

Thu. Mar 24, 2022

D202

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

[D202-2pm] 01. Education and History of Chemistry

Chair: Keiko Miyamoto, Shuichi Takahara

1:00 PM - 2:20 PM D202 (Online Meeting)

[D202-2pm-01] Practice of the hypothesis-experiment class at university and developing teaching materials aimed at forming of the metal concept

○Shuichi Takahara<sup>1</sup> (1. Okayama University of Science)

1:00 PM - 1:20 PM

[D202-2pm-02] Comprehensive Physical Chemistry Learning Based on Blended Learning: A New Laboratory Course

○Hiroto Mori<sup>1,2</sup>, Nahoko Kuroki<sup>1</sup> (1. Chuo University, 2. Institute for Molecular Science)

1:20 PM - 1:40 PM

[D202-2pm-03] A Suggestion on the Review of Several Basic Terms Used in University Organic Chemistry Classes

○Masato M. Ito<sup>1</sup> (1. Soka Univ., Fac. of Sci. & Eng.)

1:40 PM - 2:00 PM

[D202-2pm-04] Scientific English for Graduate School and University Students

○Keiko Miyamoto<sup>1</sup> (1. Rikkyo University)

2:00 PM - 2:20 PM

A204

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

[A204-2am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Kenji Sugisaki, Yuta Hori

9:00 AM - 11:20 AM A204 (Online Meeting)

[A204-2am-01] Proton conduction mechanism for anhydrous imidazolium hydrogen succinate investigated by quantum chemical calculation

○Yuta Hori<sup>1</sup>, Shun Dekura<sup>2</sup>, Tomonori Ida<sup>3</sup>, Motohiro Mizuno<sup>3</sup>, Hatsumi Mori<sup>2</sup>, Yasuteru

Shigeta<sup>1</sup> (1. University of Tsukuba, 2. The University of Tokyo, 3. Kanazawa University)

9:00 AM - 9:20 AM

[A204-2am-02] The method of calculation in spin (skyrmion and antiskyrmion)

○Tomohito Yamagishi

9:20 AM - 9:40 AM

[A204-2am-03] Development of the structure-based Gaussian expansion method: Application to hydrogen tunneling in malonaldehyde

○Kazuma Suzuki<sup>1</sup>, Manabu Kanno<sup>1</sup>, Hirohiko Kono<sup>1</sup> (1. Tohoku University)

9:40 AM - 10:00 AM

[A204-2am-04] Molecular simulation that incorporates classical equation of motion for free electrons in metal: Photo-absorption and energy relaxation of nano-particle in solution

○Atsushi Yamada<sup>1</sup> (1. University of Tsukuba)

10:00 AM - 10:20 AM

[A204-2am-05] Quantum chemical calculations on quantum computers: Development of a quantum phase difference estimation algorithm

○Kenji Sugisaki<sup>1,2,3</sup>, Chikako Sakai<sup>1</sup>, Kazuo Toyota<sup>1</sup>, Kazunobu Sato<sup>1</sup>, Daisuke Shiomi<sup>1</sup>, Takeji Takui<sup>1</sup> (1. Osaka City University, 2. JST PRESTO, 3. CQuERE/TCG CREST)

10:20 AM - 10:40 AM

[A204-2am-06] Development of anharmonic vibrational structure theory using backflow transformation

○Kiriko Ishii<sup>1</sup>, Masanori Tachikawa<sup>1</sup>, Tomomi Shimazaki<sup>1</sup>, Yukiumi Kita<sup>1</sup> (1. Yokohama city university)

10:40 AM - 11:00 AM

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

[A204-2pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Yoshiki Ishii, Shuji Ogata

1:20 PM - 3:20 PM A204 (Online Meeting)

[A204-2pm-01] First-principles simulations of protonation and adhesion weakening of organic-inorganic interface under wet conditions

○Shuji Ogata<sup>1</sup>, Masayuki Uranagase<sup>1</sup> (1. Nagoya Institute of Technology)  
1:20 PM - 1:40 PM

[A204-2pm-02] Evaluation of vibrational energies and wave functions of CO<sub>2</sub> on a quantum computer

○Erik Loetstedt<sup>1</sup>, Kaoru Yamanouchi<sup>1</sup>, Takashi Tsuchiya<sup>2</sup>, Yutaka Tachikawa<sup>2</sup> (1. The University of Tokyo, 2. DIC Corporation)  
1:40 PM - 2:00 PM

[A204-2pm-03] Comparative Study of Electron Density Distribution Maps and Crystal Structure Factors of Mg<sub>3</sub>BN<sub>3</sub> High Pressure Phase by Discrete Cosine Transform and Maximum Entropy Method

○Hideo Hiraguchi<sup>1</sup> (1. The Institution of Professional Engineers, Japan)  
2:00 PM - 2:20 PM

[A204-2pm-04] Numerical study for kinetic control of coordination self-assembly: M<sub>4</sub>L<sub>4</sub> square complex as an example

○Satoshi Takahashi<sup>1</sup>, Hirofumi Sato<sup>2,3,4</sup>, Shuichi Hiraoka<sup>1</sup> (1. Graduate School of Arts and Sciences, The University of Tokyo, 2. Department of Molecular Engineering, Kyoto University, 3. ESICB, Kyoto University, 4. Fukui Institute for Fundamental Chemistry, Kyoto University)  
2:20 PM - 2:40 PM

[A204-2pm-05] Impact of Kinetic Temperatures in Microwave Heating

○Makoto Koike<sup>1,2</sup> (1. Micro Patent Office, 2. Makoto Koike Microwave Research Institute)  
2:40 PM - 3:00 PM

[A204-2pm-06] Molecular Dynamics Analysis of Extreme Pressure Additives using Reactive and Classical Force Field

○Hitoshi Washizu<sup>1</sup>, Kyosuke Kawakita<sup>1</sup>, Yuki Iike<sup>1</sup>, Mutsuki Homma<sup>1</sup>, Riku Araki<sup>1</sup>, Yoshiki Ishii<sup>1</sup>, Hiroaki Koshima<sup>2</sup> (1. Univ. Hyogo, 2. Idemitsu Kosan)  
3:00 PM - 3:20 PM

## [F302-2pm] 03. Physical Chemistry -Structure-

Chair: Tahei Tahara, Rintaro Shimada

2:00 PM - 3:40 PM F302 (Online Meeting)

[F302-2pm-01] Complete picture of vibrational relaxation of OH stretch at the air/H<sub>2</sub>O interface:

From hydrogen-bonded OH to free OH

○Woongmo Sung<sup>1</sup>, Ken-ichi Inoue<sup>1</sup>, Satoshi Nihonyanagi<sup>1</sup>, Tahei Tahara<sup>1</sup> (1. RIKEN)  
2:00 PM - 2:20 PM

[F302-2pm-02] Ultrafast vibrational dynamics of the free OD at the air/water interface revealed by time-resolved heterodyne-detected vibrational sum frequency generation spectroscopy

○Mohammed Ahmed<sup>1,2</sup>, Satoshi Nihonyanagi<sup>1,2</sup>, Tahei Tahara<sup>1,2</sup> (1. Molecular Spectroscopy Laboratory, RIKEN, 2. Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics)  
2:20 PM - 2:40 PM

[F302-2pm-03] Elucidation of pK<sub>a</sub> Value at Silica/Water Interface Using HD-VSFG Spectroscopy and Model-Independent Spectral Decomposition

○Feng Wei<sup>1</sup>, Shu-hei Urashima<sup>1</sup>, Satoshi Nihonyanagi<sup>1,2</sup>, Tahei Tahara<sup>1,2</sup> (1. Molecular Spectroscopy Laboratory, RIKEN, Wako, Saitama, Japan, 2. Ultrafast spectroscopy Research Team, RIKEN Center for Advanced Photonics, Wako, Saitama, Japan.)  
2:40 PM - 3:00 PM

[F302-2pm-04] Probing Ring Size-Dependent Structural Dynamics of Cycloparaphenylene Using Femtosecond Stimulated Raman Spectroscopy

○Hikaru Sotome<sup>1</sup>, Yusuke Morita<sup>1</sup>, Hiroshi Miyasaka<sup>1</sup> (1. Osaka Univ.)  
3:00 PM - 3:20 PM

[F302-2pm-05] ESR study of non-TEMPO radicals incorporated in nanospace in crystalline Zn complex

○Hirokazu Kobayashi<sup>1</sup>, Kento Akiniwa<sup>2</sup>, Fumiyasu Iwahori<sup>3</sup>, Hidehiko Honda<sup>1</sup>, Masato Yamamoto<sup>1</sup> (1. Faculty of Arts and Sciences at Fujiyoshida, 2. Graduate School of Integrated Basic Sciences, College of Humanities and

F302



Sciences, Nihon University, 3. College of  
Humanities and Sciences, Nihon University)  
3:20 PM - 3:40 PM

## F203

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

### [F203-2pm] 04. Physical Chemistry -Properties-

Chair: Oshikiri Tomoya, Daichi Eguchi

1:40 PM - 3:40 PM F203 (Online Meeting)

#### [F203-2pm-01] Extrinsic Chirality by Interference between Two Plasmonic Modes on an Achiral Rectangular Nanostructure Using Multi-photon Photoemission Electron Microscopy

○Oshikiri Suganami Tomoya<sup>1</sup>, Quan Sun<sup>1</sup>, Hiroki Yamada<sup>1</sup>, Shuai Zu<sup>1</sup>, Keiji Sasaki<sup>1</sup>, Hiroaki Misawa<sup>1,2</sup> (1. Hokkaido University, 2. National Yang Ming Chiao Tung University)

1:40 PM - 2:00 PM

#### [F203-2pm-02] Surface-enhanced Raman Scattering Substrate under Modal Strong Coupling between Nanocavity and Plasmons of Gold Nanoparticles Loaded by Self-assembly Method

○Yoshiki Suganami<sup>1</sup>, Tomoya Oshikiri<sup>1</sup>, Hideyuki Mitomo<sup>1</sup>, Xu Shi<sup>1</sup>, Yasutaka Matsuo<sup>1</sup>, Kuniharu Ijiri<sup>1</sup>, Hiroaki Misawa<sup>1,2</sup> (1. Hokkaido University, 2. National Yang Ming Chiao Tung University)

2:00 PM - 2:20 PM

#### [F203-2pm-03] Near-field Distribution under Modal Strong Coupling with Coherent Interaction

○Yen-En Liu<sup>1</sup>, Xu Shi<sup>1</sup>, Tomoya Oshikiri<sup>1</sup>, Yuji Sunaba<sup>1</sup>, Keiji Sasaki<sup>1</sup>, Hiroaki Misawa<sup>1,2</sup> (1. Hokkaido University, 2. National Yang Ming Chiao Tung University)

2:20 PM - 2:40 PM

#### [F203-2pm-04] Transporting and transferring electrons across perovskite-acceptor interfaces.

○Sachith Bhagyashree Mahesha<sup>1</sup>, Takuya Okamoto<sup>1</sup>, Ghimire Sushant<sup>4</sup>, Tomokazu Umeyama<sup>1,3</sup>, Yuta Takano<sup>1</sup>, Hiroshi Imahori<sup>1,2</sup>, Vasudevanpillai Biju<sup>1</sup> (1. Hokkaido University, 2. Kyoto University, 3. University of Hyogo, 4.

University of Rostock)

2:40 PM - 3:00 PM

#### [F203-2pm-05] Processing of Ni thin film by sub-micron focusing of high-order harmonic pulses in the XUV region

○Hiroto Motoyama<sup>1</sup>, Atsushi Iwasaki<sup>1</sup>, Hidekazu Mimura<sup>2</sup>, Kaoru Yamanouchi<sup>1</sup> (1. School of Science, The University of Tokyo, 2. School of Engineering, The University of Tokyo)

3:00 PM - 3:20 PM

#### [F203-2pm-06] On-surface construction of host-guest complex and bias dependent structure switching

○Toyo Kazu Yamada<sup>1,2</sup>, Fumi Nishino<sup>1</sup>, Ryohei Nemoto<sup>1</sup>, Chi-Hsien Wang<sup>3</sup>, Masaki Horie<sup>3</sup>, Takuya Hosokai<sup>4</sup>, Yuri Hasegawa<sup>5</sup>, Keisuke Fukutani<sup>6</sup>, Satoshi Kera<sup>6</sup> (1. Chiba Univ., 2. Chiba Univ., 3. Taiwan Tsing Hua Univ., 4. AIST, 5. Ritsumeikan Univ., 6. IMS)

3:20 PM - 3:40 PM

## F102

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

### [F102-2pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Yoshiyuki Kageyama, Masashi Arakawa

1:00 PM - 2:40 PM F102 (Online Meeting)

#### [F102-2pm-01] Self-propelled Droplet Systems Using the Briggs-Rauscher Reaction

○Masakazu Kuze<sup>1</sup>, Muneyuki Matsuo<sup>1</sup>, Satoshi Nakata<sup>1</sup> (1. Graduate school of Integrated Science for Life, Hiroshima University)

1:00 PM - 1:20 PM

#### [F102-2pm-02] Self-oscillating menthylacetate swimmer

○Matsuo Muneyuki<sup>1</sup>, Satshi Nakata<sup>1</sup> (1. Hiroshima University)

1:20 PM - 1:40 PM

#### [F102-2pm-03] Interplay between collective dynamics of molecular-level reaction and self-oscillatory macroscopic transformation in an azobenzene derivative assembly under steady light irradiation

○Yoshiyuki Kageyama<sup>1</sup>, Yasuaki Kobayashi<sup>1</sup>, Daisuke Yazaki<sup>1</sup>, Tomonori Ikegami<sup>1</sup> (1. Hokkaido University)

1:40 PM - 2:00 PM

- [F102-2pm-04] Chemical reactivity of superatoms consisting of 13 group elements supported on organic surfaces  
 ○Tomoya Inoue<sup>1</sup>, Atsushi Nakajima<sup>1</sup> (1. The Univ. of Keio)

2:00 PM - 2:20 PM

- [F102-2pm-05] Photoelectron imaging of superatomic orbitals in silver cluster anions  
 ○Tasuku Nishizato<sup>1</sup>, Kento Minamikawa<sup>1</sup>, Haruki Hashimoto<sup>1</sup>, Kazuaki Matsumoto<sup>1</sup>, Masashi Arakawa<sup>1</sup>, Takuya Horio<sup>1</sup>, Akira Terasaki<sup>1</sup> (1. Department of Chemistry, Kyushu University)

2:20 PM - 2:40 PM

## D201

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

### [D201-2pm] 06. Analytical Chemistry

Chair: Daisuke Onoshima, Kenji Sueyoshi

1:40 PM - 3:40 PM D201 (Online Meeting)

- [D201-2pm-01] Analysis of membrane protein-specific lipids using gold nanoparticle-based method  
 ○Wangamnuayporn Supakorn<sup>1</sup>, Masanao Kinoshita<sup>1</sup>, Takayuki Kawai<sup>1</sup>, Nobuaki Matsumori<sup>1</sup> (1. Kyushu University)  
 1:40 PM - 2:00 PM
- [D201-2pm-02] Multifunctional Magnetic Gd Doped CuS Nanoparticles for Fluorescence/MR Bimodal Imaging-Guided Photothermal-Intensified Chemodynamic Synergetic Therapy of Targeted Tumors  
 ○Luo Minchuan<sup>1</sup>, Onoshima Daisuke<sup>2</sup>, Hiroshi Yukawa<sup>1,2,3</sup>, Baba Yoshinobu<sup>1,2,3</sup> (1. Graduate School of Engineering, Nagoya University, 2. Institute of Innovation for Future Society of Nagoya University, 3. National Institutes for Quantum and Radiological Science and Technology)  
 2:00 PM - 2:20 PM
- [D201-2pm-03] Development of single molecule electrical detection method for methylation-modified microRNA analysis  
 ○Takahito Ohshiro<sup>1</sup>, Yuki Komoto<sup>1</sup>, Ayumu

Asai<sup>1</sup>, Masamitsu Konno<sup>2</sup>, Hideshi Ishii<sup>1</sup>, Masateru Taniguchi<sup>1</sup> (1. Osaka University, 2. Tokyo University of Science)

2:20 PM - 2:40 PM

- [D201-2pm-04] Phase-separated structures in apple procyanidin-containing cell-sized liposome  
 ○Tsuyoshi Yoda<sup>1</sup> (1. Aomori Prefectural Industrial Technology Research Center, Hachinohe Industrial Research Institute)  
 2:40 PM - 3:00 PM
- [D201-2pm-05] Dark-field microscopic detection of bacteria using bacteriophage-modified SiO<sub>2</sub>@AuNP core-shell nanoparticles.  
 ○Masashi Imai<sup>1</sup>, Yosuke Niko<sup>1</sup>, Shingo Hadano<sup>1</sup>, Shigeru Watanabe<sup>1</sup>, Iyo Uchiyama<sup>3</sup>, Jumpei Uchiyama<sup>2</sup>, Shigenobu Matsuzaki<sup>4</sup> (1. Graduate School of Science, Kochi university, 2. Graduate School of Medicine Dentistry and Pharmaceutical Sciences, Okayama University, 3. Medical School, Okayama University, 4. Faculty of Health Science, Kochi Gakuen University)  
 3:00 PM - 3:20 PM
- [D201-2pm-06] Aptamer Selection Using a Microscale Electrophoretic Filtering Device  
 ○Kenji Sueyoshi<sup>1,2</sup>, Junku Takao<sup>1</sup>, Arisa Tobita<sup>1</sup>, Kaede Ueno<sup>1</sup>, Tatsuro Endo<sup>1</sup>, Hideaki Hisamoto<sup>1</sup> (1. Graduate School of Engineering, Osaka Prefecture University, 2. PRESTO, JST)  
 3:20 PM - 3:40 PM

## J401

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

### [J401-2pm] 07. Inorganic Chemistry

Chair: Takahiro Takei, Fumitaka Hayashi

1:00 PM - 3:40 PM J401 (Online Meeting)

- [J401-2pm-01] Scission of titania nanosheets via physical adsorption on a non-flat substrate  
 ○Nobuyuki Sakai<sup>1</sup>, Masahiko Suzuki<sup>1</sup>, Takayoshi Sasaki<sup>1</sup> (1. National Institute for Materials Science)  
 1:00 PM - 1:20 PM
- [J401-2pm-02] Nanofluidic Anion Transport through

# Reconstructed Membrane of Layered Double Hydroxide Nanosheets

○Fang XIAN<sup>1,2</sup>, Renzhi MA<sup>1,2</sup>, Yoshiyuki SUGAHARA<sup>2</sup>, Takayoshi SASAKI<sup>1</sup> (1. National Institute for Materials Science, 2. The Univ. of Waseda)

1:20 PM - 1:40 PM

## [J401-2pm-03] Synthesis of Fe-based (oxy)hydroxides nanosheets for oxygen evolution reaction (OER) electrocatalyst

○Lulu JIA<sup>1,2</sup>, Renzhi MA<sup>1,2</sup>, Yoshiyuki SUGAHARA<sup>2</sup>, Takayoshi SASAKI<sup>1</sup> (1. NIMS, 2. Waseda Univ.)

1:40 PM - 2:00 PM

## [J401-2pm-04] Bottom-up Synthesis of Amorphous Silica Nanosheets and Two-Dimensional Assembly

○Eisuke Yamamoto<sup>1,2</sup>, Kosuke Fujihara<sup>3</sup>, Yue Shi<sup>1</sup>, Makoto Kobayashi<sup>1</sup>, Minoru Osada<sup>1,4</sup> (1. IMASS, Nagoya University, 2. PRESTO, JST, 3. Nagoya University Graduate School, 4. WPI-MANA, National Institute for Materials Science)

2:00 PM - 2:20 PM

## [J401-2pm-05] Solution phase synthesis of borophene analogs

○Dongwan Yan<sup>1,2</sup>, Tetsuya Kambe<sup>2</sup>, Kimihisa Yamamoto<sup>2</sup> (1. KISTEC, 2. Tokyo Tech Laboratory for Chemistry and Life Science JST-ERATO)

2:20 PM - 2:40 PM

## [J401-2pm-06] Fabrication of Large-Sized MnO<sub>2</sub> Nanosheets from Layered Manganese Oxide Single Crystals and Application to Sensor Materials

○Hitomi Yano<sup>1</sup>, Akihisa Aimi<sup>1</sup>, Nobuyuki Sakai<sup>2</sup>, Takayoshi Sasaki<sup>2</sup>, Kenjiro Fujimoto<sup>1</sup> (1. Tokyo University of Science, 2. National Institute for Materials Science)

2:40 PM - 3:00 PM

## [J401-2pm-07] Flux Growth and Efficient Exfoliation of Layered Titanate and Niobate Crystals

○Fumitaka Hayashi<sup>1</sup>, Kakeru Umehara<sup>1</sup>, Nanako Tatewaki<sup>1</sup>, Furui Kenta<sup>1</sup>, Tomohito Sudare<sup>1</sup>, Maru Kashiwazaki<sup>1</sup>, Hiromasa Shiiba<sup>1</sup>, Kazunori Fujisawa<sup>1</sup>, Katsuya Teshima<sup>1</sup> (1. Shinshu

Univ.)

3:00 PM - 3:20 PM

## [J401-2pm-08] Formation of ordered structure by intercalation of phenol in organoclay investigated by molecular simulation

○Masaya Miyagawa<sup>1</sup>, Fumiya Hirosawa<sup>1</sup>, Hiromitsu Takaba<sup>1</sup> (1. Kogakuin University)

3:20 PM - 3:40 PM

## B304

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

## [B304-2pm] 08. Catalysts and Catalysis

Chair: Yusuke Kita, Kazuya Yamaguchi

1:20 PM - 3:40 PM B304 (Online Meeting)

## [B304-2pm-01] Al-doped Mesoporous Silica-supported Pd Complex Catalyst for the Tsuji-Trost Allylation

○Siming Ding<sup>1</sup>, Yuichi Manaka<sup>1,2</sup>, Ken Motokura<sup>1,3</sup> (1. Tokyo Tech., 2. AIST, 3. YNU)

1:20 PM - 1:40 PM

## [B304-2pm-02] Immobilized Iron Complex on Bipyridine-Based Periodic Mesoporous Organosilica for Hydrosilylation of Alkynes

○Xiao-Tao Lin<sup>1,2</sup>, Kazuhiro Matsumoto<sup>2</sup>, Yoshifumi Maegawa<sup>3</sup>, Kazuhiko Sato<sup>2</sup>, Norihisa Fukaya<sup>2,3</sup>, Jun-Chul Choi<sup>1,2</sup> (1. Graduate School of Pure and Applied Sciences, University of Tsukuba, 2. Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, 3. Toyota Central R&D Labs)

1:40 PM - 2:00 PM

## [B304-2pm-03] Hydrogenolysis of alcohols and carbonyl compounds to alkanes by Pt/Al(PO<sub>3</sub>)<sub>3</sub> catalyst

○Kento Oshida<sup>1</sup>, Xiongjie Jin<sup>1</sup>, Kyoko Nozaki<sup>1</sup> (1. The University of Tokyo)

2:00 PM - 2:20 PM

## [B304-2pm-04] Preparation and Catalytic Properties of Silica-Supported Pt Nanoparticles

○Toshiki Nishitoba<sup>1</sup>, Yusuke Ishizaka<sup>2</sup>, Kazuhiro Matsumoto<sup>1</sup>, Katsuhiko Takeuchi<sup>1</sup>, Norihisa Fukaya<sup>1</sup>, Kazuhiko Sato<sup>1</sup>, Jun-Chul

Choi<sup>1,2</sup> (1. National Institute of Advanced Industrial Science and Technology, 2. The Univ. of Tsukuba)

2:20 PM - 2:40 PM

[B304-2pm-05] Effect of Sodium Salt Additives on Intramolecular Cyclization of Alkynoic Acids Catalyzed by Au(0) Nanoparticles Catalysts Supported on Metal Oxides  
<sup>○</sup>Eiji Yamamoto<sup>1</sup>, Qi-An Huang<sup>1</sup>, Takaaki Ikeda<sup>1</sup>, Seiya Kawai<sup>1</sup>, Kazuki Haruguchi<sup>1</sup>, Haruno Murayama<sup>1</sup>, Tamao Ishida<sup>2</sup>, Tetsuo Honma<sup>3</sup>, Makoto Tokunaga<sup>1</sup> (1. Kyushu University, 2. Tokyo Metropolitan University, 3. Japan Synchrotron Radiation Research Institute)

2:40 PM - 3:00 PM

[B304-2pm-06] Intramolecular cycloamination of primary amines using gold nanoparticles deposited on fibrillated citric acid-modified cellulose  
<sup>○</sup>Butsaratip Suwattananuruk<sup>1</sup>, Yuta Uetake<sup>1,2</sup>, Hidehiro Sakurai<sup>1,2</sup> (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

3:00 PM - 3:20 PM

[B304-2pm-07] Enhancing the Catalytic Activity Utilizing Strong Metal-Support Interactions (SMSI) - Isomerization of Alkenes on Substituted Hydroxyapatite Supported Gold Catalysts  
<sup>○</sup>Akihiro Nakayama<sup>1</sup>, Ryusei Sodenaga<sup>1</sup>, Gangarajura Yuvaraj<sup>2</sup>, Ayako Taketoshi<sup>3</sup>, Toru Murayama<sup>1,4</sup>, Tetsuo Honma<sup>5</sup>, Norihito Sakaguchi<sup>6</sup>, Tetsuya Shimada<sup>1</sup>, Shinsuke Takagi<sup>1</sup>, Masatake Haruta<sup>1</sup>, Qiao Botao<sup>2</sup>, Wang Junhu<sup>2</sup>, Tamao Ishida<sup>1</sup> (1. Tokyo Metropolitan University, 2. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 3. Yokohama National University, 4. Yantai University, 5. Japan Synchrotron Radiation Research Institute, 6. Hokkaido University)

3:20 PM - 3:40 PM

## Organometallic Chemistry

Chair: Shiro Hikichi, Mio Kondo

9:00 AM - 11:40 AM J402 (Online Meeting)

[J402-2am-01] Electrochemical CO<sub>2</sub> Reduction Catalyzed by Metal Porphyrin Complexes: Control of the Catalytic Activity by Reaction Media  
<sup>○</sup>Kento Kosugi<sup>1</sup>, Hina Kashima<sup>1</sup>, Mio Kondo<sup>1,2</sup>, Shigeyuki Masaoka<sup>1</sup> (1. Graduate School of Engineering, Osaka University, 2. JST PRESTO)  
 9:00 AM - 9:20 AM

[J402-2am-02] Preparation of Coordination Polymer Glasses Encapsulating Metal Complex Catalysts  
<sup>○</sup>Hitoshi Izu<sup>1</sup>, Hiroyasu Tabe<sup>2</sup>, Yuji Namiki<sup>3</sup>, Takashi Kajiwarai<sup>1</sup>, Satoshi Horike<sup>2</sup> (1. National Institute of Advanced Industrial Science and Technology, 2. Kyoto University, 3. POLA Chemical Industries, Inc.)  
 9:20 AM - 9:40 AM

[J402-2am-03] pH-Insensitive Brønsted Acid-Base Site Embedded in a Pentanuclear Scaffold  
<sup>○</sup>Misa Tomoda<sup>1,2,3</sup>, Hitoshi Izu<sup>1,2</sup>, Yutaka Saga<sup>1</sup>, Mio Kondo<sup>1,4</sup>, Shigeyuki Masaoka<sup>1</sup> (1. Osaka University, 2. IMS, 3. SOKENDAI, 4. JST PRESTO)  
 9:40 AM - 10:00 AM

[J402-2am-04] Activation of a PNNP-ligated Fe complex with a base to facilitate photocatalytic CO<sub>2</sub> reduction  
<sup>○</sup>Taku Wakabayashi<sup>1</sup>, Kenji Kamada<sup>1</sup>, Jieun Jung<sup>1</sup>, Susumu Saito<sup>1,2</sup> (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)  
 10:00 AM - 10:20 AM

[J402-2am-05] Effect of hydrophobic interaction field on catalysis of metal complexes immobilized on mesoporous silica  
<sup>○</sup>Masaya Okamura<sup>1</sup>, Kou Kuwamoto<sup>1</sup>, Seiya Sakakura<sup>1</sup>, Nana Aizawa<sup>1</sup>, Shiro Hikichi<sup>1</sup> (1. Kanagawa university)  
 10:20 AM - 10:40 AM

[J402-2am-06] Highly efficient electrocatalysis by a Fe complex for water oxidation in a homogeneous solution.  
<sup>○</sup>Taichi Hayasaka<sup>1</sup>, Eman A. Mohamed<sup>1</sup>, Zaki N. Zahran<sup>1</sup>, Yuta Tsubonouchi<sup>1</sup>, Masayuki Yagi<sup>1</sup> (1. Grad. School of Sci. Tec., Niigata Univ.)

## J402

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

[J402-2am] 09. Coordination Chemistry,

10:40 AM - 11:00 AM

[J402-2am-07] Development of hydrogenation and dehydrogenation reactions based on the use of iron complexes bearing group 14 element ligands

○Yoshinao Kobayashi<sup>1</sup>, Yusuke Sunada<sup>1,2</sup> (1. School of Eng., The Univ. of Tokyo, 2. IIS, The Univ. of Tokyo)

11:00 AM - 11:20 AM

[J402-2am-08] Self-assembling behavior of polymer systems conjugated with artificial photosynthetic circuits

○Takafumi Enomoto<sup>1</sup>, Aya M Akimoto<sup>1</sup>, Ryo Yoshida<sup>1</sup> (1. Department of Materials Engineering, School of Engineering, The University of Tokyo)

11:20 AM - 11:40 AM

## J403

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

[J403-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Shinya Takaishi, Shohei Tashiro

9:00 AM - 11:40 AM J403 (Online Meeting)

[J403-2am-01] Substituent Effects on Nickel(II)

Percarboxylate Complex Formation by Ozone Oxidation of Nickel(II) Carboxylate Complexes

○Yuma Morimoto<sup>1</sup>, Ryotaro HARIKI<sup>1</sup>, Shinobu ITOH<sup>1</sup> (1. Osaka Univ.)

9:00 AM - 9:20 AM

[J403-2am-02] High valent Nickel catalyzed trifluoromethylation of arenes and heteroarenes induced by light irradiation

○Shubham Deolka Deolka<sup>1</sup>, Julia Khusnutdinova<sup>1</sup> (1. OIST, JAPAN)

9:20 AM - 9:40 AM

[J403-2am-03] Reversible Chemisorption of CO at Room Temperature on Ni(0) Complexes

○Yasuhiro Yamauchi<sup>1</sup>, Yoichi Hoshimoto<sup>1</sup>, Sensuke Ogoshi<sup>1</sup> (1. osaka university)

9:40 AM - 10:00 AM

[J403-2am-04] Structure Estimation from XANES spectra using machine learning

○Kentaro Fuku<sup>1</sup>, Takefumi Yoshida<sup>2</sup>, Hitoshi

Abe<sup>3,4,5</sup>, Hiroaki Iguchi<sup>1</sup>, Shinya Takaishi<sup>1</sup> (1. Tohoku Univ., 2. UEC, 3. KEK-IMSS, 4. SOKENDAI, 5. Ibaraki Univ.)

10:00 AM - 10:20 AM

[J403-2am-05] Structure and Magnetic Properties of a Dimerized Trinuclear Ni String Complex

○Kentaro Aoki<sup>1</sup>, Kazuya Otsubo<sup>1</sup>, Yukihiro Yoshida<sup>1</sup>, Kuniyoshi Sugimoto<sup>2</sup>, Hiroshi Kitagawa<sup>1</sup> (1. Grad. Sch. Sci., Kyoto Univ., 2. JASRI/SPRING-8)

10:20 AM - 10:40 AM

[J403-2am-06] Crystal structures and electronic states of metal-dithiolate-resorcinarene co-assemblies driven by hydrogen-bond formations

○Mikihiro Hayashi<sup>1</sup> (1. Nagasaki University)

10:40 AM - 11:00 AM

[J403-2am-07] Control of inversion motion by *in/out*-isomerization of helically twisted Pd<sub>3</sub>-macrocycles

○Tomoki Nakajima<sup>1</sup>, Shohei Tashiro<sup>1</sup>, Mitsuhiro Shionoya<sup>1</sup> (1. Grad. Sch. of Sci., The Univ. of Tokyo)

11:00 AM - 11:20 AM

[J403-2am-08] Development of substrate-specific long-range olefin migration reactions catalyzed by active palladium sites in a porous metal-macrocyclic framework

○Mengying Han<sup>1</sup>, Shohei Tashiro<sup>1</sup>, Takafumi Shiraogawa<sup>2</sup>, Masahiro Ehara<sup>3</sup>, Mitsuhiro Shionoya<sup>1</sup> (1. Graduate School of Science, The University of Tokyo, 2. Institute for Catalysis, Hokkaido University, 3. Institute for Molecular Science)

11:20 AM - 11:40 AM

## K3

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

[K3-2pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Masashi Hasegawa, Yumi Yakiyama

1:00 PM - 3:40 PM K3 (Online Meeting)

[K3-2pm-01] Electrochemical synthesis and dynamic control of [n]acene structures

○Takashi Harimoto<sup>1</sup>, Takanori Suzuki<sup>2</sup>, Yusuke

Ishigaki<sup>2</sup> (1. Graduate School of Chemical and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

1:00 PM - 1:20 PM

[K3-2pm-02] Synthesis of Novel Closed Heterohelicenes Interconvertible between Its Monomer and Dimer

○Yusuke Matsuo<sup>1</sup>, Takayuki Tanaka<sup>1</sup> (1. Kyoto University)

1:20 PM - 1:40 PM

[K3-2pm-03] Cycloparaphenylene Synthesis via a Macrocyclic Gold(I) Complex: Multiply Functionalized CPPs

○Yoshitaka Tsuchido<sup>1</sup>, Naoki Narita<sup>1</sup>, Yusuke Kurita<sup>1</sup>, Tomohito Ide<sup>3</sup>, Kohtaro Osakada<sup>2</sup>, Hidetoshi Kawai<sup>1</sup> (1. Tokyo Univ. of Sci., 2. Tokyo Inst of Tech., 3. Nat. Coll. of Tech., Tokyo Coll.)

1:40 PM - 2:00 PM

[K3-2pm-04] Synthesis of Armchair- and Chiral-Types Cyclophenylene-Naphthylene Belts by Rhodium-Catalyzed Intramolecular [2+2+2] Cycloaddition

○Juntaro Nogami<sup>1</sup>, Yuki Nagashima<sup>1</sup>, Haruki Sugiyama<sup>2</sup>, Kazunori Miyamoto<sup>3</sup>, Yusuke Tanaka<sup>3</sup>, Hidehiro Uekusa<sup>4</sup>, Atsuya Muranaka<sup>5</sup>, Masanobu Uchiyama<sup>3</sup>, Ken Tanaka<sup>1</sup> (1. Sch. Mater. & Chem. Tech., Tokyo Tech., 2. IMS, 3. Grad. Sch. of Pharm. Sci., The Univ. of Tokyo, 4. Sch. Sci., Tokyo Tech., 5. RIKEN)

2:00 PM - 2:20 PM

[K3-2pm-05] Synthesis and properties of kinetically stabilized bis-periazulene derivatives

○Koki Horii<sup>1</sup>, Akihito Konishi<sup>1</sup>, Makoto Yasuda<sup>1</sup> (1. Osaka University)

2:20 PM - 2:40 PM

[K3-2pm-06] Synthesis and Properties of Nitrogen-doped Triangulene Cation

○Shinobu Arikawa<sup>1</sup>, Akihiro Shimizu<sup>1</sup>, Daisuke Shiomi<sup>2</sup>, Kazunobu Sato<sup>2</sup>, Ryo Shintani<sup>1</sup> (1. Osaka University, 2. Osaka City University)

2:40 PM - 3:00 PM

[K3-2pm-07] Synthesis, Physical Properties, and Semiconductor Characteristics of Fluorinated Pentalene-1,4-dione Derivatives

○Soichi Yokoyama<sup>1</sup>, Yutaka Ie<sup>1</sup> (1. SANKEN, Osaka Univ.)

3:00 PM - 3:20 PM

[K3-2pm-08]  $\sigma$ -Delocalized Orbitals and Charge-Transport Properties of Polyiodobenzenes

○Yuki Takada<sup>1</sup>, Shunsuke Furukawa<sup>1</sup>, Masaichi Saito<sup>1</sup> (1. Department of Chemistry, Graduate School of Science and Engineering, Saitama University)

3:20 PM - 3:40 PM

## K1

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

[K1-2pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Kenji Matsuda, Junpey Yuasa

2:00 PM - 3:40 PM K1 (Online Meeting)

[K1-2pm-01] Synthesis and characterization of curved perylene diimide derivatives and application for organic solar cell

○Keisuke Fujimoto<sup>1</sup>, Ayumu Takahashi<sup>1</sup>, Kazuki Yamada<sup>1</sup>, Seiichiro Izawa<sup>2</sup>, Masahiro Hiramoto<sup>2</sup>, Masaki Takahashi<sup>1</sup> (1. Shizuoka University, 2. Institute for Molecular Science)

2:00 PM - 2:20 PM

[K1-2pm-02] Hole Collecting Monolayer Materials Based on Triazatruxene Skeleton for Efficient Perovskite Solar Cells

○Tsukasa Funasaki<sup>1</sup>, Lucas Ueberricke<sup>1</sup>, Wataru Nojo<sup>2</sup>, Minh Anh Truong<sup>1</sup>, Richard Murdey<sup>1</sup>, Takumi Yamada<sup>1</sup>, Tomoya Nakamura<sup>1</sup>, Shuaifeng Hu<sup>1</sup>, Yoshihiko Kanemitsu<sup>1</sup>, Takanori Suzuki<sup>2</sup>, Atsushi Wakamiya<sup>1</sup> (1. Institute for Chemical Research, Kyoto University, 2. Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

[K1-2pm-03] Synthesis, optical and singlet oxygen generation properties of phenazinone dyes

○Kazuki Ohira<sup>1</sup>, Masahiro Yamamoto<sup>1</sup>, Keiichi Imato<sup>1</sup>, Ichiro Imae<sup>1</sup>, Yousuke Ooyama<sup>1</sup> (1. Graduate School of Advanced Science and Engineering, Hiroshima University)

2:40 PM - 3:00 PM

[K1-2pm-04] Ion-Pairing Assemblies of Activated Charged  $\pi$ -Electronic Systems

○Hiroki Tanaka<sup>1</sup>, Hiromitsu Maeda<sup>1</sup> (1. Ritsumeikan University)

3:00 PM - 3:20 PM

[K1-2pm-05] Syntheses and aggregation properties of squalene receptors bearing ethylene glycol moieties

○TRAN NGOC LINH<sup>1</sup>, Takashi Arimura<sup>1</sup>, Kenichi Tominaga<sup>1</sup>, Hiroko Isoda<sup>1,2</sup>, Hideo Kigoshi<sup>2</sup> (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba)

3:20 PM - 3:40 PM

## H201

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

[H201-2am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kouki Oka, Koji Harano

9:00 AM - 11:20 AM H201 (Online Meeting)

[H201-2am-01] A strategy for obtaining supramolecular polymers dispersed in single molecular width

○Takuma Shimada<sup>1,2</sup>, Masayuki Takeuchi<sup>1</sup>, Kazunori Sugiyasu<sup>3</sup> (1. NIMS, 2. Kyushu Univ. Grad. Sch. Eng., 3. Kyoto Univ. Grad. Sch. Eng.)

9:00 AM - 9:20 AM

[H201-2am-02] Dissecting Self-folding Process of Curved Supramolecular Polymers

○Atsushi Isobe<sup>1</sup>, Shiki Yagai<sup>2</sup> (1. Graduate School of Science and Engineering, Chiba University, 2. Institute for Global Prominent Research, Chiba University)

9:20 AM - 9:40 AM

[H201-2am-03] Fabrication of a Large-Area and Highly-Uniform Proton-Conducting Nanofilm by Self-Assembly via Hydrogen-Bonding

○Hikaru Uchida<sup>1</sup>, Prince Ravat<sup>1</sup>, Ryosuke Sekine<sup>1</sup>, Ko Kamei<sup>1</sup>, Akihisa Yamamoto<sup>2</sup>, Oleg Konovalov<sup>3</sup>, Motomu Tanaka<sup>2,4</sup>, Teppei Yamada<sup>1</sup>, Koji Harano<sup>1</sup>, Eiichi Nakamura<sup>1</sup> (1. The University of Tokyo, 2. Kyoto University, 3. European Synchrotron Radiation Facility, 4. Heidelberg University)

9:40 AM - 10:00 AM

[H201-2am-04] Construction of Core-Shell Block Co-Crystals Composed of Different Spin-Crossover Metal Complexes

○Tomoya Fukui<sup>1,2</sup>, Masahiro Tsuchiya<sup>1,2</sup>, Takanori Fukushima<sup>1,2</sup> (1. Lab. Chem. Life Sci., Tokyo Tech, 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

10:00 AM - 10:20 AM

[H201-2am-05] Control of Aggregation Pathway and Self-Assembled Morphology by Partial Disabling of Hydrogen-bonding Group

○Takumi Aizawa<sup>1</sup>, Shiki Yagai<sup>2</sup> (1. Chiba University, 2. Chiba University IGPR)

10:20 AM - 10:40 AM

[H201-2am-06] Creation of Highly Reactive Supramolecular Polymers Toward Hierarchical Self-assembly

○Chisako Kanzaki<sup>1</sup>, Yoshihiro Kikkawa<sup>2</sup>, Munenori Numata<sup>1</sup> (1. Grad. Sch. Life and Env. Sci., Kyoto Pref. Univ., 2. AIST)

10:40 AM - 11:00 AM

[H201-2am-07] Multistep synthesis of supramolecular block concentric toroids

○Norihiro Sasaki<sup>1</sup>, Masayuki Takeuchi<sup>1</sup>, Kazunori Sugiyasu<sup>2</sup> (1. National Institute for Materials Science, 2. Grad. Sch. Eng., Kyoto Univ.)

11:00 AM - 11:20 AM

## K6

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

[K6-2am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Koichi Mitsudo, Toshiki Nokami

9:00 AM - 11:20 AM K6 (Online Meeting)

[K6-2am-01] Synthesis and Electrochemical Properties of Pillar[6]quinone

○Tomoki Hirohata<sup>1</sup>, Naoki Shida<sup>2</sup>, Tomoki Ogoshi<sup>3</sup>, Ikuyoshi Tomita<sup>1</sup>, Shinsuke Inagi<sup>1,4</sup> (1. Tokyo Institute of Technology, 2. Yokohama National Univ., 3. Kyoto Univ., 4. JST PRESTO)

9:00 AM - 9:20 AM

[K6-2am-02] Electrochemical Post-functionalization of Poly(3-(2-ethylhexyl)thiophene) Facilitated by Forming the Ordered Structure

○Tomoyuki Kurioka<sup>1</sup>, Takahiro Komamura<sup>1</sup>, Naoki Shida<sup>2</sup>, Teruaki Hayakawa<sup>1</sup>, Ikuyoshi Tomita<sup>1</sup>,

Shinsuke Inagi<sup>1,3</sup> (1. Sch. Mater. & Chem. Tech.,  
Tokyo Tech., 2. Grad. Sch. Eng., Yokohama  
National University, 3. JST PRESTO)  
9:20 AM - 9:40 AM

- [K6-2am-03] Synthesis of Precursors of Chitin  
Oligosaccharides by Electrochemical  
Glycosylation Polymerization  
○Azadur Md Rahman<sup>1</sup>, Kana Kuroda<sup>1</sup>, Tomoaki  
Hamada<sup>2</sup>, Hiraku Sakai<sup>2</sup>, Toshiki Nokami<sup>1</sup> (1.  
Tottori University, 2. Koganei Corporation)  
9:40 AM - 10:00 AM
- [K6-2am-04] Formation of Sterically Congested C-N  
bonds by Electrochemical Reductive  
Coupling of Amines and  $\alpha$ -Bromo  
Carboxamides  
○Titli Ghosh<sup>1</sup>, Hazuki Kaizawa<sup>1</sup>, Takashi  
Nishikata<sup>2</sup>, Toshiki Nokami<sup>1</sup> (1. Tottori University,  
2. Yamaguchi University)  
10:00 AM - 10:20 AM
- [K6-2am-05] Electrosynthesis of hypervalent iodine using  
extended  $\pi$ -system and its application to  
electrocatalysis  
○Shohei Yoshinaga<sup>1</sup>, Naoki Shida<sup>1</sup>, Mahito Atobe<sup>1</sup>  
(1. Yokohama National University)  
10:20 AM - 10:40 AM
- [K6-2am-06] Diastereoselective Electrocatalytic  
Hydrogenation of Substituted  
Cyclohexanones in a PEM Reactor  
○Yugo Shimizu<sup>1</sup>, Atsushi Fukazawa<sup>1</sup>, Naoki Shida<sup>1</sup>,  
Mahito Atobe<sup>1</sup> (1. Yokohama National  
University)  
10:40 AM - 11:00 AM
- [K6-2am-07] Hole-catalyzed selective C-C bond formation  
at benzylic position in lignin model materials  
by anodic oxidation  
○Rumi Izumiya<sup>1</sup>, Naoki Shida<sup>1</sup>, Mahito Atobe<sup>1</sup> (1.  
Yokohama National University)  
11:00 AM - 11:20 AM

## K4

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

[K4-2pm] 14. Organic Chemistry -Aromatic,  
Heterocyclic, and Heteroatom  
Compounds-

Chair: Yuki Nagashima, Satoru Kuwano  
1:00 PM - 3:40 PM K4 (Online Meeting)

- [K4-2pm-01] Cationic Rhodium(I)-Catalyzed Asymmetric  
[2+2+2] Cycloaddition of Homopropargyl  
Enamides with Alkynes  
○Kohei Fujii<sup>1</sup>, Koji Masutomi<sup>1</sup>, Yuki Nagashima<sup>1</sup>,  
Ken Tanaka<sup>1</sup> (1. Tokyo Institute of Technology)  
1:00 PM - 1:20 PM
- [K4-2pm-02] The Development of Stereoselective [2 + 3]  
Cycloaddition Reactions of Oxime  
Substituted Nitrile Oxides and Alkenes  
○Nao Umemoto<sup>1</sup>, Ayumi Imayoshi<sup>1</sup>, Kazunori  
Tsubaki<sup>1</sup> (1. Kyoto Prefectural University)  
1:20 PM - 1:40 PM
- [K4-2pm-03] Development of New Reactions by Quantum  
Chemical Calculations: the Synthesis of  
Unsymmetric DPPE via Difunctionalization of  
Ethylene  
○Hideaki Takano<sup>1,2</sup>, Hitomi Katsuyama<sup>1,2</sup>, Hiroki  
Hayashi<sup>1,2</sup>, Wataru Kanna<sup>3</sup>, Yu Harabuchi<sup>1,2,3</sup>,  
Satoshi Maeda<sup>1,2,3</sup>, Tsuyoshi Mita<sup>1,2</sup> (1. WPI-  
ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of  
Sci., Hokkaido Univ.)  
1:40 PM - 2:00 PM
- [K4-2pm-04] Synthesis of Polycyclic Aromatic Amines via  
Benzannulation of Ynamine:  $\pi$ -Extension  
Strategy for Optimization of Optical  
Properties  
○Yasuhiro Okuda<sup>1</sup>, Mayo Fujimoto<sup>1</sup>, Kazuya  
Kiyohara<sup>1</sup>, Aina Kuwayama<sup>1</sup>, Akihiro Orita<sup>1</sup> (1.  
Fac. of Eng., Okayama Univ. of Sci.)  
2:00 PM - 2:20 PM
- [K4-2pm-05] Synthesis and luminescence characteristics  
of disilane crosslinked DAD molecules  
○Yoshinori Yamanoi<sup>1</sup>, Masaki Nishio<sup>1</sup>, Hiroto  
Miyabe<sup>1</sup>, Mizuha Ujita<sup>1</sup>, Shunya Matsushita<sup>1</sup>,  
Toyotaka Nakae<sup>1</sup>, Teppei Yamada<sup>1</sup> (1. The Univ  
of Tokyo)  
2:20 PM - 2:40 PM
- [K4-2pm-06] Model Study on the Mechanism and  
Inhibition of Thyroid Hormone Activating  
Enzymes by Taking Advantage of a Cradled  
Selenopeptide  
○Ryosuke Masuda<sup>1</sup>, Satoru Kuwano<sup>1</sup>, Shohei  
Sase<sup>1</sup>, Kei Goto<sup>1</sup> (1. Tokyo Institute of



Technology)

2:40 PM - 3:00 PM

**[K4-2pm-07] Catalytic hydroboration reaction of Lewis-base stabilized hydrostannylenes**○Kazuki Nakaya<sup>1</sup>, Yoshiki Kobayashi<sup>1</sup>, Norio Nakata<sup>1</sup>, Akihiko Ishii<sup>1</sup> (1. Saitama University)

3:00 PM - 3:20 PM

**[K4-2pm-08] Sulfonyl Pyrroles: Synthetic Linchpins for Late-Stage Functionalization of Primary Sulfonamides**Tomoya Ozaki<sup>1</sup>, Hideki Yorimitsu<sup>1</sup>, ○Gregory J. P. Perry<sup>1</sup> (1. Kyoto University)

3:20 PM - 3:40 PM

**B104**

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

**[B104-2am] 16. Natural Products Chemistry, Chemical Biology**

Chair: Takuya Kaji, Ryo Tanifuji

9:00 AM - 11:40 AM B104 (Online Meeting)

**[B104-2am-01] Discovery of New Aplaminone Derivatives from *Aplysia kurodai* and Elucidation of the Origin by Molecular Networking Analysis**○Yusuke Hioki<sup>1</sup>, Ayuka Tochino<sup>2</sup>, Tatsuya Sato<sup>3</sup>, Toyoki Iwao<sup>4</sup>, Atsushi Kawamura<sup>5</sup>, Masaki Kita<sup>1</sup>

(1. Graduate School of Bioagricultural Sciences, Nagoya University, 2. School of Agricultural Sciences, Nagoya University, 3. Zakko Club, 4. Toba Fisheries Science Center, 5. Interdisciplinary Cluster for Cutting Edge Research, Shinshu University)

9:00 AM - 9:20 AM

**[B104-2am-02] Structural Study of Actin-Aplyronine A-Tubulin Heterotrimeric Complex and Development of Actin-affinity Tags**○Didik Huswo Utomo<sup>1</sup>, Akari Fujieda<sup>1</sup>, Atsunori Oshima<sup>2</sup>, Akihiro Narita<sup>3</sup>, Momoko Takahashi<sup>4</sup>, Hideo Kigoshi<sup>4</sup>, Masaki Kita<sup>1</sup> (1. Graduate

School of Bioagricultural Sciences, Nagoya University, 2. Graduate School of Pharmaceutical Sciences, Nagoya University, 3. Graduate School of Sciences, Nagoya University, 4. Degree Programs of Pure and Applied Sciences, University of Tsukuba)

9:20 AM - 9:40 AM

**[B104-2am-03] Artificial throwback strategy of jasmonate perception by ancestral jasmonate ligand dn-iso-OPDA and M. polymorpha COI1 receptor**○Takuya Kaji<sup>1</sup>, Haruka Sakurai<sup>1</sup>, Nobuki Kato<sup>1</sup>, Wang Jianxin<sup>1</sup>, Minoru Ueda<sup>1,2</sup> (1. Grad. Sch. of Science, Tohoku Univ., 2. Grad. Sch. of Life science, Tohoku Univ.)

