった。[2)]これらのゲルを分析した結果、16AG ダイマーがアルキル鎖の疎溶媒相互作用と CH···OC の弱い水素結合によって自己集合し、最小繊維幅 5.5 nm のファイバーネットワークを形成していることを明らかにした。さらに 16AG を含むパラフィンゲルの DSC 測定を行ったところ、昇温過程でゲル-ゾル相転移に相当するピーク（45 ℃）の他、8 ℃および 32 ℃に発熱および吸熱ピークが観察されたが、この温度域ではゲル状態を保ったままであった。非常にゆっくりとゲル化させたサンプルではゲル-ゾル相転移のピークのみが得られることから、複数の発熱および吸熱ピークは、ゲルが準安定状態を形成し、ゲル状態を保ったまま相転移することに相当するピークと推察した。ゲルの準安定状態を利用した蓄熱材料としての応用が期待できる。



16AG: $R_1 = R_2 = R_3 = R_4 = -C_{15}H_{31}$

1) T. Kajiki, S. Komba *J. Apply. Glycosci.*, **66**, 103 (2019). 2) R. Iwaura, S. Komba, T. Kajiki *Soft Matter*, 10.1039/D0SM02136A

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ヒドロゲルを利用したホウ素吸着に関する研究

（名市工研）○松村大植・中野万敬

Research on Adsorption of Boron using Hydrogels (*Nagoya Municipal Industrial Research Institute*) ○Daiki Matsumura, Kazunori Nakano

Hydrogels of gluconamide derivatives as an adsorbent for boron were synthesized from gluconolactone, polyetheleneimine, and crosslinking agents. The hydrogels absorbed boron effectively within 6 hours: the absorbed amount of boron reached as high as 14.3 mg/g-dry gel at maximum when the hydrogels were put into a solution containing 100 ppm borate ion. In addition, the hydrogels adsorbed boron in the wide range of pH 2-8.
Keywords : Adsorbent; Boron; Hydrogel; Gluconamide

ホウ素化合物はガラス製造業等多くの産業において幅広く使用されているが人体へ影響を及ぼすことから、2001 年に水質汚濁防止法に排水基準に「ホウ素及びその化合物」として追加された。ホウ素の排水処理法として、ホウ素と水酸基のキレート形成を利用したポリオール構造を有するイオン交換樹脂を用いた吸着法が知られている。本研究では吸着法によるホウ素処理に用いることが可能なヒドロゲルの開発を目指した。ヒドロゲルはイオン交換樹脂と異なり親水性が高く内部まで水溶液を浸透させることができる。ポリオールを導入したヒドロゲルを合成することができれば、母材表面で吸着を行うイオン交換樹脂とは異なりヒドロゲル内部でも吸着が可能となるため吸着容量が大きくなることが期待できる。

ポリエチレンイミンとグルコノラクトンを反応させたグルコンアミド誘導体をエチレングリコールジグリシジルエーテルと反応させ架橋することでホウ素吸着材となるヒドロゲルの合成を行った（図１）。このヒドロゲルを 100 ppm のホウ素溶液中にてホウ素吸着実験を行ったところ、6 時間以内に吸着は終了しホウ素の最大吸着量が 14.3 mg/g-dry gel となった。また、このヒドロゲルの pH の適用範囲は pH 2-8 と幅広いことがわかった。

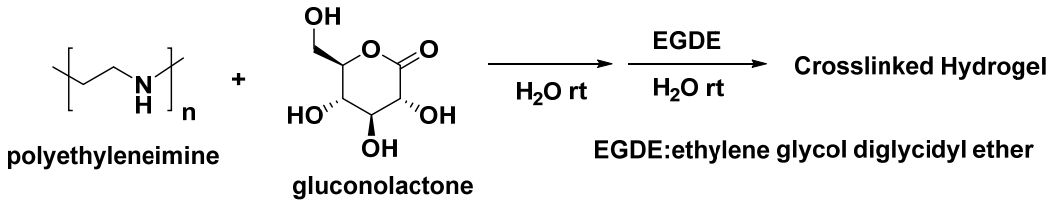

図１．ポリエチレンイミンとグルコノラクトンを用いたヒドロゲルの合成

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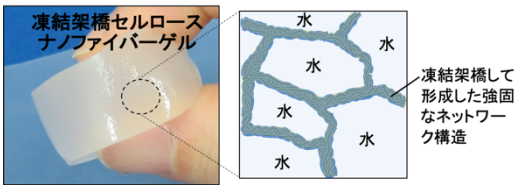
凍結架橋による高強度セルロースナノファイバーゲルの開発

(JAEA[1]・山大院工[2]・都産技[3]・東大院理[4]) ○関根 由莉奈[1]・○南川 卓也[1]・三浦 大輔[2]・柚木 俊二[2]・杉田 剛[1]・中川 洋[1]・山田 鉄兵[4]
Development of high-strength cellulose nanofiber hydrogels by freeze-crosslinking([1]*Japan Atomic Energy Agency*, [2]*Graduate School of Engineering, Yamagata University*, [3]*Tokyo Metropolitan Industrial Technology Research Institute*, [4]*Graduate School of Science, The University of Tokyo*) ○Yurina Sekine,[1] Takuya Nankawa,[1] Daisuke Miura,[2] Shunji Yunoki,[3] Tsuyoshi Sugita,[1] Hiroshi Nakagawa,[1] Teppei Yamada[4]

In this study, we developed a freeze crosslinking method to obtain a physically crosslinked hydrogel with high water content (> 94 %), high compressive strength (> 80 MPa), and high compressive recoverability from carboxymethyl cellulose nanofiber (CMCF) and citric acid (CA).[1] The CMCF hydrogel was formed by adding an aqueous solution of CA to a frozen CMCF sol and then thawing the sol. The reaction between the freeze-concentrated cellulose nanofiber and citric acid created a rigid porous structure. Without the freeze crosslinking method, the complex of the cellulose nanofiber sol and citric acid produced hydrogels, which easily collapsed under compressive stress. Because CMCF and CA are edible and are highly biodegradable, the hydrogels are non-toxic and eco-friendly, and our method does not require complicated procedures or synthetic regents other than CMCF, CA, and water.
Keywords : Carboxymethyl Cellulose Nanofiber; Freeze Concentration; High Compressive Strength; Adsorbent; Biodegradable

植物繊維由来のセルロースナノファイバー及びその誘導体は、ナノファイバーの特性とセルロースの性質を合わせ持つ、環境負荷の少ない高機能性バイオマス素材として高い注目を集めている。材料において、そのマクロな構造は物性を決定する大きな要因の一つである。本研究では、氷形成に着想を得て、極めて簡易な方法で高い圧縮強度と成型性を有するナノファイバーゲルの合成法及び材料を開発した。凍結させたカルボキシメチルセルロースナノファイバー(CMCF)溶液にクエン酸溶液を添加して溶解させたところ、氷が溶けると同時にハイドロゲルが形成した。このゲルは 80MPa 以上の高い圧縮強度を有しており、凍結過程無しに形成した CMCF―クエン酸ゲルに比べて、強度は 20 万倍以上向上していた。強度向上のメカニズムとして、氷形成時に氷の周囲に凝集した CMCF とクエン酸が反応した結果、水素結合による強固な三次元ネットワーク構造を形成し、高強度なゲルになったと考えられる。



1) Y. Sekine, T. Nankawa, S. Yunoki, T. Sugita, H. Yakagawa, T. Yamada, *ACS Appl. Polym. Mater.* **2020**, *2*, 5482-5491.