9:40 AM - 10:00 AM

**[B104-2am-04] Synthetic Study on Mollenyne A**○Nurchahyo Iman Prakoso<sup>1,2</sup>, Shi Quan<sup>1</sup>, Taiki Umezawa<sup>1</sup> (1. Hokkaido University, 2. Universitas Islam Indonesia)

10:00 AM - 10:20 AM

**[B104-2am-05] Generation of Mid-sized Alkaloidal Scaffolds Exhibiting Potent Anti-cancer Activities: Systematic Diversification of Macrocyclic Framework of Ecteinascidins**○Ryo Tanifuji<sup>1</sup>, Erina Hosono<sup>2</sup>, Hiroki Oguri<sup>1</sup> (1. The University of Tokyo, 2. Tokyo

University of Agriculture and Technology)

10:20 AM - 10:40 AM

**[B104-2am-06] Total Synthesis of Paclitaxel**○Shota Iiyama<sup>1</sup>, Keisuke Fukaya<sup>1</sup>, Yu Yamaguchi<sup>1</sup>, Ami Watanabe<sup>1</sup>, Hiroaki Yamamoto<sup>1</sup>, Shota Mochizuki<sup>1</sup>, Ryosuke Saio<sup>1</sup>, Takashi Noguchi<sup>1</sup>, Takeshi Oishi<sup>2</sup>, Takaaki Sato<sup>1</sup>, Noritaka Chida<sup>1</sup> (1. Keio University, 2. School of Medicine, Keio University)

10:40 AM - 11:00 AM

**[B104-2am-07] Identification of intracellular proteases that degrade chimeric compounds**○Kai Tahara<sup>1</sup>, Akinobu Nakamura<sup>1</sup>, Sachio Suzuki<sup>1</sup>, Yuki Ichihashi<sup>2</sup>, Yasuteru Urano<sup>2,3</sup>, Toru Komatsu<sup>2</sup>, Shinya Tsukiji<sup>1</sup> (1. Grad. Sch. of Eng., Nagoya Inst. of Tech., 2. Grad. Sch. of Phar. Sci., The Univ. of Tokyo, 3. Grad. Sch. of Med., The Univ. of Tokyo)

11:00 AM - 11:20 AM

**[B104-2am-08] A versatile inducible protein translocation tool for controlling plasma membrane signaling**○Sachio Suzuki<sup>1</sup>, Akinobu Nakamura<sup>2</sup>, Hatano Yuka<sup>1</sup>, Kazuhiro Aoki<sup>2</sup>, Shinya Tsukiji<sup>1</sup> (1. Grad. Sch. of Eng., Nagoya Inst. of Tech., 2.

ExCELLS, Natl. Inst. of Natural Sci.)

11:20 AM - 11:40 AM

**G101**

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

**[G101-2am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Tamaki Endoh, Hiromu Kashida

9:00 AM - 11:40 AM G101 (Online Meeting)

**[G101-2am-01] Photocaged chemically modified PCR primer aiming accurate and efficient DNA assembly**

○Fumitaka Hashiya<sup>1</sup>, Kaoru Onda<sup>2</sup>, Kohei Nomura<sup>2</sup>, Gao Yuino<sup>2</sup>, Hirotaka Murase<sup>2</sup>, Kosuke Nakamoto<sup>2</sup>, Masahito Inagaki<sup>2</sup>, Haruka Hiraoka<sup>2</sup>, Naoko Abe<sup>2</sup>, Yasuaki Kimura<sup>2</sup>, Natsuhisa Oka<sup>3,4,6</sup>, Goro Terai<sup>5,6</sup>, Kiyoshi Asai<sup>5,6</sup>, Hiroshi Abe<sup>1,2,6,7</sup> (1. Research Center for Material Science, Nagoya University, 2. Graduate School of Science, Nagoya University, 3. Department of Chemistry and Biomolecular Science, Gifu University, 4. Institute for Glyco-core Research (iGCORE), Gifu University, 5. Department of Computational Biology and Medical Sciences, University of Tokyo, 6. CREST, Japan Science and Technology Agency, 7. Institute for Glyco-core Research (iGCORE), Nagoya University)

9:00 AM - 9:20 AM

**[G101-2am-02] Orthogonal signal amplification circuit composed of acyclic nucleic acid for RNA visualization**

○Yanglingzhi Chen<sup>1</sup>, Keiji Murayama<sup>1</sup>, Hiroyuki Asanuma<sup>1</sup> (1. The Univ. of Nagoya)

9:20 AM - 9:40 AM

**[G101-2am-03] Improvement of inhibitory activity of SNA-based anti-miRNA-21 by introduction of pseudocomplementary bases**

○Fuminori Sato<sup>1</sup>, Keiji Murayama<sup>1</sup>, Yukiko Kamiya<sup>1</sup>, Hiroyuki Asanuma<sup>1</sup> (1. The Univ. of Nagoya)

9:40 AM - 10:00 AM

**[G101-2am-04] Staple oligomer hijacks protein translation machinery based on the conformational changes of mRNA**

structure

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

10:00 AM - 10:20 AM

**[G101-2am-05] Imidazolium-modified supports as nucleic acid adsorbents and its application to DNA amplification testing**

○Yasuaki Kakikura<sup>1</sup> (1. Osaka Research Institute of Industrial Science and Technology)

10:20 AM - 10:40 AM

**[G101-2am-06] Photo-oxidation properties of guanosine in the duplex by a small, efficient photosensitizer**

○Takashi Kanamori<sup>1</sup>, Shota Kaneko<sup>1</sup>, Kohji Hanamoto<sup>1</sup>, Chao Wang<sup>1</sup>, Ruoyu Li<sup>1</sup>, Hideya Yuasa<sup>1</sup> (1. Tokyo Institute of Technology)

10:40 AM - 11:00 AM

**[G101-2am-07] Evaluation of side-products in chemically synthesized DNA by next-generation sequencing**

○Yoshiaki Masaki<sup>1,2</sup>, Taichi Yagata<sup>1</sup>, Kohji Seio<sup>1</sup> (1. Tokyo Tech, 2. JST PRESTO)

11:00 AM - 11:20 AM

**[G101-2am-08] Effect of the ordered hydration layer for the enzymatic reactions on DNA scaffold**

○Peng Lin<sup>1</sup>, Huyen Dinh<sup>1</sup>, Eiji Nakata<sup>1</sup>, Takashi Morii<sup>1</sup> (1. Institute of Advanced Energy, Kyoto University)

11:20 AM - 11:40 AM

**G202**

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

**[G202-2am] 17. Biofunctional Chemistry,**

## Biotechnology

Chair: Hideki Mori, Kazunori Shimizu

9:00 AM - 11:40 AM G202 (Online Meeting)

### [G202-2am-01] Autonomous Arrangement of Micro-Droplets Entrapping DNA and Living Cells Generated through Micro Phase-Separation

○Mayu Shono<sup>1</sup>, Ritsuki Ito<sup>2</sup>, Fumika Fujita<sup>2</sup>, Hiroki Sakuta<sup>2</sup>, Akihisa Shioi<sup>1</sup>, Kenichi Yoshikawa<sup>2</sup> (1. Department of Chemical Engineering and Materials Science, Doshisha Univ., 2. Faculty of Life and Medical Sciences, Doshisha Univ.)

9:00 AM - 9:20 AM

### [G202-2am-02] Effect of polyunsaturated docosahexaenoic acid on the lipid-raft mimetic ordered/disordered phase separated membranes

○Masanao Kinoshita<sup>1</sup>, Akira Sorada<sup>1</sup>, Yutaro Tajima<sup>1</sup>, Nobuaki Matsumori<sup>1</sup> (1. Kyushu University)

9:20 AM - 9:40 AM

### [G202-2am-03] Detection of biological molecule using $\beta$ -barrel nanopore protein by changing number of $\beta$ -strands

○Toshiyuki Tosaka<sup>1</sup>, Koki Kamiya<sup>1</sup> (1. Gunma Univ.)

9:40 AM - 10:00 AM

### [G202-2am-04] Analysis of the Akt isoform-specific signaling pathway regulation using optogenetics and mathematical modeling

○Yuka Sekine<sup>1</sup>, Genki Kawamura<sup>1</sup>, Takeaki Ozawa<sup>1</sup> (1. The University of Tokyo)

10:00 AM - 10:20 AM

### [G202-2am-05] Optical control of Akt to analyze cellular metabolic signalling pathways

○Genki Kawamura<sup>1</sup>, Takeaki Ozawa<sup>1</sup> (1. The Univ. of Tokyo)

10:20 AM - 10:40 AM

### [G202-2am-06] Development of an evaluation system for contractility of cultured muscle tissues and its application to the screening for anti-atrophic peptides

○Kazunori Shimizu<sup>1</sup>, Kazuki Yamamoto<sup>1</sup>, Saki Ohsumi<sup>1</sup>, Takunori Nagashima<sup>1</sup>, Hirokazu Akiyama<sup>1</sup>, Hiroyuki Honda<sup>1</sup> (1. Nagoya

University)

10:40 AM - 11:00 AM

### [G202-2am-07] Single-cell analysis of immune cell cytotoxicity using a photo-reactive surface

○Takahiro Kosaka<sup>1</sup>, Satoshi Yamaguchi<sup>2</sup>, Shinya Yamahira<sup>3</sup>, Akimitsu Okamoto<sup>1,2</sup> (1. School of Engineering, The University of Tokyo, 2. Research Center for Advanced Science and Technology, The University of Tokyo, 3. St. Luke's International University)

11:00 AM - 11:20 AM

### [G202-2am-08] Nylon mesh scaffolds for the adherent culture of neural stem/progenitor cells

○Masayuki Hara Hara<sup>1</sup>, Hideki Mori<sup>1</sup> (1. Osaka Prefecture University)

11:20 AM - 11:40 AM

## G301

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

### [G301-2am] 17. Biofunctional Chemistry, Biotechnology

Chair: Takafumi Ueno, Norifumi Kawakami

9:00 AM - 11:40 AM G301 (Online Meeting)

### [G301-2am-01] Design of the heteroepitaxial vertical assembly of asymmetric protein needles

○Kosuke Kikuchi<sup>1</sup>, Takafumi Ueno<sup>1</sup> (1. Tokyo Institute of Technology)

9:00 AM - 9:20 AM

### [G301-2am-02] Enrichment of hierarchical supramolecular polymers into droplets and effect on protein functions under liquid-liquid phase separation environment

○Hiroki Obayashi<sup>1</sup>, Rie Wakabayashi<sup>1</sup>, Masahiro Goto<sup>1,2</sup>, Norihiro Kamiya<sup>1,2</sup> (1. Graduate School of Engineering, Kyusyu University, 2. Center for Future Chemistry, Kyushu University)

9:20 AM - 9:40 AM

### [G301-2am-03] Development of enzyme-mimetic oxidative protein folding promoters

○Shunsuke Okada<sup>1</sup>, Masaki Okumura<sup>2</sup>, Takahiro Muraoka<sup>1,3</sup> (1. Tokyo Univ. of Agr. and Tech., 2. Tohoku Univ., 3. KISTEC)

9:40 AM - 10:00 AM

[G301-2am-04] Construction of Functional Protein  
Needle Encapsulated in In-cell Protein  
Crystal

○THUC TOAN PHAM<sup>1</sup>, Satoshi Abe<sup>1</sup>, Kazuhiko  
Katayama<sup>2</sup>, Takafumi Ueno<sup>1</sup> (1. Tokyo  
Institute of Technology, 2. Kitasato University,  
Omura Satoshi Memorial Institute)

10:00 AM - 10:20 AM

[G301-2am-05] Functionalization of amyloid beta peptide  
into ferritin cage and observation of the  
cage disassembly.

○Basudev Maity<sup>1</sup>, Shiori Kameyama<sup>1</sup>, Satoshi  
Abe<sup>1</sup>, Takafumi Ueno<sup>1</sup> (1. TOKYO INSTITUTE  
OF TECHNOLOGY)

10:20 AM - 10:40 AM

[G301-2am-06] Encapsulation of heterologous proteins in  
an inner space of an artificial protein  
nanocage TIP60

○Norifumi Kawakami<sup>1</sup>, Keiichi Hayashi<sup>1</sup>, Mao  
Kitamura<sup>1</sup>, Kenji Miyamoto<sup>1</sup> (1. Keio  
University)

10:40 AM - 11:00 AM

[G301-2am-07] Catalytic activity of enzymes immobilized  
with ionic metal-organic cages

○Benjamin LE OUAY<sup>1</sup>, Ryosuke Minami<sup>1</sup>, Ryo  
Ohtani<sup>1</sup>, Masaaki Ohba<sup>1</sup> (1. Kyushu  
University)

11:00 AM - 11:20 AM

[G301-2am-08] Analysis of Dynamic Behavior of Aromatic  
Interactions using Protein Cages

○Yuki Hishikawa<sup>1</sup>, Asuka Asanuma<sup>1</sup>, Basudev  
Maity<sup>1</sup>, Satoru Nagatoishi<sup>2</sup>, Kouhei Tsumoto<sup>2,3</sup>,  
Satoshi Abe<sup>1</sup>, Takafumi Ueno<sup>1</sup> (1. Sch. of Life  
Sci. & Technol., Tokyo Inst. of Technol., 2. The  
Inst. of Med. Sci., The Univ. of Tokyo, 3. Sch. of  
Eng., The Univ. of Tokyo)

11:20 AM - 11:40 AM

## G201

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

### [G201-2am] 17. Biofunctional Chemistry, Biotechnology

Chair: Hiroshi Nonaka, Yusuke Yonamine  
9:00 AM - 11:40 AM G201 (Online Meeting)

[G201-2am-01] Probing the biogenesis of storage  
organelles in algal cells via Raman

imaging with stable isotope labeling

○Yusuke Yonamine<sup>1</sup>, Takuro Ito<sup>2</sup>, Yasuyuki  
Ozeki<sup>3</sup>, Yu Hoshino<sup>4</sup>, Hideyuki Mitomo<sup>1</sup>,  
Kuniharu Ijiri<sup>1</sup> (1. RIES, Hokkaido Univ., 2.  
NIT, Tsuruoka Col., 3. Grad. Sch. of Eng., The  
Univ. of Tokyo, 4. Grad. Sch. of Eng., Kyushu  
Univ.)

9:00 AM - 9:20 AM

[G201-2am-02] Ligand directed chemistry in live mouse  
brain (1): Labeling and imaging of AMPA-  
type glutamate receptor

○Kazuki Shiraiwa<sup>1</sup>, Seiji sakamoto<sup>1</sup>, Hiroshi  
Nonaka<sup>1,2</sup>, Shigeki Kiyonaka<sup>2,3</sup>, Itaru  
Hamachi<sup>1,2</sup> (1. Graduate school of  
Engineering, Kyoto University, 2. JST ERATO, 3.  
Graduate school of Engineering, Nagoya  
University)

9:20 AM - 9:40 AM

[G201-2am-03] Ligand directed chemistry in live mouse  
brain (2): Application to other  
endogenous neurotransmitter receptors  
and their life-time analysis.

○Seiji Sakamoto<sup>1</sup>, Kazuki Shiraiwa<sup>1</sup>, Shigeki  
Kiyonaka<sup>2</sup>, Nonaka Hiroshi<sup>1,3</sup>, Itaru Hamachi<sup>1,3</sup>  
(1. Kyoto University, 2. Nagoya University, 3.  
JST ERATO)

9:40 AM - 10:00 AM

[G201-2am-04] Ligand directed chemistry in live mouse  
brain (3): Pulse-chase analysis of AMPA  
receptors in the brain during postnatal  
development

○Hiroshi Nonaka<sup>1,2</sup>, Kazuki Shiraiwa<sup>1</sup>, Seiji  
Sakamoto<sup>1</sup>, Shigeki Kiyonaka<sup>2,3</sup>, Itaru  
Hamachi<sup>1,2</sup> (1. Graduate School of  
Engineering, Kyoto Univ, 2. ERATO, JST, 3.  
Graduate School of Engineering, Nagoya  
Univ)

10:00 AM - 10:20 AM

[G201-2am-05] Optical regulation of protein translocation  
using a photo-reversible protein labeling  
system

○Takato Mashita<sup>1</sup>, Toshiyuki Kowada<sup>1,2</sup>,  
Toshitaka Matsui<sup>1,2</sup>, Shin Mizukami<sup>1,2</sup> (1.  
Graduate School of Science, Tohoku

University, 2. Institute of Multidisciplinary  
Research for Advanced Materials, Tohoku  
University)

10:20 AM - 10:40 AM

[G201-2am-06] Development of fluorescent probes for  
visualizing membrane contact sites in  
living cells

○Moeka Ajiki<sup>1</sup>, Masaru Yoshikawa<sup>2</sup>, Keita  
Tsutsui<sup>2</sup>, Fubito Nakatsu<sup>3</sup>, Shinya Tsukiji<sup>1,2</sup> (1.  
Fac. of Eng., Nagoya Inst. of Tech., 2. Grad.  
Sch. of Eng., Nagoya Inst. of Tech., 3. Grad.  
Sch. of Med. and Dent. Sci., Niigata Univ.)

10:40 AM - 11:00 AM

[G201-2am-07] Development of chemical tools for  
manipulating membrane contacts in living  
cells

○Masaru Yoshikawa<sup>1</sup>, Moeka Ajiki<sup>2</sup>, Keita  
Tsutsui<sup>1</sup>, Fubito Nakatsu<sup>3</sup>, Shinya Tsukiji<sup>1</sup> (1.  
Grad. Sch. of Eng., Nagoya Inst. of Tech., 2.  
Fac. of Eng., Nagoya Inst. of Tech., 3. Grad.  
School of Niigata Univ.)

11:00 AM - 11:20 AM

[G201-2am-08] Fluorescence lifetime mapping of lipid  
compositions using an environment-  
responsive lipid droplet probe

○Keiji Kajiwara<sup>1</sup>, Yuki Ohsaki<sup>2</sup>, Masayasu Taki<sup>1</sup>,  
Shigehiro Yamaguchi<sup>1</sup> (1. Nagoya Univ., 2.  
Sapporo Medical Univ.)

11:20 AM - 11:40 AM

## C203

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

[C203-2am] 18. Polymer

Chair: Masayuki Gon, Kenichi Oyaizu

9:00 AM - 11:40 AM C203 (Online Meeting)

[C203-2am-01] Topology Transformation toward Cyclic,  
Figure-Eight-Shaped, and Cross-Linked  
Polymers via Dynamic Covalent Chemistry

○Hirogi Yokochi<sup>1</sup>, Daisuke Aoki<sup>1,2</sup>, Hideyuki  
Otsuka<sup>1</sup> (1. Tokyo Institute of Technology, 2.  
JST PRESTO)

9:00 AM - 9:20 AM

[C203-2am-02] Synthesis, Reactions, and DFT Study of  
Radical-type Mechanophores with  
Bisarylfluorene Skeletons

○Hajime Sugita<sup>1,2</sup>, Yi Lu<sup>2</sup>, Koichiro Mikami<sup>1</sup>,  
Daisuke Aoki<sup>2</sup>, Hideyuki Otsuka<sup>2</sup> (1. Sagami  
Chemical Research Institute, 2. Tokyo Institute  
of Technology)

9:20 AM - 9:40 AM

[C203-2am-03] Synthesis and Functionalities of  
Luminescent Conjugated Polymers Based  
on Dialdiminate Boron Complexes

○Shunichiro Ito<sup>1</sup>, Yuki Sakai<sup>1</sup>, Miyako  
Hashizume<sup>1</sup>, Kazuo Tanaka<sup>1</sup>, Yoshiki Chujo<sup>1</sup>  
(1. Kyoto University)

9:40 AM - 10:00 AM

[C203-2am-04] Synthesis of functional peroxide  
mechanophores and their application to  
mechanoresponsive polymer networks  
that release fluorescent molecules

○Yi Lu<sup>1</sup>, Hajime Sugita<sup>2</sup>, Koichiro Mikami<sup>2</sup>,  
Daisuke Aoki<sup>1</sup>, Hideyuki Otsuka<sup>1</sup> (1. Tokyo  
Institute of Technology, 2. Sagami Chemical  
Research Institute)

10:00 AM - 10:20 AM

[C203-2am-05] A cyclophane-based supramolecular  
mechanophore that shows ratiometric  
change in emission between monomer  
and exciplex

○Shakkeeb Thazhathethil<sup>1</sup>, Nobuyuki  
Tamaoki<sup>1</sup>, Yoshimitsu Sagara<sup>2</sup> (1. Hokkaido  
University, 2. Tokyo Institute of Technology)

10:20 AM - 10:40 AM

[C203-2am-06] A Photostable Gel that Degrades by  
Simultaneous Treatment with Acid and UV  
Light for Phototuning of Optical  
Functionalities

○Go Martin Russell<sup>1</sup>, Takashi Kaneko<sup>1</sup>, Hiroshi  
Masai<sup>1</sup>, Jun Terao<sup>1</sup> (1. The Univ. of Tokyo)

10:40 AM - 11:00 AM

[C203-2am-07] Poly(para-phenylene) ionomer  
membranes containing methyl or  
trifluoromethyl substituents

○FANGHUA LIU<sup>1</sup>, Kenji Miyatake<sup>1,2</sup> (1. Univ.  
Yamanashi, 2. Waseda Univ.)

11:00 AM - 11:20 AM

[C203-2am-08] Revealing the relationships between  
processes, structures, and properties of  
poly(phenylene ether)-based solid-state  
electrolytes by materials informatics

○Kan Hatakeyama-Sato<sup>1</sup>, Momoka Umeki<sup>1</sup>,  
Hiroki Adachi<sup>1</sup>, Kenichi Oyaizu<sup>1</sup> (1. Waseda  
University)  
11:20 AM - 11:40 AM

## C202

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

### [C202-2am] 18. Polymer

Chair: Nobuhiko Hosono, Fumitaka Ishiwari  
9:00 AM - 11:00 AM C202 (Online Meeting)

#### [C202-2am-01] Threading ultra-long polymers into MOF:

Formation of a new penetration complex  
○Tomoya Iizuka<sup>1</sup>, Hiroyuki Sano<sup>2</sup>, Nobuhiko  
Hosono<sup>2</sup>, Takashi Uemura<sup>2</sup> (1. Univ. of Tokyo,  
Grad. Sch. of Front. Sci., 2. Univ. of Tokyo,  
Grad. Sch. of Eng.)  
9:00 AM - 9:20 AM

#### [C202-2am-02] Synthesis, Properties, and Conformational Dynamics of Ladder Polymers Containing *N,N'*-Diacylated Diazacyclooctane Units in their Main Chains

○Keiki Inoue<sup>1,2</sup>, Fumitaka Ishiwari<sup>3</sup>, Takanori  
Fukushima<sup>1,2</sup> (1. Sch. of Mat. and Chem.  
Tech., Tokyo Tech, 2. CLS, Tokyo Tech, 3.  
Grad. Sch. of Eng., Osaka Univ.)  
9:20 AM - 9:40 AM

#### [C202-2am-03] Solid-state supramolecular polymers with ordered nanostructures

○Zebin Su<sup>1</sup> (1. Riken)  
9:40 AM - 10:00 AM

#### [C202-2am-04] In situ observation of polymeric vesicle formation by time-resolved ultra small- angle X-ray scattering

○Rintaro Takahashi<sup>1</sup>, Theyencheri Narayanan<sup>2</sup>,  
Shin-ichi Yusa<sup>4</sup>, Takahiro Sato<sup>3</sup> (1. Nagoya  
University, 2. ESRF-The European Synchrotron,  
3. Osaka University, 4. University of Hyogo)  
10:00 AM - 10:20 AM

#### [C202-2am-05] Thermal degradation of a poly (ethylene- co-methacrylic acid) ionomer investigated by solid-state <sup>13</sup>C NMR and ESR

○Shohei Mikage<sup>1</sup>, Atsushi Asano<sup>1</sup> (1. National  
Defense Academy of Japan)  
10:20 AM - 10:40 AM

#### [C202-2am-06] Design of Stabilizer Formulations for

### Yellowing Inhibition of Polymeric Materials based on High-Throughput Experiments and Genetic Algorithm

○Ken Takimoto<sup>1</sup>, Toshiaki Taniike<sup>1</sup> (1. Japan  
Advanced Institute of Science and  
Technology)  
10:40 AM - 11:00 AM

## C205

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

### [C205-2pm] 20. Materials Chemistry -Basic and Application-

Chair: Ryota Sato, Kazuki Yamamoto  
1:40 PM - 3:40 PM C205 (Online Meeting)

#### [C205-2pm-01] Synthesis and Properties of

Diethoxysiloxane Derivatives  
○Yohei Sato<sup>1</sup>, Ryohei Hayami<sup>2</sup>, Kazuki  
Yamamoto<sup>1</sup>, Takahiro Gunji<sup>1</sup> (1. Tokyo  
University of Science, 2. Zoome LLC)  
1:40 PM - 2:00 PM

#### [C205-2pm-02] Synthesis and Properties of Polysiloxanes from Monomers Consisting of Different Silicon Units

○Kazuki Yamamoto<sup>1</sup>, Tomoya Shimoda<sup>1</sup>,  
Takahiro Gunji<sup>1</sup> (1. Tokyo University of  
Science)  
2:00 PM - 2:20 PM

#### [C205-2pm-03] The substitution pattern effect on thermal, liquid-physical and optical properties of alkylated distyrylbenzene liquids.

○Xiao Zheng<sup>1,2</sup>, Kazuhiko Nagura<sup>2</sup>, Takashi  
Nakanishi<sup>1,2</sup> (1. Division of Soft Matter,  
Graduate School of Life Science, Hokkaido  
University, 2. International Center for Materials  
Nanoarchitectonics, National Institute for  
Materials Science)  
2:20 PM - 2:40 PM

#### [C205-2pm-04] Diffusion process of Fe immiscible with In into Pd-In alloy nanoparticles

○Kenshi Matsumoto<sup>1</sup>, Ryo Takahata<sup>1</sup>, Ryota  
Sato<sup>1</sup>, Toshiharu Teranishi<sup>1</sup> (1. Kyoto  
University)  
2:40 PM - 3:00 PM

#### [C205-2pm-05] Unusual cationic coordination network

based on boron-bridged structure

○Takeshi Kato<sup>1</sup>, Masataka Ohtani<sup>1</sup> (1. Kochi University of Technology)

3:00 PM - 3:20 PM

- [C205-2pm-06] Site-selective formation of coordination polymer consisting of Cu-thiolate ligands using metal ion-doped polymer substrate
- Takaaki Tsuruoka<sup>1</sup>, Yuri Miyashita<sup>1</sup>, Ryuki Yoshino<sup>1</sup>, Myu Fukuoka<sup>1</sup>, Yohei Takashima<sup>1</sup>, Kensuke Akamatsu<sup>1</sup> (1. Konan University)
- 3:20 PM - 3:40 PM

## D103

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

### [D103-2pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Tatsuya Kameyama, Kazuhide Kamiya  
1:00 PM - 3:40 PM D103 (Online Meeting)

- [D103-2pm-01] Carbon nanotube-based novel non-precious metal electrode catalyst with high performance
- Naotoshi Nakashima<sup>1</sup>, Ganesan Pandian<sup>1</sup>, Chearin Kim<sup>1</sup>, Jin Nishida<sup>1</sup>, Hiroki Shu<sup>2</sup>, Mitsugu Uejima<sup>2</sup>, Aleksandar Staykov<sup>1</sup> (1. Kyushu University, 2. Zeon Co.)
- 1:00 PM - 1:20 PM
- [D103-2pm-02] Synthesis of double-layer platinum nanosheets and electrocatalytic reaction
- Daisuke Takimoto<sup>1</sup>, Shino Toma<sup>1</sup>, Yuya Suda<sup>2</sup>, Masashi Matsumoto<sup>3</sup>, Hideto Imai<sup>3</sup>, Wataru Sugimoto<sup>2</sup> (1. University of the Ryukyus, 2. Shinshu University, 3. NISSAN ARC LTD.)
- 1:20 PM - 1:40 PM
- [D103-2pm-03] Bimetal oxide nanoparticles embedded in rGO as catalyst for rechargeable Zn-air batteries
- Mai Thanh Nguyen<sup>1</sup>, Wei Jian Sim<sup>1</sup>, Zixuan Huang<sup>1</sup>, Masayuki Takahashi<sup>1</sup>, Tetsu Yonezawa<sup>1</sup> (1. Hokkaido University)
- 1:40 PM - 2:00 PM
- [D103-2pm-04] Catalytic synergies in multimetallic nano and subnanoparticles for hydrogen evolution reaction (HER)
- Quan ZOU<sup>1</sup>, Yuji Akada<sup>1</sup>, Akiyoshi Kuzume<sup>2,3</sup>,

Takane Imaoka<sup>1,2</sup>, Kimihisa Yamamoto<sup>1,2</sup> (1. Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, 2. JST-ERATO, 3. University of Yamanashi)

2:00 PM - 2:20 PM

- [D103-2pm-05] Co-sintering Process of LiCoO<sub>2</sub> Cathodes and NASICON-type LATP Solid Electrolytes Studied by X-ray Absorption Fine Structure and X-ray Diffraction
- Fumihiko Ichihara<sup>1</sup>, Shogo Miyoshi<sup>1</sup>, Takuya Masuda<sup>1</sup> (1. National Institute for Materials Science)
- 2:20 PM - 2:40 PM
- [D103-2pm-06] Feasibility Studies of Graphite as a Negative Electrode Material for Mg-Ion Batteries
- Masahiro SHIMIZU<sup>1</sup>, Susumu Arai<sup>1</sup> (1. Shinshu University)
- 2:40 PM - 3:00 PM
- [D103-2pm-07] Effect of thermal maturation on the evaluation indicator for source organic matter of crude oil using naphthalene composition
- Kenta Asahina<sup>1</sup>, Koji U. Takahashi<sup>1</sup>, Kazuya Morimoto<sup>1</sup>, Takeshi Nakajima<sup>1</sup>, Yuichiro Suzuki<sup>1</sup> (1. National Institute of Advanced Industrial Science and Technology)
- 3:00 PM - 3:20 PM
- [D103-2pm-08] Electricity generation by radiolysis of water in the presence of iron oxide particles
- Momoko Shimaoka<sup>1</sup>, Sakyo Ueno<sup>1</sup>, Sana Itakura<sup>1</sup>, Sota Goto<sup>1</sup>, Shin-ichi Hashimoto<sup>1</sup>, Yusa Muroya<sup>2</sup>, Kaname Tsutsumiuchi<sup>1</sup> (1. Chubu Univ., 2. SANKEN, Osaka U.)
- 3:20 PM - 3:40 PM

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

## [D202-2pm] 01. Education and History of Chemistry

Chair: Keiko Miyamoto, Shuichi Takahara

Thu. Mar 24, 2022 1:00 PM - 2:20 PM D202 (Online Meeting)

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[D202-2pm-01] Practice of the hypothesis-experiment class at university and developing teaching materials aimed at forming of the metal concept

○Shuichi Takahara<sup>1</sup> (1. Okayama University of Science)

1:00 PM - 1:20 PM

[D202-2pm-02] Comprehensive Physical Chemistry Learning Based on Blended Learning: A New Laboratory Course

○Hiroto Mori<sup>1,2</sup>, Nahoko Kuroki<sup>1</sup> (1. Chuo University, 2. Institute for Molecular Science)

1:20 PM - 1:40 PM

[D202-2pm-03] A Suggestion on the Review of Several Basic Terms Used in University Organic Chemistry Classes

○Masato M. Ito<sup>1</sup> (1. Soka Univ., Fac. of Sci. & Eng.)

1:40 PM - 2:00 PM

[D202-2pm-04] Scientific English for Graduate School and University Students

○Keiko Miyamoto<sup>1</sup> (1. Rikkyo University)

2:00 PM - 2:20 PM



## 金属概念の形成を目指した大学での仮説実験授業の実践と教材開発

(岡山理科大学) ○高原 周一

Practice of the Hypothesis-Experiment Class at University and Developing Teaching Materials Aimed at Forming of the Metal Concept (Okayama University of Science) ○Shuichi Takahara

Understanding the common properties of metals such as metallic luster, electrical conductivity, and thermal conductivity, that is, forming of the metal concept, is important in chemical education. However, even university students are inadequate in forming of the metal concept. In order to improve this situation, the author practiced lessons and developed teaching materials with reference to the hypothesis-experiment class. The results will be reported.

*Keywords : Hypothesis-Experiment Class; University Education; Metal Concept; Development of Teaching Materials*

金属光沢、電気伝導性、熱伝導性などの金属の共通する性質を理解すること、すなわち金属概念を形成することは、化学教育において重要である。発表者は、勤務大学の教養科目「現代人の科学 A」等において、仮説実験授業の授業書<sup>1,2)</sup>を活用した金属概念に関する講義を行ってきた。表 1 に講義中にクリッカーを用いて実施した物質の電気伝導に関する問題の平均正答率 (2016～2020 年度, 11 クラス, 計 708 名分) を示す。その結果、問題 1・2 のような基本問題であっても大学生の正答率は 6 割弱であり、「全ての金属は良導体である」という認識の定着が不十分であることがわかった。これを改善するためには、仮説実験授業で行われている問題 3 (銀色の折り紙＝紙にアルミ箔を貼ってある)、問題 4 (アラザン＝砂糖の周りを銀箔でコーティングしてある) のような判断に迷う問題を扱い、金属光沢と電気伝導の関係を強く意識させることが有効であると考えられる。

そこで、これらの問題の類題を開発するため、豆電球もしくは LED 電球と乾電池のテスターを使って、幾つかの金属光沢をもつ試料について導通を調べた。その結果を表 2 示す。LED 電球のみで導通確認できた試料 (結果欄「LED 電球」) は金属蒸着膜、豆電球でも導通確認できた試料 (結果欄「豆電球」) は金属箔を使用していると思われる。発表では、これらの結果を用いた教材を提案したい。

- 1) 《電気をとおすもの・とおさないもの》, 藤沢千之, たのしい授業, **2020**, 508, 32-47.
- 2) 《自由電子が見えたなら》, 板倉聖宣, 仮説実験授業研究 (第Ⅲ期) 第 2 集, 仮説社, **1990**, 102-238.

表 1 物質の電気伝導に関する問題の平均正答率 (大学生)

問題番号	試料	平均正答率
1	1 円玉	57 %
2	5 円玉	57 %
3	銀色の折り紙	51 %
4	アラザン	51 %

注: 上記試料は全て豆電球と乾電池のテスターで導通確認が可能

表 2 様々な試料の電気伝導

試料	結果
銀色プラスチックスプーン	LED 電球
ポテトチップスの袋 *	LED 電球
イトル食品の袋 *	豆電球
漢方薬の袋 *	豆電球

注: 試料欄の \* は紙やすりで磨く必要がある試料を示す。

## ブレンデッドラーニングに基づく総合的な物理化学の学習： 新しい大学学生実験の試み

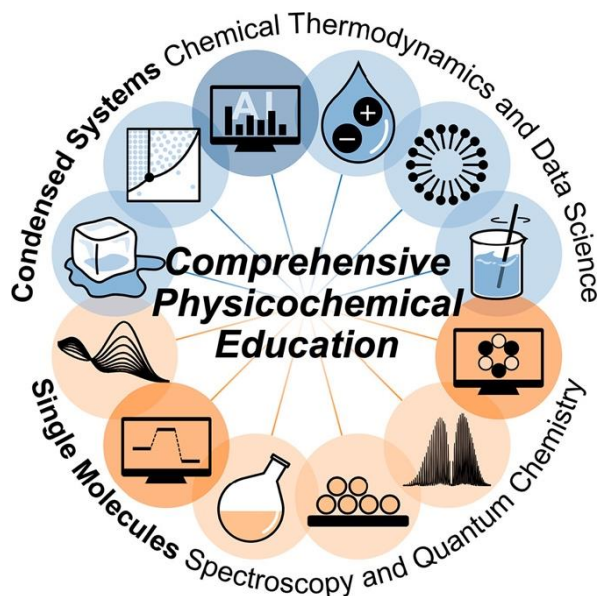
(中央大理工<sup>1</sup>・分子研<sup>2</sup>) ○森 寛敏<sup>1,2</sup>・黒木 菜保子<sup>1</sup>

Comprehensive Physical Chemistry Learning Based on Blended Learning: A New Laboratory Course (<sup>1</sup>*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*, <sup>2</sup>*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science*) ○Hiroto Mori<sup>1,2</sup>, Nahoko Kuroki<sup>1</sup>

**Keywords :** *Physical Chemistry, Computational Chemistry, Chemoinformatics, Spectroscopy, Thermodynamics*

The COVID-19 pandemic has led to an increasing amount of research on redesigning educational models. This paper describes the contents of a new laboratory course on physical chemistry based on blended learning, designed for third-year students in the Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University. We provided students with digest video materials for flipped learning, a cloud computing environment, and video conferencing tools. These materials enhanced the course contents to facilitate effective education during the pandemic. The results of a questionnaire survey showed that students were delighted with the new course, which comprehensively included experiments, computation, and data science.

コロナ禍を契機に、化学教育モデルの再設計が活発化している。本講演では、ブレンデッドラーニングに基づく物理化学の新実験授業の取組を紹介する。本授業では、反転学習用のダイジェストビデオ、クラウド計算環境、ビデオ会議ツールを学生に提供した。また、パンデミック下の効果的な教育を促進するため、授業内容を充実させた。アンケート結果、実験から情報化学まで総合的に盛り込んだ授業に、学生が満足したことが分かった。



1) Comprehensive Physical Chemistry Learning Based on Blended Learning: A New Laboratory Course, Kuroki N., Mori H., *J. Chem. Edu.* **2021**, 12, 3864-3870. ([Open Access](#))

## 大学の有機化学の授業等で用いられているいくつかの基本的な用語の見直しの提案

(創価大理工) ○伊藤 真人

A Suggestion on the Review of Several Basic Terms Used in University Organic Chemistry Classes (Faculty of Science and Engineering, Soka University) ○Masato M. Ito

Some of the terms in organic chemistry classes and textbooks for introductory education in universities has been conventionally used, although they no longer seem appropriate in view of the current theories or practices, or may cause misconception. Some examples are shown and their possible alternatives are suggested.

(1) The terms “resonance” and “resonance effect” *etc.* in terms of delocalization of electrons in conjugate systems seems inappropriate because the resonance theory, on which these terms are based, no longer holds. “delocalization” and “delocalization effect” *etc.* are suggested as alternatives. (2) The term “nucleophile” or “electrophile” has been translated as “求核 (求電子) 試薬 (剤): *kyukaku (kyudenshi)-shuiyaku (zai)*”. However, when they are used in terms of active species ( $\text{Cl}^-$ ,  $\text{NO}_2^+$  *etc.*), they shall better be translated as “求核 (求電子) 種: *kyukaku (kyudenshi)-shu*” because the term “試薬 (剤): *shiyaku (zai)*” corresponds to the chemical agents but does not well accord with the active species. (3) The traditional term “downfield (upfield)” shift in NMR to direct chemical shift change, mainly used by organic chemists, may be replaced with upfreq (downfreq) shift, in accord with the principle of the chemical shift, as has been noted by Takeuchi<sup>1)</sup> and Mori<sup>2)</sup>.

*Keywords: University Chemistry Education, Organic Chemistry, Review and Suggestion of Basic Terms, Improper Terminology*

主として有機化学の専門基礎教育の授業等で伝統的に使われている用語の中には、現在では使い方が適切ではないものや誤解を招く恐れがあると考えられるものがある。これに該当する例をいくつか取り上げ、問題点と改訂案を示す。

(1) 共役系での「共鳴」は、今日では $\pi$ 電子の非局在化を表し、「共鳴効果」はこれに基づく置換基の電子効果を表している。しかし、この用語の基になった共鳴理論は、現在では共役系の $\pi$ 電子の分布の様子を表す考え方としては用いられない。この文脈での「共鳴」は、「非局在化」で置き換えるのが妥当ではないか（例えば、「共鳴式」→「非局在化(の)式」, 「共鳴効果」→「非局在化効果」など）。(2) 求核試薬 (剤) や求電子試薬 (剤) は、対応する薬品に用いるのは問題ないが、実際の活性種 ( $\text{Cl}^-$ ,  $\text{NO}_2^+$  など) を表すときは、求核種や求電子種を用いてはどうか。(3) NMR で化学シフト変化を説明する際に用いる「低 (高) 磁場シフト」は、竹内ら<sup>1)</sup>や森<sup>2)</sup>が指摘しているように「高 (低) 周波シフト」で置き換えるべきである。

適切な用語を用いることにより内容を易しく、かつ正しく理解できるようになる。基礎教育の段階から、習慣にとらわれずに内容を適切に表す用語を用いるよう努めることが望まれる。

1) 竹内, 加藤, 「よくある質問の基本」講談社 (2012), p. 33. 2) 森, 有機合成化学, **78**, 189 (2020).

## 科学英語教育実践例

(立教大理) ○宮本 恵子

Scientific English for Graduate School and University Students (*Faculty of Science, Rikkyo University*) ○Keiko Miyamoto

There is no need to say how important for scientific students to have a good command of English. But the reality is that most students having learned English for 6 years in secondary school have hard time in reading research papers for their graduation work. Therefore, a “bridge” course to fill this gap is required. In my Scientific English classes, undergraduate students learn specific grammar useful for mastering scientific English (compound noun, compound adjective etc). They carry out listening/reading exercises to accept English without translating it into Japanese (i.e. try to receive the information contained in English in the order of words). Through these trainings, they will acquire rapid-reading skills and improve listening skills. For graduate students, writing and speaking (presentation) exercises will be added.

*Keywords : Scientific English; Specific Grammar; Rapid-reading; Listening exercises*

理工系の学生にとって科学英語力を高めることがどれほど重要であるかについては、改めて述べる必要はないだろう。中学高校大学とほぼ8年間英語を学んでいるが、いざ卒研で論文を読むとなると非常に苦勞する現実がある。大学の科学英語の授業では、科学英語特有の文法（物質名詞が普通名詞に変化するなど）を学び、英語を日本語に訳して理解するのではなく、英語のまま理解する（すなわち英語で提示された「情報」を英語の語順のまま受け取る）演習をリスニングとリーディングの両方で行う。速読力を身につけることは、リスニング力の向上にもつながり、論文を速く正確に苦勞なく読みとけるようになる。大学院の授業では、情報を発信する（書く、話す）ことに重点を置く。「Science at Hand」<sup>1)</sup>と「化学英語30講」<sup>2)</sup>を使用し、ウェブサイト<sup>3,4)</sup>も活用した学部と大学院での授業例を紹介する。



- 1) Science at Hand: Articles from Smithsonian Magazine's Smart News - スミソニアンで読む日常の科学 2020年1月発行 出版社：金星堂 978-4-7647-4103-4
- 2) 化学英語30講 2017年10月発行 出版社：朝倉書店 978-4-2541-4675-2
- 3) <http://scientific-english.moon.bindcloud.jp/>
- 4) <http://www.eng4science.com>

## [A204-2am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Kenji Sugisaki, Yuta Hori

Thu. Mar 24, 2022 9:00 AM - 11:20 AM A204 (Online Meeting)

### [A204-2am-01] Proton conduction mechanism for anhydrous imidazolium hydrogen succinate investigated by quantum chemical calculation

○Yuta Hori<sup>1</sup>, Shun Dekura<sup>2</sup>, Tomonori Ida<sup>3</sup>, Motohiro Mizuno<sup>3</sup>, Hatsumi Mori<sup>2</sup>, Yasuteru Shigeta<sup>1</sup> (1. University of Tsukuba, 2. The University of Tokyo, 3. Kanazawa University)

9:00 AM - 9:20 AM

### [A204-2am-02] The method of calculation in spin (skyrmion and antiskyrmion)

○tomohito yamagishi

9:20 AM - 9:40 AM

### [A204-2am-03] Development of the structure-based Gaussian expansion method: Application to hydrogen tunneling in malonaldehyde

○Kazuma Suzuki<sup>1</sup>, Manabu Kanno<sup>1</sup>, Hirohiko Kono<sup>1</sup> (1. Tohoku University)

9:40 AM - 10:00 AM

### [A204-2am-04] Molecular simulation that incorporates classical equation of motion for free electrons in metal: Photo-absorption and energy relaxation of nano-particle in solution

○Atsushi Yamada<sup>1</sup> (1. University of Tsukuba)

10:00 AM - 10:20 AM

### [A204-2am-05] Quantum chemical calculations on quantum computers: Development of a quantum phase difference estimation algorithm

○Kenji Sugisaki<sup>1,2,3</sup>, Chikako Sakai<sup>1</sup>, Kazuo Toyota<sup>1</sup>, Kazunobu Sato<sup>1</sup>, Daisuke Shiomi<sup>1</sup>, Takeji Takui<sup>1</sup> (1. Osaka City University, 2. JST PRESTO, 3. CQuERE/TCG CREST)

10:20 AM - 10:40 AM

### [A204-2am-06] Development of anharmonic vibrational structure theory using backflow transformation

○Kiriko Ishii<sup>1</sup>, Masanori Tachikawa<sup>1</sup>, Tomomi Shimazaki<sup>1</sup>, Yukiumi Kita<sup>1</sup> (1. Yokohama city university)

10:40 AM - 11:00 AM

## 量子化学計算によるコハク酸イミダゾリウム結晶中のプロトン伝導機構解析

(筑波大計算セ<sup>1</sup>・東大物性研<sup>2</sup>・金沢大院自然<sup>3</sup>) ○堀 優太<sup>1</sup>・出倉 駿<sup>2</sup>・井田朋智<sup>3</sup>・水野元博<sup>3</sup>・森 初果<sup>2</sup>・重田育照<sup>1</sup>

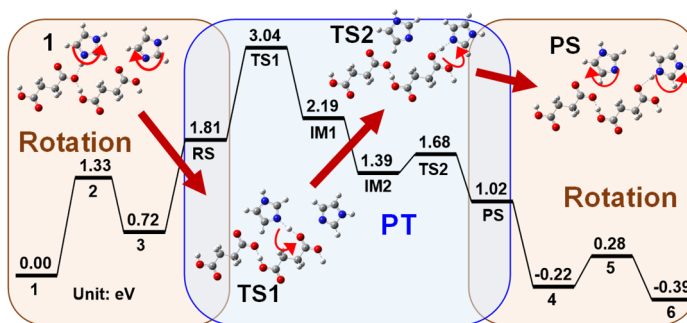
**Proton conduction mechanism for anhydrous imidazolium hydrogen succinate investigated by quantum chemical calculation** (<sup>1</sup>*Center for Computational Sciences, University of Tsukuba*, <sup>2</sup>*The Institute for Solid State Physics, The University of Tokyo*, <sup>3</sup>*Graduate School of Natural Science and Technology, Kanazawa University*) Yuta Hori,<sup>1</sup> Shun Dekura,<sup>2</sup> Tomonori Ida,<sup>3</sup> Motohiro Mizuno,<sup>3</sup> Hatsumi Mori,<sup>2</sup> Yasuteru Shigeta<sup>1</sup>

Anhydrous imidazolium hydrogen succinate (Im-Suc) exhibits high proton conduction even at temperatures exceeding 100 °C despite its crystalline nature. Proton conduction mechanisms are attractive for elucidating toward the development of solid electrolytes for fuel cells. Quantum chemical calculations are utilized for proton conduction mechanism in terms of the change of hydrogen bonds and molecular rotation in Im-Suc. The dominant proton conduction pathway and vibrational frequencies showed that the N–H stretching of imidazolium were identified as key factors for promoting efficient proton conduction in Im-Suc. The calculated potential energy surface involving proton transfer (PT) and rotational motion of imidazole showed that PT between imidazole and succinic acid was a rate-limiting step for proton transport in Im-Suc and proton conduction proceeded via the successive coupling of PT and rotational motion of imidazole based on a Grotthuss-type mechanism.

**Keywords:** Proton Conduction; Quantum Chemistry; Imidazole; Succinic Acid

コハク酸イミダゾリウム(Im-Suc)は、結晶でありながら比較的高いプロトン伝導性を示しており、そのプロトン伝導機構に興味を持たれている。本研究では、赤外分光測定と量子化学計算による振動解析から温度変化に伴う水素結合構造の変化を調べた。また、量子化学計算によって Im-Suc 中の水素結合構造、プロトン移動、分子運動を結びつけるためにポテンシャルエネルギーダイアグラム（下図）を構築した。

実験との比較により、Im-Suc 中では温度上昇に伴い、Im のディスオーダーによる水素結合環境の変化が起きていることがわかった。また、ポテンシャルエネルギーから Im-Suc 中のプロトン伝導は、Im の面内回転運動と Im と Suc 間の分子間のプロトン移動のカップリングにより効率的に引き起こされることが明らかとなった。



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



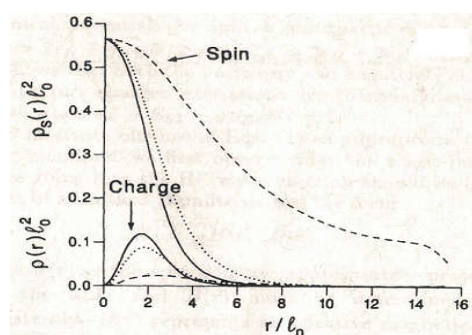
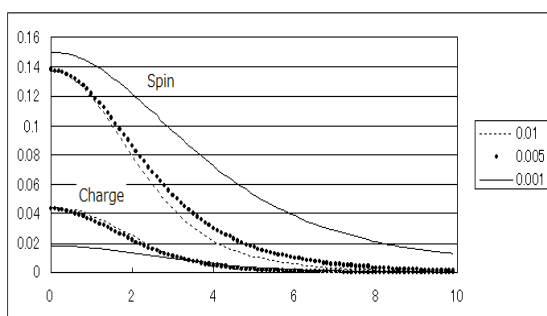
## アンチスカームイオンを用いた Hartree Fock 近似の有効範囲

山岸智仁

When a magnetic field perpendicular to a metal flat plate is applied at an extremely low temperature, all the spin directions, which is called a ferromagnetic state, are aligned. When one electron is removed from it, if the magnetic field is strong, only the part where the electron is removed becomes a hole state, but if the magnetic field becomes weak, the spin direction of electrons is slightly shifted and electrons move to fill the space, resulting in skyrmion state with a characteristic spin state. Similarly, when an electron is added in weak magnetic field, it becomes an anti-skyrmion state, which is similar to skyrmion. In the past, the Hartree Fock approximation was used to calculate skyrmion state at zero temperature, and the energy of the anti-Skyrmion state was calculated by adding a constant to it. Here, the calculation using the Hartree Fock approximation is performed for the anti-skyrmion state. I discuss exactly how much magnetic field the Hartree Fock approximation is effective for. (The following is graph different from conventional calculation result)

**Keywords :** skyrmion antiskyrmion lowtemperature

極低温で、金属平板に垂直な磁場をかけると、強磁性状態と呼ばれるスピンの方向がすべてそろった状態になる。そこから、電子を一つ取り除くと、強磁場であれば、電子が取り除かれた所だけ欠けたホール状態になるが、磁場が弱くなると、となり合う電子のスピン方向をわずかにずらしながら、欠けた所を埋めるように電子が移動しスピンの状態が特徴的なスカームイオン状態になる。また、同様に電子を一つ加え、弱磁場にするとアンチスカームイオン状態というスカームイオンに似た状態になる。従来は絶対零度のスカームイオン状態に Hartree Fock 近似を用いて計算し、それに定数を加えてアンチスカームイオン状態のエネルギーの計算をしていたが、ここではアンチスカームイオン状態に Hartree Fock 近似を用いた計算をし、正確にはどの程度の磁場までに Hartree Fock 近似が有効かを議論する。(以下は従来の計算結果と異なるグラフ)



(Phys.RevB50 より)

- 1) H.A.Fertig, Luis Brey, R.Cot, and A.H.MacDonalds ,Phys.Rev.B50.11018(1994)
- 2) Wenchen Luo and R.Cote Phys.Rev. B88. 115417 (2013)

## 構造ベースガウス基底展開法の開発:マロンアルデヒドの水素トンネリングへの適用

(東北大院理) ○鈴木 和磨・菅野 学・河野 裕彦

Development of the structure-based Gaussian expansion method: Application to hydrogen tunneling in malonaldehyde (*Graduate School of Science, Tohoku University*) ○Kazuma Suzuki, Manabu Kanno, Hirohiko Kono

For the simulation of chemical reactions including nuclear quantum effects such as tunneling effects, it is necessary to calculate the time evolution of a molecular wavefunction (nuclear wavepacket). However, in conventional methods, the number of grid points or basis functions used to expand a wavepacket increases exponentially with the system size. In order to solve this problem, we have developed a structure-based Gaussian expansion method in which Cartesian Gaussian bases corresponding to molecular structures are mainly placed around chemically critical structures and reaction pathways in the reaction of interest. This enables us to expand a molecular wavepacket with minimum bases. We applied the method to a hydrogen tunneling in malonaldehyde  $\text{CH}_2(\text{CHO})_2$ . The tunneling splitting of malonaldehyde,  $\Delta E$ , was calculated using 875 Gaussian bases mainly placed around two equilibrium structures and the intrinsic reaction coordinate (IRC) connecting them via the transition state. We performed electronic structure calculations at the MP2/6-31G(d,p) level and obtained the barrier height of  $1270 \text{ cm}^{-1}$  and  $\Delta E = 27.1 \text{ cm}^{-1}$ . This splitting is a little larger than the experimental value of  $21.6 \text{ cm}^{-1}$ , which is reasonable considering the actual barrier height of about  $1430 \text{ cm}^{-1}$ . We succeeded in analyzing and visualizing the quantum states of malonaldehyde in terms of expansion coefficients of individual Gaussians and found the contribution of a linear pathway of hydrogen transfer away from the IRC.

**Keywords :** *Quantum Molecular Dynamics; Gaussian Basis; Hydrogen Transfer; Malonaldehyde*

トンネル効果のような原子核の量子効果が関与する化学反応を理論的に調べるには、分子波動関数(核波束)の時間発展を計算する必要がある。しかし、従来の計算法には、波束の展開に用いる基底の数が自由度の増加と共に指数関数的に増加するという課題がある。この問題を解決するために、我々は分子構造に対応したデカルト座標ガウス基底を対象の化学反応において重要な構造や反応経路周辺に重点的に配置し、必要最小限の基底で分子波束を展開する構造ベースガウス基底展開法を開発した。本手法をマロンアルデヒド  $\text{CH}_2(\text{CHO})_2$  の水素トンネリングに適用した。

マロンアルデヒドの2つの平衡構造と、遷移状態を経由してそれらを結ぶ固有反応座標(IRC)周辺に重点的に配置した875個のガウス基底を用いてトンネル分裂  $\Delta E$  を計算した。電子状態計算をMP2/6-31G(d,p)レベル(障壁の高さの計算値  $1270 \text{ cm}^{-1}$ )で行ったところ、 $\Delta E = 27.1 \text{ cm}^{-1}$  を得た。実験値<sup>1)</sup>  $21.6 \text{ cm}^{-1}$  より少し大きい、実際の障壁高<sup>2)</sup>が  $1430 \text{ cm}^{-1}$  程度であることを考えれば妥当な値である。また、マロンアルデヒドの量子状態を基底の展開係数に基づいて解析・可視化することに成功し、IRCに加えてそこから離れた直線的な水素移動経路も寄与する結果を得た。

1)D. W. Firth et al., J. Chem. Phys. **94**, 1812 (1991); 2)Y. Wang et al., J. Chem. Phys. **128**, 224314 (2008).



## 金属内自由電子の古典的運動方程式を組み込んだ分子シミュレーションの開発：水溶液中ナノ粒子の光吸収とエネルギー緩和

(筑波大計セ<sup>1)</sup>) ○山田 篤志<sup>1</sup>

Molecular simulation that incorporates classical equation of motion for free electrons in metal: Photo-absorption and energy relaxation of nano-particle in solution (<sup>1</sup>Center for Computational Sciences, University of Tsukuba) ○Atsushi Yamada<sup>1</sup>

Molecular simulation that incorporates oscillating electric field and classical free electron dynamics in the framework of the force-field model has been developed to enable us to describe the optical response of metal materials in visible region. As numerical examples, we demonstrate metal-charge interaction that reproduces the classical image charge potential, calculations of dielectric functions of bulk metal, absorption spectrum of a metal nano-particle, and solvation effect on the spectrum, and simulation of visible light absorption by the plasmon resonance and succeeding thermal relaxation for metal nano-particles in the water solvent.

**Keywords :** light-metal interaction, molecular simulation, classical electron dynamics, optical response, metal nano-particle

金属は光科学分野に於いて重要な物質である。例えば金属ナノ粒子が光と相互作用することで起こるプラズモン共鳴や近接場光などの現象は基礎から応用まで幅広く研究されている。こうした系の光応答を原子レベルで解析する計算科学アプローチは第一原理手法により行われているが、高い計算コストのため小さい系に適用性が限られる。第一原理以外の実用的な計算手法の選択肢を確立することを目指し、本研究では可視領域での溶液内金属の光応答を記述することができる分子シミュレーションを開発した[1]。金属の光学特性は自由電子に由来するため、固定点電荷や断熱的な電子分極を表現する従来の力場モデルでは吸収を伴う可視光との相互作用を記述することができない。そこで本研究では、力場による分子シミュレーションの枠組みに金属内自由電子の古典運動ならびに光振動電場を組み入れることによる新たな計算手法を構築する。さらに分極可能モデルの溶媒分子を配置することで、溶液との相互作用を含む光応答を記述可能にする。計算例として、(i)金属の表面電荷と鏡像ポテンシャルの再現、(ii)バルク金属の誘電関数の計算、(iii)水溶液中の金属ナノ粒子の吸収スペクトル、(iv)可視光照射によるプラズモン共鳴励起とエネルギー緩和過程、を示す。

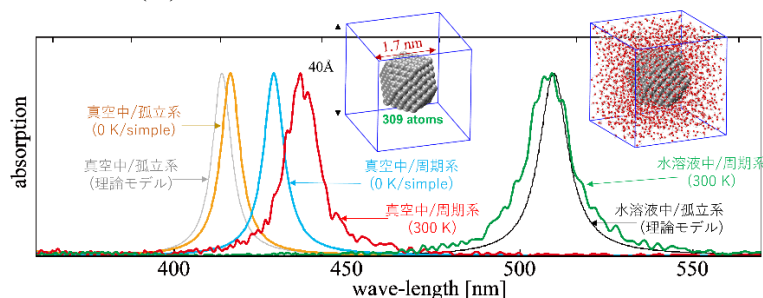


図1. 本手法で計算した真空中と水溶液中の金属ナノ粒子の可視吸収スペクトル

1) Atsushi Yamada, *J. Chem. Phys.*, **155**, 174118 (2021).

## 量子コンピュータによる量子化学計算：量子位相差推定アルゴリズムの開発

(阪市大院理<sup>1</sup>・JST さきがけ<sup>2</sup>・TCG 科学技術研究教育センター/量子工学研究所<sup>3</sup>)  
○杉崎研司<sup>1,2,3</sup>・酒井智香子<sup>1</sup>・豊田和男<sup>1</sup>・佐藤和信<sup>1</sup>・塩見大輔<sup>1</sup>・工位武治<sup>1</sup>

Quantum chemical calculations on quantum computers: Development of a quantum phase difference estimation algorithm (<sup>1</sup>Graduate School of Science, Osaka City University, <sup>2</sup>JST PRESTO, <sup>3</sup>Centre for Quantum Engineering, Research and Education, TCG Centres for Research and Education in Science and Technology) ○Kenji Sugisaki,<sup>1,2,3</sup> Chikako Sakai,<sup>1</sup> Kazuo Toyota,<sup>1</sup> Kazunobu Sato,<sup>1</sup> Daisuke Shiomi,<sup>1</sup> and Takeji Takui<sup>1</sup>

The quantum phase estimation algorithm is capable of computing the full-CI energy with a polynomial cost on a quantum computer. The total energy strongly depends on the size of molecule, but the magnitude of energy difference to be discussed is not greatly dependent on the molecular size. It is very valuable if we can calculate the energy gap directly without inspecting the total energies of molecule. In this work, we developed a Bayesian phase difference estimation algorithm, which allows us to calculate the energy gap of two electronic states directly on a quantum computer.

**Keywords :** *quantum computers, quantum chemical calculations, quantum algorithms, full configuration interaction method*

量子化学計算は量子コンピュータの近い将来の計算ターゲットとして注目を集め、非常に活発に研究が行われている。量子化学計算のための量子アルゴリズムは大別すると量子位相推定(QPE)に基づく full-CI 計算法と変分量子固有ソルバー(VQE)を用いた近似波動関数計算法がある。QPE は非常に多くの量子ゲート操作を必要とするため、誤り耐性量子コンピュータ(FTQC)が実現しないと意味のある計算結果を得ることは難しいが、古典コンピュータでは分子軌道数に対して指数関数的に増加する full-CI 計算コストが QPE を用いると多項式になることが理論的に示されているため、FTQC 時代に有力な計算手段となると期待されている。

QPE による full-CI 計算では、波動関数の時間発展により生じる位相変化にエネルギー固有値の情報が含まれていることを利用し、時間発展前後の波動関数の位相差を決定することでエネルギーを求める。一方で、量子化学計算で扱う多くの問題は全エネルギーとは桁違いに小さなエネルギー差を議論する。また、全エネルギーは分子サイズに大きく依存するが、たとえば化学反応で議論されるエネルギー差の大きさは分子サイズにほぼ依存しない。これらの理由から、量子コンピュータを用いてエネルギー差を直接計算できれば非常に有用である。今回我々は、エネルギー差を求めたい2つの電子状態の量子重ね合わせ状態を利用することで full-CI 法でのエネルギー差を直接計算することができる量子位相差推定アルゴリズム<sup>1)</sup>を開発したので報告する。

1) K. Sugisaki, C. Sakai, K. Toyota, K. Sato, D. Shiomi, T. Takui, Bayesian phase difference estimation: a general quantum algorithm for the direct calculation of energy gaps. *Phys. Chem. Chem. Phys.* **2021**, *23*, 20152–20162.

## Development of anharmonic vibrational structure theory using backflow transformation

(<sup>1</sup>Graduate School of Nanobioscience, Yokohama City University, <sup>2</sup>School of Data Science, Yokohama City University) ○Kiriko Ishii,<sup>1</sup> Masanori Tachikawa,<sup>1,2</sup> Tomomi Shimazaki,<sup>1</sup> Yukiumi Kita<sup>2</sup>

**Keywords:** Anharmonic vibrational structure theory; Vibrational Coordinate; Backflow transformation; Quantum Monte Carlo method

The anharmonic vibrational structure analysis using the first principles calculations has been widely used in molecular spectroscopy to assign peaks/bands in infrared (IR) spectra and to determine molecular geometries. In anharmonic vibrational structure theory, an accurate trial wavefunction is indispensable to describe the molecular vibrational nature. Especially, it is important for generating accurate trial wavefunction to include many-body effect in the vibrational wavefunction.

In this study, we developed new vibrational coordinates using backflow transformation (BF),<sup>1)</sup> which is one of the theoretical approaches to take a correlation effect in quantum many-body systems into account, in order to improve the vibrational trial wavefunction. In the BF approach, vibrational normal coordinates  $\{Q_m\}$  for each vibrational mode is transformed into a collective coordinate as,

$$Q_m \rightarrow Q_m + \zeta_m(Q_1, Q_2, \dots, Q_{N_v}), \quad \zeta_m = \sum_{n \neq m}^{N_v} \left( \sum_{\alpha=1}^{N_{\text{ex}}} \sum_{\beta=1}^{N_{\text{ex}}} c_{\alpha\beta}^{(mn)} Q_m^\alpha Q_n^\beta \right),$$

where a multivariable function  $\zeta_m$  is a *backflow displacement*, which determines the transformation into collective coordinates,  $N_v$  the number of vibrational modes,  $N_{\text{ex}}$  the expansion order of the polynomial, and  $c_{\alpha\beta}$  the expansion coefficient. The variational Monte Carlo method,<sup>2)</sup> which is one of the most accurate methods to solve a vibrational Schrödinger equation, was used to analyze the molecular properties of each state. The backflow transformation was applied to vibrational self-consistent field (VSCF) wavefunction. In this study, the theoretical accuracy of BF in quantum vibrational problems has been tested for fundamental tones, overtones, and combination tones of H<sub>2</sub>O molecule.

As a result, BF worked very well for improvement of frequencies. The mean absolute percentage error (MAPE) from the corresponding experimental values by BF was 0.8 %, which is around half of the MAPE by VSCF (1.3 %) and reasonably agree with the MAPE by the vibrational configuration interaction (VCI) wavefunction (0.6 %). The vibrational probability density to which the BF transformation was applied is also consistent with the VCI results and showed that the BF transformation appropriately take into account the correlation effects in quantum many-body systems.

1) P. López Ríos, et al., *Phys. Rev. E* **2006** 74, 066701. 2) R. J. Needs, et al., *J. Phys. Cond. Matter*, **2010** 22, 023201.

## [A204-2pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Yoshiki Ishii, Shuji Ogata

Thu. Mar 24, 2022 1:20 PM - 3:20 PM A204 (Online Meeting)

### [A204-2pm-01] First-principles simulations of protonation and adhesion weakening of organic-inorganic interface under wet conditions

○Shuji Ogata<sup>1</sup>, Masayuki Uranagase<sup>1</sup> (1. Nagoya Institute of Technology)

1:20 PM - 1:40 PM

### [A204-2pm-02] Evaluation of vibrational energies and wave functions of CO<sub>2</sub> on a quantum computer

○Erik Loetstedt<sup>1</sup>, Kaoru Yamanouchi<sup>1</sup>, Takashi Tsuchiya<sup>2</sup>, Yutaka Tachikawa<sup>2</sup> (1. The University of Tokyo, 2. DIC Corporation)

1:40 PM - 2:00 PM

### [A204-2pm-03] Comparative Study of Electron Density Distribution Maps and Crystal Structure Factors of Mg<sub>3</sub>BN<sub>3</sub> High Pressure Phase by Discrete Cosine Transform and Maximum Entropy Method

○Hideo Hiraguchi<sup>1</sup> (1. The Institution of Professional Engineers, Japan)

2:00 PM - 2:20 PM

### [A204-2pm-04] Numerical study for kinetic control of coordination self-assembly: M<sub>4</sub>L<sub>4</sub> square complex as an example

○Satoshi Takahashi<sup>1</sup>, Hirofumi Sato<sup>2,3,4</sup>, Shuichi Hiraoka<sup>1</sup> (1. Graduate School of Arts and Sciences, The University of Tokyo, 2. Department of Molecular Engineering, Kyoto University, 3. ESICB, Kyoto University, 4. Fukui Institute for Fundamental Chemistry, Kyoto University)

2:20 PM - 2:40 PM

### [A204-2pm-05] Impact of Kinetic Temperatures in Microwave Heating

○Makoto Koike<sup>1,2</sup> (1. Micro Patent Office, 2. Makoto Koike Microwave Research Institute)

2:40 PM - 3:00 PM

### [A204-2pm-06] Molecular Dynamics Analysis of Extreme Pressure Additives using Reactive and Classical Force Field

○Hitoshi Washizu<sup>1</sup>, Kyosuke Kawakita<sup>1</sup>, Yuki Iike<sup>1</sup>, Mutsuki Homma<sup>1</sup>, Riku Araki<sup>1</sup>, Yoshiki Ishii<sup>1</sup>, Hiroaki Koshima<sup>2</sup> (1. Univ. Hyogo, 2. Idemitsu Kosan)

3:00 PM - 3:20 PM

## 湿潤環境での無機有機界面のプロトン化と接着力低下に関する第一原理シミュレーション

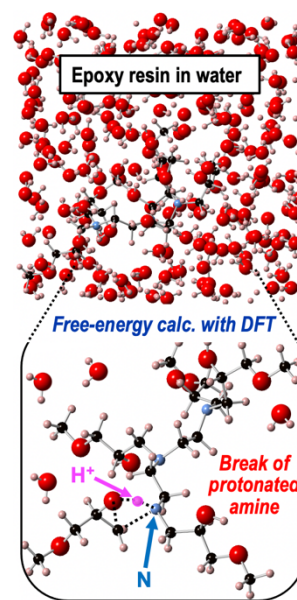
(名工大院工<sup>1</sup>) ○尾形 修司<sup>1</sup>・浦長瀬 正幸<sup>1</sup>

First-principles simulations of protonation and adhesion weakening of organic-inorganic interface under wet conditions (<sup>1</sup>*Graduate School of Engineering, Nagoya Institute of Technology*) ○Shuji Ogata,<sup>1</sup> Masayuki Uranagase<sup>1</sup>

First, we theoretically investigate the protonation of the amine group in epoxy resins prepared using amine-based curing agents. DFT-based free-energy calculations show that the amine group of the epoxy resin is protonated at equilibrium depending on the location of the amine group when the epoxy resin is embedded in neutral or acid water. The energetic barrier for breaking the ether bond of the epoxy resin is substantially lowered as a result of the cooperative effect of H<sub>2</sub>O dissociation [1]. Second, we address the issue of weakening of silane coupling agent to silica under neutral or alkaline condition. We find that the terminal -OH of silica is significantly deprotonated and that the transition-state barrier energy to break the Si-O bond of the silane coupling becomes less than 1 eV with the assistance of H<sub>2</sub>O dissociation when 50% of the terminal -OH groups on silica is deprotonated [2].

**Keywords :** DFT, Epoxy resin, Silane coupling, Wet condition, Adhesion

接着剤を用いた接着やシランカップリングによる接合は、マルチマテリアル化やコンポジット化から産業界での需要が高まっているが、湿潤環境下でその接着力や強結合強度が低下することが知られており広範な利用の障害となっている。我々は第一に、アミン系硬化剤を用いたエポキシ樹脂（接着剤）について、中性あるいは酸性環境でアミン基がプロトン化することを DFT によるプロトン移動の自由エネルギー計算で明らかにし、そのプロトン化や水分子の存在により、化学ボンド破壊に要するバリアエネルギーが大きく低下することを明らかにする[1]。第二に、有機樹脂材料に無機ナノ粒子を分散させたコンポジットの作成などで広く使われているシランカップリングに関して、水分-材料間でのプロトン移動の自由エネルギーを計算し、中性あるいはアルカリ環境でシリカ基板から脱プロトン化すること、さらにその状況ではシランカップリングの化学ボンドが弱くなることを明らかにする[2]。



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

[2] Ogata and Uranagase: J. Phys. Chem. C (2021) 125, 22907.

## Evaluation of vibrational energies and wave functions of CO<sub>2</sub> on a quantum computer

(<sup>1</sup>*School of Science, The University of Tokyo*, <sup>2</sup>*DIC Corporation*)

○Erik Lötstedt,<sup>1</sup> Kaoru Yamanouchi,<sup>1</sup> Takashi Tsuchiya,<sup>2</sup> Yutaka Tachikawa<sup>2</sup>

**Keywords:** Quantum computer; Vibrational spectroscopy; Variational quantum eigensolver

Quantum computing is beneficial for solving a variety of problems in quantum chemistry because of the possibility of storing  $2^K$  amplitudes on a quantum computer having  $K$  qubits.<sup>1</sup> By manipulating an exponentially large number of superposition states on a quantum computer, we will be able to carry out full-CI type of calculations for large molecular systems, which we cannot handle using conventional methods on classical computers. However, because of the presence of coherent and incoherent noise in quantum computing in presently available quantum computers, successful quantum chemistry calculations have been carried out using at most 10 qubits for molecular systems having up to 10 electrons.<sup>2</sup> Recently, we showed how the vibrational eigenenergies of a two-mode model of CO<sub>2</sub> can be evaluated on a quantum computer and demonstrated that quantum computers can also be applied to the vibrational eigenvalue problem.<sup>3</sup>

In this contribution, we present a new method for calculating level energies of quantum systems on a quantum computer. The method is a variation of the multistate contracted variational quantum eigensolver (MC-VQE) method.<sup>4</sup> In the MC-VQE method, we first evaluate matrix elements of the Hamiltonian on a quantum computer, and then, obtain eigenenergies by diagonalizing the Hamiltonian matrix on a classical computer. In the method we introduce, which is called a reduced MC-VQE (RMC-VQE) method, we employ a larger basis set with which the matrix elements can be evaluated efficiently on a classical computer and a smaller basis set with which the matrix elements are evaluated on a quantum computer.

We apply the RMC-VQE method to a two-mode model of CO<sub>2</sub> and execute the quantum circuits on the quantum computer *ibm\_kawasaki* at IBM Quantum. We demonstrate that we can obtain the eigenenergies of the Fermi doublet within an uncertainty of less than 0.1 cm<sup>-1</sup> after performing error mitigation to reduce the systematic errors originating from the noise. We also introduce a method by which we can construct vibrational wave functions on a quantum computer based on the measurements of the coefficients of the harmonic oscillator basis functions in the expansion of the wave function.

This research is supported by the UTokyo Quantum Initiative. We also acknowledge the use of IBM Quantum services.

1) S. McArdle, S. Endo, A. Aspuru-Guzik, S. C. Benjamin, and X. Yuan, *Rev. Mod. Phys.* **2020**, *92*, 015003. 2) Google AI Quantum and Collaborators, *Science* **2020**, *369*, 1084. 3) E. Lötstedt, K. Yamanouchi, T. Tsuchiya, and Y. Tachikawa, *Phys. Rev. A* **2021**, *103*, 062609. 4) R. M. Parrish, E. G. Hohenstein, P. L. McMahon, and T. J. Martínez, *Phys. Rev. Lett.* **2019**, *122*, 230401.

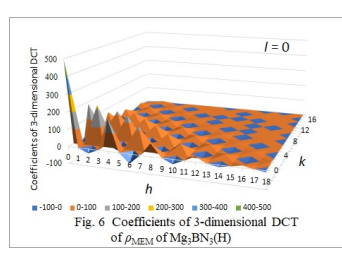
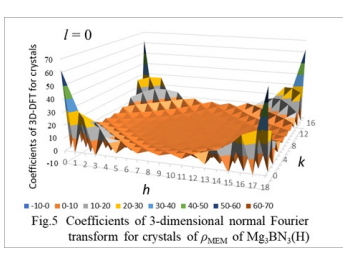
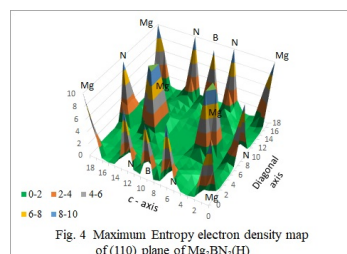
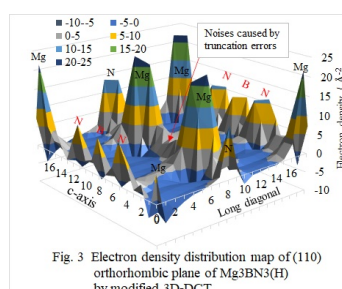
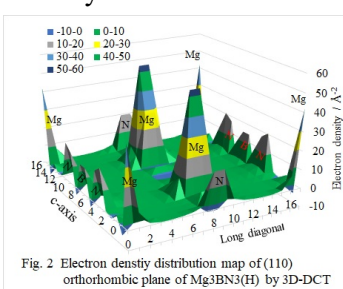
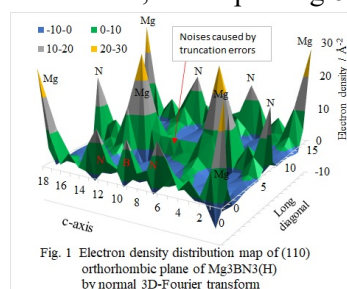
## Comparative Study of Electron Density Distribution Maps and Crystal Structure Factors of $\text{Mg}_3\text{BN}_3$ High Pressure Phase by Discrete Cosine Transform and Maximum Entropy Method

(<sup>1</sup>Professional Engineer, Japan belonging to the Institution of Professional Engineers, Japan)

○Hideo Hiraguchi <sup>1</sup>

**Keywords:** 3-dimensional DCT; Electron Density Distribution Maps; Maximum Entropy Method;  $\text{Mg}_3\text{BN}_3$  high pressure phase

It is known that the electron density distribution maps calculated by the normal Fourier transform have noises caused by truncation errors as shown in Fig.1. The Maximum Entropy method can be used to eliminate the noises by the truncation errors as shown in Fig.4. In this research, it has been found out that the 3-dimensional DCT<sup>5)</sup> can diminish the truncation errors of the electron density distribution maps of the center symmetric crystals such as  $\text{Mg}_3\text{BN}_3(\text{H})$ <sup>1)~3)</sup> (Space group : Pmmm Orthorhombic) as shown in Fig.2<sup>4)</sup>. For these calculations,  $Fhkl$  ( $h=0\sim 8, k=0\sim 8, l=0\sim 8$ ) and  $19\times 19\times 19$  voxels in the unit cell were used. Though there is no bonding electrons between Mg atoms, the noises exist in the region in Fig.1. Meanwhile, there are no electrons in the region of the 3D-DCT map in Fig.2. However, the modified 3-dimensional DCT cannot diminish the truncation errors as shown in Fig.3. To compare the coefficients between the normal Fourier transform and the DCT, the coefficients were calculated respectively as shown in Fig.5 and Fig.6. The map in Fig.5 has a symmetric center. Meanwhile, the map in Fig.6 has no symmetric center.



- 1) H. HIRAGUCHI, O. SAKATA, H. HASHIZUME, A. TAKENAKA, O. FUKUNAGA. (1990). J. Cryst. Soc. Jp. OB-11, 32.
- 2) H. HIRAGUCHI, H. HASHIZUME, O. FUKUNAGA, A. TAKENAKA, M. SAKATA. (1991). J. Appl. Cryst. 24.
- 3) H. HIRAGUCHI, H. HASHIZUME, S. SASAKI, S. NAKANO, O. FUKUNAGA. (1993). Acta Cryst. B49.4
- 4) H. HIRAGUCHI. (2021). Pacificchem2021.5
- 5) H. HIRAGUCHI. (2021). J. Appl. Cryst.



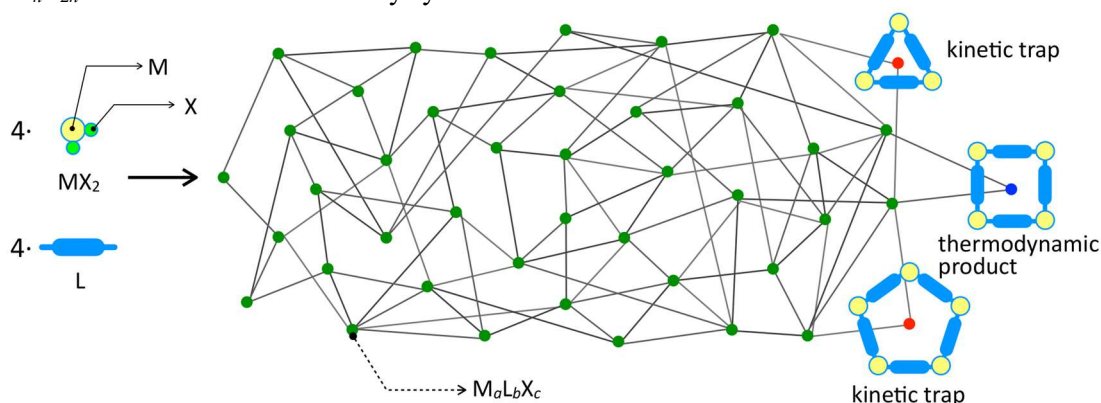
## Numerical Study for Kinetic Control of Coordination Self-Assembly: $M_4L_4$ Square Complex as an Example

(<sup>1</sup>Graduate School of Arts and Sciences, The University of Tokyo, <sup>2</sup>Department of Molecular Engineering, Kyoto University, <sup>3</sup>ESICB, Kyoto University, <sup>4</sup>Department of Fundamental Chemistry, Kyoto University) ○ Satoshi Takahashi,<sup>1</sup> Hirofumi Sato,<sup>2,3,4</sup> Shuichi Hiraoka<sup>1</sup>

**Keywords:** Molecular Self-Assembly; Chemical Master Equation; Kinetic Control

Molecular self-assembly is one of the fascinating phenomena, in which constituent atoms and molecules spontaneously assemble into the products having specific geometries depending on the types and strengths of the available chemical interactions. In most of such processes, the final products distribute in the well-known Boltzmann's manner, and so the reaction pathways of molecular self-assembly have tended to be neglected. However, if the molecular self-assembly can be carried out under kinetic control, digging into the details of reaction pathways makes us understand how to control molecular self-assembly with varying the reaction conditions and suitable design of the building blocks.

In this work, as a prototype system for numerically studying such a possibility to the kinetic chemical reaction control, we adopted the coordination self-assembly of a  $M_4L_4$  square complex composed of transition metal complexes  $MX_2$  (M and X represent the metal ion and the leaving ligand, respectively) and a ditopic ligand L. A chemical reaction network was constructed by considering all elementary reactions among 35 possible species including chain-like oligomers  $M_aL_bX_c$  ( $a = 1-10$ ) and macrocycles  $M_aL_a$  ( $a = 3-5$ ). Simulations of the self-assembly were conducted under various kinetic parameter sets and reaction conditions such as the way of mixing of the components ( $MX_2$  and L), which led to a general principle that enables us to produce most stable assembly ( $M_4L_4$ ) in higher yield by choosing a proper self-assembly pathway. This idea was experimentally confirmed for  $Pd_nL_{2n}$  coordination self-assembly systems.



Schematic representation of the self-assembly of a  $M_4L_4$  square in a chemical reaction network.



## Impact of Kinetic Temperatures in Microwave Heating

(<sup>1</sup>*Micro Patent Office*, <sup>2</sup>*Makoto Koike Microwave Research Institute*) ○Makoto Koike<sup>1,2</sup>

**Keywords:** Microwave Heating; Microwave Chemistry; Reaction Rate; Kinetic Temperatures; Arrhenius Equation

Microwave heating in polar solvents provides for an increased reaction rate constant and an improved yield compared to the conventional heating by thermal conduction,<sup>1</sup> which provides a thermal equilibrium with a homogeneous temperature: molecules, atoms and electrons have the same temperature.

This presentation pursues a theory for the microwave effect herein. Under the microwave irradiation, the reaction system is in a non-thermal equilibrium with heterogeneous kinetic temperatures, each of which correlates to an average kinetic energy of particles.

In the prominent Arrhenius equation (1) shown below, where  $k$  is a reaction rate constant;  $A$  is a frequency factor;  $E$  is the activation energy;  $R$  is the universal gas constant; and  $T$  should be an electron temperature, which is a kinetic temperature of electrons, instead of absolute temperatures defined in the thermal-equilibrium thermodynamics. Any chemical reaction involves the cleavage and formation of chemical bonds, which correspond to the changes in the spatial distribution of the electron probability density, and the electrons in the reactants play the dominant role during the chemical reaction. The external electric field by microwave gives drastically increased electron temperatures in any ion, which includes carbocations, carbanions and electrolytes, compared to kinetic temperatures of the atoms in the ion since the external electric field at the positions of the atoms are shielded by the electrons. With regard to the frequency factor  $A$ , the electromagnetic energy of microwave increases rotations of the polar solvent, which is equivalent to an increased kinetic temperature of the polar solvent in rotation in contrast to the kinetic temperature of the polar solvent in translation, so as to give the increased frequency factor.

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

- 1) Á. Díaz-Ortiz, P. Prieto, A. De La Hoz. *Chem. Rec.* **2019**, 19(1), 85.

## 反応力場と古典力場による極圧添加剤の分子動力学解析

(兵庫県大院情報<sup>1</sup>・出光興産<sup>2</sup>) ○鷺津 仁志<sup>1</sup>・河北 恭佑<sup>1</sup>・井池 祐貴<sup>1</sup>・本間 睦己<sup>1</sup>・荒木 陸<sup>1</sup>・石井 良樹<sup>1</sup>・甲嶋 宏明<sup>2</sup>

Molecular Dynamics Analysis of Extreme Pressure Additives using Reactive and Classical Force Field (<sup>1</sup>*Graduate School of Information Science, University of Hyogo*, <sup>2</sup>*Idemitsu Kosan Ltd.*) ○Hitoshi Washizu<sup>1</sup>, Kyosuke Kawakita<sup>1</sup>, Yuki Iike<sup>1</sup>, Mutsuki Homma<sup>1</sup>, Riku Araki<sup>1</sup>, Yoshiki Ishii<sup>1</sup>, Hiroaki Koshima<sup>2</sup>

The extreme pressure additives in lubrication oil make surface film reacting on the metal surface under high temperature and high share and bring low friction and wear. The mechanism is not easy to understand since they include many process. Additive molecules make reverse micelle in normal condition. Then the molecules adsorb on metal surface under lubricating condition. We used molecular dynamics simulation to understand the stability of reverse micelle in room temperature. Then used reactive force field to analyze surface reaction on metal surfaces and results revealed the mechanism.

**Keywords :** *Molecular Dynamics, Extreme Pressure Agent, Friction, Wear, Reverse Micelle*

潤滑油の添加剤<sup>1,2)</sup>の中でも、極圧添加剤についての理解は大変難しい。これは、高温、高せん断の曲圧状態において金属表面において化学反応により皮膜を形成し、低摩擦および低摩耗を実現するためである。我々は、古典力場を用いて常温において極圧剤が作用しない理由、すなわち逆ミセル形成による安定化について検討した。次に、反応力場を用いて金属および金属酸化物表面における反応を解析し、分子形状の違いによる物理・化学吸着挙動の発現機構について明らかにした。

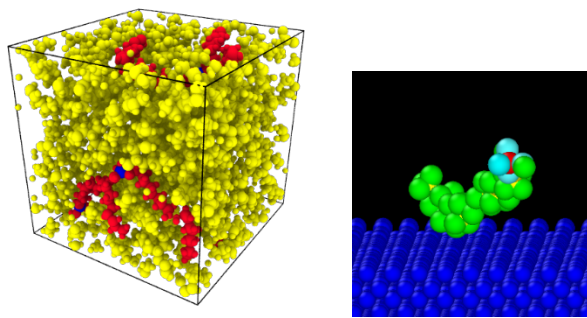


Fig. 1 Molecular dynamics simulation of mono-Oleyl phosphate. Classical molecular dynamics of reverse-micelle formation (left) and reactive molecular dynamics of surface adsorption (right).

1) M. Konishi, H. Washizu, *Trib. Intl.*, **2020**, *149*, 105568.

2) K. Nishikawa, H. Akiyama, K. Yagishita, H. Washizu, *Jurnal Tribologi*, **2019**, *21*, 63.

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Academic Program [Oral B] | 03. Physical Chemistry -Structure- | Oral B**[F302-2pm] 03. Physical Chemistry -Structure-**

Chair: Tahei Tahara, Rintaro Shimada

Thu. Mar 24, 2022 2:00 PM - 3:40 PM F302 (Online Meeting)

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**[F302-2pm-01] Complete picture of vibrational relaxation of OH stretch at the air/H<sub>2</sub>O interface: From hydrogen-bonded OH to free OH**○Woongmo Sung<sup>1</sup>, Ken-ichi Inoue<sup>1</sup>, Satoshi Nihonyanagi<sup>1</sup>, Tahei Tahara<sup>1</sup> (1. RIKEN)

2:00 PM - 2:20 PM

**[F302-2pm-02] Ultrafast vibrational dynamics of the free OD at the air/water interface revealed by time-resolved heterodyne-detected vibrational sum frequency generation spectroscopy**○Mohammed Ahmed<sup>1,2</sup>, Satoshi Nihonyanagi<sup>1,2</sup>, Tahei Tahara<sup>1,2</sup> (1. Molecular Spectroscopy Laboratory, RIKEN, 2. Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics)

2:20 PM - 2:40 PM

**[F302-2pm-03] Elucidation of pK<sub>a</sub> Value at Silica/Water Interface Using HD-VSFG Spectroscopy and Model-Independent Spectral Decomposition**○Feng Wei<sup>1</sup>, Shu-hei Urashima<sup>1</sup>, Satoshi Nihonyanagi<sup>1,2</sup>, Tahei Tahara<sup>1,2</sup> (1. Molecular Spectroscopy Laboratory, RIKEN, Wako, Saitama, Japan, 2. Ultrafast spectroscopy Research Team, RIKEN Center for Advanced Photonics, Wako, Saitama, Japan.)

2:40 PM - 3:00 PM

**[F302-2pm-04] Probing Ring Size-Dependent Structural Dynamics of Cycloparaphenylene Using Femtosecond Stimulated Raman Spectroscopy**○Hikaru Sotome<sup>1</sup>, Yusuke Morita<sup>1</sup>, Hiroshi Miyasaka<sup>1</sup> (1. Osaka Univ.)

3:00 PM - 3:20 PM

**[F302-2pm-05] ESR study of non-TEMPO radicals incorporated in nanospace in crystalline Zn complex**○Hirokazu Kobayashi<sup>1</sup>, Kento Akiniwa<sup>2</sup>, Fumiyasu Iwahori<sup>3</sup>, Hidehiko Honda<sup>1</sup>, Masato Yamamoto<sup>1</sup> (1. Faculty of Arts and Sciences at Fujiyoshida, 2. Graduate School of Integrated Basic Sciences, College of Humanities and Sciences, Nihon University, 3. College of Humanities and Sciences, Nihon University)

3:20 PM - 3:40 PM

## Complete picture of vibrational relaxation of OH stretch at the air/H<sub>2</sub>O interface: From hydrogen-bonded OH to free OH

(<sup>1</sup>Molecular Spectroscopy Laboratory, RIKEN, <sup>2</sup>Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics)

○Woongmo Sung,<sup>1</sup> Ken-ichi Inoue,<sup>1</sup> Satoshi Nihonyanagi,<sup>1,2</sup> Tahei Tahara<sup>1,2</sup>

**Keywords:** Interface, Water, Dynamics, Nonlinear spectroscopy, Vibrational spectroscopy

It has been a long-lasting question how the vibrational dynamics of water at the interface differs from that of bulk water. Until now, even a very fundamental quantity such as the vibrational relaxation ( $T_1$ ) time of the OH stretch at the air/water interface has been controversial.<sup>1,2</sup> In the present study, we used time-resolved heterodyne-detected vibrational sum-frequency generation (TR-HD-VSFG) to determine the  $T_1$  time of the OH stretch of water at the air/water interface. For obtaining reliable  $T_1$  values, we monitored the temporal evolution of the hot band (1 $\rightarrow$ 2 transition) in the hydrogen-bonded (HB) OH stretch. By tuning the pump frequency, we selectively excited the OH stretch vibration at different frequencies, in a wide range covering both the HB OH and non-hydrogen-bonded OH (free-OH). When the HB OH was excited with the pump of 3200-3500 cm<sup>-1</sup>, the  $T_1$  time in the range of 200-400 fs was obtained directly through the decay of the hot band of HB OH. Upon excitation of the free-OH (3700 cm<sup>-1</sup>), in contrast, we observed a delayed rise and a decay of the hot band of the HB OH, reflecting the conversion from the excited free OH to the excited HB OH ( $T_{1,\text{free}} \sim 840 \pm 80$  fs)<sup>3</sup> and the subsequent vibrational relaxation of the converted HB OH ( $T_{1,\text{HB}} \sim 340 \pm 60$  fs). The present TR-HD-VSFG study successfully provides reliable and consistent  $T_1$  time of the OH stretch at the air/H<sub>2</sub>O interface, as well as a coherent view of the vibrational relaxation dynamics of the interfacial OH stretch.

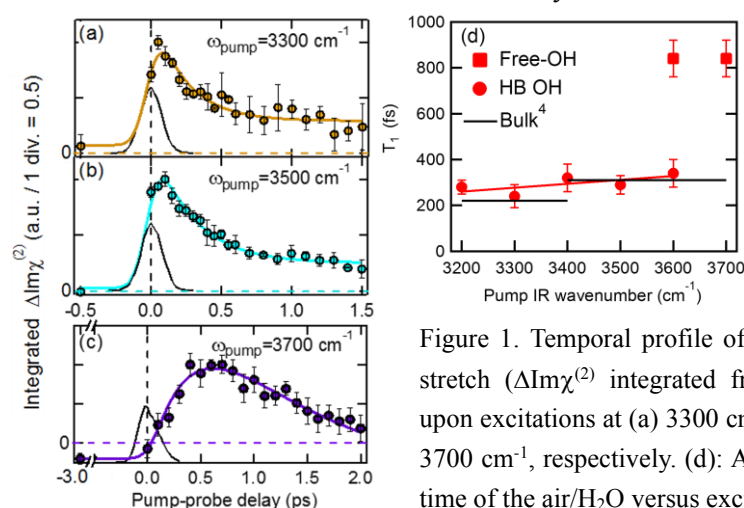


Figure 1. Temporal profile of the hot band of HB OH stretch ( $\Delta \text{Im}\chi^{(2)}$  integrated from 2900 to 3050 cm<sup>-1</sup>) upon excitations at (a) 3300 cm<sup>-1</sup>, (b) 3500 cm<sup>-1</sup>, and (c) 3700 cm<sup>-1</sup>, respectively. (d): A graph of summary on  $T_1$  time of the air/H<sub>2</sub>O versus excitation frequencies.

- 1) S. T. van der Post et al., *Nat. Commun.* **2015**, 6, 8384. 2) K. Inoue et al., *J. Phys. Chem. Lett.* **2016**, 7, 1811. 3) K. Inoue et al., *Nat. Commun.* **2020**, 11, 5344. 4) L. De Marco et al., *J. Chem. Phys.* **2016**, 145, 094501.

## Ultrafast vibrational dynamics of the free OD at the air/water interface revealed by time-resolved heterodyne-detected vibrational sum frequency generation spectroscopy

(<sup>1</sup>Molecular Spectroscopy Laboratory, RIKEN, <sup>2</sup>Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics)

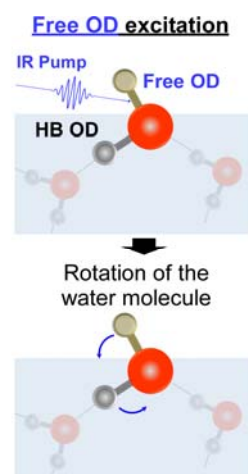
○Mohammed Ahmed<sup>1,2</sup>, Satoshi Nihonyanagi<sup>1,2</sup>, and Tahei Tahara,<sup>1,2</sup>

**Keywords:** Interface, vibrational relaxation, ultrafast dynamics, vibrational sum frequency generation, heterodyne detection

Vibrational relaxation dynamics of the OH stretch of water at the water surface has been a subject of intensive research facilitated by recent developments in ultrafast interface-selective nonlinear spectroscopy.<sup>1</sup> We previously reported the vibrational relaxation of the free OH at the air/water interface for pure H<sub>2</sub>O and isotopically diluted water (HOD-D<sub>2</sub>O) using time-resolved heterodyne-detected VSFG (TR-HD-VSFG) spectroscopy.<sup>2</sup> In sharp contrast to a former homodyne TR-VSFG study,<sup>3</sup> we found that the vibrational relaxation  $T_1$  time of the free OH at the air/H<sub>2</sub>O and air/HOD-D<sub>2</sub>O interfaces does not change with isotopic dilution. Based on the absence of the isotopic dilution effect on the  $T_1$  time, it was concluded that the vibrational relaxation of the free OH proceeds predominantly with the reorientation of the topmost water molecule having the free OH, not by intramolecular energy transfer as believed so far.

In this presentation, we report the vibrational relaxation dynamics of the free OD at the air/neat D<sub>2</sub>O and isotopically diluted HOD-H<sub>2</sub>O interfaces using TR-HD-VSFG spectroscopy. The obtained results show that the  $T_1$  time of the free OD does not show any detectable change with the isotopic dilution within the experimental error, as in the case of the free OH in the OH stretch region. This result further confirms that the vibrational relaxation of the free OD/OH at the water surface predominantly proceeds with the diffusive rotation mechanism and negates the predominant contribution of intermolecular energy transfer in the relaxation of the free OH that has been argued based on a recent MD simulation.<sup>4</sup> We also found that the  $T_1$  time of the free OD is about twice larger than that of the free OH, being consistent with the reorientation mechanism of the vibrational relaxation.

The observed large difference in the  $T_1$  time between the free OD and the free OH may suggest the involvement of the non-classical isotope effect, i.e., the nuclear quantum effect.



**Figure 1.** Schematic of the vibrational relaxation mechanism of the free OD.

- 1) S. Nihonyanagi *et al.*, *Chem. Rev.* **117**, 10665 (2017). 2) K. Inoue *et al.*, *Nat. Commun* **11**, 5344 (2020).
- 3) C.-S. Hsieh *et al.*, *PNAS* **110**, 18780 (2013). 4) T. Ishiyama, *J. Chem. Phys.* **154**, 104708 (2021).

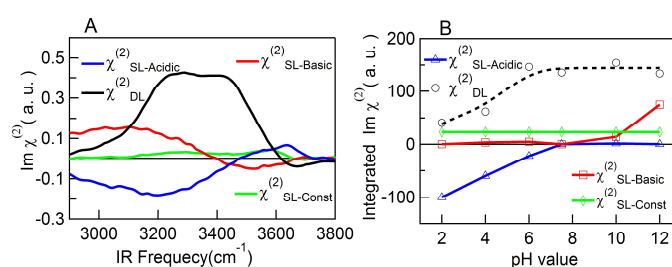
## Elucidation of $pK_a$ Value at Silica/Water Interface Using HD-VSFG Spectroscopy and Model-Independent Spectral Decomposition

(<sup>1</sup>Molecular Spectroscopy Laboratory, RIKEN, Wako, Saitama, Japan. <sup>2</sup>Ultrafast spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), Wako, Saitama, Japan.)

○Feng Wei<sup>1</sup>, Shu-hei Urashima<sup>1</sup>, Satoshi Nihonyanagi<sup>1, 2</sup>, Tahei Tahara<sup>1, 2</sup>

**Keywords:** silica/water interface, electrical double layer, HD-VSFG, charge density,  $pK_a$  value.

The silica/water buried interface is one of the most fundamental charged interfaces in nature.<sup>1</sup> In the present study, we applied heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy to obtain a molecular-level picture of silica surface,<sup>2</sup> by collecting the second-order nonlinear susceptibility ( $\chi^{(2)}$ ) spectra with different NaCl concentrations in a wide pH range. The obtained salt-dependent  $\chi^{(2)}$  spectra at each pH value were separated into the spectral components associated with water in the Stern layer (SL) and diffusely held Gouy-Chapman layer (DL) by model-independent SVD analysis. As shown in Figure A, the DL water spectrum (black line) show OH bands at 3200  $\text{cm}^{-1}$  and 3450  $\text{cm}^{-1}$ , which originate from the bulk-like water molecules in DL. The DL water contribution of the silica/water interface are positive at all pH studied, indicating that the silica surface is negatively charged in the pH range of 2.0 – 12.0. As shown in Figure B, the DL water contributions (black circles ○) show only one significant change between pH 2.0 – 6.0, which can be fitted with one  $pK_a$  value ( $3.7 \pm 0.4$ ) using the modified Gouy-Chapman model. On the other hand, the spectral component of SL water exhibits pH-dependent changes, which is explained by three spectral components (Figure A). It was found that the SL water at acidic pH (blue line) and basic pH conditions (red line) have the different conformations.



**Figure** (A) The spectral components of the water molecules at the silica/water interface: DL water ( $\chi^{(2)}_{\text{DL}}$ ) at 0.01 M and SL water ( $\chi^{(2)}_{\text{SL-Acidic}}$ ,  $\chi^{(2)}_{\text{SL-Basic}}$  and  $\chi^{(2)}_{\text{SL-Const}}$ ) at 5.0 M. (B) The pH dependent curves of integrated amplitude of each component of DL water and SL water.

1) Limo, M. J.; Sola-Rabada, A.; Boix, E.; Thota, V.; Westcott, Z. C.; Puddu, V.; Perry, C. C., *Chem. Rev.* **2018**, *118*, 11118-11193. 2) a) Myalitsin, A.; Urashima, S.-h.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T., *J. Phys. Chem. C* **2016**, *120*, 9357-9363. b) Urashima, S.-h.; Myalitsin, A.; Nihonyanagi, S.; Tahara, T., *J. Phys. Chem. Lett.* **2018**, *9*, 4109-4114.

## フェムト秒誘導ラマン分光で観るリングサイズに依存したシクロパラフェニレンの構造変形ダイナミクス

(阪大院基礎工<sup>1</sup>) ○五月女 光<sup>1</sup>・森田 悠介<sup>1</sup>・宮坂 博<sup>1</sup>

Probing Ring Size-Dependent Structural Dynamics of Cycloparaphenylene Using Femtosecond Stimulated Raman Spectroscopy (<sup>1</sup>*Graduate School of Engineering Science, Osaka University*) ○Hikaru Sotome,<sup>1</sup> Yusuke Morita,<sup>1</sup> Hiroshi Miyasaka,<sup>1</sup>

Cycloparaphenylene (CPP) derivatives are one of molecular nanocarbon and show unique physical properties owing to their distorted and strained ring structure. Such properties originate from the structural change in the excited state, as represented by fluorescence with large Stokes shift. In this context, it is important to elucidate the structure-property correlation in the excited state. In the present study, to this end, we have investigated the structural dynamics of several CPP derivatives with different ring size using transient absorption and femtosecond stimulated Raman spectroscopies.