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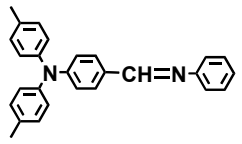
ベンジリデンアニリン系アモルファス分子材料－有機酸複合膜の発光特性

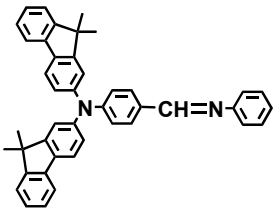
（室蘭工大）○塚田 琢真・北村 侑也・中野 英之
Emission Properties of Hybrid Films of Benzylideneaniline-based Amorphous Molecular Materials with Organic Acids (*Muroran Inst. Tech.*) ○Takuma Tsukada, Yuya Kitamura, Hideyuki Nakano

Novel moisture-sensitive hybrid films that exhibit reversible change in fluorescent color have been created using fluorescent amorphous molecular materials, BMBZA and BFBZA, with organic acids such as pentafluorobenzoic acid and benzoic acid. Orange fluorescent color of the films under ambient dry atmosphere was found to change drastically to greenish blue under wet atmosphere. It was suggested that such change in fluorescent color was due to switching the excited species between amorphous molecular materials and their protonated iminium cations. In addition, excited-state intermolecular proton transfer was suggested to contribute the orange fluorescence under dry atmosphere.
Keywords : Emitting Amorphous Molecular Material; Organic Acid; Reversible Emission Color Change; Excited-state Intermolecular Proton Transfer

外部刺激に応答して色彩や発光色が可逆的に変化する材料は、基礎科学的観点からのみならず、応用的観点からも興味がもたれる。われわれは最近、アモルファス分子材料と有機酸との複合による新機能の開拓を目的とした研究を進めており、水蒸気に応答して可逆的に色彩が変化する複合材料や、[1,2] 蛍光の OFF−ON が行える複合材料を報告している。[3] 本研究では、水蒸気に応答して発光色が変化するアモルファス分子材料と有機酸との複合膜の開拓と機構解明を目的として、ベンジリデンアニリン系アモルファス分子材料である BMBZA および BFBZA と様々な有機酸との複合膜を作製し、その発光挙動を検討した。



BMBZA



BFBZA

BMBZA ならびに BFBZA の単独膜は青緑色の発光を示すのに対し、有機酸としてペンタフルオロ安息香酸や安息香酸を用いた複合膜は乾燥雰囲気下で橙色発光を示した。この膜に水蒸気を吹きかけると発光色が青緑色に変化した。この現象は有機酸によるプロトン化と水蒸気の影響による脱プロトン化に基づくと考えられる。また、橙色の発光種の生成には、励起状態での分子間プロトン移動が関与していることを示唆する結果を得た。

1) H. Nakano et al., *RSC Adv.*, **2015**, 5, 2934. 2) H. Nakano et al., *Mater. Chem. Front.*, **2018**, 2, 90.
3) H. Nakano et al., *ChemistrySelect*, **2016**, 1, 1737.

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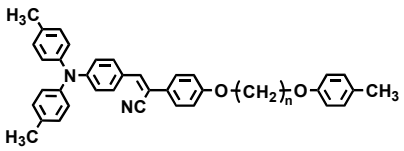
シアノスチルベン系アモルファス分子材料の発光と光反応

（室蘭工大[1]・東工大[2]・北大電子研[3]）○福島 寛也[1]・森 健介[1]・相良 剛光[2]・小門 憲太[3]・中村 貴義[3]・玉置 信之[3]・中野 英之[1]
Emission and Photochemical Reactions of Cyanostilbene-based Amorphous Molecular Materials ([1]*Muroran Inst. Tech.,* [2]*TITEC,* [3]*RIES, Hokkaido Univ.*) ○Hiroya Fukushima,[1] Kensuke Mori,[1] Yoshimitsu Sagara,[2] Kenta Kokado,[3] Takayoshi Nakamura,[3] Nobuyuki Tamaoki,[3] Hideyuki Nakano[1]

For the purpose of creating emitting amorphous molecular materials with photochemical reactivity, we have designed and synthesized noble cyanostilbene-based molecules, *N*,*N*-bis(4-methylphenyl)-4-(2-cyano-2-{4-[5-(4-methylphenyloxy)pentyloxy]-pentyl}ethenyl)aniline (BMAC5) and *N*,*N*-bis(4-methylphenyl)4-(2-cyano-2-{4-[6-(4-methylphenyloxy)hexyloxy]-phenyl}ethenyl)aniline (BMAC6), and investigate their emitting behaviors and photochemical reactivities in solid states as well as in solutions.
Keywords : Emitting Amorphous Molecular Material; Cyanostilbene; Solvatochromic Emission; Mechanochromic Emission; Photochemical Reaction

われわれは最近、1,4-bis(2-cyano-2-{4-[5-(4-methylphenyloxy)pentyloxy]phenyl}-ethenyl)-2,5-dimethoxybenzene (CSB-5) を設計・合成し、その結晶膜およびアモルファス膜が橙色の発光を示すこと、アモルファス膜の発光色が光照射に伴って変化していくこと、このことを利用して膜の発光パターニングを行えることを報告している [1]。本研究では、CSB-5 と同様の光機能を有するとともに、よりアモルファス化しやすい新たな発光性アモルファス分子材料の創製を目指して、新規シアノスチルベン系アモルファス分子材料 BMAC5 および BMAC6 を設計・合成し、それらの発光挙動ならびに光反応性について検討した。



BMACn (n=5,6)

BMAC5 のトルエン溶液は 500 nm 付近に極大を有する蛍光を示した。また、結晶試料は 530 nm に極大を有する緑色の蛍光を示すのに対し、アモルファス膜の極大蛍光波長は 540 nm であった。BMAC6 のトルエン溶液およびアモルファス膜の蛍光極大はそれぞれ BMAC5 のそれらと一致した。しかし、結晶試料は BMAC5 とは異なり 580 nm に極大を有する黄色の蛍光を示した。これは、結晶中におけるシアノスチルベン骨格部分の平面性が BMAC5 と BMAC6 で異なることに基づくと考えられる。

次に、光反応について検討をおこなった。BMAC5 の溶液中ならびにアモルファス膜中では 450 nm 光の照射に伴って光化学反応が進行し、電子吸収スペクトルが大きく変化していくとともに発光強度が大きく減衰した。これに対して、結晶試料に光を照射しても光化学反応は進行しなかった。BMAC6 も同様に、溶液中およびアモルファス膜中で光反応が進行するのに対し、結晶中で光反応は進行しなかった。

1) R. Kaneko, Y. Sagara, S. Katao, N. Tamaoki, C. Weder, H. Nakano, *Chem. Eur. J.*, **2019**, *25*, 6162.

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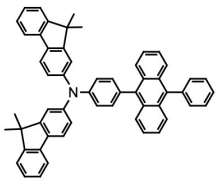
ジフェニルアントラセン骨格を有する新規アモルファス分子材料の発光と光反応

（室蘭工大）○松井 諒真・浅沼 宏紀・中野 英之
Emission and Photochemical Reaction of a Novel Amorphous Molecular Material Possessing Diphenylanthracene Moiety (*Muroran Inst. Tech.*) ○ Ryoma Matsui, Hiroki Asanuma, Hideyuki Nakano

We have designed and synthesized a novel amorphous molecular material, 9-{4-[bis(9,9-dimethylfluoren-2-yl)amino}phenyl]-10-phenylanthracene (BFAPA). BFAPA formed readily an amorphous glass with a glass-transition temperature of 157 °C. BFAPA in solution was found to exhibit solvatochromic emission, the spectrum being shifted to longer wavelength with increasing solvent polarity. It was also found that the crystalline sample of BMAPA exhibited fluorescence emission and that the emission color was changed from blue to light green by mechanical grinding. In addition, the photochemical reactions of BFAPA were found to take place both in solution and solid state.
Keywords : Amorphous Molecular Material; Diphenylanthracene; Solvatofluorochromism; Mechanofluorochromism; Photochemical Reaction

摩砕や加圧などの力学的刺激により可逆的に発光色が変化するメカノクロミック発光が注目を集めている。われわれは、励起状態で大きく構造が変化し、かつ容易にアモルファスガラスを形成することが期待される分子が、メカノクロミック発光材料創出のための分子設計指針となることを示している。[1-4] この指針に基づいて本研究では、新たなメカノクロミック発光性アモルファス分子材料の創出を目指して、ジフェニルアントラセン骨格を有する新規アモルファス分子材料 9-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}-10-phenylanthracene (BFAPA) を設計・合成し、溶液中ならびに固相における発光挙動を検討した。


BFAPA

BFAPA は溶融状態を冷却することで容易にアモルファスガラスを形成した（Tg = 157 °C）。また、溶媒極性の増大に伴って発光スペクトルが長波長シフトするソルバトクロミック発光を示した。さらに BFAPA の結晶が青色に発光するのに対し、磨砕により発光色は淡緑色に変化し、さらにアセトンに浸すことでもとに戻るメカノクロミック発光を示すことが確認できた。

BFAPA の結晶およびアモルファス膜における蛍光量子収率は、測定ごとのばらつきがあったものの、結晶で 0.50～0.65、アモルファス膜で 0.30～0.40 となった。さらに検討をすすめていくなかで、結晶中やアモルファス膜中で BFAPA の光反応が進行していることを示唆する結果を得た。

1) K. Mizuguchi, H. Kageyama, H. Nakano, *Mater. Lett*., **2011**, *65*, 2658. 2) K. Mizuguchi, H. Nakano, *Dyes Pigm*., **2013**, *96*, 76. 3) K. Okoshi, H. Nakano, *J. Photopolym. Sci. Tech*., **2014**, *27*, 535. 4) S. Manabe, E. Nagata, H. Nakano, *Rapid Commun. Photosci*., **2014**, *3*, 38.