**Keywords :** Cycloparaphenylene; Femtosecond Stimulated Raman Spectroscopy; Structural Dynamics; Transient Absorption Spectroscopy

シクロパラフェニレン (CPP, Figure 1a) は分子ナノカーボンのひとつであり、それを構成するベンゼン環同士のねじれたリング状構造に由来する特異な物性を示す。こうした物性は、ストークスシフトの大きな蛍光に代表されるように、光励起状態における構造変化に起因している。本研究では、リングサイズの異なる種々の CPP を対象に、その励起状態における構造変形の解明を目的として、過渡吸収分光とフェムト秒誘導ラマン分光 (FSRS) を用い、光励起後フェムト・ピコ秒時間領域の構造ダイナミクスを測定した。Figure 1b, c に [12]CPP と [8]CPP の FSRS スペクトルを示す。[12]CPP では、803, 1215, 1580  $\text{cm}^{-1}$  のラマンバンドが観測され、それぞれ C-H 面外変角、C-H 面内変角、芳香環 C=C 伸縮振動に帰属された。これらのバンドは振動数に変化はないものの、励起後 1 ps 程度の時定数で部分的に強度を失った。一方、[8]CPP の C-H 面内変角と C=C 伸縮振動に対応するバンドでは、強度低下に加えてバンド形状の変化も観測された。この結果は、リングサイズが小さな CPP の方が、励起状態に遷移後、隣接するベンゼン環同士のねじれの解消が顕著に進行することを示唆している。

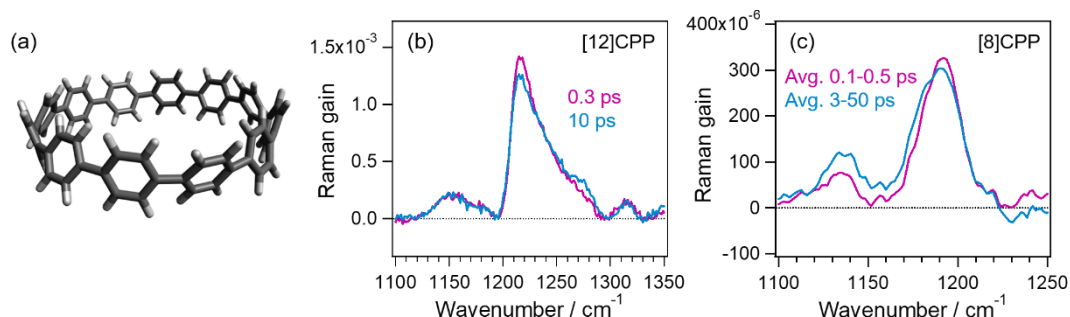


Figure 1. (a) Chemical structure of cycloparaphenylene (CPP). (b,c) Femtosecond stimulated Raman spectra of [12]CPP and [8]CPP in tetrahydrofuran.



## 多孔性亜鉛錯体結晶中の細孔における非 TEMPO 系ラジカルの ESR 測定

(昭和大教<sup>1</sup>・日大院総合基礎<sup>2</sup>・日大文理<sup>3</sup>) ○小林 広和<sup>1</sup>・秋庭 健人<sup>2</sup>・岩堀 史靖<sup>3</sup>・本多 英彦<sup>1</sup>・山本 雅人<sup>1</sup>

ESR study of non-TEMPO radicals incorporated in nanospace in crystalline Zn complex (<sup>1</sup>Dep. Arts and Sci., Showa Univ., <sup>2</sup>Grad. Sch. Integ. Basic Sci., Col. of Humanities and Sci., Nihon Univ., <sup>3</sup>Humanities and Sci., Nihon Univ.) ○ Hirokazu Kobayashi,<sup>1</sup> Kento Akiniwa,<sup>2</sup> Fumiyasu Iwahori,<sup>1</sup> Hidehiko Honda,<sup>1</sup> Masato Yamamoto<sup>1</sup>

A new electron spin resonance (ESR) spin probe technique with nitronitroxide, iminonitroxide, and benzonitronitroxide radicals used as probe molecules has been developed for organic 1D porous nanochannels or polymers over the last decade. In the present study, room temperature ESR measurements were conducted for these radicals incorporated in a porous metal-organic complex, [(ZnI<sub>2</sub>)<sub>3</sub>(tris(4-pyridyl)-1,3,5-triazine)<sub>2</sub>] (ZnTPT). The principal values of *g* and hyperfine coupling (*A*) tensors were estimated according to the spectral reproduction. The ESR spectra showed rotational diffusion for the iminonitroxide radicals, which indicates that ZnTPT contains cylindrical nanospaces.

**Keywords :** ESR, nanospace, MOF, *g* value, hyperfine coupling

近年、非 TEMPO 系ラジカル(例えば nitronitroxide (NN), benzonitronitroxide (BzNN)および iminonitronitroxide (IN))を用いた ESR スピンプローブ法の開発が行われており、有機 1 次元ゼオライトやアクリル樹脂などの有機マトリックスの細孔に対して有効であることが報告されている<sup>1)</sup>。本研究では多孔性配位高分子 (MOF/PCP) である [(ZnI<sub>2</sub>)<sub>3</sub>(tris(4-pyridyl)-1,3,5-triazine)<sub>2</sub>] (ZnTPT)<sup>2)</sup>に包接された非 TEMPO 系ラジカルの ESR スペクトルを測定した。スペクトルシミュレーションにより、各ラジカルの *g* および超微細結合テンソルが得られた。このうち IN ラジカル誘導体を包接した場合において、一軸性回転拡散を示すスペクトルが得られた。これは ZnTPT が軸対称かそれに近い形状の細孔を有することを表わす。これらの結果は、MOF 中でも非 TEMPO 系 ESR スピンプローブ法が有効である可能性を示唆している。当日詳細を述べる。

1) Investigation of various organic radicals dispersed in polymethylmethacrylate matrices using the Electron Spin Resonance spectroscopy technique has been reported. H. Kobayashi, *et al.*, *ACS Omega* **2021**, 6, 20855.

2) X-ray analysis on the nanogram to microgram scale using porous complexes has been reported. Y. Inokuma, *et al.*, *Nature* **2013**, 495, 461.

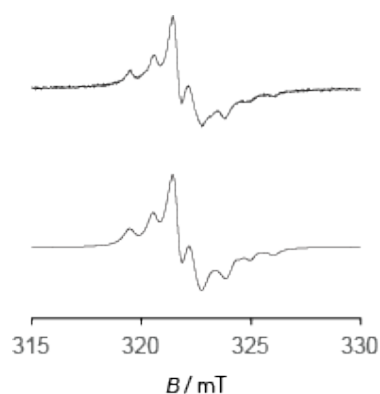


図 ZnTPT 中に包接された 2-phenyl-IN ラジカルの ESR スペクトル (上) とシミュレーションの結果 (下)。



**[F203-2pm] 04. Physical Chemistry -Properties-**

Chair: Oshikiri Tomoya, Daichi Eguchi

Thu. Mar 24, 2022 1:40 PM - 3:40 PM F203 (Online Meeting)

**[F203-2pm-01] Extrinsic Chirality by Interference between Two Plasmonic Modes on an Achiral Rectangular Nanostructure Using Multi-photon Photoemission Electron Microscopy**○Oshikiri Suganami Tomoya<sup>1</sup>, Quan Sun<sup>1</sup>, Hiroki Yamada<sup>1</sup>, Shuai Zu<sup>1</sup>, Keiji Sasaki<sup>1</sup>, Hiroaki Misawa<sup>1,2</sup> (1. Hokkaido University, 2. National Yang Ming Chiao Tung University)

1:40 PM - 2:00 PM

**[F203-2pm-02] Surface-enhanced Raman Scattering Substrate under Modal Strong Coupling between Nanocavity and Plasmons of Gold Nanoparticles Loaded by Self-assembly Method**○Yoshiki Suganami<sup>1</sup>, Tomoya Oshikiri<sup>1</sup>, Hideyuki Mitomo<sup>1</sup>, Xu Shi<sup>1</sup>, Yasutaka Matsuo<sup>1</sup>, Kuniharu Ijiri<sup>1</sup>, Hiroaki Misawa<sup>1,2</sup> (1. Hokkaido University, 2. National Yang Ming Chiao Tung University)

2:00 PM - 2:20 PM

**[F203-2pm-03] Near-field Distribution under Modal Strong Coupling with Coherent Interaction**○Yen-En Liu<sup>1</sup>, Xu Shi<sup>1</sup>, Tomoya Oshikiri<sup>1</sup>, Yuji Sunaba<sup>1</sup>, Keiji Sasaki<sup>1</sup>, Hiroaki Misawa<sup>1,2</sup> (1. Hokkaido University, 2. National Yang Ming Chiao Tung University)

2:20 PM - 2:40 PM

**[F203-2pm-04] Transporting and transferring electrons across perovskite-acceptor interfaces.**○Sachith Bhagyashree Mahesha<sup>1</sup>, Takuya Okamoto<sup>1</sup>, Ghimire Sushant<sup>4</sup>, Tomokazu Umeyama<sup>1,3</sup>, Yuta Takano<sup>1</sup>, Hiroshi Imahori<sup>1,2</sup>, Vasudevanpillai Biju<sup>1</sup> (1. Hokkaido University, 2. Kyoto University, 3. University of Hyogo, 4. University of Rostock)

2:40 PM - 3:00 PM

**[F203-2pm-05] Processing of Ni thin film by sub-micron focusing of high-order harmonic pulses in the XUV region**○Hiroto Motoyama<sup>1</sup>, Atsushi Iwasaki<sup>1</sup>, Hidekazu Mimura<sup>2</sup>, Kaoru Yamanouchi<sup>1</sup> (1. School of Science, The University of Tokyo, 2. School of Engineering, The University of Tokyo)

3:00 PM - 3:20 PM

**[F203-2pm-06] On-surface construction of host-guest complex and bias dependent structure switching**○Toyo Kazu Yamada<sup>1,2</sup>, Fumi Nishino<sup>1</sup>, Ryohei Nemoto<sup>1</sup>, Chi-Hsien Wang<sup>3</sup>, Masaki Horie<sup>3</sup>, Takuya Hosokai<sup>4</sup>, Yuri Hasegawa<sup>5</sup>, Keisuke Fukutani<sup>6</sup>, Satoshi Kera<sup>6</sup> (1. Chiba Univ., 2. Chiba Univ., 3. Taiwan Tsing Hua Univ., 4. AIST, 5. Ritsumeikan Univ., 6. IMS)

3:20 PM - 3:40 PM

## Extrinsic Chirality by Interference between Two Plasmonic Modes on an Achiral Rectangular Nanostructure Using Multi-photon Photoemission Electron Microscopy

(<sup>1</sup>Research Institute for Electronic Science, Hokkaido University, <sup>2</sup>Center for Emergent Functional Matter Science, National Chiao Tung University, Taiwan) ○Tomoya Oshikiri,<sup>1</sup> Quan Sun,<sup>1</sup> Hiroki Yamada,<sup>1</sup> Zu Shuai,<sup>1</sup> Keiji Sasakai,<sup>1</sup> Hiroaki Misawa<sup>1,2</sup>

**Keywords:** Chirality; Localized surface plasmon resonance; Photoemission electron microscopy; Near-field imaging; Mode interference

Localized surface plasmon resonances (LSPRs), which are collective oscillations of conductive electrons at the surfaces of metallic nanostructures, harvest light incident on the nanostructures and enhance the local electric field, which is called the near field (NF). The NF induced by circularly polarized light (CPL) irradiation on the plasmonic structure is a hot scientific topic. Recently, Okamoto *et al.* observed a nanoscale two-dimensional chiral NF distribution on achiral rectangular gold nanostructures.<sup>1</sup>

In this study, we observed a chiral NF intensity distribution on a series of achiral gold nanorectangular structures (Au-NRs) under CPL irradiation by using multiphoton photoemission electron microscopy (MP-PEEM).<sup>2</sup> Additionally, the differential NF spectra under left and right CPL irradiation, which represent the asymmetry of the NF intensity distribution, were investigated. We propose an interpretation that the chiral NF intensity distribution on an achiral metallic nanostructure is extrinsically generated by the interference between two LSPR modes by combining state-of-the-art MP-PEEM techniques and the classical oscillator model. Not only the NF intensity distribution but also the observed peak wavelength of the DNF spectra in both the experiment and numerical simulation are well explained by our interpretation. Furthermore, it was proven that not only the dipole mode but also the hexapole mode could interfere with another mode and generate a chiral NF intensity distribution. A series of experiments revealed that the intensity of the NF and its phase angle of each mode are critical factors for the generation of the chiral NF intensity distribution. Importantly, both control factors can be estimated from the NF spectra under linearly polarized light irradiation without CPL irradiation.

1) S. Hashiyada, T. Narushima, H. Okamoto, J. Phys. Chem. C 2014, 118, 22229.

2) T. Oshikiri, Q. Sun, H. Yamada, S. Zu, K. Sasaki, H. Misawa, ACS Nano 2021, 15, 16802.

## Surface-enhanced Raman Scattering Substrate under Modal Strong Coupling between Nanocavity and Plasmons of Gold Nanoparticles Loaded by Self-assembly Method

(<sup>1</sup>Research Institute for Electronic Science, Hokkaido University, <sup>2</sup>Creative Research Institution, Hokkaido University, <sup>3</sup>Center for Emergent Functional Matter Science, National Chiao Tung University, Taiwan) ○Yoshiki Suganami<sup>1</sup>, Tomoya Oshikiri<sup>1</sup>, Hideyuki Mitomo<sup>1</sup>, Xu Shi<sup>2</sup>, Yasutaka Matsuo<sup>1</sup>, Kuniharu Ijiri<sup>1</sup>, Hiroaki Misawa<sup>1,3</sup>

**Keywords:** Surface-enhanced Raman scattering; Localized surface plasmon resonance; Modal strong coupling; Self-assembly

Recently, we found that the localized surface plasmon resonance of gold nanoparticles (Au-NPs) coupled with the Fabry-Pérot (FP) nanocavity improves the surface-enhanced Raman scattering (SERS) properties<sup>1</sup>. In this study, we have fabricated the modal strong coupling structure with large coupling strength composed of a high number density of Au-NPs on FP nanocavity using self-assembly methods and investigated their SERS properties because it is known that the strong coupling strength in the light-matter coupling system is proportional to the square root of the number density of oscillators<sup>2</sup>.

An FP nanocavity was fabricated by depositing 100 nm of gold on a SiO<sub>2</sub> substrate using a sputtering method, followed by the deposition of 31 nm of TiO<sub>2</sub> using an atomic layer deposition method. A self-assembled monolayer of Au-NPs was formed on the water surface by dropping a chloroform solution of Au-NPs modified with dodecanethiol (DDT) ligand into ultrapure water. The Au-NPs monolayer was then transferred onto the TiO<sub>2</sub> surface to fabricate the DDT-modified Au-NPs/TiO<sub>2</sub>/Au film (DDT-ATA) structure. Finally, the ozone cleaning process was performed to remove DDT molecules on DDT-ATA. From the SEM images, the surface coverage ratios with Au-NPs on the surface of DDT-ATA were calculated to be 48 %. The absorption spectra of DDT-ATA split into two peaks due to the hybrid modes associated with the modal strong coupling formation, and the splitting energy was calculated to be 670 meV from the dispersion curve. This value was almost twice the conventional ATA, whose coverage ratio was ca. 30%. In addition, the SERS performance of DDT-ATA substrate was investigated by using crystal violet as a probe molecule with an excitation wavelength of 785 nm. The Raman intensity of DDT-ATA substrate was 14-times higher than that of Au-NPs/TiO<sub>2</sub> substrate without FP nanocavity.

1) X. Zang, X. Shi, T. Oshikiri, K. Ueno, Y. Sunaba, K. Sasaki, and H. Misawa, *J. Phys. Chem. C* **2021**, 125, 19880.

2) M. Suzuki, K. Nishiyama, N. Kani, X. Yu, K. Uzumi, M. Funahashi, F. Shimokawa, S. Nakanishi, and N. Tsurumachi, *Appl. Phys. Lett.* **2019**, 114, 191108.

## Near-field Distribution under Modal Strong Coupling with Coherent Interaction

(<sup>1</sup>Research Institute for Electronic Science, Hokkaido University, <sup>2</sup>Creative Research Institution, Hokkaido University, <sup>3</sup>Center for Emergent Functional Matter Science, National Chiao Tung University, Taiwan) ○Yen-En Liu,<sup>1</sup> Xu Shi,<sup>2</sup> Tomoya Oshikiri,<sup>1</sup> Yuji Sunaba,<sup>1</sup> Keiji Sasaki,<sup>1</sup> Hiroaki Misawa<sup>1,3</sup>

**Keywords:** Localized surface plasmon resonance; Modal strong coupling; Coherent interaction; Photoemission electronic microscopy

The modal strong coupling system between localized surface plasmon and Fabry–Pérot (FP) nanocavity modes was demonstrated to enhance the photocurrent generation efficiency and the quantum efficiency of the water splitting photoreaction.<sup>1,2</sup> Moreover, we have discovered the enhancement of the hot carrier generation efficiencies in the Au nanodisks (Au NDs) on thin-film TiO<sub>2</sub>/Au-film (ATA) FP nanocavity modal strong coupling structure. We hypothesized that the coherent interaction between Au NDs through the FP nanocavity enhances hot carrier transfer efficiencies. In the present study, we further applied photoemission electronic microscopy (PEEM) to investigate the coherent interaction and the coherence area by discussing the near-field properties and the photoemission distributions.

In order to quantitatively observe the coherence area, we fabricated the ATA structures with different particle numbers (PNs) of the 80-nm Au NDs hexagonal clusters. First, the near-field intensity spectra were observed by the PEEM measurement, and we found the near-field intensity peaks of the ATAs were at 710-730 nm. Next, we took the photoemission distribution images of the Au NDs clusters with different PNs at the peak wavelength excitation. We found that the Au NDs located in the rim part of the cluster showed obviously stronger photoemission intensities than the central part when PNs were larger than 7. This result indicates that Au NDs clusters exhibit the different modes from the individual plasmonic mode of single Au ND due to the coherent interaction through the FP nanocavity. Similar phenomena were also observed in the numerical simulation using the finite element method.

1) X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki and H. Misawa, *Nat. Nanotechnol.* **2018**, 13, 953.

2) Y. Suganami, T. Oshikiri, X. Shi, H. Misawa, *Angew. Chem. Int. Ed.* **2021**, 60, 18438.

## Transporting and transferring electrons across perovskite-acceptor interfaces

(<sup>1</sup>Graduate School of Environmental Science, Hokkaido University, <sup>2</sup>University of Rostock, <sup>3</sup>University of Hyogo, <sup>4</sup>Kyoto University) ○Sachith Bhagyashree Mahesha,<sup>1</sup> Takuya Okamoto,<sup>1</sup> Ghimire Sushant,<sup>2</sup> Tomokazu Umeyama,<sup>3</sup> Yuta Takano,<sup>1</sup> Hiroshi Imahori,<sup>4</sup> Vasudevanpillai Biju<sup>1\*</sup>

**Keywords:** halide perovskite; nanocrystals; interfacial electron transfer; fullerene

Halide perovskite nanocrystals (PNCs) become attractive due to their high photoluminescence (PL) quantum yields, tunable bandgap, and straightforward synthesis.<sup>1</sup> As a result, these materials become superior light absorbers in perovskite solar cells (PSCs) and the certified power conversion efficiency of a PSC exceeds 25%. Recently, photoinduced electron transfer (PET) studies in PNC-based electron donor-acceptor (D-A) systems receive great momentum, which is owing to the general interest to optimize the perovskite solar cell technology.<sup>2</sup> Radiative and nonradiative carrier losses adversely affect the energy conversion efficiency in thick perovskite films.<sup>3</sup> Both the PL lifetime and transient absorption measurements in the presence of electron- and hole-accepting materials reveal the high charge mobility in perovskite films. However, the distance- or thickness-dependent recombination dynamics of photogenerated excitons/charge carriers at the perovskite-electron acceptor interfaces are yet to be completely understood.

We reveal the extent of diffusion, the degree of radiative loss, and the rate of diffusion-controlled interfacial electron transfer in heterojunction films of cesium or formamidinium lead bromide (Cs/FAPbBr<sub>3</sub>) PNCs and C<sub>60</sub> or TiO<sub>2</sub>. Self-assembled PNC films prepared from FAPbBr<sub>3</sub> show a longer PL lifetime than a solution, showing a long-range carrier migration or efficient carrier-trapping de-trapping cycles. To examine the nature of PET from PNCs, we perform PL studies of PNC solutions in the absence or presence of C<sub>60</sub>. The acceptor quenches the PL intensity but not the lifetime in a solution, revealing a static electron transfer. Conversely, the distance-dependent electron transfer in films changes from dynamic to static by moving the pump-probe towards the donor-acceptor interface.<sup>4</sup> While radiative recombination dominates the electron transfer at 800 μm or farther, the acceptors quantitatively scavenge the photogenerated carriers within 100 μm.

In summary, the adsorption of C<sub>60</sub> molecules onto the hydrophobic-caped surface of a PNC leads to static and quantitative PL quenching by electron transfer. Also, the electron transfer efficiency is appreciably high for excitons generated within 800 μm of a D-A interface. The migrating or trapped photogenerated charge carriers in the D-A films enable diffusion-controlled interfacial electron transfer.

1) S. Ghimire, et al. *ACS Energy Lett.* 4 (2019) 133. 2) L. Chouhan, et al. *Chem. Soc. Rev.* 49 (2020) 2869. 3) V. C. Nair, et al. *Angew. Chem. Int. Ed.* 56 (2017) 1214. 4) B. M. Sachith et al. *J. Phys. Chem. Lett.* 12 (2021), 8644.

## Processing of Ni thin film by sub-micron focusing of high-order harmonic pulses in the XUV region

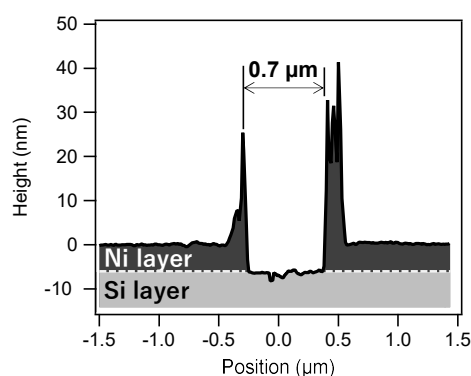
(<sup>1</sup>*School of Science, The University of Tokyo*, <sup>2</sup>*School of Engineering, The University of Tokyo*) ○Hiroto Motoyama,<sup>1</sup> Atsushi Iwasaki,<sup>1</sup> Hidekazu Mimura,<sup>2</sup> Kaoru Yamanouchi<sup>1</sup>

**Keywords:** High-order harmonic generation, Laser processing

Non-thermal laser processing using femtosecond near-infrared (NIR) laser pulses has been widely used for microfabrication because of its high processing resolution. However, considering the diffraction-limited size of the NIR laser pulses, the spatial resolution is limited to a few micrometers due to the long wavelength of around 1  $\mu\text{m}$ . Therefore, a laser processing technique with a sub-micron spatial resolution has been awaited for further development of micro- and nano-fabrication processes.

To meet this demand, we have been developing a laser processing system using femtosecond laser pulses in the extreme ultraviolet (XUV) region of around 30 nm [1, 2]. By focusing femtosecond NIR laser pulses on a rare-gas medium, we generated femtosecond XUV pulses as the high-order harmonics and irradiated a thin acrylic resin film with the focused XUV pulses to drill sub-micron holes on the surface [2].

In the present study, we demonstrate sub-micron machining of metallic materials having a much higher damage threshold than an acrylic resin. Using a Wolter mirror with a large aperture, we focus the generated XUV pulses whose pulse energy is at most 1 nJ into a sub-micron spot to achieve a sufficiently high fluence of 100 mJ/cm<sup>2</sup>. We irradiate Ni thin films with the focused XUV pulses and measure the surface morphology of the irradiated position using an atomic force microscope. We have revealed that, when the thickness of the Ni thin film coated on a silicon substrate is 5 nm, Ni atoms in the irradiated area whose diameter is  $\sim 1 \mu\text{m}$  are removed and the surface of the silicon substrate is exposed to the vacuum as shown in Fig. 1, indicating that laser machining of a variety of metallic materials with a sub-micrometer resolution can be achieved using our submicron XUV focusing system.



**Fig. 1** The cross-section profile of the atomic force microscope image of the sub-micron structure on the Ni surface created by the irradiation of the focused ultrashort XUV laser pulses.

1) H. Motoyama, A. Iwasaki, Y. Takei, T. Kume, S. Egawa, T. Sato, K. Yamanouchi, and H. Mimura, *Appl. Phys. Lett.* **114**, 241102 (2019).

2) K. Sakaue, H. Motoyama, R. Hayashi, A. Iwasaki, H. Mimura, K. Yamanouchi, T. Shibuya, M. Ishino, T-H Dinh, H. Ogawa, T. Higashiguchi, M. Nishikino, and R. Kuroda, *Opt. Lett.* **45**, 2926 (2020).

## Cu(111)上の環状ホスト分子配列へのゲスト分子吸着による包接化合物作製と電圧依存ゲスト分子構造変化

(千葉大院工<sup>1</sup>・千葉大キラ研<sup>2</sup>・台湾清華大<sup>3</sup>・産総研<sup>4</sup>・立命館大<sup>5</sup>・分子研<sup>6</sup>) ○山田 豊和<sup>1,2</sup>, 西野 史<sup>1</sup>, 根本 諒平<sup>1</sup>, 王 祺嫻<sup>3</sup>, 堀江 正樹<sup>3</sup>, 細貝 拓也<sup>4</sup>, 長谷川 友里<sup>5</sup>, 福谷 圭祐<sup>6</sup>, 解良 聡<sup>6</sup>

On-Surface Construction of Host-Guest Complex and Bias Dependent Structure Switching (<sup>1</sup>Graduate School of Engineering, Chiba Univ., <sup>2</sup>Chiral Research Center, Chiba Univ., <sup>3</sup>Taiwan Tsing Hua Univ., <sup>4</sup>AIST, <sup>5</sup>Ritsumeikan Univ. <sup>6</sup>IMS) ○Toyo Kazu Yamada<sup>1,2</sup>, Fumi Nishino<sup>1</sup>, Ryohei Nemoto<sup>1</sup>, Chi-Hsien Wang<sup>3</sup>, Masaki Horie<sup>3</sup>, Takuya Hosokai<sup>4</sup>, Yuri Hasegawa<sup>5</sup>, Keisuke Fukutani<sup>6</sup> and Satoshi Kera<sup>6</sup>

A growth of [ferrocenylmethyl(methy)-ammonium]<sup>+</sup> (PF<sub>6</sub>)<sup>-</sup> (Fc-amm) guest molecules adsorbed on a 4,4', 5,5'-tetrabromodibenzo[18] crown-6 ether (Br-CR) (7×4) host ring molecular array<sup>1)</sup> was studied by means of ultra-high vacuum low-temperature scanning tunneling microscopy (STM). The well-ordered Br-CR array grown on an atomically-flat and clean Cu(111) substrate showed an ability to catch the guest Fc-amm molecules, which form an ordered assembly array. Scanning tunneling spectroscopy found the highest occupied molecular orbitals (HOMO) at -1.3 and -1.5 eV below the Fermi energy. Markedly, the Fc-amm array showed bias voltage dependent structure variations around the negative bias voltages.

**Keywords :** Host-Guest Complex; Inclusion Compound; Crown Ether; Ferrocene; Scanning Tunneling Microscopy

単分子レベルで外部刺激応答性を示す包接化合物を、超高真空中にて固体表面上で作製した。超高真空・低温・走査トンネル顕微鏡 (STM)/ 走査トンネル分光 (STS) による、吸着構造と電子状態の変化を探った。ホスト分子として、4,4', 5,5' - tetrabromodibenzo[18] crown-6 ether (Br-CR) を用いた。Br-CR は Cu(111) 上で (7×4) 超周期構造をとる<sup>1)</sup>。ゲスト分子には [ferrocenylmethyl(methy)-ammonium]<sup>+</sup> (PF<sub>6</sub>)<sup>-</sup> (Fc-amm) を使用した。

Br-CR 島上に吸着した Fc-amm 分子を STM 観察した。Fc-amm 分子は 5 つの輝点からなる集合体 (大きさ 0.9×1.4 nm) を形成した。Fc-amm 集合体は、Br-CR 単層膜上で周期配列 (約 2 nm×3 nm) した。大事な点は、Fc-amm 集合体が Br-CR 格子に従って吸着していたことである。つまり、ゲスト分子である Fc-amm は Br-CR にトラップされており包接化合物を形成している可能性が確認できた。さらに、STM/STS より HOMO -1.3 eV から -1.5 eV で確認した。STS dI/dV 像は Fc-amm 集合体内で電子状態密度分布に差があることを示した。さらに 1 個の集合体内の電子状態密度分布が電圧依存して変化する様子 (回転) を dI/dV 像は鮮明にとらえた。詳細を報告する。

1) Well-Ordered Monolayer Growth of Crown-Ether Ring Molecules on Cu(111) in Ultra-High Vacuum: A STM, UPS, and DFT Study. R. Nemoto, P. Krueger, A. N. P. Hartini, T. Hosokai, M. Horie, S. Kera, T K. Yamada, *J. Phys. Chem. C* **2019**, *123*, 18939.

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

## [F102-2pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Yoshiyuki Kageyama, Masashi Arakawa

Thu. Mar 24, 2022 1:00 PM - 2:40 PM F102 (Online Meeting)

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### [F102-2pm-01] Self-propelled Droplet Systems Using the Briggs-Rauscher Reaction

○Masakazu Kuze<sup>1</sup>, Muneyuki Matsuo<sup>1</sup>, Satoshi Nakata<sup>1</sup> (1. Graduate school of Integrated Science for Life, Hiroshima University)

1:00 PM - 1:20 PM

### [F102-2pm-02] Self-oscillating menthylacetate swimmer

○Matsuo Muneyuki<sup>1</sup>, Satshi Nakata<sup>1</sup> (1. Hiroshima University)

1:20 PM - 1:40 PM

### [F102-2pm-03] Interplay between collective dynamics of molecular-level reaction and self-oscillatory macroscopic transformation in an azobenzene derivative assembly under steady light irradiation

○Yoshiyuki Kageyama<sup>1</sup>, Yasuaki Kobayashi<sup>1</sup>, Daisuke Yazaki<sup>1</sup>, Tomonori Ikegami<sup>1</sup> (1. Hokkaido University)

1:40 PM - 2:00 PM

### [F102-2pm-04] Chemical reactivity of superatoms consisting of 13 group elements supported on organic surfaces

○Tomoya Inoue<sup>1</sup>, Atsushi Nakajima<sup>1</sup> (1. The Univ. of Keio)

2:00 PM - 2:20 PM

### [F102-2pm-05] Photoelectron imaging of superatomic orbitals in silver cluster anions

○Tasuku Nishizato<sup>1</sup>, Kento Minamikawa<sup>1</sup>, Haruki Hashimoto<sup>1</sup>, Kazuaki Matsumoto<sup>1</sup>, Masashi Arakawa<sup>1</sup>, Takuya Horio<sup>1</sup>, Akira Terasaki<sup>1</sup> (1. Department of Chemistry, Kyushu University)

2:20 PM - 2:40 PM



## 化学振動反応である Briggs-Rauscher 反応を用いた自己駆動液滴系の開発

(広島大院統合生命<sup>1</sup>) ○久世 雅和<sup>1</sup>・松尾 宗征<sup>1</sup>・中田 聡<sup>1</sup>

Self-propelled Droplet Systems Using the Briggs-Rauscher Reaction

(<sup>1</sup>Graduate School of Integrated Sciences for Life, Hiroshima University) ○Masakazu Kuze,<sup>1</sup> Muneyuki Matsuo,<sup>1</sup> Satoshi Nakata<sup>1</sup>

The Briggs-Rauscher (BR) reaction is well known as an oscillating chemical reaction, in which the concentration of iodine oscillates spontaneously. In this study, a droplet of the BR reactive solution (BR droplet) was placed in an oil phase containing monoolein as a surfactant. A self-propelled motion of the BR droplet was observed depending on the volume of the droplet and the concentration of a surfactant in the oil phase.

The accumulation of iodine was observed in the aqueous phase after the droplet was placed in the oil phase. Here, the amount of iodine increased with an increase in the volume of the droplet,  $V$ . No production of the iodine and no droplet's motion were observed in small  $V$ , while accumulation of iodine and a shaking of the droplet itself were observed in large  $V$ . As the reaction progressed, an iodine phase was clearly observed inside the droplet. Furthermore, it was released from the droplet to the oil phase, as a result, the BR droplet was driven in the opposite direction to the release. In addition, a continuous motion was also observed depending on the concentration of the hydrogen peroxide in the BR solution. These results suggest that the inhomogeneous flow generated by the reaction of iodine with monoolein at the oil/water interface affects the motion of the BR droplet, and that the rate of iodine production in the BR reaction may play an important role in the bifurcation of the self-propelled motion.

**Keywords :** *Oscillatory reaction, Self-propelled motion, Nonlinear phenomena*

本研究では化学振動反応系として知られる Briggs-Rauscher (BR) 反応を用いて、自律性の高い無生物自己駆動系の構築を目指した。BR 反応では、ヨウ素とヨウ化物イオンの濃度が自発的に振動する。本研究では、界面活性分子であるモノオレインを含む油相中に BR 水溶液を滴下して液滴 (BR 液滴) を調製した。この BR 液滴の挙動について報告する。

BR 溶液量  $V$  が少ない場合は、ヨウ素の生成や液滴の駆動は観察されなかった。一方、 $V$  が多い場合では、液滴内部でのヨウ素の蓄積と同時に、液滴自身の小刻みな揺れが見られた。さらに反応が進行すると、蓄積したヨウ素が液滴外に放出され、その放出とは逆方向に液滴が数 mm 程度駆動した。すなわち、小刻みな揺れと大きな駆動を繰り返す振動運動が見られた。また、BR 反応溶液中の過酸化水素濃度に依存して、一方向への連続的な駆動も見られた (連続運動)。これらの結果より、BR 反応で生成したヨウ素と、油水界面に局在化したモノオレインとの反応が運動の駆動力となっていること、また、BR 反応におけるヨウ素の生成速度が、連続運動と振動運動の分岐において重要な役割を果たしている可能性が示唆された。

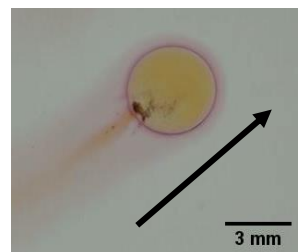


図 1. 連続運動する BR 液滴 (Top view). 矢印は運動の方向.

## 自励振動する自己駆動液滴

(広島大院統合生命) ○松尾 宗征・中田 聡

Self-oscillating menthylacetate swimmer (*Graduated School of Integrated Sciences for Life, Hiroshima University*) ○Muneyuki Matsuo, Satoshi Nakata

In this study, we constructed a self-oscillating droplet swimmer composed of menthylacetate (MA) to demonstrate the emergence of recursiveness of molecular aggregates under the condition in which there are no oscillating chemical reactions and perturbations.

MA is readily hydrolyzed to menthol (MOH) and acetic acid. When MA (2-8  $\mu\text{L}$ ) was dropped onto 3 mL of NaOH aqueous solution (0.1-10 mM) or ultrapure water which filled a glass Petri dish, MA spread wet on the surface of an aqueous solution. However, MA gradually re-aggregated, and MA droplets were formed. The formed droplets exhibited self-propulsion. Surface tension measurements revealed that the hydrolysis product MOH reduced the interfacial tension by up to 13 mN/m. Droplets composed of decyl acetate, in which MOH was replaced by decanol, did not exhibit self-propulsion. These results strongly suggest that self-propulsion is induced by the MOH-derived inhomogeneity of the surface tension (Fig. 1).

Furthermore, at a NaOH concentration of 10 mM, MA droplets with an initial volume of more than 6  $\mu\text{L}$  exhibited oscillatory self-propulsion, i.e., repeatedly stopped and moved (Fig. 2). The oscillation was driven by the deformation of the droplet. When a droplet position was fixed, a droplet beat, i.e., repeatedly swelled and shrank. When a petri dish was covered with a cap, no oscillation and beating were observed. These results indicate that the oscillatory motion of the droplets is due to the synergy of MOH production and sublimation.

**Keywords :** Self-oscillation; Self-propelled droplet; Self-propulsion; Active matter; Synergy

本研究では、振動性の化学反応や摂動がない環境下での無生物的な分子集合体における再帰性の創発を実証するため、メントール (MOH) と酢酸に容易に加水分解されるメンチルアセテート (MA) からなる自励振動する自己駆動液滴を構築した。

ガラスシャーレを満たした NaOH 水溶液 (0.1~10 mM) または超純水 3 mL 上に MA (2~8  $\mu\text{L}$ ) を滴下すると、水面に濡れ広がり、油膜を形成した。しかし、加水分解が進行するにつれ MA が再度凝集し、液滴が形成された。さらに、液滴は自己駆動した。表面張力測定により、加水分解産物である MOH が水の表面張力を最大で 13 mN/m 下げることが明らかになった。また、MOH をデカノールに置換したデシルアセテート液滴では、自己駆動が抑制された。これらの結果は、液滴から生成される MOH 由来の表面張力の不均一性が自己駆動を誘起することを意味している (図 1)。

さらに、NaOH 濃度が 10 mM のとき、MA の初期体積が 6  $\mu\text{L}$  以上の液滴は停止と自己駆動を繰り返す振動運動を発現した (図 2)。この振動は、液滴の変形に先導されていた。液滴は固定されると、膨潤と収縮を繰り返し拍動した。振動運動や拍動はシャーレに蓋をすると観測されなかった。これらの結果は、液滴が MOH の生成と昇華の協同効果で振動することを示唆している。

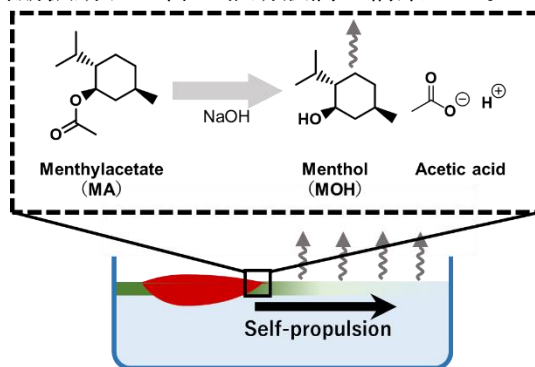


Figure 1. Self-propulsion mechanism of MA droplet

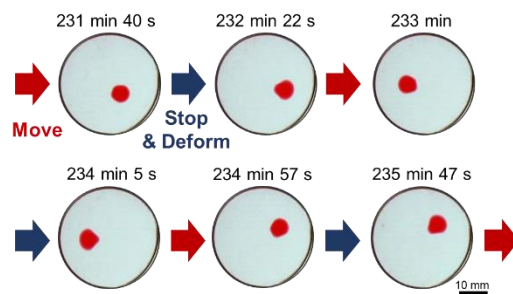


Figure 2. Self-oscillatory motion of MA droplet

## 定常光照射下で自励振動するアゾベンゼン分子集合体にみられる分子レベル継続ダイナミクスの集団化と巨視的ダイナミクス

(北大院理<sup>1</sup>・北大電子研<sup>2</sup>) ○景山 義之<sup>1</sup>・小林 康明<sup>2</sup>・矢崎 大介<sup>1</sup>・池上 智則<sup>1</sup>  
 Interplay between collective dynamics of molecular-level reaction and self-oscillatory macroscopic transformation in an azobenzene derivative assembly under steady light irradiation (<sup>1</sup>*Faculty of Science, Hokkaido University*, <sup>2</sup>*Research Institute for Electronic Science, Hokkaido University*) ○Yoshiyuki Kageyama,<sup>1</sup> Yasuaki Kobayashi,<sup>2</sup> Daisuke Yazaki,<sup>1</sup> Tomonori Ikegami<sup>2</sup>

Self-organization is the phenomenon where excited microscopic dynamics are converted into macroscopic dynamics. We reported self-oscillatory flipping motion of an azobenzene crystal, the motion of which is driven by the photoinduced repetitive isomerization of the azobenzene derivative. However, there are huge difference in size between the millimeter length crystal and the nanometer length molecule, and therefore, the mechanism for realizing the spatio-and-temporally patterned dynamics is not self-evident. In this work, we construct a simple mathematical model that demonstrates the periodic deformation of an elastic plate object, in which repetitive photoisomerization and crystalline phase transition are incorporated, as observed experimentally. By employing a kinetic equation which depend on the accepted light intensity ( $I$ ) and the phase-state ( $\phi$ ) (eq. 1), a Landau's function for a mean-field approximation for the first order phase transitions (eq. 2), and an equation for the spring elasticity between the elements, the model plate showed periodic flipping motion like as the observed crystal. Self-organizing behavior across the three levels of hierarchy is included in the modeled dynamic.

**Keywords :** *Self-organization, Hierarchization, Collective Dynamics, Molecular Motor, Discrete Mathematical Model*

自己組織化とは、エネルギー消費を伴うミクロなダイナミクスによって、マクロなダイナミクスが発現する現象である。我々は、定常光照射下で継続するアゾベンゼンの光異性化反応によって駆動される、アゾベンゼン含有結晶の自励振動現象を報告してきた。しかし、ナノメートルサイズの分子のダイナミクスが、どのようにミリメートルサイズの結晶の時空間秩序をもった運動を実現しているかは自明ではない。この解決を目指し、本研究では、光異性化と結晶相転移が組み込まれた弾性を有する板状物体の周期的変形を示す粗視化数理モデルを構築した。結晶の微視的領域における相状態( $\phi$ )と受容光強度( $I$ )に依存した光異性化反応速度式 (式 1)、ランダウの平均場近似を転用した異性化率( $\chi$ )と  $\phi$  との関係式 (式 2)、 $\phi$  に依存した板の自発曲率等を設定したモデルにおいて、粘弾性を持つ板は、観測結晶と同様に周期的な振動運動を示した。ここには、二つの階層にまたがる自己組織化挙動が含まれている。

$$\frac{d}{dt}\chi = (\alpha(\phi) - (\alpha(\phi) + \beta(\phi))\chi)I \quad (1)$$

$$f(\phi, \chi) = \frac{\Lambda(\chi)}{2}\phi^2 + \frac{B}{4}\phi^4 + \frac{C}{6}\phi^6 \quad (2)$$

謝辞: プログラミングと数値計算については、清水敏明氏 (WDB(株)) の協力を受けて行った。

## 有機表面上に担持された 13 族超原子の化学反応性

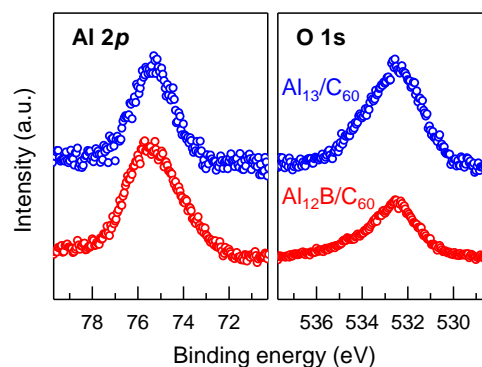
(慶大理工<sup>1</sup>) ○井上 朋也<sup>1</sup>・中嶋 敦<sup>1</sup>

Chemical Reactivity of Superatoms Consisting of 13 Group Elements Supported on Organic Surfaces (<sup>1</sup>*Faculty of Science and Technology, Keio University*) ○Tomoya Inoue,<sup>1</sup> Atsushi Nakajima<sup>1</sup>

Nanoclusters which have atom-like electronic states are called as superatoms (SAs) and their chemical properties strongly depend on charge state. SAs of  $\text{Al}_{13}$  and  $\text{Al}_{12}\text{B}$  consisting of 13 elements show rare-gas-like high chemical stabilities in monovalent anion state because they satisfy 2P superatomic orbitals of 40 electrons and simultaneously take icosahedral close-packed structures. In the gas phase experiment,  $\text{Al}_{12}\text{B}^-$  is more stable than  $\text{Al}_{13}^-$  due to relaxing geometric strains by encapsulating a small B atom.<sup>1</sup> To utilize such SAs as novel nanomaterials, the surface support methods that retains the charge state of SAs are required. In this study, mass selected  $\text{Al}_{13}^-$  and  $\text{Al}_{12}\text{B}^-$  were deposited on the substrate pre-decorated by fullerene ( $\text{C}_{60}$ ), and their chemical states were examined with X-ray photoelectron spectroscopy (XPS). Fig. 1 shows the XPS spectra of  $\text{Al}_{13}$  and  $\text{Al}_{12}\text{B}$  deposited on  $\text{C}_{60}$  substrate. The Al 2p peak of  $\text{Al}_{12}\text{B}$  (bottom) spread to the low binding energy side and the O 1s signal intensity of  $\text{Al}_{12}\text{B}$  was less than that of  $\text{Al}_{13}$  (top). The results show that  $\text{Al}_{12}\text{B}$  exhibits higher robustness than  $\text{Al}_{13}$  on  $\text{C}_{60}$  surfaces, while both SAs were oxidized after depositions on  $\text{C}_{60}$  substrate.

**Keywords :** Superatoms; Aluminum; Oxidized Reaction; X-ray Photoelectron Spectroscopy

原子様の電子状態を有するナノクラスターは超原子と呼ばれ、その化学特性は電荷状態に大きく依存する。13 族超原子である  $\text{Al}_{13}$  および  $\text{Al}_{12}\text{B}$  は-1 価の負イオンにおいて、40 電子の 2P 超原子軌道を閉殻にし、正二十面体の最密充填構造をとるため希ガス原子様の特異な化学的安定性を示す。特に、 $\text{Al}_{12}\text{B}^-$  は原子半径の小さな B 原子が内包されることによって、 $\text{Al}_{13}^-$  よりも幾何的に安定となることが実験的に見出されている<sup>1</sup>。この超原子を新規ナノ物質群として活用する上では、超原子の電荷状態を保持した表面担持法が求められる。本研究では、原子 1 個単位で質量選別された  $\text{Al}_{13}^-$  および  $\text{Al}_{12}\text{B}^-$  を、フラーレン( $\text{C}_{60}$ )分子で表面修飾した基板に蒸着し、その化学状態を X 線光電子分光(XPS)で調べた。Fig. 1 には  $\text{Al}_{13}^-$  と  $\text{Al}_{12}\text{B}^-$  を  $\text{C}_{60}$  基板上に蒸着した後の XPS スペクトルを示す。いずれも、Al 2p ピークは酸化されていることを示し、蒸着後に O 1s ピークが観測された。 $\text{Al}_{12}\text{B}$  の Al 2p ピークは低束縛エネルギー側に裾を引いており、O 1s の信号強度は  $\text{Al}_{13}$  の場合よりも小さい。これは、13 族超原子は  $\text{C}_{60}$  基板上では酸化されてしまうものの、表面上において  $\text{Al}_{12}\text{B}$  の方が  $\text{Al}_{13}$  よりも安定化されることを示している。



**Fig. 1.** XPS spectra for  $\text{Al}_{13}$  and  $\text{Al}_{12}\text{B}$  (0.6 monolayer) deposited on a  $\text{C}_{60}$  substrate around Al 2p (left) and O 1s (right) core levels

1) A. Nakajima, T. Sugioka, T. Kishi, K. Kaya, *Chem. Phys. Lett.*, **1991**, 187, 239-244.

## 光電子イメージングによる銀クラスター負イオンの超原子軌道の探究

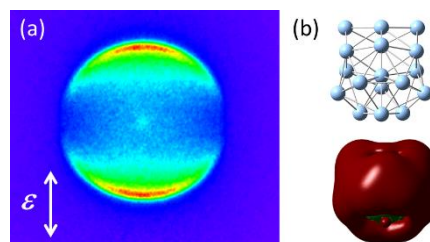
(九大院理) ○西里将・南川賢人・橋本治暉・松本一陽・荒川雅・堀尾琢哉・寺寄亨  
 Photoelectron imaging of superatomic orbitals in silver cluster anions  
 (Department of Chemistry, Kyushu University) ○Tasuku Nishizato, Kento Minamikawa,  
 Haruki Hashimoto, Kazuaki Matsumoto, Masashi Arakawa, Takuya Horio, Akira Terasaki

Physical and chemical properties of metal clusters dramatically change by a single difference in the number of constituent atoms due to modification in their electronic structures. The spherical jellium model predicts that valence electrons of metal clusters occupy so-called superatomic orbitals (1S, 1P, 1D, 2S, ...). While the discrete energy levels have indeed been observed for various metal clusters by anion photodetachment spectroscopy, the angular momentum characters, S, P, D, ..., have not been fully explored so far. Herein, we apply our recently-developed novel photoelectron imaging apparatus to investigation of metal-cluster superatomic orbitals from the angular-momentum point of view. In this talk, we present our first results obtained for size-selected silver cluster anions,  $\text{Ag}_n^-$ .

**Keywords :** Silver Cluster; Photoelectron Imaging; Superatomic Orbitals; Photoelectron Emission Angular Distribution; Electronic Structure

アルカリ金属や貨幣金属のクラスター中の価電子は、エネルギーと軌道角運動量が量子化された超原子軌道 (1S, 1P, 1D, 2S, ...) を形成することがジェリウムモデルの下で示される[1]。この電子構造は、サイズに依存したクラスターの物性発現の鍵であり、負イオン光電子分光法が量子準位のエネルギーを測定する有効な手段となっている。しかし、軌道角運動量状態にまで及ぶ議論はこれまで十分になされて来なかった。最近我々は、金属クラスター連続発生装置[2]と光源に CW レーザーを用いた新たな光電子画像観測法を提案し、この問題に取り組み始めた。本発表では銀クラスター負イオンについて得られた結果を報告する。

総価電子数が 19 個の  $\text{Ag}_{18}^-$  について得られた光電子イメージ (3 次元分布の 2 次元射影像) を図 1(a) に示す。光電子脱離には波長 404 nm (3.07 eV) の直線偏光レーザーを使用した。放出された光電子はレーザーの偏光軸方向  $\epsilon$  に著しい異方性を示しており、異方性パラメータ ( $\beta$ ) は約 1.9 と求まった。原子負イオンでは、直線偏光のレーザーで s 電子を脱離させると p 波が放出し、偏光軸方向に著しい異方性を示すことが知られている[3]。つまり、図 1(a) の結果は、電子がもともと超原子 S 軌道を占有していたことを示唆している。実際、図 1(b) に示すように、密度汎関数理論で予測される  $\text{Ag}_{18}^-$  の HOMO は超原子 2S 軌道と見なすことができ、理論的にも支持される。また、図 1(a) の結果は、同じく超原子 2S 軌道が HOMO となる  $\text{Na}_{19}^-$  について得られた結果[4]とも矛盾しない。このような手法を用いて金属クラスターの軌道角運動量の探究が可能となった。



**Figure 1**  
 (a) Photoelectron image observed for  $\text{Ag}_{18}^-$   
 (b) Optimized structure and HOMO of  $\text{Ag}_{18}^-$

- [1] de Heer, *Rev. Mod. Phys.* **65**, 611 (1993). [2] Sarugaku *et al.*, *J. Phys. Chem. C* **123**, 25890 (2019).  
 [3] Cooper and Zare, *J. Chem. Phys.* **48**, 942 (1968). [4] Bartels *et al.*, *Science* **323**, 1323 (2009).



**[D201-2pm] 06. Analytical Chemistry**

Chair: Daisuke Onoshima, Kenji Sueyoshi

Thu. Mar 24, 2022 1:40 PM - 3:40 PM D201 (Online Meeting)

**[D201-2pm-01] Analysis of membrane protein-specific lipids using gold nanoparticle-based method**○Wangamnuyaporn Supakorn<sup>1</sup>, Masanao Kinoshita<sup>1</sup>, Takayuki Kawai<sup>1</sup>, Nobuaki Matsumori<sup>1</sup> (1. Kyushu University)

1:40 PM - 2:00 PM

**[D201-2pm-02] Multifunctional Magnetic Gd Doped CuS Nanoparticles for Fluorescence/MR Bimodal Imaging-Guided Photothermal-Intensified Chemodynamic Synergetic Therapy of Targeted Tumors**○Luo Minchuan<sup>1</sup>, Onoshima Daisuke<sup>2</sup>, Hiroshi Yukawa<sup>1,2,3</sup>, Baba Yoshinobu<sup>1,2,3</sup> (1. Graduate School of Engineering, Nagoya University, 2. Institute of Innovation for Future Society of Nagoya University, 3. National Institutes for Quantum and Radiological Science and Technology)

2:00 PM - 2:20 PM

**[D201-2pm-03] Development of single molecule electrical detection method for methylation-modified microRNA analysis**○Takahito Ohshiro<sup>1</sup>, Yuki Komoto<sup>1</sup>, Ayumu Asai<sup>1</sup>, Masamitsu Konno<sup>2</sup>, Hideshi Ishii<sup>1</sup>, Masateru Taniguchi<sup>1</sup> (1. Osaka University, 2. Tokyo University of Science)

2:20 PM - 2:40 PM

**[D201-2pm-04] Phase-separated structures in apple procyanidin-containing cell-sized liposome**○Tsuayoshi Yoda<sup>1</sup> (1. Aomori Prefectural Industrial Technology Research Center, Hachinohe Industrial Research Institute)

2:40 PM - 3:00 PM

**[D201-2pm-05] Dark-field microscopic detection of bacteria using bacteriophage-modified SiO<sub>2</sub>@AuNP core-shell nanoparticles.**○Masashi Imai<sup>1</sup>, Yosuke Niko<sup>1</sup>, Shingo Hadano<sup>1</sup>, Shigeru Watanabe<sup>1</sup>, Iyo Uchiyama<sup>3</sup>, Jumpei Uchiyama<sup>2</sup>, Shigenobu Matsuzaki<sup>4</sup> (1. Graduate School of Science, Kochi university, 2. Graduate School of Medicine Dentistry and Pharmaceutical Sciences, Okayama University, 3. Medical School, Okayama University, 4. Faculty of Health Science, Kochi Gakuen University)

3:00 PM - 3:20 PM

**[D201-2pm-06] Aptamer Selection Using a Microscale Electrophoretic Filtering Device**○Kenji Sueyoshi<sup>1,2</sup>, Junku Takao<sup>1</sup>, Arisa Tobita<sup>1</sup>, Kaede Ueno<sup>1</sup>, Tatsuro Endo<sup>1</sup>, Hideaki Hisamoto<sup>1</sup> (1. Graduate School of Engineering, Osaka Prefecture University, 2. PRESTO, JST)

3:20 PM - 3:40 PM

## Analysis of membrane protein-specific lipids using gold nanoparticle-based method

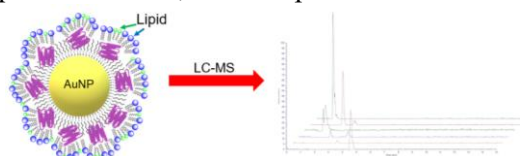
(<sup>1</sup>Graduate School of Science, Kyushu University) ○Supakorn Wangamnuayporn,<sup>1</sup> Masanao Kinoshita<sup>1</sup>, Takayuki Kawai<sup>1</sup>, Nobuaki Matsumori<sup>1</sup>

**Keywords:** Gold Nanoparticle, Membrane Protein, Bacteriorhodopsin, Lipid, Liquid chromatography–mass spectrometry

The interaction between membrane proteins (MPs) and surrounding lipids is important to regulate biological properties and stabilize the structure of MPs. In order to understand the MPs-lipid interaction, the analytical method was recently developed based on the surface plasmon resonance (SPR).<sup>1</sup> Briefly, the gold surface of SPR sensor chips was coated by self-assembled monolayer (SAM) containing mercaptohexanol and mercaptohexanoic acid which significantly enhance MP immobilization due to partly hydrophobic environment. After that, MP-lipid interaction was detected by introducing lipid into the MP-immobilized sensor chips. Applying this method to seven-transmembrane bacteriorhodopsin (bR), we found that a halobacterial lipid S-TGA-1 has the highest affinity to bR.<sup>2</sup> However, lipid isolation from the lipid mixtures extracted from biological membranes is necessary prior to the SPR analysis. Therefore, to overcome the limitation, a new method to identify MP-specific lipids without lipid purification was developed by using SAM-coated gold nanoparticles (AuNPs) based on the idea of SAM-based SPR method.

In this study, AuNPs were coated by SAM, followed by immobilization of bR through the EDC/NHS activation. The effects of SAM chain length, AuNPs size, and the ratio of mercaptoalcohol/mercaptocarboxylic acid were examined for the highest bR immobilization. Then, the lipid mixture extracted from purple membrane was incubated with the bR-immobilized AuNPs. The MP-bound lipid species were quantified by LC-MS and the affinity of each lipid to bR was roughly estimated by introducing the binding index which is the comparison of the MS peak intensity ratio between MP-bound lipids and the extracted lipid mixture. The bR-immobilized AuNPs successfully detected S-TGA-1 as bR-specific lipid which confirmed the result from the SPR-based method. More interestingly, the AuNPs-based method also identified S-TeGA-1 as the lipid with high affinity to bR, providing a new information about the bR-lipid interaction.

In conclusion, the AuNPs-based method, which enables simultaneous lipid screening, does not only reproduce the result for the bR-specific lipid, but also identify a new specific lipid otherwise undetected. This method can be further applied to various MPs to improve understanding on MP-lipid interactions, and thus provide a breakthrough for the study of lipids.



- 1) M. Inada, M. Kinoshita, A. Sumino, S. Oiki, N. Matsumori, *Anal. Chim. Acta* **2019**, *1059*, 103-112.
- 2) M. Inada, M. Kinoshita, N. Matsumori, *ACS Chem Biol.* **2020**, *15*(1), 197-204.

## 標的腫瘍の蛍光/ MR バイ モーダル イメージング ガイド 光熱増強 化学力学的相乗療法のための多機能磁性 Gd ドープ CuS ナノ粒子

(名大院工<sup>1</sup>・名大未来社会創造機構<sup>2</sup>・量子科学技術研究開発機構<sup>3</sup>) Luo Minchuan<sup>1</sup>、小野島 大介<sup>2</sup>、湯川 博<sup>1,2,3</sup>、馬場 嘉信<sup>1,2,3</sup>

Multifunctional Magnetic Gd Doped CuS Nanoparticles for Fluorescence/MR Bimodal Imaging-Guided Photothermal-Intensified Chemodynamic Synergetic Therapy of Targeted Tumors (<sup>1</sup>Graduate School of Engineering, Nagoya University, <sup>2</sup>Institute of Innovation for Future Society of Nagoya University, <sup>3</sup>National Institutes for Quantum and Radiological Science and Technology) Luo Minchuan<sup>1</sup>, Onoshima Daisuke<sup>2</sup>, Hiroshi Yukawa<sup>1,2,3</sup>, Baba Yoshinobu<sup>1,2,3</sup>

Chemodynamic therapy (CDT) that generate reactive oxygen species (ROS) and causes oxidative damage to tumor cells shows tremendous promise for advanced cancer treatment. Herein, we report a multifunctional nanoprobe integrating bimodal imaging and photothermal-enhanced CDT of targeted tumor, which is produced by covalent conjugation of bovine serum albumin-stabilized CuS/Gd<sub>2</sub>O<sub>3</sub> nanoparticles with Cy5.5 fluorophore and tumor-targeting ligand RGD. It was used for both sensitive fluorescence imaging and high-spatial-resolution magnetic resonance imaging of tumor in vivo. Moreover, owing to the strong NIR absorbance from internal CuS NPs, BCGCR can generate localized heat under 980 nm laser irradiation, which enables photothermal therapy (PTT) and further intensifies ROS generation for enhanced CDT. This synergetic effect takes on such an excellent therapeutic efficacy that it can ablate xenografted tumors in vivo.

**Keywords :**

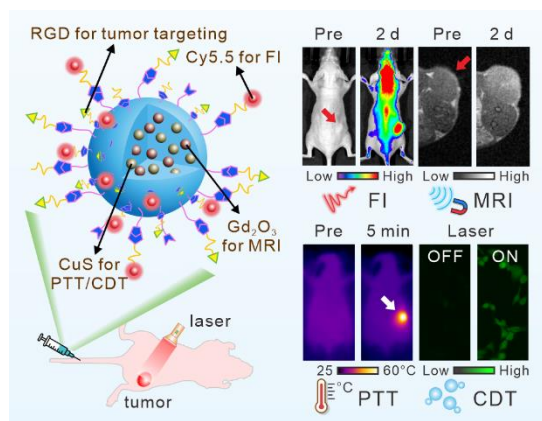
*copper sulfide,*

*fluorescence imaging,*

*magnetic resonance imaging,*

*photothermal therapy,*

*enhanced chemodynamic therapy*



活性酸素種 (ROS) を生成し、腫瘍細胞に酸化的損傷を引き起こす化学力学的療法 (CDT) は、高度な癌治療に大きな期待を寄せています。ここでは、Cy5.5 フルオロフォアと腫瘍標的リガンド RGD 修飾したウシ血清アルブミン安定化硫化銅 / 酸化ガドリニウムナノ粒子の共有結合によって標的腫瘍のバイモーダルイメージングと光熱増強 CDT を統合する多機能ナノプローブ (BCGCR) を報告します。これは、in vivo での腫瘍の高感度蛍光イメージングと高空間分解能磁気共鳴イメージングの両方に使用されました。さらに、硫化銅からの強い NIR 吸収により、BCGCR はレーザー照射下で局所的な熱を発生させることができ、光熱治療 (PTT) を可能にし、CDT を強化するための ROS 生成をさらに促進します。この相乗効果は、非常に優れた治療効果を発揮し、生体内で異種移植された腫瘍の縮小に貢献します。



## メチル化修飾マイクロ RNA 解析のための単分子検出法の開発

(阪大<sup>1</sup>・東理大<sup>2</sup>) 大城 敬人<sup>1</sup>、小本 祐貴<sup>1</sup>、浅井 歩<sup>1</sup>、今野 雅允<sup>2</sup>、石井 秀始<sup>1</sup>、谷口 正輝<sup>1</sup>

Development of single molecule detection method for methylation-modified microRNA analysis (<sup>1</sup>Osaka University, <sup>2</sup> Tokyo University of Science) ○Takahito Ohshiro<sup>1</sup>, Yuki Komoto<sup>1</sup>, Ayumu Asai<sup>1</sup>, Masamitsu Konno<sup>2</sup>, Hideshi Ishii<sup>1</sup>, Masateru Taniguchi<sup>1</sup>

We focused on the methylation of m6A in microRNA and evaluated the methylation modification rate. As a result, when comparing the samples of the patient group with signal pancreatic cancer and the healthy subject group, it was detected that the proportion containing the signal of m6A increased. This was confirmed by mass spectrometry. From the above, it can be said that it is possible to easily diagnose the disease by evaluating the methylation-modified state of a specific microRNA by this method.

**Keywords :** RNA; Single-Molecule Detection; Tunnel-Current; Epigenetics

本研究では、尿中のマイクロ RNA 中の m6A のメチル化に注目し、各アデニン部位でのメチル化修飾率を評価した。これまでがん診断として、マイクロ RNA 解析(RNA-seq)が注目されてきた。しかし、その解析は種類や量となり、それだけの識別精度は十分でないことが分かっている。一方、特定のマイクロ RNA で、メチル化を指標として高精度に識別される可能性が示唆されている。ここでは、ナノギャップ電極デバイスによってマイクロ RNA の単分子トンネル電流計測を行い、m6A (N6-methyladenosine)の修飾を分子ごとの電気伝導度により検出し、定量が可能であるかについて検討を行った。

試料となる修飾塩基としては、m6A とした。この核酸塩基モノマー、m6A を含む合成オリゴ、あるいは抽出した mRNA を含む水溶液 1μM の濃度に調整し、室温・大気圧下で計測を行った。尿中に存在するエクソソームを、ナノワイヤーデバイスにより抽出した。計測に用いる nano-MCBI デバイスにより電極間距離をトンネル電流測定可能な距離に制御し、電気計測を行った。一方、同じく抽出した RNA についてイルミナによる RNA 種の特定制を行い、RNA 量の多いマイクロ RNA に対して m6A への修飾割合について評価を行った。まず、ガン患者由来の人のサンプルから hsa-let7a-5p に相当とするシグナルを検出した。このうち、hsa-let7a-5p の#3 について、A のコンダクタンス値をもつシグナルと m6A のコンダクタンス値をもつシグナルを比較した。その結果、シグナル膀胱がんの患者群のサンプル中では、m6A のシグナルを含む割合は、健常者群と比べ著しく増加していることが分かった。以上のことから、本計測法が、特定のマイクロ RNA のメチル化修飾状態について評価でき、疾患の診断に供する可能性があることが示されたといえる。

1) Single-Molecule RNA Sequencing for Simultaneous Detection of m6A and 5mC, Ohshiro T, Konno M, Asai A, Komoto Y, Satoh T, Eguchi H, Doki Y, Taniguchi M, Ishii H, *Sci. Rep.* **2021**, *11*, 19304

## リンゴプロシアニジンを含む細胞サイズリポソームの相分離構造

(青森産技八工研<sup>1</sup>) ○依田 毅<sup>1</sup>

Phase-separated Structures in Apple procyanidin-containing Cell-sized Liposomes (<sup>1</sup>Aomori Prefectural Industrial Technology Research Center, Hachinohe Industrial Research Institute)

○Tsuyoshi Yoda<sup>1</sup>

Procyanidin extracted from fruits such as apples has been shown to improve lipid metabolism. Recently, studies have revealed that procyanidin interacts with lipid molecules in membranes, enhancing lipid metabolism. Nevertheless, direct evidence of the interaction between procyanidin and lipid membranes has not been demonstrated. In this study, the phase behaviors and changes of membrane fluidity in cell-sized liposomes containing apple procyanidin, procyanidin B2 (PB2) were demonstrated. Phase separation in 1,2-Dioleoyl-sn-glycero-3-phosphocholine/1,2-dipalmitoyl-sn-glycero-3-phosphocholine/cholesterol ternary membranes decreased significantly after addition of a PB2 concentration. The prospect of applying procyanidin content measurements using the results of this study and commercial apple juices was also assessed. At the presentation, the mechanism through which procyanidin improves lipid metabolisms through membrane fluidity regulation was discussed.

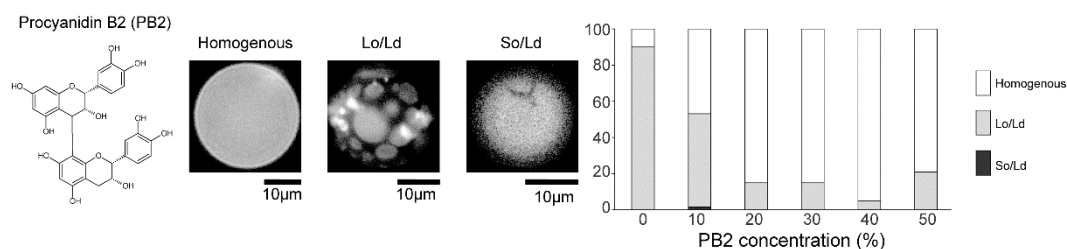
**Keywords :** Procyanidin, Model Biomembranes, Liposomes, Phase-separated Structures

### 【背景・方法】

リンゴなどの果物から抽出されたプロシアニジンは、脂質代謝を改善することが示されている。プロシアニジンと脂質膜の間の相互作用の直接的な証拠は実証されていなかった。この研究では、リンゴのプロシアニジンであるプロシアニジン B2 (PB2) を含む細胞サイズリポソームの相分離構造と膜流動性の変化を蛍光顕微鏡観察により調べた。

### 【結果・考察】

1,2-ジオレオイル-sn-グリセロ-3-ホスホコリン (DOPC) / 1,2-ジパルミトイル-sn-グリセロ-3-ホスホコリン (DPPC) / コレステロール三成分からなる相分離構造(液体秩序相/液体無秩序相, Lo/Ld 等)をする細胞サイズリポソームの割合は、PB2 を添加した時、大幅に減少し均一な構造(Homogenous)が増えた。この研究の結果を参考にした、市販のリンゴジュースを使用した実験により、プロシアニジン含有量測定に適用する可能性を評価した。発表では、プロシアニジンが膜流動性調節を通じて脂質代謝を改善するメカニズムについても議論する。

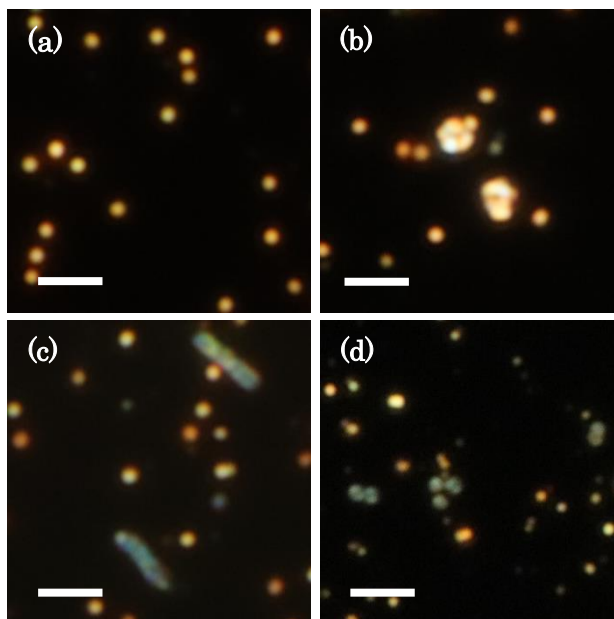


## Dark-field microscopic detection of bacteria using bacteriophage-modified SiO<sub>2</sub>@AuNP core-shell nanoparticles.

(<sup>1</sup>Graduate school of science, Kochi University, <sup>2</sup>Graduate School of Medicine Dentistry and Pharmaceutical sciences, Okayama University, <sup>3</sup>Medical school, Okayama University, <sup>4</sup>Faculty of Health Science, Kochi Gakuen University ) ○Masashi Imai,<sup>1</sup> Yosuke Niko,<sup>1</sup> Shingo Hadano,<sup>1</sup> Shigeru Watanabe,<sup>1</sup> Jumpei Uchiyama,<sup>3</sup> Iyo Uchiyama,<sup>2</sup> Shigenobu Matsuzaki,<sup>4</sup>

**Keywords:** Bacteriophage; Bacterial detection; Dark-field microscopy; Gold nanoparticle; Metal nanoparticle

Bacterial infections are serious worldwide threat to public health, and so the accurate and rapid detection and identification. Bacteriophages are naturally occurring viruses of bacteria that only infect bacterial cells and are harmless to mammals. Among a wide variety of biological materials, bacteriophages have received increasing attention as promising alternatives to antibodies in biosensor applications. Herein we present a rapid and highly selective detection method for pathogenic bacteria, which combines dark-field light scattering imaging with a plasmonic biosensor. The biosensor was prepared by immobilizing phages on the surfaces of the SiO<sub>2</sub>@AuNPs core-shell nanoparticles. The biosensor selectively bound to *S. aureus* and significantly increased the scattering contrast of *S. aureus* (**Figure 1**). This method is capable of discrimination not only at the genus level but also at the species level. The detection limit for *S.aureus* was  $\sim 1 \times 10^4$  cfu/mL, and the quantification of target bacteria over a wide range of concentrations was accomplished within 15-20 min after addition of the biosensors to the bacterial solution.



**Figure 1.** Dark field images of SiO<sub>2</sub>@AuNPs mixed with (a) *S.aureus*, (b) *E.coli* and (c) *S.pseudintermedius*. Scale bar is 10  $\mu$ m.

Imai, Masashi, *et al.*, *Anal.Chem.* **2019**, *19*, 12352-12357.

## ミクروسケール電気泳動フィルタリングデバイスを用いた核酸アプタマー選抜

(阪府大院工<sup>1</sup>・JST さきがけ<sup>2</sup>) ○末吉 健志<sup>1,2</sup>・高尾 隼空<sup>1</sup>・飛田 安梨沙<sup>1</sup>・上野楓<sup>1</sup>・遠藤 達郎<sup>1</sup>・久本 秀明<sup>1</sup>

Aptamer Selection Using a Microscale Electrophoretic Filtering Device (<sup>1</sup>*Graduate School of Engineering, Osaka Prefecture University*, <sup>2</sup>*PREST, JST*) ○Kenji Sueyoshi,<sup>1,2</sup> Junku Takao,<sup>1</sup> Arisa Tobita,<sup>1</sup> Kaede Ueno,<sup>1</sup> Tatsuro Endo,<sup>1</sup> Hideaki Hisamoto<sup>1</sup>

Recently, DNA aptamer specifically binding with their target is expected to be a novel molecular probe instead of antigens. Here, an aptamer selection method using a microscale electrophoretic filtering device was newly developed. Experimentally, target proteins electrokinetically introduced into a capillary partially plugged with a hydrogel were trapped by molecular sieving effect. DNAs with different random sequence are then introduced into the capillary for binding reaction with the trapped protein. After washing the unbound DNAs, the remaining DNAs (aptamer candidates) were eluted and sequenced. As a result, the DNAs resembling the reported aptamers were found from the obtained candidates in the eluent.

**Keywords :** *Aptamer Selection; Microscale electrophoretic Filtering*

核酸アプタマーは、標的分子に対して特異的に結合する配列を持つ核酸群の総称であり、生体由来の抗体に代わる分子認識プローブとして近年注目されている。その選抜法として、一般的に Systematic Evolution of Ligands by Exponential Enrichment (SELEX) 法が利用されているが、混合・分離・増幅などの煩雑な実験操作を 10 数回繰り返す必要があり、その簡略化が望まれている。そこで、本研究ではミクروسケール電気泳動フィルタリングデバイスを用いた新規アプタマー選抜法を開発した。本法では、ポリアクリルアミド (PAAm) ゲルが部分充填されたキャピラリーデバイス内に試料分子を電気泳動導入し、分子ふるい効果によって捕捉する。試料分子捕捉後、ランダム配列核酸ライブラリを電気泳動導入し、結合・解離反応を順次行う。その際、高い結合能を示す核酸のみが捕捉された試料分子と結合して濃縮される。さらに洗浄・溶離後に回収された核酸群を PCR で増幅し、次世代シーケンサーで配列を解析する。

免疫グロブリン G (IgG) および E (IgE)、癌胎児性抗原、テトラスパニン類などをモデル標的分子として、提案した手法に基づくアプタマー選抜をそれぞれに対して行った。作製したデバイスに蛍光標識 IgG を導入したところ、試料導入時間に対する経時的な蛍光強度増加が観察され、PAAm ゲルの分子ふるい効果に基づく IgG 捕捉が確認された。また、非標識 IgE を捕捉後に蛍光標識核酸ライブラリを導入した結果、蛍光標識核酸の結合に伴う蛍光強度増加と洗浄時の解離に伴う蛍光強度減少がそれぞれ観察された。そこで、最終的にデバイス内に残存した核酸分子を溶離・回収して配列解析を行ったところ、モデル試料に対して SELEX 法で得られた既知アプタマー配列に類似した核酸が、本法による 1 回の選抜操作で得られた核酸群の中にそれぞれ確認された。現在、各アプタマー候補の結合能および選択性について評価中である。

**[J401-2pm] 07. Inorganic Chemistry**

Chair: Takahiro Takei, Fumitaka Hayashi

Thu. Mar 24, 2022 1:00 PM - 3:40 PM J401 (Online Meeting)

**[J401-2pm-01] Scission of titania nanosheets via physical adsorption on a non-flat substrate**○Nobuyuki Sakai<sup>1</sup>, Masahiko Suzuki<sup>1</sup>, Takayoshi Sasaki<sup>1</sup> (1. National Institute for Materials Science)

1:00 PM - 1:20 PM

**[J401-2pm-02] Nanofluidic Anion Transport through Reconstructed Membrane of Layered Double Hydroxide Nanosheets**○Fang XIAN<sup>1,2</sup>, Renzhi MA<sup>1,2</sup>, Yoshiyuki SUGAHARA<sup>2</sup>, Takayoshi SASAKI<sup>1</sup> (1. National Institute for Materials Science, 2. The Univ. of Waseda)

1:20 PM - 1:40 PM

**[J401-2pm-03] Synthesis of Fe-based (oxy)hydroxides nanosheets for oxygen evolution reaction (OER) electrocatalyst**○Lulu JIA<sup>1,2</sup>, Renzhi MA<sup>1,2</sup>, Yoshiyuki SUGAHARA<sup>2</sup>, Takayoshi SASAKI<sup>1</sup> (1. NIMS, 2. Waseda Univ.)

1:40 PM - 2:00 PM

**[J401-2pm-04] Bottom-up Synthesis of Amorphous Silica Nanosheets and Two-Dimensional Assembly**○Eisuke Yamamoto<sup>1,2</sup>, Kosuke Fujihara<sup>3</sup>, Yue Shi<sup>1</sup>, Makoto Kobayashi<sup>1</sup>, Minoru Osada<sup>1,4</sup> (1. IMASS, Nagoya University, 2. PRESTO, JST, 3. Nagoya University Graduate School, 4. WPI-MANA, National Institute for Materials Science)

2:00 PM - 2:20 PM

**[J401-2pm-05] Solution phase synthesis of borophene analogs**○Dongwan Yan<sup>1,2</sup>, Tetsuya Kambe<sup>2</sup>, Kimihisa Yamamoto<sup>2</sup> (1. KISTEC, 2. Tokyo Tech Laboratory for Chemistry and Life Science JST-ERATO)

2:20 PM - 2:40 PM

**[J401-2pm-06] Fabrication of Large-Sized MnO<sub>2</sub> Nanosheets from Layered Manganese Oxide Single Crystals and Application to Sensor Materials**○Hitomi Yano<sup>1</sup>, Akihisa Aimi<sup>1</sup>, Nobuyuki Sakai<sup>2</sup>, Takayoshi Sasaki<sup>2</sup>, Kenjiro Fujimoto<sup>1</sup> (1. Tokyo University of Science, 2. National Institute for Materials Science)

2:40 PM - 3:00 PM

**[J401-2pm-07] Flux Growth and Efficient Exfoliation of Layered Titanate and Niobate Crystals**○Fumitaka Hayashi<sup>1</sup>, Kakeru Umehara<sup>1</sup>, Nanako Tatewaki<sup>1</sup>, Furui Kenta<sup>1</sup>, Tomohito Sudare<sup>1</sup>, Maru Kashiwazaki<sup>1</sup>, Hiromasa Shiiba<sup>1</sup>, Kazunori Fujisawa<sup>1</sup>, Katsuya Teshima<sup>1</sup> (1. Shinshu Univ.)

3:00 PM - 3:20 PM

**[J401-2pm-08] Formation of ordered structure by intercalation of phenol in organoclay investigated by molecular simulation**○Masaya Miyagawa<sup>1</sup>, Fumiya Hirose<sup>1</sup>, Hiromitsu Takaba<sup>1</sup> (1. Kogakuin University)

3:20 PM - 3:40 PM

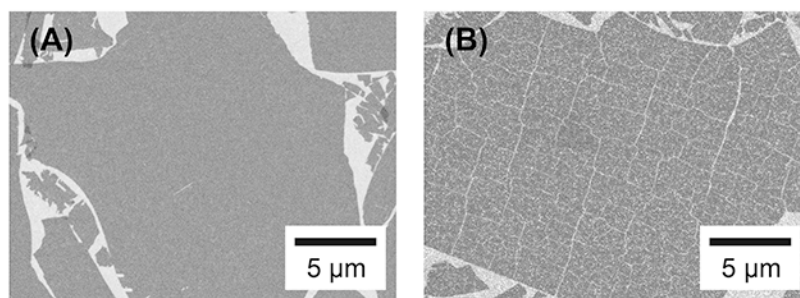
## 非平坦基板への物理吸着による酸化チタンナノシートの切断

(物質・材料研究機構) ○坂井 伸行・鈴木 雅彦・佐々木 高義

Scission of Titania Nanosheets via Physical Adsorption on a Non-Flat Substrate (*National Institute for Materials Science*) ○Nobuyuki Sakai, Masahiko Suzuki, Takayoshi Sasaki

Secondary processing such as drilling and cutting of 2D nanosheets is an important technique for modulation of their properties and fabrication of devices based on the nanosheets. In the present study, we found that titania nanosheets can be orthogonally sectioned into substantially rectangular-shaped fragments when deposited on a non-flat substrate via spin-coating their suspension (Figure 1). Upon adsorption on the substrate, the nanosheet experiences tensile stress along its lateral direction, which is based on the integrated intermolecular forces acting between the nanosheet and the substrate surface. Due to the high 2D anisotropy, the integrated intermolecular forces can be large enough to cleave the chemical bonds in the nanosheets, leading to the scission of the nanosheets. This interesting finding may offer a new processing technique for cutting and shaping various 2D materials along their crystallographic orientation. **Keywords** : 2D Materials; Secondary Processing; Intermolecular Forces; Tensile Stress

切断や穿孔などナノシートを二次加工することはデバイス作製や特性向上において重要な技術である。本研究では、非平坦基板への吸着により酸化チタンナノシートが結晶軸方位に沿って切断されることを見出した(図 1)。スピncコート法による吸着過程において、液面に浮かぶ個々のナノシートは非平坦基板の複数の凸部に接触し、基板表面の凹凸に追従して吸着し始める。しかし、ナノシートの面積は非平坦基板の実面積より小さいためナノシートは面内方向に引張応力を受け、吸着面積の増加とともに増大する引張応力によりナノシート内部に亀裂が生じる。引張応力の起源はナノシートと基板の間に働く分子間力であり、ナノシートの高い二次元性により一定の面積に働く分子間力の合計はナノシート内部の化学結合を切断するのに十分な大きさを持ち、ナノシートを切断できると考えられる。亀裂は互いに直交する傾向が認められ、結晶軸方位に沿ってナノシートが切断されることが示唆された。



**Figure 1.** SEM images of titania nanosheets adsorbed on ITO substrates with (A) a flat surface and (B) a bumpy surface.

## Nanofluidic Anion Transport through Reconstructed Membrane of Layered Double Hydroxide Nanosheets

(<sup>1</sup>International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), <sup>2</sup>Graduate School of Advanced Science and Engineering, Waseda University) ○Fang Xian, <sup>1,2</sup> Renzhi Ma, <sup>1,2</sup> Yoshiyuki Sugahara, <sup>2</sup> Takayoshi Sasaki, <sup>1</sup>

**Keywords:** Layered double hydroxide; Nanosheets; Nanofluidics; Anion transport; Ion pump

Two-dimensional (2D) materials have been widely studied due to their novel properties distinct from the bulk counterpart compounds.<sup>1,2</sup> Recently, a number of nanosheets with molecular thickness have been successfully obtained by exfoliating their bulk layer materials, thus further accelerating the research on 2D materials.<sup>2</sup> In particular, reconstruction or restacking of nanomaterials creates nanochannels with excellent nanofluidic transport characteristics for applications in bio-sensing, seawater desalination and energy harvesting.<sup>3</sup> There have been previous reports on fabrication of cationic transport devices based on 2D materials such as graphene oxide (GO).<sup>4</sup> However, construction of anionic transport membranes is very rare.

In the present work, a membrane-type nanofluidic device was prepared by self-assembling MgAl LDH nanosheets, which exhibited a remarkable OH<sup>-</sup> conductivity of  $\sim 2 \times 10^{-2} \text{ S cm}^{-1}$  (Fig. 1). The conductivity is much higher than that reported for GO membranes ( $\sim 0.2 \times 10^{-2} \text{ S cm}^{-1}$ ). By further tuning the LDH membrane into a triangular shape, a diode behavior for anionic transport has been confirmed. The result demonstrates a great application prospect of using LDH membrane as ion-pump for uphill transport against the concentration gradient.

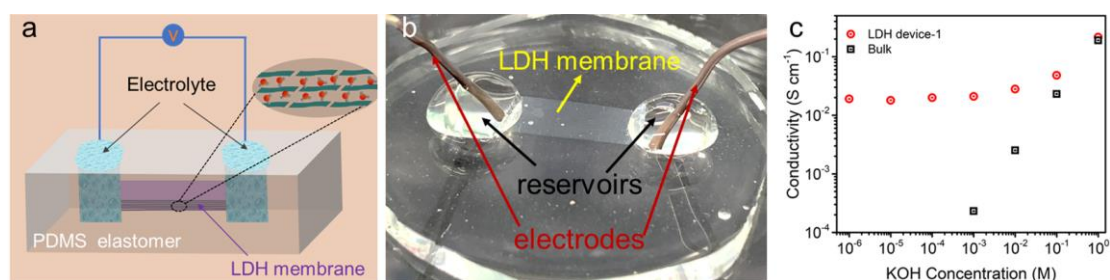


Figure 1. (a) Schematic illustration and (b) digital photo of LDH membrane-based nanofluidic device. (c) Ionic conductivity as a function of KOH concentration. The corresponding conductivities of bulk solution are displayed as references.

- 1) X. Cai, et al., *Chem. Soc. Rev.*, **2018**, 47, 6224-6266. 2) P. Xiong, et al., *Adv. Mat.*, **2020**, 32, 1902654. 3) a) J. Feng, et al., *Nature*, **2016**, 536, 197-200. b) Z. Zhang, et al., *Nat. Commun.*, **2019**, 10, 1-9. 4) a) K. Raidongia, et al., *J. Am. Chem. Soc.*, **2012**, 134, 16528-16531. b) X. Zhang, et al., *ACS Nano*, **2019**, 13, 4238-4245.



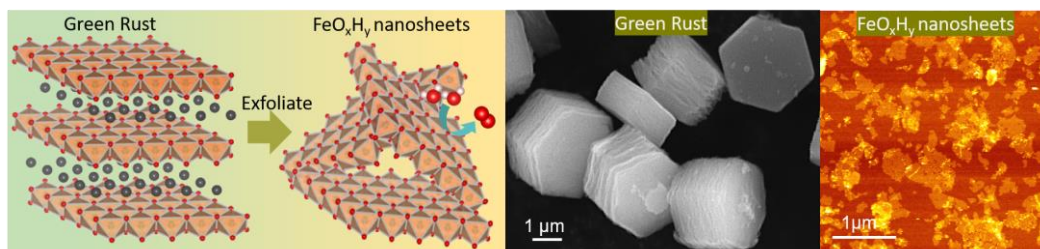
## Synthesis of Fe-based (oxy)hydroxide nanosheets for oxygen evolution reaction (OER) electrocatalyst

(<sup>1</sup>International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), <sup>2</sup>Graduate School of Advanced Science and Engineering, Waseda University) ○Lulu Jia,<sup>1,2</sup> Renzhi Ma,<sup>1,2</sup> Yoshiyuki Sugahara,<sup>2</sup> Takayoshi Sasaki<sup>1</sup>

**Keywords:** Hydroxide nanosheets; Iron (oxy)hydroxide; Electrocatalyst

Two-dimensional (2D) nanosheets beyond graphene such as metal dichalcogenides, oxides and hydroxides, carbides have received widespread attention for potential applications in various fields including electronics, optics, magnetism, and catalysis due to their unique structural anisotropy and compositional tunability. Among them, 3d transition metal (Fe, Co, Ni)-based (oxy)hydroxides nanosheets exhibit promising electrocatalytic properties in water splitting under alkaline conditions. In our previous reports, we have systematically studied the synthetic chemistry of layered double hydroxide (LDH) nanosheets based on the combination of different transition elements (Ni(Co)-Fe, Co(Ni)-Ni, and Co-Co).<sup>1-3</sup> However, the synthesis of pure Fe hydroxide nanosheets is still challenging.

In the current work, we have succeeded in preparation of pure Fe (oxy)hydroxide ( $\text{FeO}_x\text{H}_y$ ) nanosheets with a unilamellar thickness of 1 nm and lateral dimension of several hundred nm by using highly crystalline Green Rust (GR) as parent layered material. GR, a  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  LDH with a general formula of  $[\text{Fe}_{1-x}^{2+}\text{Fe}_x^{3+}(\text{OH})_2]^{+x} [\text{A}^{n-}/m \cdot m\text{H}_2\text{O}]^{-x}$  where A representing interlayer anions ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.), can be conventionally synthesized through co-precipitation of ferrous and ferric salts. However, low crystallinity and small lateral size of the co-precipitation product pose a great hurdle for obtaining well-defined nanosheets. We employed a topochemical oxidation and intercalation process to prepare highly crystalline GR intercalated with iodide ( $\text{I}^-$ ) based on brucite-like  $\text{Fe}(\text{OH})_2$ . Taking advantage of facile anion exchangeability, GR intercalated with dodecyl sulfate ( $\text{DS}^-$ ) were converted for the delamination into  $\text{FeO}_x\text{H}_y$  nanosheets. As synthesized nanosheets were explored as electrocatalysts for oxygen evolution reaction (OER) under alkaline conditions.



**Fig. 1** Exfoliate Green Rust to unilamellar  $\text{FeO}_x\text{H}_y$  nanosheets

1) W. Ma, et al., *ACS Nano*, **2015**, 9, 1977-1984. 2) R. Ma, et al., *J. Am. Chem. Soc.*, **2011**, 133, 613-620. 3) L. Jia, et al., *ChemSusChem*, **2019**, 12, 5274-5281.

## アモルファスシリカナノシートのボトムアップ合成と精密集積

(名大未来研<sup>1</sup>・JST さきがけ<sup>2</sup>・名大院工<sup>3</sup>・物材機構 WPI-MANA<sup>4</sup>) ○山本 瑛祐<sup>1,2</sup>・藤原 康輔<sup>3</sup>・施 越<sup>1</sup>・小林 亮<sup>1</sup>・長田 実<sup>1,4</sup>

Bottom-up Synthesis of Amorphous Silica Nanosheets and Two-Dimensional Assembly (<sup>1</sup>IMaSS, Nagoya University, <sup>2</sup>PRESTO, JST, <sup>3</sup>Nagoya University Graduate School, <sup>4</sup>WPI-MANA, NIMS) ○Eisuke Yamamoto<sup>1,2</sup>, Kosuke Fujihara<sup>3</sup>, Yue Shi<sup>1</sup>, Makoto Kobayashi<sup>1</sup>, Minoru Osada<sup>1,4</sup>

Amorphous nanosheets have attracted much attention because they exhibit unique properties distinct from bulk counterparts. In particular, amorphous silica nanosheets have been synthesized through various templating methods. However, the resultant nanosheets had rather thick, and those were not atomically thin and obtained as aggregates. In this study, surfactant-silica lamellar hybrids templated Brij52 ( $\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_2\text{OH}$ ) were exfoliated into amorphous silica nanosheets with 0.9 nm in thickness. The obtained colloidal solution showed high colloidal stability, which allowed us to construct the Langmuir film. The obtained Langmuir film was transferred into Si substrate, and the monolayer nanosheets were two-dimensionally packed as shown by AFM image. Furthermore, multi layered films were also prepared through repeating the deposition process, which are expected to be used for various devices.

**Keywords :** Nanosheet, Amorphous silica, Non-ionic surfactant, Lamellar

アモルファス原子膜(ナノシート)はバルク材料とは異なる構造的特徴を有しており、ありふれた材料も 1 nm 以下の原子膜化に伴い、電気的特性や機械的特性が大きく変化する。近年では、アモルファスシリカナノシートが注目を集めているが、一般的な合成手法であるカチオン性界面活性剤-シリカ層状複合体の剥離ではシリカ層が数層分重なった厚いナノシートの凝集体しか得られていない。本研究では非イオン性界面活性剤である Brij52( $\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_2\text{OH}$ )を含む層状複合体<sup>1)</sup>をエタノール中で剥離することで、厚み 0.9 nm のアモルファスシリカナノシートのコロイド分散液を合成した。得られたナノシート分散液を用いてラングミュア膜を構築した後に、シリコン基板上にナノシート集積膜を転写できた (Fig.1 (a))。ナノシート同士は密に敷き詰まっており、緻密な集積膜の構築に成功している (Fig.1 (b))。積層操作を繰り返すことで、ナノシート多層膜の作製にも成功しており、今後様々なデバイスへの展開も期待される。

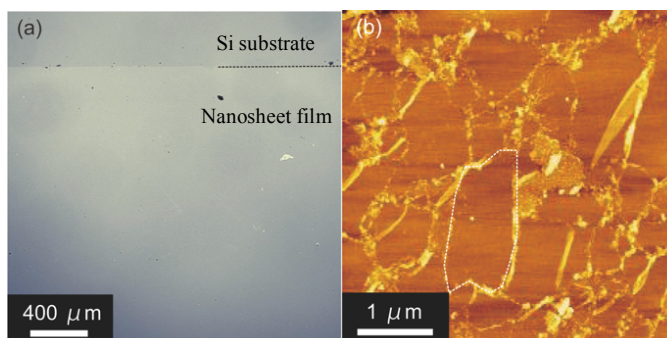


Fig. 1 (a) Confocal laser microscope image and (b) AMF image of the amorphous silica nanosheets film.

1) D. Zhao *et al.*, *J. Am. Chem. Soc.* **1998**, 120, 6024.

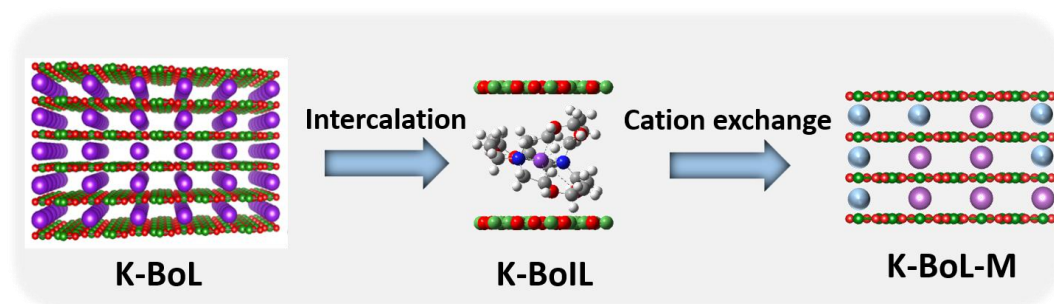
## Solution phase synthesis of borophene analogues

(<sup>1</sup>Kanagawa Institute of Industrial Science and Technology, Tokyo Tech, <sup>2</sup>Laboratory for Chemistry and Life Science JST-ERATO, Tokyo Tech) ○ Dongwan Yan<sup>1</sup>, Tetsuya Kambe<sup>2</sup>, Kimihisa Yamamoto<sup>2</sup>

**Keywords:** Borophene analogues; Solution phase synthesis; Cation exchange

Single-atom layer materials, such as graphene, phosphorene, and stanine, are usually raised unique electrochemistry properties. Borophene is reported as an allotrope of boron with two-dimensional (2D) boron sheets which has been firstly experimentally confirmed in 2015.<sup>1</sup> By far, the synthesis methods relied on metal substrates and usually under ultra-high vacuum systems. Due to the strict synthesis environment of borophene, it is hard to develop utilize properties practically. Our group reported potassium cations intercalated borophene-oxygen layers (BoLs) synthesized in solution phase with anisotropic conductivity.<sup>2</sup> The atomospheric pressure and substrate-free preparation are also adapted in other borophene analogues.

In this report, we mainly focus on a cation-exchange approach by exchanging the cations of K-BoLs with other metal cations in a solution phase. Because of the unique structure of the BoLs, single borophene-oxide layers can be obtained by peeling off the crystal stacking layers in solutions. Therefore, changing the cations between these B-O layers are theoretically feasible. Crown ethers were used for intercalating the cations of BoLs in solutions and the achieved K-BoLs intercalated with crown ethers (BoIL) were then conducting the cation exchange steps. A series of borophene analogues have been successfully synthesized and the members of the borophene analogues are enriched. The cation-exchanged BoLs are well confirmed and compared by character approaches, such as FT-IR, XRD, SEM and EDX.



- 1) a) Mannix, Andrew J., et al. Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs. *Science* **2015**, 350, 6267, 1513-1516. b) Feng, Baojie et al. Experimental realization of two-dimensional boron sheets. *Nature Chem.* **2016**, 8, 6, 563-568.
- 2) T. Kambe, et al. Solution Phase Mass Synthesis of 2D Atomic Layer with Hexagonal Boron Network., *J. Am. Chem. Soc.* **2019**, 141, 33, 12984-12988.

## Fabrication of Large-Sized MnO<sub>2</sub> Nanosheets from Layered Manganese Oxide Single Crystals and Application to Sensor Materials

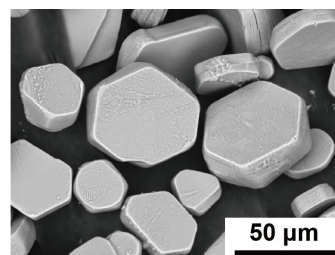
(<sup>1</sup>Graduate School of Science and Technology, Tokyo University of Science, <sup>2</sup>International Center for Materials Nanoarchitectonics, National Institute for Materials Science)

○Hitomi Yano,<sup>1</sup> Akihisa Aimi,<sup>1</sup> Nobuyuki Sakai,<sup>2</sup> Takayoshi Sasaki,<sup>2</sup> Kenjiro Fujimoto<sup>1</sup>

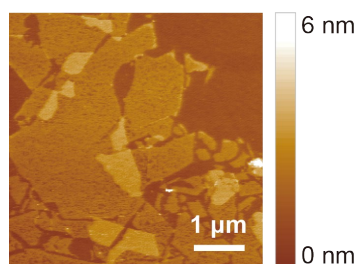
**Keywords:** Single Crystals; Manganese Oxide; Flux Method; Nanosheets; Gas Sensors

Nanosheets have been known to have a unique two-dimensional structure with a molecular thickness. Manganese oxide nanosheets are known to possess superior redox properties and conductivity.<sup>1</sup> To bring out their performance, nanosheets with large lateral size are needed. However, preparation of large-sized nanosheets was difficult because layered metal oxide crystals tend to fragment into small pieces during exfoliation process. Lateral size control of the nanosheets have been studied on such as Ti<sub>0.87</sub>O<sub>2</sub>.<sup>2</sup> On the other hand, few studies have been reported on the size control of MnO<sub>2</sub> nanosheets.<sup>3</sup> In this study, we prepared large MnO<sub>2</sub> nanosheets by using large-sized mother phase of layered manganese oxide single crystals and optimizing an exfoliation process, and investigated its gas sensor properties.

Single crystals of layered manganese oxide, K<sub>0.3</sub>MnO<sub>2</sub>, were synthesized by a flux method. K<sub>2</sub>MoO<sub>4</sub> and K<sub>0.45</sub>MnO<sub>2</sub> polycrystals were used as a flux agent and a crystal source, respectively. After the melting at 1000 °C and gradual cooling, hexagonal plate-shaped single crystals of K<sub>0.3</sub>MnO<sub>2</sub> with smooth surface were obtained (**Figure 1**). HCl or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was used for removal of interlayer K<sup>+</sup> and protonation of K<sub>0.3</sub>MnO<sub>2</sub>. The crystals cracked by protonating with HCl, while relatively smooth surface remained by protonating with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The reaction of the protonated crystals with delaminating agents resulted in MnO<sub>2</sub> nanosheets with a thickness of ~1 nm and a lateral size of up to 3 μm which is larger than conventional nanosheets derived from polycrystals (~0.3 μm) (**Figure 2**). Furthermore, MnO<sub>2</sub> nanosheet thin films were fabricated to evaluate hydrogen gas responsiveness based on electric resistance. The resistance changed rapidly under H<sub>2</sub>-mixed gas exposure at 200 °C, suggesting that the MnO<sub>2</sub> nanosheets have H<sub>2</sub> sensing abilities.



**Figure 1.** SEM image of K<sub>0.3</sub>MnO<sub>2</sub> single crystals



**Figure 2.** AFM image of MnO<sub>2</sub> nanosheets

1) L.-Z. Wang, Y. Omomo, N. Sakai, K. Fukuda, I. Nakai, Y. Ebina, K. Takada, M. Watanabe, T. Sasaki, *Chem. Mater.* **2003**, *15*, 2873.

2) T. Tanaka, Y. Ebina, K. Takada, K. Kurashima, T. Sasaki, *Chem. Mater.* **2003**, *15*, 3564.

3) X.-J. Yang, Y. Makita, Z.-H. Liu, K. Sakane, K. Ooi, *Chem. Mater.* **2004**, *16*, 5581.



## 層状チタン酸・ニオブ酸塩結晶のフラックス育成とその高効率剥離

(信州大工<sup>1</sup>・信州大 RISM 研<sup>2</sup>) ○林 文隆<sup>1</sup>・梅原 翔<sup>1</sup>・帯刀 菜奈子<sup>1</sup>・古井 健太<sup>1</sup>・簾 智仁<sup>2</sup>・柏崎 真瑠<sup>1</sup>・椎葉 寛将<sup>2</sup>・藤澤 一範<sup>2</sup>・手嶋 勝弥<sup>1,2</sup>

Flux growth and exfoliation of layered titanate and niobate crystals and their efficient exfoliation (<sup>1</sup>*Faculty of Engineering, Shinshu University*, <sup>2</sup>*RISM, Shinshu University*) ○ Fumitaka Hayashi,<sup>1</sup> Kakeru Umehara,<sup>1</sup> Nanako Tatewaki,<sup>1</sup> Kenta Furui,<sup>1</sup> Tomohito Sudare,<sup>2</sup> Maru Kashiwazaki,<sup>1</sup> Hiromasa Shiiba,<sup>1</sup> Kazunori Fujisawa,<sup>2</sup> Katsuya Teshima<sup>1,2</sup>

Two-dimensional (2D) materials have attracted great attentions of chemists and physicists because of their unexpected physical, chemical, electronic, and optical properties. However, there remain several challenges; for example, the yield, the lateral size control, and the crystallinity should be improved. The present study demonstrate the efficient and environmentally begin methodology for nanosheet preparation. That is, we demonstrate the flux-evaporation-assisted growth of millimeter-sized five-coordinate  $K_2Ti_2O_5$  and multicomponent hexaniobate  $K_4(Nb,M_x)_6O_{17}$  ( $x = 1\sim4$ ,  $M = Ti, Zr, Hf, Ta, Sb$ , etc.) single crystals and the exfoliation of the resultant KTO crystals under the hydrothermal conditions without the use of acids and bases.