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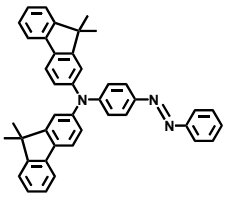
アゾベンゼン系分子ガラス微粒子の光誘起らせん構造形成

（室蘭工大）○松原 情菜・鵜飼 裕康・倉賀野 正弘・徳楽 清孝・中野 英之
Photoinduced Helical Structure Formation of Azobenzene-based Molecular Glass Particles (*Muroran Inst. Tech.*) ○Motona Matsubara, Hiroyasu Ukai, Masahiro Kuragano, Kiyotaka Tokuraku, Hideyuki Nakano

We have reported that azobenzene-based molecular glass particles fixed in an agar gel exhibited not only photo-elongation in the polarization direction but also undulatory motion upon irradiation polarized laser beam. In the present study, we have found that the ends of the photo-elongated glass particles took helical structures, and investigated the mechanism of such photoinduced helical structure formation.
Keywords : Photomechanical Effect; Molecular Glass; Azobenzene; Agar Gel; Polarized Light

われわれは、アゾベンゼン系分子材料が示すフォトメカニカル挙動に関する研究を進めている。最近では、寒天ゲル中に固定したアゾベンゼン系分子材料の BFlAB 微粒子にレーザー光の偏光を照射すると、偏光方向に伸長すると同時に持続的にうねり運動を示すことを見出している [1,2]。本研究では、この光うねり運動について詳細な知見を得ることを目的として、以下の検討を行った。



BFlAB

寒天ゲル中に保持した BFlAB 粒子に 60 分間偏光を照射し光伸長させた粒子の末端部分を共焦点蛍光顕微鏡で観察すると、らせん構造を形成していることが明らかになった (Fig. 1)。多数の粒子の末端部分の巻方向を確認した結果、右ねじ形よりも左ねじ形のほうが多く見られた。らせんの巻方向が偏るのは、粒子が光うねり運動をする際、周囲の寒天ゲルのキラリティーの影響を受けたためであると考えられる。

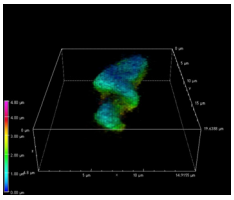


Fig. 1. 3D image of a BFlAB particle elongated in agar gel by 60 min irradiation with polarized laser beam.

巻方向の偏りが伸長し始めるときに決まっているのか、あるいは光照射時間とともに変化しているのかを明らかにするため、粒子のうねり運動の様子を 120 分間連続で撮影した。その結果、粒子が偏光方向と平行方向に伸長するだけではなく、伸びたり縮んだりを繰り返していることがわかった。さらに、縮んでから改めて伸長する際に、巻方向が逆転する場合があることが確認できた。これは、光照射中にいったん粒子の末端が縮むと、再び伸長する際に周囲のゲルの影響を受けなおして巻方向が決まるからだと予想される。

1) R. Ichikawa, H. Nakano, *RSC Adv,*. **2016**, 6, 36761.
2) H. Nakano, R. Ichikawa, H. Ukai, A. Kitano, *J. Phys. Chem. B*, **2018,** 122, 777

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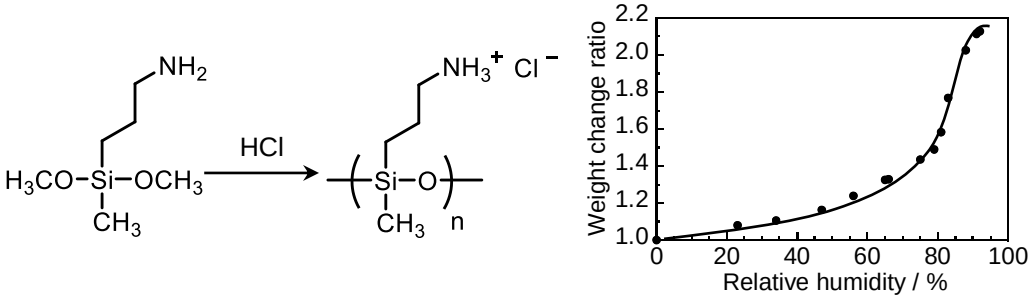
特異な力学物性を示す直鎖状シリコーンの開発

（名大院工[1]・立教大理[2]）○原 光生[1]・飯島雄太[1]・永野修作[2]・関 隆広[1]
Development of linear silicones with unique mechanical properties ([1]*Graduate School of Engineering, Nagoya University*, [2]*Department of Chemistry, Rikkyo University*) ○Mitsuo Hara,[1] Yuta Iijima,[1] Shusaku Nagano,[2] Takahiro Seki[1]

Ionic polysiloxane containing alkylamine hydrochloride side chains was synthesized by sol-gel reaction of silane coupling agents. The resulting polysiloxane was a viscous substance due to hygroscopic nature at room temperature and atmospheric pressure. However, its storage elastic modulus (G') increased to ca. 100 million times. The value of G' was 10^9 Pa, which was comparable to typical plastics. This large modulus change is due to multipoint crosslinking among ionic groups of the polysiloxane. Furthermore, we demonstrated that the ionic polysiloxane had a potential as an adhesive material.
Keywords : Polysiloxane; Moisture Absorption; Polyelectrolyte; Adhesion; Thermoset

直鎖状シリコーンは一般に、ガラス転移温度が低く、室温で粘性体の性状を示す。しかし、最近我々は、アルキルアミン塩酸塩を側鎖にもつポリシロキサンがプラスチックに匹敵する弾性率を有することを見出した[1)]。また、このポリシロキサンの弾性率は吸湿量に応じて最大で 1 億倍変化し、弾性率の高さだけでなく、弾性率の変化幅も特異的であった。

具体的には、3-アミノプロピルジメトキシシランを塩酸の存在下で重縮合させることで、アルキルアミン塩酸塩を側鎖にもつ直鎖状シリコーンを合成した。このシリコーン材料は、相対湿度 90%（RH=90%）において自重と同等の水分を吸湿し、高い吸湿性を示した。RH=80%の環境下で吸湿させたシリコーン材料の貯蔵弾性率は約 10 Pa であったが、乾燥させることで約 1 GPa まで増大した。1 GPa という値は、汎用プラスチックに相当する。柔軟材料の代名詞でもある直鎖状シリコーンがプラスチックに相当する弾性率を示したのは、アミン塩酸塩を介した多点イオン架橋による三次元ネットワークの形成が関係していると考えられる。また、この直鎖状シリコーン材料は接着材料としても機能し、高温下で接着力が増す特異な性質を示した。



1) "ポリシロキサン、接着剤および湿度センサ", 関 隆広, 原 光生, 飯島雄太, 竹下智也, 特願 2020-083502, 名古屋大学.

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乳酸-グリコール酸共重合体(PLGA)ナノカプセルゾルの透過型電子顕微鏡(TEM)測定

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Transmission Electron Microscope (TEM) Measurements of the PLGA Nanocapsule sol

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When the TEM measurements of the new nanocapsule sol, expected as medical materials such as MRI contrast agents (aquatic functional materials), was measured with and without various contrast media, it could be directly observed spherical. We will also report what we learned from these TEM measurement results.

Keywords : Nanocapsule sol ; Transmission Electron Microscope (TEM) ; Magnetic Resonance bio-Imaging(MRI); Manganese (Mn) ; Aquatic Functional Materials(AFM)

検診や治療に役立つ生体用磁気共鳴イメージング（MRI）を研究している。MRI 造影剤として利用可能な、マンガン（Mn）含有の乳酸-グリコール酸共重合体（PLGA）ナノカプセルゾルを創製し[1]、造影剤としての有用性[2]や Mn イオン保持性、徐放性および粒子径の均一性､安定性などの物性[3]を紹介してきた。さらに透過型電子顕微鏡(TEM)測定で物性について新たな知見が得られたので報告する。

【実験】試料のナノカプセルゾルは文献[4]を参考に各種改良し Mn 濃度を高め、平均粒子径 50～200nm で調製した[1]。透過型電子顕微鏡測定は、リンタングステン酸を用いたネガティブ染色（日立製 H-7100FA)、酢酸ウラニルを用いたネガティブ染色および無染色（日本電子製 JEM-1400 および JEM-2100）である。

【結果と考察】ウラン染色 TEM（図１）により真球のゾルであることが確認できた。さらに無染色 TEM-EDS により内水層(Mn)が確認できた(図２)。矢印の先の中心の黒点が Mn である。文献[4]およびその調製法からの推定で、粒子最深部に Mn 水溶液、中間層に PLGA、表面にポリエチレングリコール（PEG）リン脂質のダブルエマルジョン型微粒子ゾルと考えていたが、今回の TEM 測定結果はこれを支持している。なお、PEG リン脂質由来とみられる小微粒子径約 6～8nm が近接共存していた。動的光散乱（DLS）ではこの小微量子を含めて一粒子と捉えていたと考えている。