**Keywords :** Layered material; nanosheet; exfoliation; high entropy ceramics, flux growth

無機ナノシートは、無機層状結晶を剥離することにより得られる二次元ナノ結晶であり、 $10^4$ を超える大きな異方性比と最大  $100\ \mu\text{m}$  にもなる大きな二次元方向サイズを特徴とする。無機ナノシートの中でも、酸化チタンやニオブナノシートは優れた半導体・(光)触媒特性を示し、その機能を活かしてエネルギー変換・環境浄化デバイスへの応用が展開されている。一般に層電荷密度の高い結晶を剥離するには、酸への浸漬、嵩高い塩基による中和、未剥離体との分離からなる多段階プロセスを必要とする。本研究では、5 配位チタン酸塩  $K_2Ti_2O_5$  (KTO) 結晶と多成分置換六ニオブ酸カリウム  $K_4(Nb,M_x)_6O_{17}$  ( $x = 1\sim4$ ,  $M = Ti, Zr, Hf, Ta, Sb$ , etc.) をホスト結晶として着目し、より簡便なナノシートの作製法を検討した。具体的には、フラックス法を用いて、サブミリ～ミリメートルサイズのチタン・ニオブ酸塩単結晶を育成し、酸や塩基を使わずに水熱処理のみで剥離した。一例として、Fig.1 に、 $K_4(Nb,M_x)_6O_{17}$  ( $x = 1\sim4$ ,  $M = Ti, Hf, Ta, Sb$ ) 結晶を剥離して得られたナノシートの AFM 像を示す。得られたナノシートの厚みはおよそ  $2.5\ \text{nm}$  であることを確認した。

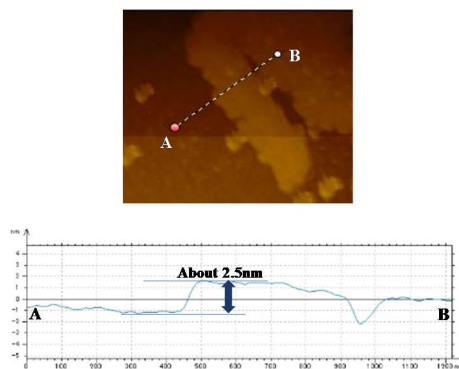


Fig.1 AFM image of nanosheets obtained from  $K_4(Nb,M_x)_6O_{17}$  ( $x = 1\sim4$ ,  $M = Ti, Hf, Ta, Sb$ ).

謝辞：本研究の一部は、科研費 (Grant No. 20K05074, 20H05214), JST-CREST (JPMJCR20H3), および JST-COI 事業 (JPMJCE1316, R1WD11-13) の支援をうけた。記して謝意を表する。

## 有機粘土へのフェノール吸着で形成される秩序構造の分子シミュレーションによる解明

(工学院大<sup>1</sup>) ○宮川 雅矢<sup>1</sup>・廣澤 史也<sup>1</sup>・高羽 洋充<sup>1</sup>

Formation of ordered structure by intercalation of phenol in organoclay investigated by molecular simulation (<sup>1</sup>*School of Advanced Engineering, Kogakuin University*) ○Masaya Miyagawa,<sup>1</sup> Fumiya Hirose,<sup>1</sup> Hiromitsu Takaba<sup>1</sup>

In the present study, we investigated structural changes in methylviologen-modified montmorillonite (Mont-MV) by molecular dynamics simulation. In Mont-MV, the MV cations are oriented horizontally. By initial stage of intercalation of phenol, the phenol is interacted with siloxane surface of Mont while the interlayer structure does not change significantly. As more phenol molecules are intercalated, however, both the MV cations and phenol molecules get tilted. This morphology sufficiently rationalizes charge-transfer complex observed experimentally. Therefore, it is concluded that the MV cation plays as pillar and the formation of the complex is the secondarily derived function.

**Keywords** : Montmorillonite, Molecular dynamics simulation, Organoclay, Methylviologen, Intercalation

モンモリロナイトの層間カチオンをメチルビオロゲンに交換すると、複合体 (Mont-MV) はフェノール類を吸着するだけでなく呈色反応を示す。<sup>1)</sup>これはフェノールと MV が電荷移動錯体を形成するためと考えられているが、このような機能の発現メカニズムにおいて層および層間カチオンが果たす役割を解明することは容易ではない。我々は最近、分子動力学 (MD) 法を用いて有機粘土およびアントラセン吸着時の層間構造を報告した。<sup>2)</sup>本研究ではフェノール吸着にともなう Mont-MV の構造変化の解明を目的とした。Mont の力場には interface を、<sup>3)</sup>それ以外には pcff を用いた。

Mont-MV のスナップショットを Fig. 1(a)に示す。基本面間隔は 12.4 Å と実験値をよく再現し、MV は Mont 層に対して平行に配向している。フェノールを各層間に 6 分子含む複合体のスナップショットを Fig. 1(b)に示す。フェノールの OH 基は面外に飛び出し Mont 層のシロキサン表面と相互作用しているが、フェノール・MV どちらも大きな配向変化は見られない。しかし、フェノールを 24 分子含む複合体ではどちらも粘土層に対して傾き、互いにおおよそ平行で錯形成に十分な構造を形成している。すなわち、Mont-MV へのフェノール吸着では、層との相互作用が重要であり、MV との錯形成は副次的な機能であることがわかる。

1) T. Okada, M. Ogawa, Chem. Lett. **2002**, 31, 812. 2) M. Miyagawa, F. Hirose, H. Higuchi, H. Takaba, ACS Omega **2021**, 6, 19314. 3) H. Heinz et al., Langmuir 2013, 20, 1754.

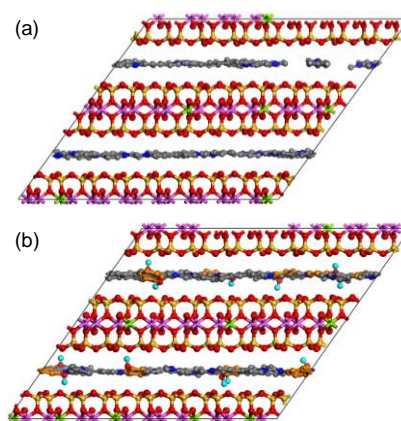


Fig. 1. Snapshots of (a) Mont-MV and (b) Mont-MV containing 6 phenols.

**[B304-2pm] 08. Catalysts and Catalysis**

Chair: Yusuke Kita, Kazuya Yamaguchi

Thu. Mar 24, 2022 1:20 PM - 3:40 PM B304 (Online Meeting)

**[B304-2pm-01] Al-doped Mesoporous Silica-supported Pd Complex Catalyst for the Tsuji-Trost Allylation**○Siming Ding<sup>1</sup>, Yuichi Manaka<sup>1,2</sup>, Ken Motokura<sup>1,3</sup> (1. Tokyo Tech., 2. AIST, 3. YNU)

1:20 PM - 1:40 PM

**[B304-2pm-02] Immobilized Iron Complex on Bipyridine-Based Periodic Mesoporous Organosilica for Hydrosilylation of Alkynes**○Xiao-Tao Lin<sup>1,2</sup>, Kazuhiro Matsumoto<sup>2</sup>, Yoshifumi Maegawa<sup>3</sup>, Kazuhiko Sato<sup>2</sup>, Norihisa Fukaya<sup>2,3</sup>, Jun-Chul Choi<sup>1,2</sup> (1. Graduate School of Pure and Applied Sciences, University of Tsukuba, 2. Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, 3. Toyota Central R&D Labs)

1:40 PM - 2:00 PM

**[B304-2pm-03] Hydrogenolysis of alcohols and carbonyl compounds to alkanes by Pt/Al(PO<sub>3</sub>)<sub>3</sub> catalyst**○Kento Oshida<sup>1</sup>, Xiongjie Jin<sup>1</sup>, Kyoko Nozaki<sup>1</sup> (1. The University of Tokyo)

2:00 PM - 2:20 PM

**[B304-2pm-04] Preparation and Catalytic Properties of Silica-Supported Pt Nanoparticles**○Toshiki Nishitoba<sup>1</sup>, Yusuke Ishizaka<sup>2</sup>, Kazuhiro Matsumoto<sup>1</sup>, Katsuhiko Takeuchi<sup>1</sup>, Norihisa Fukaya<sup>1</sup>, Kazuhiko Sato<sup>1</sup>, Jun-Chul Choi<sup>1,2</sup> (1. National Institute of Advanced Industrial Science and Technology, 2. The Univ. of Tsukuba)

2:20 PM - 2:40 PM

**[B304-2pm-05] Effect of Sodium Salt Additives on Intramolecular Cyclization of Alkynoic Acids Catalyzed by Au(0) Nanoparticles Catalysts Supported on Metal Oxides**○Eiji Yamamoto<sup>1</sup>, Qi-An Huang<sup>1</sup>, Takaaki Ikeda<sup>1</sup>, Seiya Kawai<sup>1</sup>, Kazuki Haruguchi<sup>1</sup>, Haruno Murayama<sup>1</sup>, Tamao Ishida<sup>2</sup>, Tetsuo Honma<sup>3</sup>, Makoto Tokunaga<sup>1</sup> (1. Kyushu University, 2. Tokyo Metropolitan University, 3. Japan Synchrotron Radiation Research Institute)

2:40 PM - 3:00 PM

**[B304-2pm-06] Intramolecular cycloamination of primary amines using gold nanoparticles deposited on fibrillated citric acid-modified cellulose**○Butsaratip Suwattananuruk<sup>1</sup>, Yuta Uetake<sup>1,2</sup>, Hidehiro Sakurai<sup>1,2</sup> (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

3:00 PM - 3:20 PM

**[B304-2pm-07] Enhancing the Catalytic Activity Utilizing Strong Metal-Support Interactions (SMSI) - Isomerization of Alkenes on Substituted Hydroxyapatite Supported Gold Catalysts**○Akihiro Nakayama<sup>1</sup>, Ryusei Sodenaga<sup>1</sup>, Gangarajura Yuvaraj<sup>2</sup>, Ayako Taketoshi<sup>3</sup>, Toru Murayama<sup>1,4</sup>, Tetsuo Honma<sup>5</sup>, Norihito Sakaguchi<sup>6</sup>, Tetsuya Shimada<sup>1</sup>, Shinsuke Takagi<sup>1</sup>

, Masatake Haruta<sup>1</sup>, Qiao Botao<sup>2</sup>, Wang Junhu<sup>2</sup>, Tamao Ishida<sup>1</sup> (1. Tokyo Metropolitan University, 2. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 3. Yokohama National University, 4. Yantai University, 5. Japan Synchrotron Radiation Research Institute, 6. Hokkaido University)

3:20 PM - 3:40 PM



## Al-doped Mesoporous Silica-supported Pd Complex Catalyst for the Tsuji-Trost Allylation

(<sup>1</sup>*School of Material and Chemical Technology, Tokyo Institute of Technology*, <sup>2</sup>*Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology*, <sup>3</sup>*Yokohama National University*) ○Siming Ding<sup>1</sup>, Yuichi Manaka<sup>1,2</sup>, Ken Motokura<sup>1,3</sup>

**Keywords:** Pd complex, allylation, supported catalyst, mesoporous silica, Al doping

Allylation using allylic alcohol is friendly to the environment because the water is the only byproduct. Allylic alcohol is one of the most unreactive allylating agents in the most homogeneous Pd-catalyzed allylation reaction systems.[1,2] Heterogeneous catalysts are known for their unique catalytic performance caused by the concerted catalysis effect with both immobilized metal center and supporting material surface. Our laboratory has developed a mesoporous silica supported Pd complex catalyst recently, which promotes the Tsuji-Trost type allylation of dicarbonyl and cyanide compounds using allylic alcohol and its derivatives.[3] The catalyst promotes the reaction by activating the unactivated allylic alcohol through the establish of hydrogen bonds between allylic alcohol and surficial silanol groups. Otherwise, the doping of alumina into silica would increase the acidity on the surface, by the electron withdrawing effect and its unoccupied orbitals.

In this work, a series of aluminium doped mesoporous silica (MS-Al) supported Pd complexes with diphenyl phosphine ligand (Figure 1) were synthesized and characterized through NMR, FT-IR, ICP and XAFS. FT-IR pyridine adsorption experiment found bare Brønsted acid sites but abundant Lewis acid sites after immobilization, which may activate the allylic alcohol in the reaction acceleration. In the case of allylic alcohol scope, we found that modifying the surface acidity by the addition of Al can affect their reactivity. Other supports like pure mesoporous silica (MS/PP-Pd) and calcinated mesoporous silica (MS(cal)/PP-Pd) were also examined. The catalytic performance for simple allylic alcohol was increased by Al-doping, while the reactivity enhanced further in the case of allylic alcohols with substitution groups. Acidic activation of the substituted allylic alcohols by Al site may promote the C-O bond cleavage. On the other hand, the MS(cal) support showed the low activity due to the decreased Si-OH group on its surface.

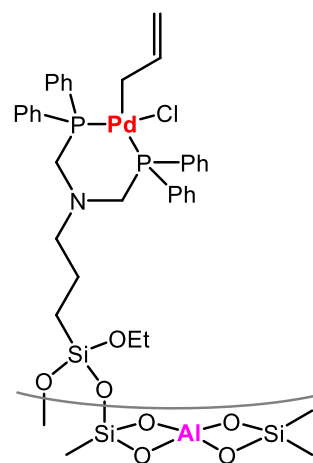


Figure 1. Structure of MS-Al/PP-Pd

- 1) N. A. Butt and W. Zhang, *Chem. Soc. Rev.* **2015**, 44, 7929-7967.
- 2) S. Ding and K. Motokura, *ChemPlusChem* **2020**, 85, 2428-2437.
- 3) K. Motokura, M. Ikeda, M. Kim, K. Nakajima, S. Kawashima, M. Nambo, W. Chun and S. Tanaka, *ChemCatChem* **2018**, 10, 4536.

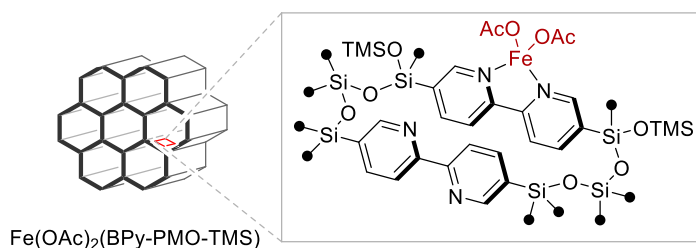
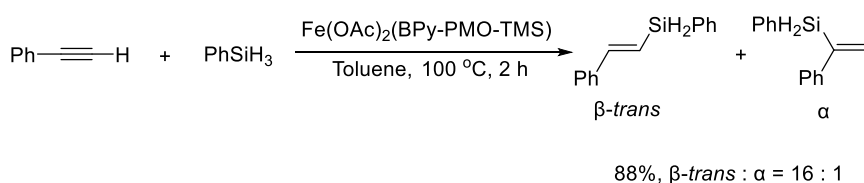
## Immobilized Iron Complex on Bipyridine-Based Periodic Mesoporous Organosilica for Hydrosilylation of Alkynes

(<sup>1</sup>Graduate School of Pure and Applied Sciences, University of Tsukuba, <sup>2</sup>Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, <sup>3</sup>Toyota Central R&D Labs.) ○Xiao-Tao Lin,<sup>1,2</sup> Kazuhiro Matsumoto,<sup>2</sup> Yoshifumi Maegawa,<sup>3</sup> Kazuhiko Sato,<sup>2</sup> Shinji Inagaki,<sup>2,3</sup> Jun-Chul Choi<sup>1,2</sup>

**Keywords:** Mesoporous Organosilica; Bipyridine; Iron Complex; Hydrosilylation; Immobilized Catalyst

Periodic mesoporous organosilica containing 2,2'-bipyridine groups (BPy-PMO) in the organosiloxane framework has been applied as a solid ligand for a wide variety of metal complexes.<sup>1)</sup> In BPy-PMO, the BPy units are arranged in the hexagonal mesopore wall and the relative position of the BPy groups are highly regulated by the framework. By taking advantage of this feature, we hypothesized that a 1 : 1 iron complex of BPy, which is difficult to synthesize in a solution state, would be selectively formed on the pore surfaces of BPy-PMO.

Fe(OAc)<sub>2</sub> was successfully immobilized on TMS-endcapped BPy-PMO by simply mixing Fe(OAc)<sub>2</sub> and BPy-PMO-TMS in EtOH. The immobilized Fe complex, Fe(OAc)<sub>2</sub>(BPy-PMO-TMS), showed high catalytic activity and regioselectivity in hydrosilylation of alkynes. In contrast, the corresponding homogeneous complex Fe(OAc)<sub>2</sub>/BPy and a grafted Fe(OAc)<sub>2</sub>/BPy on MCM-41 exhibited low activity and regioselectivity. Furthermore, Fe(OAc)<sub>2</sub>(BPy-PMO-TMS)-catalyzed hydrosilylation can be applied for various alkynes including terminal alkynes and internal alkynes, and it can be reused at least five times.



1) M. Waki, Y. Maegawa, K. Hara, Y. Goto, S. Shirai, Y. Yamada, N. Mizoshita, T. Tani, W.-J. Chun, S. Muratsugu, M. Tada, A. Fukuoka, S. Inagaki, *J. Am. Chem. Soc.* **2014**, 136, 4003.

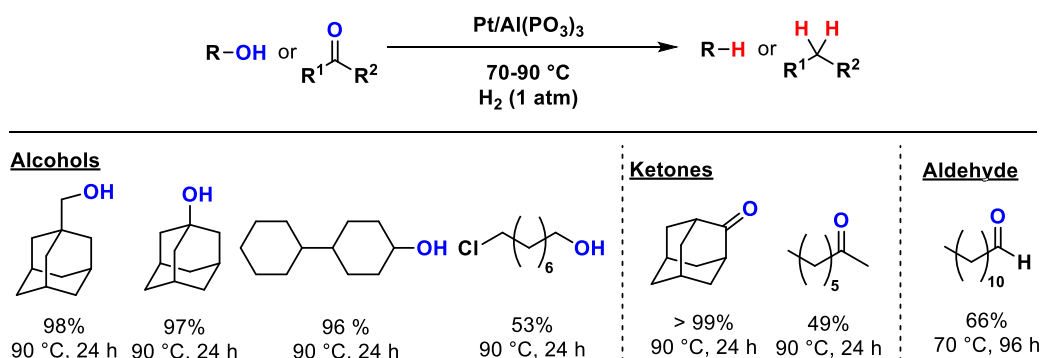
## Hydrogenolysis of alcohols and carbonyl compounds to alkanes by Pt/Al(PO<sub>3</sub>)<sub>3</sub> catalyst

(<sup>1</sup>The University of Tokyo) ○Kento Oshida,<sup>1</sup> Xionjie Jin,<sup>1</sup> Kyoko Nozaki<sup>1</sup>

**Keywords:** Alcohols; Carbonyl compounds; Aluminum metaphosphate; Platinum; Hydrogenolysis

Deoxygenation of alcohols and carbonyl compounds have been widely used in fine chemical synthesis and biomass conversion. Hydrogenolysis using molecular hydrogen as hydride source has the highest atomic efficiency among the deoxygenation reactions and is ideal because it produces only water as a byproduct. Various catalytic systems<sup>1,2)</sup> have been reported so far, but they either require harsh reaction conditions (>150 °C or high-pressure conditions) or have limited substrate scope.

In this study, we developed the hydrogenolysis of alcohols and carbonyl compounds to alkanes by metal–support cooperative catalysis of Pt nanoparticles supported on aluminum metaphosphate (Pt/Al(PO<sub>3</sub>)<sub>3</sub>). Pt/Al(PO<sub>3</sub>)<sub>3</sub> was applicable to all primary, secondary, and tertiary alcohols under relatively low temperature (<90 °C) and ambient pressure of hydrogen gas. The corresponding alkanes were obtained in high yields from various alcohols and aliphatic carbonyl compounds, including primary alcohols without hydrogen at the β-position, polycyclic alcohols with a hydroxy group at the bridgehead position and halogen-substituted alcohols. Hydrogenolysis of alcohols did not proceed by using Pt/γ-Al<sub>2</sub>O<sub>3</sub> as the catalyst, suggesting metaphosphate anion in Al(PO<sub>3</sub>)<sub>3</sub> contributed to the high efficiency. For the hydrogenolysis of aliphatic primary and secondary alcohols, it is suggested that the reaction likely proceeds through S<sub>N</sub>2 mechanism with the accumulation of positive charge on the transition state for C–O bond activation. As for tertiary alcohols, the hydrogenolysis likely proceeds through the dehydration-hydrogenation pathway or S<sub>N</sub>1 like mechanism.



1) T. Schwob, P. Kunas, N. de Jonge, C. Papp, H. P. Steinrück, R. Kempe, *Sci. Adv.* **2019**, 5, No. eaav3680. 2) N. Antil, A. Kumar, N. Akhtar, R. Mewar, W. Begum, K. Manna, *Inorg. Chem.* **2021**, 60, 9029-9039.

## シリカ固定化白金ジシリケート錯体からのシリカ担持 Pt ナノ粒子の調製と触媒特性

(産総研<sup>1</sup>・筑波大<sup>2</sup>) ○西島羽 俊貴<sup>1</sup>、石坂 悠介<sup>2</sup>、松本 和弘<sup>1</sup>、竹内 勝彦<sup>1</sup>、深谷 訓久<sup>1</sup>、佐藤 一彦<sup>1</sup>、崔 準哲<sup>1,2</sup>

Preparation and Catalytic Properties of Silica-Supported Pt Nanoparticles (<sup>1</sup>National Institute of Advanced Industrial Science and Technology, <sup>2</sup>University of Tsukuba) ○Toshiki Nishitoba,<sup>1</sup> Yusuke Ishizaka,<sup>2</sup> Kazuhiro Matsumoto,<sup>1</sup> Katsuhiko Takeuchi,<sup>1</sup> Norihisa Fukaya,<sup>1</sup> Kazuhiko Sato,<sup>1</sup> Jun-Chul Choi<sup>1,2</sup>

In this study, we prepared silica-supported Pt nanoparticles by calcination and reduction of silica-grafted Pt disilicate complexes, and evaluated their physical properties and catalytic activity. The silica-supported Pt nanoparticles have a smaller average particle size and a higher dispersibility than those prepared by the impregnation method. Regardless of the calcination and reduction temperatures in the range of 150-450 °C, our silica-supported Pt nanoparticles shows high catalytic activity in alkene hydrogenation.

**Keywords :** Pt nanoparticles, Supported metal complex catalysts, Hydrogenation

担持 Pt ナノ粒子は、触媒として幅広く利用されており、盛んに研究されている。非晶質担体上への担持を行う場合、担持金属種は多様な表面状態を取り、生成した Pt 種の均一化が困難だと言われている<sup>1)</sup>。本研究では、白金ジシリケート錯体をシリカに固定化した後、担持白金ナノ粒子を調製することで、調製時の凝集や非晶質シリカ担体由来の不均一性の影響を取り除いた Pt ナノ粒子の調製を行った。固定化錯体を経由して得られたシリカ担持 Pt ナノ粒子 (Pt/Silica-錯体法) は含浸法で調製したものよりも平均粒子径が小さく、高分散な Pt 種が生成していた。また、焼成・還元温度を 150~450 °C まで変化させたところ、どの温度域においても高い活性を示した。

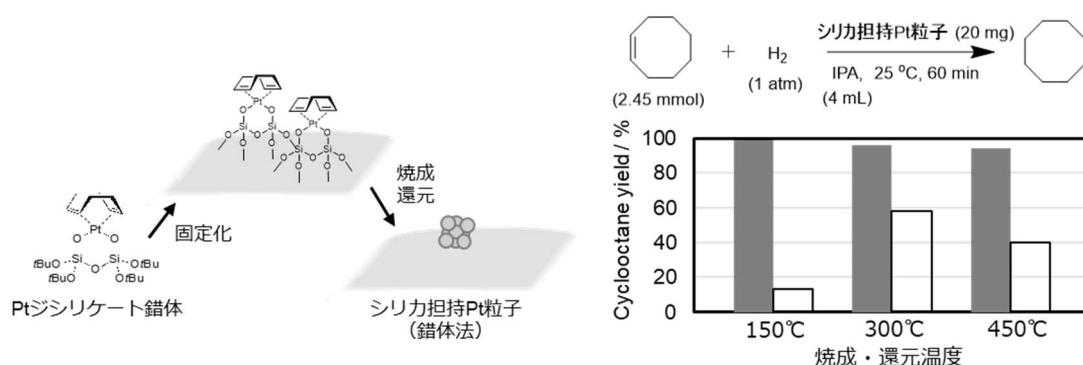


図 固定化 Pt ジシリケート錯体を前駆体とした担持 Pt 粒子の触媒調製法 (左) とシクロオクテン水素化活性と焼成・還元温度の関係 (右) ■: 錯体法、□: 含浸法

1) C. S. Ewing et al., J. Phys. Chem. C 119 (2015) 2503

## 担持 0 価金ナノ粒子触媒によるアルキニルカルボン酸の分子内環化反応におけるナトリウム塩添加効果

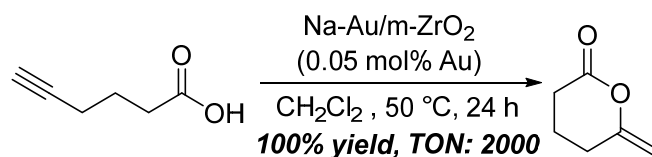
(九大院理<sup>1</sup>・都立大<sup>2</sup>・JASRI<sup>3</sup>) ○山本英治<sup>1</sup>・黄 啓安<sup>1</sup>・池田孝明<sup>1</sup>・川相誓也<sup>1</sup>・春口一騎<sup>1</sup>・村山美乃・石田玉青<sup>2</sup>・本間徹生<sup>3</sup>・徳永 信<sup>1</sup>

Effect of Sodium Salt Additives on Intramolecular Cyclization of Alkynoic Acids Catalyzed by Au(0) Catalysts Supported on Metal Oxides (<sup>1</sup>*Graduate School of Science, Kyushu University*, <sup>2</sup>*Graduate Course of Urban Environmental Sciences, Tokyo Metropolitan University*, <sup>3</sup>*Japan Synchrotron Radiation Research Institute (JASRI)*) ○Eiji Yamamoto,<sup>1</sup> Qi-An Huang,<sup>1</sup> Takaaki Ikeda,<sup>1</sup> Seiya Kawai,<sup>1</sup> Kazuki Haruguchi,<sup>1</sup> Haruno Murayama,<sup>1</sup> Tamao Ishida,<sup>2</sup> Tetsuo Honma,<sup>3</sup> Makoto Tokunaga<sup>1</sup>

The intramolecular cyclization of alkynoic acids is an important reaction with high atomic efficiency that gives useful enol lactones. However, existing heterogeneous catalysts still leave room for improvement in terms of reusability and simplicity of catalyst preparation. In this study, we found that ZrO<sub>2</sub>-supported Au(0) catalysts effectively promoted the cyclization of 5-hexynoic acid in CH<sub>2</sub>Cl<sub>2</sub> at 50 °C (100% yield, TON = 2000). Furthermore, catalyst characterization by XAFS, XPS, and TEM revealed that a very small amount of Na salt has a greater effect on the catalytic activity than the particle size or electronic state of the Au nanoparticles. In the presentation, the details of the reaction mechanism will be also discussed based on kinetic experiments.

**Keywords :** *Au Nanoparticles; Alkynoic Acids; Intramolecular Cyclization; Sodium Salt Additives; Heterogeneous Catalysis*

アルキニルカルボン酸の分子内環化は、合成中間体として有用なエノールラクトンを与える原子効率の高い重要な反応である。しかし、既存の不均一系触媒には再利用性や触媒調製の簡便さの観点から改善の余地が残されていた。本研究では、実用性が高く、簡便に調製可能な固体触媒の開発を目指して種々検討を行った結果、ZrO<sub>2</sub>担持Au(0)ナノ粒子触媒(Na-Au/m-ZrO<sub>2</sub>)がCH<sub>2</sub>Cl<sub>2</sub>中、50℃の条件下で5-ヘキシノ酸の環化反応を効果的に促進することを見出した(100%収率、TON=2000)。さらに、XAFS、XPS、TEMによる詳細な触媒のキャラクタリゼーションを行った結果、本反応系では、金ナノ粒子の粒子径や電子状態よりも極少量のNa塩の有無が触媒活性に大きな影響を与えることを明らかにした。また、この触媒を用いて流通式反応を検討したところ、反応の総TONは最大9000まで到達した。講演では、重水素同位体効果を含む速度論実験などの結果も踏まえて反応機構の詳細について議論する予定である。



### ■ Detailed Mechanistic Studies

• XPS, TEM, XAFS, Kinetic study

### ■ Flow System Available

• total TON = up to 9000

## Intramolecular cycloamination of primary amines using gold nanoparticles deposited on fibrillated citric acid-modified cellulose

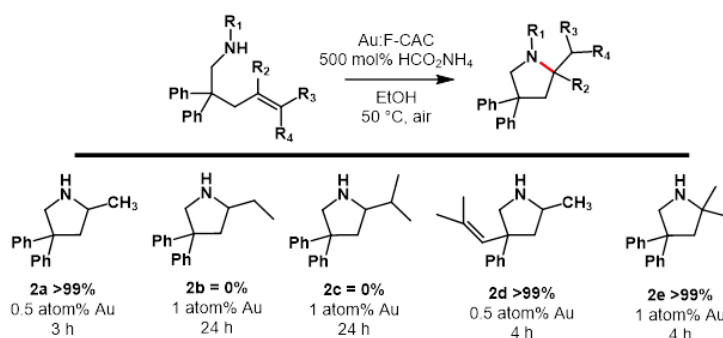
(<sup>1</sup>Grad. Sch. Eng., Osaka Univ., <sup>2</sup>ICS-OTRI, Osaka Univ.)

○Butsaratip Suwattananuruk,<sup>1</sup> Yuta Uetake,<sup>1,2</sup> Hidehiro Sakurai<sup>1,2</sup>

**Keywords:** gold nanoparticles, citric acid-modified cellulose, intramolecular hydroamination.

Gold nanoparticles (AuNPs) stabilized by biomacropolymers, such as cellulose and/or chitosan, show unique catalytic properties, and therefore, attracted much attention from the viewpoint of sustainable development. Recently, we have reported a size-selective preparation method of AuNPs deposited on a fibrillated citric acid-modified cellulose (F-CAC),<sup>1</sup> and the thus-prepared Au:F-CAC was applied to aerobic oxidation of benzyl alcohol.<sup>2</sup> The high tolerance of cellulose toward organic solvents allowed us to perform the reactions in various organic solvents. Meanwhile, we have reported that the Lewis-acidic nature of O<sub>2</sub>-adsorbed AuNP catalyzed cycloamination reaction of primary amines under aerobic conditions.<sup>3</sup> In this study, we investigated the catalytic activity of Au:F-CAC catalyst toward the cycloamination reaction.

After optimization of reaction conditions, it was found that the intramolecular cyclization of **1a** proceeded in the presence of 0.2 atom% of Au:F-CAC catalyst to give pyrrolidine **2a** in 99% yield after 8 h without any side products. Then, we investigated the substrate scope of this reaction and found that this reaction conditions were sensitive to the steric factors. Contrary to the case of substrates having terminal olefins, the reaction did not proceed in the case of those having crotyl (**2b**) and prenyl (**2c**) groups. Based on this observation, the substrate bearing both allyl and prenyl groups (**2d**) was examined and found that the cyclization occurred at less hindered allyl moiety in complete regioselectivity, showing the unique catalytic activity of the Au:F-CAC catalyst.



1) X. Cui, T. Honda, T.-A. Asoh, H. Uyama, *Carbohydr. Polym.* **2020**, 230, 115662.

2) T. Chutimasakul, Y. Uetake, J. Tantirungrotechai, T. Asoh, H. Uyama, H. Sakurai, *ACS Omega*. **2021**, 5, 33206.

3) H. Kitahara, H. Sakurai, *Chem. Lett.* **2010**, 39, 46.

## Enhancing the Catalytic Activity Utilizing Strong Metal-Support Interactions (SMSI) - Isomerization of Alkenes on Substituted Hydroxyapatite Supported Gold Catalysts

(<sup>1</sup>Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, <sup>2</sup>Mössbauer Effect Data Center, Dalian Institute of Chemical Physics, <sup>3</sup>CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, <sup>4</sup>Graduate School of Engineering, Yokohama National University, <sup>5</sup>School of Chemistry & Chemical Engineering, Yantai University, <sup>6</sup>Japan Synchrotron Radiation Research Institute (JASRI), <sup>7</sup>Faculty of Engineering, Hokkaido University) ○Akihiro Nakayama,<sup>1</sup> Ryusei Sodenaga,<sup>1</sup> Yuvaraj Gangarajula,<sup>2,3</sup> Ayako Taketoshi,<sup>4</sup> Toru Murayama,<sup>1,5</sup> Tetsuo Honma,<sup>6</sup> Norihito Sakaguchi,<sup>7</sup> Tetsuya Shimada,<sup>1</sup> Shinsuke Takagi,<sup>1</sup> Masatake Haruta,<sup>1</sup> Botao Qiao,<sup>3</sup> Junhu Wang,<sup>2</sup> Tamao Ishida<sup>1</sup>

**Keywords:** Au Nanoparticles; Strong Metal-Support Interaction; Hydroxyapatite; Isomerization of Alkene

A thin layer of hydroxyapatite (HAP) covers surfaces of gold nanoparticles (Au NPs) by heat treatment in an oxidative atmosphere, which is the so-called oxidative SMSI.<sup>1</sup> The oxidative SMSI makes Au positively charged, which is beneficial to use Au as a soft Lewis acid catalyst. In this work, we exploited apatite-supported Au catalysts with oxidative SMSI for  $\pi$ -activation reaction of an alkene. The cationic property of Au was carefully analyzed by diffuse reflectance FT-IR studies of the CO adsorption (CO-DRIFT). The Au-CO peak shifted to a higher wavenumber by partial substitutions of Ca or Sr with Mg and Ce, and by a formation

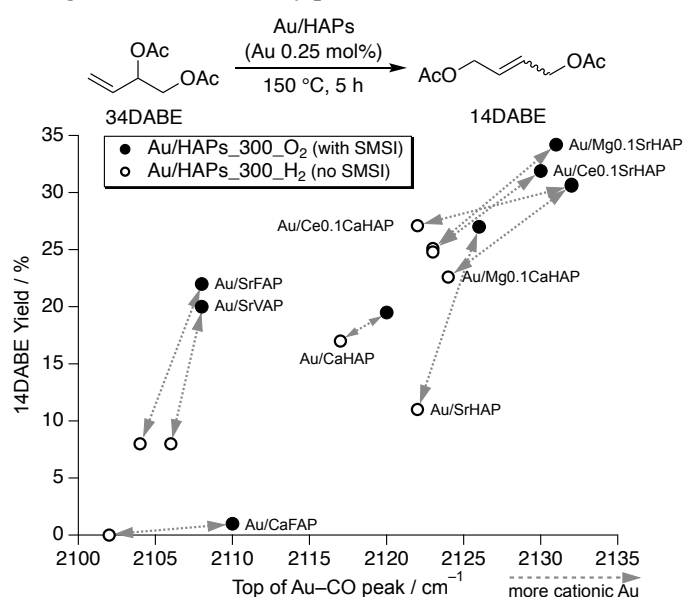


Figure 1. Relationship between the catalytic activity for 34DABE isomerization and the cationic properties of Au.

of the oxidative SMSI, meaning that Au NPs became more cationic. The catalytic activity for isomerization of 3,4-diacetoxybut-1-ene (34DABE) to 14DABE was correlated well to the cationic properties of Au (Figure 1). Precise control of the oxidative SMSI enhanced soft Lewis acidity of Au, resulting in improved catalytic activity.

1) a) H. Tang, J. Wei, F. Liu, B. Qiao, X. Pan, L. Li, J. Liu, J. Wang, T. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 56; b) X. Du, H. Tang, B. Qiao, *catalysts* **2021**, *11*, 896.

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[J402-2am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Shiro Hikichi, Mio Kondo

Thu. Mar 24, 2022 9:00 AM - 11:40 AM J402 (Online Meeting)

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**[J402-2am-01] Electrochemical CO<sub>2</sub> Reduction Catalyzed by Metal Porphyrin Complexes: Control of the Catalytic Activity by Reaction Media**○Kento Kosugi<sup>1</sup>, Hina Kashima<sup>1</sup>, Mio Kondo<sup>1,2</sup>, Shigeyuki Masaoka<sup>1</sup> (1. Graduate School of Engineering, Osaka University, 2. JST PRESTO)

9:00 AM - 9:20 AM

**[J402-2am-02] Preparation of Coordination Polymer Glasses Encapsulating Metal Complex Catalysts**○Hitoshi Izu<sup>1</sup>, Hiroyasu Tabe<sup>2</sup>, Yuji Namiki<sup>3</sup>, Takashi Kajiwara<sup>1</sup>, Satoshi Horike<sup>2</sup> (1. National Institute of Advanced Industrial Science and Technology, 2. Kyoto University, 3. POLA Chemical Industries, Inc.)

9:20 AM - 9:40 AM

**[J402-2am-03] pH-Insensitive Brønsted Acid-Base Site Embedded in a Pentanuclear Scaffold**○Misa Tomoda<sup>1,2,3</sup>, Hitoshi Izu<sup>1,2</sup>, Yutaka Saga<sup>1</sup>, Mio Kondo<sup>1,4</sup>, Shigeyuki Masaoka<sup>1</sup> (1. Osaka University, 2. IMS, 3. SOKENDAI, 4. JST PRESTO)

9:40 AM - 10:00 AM

**[J402-2am-04] Activation of a PNNP-ligated Fe complex with a base to facilitate photocatalytic CO<sub>2</sub> reduction**○Taku Wakabayashi<sup>1</sup>, Kenji Kamada<sup>1</sup>, Jieun Jung<sup>1</sup>, Susumu Saito<sup>1,2</sup> (1. Grad. Sch. Sci., Nagoya Univ., 2. RCMS, Nagoya Univ.)

10:00 AM - 10:20 AM

**[J402-2am-05] Effect of hydrophobic interaction field on catalysis of metal complexes immobilized on mesoporous silica**○Masaya Okamura<sup>1</sup>, Kou Kuwamoto<sup>1</sup>, Seiya Sakakura<sup>1</sup>, Nana Aizawa<sup>1</sup>, Shiro Hikichi<sup>1</sup> (1. Kanagawa university)

10:20 AM - 10:40 AM

**[J402-2am-06] Highly efficient electrocatalysis by a Fe complex for water oxidation in a homogeneous solution.**○Taichi Hayasaka<sup>1</sup>, Eman A. Mohamed<sup>1</sup>, Zaki N. Zahran<sup>1</sup>, Yuta Tsubonouchi<sup>1</sup>, Masayuki Yagi<sup>1</sup> (1. Grad. School of Sci. Tec., Niigata Univ.)

10:40 AM - 11:00 AM

**[J402-2am-07] Development of hydrogenation and dehydrogenation reactions based on the use of iron complexes bearing group 14 element ligands**○Yoshinao Kobayashi<sup>1</sup>, Yusuke Sunada<sup>1,2</sup> (1. School of Eng., The Univ. of Tokyo, 2. IIS, The Univ. of Tokyo)

11:00 AM - 11:20 AM

**[J402-2am-08] Self-assembling behavior of polymer systems conjugated with artificial photosynthetic circuits**○Takafumi Enomoto<sup>1</sup>, Aya M Akimoto<sup>1</sup>, Ryo Yoshida<sup>1</sup> (1. Department of Materials



Engineering, School of Engineering, The University of Tokyo)

11:20 AM - 11:40 AM

## Electrochemical CO<sub>2</sub> Reduction Catalyzed by Metal Porphyrin Complexes: Control of the Catalytic Activity by Reaction Media

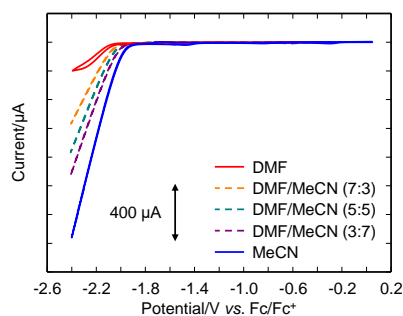
(<sup>1</sup>Graduate School of Engineering, Osaka University, <sup>2</sup>JST PRESTO)

○Kento KOSUGI,<sup>1</sup> Hina KASHIMA,<sup>1</sup> Mio KONDO,<sup>1,2</sup> Shigeyuki MASAOKA<sup>1</sup>

**Keywords:** CO<sub>2</sub> Reduction; Solvation Effect; Electrochemistry; Porphyrin; Catalyst

The development of artificial molecular catalysts for CO<sub>2</sub> reduction is the key to solving energy and environmental problems. Although chemical modification can generally improve the catalytic activity of this class of compounds, they often require complicated synthetic procedures. Here, we report the simple procedures that dramatically enhance electrochemical CO<sub>2</sub> reduction activity by metal porphyrin complexes focusing on the effect of the reaction medium.

We began by reinvestigating CO<sub>2</sub> reduction by a commercially available catalyst, iron(III) tetraphenylporphyrin chloride (**FeTPP-Cl**), in DMF. DMF is a common solvent for iron porphyrin systems, as it can dissolve both the complex and CO<sub>2</sub> at high concentration. **FeTPP-Cl** indeed exhibited a large irreversible current under CO<sub>2</sub>, corresponding to the electrocatalytic reduction of CO<sub>2</sub> (Figure 1, red line). Unexpectedly, the intensity of the irreversible current increased when acetonitrile (MeCN) was added (Figure 1, dashed lines). Furthermore, **FeTPP-CIO<sub>4</sub>**, a perchlorate salt of **FeTPP** that is well soluble in various solvent, exhibited the largest irreversible current in pure MeCN (Figure 1, blue line). To quantify the catalytic product, controlled potential electrolysis experiment of **FeTPP-CIO<sub>4</sub>** (0.01 mM) was then performed in MeCN with 1.0 M TFE under CO<sub>2</sub> at –2.35 V vs. Fc/Fc<sup>+</sup>. The total amount of charge passed over a period of 60 min was 75.9 C, and CO was formed with a Faradaic efficiency of 97.3%. Subsequently, turnover frequency (TOF) for CO production was evaluated. Surprisingly, TOF reached 7.30×10<sup>6</sup> s<sup>–1</sup>, which is the highest among those of current best-in-class molecular catalysts.<sup>1</sup> These results clearly demonstrate that the electrocatalytic activity of **FeTPP** for CO<sub>2</sub> reduction is significantly enhanced in MeCN.



**Figure 1.** Cyclic voltammograms of **FeTPP** in TBAP/solvent under CO<sub>2</sub> with 1.0 M TFE (scan rate: 100 mV s<sup>–1</sup>).

The effect of reaction medium on the catalytic activity was also observed for other metal porphyrin complex. In MeCN, a copper porphyrin complex bearing strong electron-withdrawing substituents, copper(II) tetrakis(pentafluorophenyl)porphyrin (**CuTPFP**), exhibited a TOF of 1.46×10<sup>6</sup> s<sup>–1</sup> at an overpotential of 0.85 V.<sup>2</sup> Surprisingly, this value is more than 10<sup>6</sup> times higher than those of other reported copper-based catalysts (TOF≤1.15 s<sup>–1</sup>). The details of the reaction medium on the catalytic mechanisms will be discussed in the presentation.

1) K. Kosugi *et al.*, *Angew. Chem. Int. Ed.* **2021**, 60, 22070. 2) K. Kosugi *et al.*, *Chem. Commun. in press*.

## Preparation of Coordination Polymer Glasses Encapsulating Metal Complex Catalysts

(<sup>1</sup>National Institute of Advanced Industrial Science and Technology, <sup>2</sup>Kyoto University, <sup>3</sup>POLA Chemical Industries, Inc.) ○Hitoshi Izu,<sup>1</sup> Hiroyasu Tabe,<sup>2</sup> Yuji Namiki,<sup>3</sup> Takashi Kajiwara,<sup>1</sup> Satoshi Horike<sup>2</sup>

**Keywords:** Coordination Polymer Glasses; Photocatalytic CO<sub>2</sub> Reduction; Iron Porphyrin

Coordination polymers (CPs) are crystalline compounds composed of metal ions and bridging ligands. Recent reports indicate that several CPs transform to a glassy state by a melt-quench process<sup>1</sup>. A typical example is a coordination polymer composed of zinc (II) ions, (di)hydrogen phosphate ions, and imidazolium ([Zn<sup>II</sup>(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>](ImH<sub>2</sub>)<sub>2</sub> (ZnPIIm, Im = imidazolate) (Fig.1-a). The amorphous nature of ZnPIIm glass resulted in the enhancement of proton (H<sup>+</sup>) conductivity than ZnPIIm in the crystalline state due to the highly flexible nature of imidazole and (di)hydrogen phosphate ions<sup>2</sup>.

In addition, crystal-glass transformation of CPs via melt-quenching offers diverse accessibility to unique processing abilities and properties by using immobilized guest molecules. Such an immobilization technique can be applied to the heterogenization of metal complex catalysts. The interaction between metal complex catalysts and organic ligands liberated in the vitrification process results in facile immobilization of the catalysts in CP glasses, resulting in the heterogenization of the catalysts with high durability.

Herein, we prepared a film of ZnPIIm glass containing iron(III) 5,10,15,20-tetraphenyl-21H,23H-porphyrin (Fe<sup>III</sup>(TPP)) ion via a melt-quenching process. The films supported on slide plates have a smooth surface and thickness of 3-9 μm (Fig. 1-b). Fe<sup>III</sup>(TPP) was stably immobilized in the ZnPIIm glass by the coordination of imidazolate liberated from ZnPIIm frameworks during the melt-quench process. The films exhibited catalytic activity for the carbon dioxide reduction under the visible-light irradiation by taking advantage of electron-donation to the active Fe<sup>III</sup> site by imidazolate. The ZnPIIm glass film with a thickness of 9 μm exhibited three-times higher activity than those of 3 μm, indicating that CO<sub>2</sub> molecules efficiently access Fe<sup>III</sup>(TPP) immobilized in the subsurface of ZnPIIm glass film.

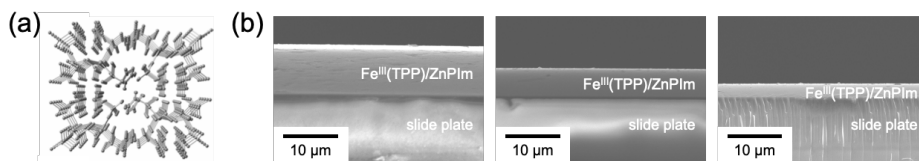


Fig. 1 (a) Crystal structure of ZnPIIm and (b) scanning electron microscope (SEM) images from the side of ZnPIIm glass containing Fe<sup>III</sup>(TPP) with thickness of 9 μm (left), 7 μm (middle), and 3 μm (right).

- 1) S. Horike, S. S. Nagarkar, T. Ogawa, S. Kitagawa, *Angew. Chem. Int. Ed.* **2020**, *59*, 6652.
- 2) D. Umeyama, S. Horike, M. Inukai, T. Itakura, S. Kitagawa, *J. Am. Chem. Soc.* **2015**, *137*, 864.

## pH-Insensitive Brønsted Acid-Base Site Embedded in a Pentanuclear Scaffold

(<sup>1</sup>Graduate School of Engineering, Osaka University, <sup>2</sup>Institute for Molecular Science, <sup>3</sup>SOKENDAI, <sup>4</sup>JST PRESTO) ○Misa Tomoda,<sup>1,2,3</sup> Hitoshi Izu,<sup>1,2</sup> Yutaka Saga,<sup>1</sup> Mio Kondo,<sup>1,4</sup> Shigeyuki Masaoka<sup>1</sup>

**Keywords:** Heterometallic Multinuclear Complex; Acid-Base Response; Hydrogen Evolution Reaction; Changes in Catalytic Activity

Hydrogen ion ( $H^+$ ) is a cation which consists of a single proton and exhibits the highest positive charge density. The behaviors of  $H^+$  play an essential role as the origin of functions in both biological systems and artificial functional materials. In general, the behaviors of  $H^+$  can be interpreted by the conventional Brønsted-Lowry acid-base theory. According to the theory, the behavior of  $H^+$  is quite sensitive to the concentration of  $H^+$  (*i.e.*, pH), and it is quite difficult to maintain the properties/function of compounds bearing Brønsted acid/base sites throughout a wide range of pH. Here, we successfully developed an unconventional Brønsted acid/base site, which exhibits pH-insensitive nature.

Our study started with the investigation on acid-base responding behaviors of heterometallic pentanuclear complexes, **Ru<sub>2</sub>Co<sub>3</sub>OH** and **Ru<sub>2</sub>Co<sub>3</sub>O** (Figure 1). Upon addition of 3 eq. of a strong base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU,  $pK_a = 24.3$ ) to an acetonitrile solution containing **Ru<sub>2</sub>Co<sub>3</sub>OH**, no UV-vis absorption spectral change was observed, indicating that no deprotonation reaction proceed. Additionally, the protonation reaction of **Ru<sub>2</sub>Co<sub>3</sub>O** was conducted by using the conjugated acid of DBU, DBU- $H^+$ . In this case, protonation reaction also did not proceed. These unusual acid-base responding behaviors of the complexes indicated that Brønsted acid-base sites at the triangular core are in the unique environment.

Subsequently, we investigated redox behaviors of **Ru<sub>2</sub>Co<sub>3</sub>OH** and **Ru<sub>2</sub>Co<sub>3</sub>O** (Figure 2), and it was revealed that the confined  $H^+$  largely affects their redox behaviors. We also found that the catalytic activity for hydrogen evolution reaction can be controlled by the presence/absence of  $H^+$  at the sites. Current study offers a new class of compounds, which can maintain the properties/function as a Brønsted acid/base in a wide range of pH.

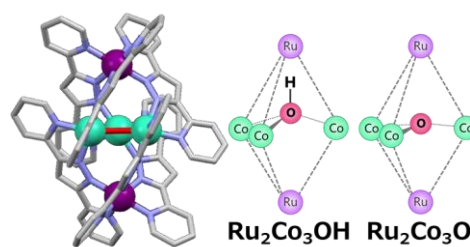


Figure 1. The molecular structures of heterometallic pentanuclear complexes, **Ru<sub>2</sub>Co<sub>3</sub>OH** (left) and **Ru<sub>2</sub>Co<sub>3</sub>O** (right).

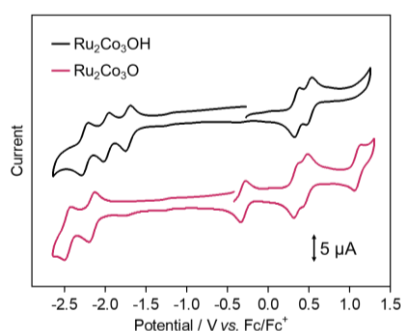


Figure 2. CVs of **Ru<sub>2</sub>Co<sub>3</sub>OH** and **Ru<sub>2</sub>Co<sub>3</sub>O**.