図１ TEM（JEM-1400）

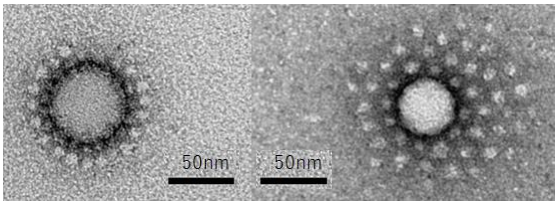
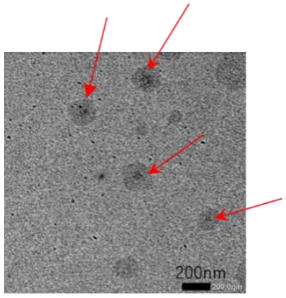


図２ TEM-EDS（JEM-2100）



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3) 新井,城,村山,青木,佐賀、日本化学会第 96 年会、3PA-069 (2016)
4) H.Sneh-Edri,D.Likhtenshtein,D.Stepensky,Mol.Pharmaceutics, 2011(8),1266-1275

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液中通電法を用いた金微粒子作製の検討

（防衛大機能材料）○小澤 真一郎・岩﨑 裕一郎・西尾 将也・齊藤 遼・宮﨑 尚・岡本 庸一

A Study on The Preparation of Gold Nanoparticle using The Electric Current Application in Electrolyte Solution (*Department of Materials Science and Engineering, National Defense Academy*) ○ Shinichirou Ozawa, Yuichiro Iwasaki, Masaya Nishio, Ryo Saito, Hisashi Miyazaki, Yoichi Okamoto

Previously, the formation of gold nanoparticles has reported in the electrolytic cell using gold wire as the electrode and inorganic salts (Na_2SiO_3, Na_2CO_3, Na_2SO_4, etc.) as the electrolyte by the electric current application.[1)] In this study, organic acids (acetic acid, citric acid, ascorbic acid) and their sodium salts were used as electrolytes for the preparation of gold nanoparticles by the electric current application. The electric current application was carried out in a 1 mole/l aqueous solution of six different electrolytes. The presence or absence of precipitates and the composition of the precipitates after energization are shown in Table 1 and the precipitates were identified by X-ray diffraction (XRD). In the case of electrolytes other than sodium ascorbate, precipitates were observed and confirmed to be gold by XRD. The obtained gold particles and electrolyte solutions are reported along with the results of optical and electrochemical methods of investigation.

Keywords : Electric Current Application; Gold Nanoparticles; Electrolyte; Sodium Ascorbate; New Materials

電解質に無機塩(Na_2SiO_3, Na_2CO_3, Na_2SO_4 など)を用いた電解質溶液を調整し、電極に金ワイヤ(ϕ 1.0 × 20 mm)をビーカーに設置して、数時間、液中通電することにより、金微粒子の生成を確認したことが報告されている [1)]。今回、有機酸（酢酸, クエン酸, アスコルビン酸）ならびにそれらのナトリウム塩を電解質に選定し、液中通電法による金微粒子作製の検討を行った。

液中通電法は、6 種類の電解質の 1.0 mole / l 水溶液中にて実施した。通電後の析出物の有無ならびに析出物の組成を Table 1 に示した。なお、析出物の同定は、X 線回折法(XRD)により行なった。アスコルビン酸ナトリウム以外の電解質の場合、析出物が確認され、XRD により金であることが確認された。得られた金微粒子および電解質溶液の光学的、電気化学的手法により調査した結果と合わせて、金微粒子作製について考察する。

Table 1 The summary of presence or absence and identification (XRD) of precipitates

electrolyte	precipitates	XRD / 2 θ (deg.)
Acetic acid	presence	Au / 38.21
Sodium acetate	presence	Au / 38.23
Citric acid	presence	Au / 38.21
Sodium citrate	presence	Au / 38.23
Ascorbic acid	presence	Au / 38.23
Sodium ascorbate	absence	-

1) Proposal of New Fabrication Method for Metal Nano-dots -Electric Current Apllication in Electrolyte Solution-. Y. Okamoto, K. Nimura, H. Nakatsugawa, H. Miyazaki, *J. Jpn. Soc. Powder Powder Metallurgy.* **2018**, *65*, 548-553.

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フレキシブル薄膜トランジスタ応用に向けた架橋性アミンポリマーを用いたカーボンナノチューブ薄膜の製膜

(名大院理[1]・名大院工[2]・名大未来研[3]・名大物国センター[4]) 松本 海成[1]・上野 和樹[1]・廣谷 潤[2]・大野 雄高[2,3]・○大町 遼[1,4]
Fabrication of Carbon Nanotube Thin Films for Flexible Transistor Applications using a Cross-linked Amine Polymer ([1]*Graduate School of Science,* [2]*Graduate School of Engineering, Nagoya University*, *Institute of Materials and Systems for Sustainability*, [3]*Nagoya University*, [4]*Research Center for Materials Science, Nagoya University*) Kaisei Matsumoto[1], Kazuki Ueno[1], Jun Hirotani[2], Yutaka Ohno[2,3], ○Haruka Omachi[1,4]

We report a solution-based SWCNT film fabrication using methoxycarbonyl polyallylamine (Moc-PAA). The NH_2-teminated surface of the cross-linked Moc-PAA layer enables the formation of highly dense and uniform SWCNT networks on both rigid and flexible substrates. TFTs that use the fabricated SWCNT thin film exhibited excellent performance with small variations.
Keywords : Carbon Nanotube, Cross-linking Reaction, Thin Film Transistor, Polyallylamine, Flexible TFT

単層カーボンナノチューブを用いた薄膜トランジスタ（SWCNT-TFT）は、その顕著な特性により、様々なフレキシブルエレクトロニクスへの利用が期待されている。TFT 用の SWCNT チャネル形成には通常、アミノ基で覆われた自己組織化単分子膜（SAM）上での薄膜形成法が使用されている。しかし、この方法は高度に酸化された基板表面が必須であり、フレキシブルトランジスタの土台となる柔軟な高分子基板には適していない。

今回我々は、メトキシカルボニルポリアリルアミン（Moc-PAA）を利用した液相プロセスでの SWCNT 薄膜形成法を開発した [1)]。Moc-PAA を基板上で架橋させることにより、表面がアミノ基で覆われた SWCNT 固定層を作製した。この SWCNT 固定層により、剛性基板と柔軟性基板のどちらにおいても高密度で均一な SWCNT 薄膜を製膜できることを確認した（図 1a）。この方法を用いて作製したフレキシブル SWCNT-TFT は、基板内においてほぼ均一かつ優れた性能を示した（図 1b）。

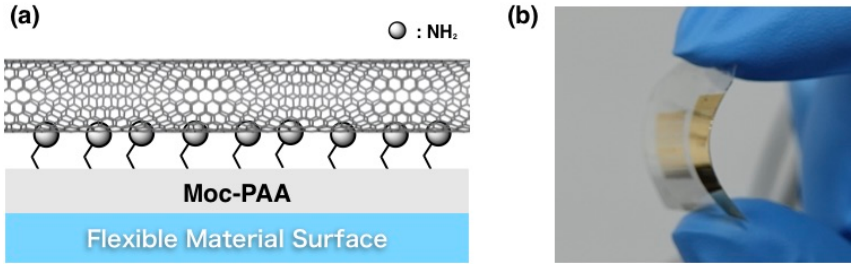

図 1. (a) Moc-PAA を利用した SWCNT 薄膜作製の模式図. (b)実際に作製したフレキシブル SWCNT-TFT.

1) Matsumoto, K.; Ueno, K.; Hirotani, J.; Ohno, Y.; Omachi, H. *Chem. Eur. J.* **2020**, *26*, 6118. ***Selected as "HOT PAPER"***

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ライブラリー vs. ライブラリーの共進化実験を通じた直交性 RNA-RNA 結合タンパク質の探索

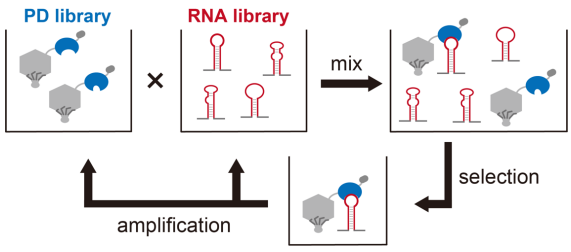
（OIST）○福永 圭佑・横林 洋平
Identification of orthogonal RNA-RNA-binding protein pairs through library-versus-library in vitro selection (*Nucleic Acid Chemistry and Engineering Unit, Okinawa Institute of Science and Technology Graduate University*) ○Keisuke Fukunaga, Yohei Yokobayashi