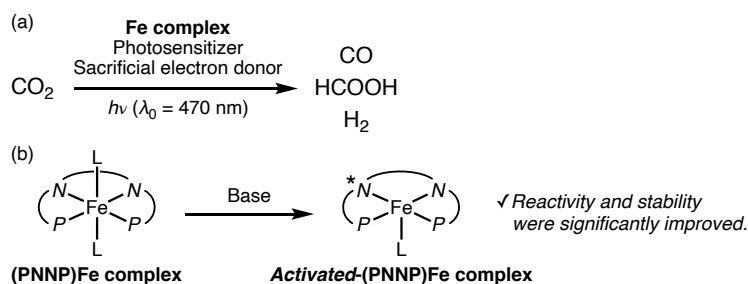
## Activation of a PNNP-ligated Fe complex with a base to facilitate photocatalytic CO<sub>2</sub> reduction

(<sup>1</sup>Graduate School of Science, Nagoya University, <sup>2</sup>RCMS, Nagoya University) ○ Taku Wakabayashi,<sup>1</sup> Kenji Kamada,<sup>1</sup> Jung Jieun,<sup>1</sup> Susumu Saito,<sup>1,2</sup>

**Keywords:** Carbon dioxide, Iron complex, Photoreaction, Transient absorption spectroscopy, Reduction reaction

Carbon dioxide (CO<sub>2</sub>) could be a ubiquitous raw material in terms of cheapness and low toxicity to achieve a sustainable society. There is a great demand to use earth-abundant metals instead of noble metals for the integration of the catalysts into economically viable devices. We have recently reported iridium<sup>1</sup> and ruthenium<sup>2</sup> complexes bearing PNNP-type tetradentate ligands for photocatalytic CO<sub>2</sub> reduction. They both worked as self-photosensitized reduction catalysts, converting CO<sub>2</sub> into formic acid (HCO<sub>2</sub>H) and carbon monoxide (CO) with high reactivity and stability under visible light irradiation in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as a sacrificial electron donor. We anticipate that the introduction of a bulky PNNP ligand prevents catalyst deterioration and promotes efficient catalysis. However, as mentioned above, it is necessary to use earth-abundant base metals instead of precious metals in an attempt to implement technologies based on CO<sub>2</sub> utilization.

Herein, we have developed a novel iron complex bearing a PNNP-type tetradentate ligand. This complex was found to convert CO<sub>2</sub> into CO mainly under blue light irradiation in the presence of Ir(ppy)<sub>3</sub> (tris(2-phenylpyridinato)iridium(III)) as a photosensitizer and BIH as a sacrificial electron donor (Scheme 1 (a)). The catalytic ability and durability were significantly improved by pre-activation of the Fe complex with the addition of a base (Scheme 1 (b)). Employing this catalyst activation, the turnover number for more reduced carbon products increased more than four times in 24 h light irradiation. The catalytic mechanism was interrogated in detail by picosecond laser flash photolysis measurements.



**Scheme 1. (a) CO<sub>2</sub> photoreduction and (b) activation of an Fe complex by adding a base.**

1) K. Kamada, J. Jung, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *J. Am. Chem. Soc.* **2020**, *142*, 10261. 2) K. Kamada, H. Okuwa, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, J. Jung, S. Saito, *Synlett* (Invited for a Cluster to honor Prof. Shunichi Fukuzumi on the occasion of his 70th birthday) **2022**, Article ASAP. DOI: 10.1055/a-1709-0280 (accessed 2022-1-11).

## メソポーラスシリカに固定化した錯体触媒における疎水的反応場の効果

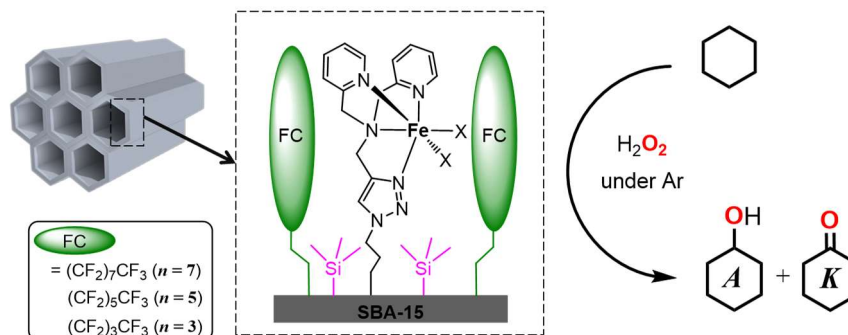
(神奈川大工<sup>1</sup>) ○岡村 将也<sup>1</sup>・桑本 航<sup>1</sup>・坂倉 星哉<sup>1</sup>・鮎澤 七南<sup>1</sup>・引地 史郎<sup>1</sup>  
 Effect of hydrophobic interaction field on catalysis of metal complexes immobilized on mesoporous silica (<sup>1</sup>*Graduate School of Engineering, Kanagawa University*) ○Masaya Okamura<sup>1</sup>, Kou Kuwamoto<sup>1</sup>, Seiya Sakakura<sup>1</sup>, Nana Aizawa<sup>1</sup>, Shiro Hikichi<sup>1</sup>

In this work, metal complexes were immobilized on mesoporous silica (SBA-15) and the surface of the silica support was modified with hydrophobic substituents to investigate the effect of the hydrophobic interaction field on the catalytic properties in alkane oxidation and alkene epoxidation reactions. In the immobilized iron complex catalyst shown in Scheme 1, the silica surface was doubly modified with two kinds of hydrophobic groups (long-chain fluoroalkyl and trimethylsilyl (TMS)), and the oxidation of cyclohexane was examined using H<sub>2</sub>O<sub>2</sub> as an oxidant. The results showed that the alcohol selectivity was improved compared with that of the hydrophobic modification only TMS, and the selectivity increased with the length of the fluoroalkyl chain.

**Keywords :** Oxidation reaction; Catalyst; Hydrogen Peroxide; Mesoporous silica

生体内における酵素の触媒機能は、中心となる金属錯体の性質と共に、その周囲を取り囲む反応場（親水性/疎水性）にも依存している。本研究では、メソポーラスシリカ（SBA-15）の細孔内を反応場として捉え、シリカ担体表面のシラノール基（Si-OH）を疎水性の置換基で修飾した固定化金属錯体触媒を開発し、アルカン酸化反応やアルケンのエポキシ化反応における疎水的反応場の効果を検証した。

Scheme1 に示す tris(2-pyridylmethyl)amine(TPA)類似配位子による固定化鉄錯体触媒では、シリカ表面を二種類の疎水基（長鎖フルオロアルキル基、及びトリメチルシリル (TMS) 基）で二重に修飾し、H<sub>2</sub>O<sub>2</sub>を酸化剤としたシクロヘキサンの酸化反応を行った。その結果、TMS 基のみで疎水化した場合と比べて、アルコールの選択性が向上し、疎水基の長さが長くなるほど選択性が高くなることが分かった。これは、疎水基によって錯体触媒が安定化させると共に、酸化生成物の分離を促進する働きがあるためだと考えられる。



Scheme 1. Cyclohexane oxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by immobilized catalysts.

## 平面型 N<sub>4</sub> 配位子を有する単核鉄錯体による高効率酸素発生触媒反応

(新潟大院自然) ○早坂 太智・モハメド エマン・ザハラン ザキ・坪ノ内 優太・八木 政行

Highly efficient electrocatalysis by a Fe complex for water oxidation in a homogeneous solution (*Grad. School of Sci. and Tec., Niigata Univ.*) ○Taichi Hayasaka, Eman A. Mohamed, Zaki N. Zahran, Yuta Tsubonouchi, Masayuki Yagi

Electrochemical water splitting coupled with renewably generated electricity has attracted much attention as a promising technology to produce H<sub>2</sub> from water. Since water oxidation is considered to be a bottleneck in water splitting, much effort has been made to develop highly active and durable water oxidation catalysts (WOCs) of earth-abundant metal complexes. In this context, we found that a mononuclear Fe complex with a planer tetradentate ligand (**FeL**) serves as a highly efficient electrochemical WOC in a homogeneous solution. The cyclic voltammogram of 0.01 mM **FeL** in an acetonitrile solution containing 9.1 vol.% water showed the higher catalytic current density for water oxidation of 4.7 mA cm<sup>-2</sup> at 1.37 V vs. Fc/Fc<sup>+</sup> (Fig.1). A decrease of the catalytic current was observed when the concentration of **FeL** was increased beyond 0.02 mM probably due to the formation of a catalytically inactive or less active multimer of **FeL**.

**Keywords :** Artificial Photosynthesis; Water Oxidation; Molecular Catalysts; Homogeneous Catalysts; Iron Complexes

昨今の環境・エネルギー問題を背景に、再生可能エネルギー由来の電力を利用した水電解による水素製造に高い関心が寄せられている。高効率な水電解システムの構築には、水からの酸素発生反応を効果的に促進する触媒の開発が重要である。これまで報告されている触媒の多くはRuやIrなどの貴金属元素を用いており、実用的な水電解システムの構築には安価で高活性な卑金属触媒の開発が不可欠である。本研究では、平面型窒素ドナー配位子を有する単核鉄錯体**FeL**が高活性かつ高安定な均一系酸素発生触媒として機能することを明らかにした。

0.01 mM の **FeL** のアセトニトリル溶液に水を添加した際のサイクリックボルタモグラム (CV) では、水の添加量に応じて酸素発生に由来する触媒電流の増大が観測された。9.1 vol.%の水存在下、1.37 V vs. Fc/Fc<sup>+</sup>における触媒電流値は 4.7 mA cm<sup>-2</sup> に到達した (Fig. 1)。触媒電流値は、錯体濃度が 0.01 mM まで直線的に増加し、それ以上の高濃度では減少することが明らかになった。分光電気化学測定から、高濃度条件における触媒活性の低下は、低活性種である **FeL** の多量体の生成に由来することが示唆された。

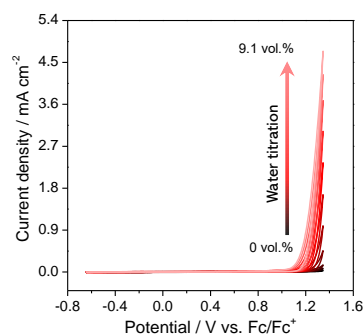


Fig. 1 CVs of 0.01 mM **FeL** in CH<sub>3</sub>CN containing 0.1 M TBAP with different water contents of 0 to 9.1 vol.% at a scan rate of 50 mV s<sup>-1</sup> under Ar.

## Development of hydrogenation and dehydrogenation reactions based on the use of iron complexes bearing group 14 element ligands

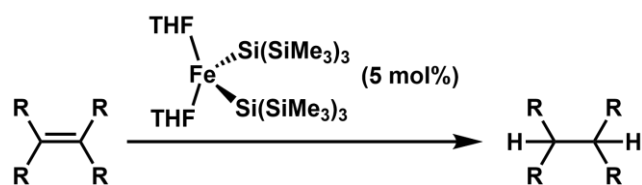
(<sup>1</sup>*School of Engineering, and* <sup>2</sup>*Institute of Industrial Science, The University of Tokyo*) ○ Yoshinao Kobayashi<sup>1</sup>, Yusuke Sunada<sup>1,2</sup>

**Keywords:** Base metal; Iron catalysts; Group 14 elements; Hydrogenation; Dehydrogenation

Hydrogenative and dehydrogenative reactions are one of the most fundamental reactions in modern organic and organometallic chemistry. In the conventional catalysis, precious metal catalysts are generally for these reactions. However, due to the increasing interest in the development of cheap and environmentally benign catalytic reactions, development of base metal catalyst has recently received much attention. In this presentation, we wish to report the development of two types of reactions, namely, hydrogenation of alkenes as well as dehydrogenation of group 14 hydrides, in which iron species bearing group 14 elements ligands acted as a key species.

First, we found that iron(II) disilyl complex  $\text{Fe}[\text{Si}(\text{SiMe}_3)_3]_2(\text{THF})_2$  (**1**)<sup>1</sup> showed good catalytic performance toward hydrogenation of various alkenes including sterically hindered ones. In a general catalysis, hydrogenation of alkenes were achieved in toluene at 80 °C in the presence of 5 mol% of **1** (Scheme 1). It should be mentioned that unfunctionalized multi-substituted alkenes such as 2,3-dimethyl-2-butene or limonene were also hydrogenated by this catalytic system.<sup>2</sup>

Second, dehydrogenative coupling of group 14 hydrides catalyzed by iron complexes was achieved. As the representative, dehydrogenative coupling of  $\text{Ph}_2\text{GeH}_2$  to afford  $\text{Ph}_{10}\text{Ge}_5$  proceeded quantitatively mediated by  $\text{Fe}(\text{Mes})_2(\text{I}^t\text{Pr}_2\text{Me}_2)_2$  ( $\text{Mes}$  = 2,4,6-trimethylbenzene,  $\text{I}^t\text{Pr}_2\text{Me}_2$  = 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene).



**Scheme 1.** Hydrogenation of unfunctionalized alkenes.

1) Arata, S.; Sunada, Y. *Dalton Trans.* **2019**, 48, 2891-2895.

2) Kobayashi, Y.; Sunada, Y. *ACS Sustain. Chem. Eng.* accepted.

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



## 人工光合成回路を内包する高分子システムの自己集合挙動

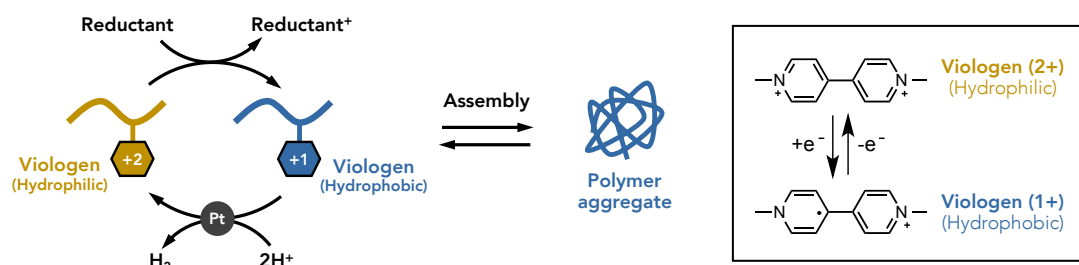
(東大院工) ○榎本 孝文・秋元 文・吉田 亮

Self-assembling Behavior of Polymer Systems Conjugated with Artificial Photosynthetic Circuits (*Graduate School of Engineering, The University of Tokyo*) ○Takafumi Enomoto, Aya M. Akimoto, Ryo Yoshida

Living systems are maintained by out-of-equilibrium self-assemblies driven by chemical reactions which control the association and dissociation of building blocks. In this work, we designed a viologen-containing polymer for constructing the out-of-equilibrium self-assembly system driven by a catalytic hydrogen evolving reaction. Due to their excellent electron storing ability, viologens are widely used as electron mediators for artificial photosynthetic systems, such as photochemical hydrogen evolving systems. We revealed that the viologen-containing polymer shows redox-responsive self-assembling behaviors in water at a constant temperature. In the presentation, the self-assembling behaviors of the viologen-containing polymers coupled with the hydrogen evolving reaction will be discussed.

**Keywords** : *Self-assembly, Stimuli-responsive polymer, Out-of-equilibrium, Artificial photosynthesis*

生体は外界から取り入れた養分をエネルギー源として個体の構造を維持する、非平衡な分子集合体である。平衡系における自己集合では熱力学的な安定性によって集合体の構造が一意的に決定されてしまうのに対し、非平衡な自己集合体ではエネルギーの流入量によってその形成と崩壊を制御することが可能であるため、高い時空間制御性を有している。本研究では、酸化還元応答性部位を持つ高分子の相転移を水の還元反応と共役させることによって、外界から供給されるエネルギーを消費しながら自己集合する高分子システムの構築に成功した (**Figure 1**)。まず、温度応答性高分子である poly(*N*-isopropylacrylamide)(PNIPAAm)を主骨格とする高分子に、可逆的な酸化還元特性を有するビオロゲン骨格を導入することで、酸化状態に応じて凝集状態を変化させる酸化還元応答性高分子を合成した。ビオロゲン化合物はプロトン、還元剤および白金触媒の共存下において良い電子受容体として作用し、水素発生反応の進行を促進させることが知られている。還元剤によるビオロゲン骨格の還元と、白金触媒によるビオロゲン骨格の酸化が競合する水素発生反応条件下において、ビオロゲン含有高分子は還元力を消費しながら定常的に自己集合体を形成することが明らかになった。



**Figure 1.** Schematic illustration of self-assembling processes of viologen containing polymers coupled with a hydrogen evolving reaction.

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[J403-2am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Shinya Takaishi, Shohei Tashiro

Thu. Mar 24, 2022 9:00 AM - 11:40 AM J403 (Online Meeting)

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**[J403-2am-01] Substituent Effects on Nickel(II) Percarboxylate Complex Formation by Ozone Oxidation of Nickel(II) Carboxylate Complexes**○Yuma Morimoto<sup>1</sup>, Ryotaro HARIKI<sup>1</sup>, Shinobu ITOH<sup>1</sup> (1. Osaka Univ.)

9:00 AM - 9:20 AM

**[J403-2am-02] High valent Nickel catalyzed trifluoromethylation of arenes and heteroarenes induced by light irradiation**○Shubham Deolka Deolka<sup>1</sup>, Julia Khusnutdinova<sup>1</sup> (1. OIST, JAPAN)

9:20 AM - 9:40 AM

**[J403-2am-03] Reversible Chemisorption of CO at Room Temperature on Ni(0) Complexes**○Yasuhiro Yamauchi<sup>1</sup>, Yoichi Hoshimoto<sup>1</sup>, Sensuke Ogoshi<sup>1</sup> (1. osaka university)

9:40 AM - 10:00 AM

**[J403-2am-04] Structure Estimation from XANES spectra using machine learning**○Kentaro Fuku<sup>1</sup>, Takefumi Yoshida<sup>2</sup>, Hitoshi Abe<sup>3,4,5</sup>, Hiroaki Iguchi<sup>1</sup>, Shinya Takaishi<sup>1</sup>  
(1. Tohoku Univ., 2. UEC, 3. KEK-IMSS, 4. SOKENDAI, 5. Ibaraki Univ.)

10:00 AM - 10:20 AM

**[J403-2am-05] Structure and Magnetic Properties of a Dimerized Trinuclear Ni String Complex**○Kentaro Aoki<sup>1</sup>, Kazuya Otsubo<sup>1</sup>, Yukihiro Yoshida<sup>1</sup>, Kuniyoshi Sugimoto<sup>2</sup>, Hiroshi Kitagawa<sup>1</sup> (1. Grad. Sch. Sci., Kyoto Univ., 2. JASRI/SPRING-8)

10:20 AM - 10:40 AM

**[J403-2am-06] Crystal structures and electronic states of metal-dithiolate-resorcinarene co-assemblies driven by hydrogen-bond formations**○Mikihiro Hayashi<sup>1</sup> (1. Nagasaki University)

10:40 AM - 11:00 AM

**[J403-2am-07] Control of inversion motion by *in/out*-isomerization of helically twisted Pd<sub>3</sub>-macrocycles**○Tomoki Nakajima<sup>1</sup>, Shohei Tashiro<sup>1</sup>, Mitsuhiro Shionoya<sup>1</sup> (1. Grad. Sch. of Sci.; The Univ. of Tokyo)

11:00 AM - 11:20 AM

**[J403-2am-08] Development of substrate-specific long-range olefin migration reactions catalyzed by active palladium sites in a porous metal-macrocyclic framework**○Mengying Han<sup>1</sup>, Shohei Tashiro<sup>1</sup>, Takafumi Shiraogawa<sup>2</sup>, Masahiro Ehara<sup>3</sup>, Mitsuhiro Shionoya<sup>1</sup> (1. Graduate School of Science, The University of Tokyo, 2. Institute for Catalysis, Hokkaido University, 3. Institute for Molecular Science)

11:20 AM - 11:40 AM

## ニッケル(II)-カルボン酸錯体のオゾン酸化による有機過酸錯体の生成反応における置換基効果

(阪大院工) ○森本 祐麻・播木 亮太朗・伊東 忍

Substituent Effects on Formation Reaction of Nickel(II)-percarboxylate Complex by Ozone Oxidation of Nickel(II)-carboxylate Complexes

(Graduate School of Engineering, Osaka University) ○Yuma Morimoto, Ryotaro Hariki, Shinobu Itoh

Reductive cleavage of O–O bonds are usually endothermic process, which is a driving force of oxidation reactions by peroxide or peracid oxidant. The reverse process is an energetically unfavorable process, so that a limited number of direct observation of the O–O bond formation reaction has been reported. We herein report Ni(II)-percarboxylate complexes formation by ozone oxidation of the corresponding Ni(II)-carboxylate complexes.

Introduction of ozone gas into a 1,1,1,3,3,3-hexafluoro-2-propanol solution of  $[\text{Ni}^{\text{II}}(\text{tmpa})(m\text{-CBA})(\text{OH}_2)](\text{PF}_6)$  (tmpa: tris(2-pyridylmethyl)amine,  $m\text{-CBA}^-$ :  $m$ -chlorobenzoate) (**1**, 30  $\mu\text{M}$ ) containing triphenylborane (0.30 mM) produced a characteristic absorption band at 393 nm ( $\epsilon = 3.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). The same spectrum was obtained by the reaction of nickel(II) complexes with  $m$ -chloroperbenzoic acid. The generated species was characterized as  $[\text{Ni}^{\text{II}}(m\text{-CPBA})(\text{tmpa})]^+$  ( $m\text{-CPBA}^-$ :  $m$ -chloroperbenzoate) (**2**) in a spin-triplet ground state with ESI-mass, Raman, IR, and  $^1\text{H}$ -NMR spectroscopies. Employment of  $^{18}\text{O}$ -labeled complex endorsed the occurrence of O–O bond formation between the oxygen of the benzoate ligand and that of ozone (Scheme 1). Nickel(II) complexes with other carboxylate ligands were also converted to the corresponding peracid complexes in the similar manner. The yields of peracid complex became higher when the carboxylate ligands with lower electron donor ability were employed.

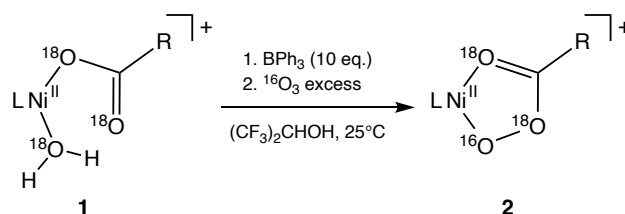
**Keywords:** *Percarboxylate Ni(II)-complex; O–O Bond Formation; Ozone; Fluorous Solvent*

酸素-酸素結合の還元的開裂は大きな発熱過程であり、これはペルオキシドや過酸による酸化反応の駆動力となっている。その逆反応である酸素-酸素結合形成反応は熱的に不利な過程であるため、直接この過程を観

測した例は限られている。本発表ではニッケル(II)-カルボン酸錯体のオゾン酸化によるニッケル(II)-有機過酸錯体生成反応について検討した結果を報告する。

$[\text{Ni}^{\text{II}}(\text{tmpa})(m\text{-CBA})(\text{OH}_2)](\text{PF}_6)$  (30  $\mu\text{M}$ ) (tmpa: トリス(2-ピリジルメチル)アミン) (**1**) の  $\text{CF}_3\text{CH}(\text{OH})\text{CF}_3$  溶液に、トリフェニルボラン (0.30 mM) を加えオゾンを流通させると、瞬時に 393 nm ( $\epsilon = 3.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) に吸収極大を有する化学種が生成した (Scheme 1)。この吸収帯はニッケル(II)錯体にメタクロロ過安息香酸を加えることでも生成した。質量分析および各種分光法より、生成物をメタクロロ過安息香酸のニッケル(II)錯体 **2** と帰属した。 $^{18}\text{O}$  同位体標識実験よりカルボン酸アニオンの酸素とオゾンの酸素の間の結合生成を確認した。同様にして他のニッケル(II)カルボン酸錯体も、対応する過酸錯体へと転換することが可能であった。電子供与性が低いカルボン酸のニッケル(II)錯体を用いた際に、より高い収率で反応が進行した。

Scheme 1. Ozone oxidation of **1** to form **2**.

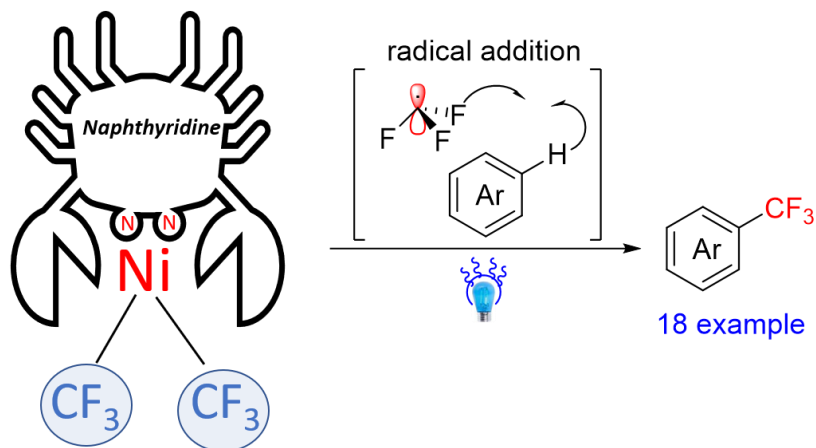


## High valent nickel-catalyzed trifluoromethylation of arenes and heteroarenes induced by light irradiation

(<sup>1</sup>Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University) ○Shubham Deolka,<sup>1</sup>, Govindarajan Ramadoss<sup>1</sup>, Eugene Khaskin,<sup>1</sup> Julia R. Khusnutdinova\*<sup>1</sup>.

**Keywords:** Nickel; Naphthyridine; Trifluoromethylation; Blue Light.

Trifluoromethylation<sup>1</sup> of C-H bonds is an industrially important reaction for the synthesis of pharmaceutical compounds, with a functional group that can significantly change the pharmacokinetics of a known drug. While many protocols are known for metal-catalyzed trifluoromethylation of C-H bonds in arenes and heteroarenes, it would be practically advantageous to develop photoinduced trifluoromethylation as a way to control the reactivity. Although photoredox catalysis has been reported in radical trifluoromethylation, the typical protocols utilize precious metal catalysts based on Ru or Ir, and no examples are known for photoinduced reactivity that would involve only inexpensive base metal complexes.



In the currently presented work, we developed<sup>2</sup> a family versatile Ni catalysts supported by N-donor naphthyridine based chelating ligands that efficiently catalyzes C-H bond trifluoromethylation of arenes and heteroarenes in the presence of visible light using two alternative protocols including Langlois or Umemoto reagents.

Interestingly, we were able to obtain stable and robust Ni(III) complexes simply by aerobic oxidation of Ni(II) precursors. EPR studies reveal that such Ni(III) trifluoromethyl complexes undergo light-induced Ni-CF<sub>3</sub> bond homolysis. We further developed it into catalytic protocols for C-H bond trifluoromethylation in the presence of blue LED irradiation. A number of electron-rich simple arenes or heterocycles (pyrroles, indoles) could be trifluoromethylated under these conditions.

Preliminary mechanistic studies suggest a radical mechanism via NiII/NiIII couple. This reactivity is an important example of the merge of Ni and photoredox catalysis into one system that utilizes only simple N-donor ligands and nickel as an inexpensive first row transition metal.

### References:

1. Nagib, D.et.al, Nature. 2011, 480, 224–228.
2. Deolka, S.et.al, Angew. Chem., Int. Ed. 2021, 60, 24620–24629

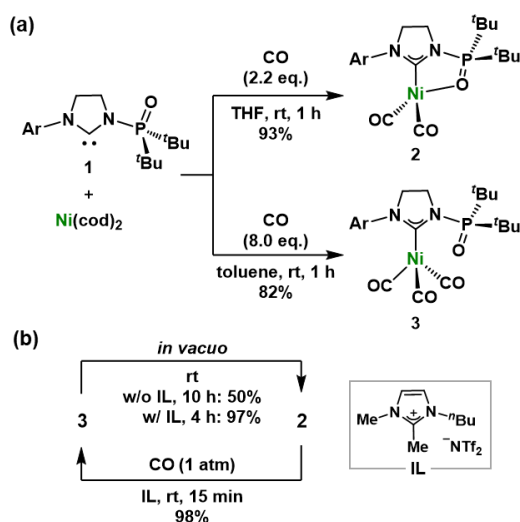
## Reversible Chemisorption of CO at Room Temperature on Ni(0) Complexes

(Graduate School of Engineering, Osaka University) ○ Yasuhiro Yamauchi, Yoichi Hoshimoto, Sensuke Ogoshi

**Keywords:** Chemisorption; Nickel-Carbonyl Complex; *N*-Heterocyclic Carbene; Ionic Liquid

Carbon monoxide (CO) is a key C1 source for many chemicals, including alcohols, acetic acid, and copolymers comprising CO and olefins. The development of an effective method for the separation/purification of CO is valuable, especially when the method can be conducted under less energy-consuming conditions. As such a procedure to separate/purify CO, the reversible chemisorption of CO has been exclusively studied using higher-valent metal complexes.<sup>1)</sup> However, in general, a temperature higher than that used in the adsorption process was required to achieve an efficient desorption process. Herein, we report a room-temperature chemisorption of CO using the interconversion between zero-valent nickel di- and tri-carbonyl complexes bearing *N*-phosphine oxide-substituted imidazolynylidene<sup>2)</sup>, which can be driven only by the change of the pressure.

Treatment of a THF solution of **1** and Ni(cod)<sub>2</sub> with 2.2 equivalents of CO afforded ( $\kappa$ -C,*O*-1)Ni(CO)<sub>2</sub> (**2**) in 93% yield (Figure 1a). On the other hand, the reaction using 8.0 equivalents of CO in toluene furnished ( $\kappa$ -C-1)Ni(CO)<sub>3</sub> (**3**) in 82% yield. Stirring a crystalline powder of **3** under the reduced pressure for 10 h resulted in the formation of **2** in 50% yield (Figure 1b). To improve the efficiency, imidazolium-based ionic liquid (**IL**) was used as a dispersant for **3**, resulting in the formation of **2** in 97% yield. Stirring **2** with **IL** in the presence of CO (1 atm) at room temperature afforded **3** in 98% yield within 15 min.



**Figure 1.** (a) Synthesis of **2** and **3** (Ar = 2,6-diisopropylphenyl). (b) Chemisorption of CO with **2/3**.

1) For examples, see: a) D. Benito-Garagorri, M. Puchberger, K. Mereiter, K. Kirchner, *Angew. Chem. Int. Ed.* **2008**, 47, 9142. b) H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata, S. Kitagawa, *Science* **2014**, 343, 167. 2) Y. Hoshimoto, S. Ogoshi, *Bull. Chem. Soc. Jpn.* **2021**, 94, 327.

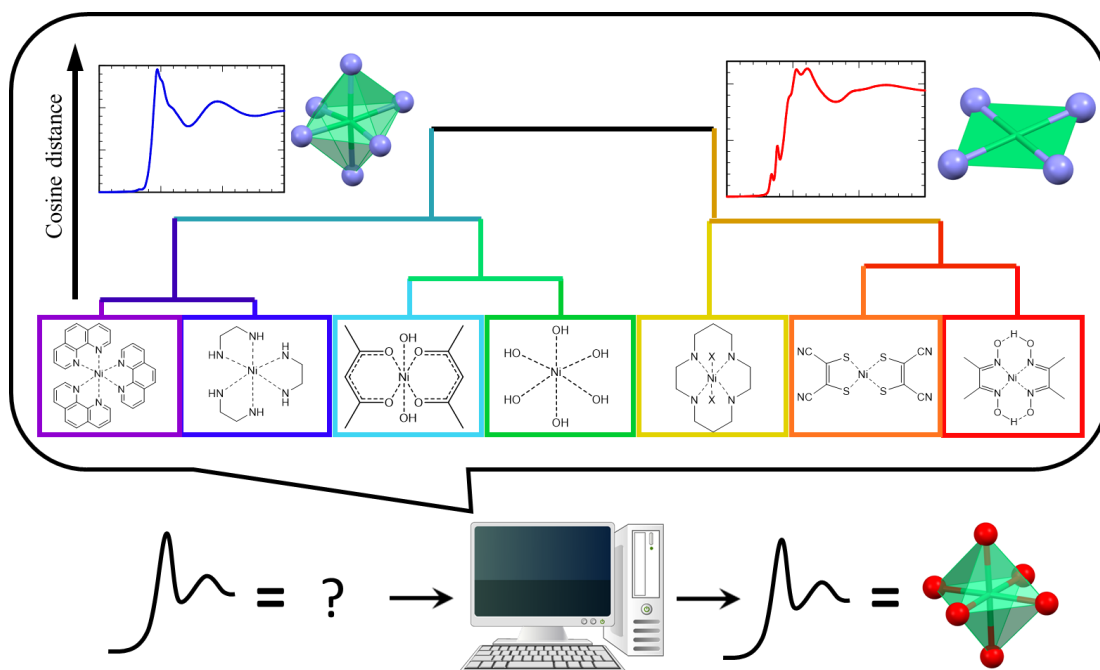
## Structure Estimation from XANES spectra using machine learning

(<sup>1</sup>Graduate School of Science, Tohoku University, <sup>2</sup>Innovation Research Center for Fuel Cells, The University of Electro-Communications, <sup>3</sup>Institute of Materials Structure Science High Energy Accelerator Research Organization (KEK), <sup>4</sup>School of High Energy Accelerator Science, SOKENDAI, <sup>5</sup>Graduate School of Science and Engineering, Ibaraki University)

○Kentarō Fuku,<sup>1</sup> Takefumi Yoshida,<sup>2</sup> Hitoshi Abe,<sup>3,4,5</sup> Hiroaki Iguchi,<sup>1</sup> Shinya Takaishi<sup>1</sup>

**Keywords:** Machine Learning; XAFS; Structure Estimation;

In coordination chemistry, the only methods for structure estimation have been single crystal X-ray structure analysis or DFT calculations. Recently, X-ray absorption fine structure (XAFS) has been attracting attention as a method for estimating coordination environments. However, the use of XAFS (especially XANES) in coordination chemistry is not common technique, and the most of its use are limited to "fingerprint matching" such as comparison with reference samples. In this study, we measured the XAFS spectra of Ni complexes, and aimed to estimate the coordination environment conveniently by spectral clustering using machine learning. As a result of our experiments, we succeeded in cluster partitioning by the number of coordination and the chemical environment of the coordinating atoms. And the clusters to which they belonged were changed following the ligand exchange reaction by adding ligands. These results suggest that the combination of XANES and machine learning will make it possible to estimate the coordination environment more easily.



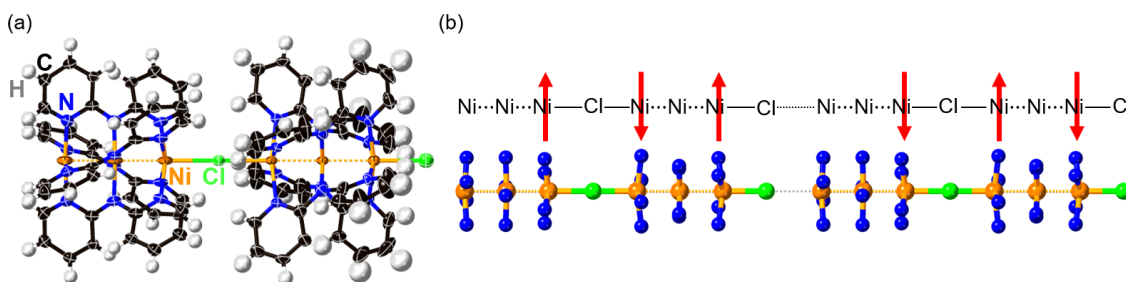
## Structure and Magnetic Properties of a Dimerized Trinuclear Ni String Complex

(<sup>1</sup>Graduate School of Science, Kyoto University, <sup>2</sup>JASRI/SPRING-8) ○Kentaro Aoki,<sup>1</sup> Kazuya Otsubo,<sup>1</sup> Yukihiro Yoshida,<sup>1</sup> Kuniyoshi Sugimoto,<sup>2</sup> Hiroshi Kitagawa<sup>1</sup>

**Keywords:** Multinuclear Complex; Metal String Complex; Oligomers; Electronic Absorption; Magnetic Properties

Metal string complexes, composed of a linear polymetallic core surrounded by the multidentate organic ligands, have attracted great interest for the study of metal–metal interactions and the application as conductive molecular nanowires.<sup>1</sup> Since the first report of the metal string complex  $\text{Ni}_3\text{Cl}_2(\text{dpa})_4$  ( $\text{dpa}^-$  = dipyridylamido anion),<sup>2</sup> various kinds of  $\text{Ni}^{\text{II}}$  string complexes have been synthesized.<sup>3</sup> However, there is no report of connecting several metal string units. Here, we synthesized a novel dimerized Ni string complex  $[\text{Ni}_6\text{Cl}_2(\text{dpa})_8](\text{I}_5)_2 \cdot 0.25\text{I}_2$  (**1**), and investigated its physical properties.

**1** was synthesized by a reaction of the trinuclear complex  $\text{Ni}_3\text{Cl}_2(\text{dpa})_4$  and  $\text{I}_2$  in mesitylene, and its molecular structure was determined from single-crystal X-ray study (**Figure 1a**). Two trinuclear moieties are bridged by a chloride to form the dimer structure, and this is the first example that two Ni string units are connected and isolated. The valence of all Ni ions in a dimer was confirmed to be divalent according to the charge balance, bond length analysis and X-ray photoelectron spectroscopy. Optical studies and DFT calculations revealed the electronic absorption bands and a vibration mode characteristic of a dimer structure. Moreover, in the solid state, the dimer string units align one-dimensionally in an MMMXMMM (M = Ni and X = Cl) manner, leading to the intra- and inter-dimer antiferromagnetic interactions (**Figure 1b**). Details are discussed.



**Figure 1.** (a) Molecular structure of **1** at 100 K. The thermal ellipsoids are drawn with a 50% probability, and counter anions are omitted for clarity. (b) The spin arrangements of **1** in the solid state. Red arrows denote the  $S = 1$  spins.

- 1) F. A. Cotton *et al.*, *Multiple Bonds Between Metal Atoms*. Springer: Boston (2005).
- 2) T. J. Hurley *et al.*, *Inorg. Chem.* **1968**, 7, 33.
- 3) P. Braunstein *et al.*, *Chem. Rev.* **2021**, 121, 7346.



## Crystal structures and electronic states of metal-dithiolate–resorcinarene co-assemblies driven by hydrogen-bond formations

(Faculty of Education, Nagasaki University) ○Mikihiro Hayashi

**Keywords:** hydrogen bond; dithiolene complex; resorcinarene; Pourbaix Diagram

**[Introduction]** Molecular assemblies driven by Hydrogen-bond (H-bond) formations have gathered attention in research fields of crystal engineering and supramolecular chemistry. As components of such assemblies, of interesting are molecules offering electronic structures impacted by protonation/deprotonation processes, such as quinone derivatives, because of potentials to develop materials exhibiting electronic functions depending on H-bond states.<sup>1</sup> Previously, I reported that bis(pyrazine-2,3-dithiolene)metal complexes;  $[M(pdt)_2]^{2-}$  ( $M = Ni, Pd, Pt$ ) shows  $d$ -element dependency of electron-donor-ability changes by their protonation in solution states;<sup>2</sup> however, their potential to build H-bond assemblies dealing with proton and electron transfers remain an issue. Herein, I report that tetraethylammonium salts of  $[M(pdt)_2]^{2-}$  ( $M = Ni, Pd, Pt$ ) are crystallized with tetra(isobutyl)resorcine[4]arene (**RCArene**) to afford a series of H-bonded 1:1 assemblies (**MArene**), and I discuss electronic states of metalladithiolate composing **MArene** by investigating their optical and magnetic properties.

**[Results and discussion]** As shown in Figure 1, crystal structures of **MArene** are an isotypic structure containing head-to-head arranged **RCArene** pairs linked by six  $[M(pdt)_2]^{2-}$  units with forming one-dimensional H-bonds between hydroxyl oxygen and pyrazine nitrogen atoms along  $c$  axis. With cooperation from intramolecular H-bonds of **RCArene** units, strongly bonded characters of the intermolecular H-bonds were indicated by broaden absorption bands of **MArene** from 3600 to 2000  $\text{cm}^{-1}$ . Electronic absorption spectra of all **MArene** shows both protonated and deprotonated states of metalladithiolate were composed. Partial oxidations of **NiArene** and **PdArene** provide different shapes of EPR signals, i.e. the Ni species has a large contribution of the metallacycle spin, and the Pd species contains both of metallacycle and hydroxyl radicals. These results are considered to come from a  $d$ -element dependency of pH-dependent redox of  $[M(pdt)_2]^{2-}$ , where values of oxidation potentials of  $[Pd(pdt)_2]^{2-}$  are reversed by those of **RCArene** with decreasing the activity of proton, as indicated by their Pourbaix Diagrams.

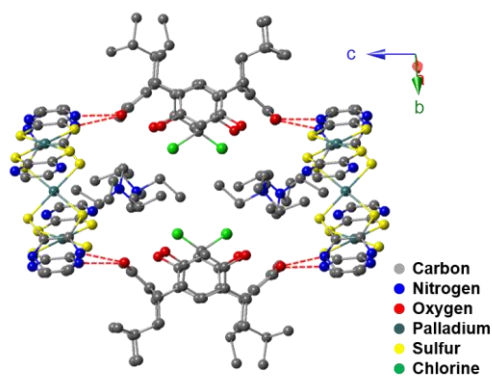


Figure 1 A key structure composed of **PdArene**.  $\text{CH}_2\text{Cl}_2$  are contained in the pair of **RCArene**. H-bonds are indicated as red dotted lines. Hydrogen atoms were omitted for clarity.

- 1) a) Y. Hirao, *et al. Angew. Chem. Int. Ed.* **2015**, 54, 2402. b) K. Nakasuji, *et al. J. Am. Chem. Soc.* **1991**, 113, 1862. 2) M Hayashi, *et al. J. Am. Chem. Soc.* **2019**, 141, 11686.



## Control of inversion motion by *in/out*-isomerization of helically twisted Pd<sub>3</sub>-macrocycles

(<sup>1</sup>Graduate School of Science, The University of Tokyo) ○Tomoki Nakajima,<sup>1</sup> Shohei Tashiro,<sup>1</sup> Mitsuhiro Shionoya<sup>1</sup>

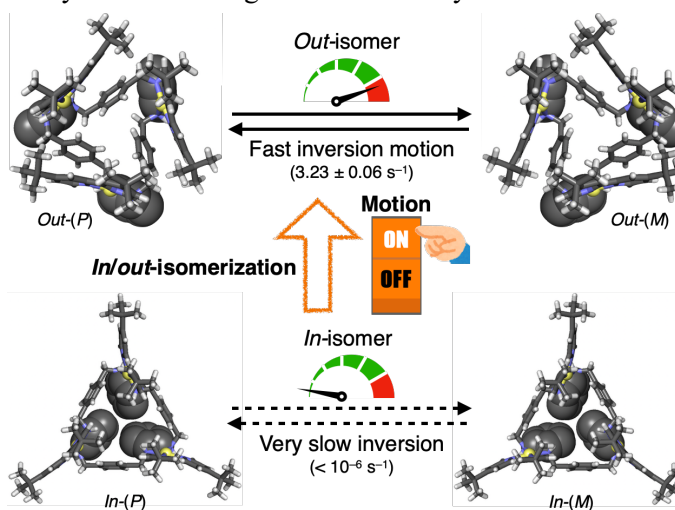
**Keywords:** Isomerization; Helicity inversion; Pd complex; Multinuclear complex; Macrocyclic compound

Isomerization is one of the most important factors in controlling molecular motions such as rotation and gearing. Photo-induced *cis/trans*-isomerization has been used in many molecular machines, but control of molecular motions based on other isomerization reactions is still challenging. Previously, our group reported an inversion motion between (*P*)- and (*M*)-enantiomers of a helically twisted Pd<sub>3</sub>-macrocycle, [Pd<sub>3</sub>LCl<sub>6</sub>], but precise control of the inversion motion has not been achieved.<sup>[1]</sup> In this study, we found that helically twisted Pd<sub>3</sub>-macrocycles, [Pd<sub>3</sub>L('Bu<sub>2</sub>bpy)<sub>3</sub>](OTf)<sub>6</sub>, form two markedly different structural isomers, *in*- and *out*-isomers, and that each isomer is in equilibrium as a racemic mixture of the (*P*)- and (*M*)-forms. The inversion kinetics of these two sets of enantiomers were remarkably different, indicating the possibility that they could be involved in an excellent molecular switching system *via* the “inside-out” isomerization.

The *in*- and *out*-isomers of the Pd<sub>3</sub>-macrocycles were selectively synthesized under different conditions and their structures were determined by single-crystal XRD and <sup>1</sup>H NMR analyses. The *out*-isomer showed conformational inversion between the *out*-(*P*)- and (*M*)-enantiomers, and the inversion rate was evaluated to be  $3.23 \pm 0.06 \text{ s}^{-1}$  at 300 K in acetone-*d*<sub>6</sub> by EXSY analysis. In stark contrast, the inversion between the *in*-(*P*)- and (*M*)-isomers was not observed in 4 days ( $< 10^{-6} \text{ s}^{-1}$ ) because it requires configurational changes of all amine nitrogen atoms.

In addition, we found that the very slow reversing *in*-isomer slowly isomerizes into the fast reversing *out*-isomer, and the rate of this *in*-to-*out* isomerization was estimated by time course NMR analysis. We will also discuss how this entire system can be controlled by external stimuli.

[1] R. Kubota, S. Tashiro, M. Shionoya, *Chem. Sci.* **2016**, 7, 2217–2221.



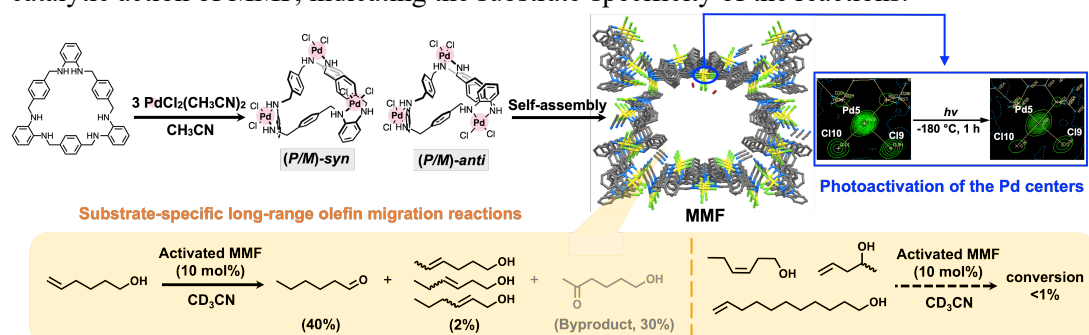
## Development of substrate-specific long-range olefin migration reactions catalyzed by active palladium sites in a porous metal-macrocycle framework

(<sup>1</sup>Graduate School of Science, the University of Tokyo, <sup>2</sup>Institute for Catalysis, Hokkaido University, <sup>3</sup>Institute for Molecular Science) ○Mengying Han,<sup>1</sup> Shohei Tashiro,<sup>1</sup> Takafumi Shiraogawa,<sup>2</sup> Masahiro Ehara,<sup>3</sup> Mitsuhiro Shionoya<sup>1</sup>

**Keywords:** Self-assembly; Porous crystal; Pd complex; Olefin migration; Heterogeneous catalyst

Encapsulation of substrates into the confined space of porous crystals with well-defined active sites on the pore surfaces improves reaction efficiency and selectivity, making them promising heterogeneous catalysts. Our group has previously reported the synthesis of metal-macrocycle frameworks (MMFs), novel porous crystals formed by the self-assembly of four stereoisomers of the trinuclear Pd<sup>II</sup> complexes of macrocyclic hexamines. MMF has one-dimensional channels with a pore size of  $1.4 \times 1.9 \text{ nm}^2$  and five enantiomerically-paired binding sites. Furthermore, the Pd-Cl bonds at the ceiling of the MMF channels were partially dissociated by photo-irradiation, and the activated Pd centers were found to function as the reaction sites for the olefin migration reaction of many aromatic substrates.<sup>[1]</sup> In this study, we developed a method to use photo-activated MMF as a heterogeneous catalyst for olefin migration reactions<sup>[2]</sup> and further extended the substrate range to several alkenyl alcohols. In particular, substrate-specific long-range olefin migration reactions were examined using MMF catalyst.

When 10 mol% photo-activated MMF was used as a catalyst, 5-hexen-1-ol underwent a long-range olefin migration reaction to give hexanal (40% conversion) as the main product. The total conversion of the internal olefin species was less than 2% throughout the reaction, indicating that the reaction proceeds by a chain-walking mechanism. On the other hand, the olefin migration using a homogeneous PdCl<sub>2</sub>(MeCN)<sub>2</sub> catalyst proceeded in a stepwise manner, giving internal olefins as the main products. Theoretical calculations were applied to simulate the reaction pathway of the long-range migration reaction to further support the proposed reaction mechanism. Furthermore, due to the spatial effect of the MMF channels, alcohol substrates with long or branched chains and internal olefin structures hardly reacted under the catalytic action of MMF, indicating the substrate-specificity of the reactions.



[1] M. Shionoya, *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 16610. [2] M. Shionoya, *et al.*, *Chem. Asian J.* **2021**, *16*, 202.

**[K3-2pm] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Masashi Hasegawa, Yumi Yakiyama

Thu. Mar 24, 2022 1:00 PM - 3:40 PM K3 (Online Meeting)

**[K3-2pm-01] Electrochemical synthesis and dynamic control of [n]acene structures**○Takashi Harimoto<sup>1</sup>, Takanori Suzuki<sup>2</sup>, Yusuke Ishigaki<sup>2</sup> (1. Graduate School of Chemical and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

1:00 PM - 1:20 PM

**[K3-2pm-02] Synthesis of Novel Closed Heterohelicenes Interconvertible between Its Monomer and Dimer**○Yusuke Matsuo<sup>1</sup>, Takayuki Tanaka<sup>1</sup> (1. Kyoto University)

1:20 PM - 1:40 PM

**[K3-2pm-03] Cycloparaphenylene Synthesis via a Macrocyclic Gold(I) Complex: Multiply Functionalized CPPs**○Yoshitaka Tsuchido<sup>1</sup>, Naoki Narita<sup>1</sup>, Yusuke Kurita<sup>1</sup>, Tomohito Ide<sup>3</sup>, Kohtaro Osakada<sup>2</sup>, Hidetoshi Kawai<sup>1</sup> (1. Tokyo Univ. of Sci., 2. Tokyo Inst of Tech., 3. Nat. Coll. of Tech., Tokyo Coll.)

1:40 PM - 2:00 PM

**[K3-2pm-04] Synthesis of Armchair- and Chiral-Types Cyclophenylene-Naphthylene Belts by Rhodium-Catalyzed Intramolecular [2+2+2] Cycloaddition**○Juntaro Nogami<sup>1</sup>, Yuki Nagashima<sup>1</sup>, Haruki Sugiyama<sup>2</sup>, Kazunori Miyamoto<sup>3</sup>, Yusuke Tanaka<sup>3</sup>, Hidehiro Uekusa<sup>4</sup>, Atsuya Muranaka<sup>5</sup>, Masanobu Uchiyama<sup>3</sup>, Ken Tanaka<sup>1</sup> (1. Sch. Mater. & Chem. Tech., Tokyo Tech., 2. IMS, 3. Grad. Sch. of Pharm. Sci., The Univ. of Tokyo, 4. Sch. Sci., Tokyo Tech., 5. RIKEN)

2:00 PM - 2:20 PM

**[K3-2pm-05] Synthesis and properties of kinetically stabilized bis-periazulene derivatives**○Koki Horii<sup>1</sup>, Akihito Konishi<sup>1</sup>, Makoto Yasuda<sup>1</sup> (1. Osaka University)

2:20 PM - 2:40 PM

**[K3-2pm-06] Synthesis and Properties of Nitrogen-doped Triangulene Cation**○Shinobu Arikawa<sup>1</sup>, Akihiro Shimizu<sup>1</sup>, Daisuke Shiomi<sup>2</sup>, Kazunobu Sato<sup>2</sup>, Ryo Shintani<sup>1</sup> (1. Osaka University, 2. Osaka City University)

2:40 PM - 3:00 PM

**[K3-2pm-07] Synthesis, Physical Properties, and Semiconductor Characteristics of Fluorinated Pentalene-1,4-dione Derivatives**○Soichi Yokoyama<sup>1</sup>, Yutaka Ie<sup>1</sup> (1. SANKEN, Osaka Univ.)