Keywords : Phage Display; SELEX; in vitro evolution; NGS; Synthetic Biology

進化分子工学の手法では通常、単一のターゲット分子に対してライブラリーの選択を行うが、“ライブラリー vs. ライブラリー”の共進化実験を行うことで相互作用するペアの情報を網羅的に取得しようとする試みがある。そこで我々は（1）“タンパク質”と“RNA”、2 種類のライブラリーを in vitro で共進化させることによって、RNA-タンパク質複合体（RNP）ペアを複数取得することができ、また（2）その中に互いに直交性を示す RNP ペアが含まれるのではないかと考えた。

まずは概念実証のためモデル系の立ち上げを行った。翻訳制御など合成生物学のツールとして利用されている（1）古細菌由来の RNA 結合タンパク質 L7Ae を提示するファージ粒子と（2）RNA 結合に関わるアミノ酸に変異を導入した iL7Ae を提示するファージ粒子を作製した。また、in vitro 転写で（3）L7Ae に結合する Kink-turn (Kt) RNA と（4）その変異体である dKt を調製した。この 4 者の中で相互作用しうるペアは L7Ae − Kt の組み合わせのみである。ファージ、RNA それぞれ 2 種類を試験管内で混ぜ、ファージ–RNA 複合体のみを選択・増幅したところ、正しいペアの濃縮が確認された。

次に、L7Ae の RNA 結合面周辺のアミノ酸をランダム化したファージディスプレイ（PD）ライブラリーを構築した。PD ライブラリーと RNA プールを試験管内で混ぜ合わせ、ファージ-RNA 複合体の選択・増幅を行うサイクルを複数回繰り返した（右図）。次世代シーケンシング（NGS）で配列を解析したところ、タンパク質ライブラリー、RNA ライブラリーともに一定の濃縮が見られ、複数のタンパク質-RNA ペアが選択されていることが示唆された。次にどのタンパク質と RNA が対応しているのかを調べるため、配列が濃縮されたタンパク質（LSx）を 20 種類リコンビナントタンパク質として調製し、これら個別の LSx に対して RNA ライブラリーの再選択を行い、結合ペアの特定を行った。現在、表面プラズモン共鳴装置を用いた分子間相互作用解析を進めているところである。



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グラフェンの二酸化塩素光酸化改質による生体分子固定化

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Immobilization of Biomolecules by Photoinduced Oxygenation of Graphene Surface with Chlorine Dioxide ([1]*Graduate School of Pharmaceutical Sciences, Osaka University*, [2]*Institute for Open and Transdisciplinary Research Initiatives, Osaka University*, [3]*Graduate School of Frontier Biosciences, Osaka University,* [4]*Institute for Advanced Co-Creation Studies, Osaka University*) ○Haruyasu Asahara,[1,2] Shota Kumano,[1] Junso Fujita,[3] Kei Ohkubo,[2,4] Tsuyoshi Inoue,[1,2]

Immobilization of biomolecules on graphene is an important technology due to the interesting applications of developing areas in the fields of biosensing, biofuel cells, nanobiocatalysis, and so on. Although covalent bond formation with a functional group on graphene is the most stable immobilization method, it is difficult to introduce functional groups to graphene surface due to their poor reactivity. In this study, we report herein photochemical introduction of oxygen functional groups to graphene with chlorine dioxide. We also examined the protein immobilization on oxidized graphene synthesized by the chlorine dioxide oxidation method.

Keywords : Graphene, Biomolecule, Chlorine Dioxide, Photo-oxidation, Cryo-EM

sp^2 結合炭素からなる二次元構造を有するグラフェンへの生体分子の固定化は、電子顕微鏡による直接観察やバイオセンサーの開発に繋がる重要な基盤技術である。しかし、グラフェンは反応性に乏しく生体分子固定の足がかりとなる官能基を導入することが困難である。目的基板上に担持されたグラフェン膜への官能基導入例として過マンガン酸カリウムなどの強力な酸化剤処理や、プラズマ処理のような物理的処理が報告されているものの、過剰酸化によるグラフェン骨格の損傷などの問題があり、グラフェンの構造的特徴を維持したままでの高効率な改質処理法の開発が強く望まれている。これに対し、本研究では最近我々が開発した二酸化塩素への光活性化に基づく新規酸化官能基導入法 [1,2] を用いてグラフェンへの酸素官能基導入を検討した。

金属基板上に担持したグラフェン薄膜に対し、二酸化塩素（$ClO_2^{\cdot}$）を作用させながら、常温・常圧下、LED ランプ（365 nm, 60 W）を用いた 10 分間の光照射により酸化改質を行った。酸化処理前後のグラフェン膜に対する水の接触角測定から本処理によって親水性が向上していることがわかった。また、X 線光電子分光（XPS）測定から、光二酸化塩素改質処理により C-O 結合や C=O 結合に由来する 286.0 と 288.0 eV のピークが増大していることが明らかとなり、酸素官能基が導入されていることが明らかとなった。その他、種々の分光測定結果とともに本酸化改質グラフェンの詳細な構造と反応メカニズム、本改質法により導入された官能基を利用したグラフェンへの蛋白質固定化についても合わせて報告する。

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2) Jia, Y.; Chen, J.; Asahara, H.; Asoh, T.; Uyama, H. *ACS Appl. Polym. Mater.*, **2019**, *1*, 3452.

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長時間・高感度のバイオイメージングを目指した生物発光基質フリマジン誘導体の開発

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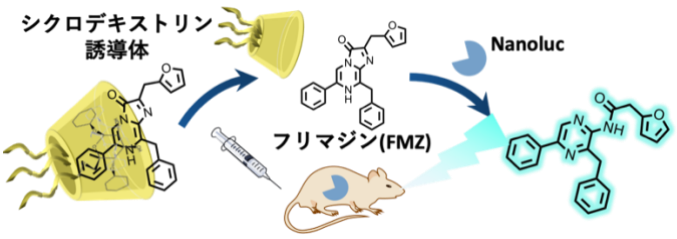
The Development of Furimazine Derivatives for Long-Term and High-Sensitive Bioluminescence Imaging ([1]Faculty of Science and Technology, Keio University, [2]Department of Chemistry, The Univesity of Tokyo) ○Mariko Orioka,[1] Yuki Mizui,[1] Masatoshi Eguchi,[2] Yuma Ikeda,[1] Hideaki Yoshimura,[2] Takeaki Ozawa,[2] Daniel Citterio,[1] Yuki Hiruta[1]

Bioluminescence imaging is a technique to visualize life phenomena by using light. It has attracted attention because of its non-invasiveness and high sensitivity. Among the bioluminescence systems, Nanoluc-Furimazine (FMZ) system is known for its high brightness. On the other hand, the bioluminescent substrate, FMZ has low solubility and stability, causing less sensitive and short-term *in vivo* imaging. Thus, the development of the novel FMZ derivatives that improve those properties are in need. Previously, we synthesized the FMZ derivatives which have the protective groups and achieved the improvement of stability[1)]. However, the solubility was still low. Thus, in this research, we developed the complex of FMZ (guest molecule) and cyclodextrin derivatives (host molecule). It showed higher solubility, stability, and longer-term luminescence. Now, we are aiming for the further improvement to achieve long-term bioluminescence imaging application.
Keywords : Bioimaging; Bioluminescence; Furimazine; Cyclodextrin

酵素基質反応で生じる光により生体内を可視化する生物発光イメージングは、非侵襲・高感度の観察を可能にする技術として注目を集めている。中でも人工生物発光酵素・基質である Nanoluc-Furimazine（FMZ）は、発光輝度の高さを特長とする。一方で基質 FMZ の水溶性および安定性の低さが、*in vivo* イメージングへの応用において障壁となっており、これらの物性を改善する新規 FMZ 誘導体の開発が望まれている。当研究室ではこれまで、FMZ の酸化分解を抑えるため、保護基を導入した誘導体を開発し、安定性の向上を達成したが [1)]、依然として水溶性は低いままである。そこで本研究では、基質 FMZ をゲスト分子、シクロデキストリン誘導体をホスト分子とする複合体を開発し、FMZ 単体よりも高い水溶性と安定性、酵素存在下での持続的な発光を示すことを確認した。さらに現在、長時間生物発光イメージングへの応用に向け、基質 FMZ の構造改変と組み合わせることで、さらなる物性の改善を目指している。



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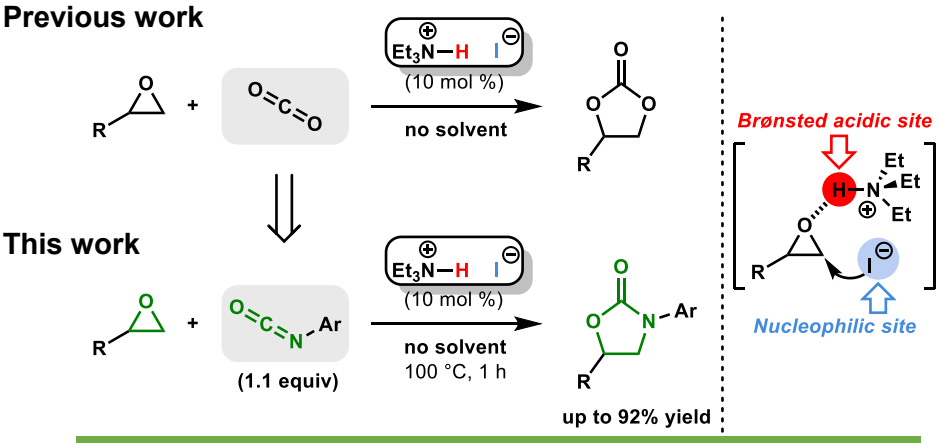
トリエチルアミンヨウ化水素酸塩を触媒とした 2-オキサゾリジノン類の実用的合成

（長崎大院水環）○奥野研・西依隆一・白川誠司
Practical Synthesis of 2-Oxazolidinones Using a Triethylamine Hydroiodide Catalyst (*Graduate School of Fisheries and Environmental Sciences, Nagasaki University*) ○Ken Okuno, Ryuichi Nishiyori, Seiji Shirakawa

Efficient synthesis of 2-oxazolidinones was achieved by cycloaddition reactions of epoxides and aryl isocyanates under the influence of triethylamine hydroiodide as a bifunctional organocatalyst. The importance of the bifunctional feature of the catalyst was clarified in the present work. The atom economical reactions efficiently proceeded under solvent-free conditions to provide important 2-oxazolidinone products in good to high yields.
Keywords : Bifunctional Catalysts; Organocatalysts; Heterocycles; Green Chemistry; Oxazolidinones

当研究室では最近、トリエチルアミンヨウ化水素酸塩触媒が、エポキシドと二酸化炭素の環化付加反応による環状カーボネートの合成に極めて有効であることを明らかにしている [1]。この報告を基に本研究では、二酸化炭素に代わりイソシアネートを反応基質として用いることで、トリエチルアミンヨウ化水素酸塩触媒下での 2-オキサゾリジノン合成が可能になると考え、検討した。

トリエチルアミンヨウ化水素酸塩触媒存在下、エポキシドとアリールイソシアネートの無溶媒下での環化付加反応を実施した [2]。その結果、対応する 2-オキサゾリジノン類が良好な収率で得られた。本反応では、入手容易なトリエチルアミンヨウ化水素酸塩が、ブレンステッド酸性部位と求核性部位を併せ持つ二官能性触媒として機能する。本手法は、医薬品開発における重要な骨格として知られる 2-オキサゾリジノン類の実用的合成法を提供する。



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2) R. Nishiyori, K. Okuno, S. Shirakawa, *Eur. J. Org. Chem.* **2020**, 4937.

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窒素上無保護ケチミンの新規触媒的直接合成法の開発とワンポット無保護アミン・アミノ酸類合成への応用

（九大院薬）○森本 浩之・近藤 優太・門田 哲弥・平澤 禎将・森崎 一宏・大嶋 孝志

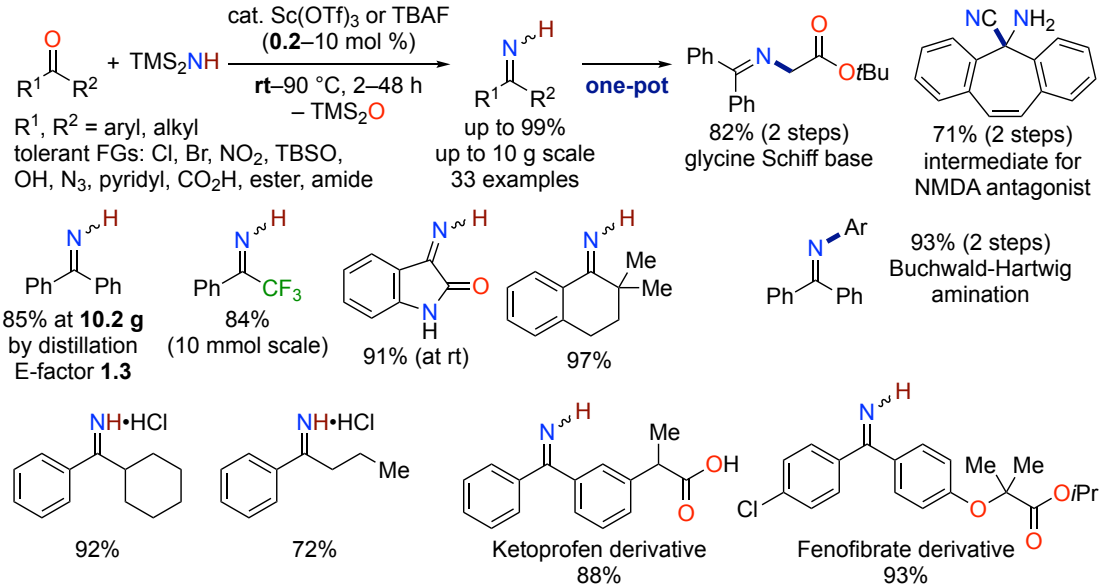
Development of New Catalytic Synthetic Methods of *N*-Unprotected Ketimines and its Applications to One-Pot Synthesis of *N*-Unprotected Amines and Amino Acid Derivatives

([1]*Graduate School of Pharmaceutical Science, Kyushu University*) ○Hiroyuki Morimoto, Yuta Kondo, Tetsuya Kadota, Yoshinobu Hirazawa, Kazuhiro Morisaki, Takashi Ohshima

Herein we report novel direct catalytic synthetic methods of *N*-unprotected ketimines from various carbonyl compounds. The reactions proceeded in the presence of commercially available Lewis acid or base catalysts even at a 10 g scale with broad functional group tolerance. Furthermore, the methods are applicable for efficient one-pot synthesis of various nitrogen-containing compounds such as amines and amino acid derivatives thanks to the low reactivity of the co-product.

Keywords : N-unprotected ketimine; catalyst; carbonyl compound; one-pot reaction; N-unprotected amines and amino acid derivatives

今回我々は、様々な含窒素化合物合成に利用可能な窒素上無保護ケチミン[1]を、入手容易なカルボニル化合物から直接合成可能な新規触媒的手法の開発に成功した[2]。本反応は市販のルイス酸またはルイス塩基触媒存在下 10 g スケールでも問題なく進行し、様々な置換基が共存可能だった。また、共生成物が低反応性である利点を活用し、ワンポット反応による様々な無保護アミン・アミノ酸類の効率的合成も実現したので、合わせて発表する。



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2) H. Morimoto,* T. Ohshima,* et al. JP 2018-082703, 2018, PCT/JP2019/12006, 2019; *Org. Process Res. Dev*. **2019**, *23*, 1718; *Org. Lett*. **2020**, *22*, 120; an additional manuscript in preparation.

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芳香族カルボニル化合物のα-ヒドロキシベンジルアニオン等価体への極性転換と二酸化炭素によるカルボキシル化反応

（分子研）○奥村　慎太郎・魚住　泰広
New umpolung strategy of aromatic carbonyl compounds to α-hydroxybenzyl anion equivalents: carboxylation with carbon dioxide (*Institute for molecular science*)○Shintaro Okumura, Yasuhiro Uozumi

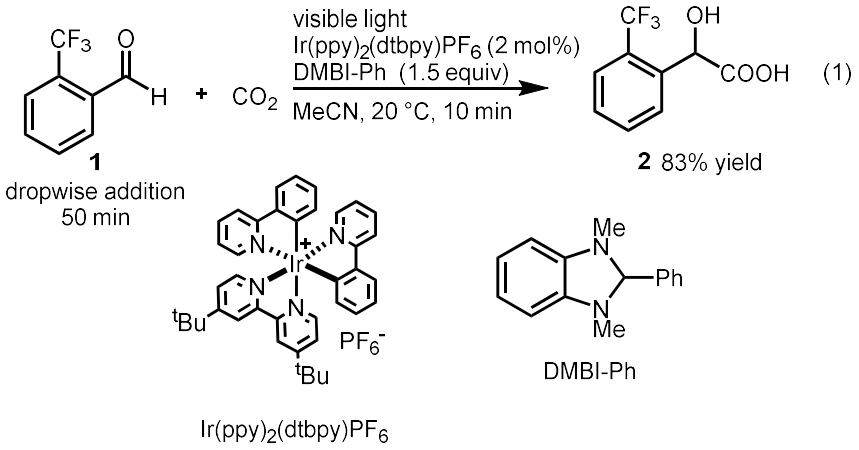
Nucleophilic addition to carbonyl groups is one of the most fundamental reactions in organic synthesis. Aromatic aldehydes and ketones generally serve as α-hydroxybenzyl cation equivalents and react with nucleophiles to give the benzyl alcohol derivatives.

On the other hand, umpolung is a useful strategy for designing reactions between electrophiles or nucleophiles. In this study, it was revealed that aromatic aldehydes and ketones served as α-hydroxybenzyl anion equivalents under photocatalytic reaction conditions. Aldehyde **1** reacted with carbon dioxide via α-hydroxybenzyl anion equivalent in the presence of an Ir photoredox catalyst, 1,3-dimethyl-2-phenylbenzimidazoline (DMBI-Ph) under visible light irradiation to give the mandelic acid derivative **2** in 83% yield (eq. 1).

Keywords : Iridium, benzimidazoline, photoredox catalysis, umpolung, carbon dioxide

カルボニルへの付加反応は最も基本的な有機反応のひとつであり、求電子的なカルボニルは求核剤と反応する。したがって芳香族アルデヒド、ケトンは通常 α-ヒドロキシベンジルカチオン等価体として挙動し、求核剤との反応によって、ベンジルアルコール誘導体を与える。

一方、カルボニルを求核的に極性転換できれば、求電子剤との反応が可能になる。本研究では、光触媒反応条件下において、芳香族アルデヒド、ケトンが極性転換し、求核的なα-ヒドロキシベンジルアニオン等価体として挙動することを明らかにした。Ir 光触媒と 1,3-ジメチル-2-フェニルベンゾイミダゾリン(DMBI-Ph)を含むアセトニトリル溶液に、可視光を照射しながら、芳香族アルデヒド **1** を滴下する事で、求電子剤である二酸化炭素への付加が進行し、マンデル酸誘導体 **2** が 83%収率で得られた（式 1）。



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ハスモンヨトウ幼虫による分子ナノカーボンの生物変換

（名大院理[1]・名大 WPI-ITbM[2]）○宇佐見 享嗣[1]・天池 一真[1]・伊丹 健一郎[1,2]
Biotransformation of Molecular Nanocarbon by *Spodoptera litura* ([1] *Graduate School of Science, Nagoya University,* [2] *Institute of Transformative Bio-Molecules (WPI-ITbM)*)
○Atsushi Usami,[1] Kazuma Amaike,[1] Kenichiro Itami[1,2]

Nanocarbons are nanometer-sized carbon materials composed of a benzene unit. Although we have already synthesized several molecular nanocarbons using the bottom-up method,[1] their direct derivatization methods are limited.[2,3]

We herein focused on a biotransformation reaction, known as a highly site-selective transformation reaction, to prepare nanocarbon molecule derivatives. *Spodoptera litura* larvae, which are resistant to various organic compounds, was used as a biocatalyst. In this presentation, the selective oxidation reaction of nanocarbon molecules and its partial structures by the *S. litura* larvae will be reported.

Keywords : Molecular Nanocarbon; Biotransformation; Spodoptera litura

ナノカーボンはベンゼン環を基本ユニットとするナノメートルサイズの炭素物質であり、興味深い物性を有した次世代マテリアルである。当研究室ではこれまでにボトムアップ式に分子として純粋な分子ナノカーボンの合成を達成している[1]。一方で分子ナノカーボンの直接誘導化に関しては、C–H 結合ホウ素化反応やクロム錯体を経由した反応が報告されているものの限定的である[2,3]。そのため、依然として分子ナノカーボンを直接誘導化する方法の開発は求められている。

そこで高選択的に官能基化が進行する生物変換反応に着目した。分子ナノカーボンである多環芳香族炭化水素の多くは環境汚染物質であるため、環境浄化を目的とした微生物による生物分解反応が実施されている[4]。しかしながら、有用物質への生物変換や昆虫に関した知見は皆無である。本研究では、多くの化合物に対し耐性を有するハスモンヨトウ幼虫を用いた分子ナノカーボンおよびその部分骨格の選択的な酸化反応をおこなった。

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3) Kubota. N.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 1356.

4) Liang, C.; Huang, Y.; Wang, H. *Appl. Environ. Microbiol.* **2019**, *85*, e02399-18.

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フェニルアルキル側鎖を持つロバストな高移動度 n 型有機半導体の開発と有機トランジスタへの応用

（東大院新領域 [1]・筑波大数物 [2]・北里大理 [3]・富士フイルム [4]・産総研東大 OPERANDO-OIL[5]・物材機構 [6]・JST さきがけ [7]）○熊谷 翔平 [1]・石井 宏幸 [2]・渡辺 豪 [3]・福﨑 英治 [4]・安中 辰朗 [1]・谷 征夫 [4]・杉浦 寛記 [4]・渡邉 哲也 [4]・黒澤 忠法 [1]・渡邉 峻一郎 [1,5]・竹谷 純一 [1,5,6]・岡本 敏宏 [1,5,7]

Synthesis and transistor applications of robust and high-mobility n-type organic semiconductors having phenylalkyl side chains ([1]*Graduate School of Frontier Sciences, The University of Tokyo,* [2]*Faculty of Pure and Applied Sciences, University of Tsukuba,* [3]*School of Science, Kitasato University,* [4]*FUJIFILM Corporation,* [5]*AIST-UTokyo OPERANDO-OIL,* [6]*WPI-MANA, NIMS,* [7]*PRESTO, JST*) ○Shohei Kumagai,[1] Hiroyuki Ishii,[2] Go Watanabe,[3] Eiji Fukuzaki,[4] Tatsuro Annaka,[1] Yukio Tani,[4] Hiroki Sugiura,[4] Tetsuya Watanabe,[4] Tadanori Kurosawa,[1] Shun Watanabe,[1,5] Jun Takeya,[1,5,6] Toshihiro Okamoto[1,5,7]

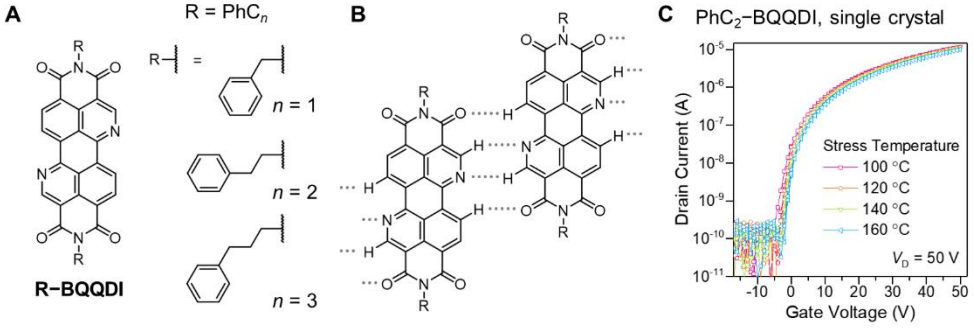
Organic semiconductors (OSCs) have attracted much attention as key materials for organic electronics. For practical application, OSCs are required to exhibit high carrier mobility, air stability, thermal-stress and processing durability, etc. In addition, it is desired that OSCs are compatible with solution processes although vacuum deposition is still a key technology.

Based on these demands, in this work, n-type OSCs were developed by a π-conjugated skeleton (3,4,9,10-benzo[*de*]isoquinolino[1,8-*gh*]quinolinetetracarboxylic diimide: BQQDI; Fig. A) and side chains for robust aggregated structures (Fig. B). PhC_n−BQQDI analogues (Fig. A) were successfully employed in air-stable thin-film transistors *via* either vacuum-deposition or solution-crystallization methods. For instance, the robustness was demonstrated by thermal durability of single-crystal PhC_2−BQQDI transistors (Fig. C).

Keywords : n-Type Organic Semiconductors; Thin-Film Transistors; Solution Process; Vacuum Deposition

有機半導体は有機エレクトロニクスデバイスの鍵材料として注目されており，実用的な観点から特に，高電荷移動度，大気安定性，熱ストレスやプロセスへの耐性に優れることなどが望まれる。また，高い結晶性を有する薄膜を作製するために，真空蒸着法や溶液法との適合性が重要である。

このような背景から，本研究では，集合構造のロバストネスを指向した π 電子系骨格および置換基設計により，n 型有機半導体ベンゾ[*de*]イソキノリノ[1,8-*gh*]キノリンテトラカルボン酸ジイミド（BQQDI）の開発をおこない，集合体構造および薄膜トランジスタ特性を明らかにすることで，本分子設計の有用性を示した。



Refs. T. Okamoto, S. Kumagai, J. Takeya *et al*, *Sci. Adv.*, 2020, **6**, eaaz0632.; *Chem. Mater.*, 2020, **32**, 9115.; *Adv. Mater.*, 2020, **32**, 202003245.

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薬用植物抽出物を基質とした Ugi 反応による天然物連結型分子の合成

（九大基幹[1]・九大院理[2]）○友原 啓介[1]・大橋 奈央[2]・野瀬 健[1,2]

Synthesis of natural product-connected molecules by Ugi reaction using medicinal plant extracts as substrates ([1]*Facultry of Arts and Science, Kyushu University*, [2]*Graduate School of Science, Kyushu University*) ○Keisuke Tomohara,[1] Nao Ohashi,[2] Takeru Nose[1,2]

A chemical engineering of natural product extracts has been recognized as a simultaneous synthetic method of natural product-like molecules. This study presents the first example of chemical engineering of a mixture of natural plant extracts to synthesize a natural product-connected molecule. Under the optimized Ugi reaction conditions, a mixture of castor oil and the methanol extract of *Curcuma zedoaria* in the presence of benzyl amine and cyclohexyl isocyanide afforded a novel natural product-connected molecule **1**.

Keywords : Natural product-like Ugi adduct; Medicinal plant extract; Chemical engineering of natural product extract; Ugi reaction

天然物抽出物そのものを基質とした合成反応（天然物抽出物のケミカルエンジニアリング）は、天然資源を起点とした天然物様分子の一斉合成法として注目されている。一方で、申請者のこれまでの研究[1]並びに国内外の関連研究[2]のいずれもが、抽出物に含まれる単独の官能基成分を標的とした並列分子変換であった。そのため、当該成分を単離したのち個別に誘導化する既存の研究手法に対する本法の優位性が低いという点に課題を残していた。そこで本研究では、天然物抽出物の混合物を基質とした Ugi 4 成分連結反応を行い、起源の異なる複数の天然有機分子が反応して同一分子に組み込まれた天然物連結型分子の合成を目指すこととした。

別途最適化した Ugi 反応条件を用いて、Ugi 反応の基質 4 成分のうち 2 つを薬用植物抽出物とした反応を試みた。すなわち、トウゴマ (*Ricinus communis*) 由来の脂肪酸混合物をカルボン酸源、ガジュツ (*Curcuma zedoaria*) のメタノール抽出物をケトン源として混合したものに対して、ベンジルアミンとシクロヘキシルイソシアニド（いずれも化成品）を添加したところ、トウゴマ成分の ricinoleic acid とガジュツ成分の curcumenone が反応して連結した新規天然物連結型 Ugi 付加体 **1** を得ることができた (Fig. 1)。**1** は、特異な縮環構造と 3 連続不斉炭素、並びに新規四置換不斉炭素を有していることから、合成化学と天然物化学の双方の長所を併せ持った本分子変換法ならではの反応成績体と言える。本結果は、天然物抽出物のケミカルエンジニアリングによって天然物連結型分子の合成に成功した初めての研究例である。

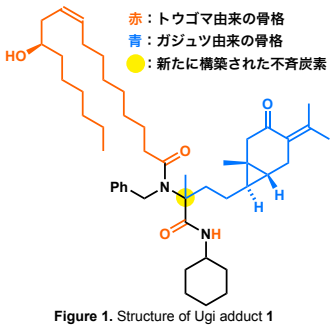

Figure 1. Structure of Ugi adduct **1**

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2) Recent review: R. L. E. Furlan *et al. Studies in Natural Products Chemistry* **2019**, *60*, 371.

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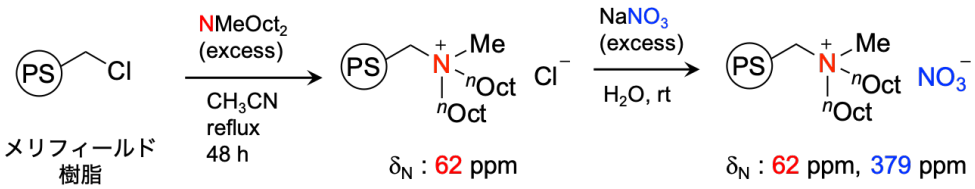
固体 DNP-NMR を活用するポリマー担持型有機分子触媒の開発

（産総研触媒化学融合 RC）○田中 真司・中島 裕美子・佐藤 一彦
Solid-state DNP-NMR spectroscopy for polymer-supported organocatalysts (*Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)*) ○Shinji Tanaka, Yumiko Nakajima, Kazuhiko Sato

Due to high reusability and separable nature, solid-supported catalysts are useful for practical organic synthesis. Organic polymers such as cross-linked polystyrene (PS) are relatively stable under acidic and basic conditions, and thereby a suitable solid support for acid-base mediated catalysis. A general issue of solid-supported catalysts is the ambiguity of structure due to limited analytical methods compared with those for molecular catalysts. Herein we demonstrated that the detailed structure of polymer-supported organocatalysts is elaborated by solid-state DNP-NMR spectroscopy, which enabled the observation of NMR signals with high sensitivity.
Keywords : solid-supported catalyst; solid-state NMR; organocatalyst

固体担持型触媒は、触媒除去や再利用性の高さから均一系触媒に比べて実用的であるものの、分析手法の乏しさから構造が不確定のまま反応に用いられることが多かった。我々は以前に、四級アルキルアンモニウム塩がグリシドール存在下でエステル交換反応に活性を示すことを見出し、グリシジルエステルの効率的な合成法となることを報告した [1),2)]。今回、本触媒をポリマー担持型へと展開するにあたり、近年注目されている高感度固体 NMR 測定手法である固体 DNP-NMR の活用に着目し、本分析法が触媒開発の強力な構造解析ツールとなること見出したので報告する。

最適なポリマー担持型アルキルアンモニウム塩として、Oct 基と Me 基を有し、アニオンとして硝酸イオンを有する構造を設計した（下図）。しかし、本触媒の調製においては、反応中のアンモニウム塩の三級アミンへの分解が懸念される。そこで各触媒調製段階において、固体 DNP-NMR を用いる天然存在比での ^{15}N NMR により、窒素官能基の状態を分析した。触媒担持後は四級窒素に相当する ^{15}N シグナルが 62 ppm 付近に観測された。このシグナルは塩素から硝酸イオンへのアニオン交換後も変化せず、新たに硝酸イオンのシグナルが 379 ppm 付近に観測された。固体 DNP-NMR 測定により構造を明確化できた本触媒は、狙い通りメチルエステルとグリシドールのエステル交換反応に高い活性を示した。さらに、固体 DNP-NMR を用いる触媒活性種や劣化種の同定も進めたので報告する。



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Deep Learning Analysis of SARS-CoV-2 Using the Codification Techniques of Conformations

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Keywords: Conformation; Deep Neural Network; Maximal Common Substructure; COVID-19; IUPAC Nomenclature

Theoretical calculations including density functional theory calculations can reproduce various observed spectra. However, there has been an increased need for ways to propose highly reliable candidates for a breakthrough on function development of organic molecules. The present calculation techniques cannot overcome this purpose. Big data of properly selected maximal common substructures (MCSs) may avoid the heavy loads of theoretical calculations and may be available for the design of new functional molecules. For this purpose, the codification techniques of conformations for a comparison of MCSs have been developed. In this presentation, an application of deep neural network-based software using protein supersecondary structure code (SSSC)[1,2] for the prediction of conformational variability to SARS-CoV-2 is described.

The deep neural network-based program for sequence-based prediction of SSSCs (SSSCPrediction) and the comparison program (SSSCPreds) of three deep neural network-based prediction systems (SSSCPred200, SSSCPred100, and SSSCPred) to predict the flexibility and conformational change of proteins were constructed.[3] The benchmarks (average concordance rates) of the three systems were as follows: for SSSCPred200, CullPDB, 0.905 (9851 subunits) and CB513, 0.911 (361 subunits); for SSSCPred100, CullPDB, 0.896 (17,169 subunits) and CB513, 0.907 (612 subunits); and for SSSCPred, CullPDB, 0.861 (17,169 subunits) and CB513, 0.882 (612 subunits).[3] SSSCPreds predicted the degree of flexibility for the receptor-binding motif of SARS-CoV-2 spike protein and the rigidity of the unique motif (SSSC: SSSHSSHHHH) at the S2 subunit.[3] Furthermore, the predicted SSSCs of D614G (Fig. 1) explained well the reduction of S1 shedding and increased infectivity without the latch between Asp614 and Thr859. Gly614 has the same stable conformation, which is found in a left-handed (LH) α-helix.

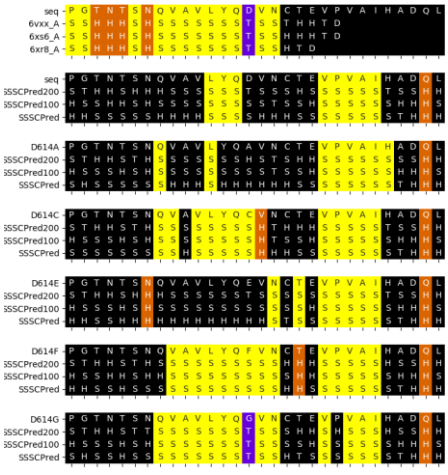

Fig. 1. Conformational variability prediction of D614G.

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