3:00 PM - 3:20 PM

**[K3-2pm-08]  $\sigma$ -Delocalized Orbitals and Charge-Transport Properties of Polyiodobenzenes**○Yuki Takada<sup>1</sup>, Shunsuke Furukawa<sup>1</sup>, Masaichi Saito<sup>1</sup> (1. Department of Chemistry, Graduate School of Science and Engineering, Saitama University)

3:20 PM - 3:40 PM

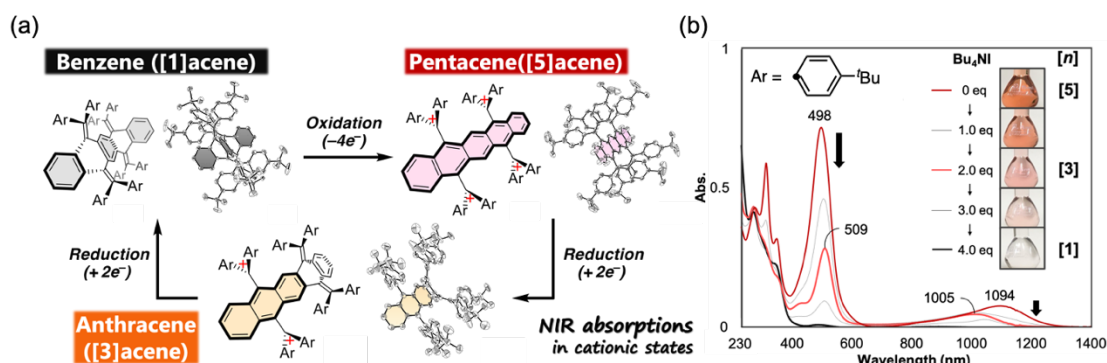
## Electrochemical synthesis and dynamic control of $[n]$ acene structures

(<sup>1</sup>Graduate School of Chemical and Engineering, Hokkaido University, <sup>2</sup>Faculty of Science, Hokkaido University) ○Takashi Harimoto,<sup>1</sup> Takanori Suzuki,<sup>1</sup> Yusuke Ishigaki<sup>2</sup>

**Keywords:** Redox System, NIR Absorption, Acene, Oligocation, Hydrocarbon

$[n]$ Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings ( $n$  indicates the number of annulated benzene rings).  $[n]$ Acenes are highly attractive molecules because their HOMO/LUMO levels and small band gap can be easily modulated by a change in  $n$ . Thus, their physical properties can be fine-tuned, and  $[n]$ acenes are widely used as functional organic materials such as semiconductors. In addition,  $[n]$ acenes have been reported to show dynamic interconversion through photo and thermal dimerization/dissociation and reversible endoperoxidation reactions. While these switching behaviors are fascinating from the viewpoint of control of HOMO/LUMO levels arising from the change in acene units, it is still challenging to attain reversible and selective switching of  $[n]$ acene units that can be observed in a unimolecular fashion rather than as an intermolecular reaction of two molecules.

Herein, we designed and synthesized zigzag-structured bisquinodimethanes (BQDs) with non-fused benzene rings, which undergo one-stage four-electron oxidation to produce tetracationic [5]acenes with a doubly twisted conformation. When tetracationic [5]acenes were reduced, two-stage two-electron reduction occurred via dicationic [3]acenes to the original BQDs (Figure a). Such hysteretic three-state redox interconversion among them demonstrates perfect control of  $n$  ( $1 \rightarrow 5 \rightarrow 3 \rightarrow 1$ ) in the  $[n]$ acene structure by redox conversion. Moreover, since these cations exhibit significantly red-shifted NIR absorptions ( $\sim 1400$  nm) based on an intramolecular charge-transfer interaction, changes in structure as well as UV-vis-NIR absorptions can be controlled by electrochemical input (Figure b). All structures were determined by X-ray analyses, and their properties were characterized by spectroscopic and theoretical studies.<sup>1</sup> Recent progress will be also presented.



1) Y. Ishigaki, **T. Harimoto**, K. Sugawara, T. Suzuki, *J. Am. Chem. Soc.* **2021**, *143*, 3306.

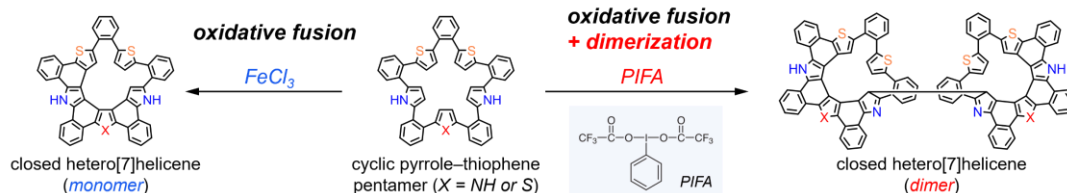
## Synthesis of Novel Closed Heterohelicenes Interconvertible between Its Monomer and Dimer

(<sup>1</sup>Graduate School of Engineering, Kyoto University) ○Yusuke Matsuo,<sup>1</sup> Takayuki Tanaka<sup>1</sup>

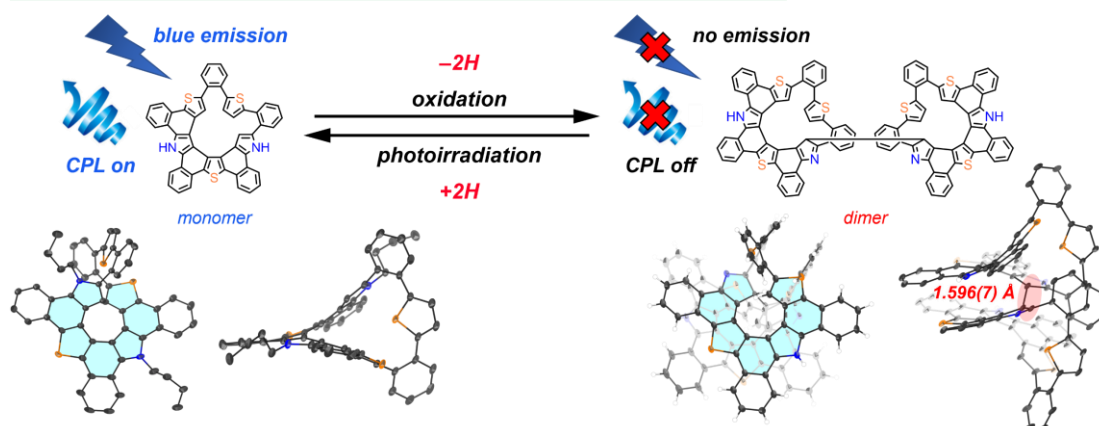
**Keywords:** Nanographene; Heterohelicene; Oxidative fusion reaction; Bond dissociation; Oxidative dimerization

Oxidative fusion reaction is an effective method for the synthesis of nanographenes. Recently, we have reported the “Fold-in” synthesis of tetraaza[8]circulene and pentaaza[10]circulene as novel N-doped nanographenes by the oxidative fusion reaction of cyclic pyrrole oligomers.<sup>1,2</sup> Herein, we examined an oxidative fusion reaction with *ortho*-phenylene-bridged cyclic pyrrole–thiophene hybrid pentamers, which afforded partially fused closed-hetero[7]helicenes exclusively. These helicenes dimerized upon addition of PIFA to make a new C–C bond with nearly 1.6 Å length. Photoirradiation to the obtained helicene-dimer reverted the monomer quantitatively, thus demonstrating a reversible dimerization process in novel closed-heterohelicenes. An enantiomer of the monomeric closed-helicene shows circularly polarized luminescence, while the dimer does not show it, thus demonstrating a stimuli-responsive ability. We will disclose their detailed structures, optical properties, and mechanisms of monomer–dimer interconversion.

### • Oxidative fusion reaction of cyclic pyrrole–thiophene hybrid pentamer



### • Interconversion between helicene monomer and dimer (X = S)



1) F. Chen, Y. S. Hong, S. Shimizu, D. Kim, T. Tanaka, A. Osuka, *Angew. Chem. Int. Ed.* **2015**, 54, 10639. 2) Y. Matsuo, K. Kise, Y. Morimoto, A. Osuka, T. Tanaka, *Angew. Chem. Int. Ed.* **2022**. DOI: 10.1002/anie.202116789.

## 大環状金(I)錯体を鍵中間体としたシクロパラフェニレン類の新規合成法：多重官能基化された CPP の合成と機能

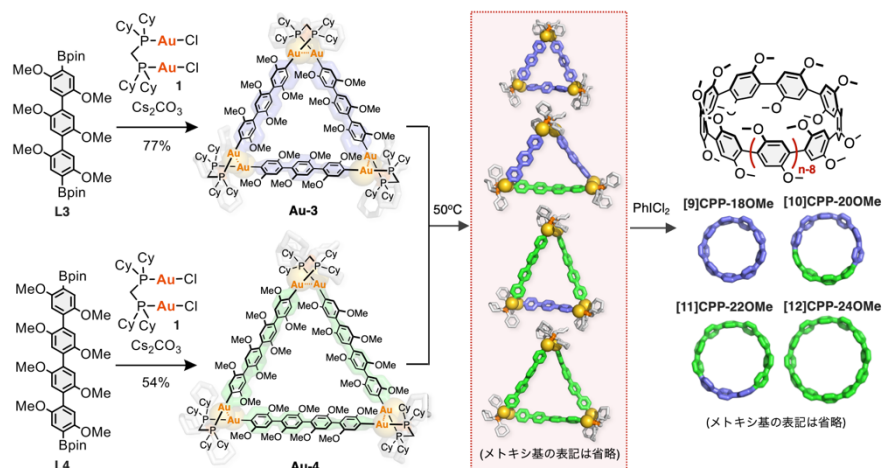
(東理大理<sup>1</sup>・東工大化生研<sup>2</sup>・東京高専物質工<sup>3</sup>) ○土戸 良高<sup>1</sup>・成田 直生<sup>1</sup>・栗田 祐輔<sup>1</sup>・井手 智仁<sup>3</sup>・小坂田 耕太郎<sup>2</sup>・河合 英敏<sup>1</sup>

Cycloparaphenylene Synthesis via a Macrocyclic Gold(I) Complex: Multiply Functionalized CPPs (<sup>1</sup>Tokyo University of Science, <sup>2</sup>Tokyo Institute of Technology, <sup>3</sup>National Institute of Technology, Tokyo College) ○Yoshitaka Tsuchido,<sup>1</sup> Naoki Narita,<sup>1</sup> Yusuke Kurita,<sup>1</sup> Tomohito Ide,<sup>3</sup> Kohtaro Osakada,<sup>2</sup> Hidetoshi Kawai<sup>1</sup>

We have synthesized a series of [n]cycloparaphenylenes (n = 9 – 12) with methoxy groups at the 2,5-positions of all benzene rings. The transmetalation between two macrocyclic Au complexes, [Au<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>-2,5-(OMe)<sub>2</sub>)<sub>n</sub>(Cy<sub>2</sub>PCH<sub>2</sub>PCy<sub>2</sub>)<sub>3</sub>] (n = 3, **Au-3**; n = 4, **Au-4**), was conducted at 50 °C. The resulting reaction mixture was directly treated with PhICl<sub>2</sub> afforded a mixture of [n]CPP-2n(OMe) (n = 9 – 12). This result indicates the formation of isosceles triangular macrocyclic complexes in which were incorporated two different oligoarylene linkers reorganized from **Au-3** and **Au-4** though the dynamic Au(I)-C bond exchange process. **Keywords:** Cycloparaphenylene, Gold(I) complex, Functionalization, Host-Guest Chemistry

シクロパラフェニレン(CPP)は、ベンゼン環がパラ位で環状に結合した分子であり、湾曲したベンゼン環に起因した光物性や電気化学物性を有する。我々は大環状金錯体を経由する新規 CPP 合成法を開発し<sup>[1]</sup>, さらに本手法を応用することで全てのベンゼン環に 2,5-ジメトキシ基が導入された[6]CPP 誘導体の合成にも成功している<sup>[2]</sup>。本研究では環サイズの大きい[n]CPP-2n(OMe) (n = 9, 10, 11, 12)を合成した。

オリゴフェニレンボロン酸 (**L3, L4**) と金クロライド錯体(**1**)を反応させることで大環状金錯体 (**Au-3, Au-4**) をそれぞれ得た。二種類の大環状金錯体を 1:1



のモル比で加熱混合した後、PhICl<sub>2</sub> で処理すると[9]CPP-18OMe, [12]CPP-24OMe に加えて[10]CPP-20OMe, [11]CPP-22OMe が生成していることが NMR・MS より確認された。これは動的な Au(I)-C 結合によって錯体間で結合交換が起き<sup>[1b]</sup>, 異なるリンカーが組み込まれた大環状金錯体が生成したことを示唆している。

[1] a) Y. Tsuchido, *et al. Angew. Chem. Int. Ed.* **2020**, 59, 22928; b) *ChemRxiv*, **2021**, DOI: 10.33774/chemrxiv-2021-v89w1; [2] 土戸ら, 日本化学会第 101 回春季年会, **2021**, A17-3am-16.



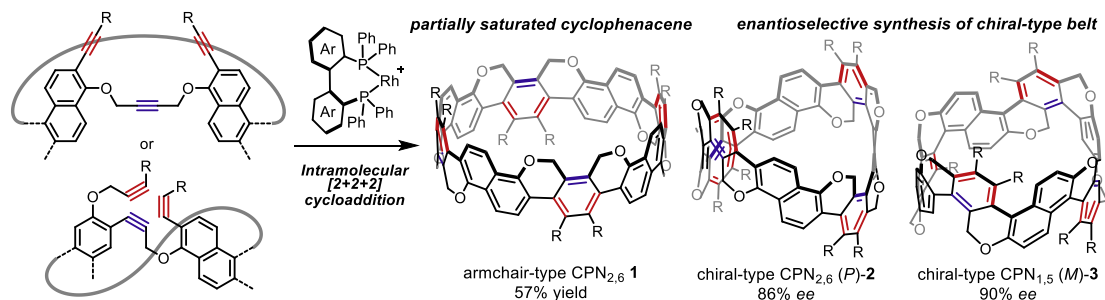
## Synthesis of Armchair- and Chiral-Types Cyclophenylene-Naphthylene Belts by Rhodium-Catalyzed Intramolecular [2+2+2] Cycloaddition

(<sup>1</sup>Sch. Mater. & Chem. Tech., Tokyo Tech., <sup>2</sup>IMS, <sup>3</sup>Grad. Sch. of Pharm. Sci., The Univ. of Tokyo, <sup>4</sup>Sch. Sci., Tokyo Tech., <sup>5</sup>RIKEN) ○Juntaro Nogami,<sup>1</sup> Yuki Nagashima,<sup>1</sup> Haruki Sugiyama,<sup>2</sup> Kazunori Miyamoto,<sup>3</sup> Yusuke Tanaka,<sup>3</sup> Hidehiro Uekusa,<sup>4</sup> Atsuya Muranaka,<sup>5</sup> Masanobu Uchiyama,<sup>3</sup> Ken Tanaka<sup>1</sup>

**Keywords:** Carbon Nanobelt; Cycloparaphenylene; Rhodium; Cyclotrimerization; Asymmetric Synthesis

Belt-shaped  $\pi$ -conjugated molecules such as carbon nanobelts (CNBs) have fascinated organic chemists for decades due to their aesthetic structures and potential applications.<sup>1</sup> Several bottom-up syntheses of these belt molecules have been reported in recent years, however, there are still unachieved synthetic targets. For example, the bottom-up synthesis of [*n*]cyclophenacene,<sup>2</sup> which is the simplest and shortest belt-type segment of armchair carbon nanotube (CNT), has not been achieved. The synthesis of chiral-type CNBs is also limited to a single racemic synthesis in Miao's report,<sup>3</sup> and the synthetic research is hardly advanced compared with the zigzag- and armchair-types CNBs.

Herein, we report the synthesis of cyclophenylene-type cyclophenylene-naphthylene (CPN) belt **1** in 57% yield, and the enantioselective synthesis of chiral-type CPN belts (*P*)-**2** and (*M*)-**3** with up to >99% ee by the cationic rhodium(I)-catalyzed intramolecular [2+2+2] cycloadditions of cyclic polyynes (Figure 1). The cylindrical unimolecular structures and the packing structures of these CPN belts were successfully confirmed by X-ray crystallographic analyses. Unfortunately, in the attempted synthesis of vertically expanded CPN belt, the final intramolecular [2+2+2] cycloaddition did not proceed and one triyne unit remaining was isolated in a low yield of 15%. These successful and unsuccessful reactions showed the capability and limitation of the cationic rhodium(I)-catalyzed intramolecular [2+2+2] cycloaddition of the cyclic polyynes.



**Figure 1.** Synthesis of cyclophenylene-naphthylene (CPN) belts.

1) E. R. Darzi, R. Jasti, *Chem. Soc. Rev.* **2015**, *44*, 6401. 2) K. Y. Cheung, S. Gui, C. Deng, H. Liang, Z. Xia, Z. Liu, L. Chi, Q. Miao, *Chem* **2019**, *5*, 838. 3) E. Nakamura, K. Tahara, Y. Matsuo, M. Sawamura, *J. Am. Chem. Soc.* **2003**, *125*, 2834.

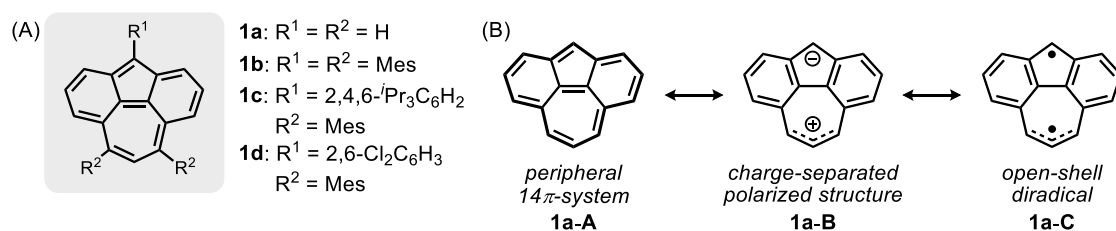
## Synthesis and Properties of Kinetically Stabilized Bis-periazulene Derivatives

(Graduate School of Engineering, Osaka University) ○Koki Horii, Akihito Konishi, Makoto Yasuda

**Keywords:** Bis-periazulene, Azulene, Non-alternant Hydrocarbon, Open-shell Character, Zwitterion

In polycyclic hydrocarbons (PAHs), the topological difference of the  $\pi$ -conjugation highly affects their electronic properties, such as aromaticity, redox ability and/or spin state.<sup>1</sup> For example, azulene, which is a non-alternant isomer of naphthalene, has engaged many chemists' attentions as a building block of  $\pi$ -extended molecules and as a great candidate of optoelectronics because of its deep blue color and polarized structure.<sup>2</sup> Bis-periazulene **1a**, a non-alternant isomer of pyrene, is theoretically predicted to be a Kekulé molecule with a triplet ground state due to a *m*-quinodimethane subunit.<sup>3</sup> Although many syntheses of **1a** or its derivatives have been attempted, they have not been achieved due to the difficulty in forming odd-membered rings and the lack of sufficient kinetic stabilization.<sup>4</sup>

In order to unveil the electronic structures of bis-periazulene, including the actual ground state, we designed kinetically stabilized derivatives **1b–d** (Figure 1A). The desired molecules **1b–d** were successfully synthesized in 8 steps using indium-catalyzed cyclization as a key step to construct a seven-membered ring. The structures of **1b–d** were fully characterized by X-ray crystallographic analyses. The electronic and magnetic measurements, and quantum chemical calculations of **1b–d** indicated that bis-periazulene **1a** contains three aspects of  $\pi$ -conjugation: peripheral 14 $\pi$ -system (**1a-A**), charge-separated polarized structure (**1a-B**) and open-shell  $\pi$ -conjugations (**1a-C**, Figure 1B). Due to the three aspects of  $\pi$ -conjugation of bis-periazulene, the introduced aryl groups affect the energy gap between the lowest singlet and triplet states. The details of the molecular structure and physical properties will be presented.



**Figure 1.** (A) Structure of bis-periazulene **1a–d**. (B) Resonance structure of bis-periazulene **1a**.

(1) (A) Tobe, Y. *Chem. Rec.* **2015**, *15*, 86. (B) A. Konishi, M. Yasuda, *Chem. Lett.* **2021**, *51*, 195. (2) Selected paper: H. Xin, B. Hou, X. Gao, *Acc. Chem. Res.* **2021**, *54*, 1737. (3) (A) P. Baumgartner, E. Weltin, G. Wagnière, E. Heilbronner, *Helv. Chim. Acta* **1965**, *48*, 751. (B) M. Nendel, B. Goldfuss, K. N. Houk, U. Grieser, K. Hafner, *Theor. Chem. Acc.* **1999**, *102*, 397. (4) (A) D. H. Reid, W. H. Stafford, J. P. Ward, *J. Chem. Soc.* **1955**, *84*, 1193. (B) R. Munday, I. O. Sutherland, *J. Chem. Soc. C* **1969**, 1427. (C) U. Grieser, K. Hafner, *Chem. Ber.* **1994**, *127*, 2307. (D) S. Das, J. Wu, *Org. Lett.* **2015**, *17*, 5854.



## 含窒素トリアンギュレンカチオンの合成と物性

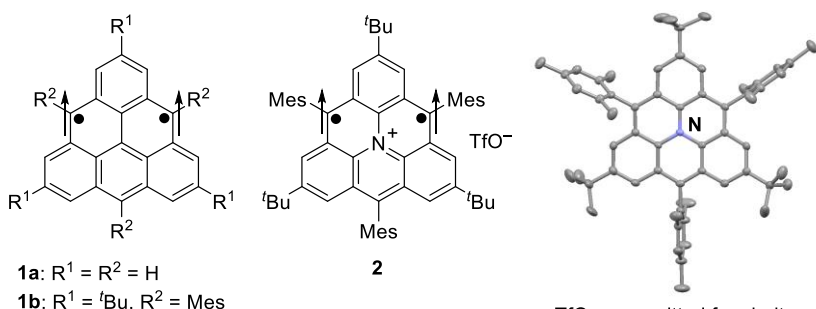
(阪大院基礎工<sup>1</sup>・阪市大院理<sup>2</sup>) ○有川 忍<sup>1</sup>・清水 章弘<sup>1</sup>・塩見 大輔<sup>2</sup>・佐藤 和信<sup>2</sup>・新谷 亮<sup>1</sup>

Synthesis and Properties of Nitrogen-doped Triangulene Cation (<sup>1</sup>Graduate School of Engineering Science, Osaka University, <sup>2</sup>Graduate School of Science, Osaka City University)  
Shinobu Arikawa,<sup>1</sup> Akihiro Shimizu,<sup>1</sup> Daisuke Shiomi,<sup>2</sup> Kazunobu Sato,<sup>2</sup> Ryo Shintani<sup>1</sup>

Triangulene (**1a**), known as Clar's hydrocarbon, is a molecule with a triplet ground state. We have recently synthesized and characterized a kinetically stabilized derivative **1b**.<sup>1</sup> On the other hand, introduction of heteroatoms into **1a** has attracted attention in recent years because of the modulation of electronic structure and the expression of specific properties.<sup>2</sup> However, hetero-triangulenes synthesized so far have a singlet ground state, and no triplet hetero-triangulene has been synthesized despite its usefulness as magnetic material. Herein, we synthesized and isolated a kinetically stabilized nitrogen-doped triangulene cation **2**. Magnetic measurements show that **2** has a triplet ground state with a large exchange interaction of unpaired electrons similar to **1b**. Electrochemical measurements show that **2** has higher oxidation and reduction potentials than **1b** due to the effect of the nitrogen atom.

**Keywords** : Triangulene; Triplet; Diradical; Cation; ESR

クラールの炭化水素として知られるトリアンギュレン (**1a**) は、基底三重項分子である。最近、我々は速度論的に安定化したトリアンギュレン誘導体 **1b** の単離と物性解明に成功している<sup>1</sup>。一方、**1a** に対するヘテロ原子の導入は、電子状態を変調し特異的な物性を発現するため、近年注目を集めている<sup>2</sup>。しかし、これまでに合成されたヘテロトリアンギュレンは基底一重項であり、磁性材料として有用な三重項ヘテロトリアンギュレンの合成はこれまで達成されていない。今回我々は、速度論的に安定化した含窒素トリアンギュレンカチオン **2** を合成・単離し、基礎的物性を明らかにした。磁気測定から、**2** は **1b** と同様に、不対電子の大きな交換相互作用をもつ基底三重項分子であることがわかった。また、電気化学測定では、窒素原子導入効果による **2** の酸化および還元電位の上昇が確認された。



- 1) Arikawa, S.; Shimizu, A.; Shiomi, D.; Sato, K.; Shintani, R. *J. Am. Chem. Soc.* **2021**, *143*, 19599.
- 2) Nakatsuka, S.; Gotoh, H.; Kinoshita, K.; Yasuda, N.; Hatakeyama, T. *Angew. Chem., Int. Ed.* **2017**, *56*, 5087.

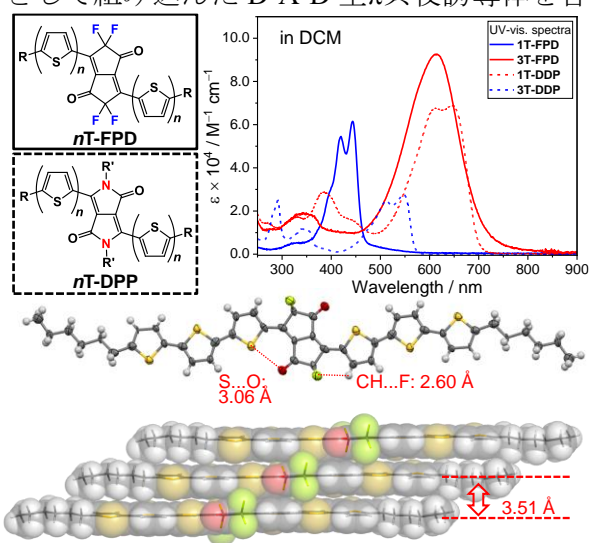
## フッ素化ペンタレンジオン誘導体の合成、物性ならびに半導体特性評価

(阪大産研) ○横山 創一・家 裕隆

Synthesis, Physical Properties, and Semiconductor Characteristics of Fluorinated Pentalene-1,4-dione Derivatives (*SANKEN, Osaka University*) ○Soichi Yokoyama, Yutaka Ie

It is well-known that D-A type  $\pi$ -conjugated molecules including diketopyrrolopyrrole (DPP) as an electron-accepting unit show high carrier mobility in its aggregate because of the strong D-A interaction in the packing structure. In this work, we designed and developed a fluorinated pentalene-1,4-dione (FPD) unit as a novel electron acceptor to enhance electron affinity and intra-/intermolecular interaction. Furthermore, we synthesized D-A type  $\pi$ -conjugated derivatives containing terminal oligothiophenes ( $n$ T) and the central FPD unit toward organic electronic materials, and investigated their photophysical/electrochemical properties, thermal properties, and packing structures. UV-vis absorption spectra of the **3T-FPD** with terthiophenes showed a large absorption band at 612 nm ( $\epsilon = 9.26 \times 10^4 \text{ M}^{-1}$ ) in dichloromethane, which is shorter absorption wavelength and higher molecular absorption coefficient compared to the corresponding **3T-DPP**. From the result of X-ray diffraction, **3T-FPD** molecule formed highly planar structure by intramolecular interaction and  $\pi$ - $\pi$  stacking structure derived from D-A intermolecular interaction. *Keywords*: Pentalenedione; Fluorinated compound;  $\pi$ -conjugated molecule; Diketopyrrolopyrrole; Organic Semiconductor

電子受容性ユニットであるジケトピロロピロール (DPP) は、D-A 型 $\pi$ 共役分子構造に組み込むことによって優れた電荷輸送特性を示すことから有機半導体材料への応用が期待されている。一方、DPP 中に含まれる電子豊富な窒素原子により、DPP 単体で見ると HOMO、LUMO 準位は決して深くはない。本研究では、DPP ユニット内の窒素原子を電子求引性である  $\text{CF}_2$  基に組み替えたフッ素化ペンタレンジオン (FPD) を設計し、アクセプターユニットとして組み込んだ D-A-D 型 $\pi$ 共役誘導体を合成し、その基礎物性ならびに半導体特性を評価した。FPD の両末端にターチオフェンを組み込んだ **3T-FPD** は、**3T-DPP** よりも短波長側に極大吸収波長 (612 nm,  $\epsilon = 9.26 \times 10^4 \text{ M}^{-1}$ ) を示した。単結晶 X 線構造解析結果から、**3T-FPD** は高い平面性を示し、 $\pi$ - $\pi$ スタッキング構造を形成した。また、このスタッキング内の移動積分は、ホール輸送に対して 118 meV、電子輸送に対して 49 meV と大きな値を示し、電荷輸送に対して有利に働くことが示唆された。



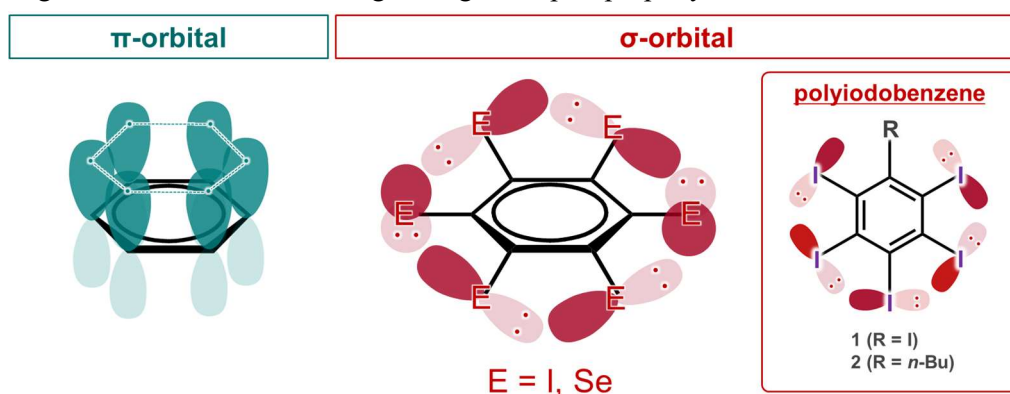
## $\sigma$ -Delocalized Orbitals and Charge-Transport Properties of Polyiodobenzenes

(Department of Chemistry, Graduate School of Science and Engineering, Saitama University) ○Yuki Takada; Shunsuke Furukawa; Masaichi Saito

**Keywords:** polyiodobenzene;  $\sigma$ -orbital interaction; OFET; charge transport

The major focus of organic semiconductors has been on  $\pi$ -conjugated molecules, and the origin of charge transport has been the interaction between  $\pi$ -orbitals (Figure 1, left). However, the intermolecular interactions of these compounds are constrained by planar extended  $\pi$ -orbitals, and the molecular packings are restricted to one-dimensional or two-dimensional manner. These molecular packing results in an anisotropy of charge transport, which suppresses efficient charge transport. In order to expand the dimensional diversity of charge transport, we have focused on cyclic delocalized orbitals with  $\sigma$ -symmetry (Figure 1, right). We hypothesized that this type of an orbital would contribute to the multi-dimensional charge transport thanks to the  $\sigma$ -delocalized orbital orthogonal to the conventional  $\pi$ -orbitals.

In this work, we have designed polyiodobenzenes **1** and **2** bearing more than five iodine atoms on a benzene platform as the target molecules and investigated their charge transport properties. Calculated reorganization energies and transfer integrals of these molecules indicated that the polyiodobenzenes possess a three-dimensional pathway for charge transport. Time-resolved microwave conductivity (TRMC) measurements of these compounds revealed that a photoconductivity of the polyiodobenzenes ( $5.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , for **1**,  $1.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , for **2**) is the same order as that of general organic semiconductors (e.g.  $6.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , for rubrene)<sup>1</sup>, suggesting that the molecules bearing  $\sigma$ -orbitals should have a high charge transport property.



**Figure 1.** Schematic drawings of a  $\pi$ -orbital (left) and a  $\sigma$ -orbital (right), and chemical structures of the target molecules **1** and **2**.

1) Okamoto, T.; Nakahara, K.; Saeki, A.; Seki, S.; Oh, J. H.; Akkerman, H. B.; Bao, Z.; Matsuo, Y. *Chem. Mater.* **2011**, *23*, 1646–1649.

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Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[K1-2pm] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Kenji Matsuda, Junpey Yuasa

Thu. Mar 24, 2022 2:00 PM - 3:40 PM K1 (Online Meeting)

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**[K1-2pm-01] Synthesis and characterization of curved perylene diimide derivatives and application for organic solar cell**<sup>○</sup>Keisuke Fujimoto<sup>1</sup>, Ayumu Takahashi<sup>1</sup>, Kazuki Yamada<sup>1</sup>, Seiichiro Izawa<sup>2</sup>, Masahiro Hiramoto<sup>2</sup>, Masaki Takahashi<sup>1</sup> (1. Shizuoka University, 2. Institute for Molecular Science)

2:00 PM - 2:20 PM

**[K1-2pm-02] Hole Collecting Monolayer Materials Based on Triazatruxene Skeleton for Efficient Perovskite Solar Cells**<sup>○</sup>Tsukasa Funasaki<sup>1</sup>, Lucas Ueberricke<sup>1</sup>, Wataru Nojo<sup>2</sup>, Minh Anh Truong<sup>1</sup>, Richard Murdey<sup>1</sup>, Takumi Yamada<sup>1</sup>, Tomoya Nakamura<sup>1</sup>, Shuaifeng Hu<sup>1</sup>, Yoshihiko Kanemitsu<sup>1</sup>, Takanori Suzuki<sup>2</sup>, Atsushi Wakamiya<sup>1</sup> (1. Institute for Chemical Research, Kyoto University, 2. Faculty of Science, Hokkaido University)

2:20 PM - 2:40 PM

**[K1-2pm-03] Synthesis, optical and singlet oxygen generation properties of phenazinone dyes**<sup>○</sup>Kazuki Ohira<sup>1</sup>, Masahiro Yamamoto<sup>1</sup>, Keiichi Imato<sup>1</sup>, Ichiro Imae<sup>1</sup>, Yousuke Ooyama<sup>1</sup> (1. Graduate School of Advanced Science and Engineering, Hiroshima University)

2:40 PM - 3:00 PM

**[K1-2pm-04] Ion-Pairing Assemblies of Activated Charged  $\pi$ -Electronic Systems**<sup>○</sup>Hiroki Tanaka<sup>1</sup>, Hiromitsu Maeda<sup>1</sup> (1. Ritsumeikan University)

3:00 PM - 3:20 PM

**[K1-2pm-05] Syntheses and aggregation properties of squalene receptors bearing ethylene glycol moieties**<sup>○</sup>TRAN NGOC LINH<sup>1</sup>, Takashi Arimura<sup>1</sup>, Kenichi Tominaga<sup>1</sup>, Hiroko Isoda<sup>1,2</sup>, Hideo Kigoshi<sup>2</sup> (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba)

3:20 PM - 3:40 PM

## 湾曲型ペリレンジイミド誘導体の合成・物性と有機太陽電池への応用

(静岡大工<sup>1</sup>・分子研<sup>2</sup>) ○藤本 圭佑<sup>1</sup>・高橋 歩<sup>1</sup>・山田 一機<sup>1</sup>・伊澤 誠一郎<sup>2</sup>・平本 昌宏<sup>2</sup>・高橋 雅樹<sup>1</sup>

Synthesis and Characterization of Curved Perylene Diimide Derivatives and Application for Organic Solar Cell (<sup>1</sup>*Faculty of Engineering, Shizuoka University*, <sup>2</sup>*Institute for Molecular Science*) ○Keisuke Fujimoto,<sup>1</sup> Ayumu Takahashi,<sup>1</sup> Kazuki Yamada,<sup>1</sup> Seichiro Izawa,<sup>1</sup> Masahiro Hiramoto,<sup>2</sup> Masaki Takahashi<sup>1</sup>

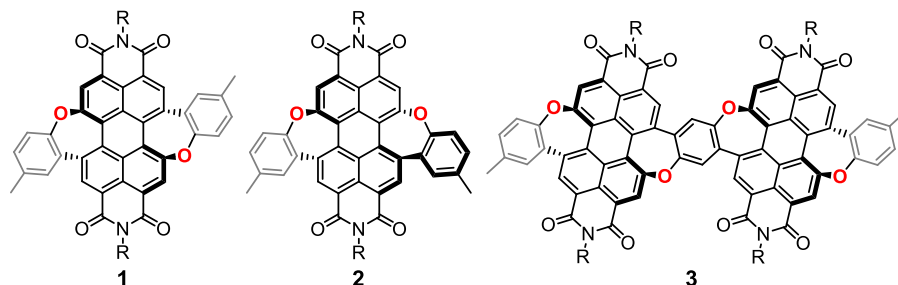
Curved perylene diimides **1** have been developed by attaching fused seven-membered rings at the bay positions<sup>1)</sup>. Owing to the curved structure, the perylene diimides showed high solubility despite the absence of bulky substituents.

In this work, we developed isomers **2** that possess different structural pattern of the seven-membered rings and dimers **3** fused with hydroquinone-based linker. For these compounds, we investigated the structural dynamics, photophysical properties, and performance as acceptor materials in a solution-processed bulk heterojunction organic solar cells.

**Keywords** : Perylene Diimide; Seven-membered Ring; Curved Structure; Organic Solar Cell

代表的な有機半導体材料であるペリレンジイミドは、溶解性が著しく低いため、誘導体合成や溶液プロセスへの応用には立体障害の大きな置換基の導入による可溶化が必要とされてきた。これに対し、最近我々は七員環構造を導入した湾曲型ペリレンジイミド **1** が立体障害を導入せずとも高い溶解性を示し、有機太陽電池のアクセプター材料として有望であることを明らかにした<sup>1)</sup>。

本研究では、新たな誘導体として七員環の向きの異なる異性体 **2** や二量体 **3** の合成を行った。化合物 **1** の円弧状湾曲構造とは対照的に、異性体 **2** は波状湾曲構造を示した。また、二量体 **3** は曲面構造の異なる二つの配座異性体をとることが明らかとなった。得られた化合物の会合特性や湾曲構造の動的挙動および光物理学的特性について構造—物性相関を調査するとともに、有機太陽電池のアクセプター材料としての応用を検討した。



1) K. Fujimoto, S. Izawa, A. Takahashi, T. Inuzuka, K. Sanada, M. Sakamoto, Y. Nakayama, M. Hiramoto, M. Takahashi, *Chem. Asian J.* **2021**, *16*, 690–695.

## トリアザトリキセン骨格を用いた高性能ペロブスカイト太陽電池の正孔回収単分子膜材料の開発

(京大化研<sup>1</sup>・北大院理<sup>2</sup>) ○舟崎 司<sup>1</sup>・ユーバリッケ ルーカス<sup>1</sup>・能條 航<sup>1,2</sup>・チョン ミンアン<sup>1</sup>・マーディー リチャード<sup>1</sup>・山田 琢允<sup>1</sup>・フ シュアイフエン<sup>1</sup>・中村 智也<sup>1</sup>・金光 義彦<sup>1</sup>・鈴木 孝紀<sup>2</sup>・若宮 淳志<sup>1</sup>

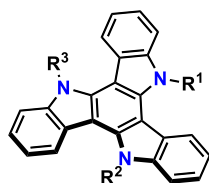
Hole Collecting Monolayer Materials Based on Triazatruxene Skeleton for Efficient Perovskite Solar Cells (<sup>1</sup>*Institute for Chemical Research, Kyoto University*, <sup>2</sup>*Department of Chemistry, Faculty of Science, Hokkaido University*) ○Tsukasa Funasaki,<sup>1</sup> Lucas Ueberricke,<sup>1</sup> Wataru Nojo,<sup>2</sup> Minh Anh Truong,<sup>1</sup> Richard Murdey,<sup>1</sup> Takumi Yamada,<sup>1</sup> Shuaifeng Hu,<sup>1</sup> Tomoya Nakamura,<sup>1</sup> Yoshihiko Kanemitsu,<sup>1</sup> Takanori Suzuki,<sup>2</sup> Atsushi Wakamiya<sup>1</sup>

The development of perovskite solar cells (PSCs) has been accompanied by an intensive search of suitable charge collecting materials. Compared to conventional organic hole collecting materials, monolayer materials are more suitable for scalable and stable PSCs due to their simple processing without the requirement of dopants. In this study, we designed and synthesized a series of triazatruxene derivatives bearing phosphonic anchoring groups for effective hole collecting monolayers (Figure 1). The PSCs using these hole collecting monolayers showed power conversion efficiencies of up to 23.0% (Figure 2). The detail molecular design, characterization as well as device evaluation will be discussed.

**Keywords:** Phosphonic Acid; Monolayer; Perovskite Solar Cells; *p*-Type Organic Semiconductors; Hole Collecting Material

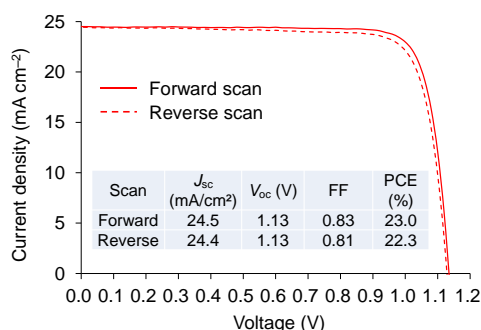
ペロブスカイト太陽電池の高性能化には、ペロブスカイト層で光吸収により生成する電荷を効率的に回収する半導体材料の開発が重要となっている。

本研究では、トリアザトリキセン骨格に金属酸化物表面への強い吸着力を有するホスホン酸が一つ、二つまたは三つ導入された一連の正孔回収材料の開発をおこなってきた (図 1)。これらをドーパントフリー正孔回収単分子膜材料として用いたペロブスカイト太陽電池は 23% の光電変換効率 (図 2) と共に優れた安定性を示すことがわかった。本発表では、分子のデザインからペロブスカイト太陽電池の作製と特性評価について詳細に報告する。



**1PATAT-C3:** R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = (CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>H<sub>2</sub>  
**2PATAT-C3:** R<sup>1</sup> = H, R<sup>2</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>H<sub>2</sub>  
**3PATAT-C3:** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>H<sub>2</sub>  
**3PATAT-C4:** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>4</sub>PO<sub>3</sub>H<sub>2</sub>

**Figure 1.** Chemical structures of synthesized hole-collecting materials.



**Figure 2.** *J*-*V* curves of the champion device based on 3PATAT-C3.



## フェナジノン系色素の合成, 光学特性と一重項酸素発生特性

(広島大院先進理工) ○大平 一輝・山本 真洋・今任 景一・今榮 一郎・大山 陽介  
 Synthesis, optical and singlet oxygen generation properties of phenazinone dyes (*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kazuki Ohira, Masahiro Yamamoto, Keiichi Imato, Ichiro Imae, Yousuke Ooyama

Phenazines as a heteroanthracene compound have been used as a functional dye in various applications such as optical sensors for metal ions and redox-responsive molecular switches. However, there are few studies that focus on its function as a photosensitizer (PS) possessing the ability to produce singlet oxygen ( $^1\text{O}_2$ ). Thus, in this study, we have designed and synthesized phenazine dyes **PZ1**, **PZ4** and **PZ5** and phenazinone dyes **PZ2**, **PZ6** and **PZ7**, and their photophysical and  $^1\text{O}_2$  generation properties have been investigated. Phenazinone dyes exhibit strong photoabsorption bands at 400–600 nm, and  $\Phi_\Delta$  of phenazinone dyes are superior to that of phenazine dyes. In particular, **PZ2** produced  $^1\text{O}_2$  quantitatively ( $\Phi_\Delta \approx 1$ ). In this presentation, we will discuss about the photophysical and  $^1\text{O}_2$  generation properties of **PZ1**–**7**.  
*Keywords* : Photosensitizers; Phenazinone skeleton; Singlet oxygen; Functional dye

ヘテロアントラセン化合物であるフェナジン骨格は、金属イオンの光学センサー、レドックス応答性分子スイッチなど様々な応用を見据えた機能性色素母体骨格として利用されてきたが、一重項酸素( $^1\text{O}_2$ )を生成する光増感色素(PS)としての開発はほとんどなされていない。本研究では、フェナジン系色素 **PZ1**、**PZ4** および **PZ5** と、分子内にカルボニル部位と 3 級アミノ部位を兼ね備えたフェナジノン系色素 **PZ2**、**PZ6** および **PZ7** を分子設計・合成し、それらの光学特性と  $^1\text{O}_2$  発生量子収率( $\Phi_\Delta$ )を調査した(図 1)。フェナジン系色素に比べて、フェナジノン系色素は 400–600 nm に強い光吸収帯を持ち、優れた  $\Phi_\Delta$  を示した。特に、**PZ2** はほぼ定量的に  $^1\text{O}_2$  を生成することがわかった( $\Phi_\Delta \approx 1$ )。本講演では、これらの化合物の光学特性および  $^1\text{O}_2$  発生特性について詳しく調査した結果を報告する。

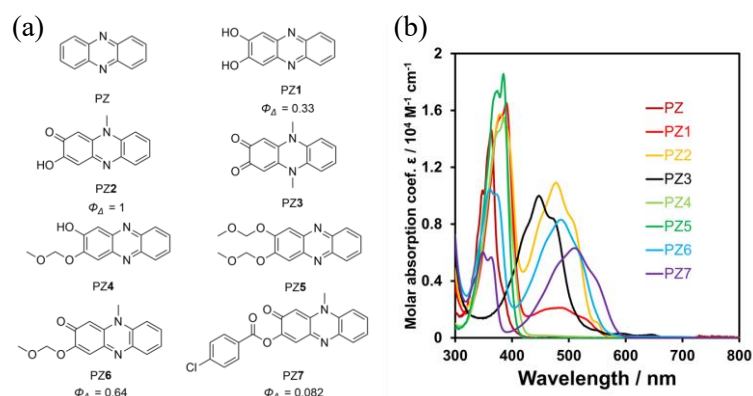


図 1. (a)フェナジン系色素 **PZ1**、**PZ4** および **PZ5** とフェナジノン系色素 **PZ2**、**PZ6** および **PZ7** の  $^1\text{O}_2$  発生量子収率( $\Phi_\Delta$ )と(b)THF 中における UV/vis 吸収スペクトル

## 活性化された荷電 $\pi$ 電子系のイオンペア集合化

(立命館大生命科学) ○田中 宏樹・前田 大光

Ion-Pairing Assemblies of Activated Charged  $\pi$ -Electronic Systems (*College of Life Sciences, Ritsumeikan University*) ○Hiroki Tanaka, Hiromitsu Maeda

$\pi$ -Electronic ion pairs are of interest for the fabrication of electronic materials, with potential ferroelectric and electric conductive properties, that use electrostatic and dispersion forces ( $i\pi-i\pi$  interaction) to produce dimension-controlled assemblies. In particular, porphyrin ions, which delocalize the charge in the core units, are suitable for the ordered arrangement and assemblies by ion pairing. In this study, charged porphyrins were found to form solid-state assemblies along with solution-state stacking ion pairs. Furthermore, the electronic states of the charged  $\pi$ -electronic systems were controlled, and the electron transfer by external stimuli such as light and solvents was suggested.

**Keywords :**  $\pi$ -electronic systems; porphyrin ions; ion pairs; electron transfer; radicals

荷電  $\pi$  電子系は静電力および分散力をおもな相互作用 ( $i\pi-i\pi$  相互作用) とし、溶液中で積層構造や、バルク状態における次元制御型集合体を形成することから、機能性材料の創製が可能である。<sup>1)</sup> 多様な周辺修飾が可能なポルフィリノイドに対し、電荷を完全に補償しない金属イオンの導入は、荷電  $\pi$  電子系の重要な形成戦略の一つである。そこで本研究では、ポルフィリンの  $\text{Au}^{\text{III}}$  錯体<sup>2)</sup>やメゾヒドロキシポルフィリンの脱プロトン体<sup>3)</sup>を導入したイオンペアを合成し、適切な置換基導入による機能発現および集合化を検討した (Figure 1)。溶液中における積層イオンペアの形成が、環電流効果と対イオンの近接に起因した  $^1\text{H}$ NMR 化学シフトから示唆された。さらに、荷電  $\pi$  電子系の電子状態を制御し、光や溶媒などの外部刺激による電子移動が示唆された (Figure 2)。<sup>4)</sup>

Figure 1

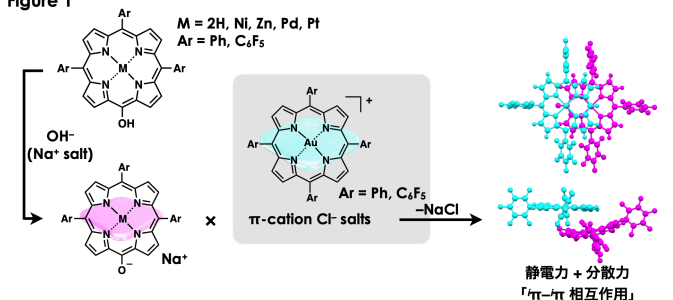
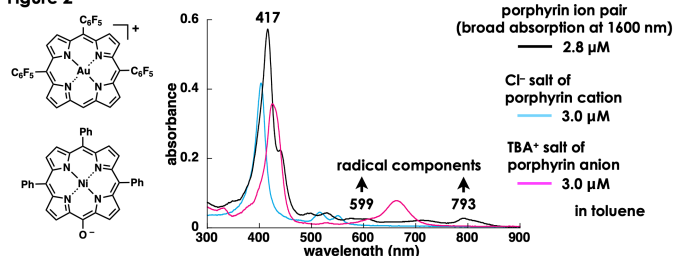


Figure 2



1) (a) Haketa, Y. et al. *Mol. Syst. Des. Eng.* **2020**, 5, 7571; (b) Yamasumi, K. et al. *Bull. Chem. Soc. Jpn.* **2021**, 94, 2252; (c) Yamasumi, K. et al. *J. Synth. Org. Chem. Jpn.* **2022**, 80(3), in press.

2) (a) Haketa, Y. et al. *iScience* **2019**, 14, 241; (b) Tanaka, H. et al. *Chem. Asian J.* **2019**, 14, 2129.

3) (a) Sasano, Y. et al. *Dalton Trans.* **2017**, 46, 8924; (b) Sasano, Y. et al. *Chem. Eur. J.* **2019**, 25, 6712; (c) Sasano, Y.; Tanaka, H. et al. *Chem. Sci.* **2021**, 12, 9625.

4) Tanaka, H. et al. to be submitted.



## エチレングリコール基を有するスクアレンレセプターの合成と会合特性

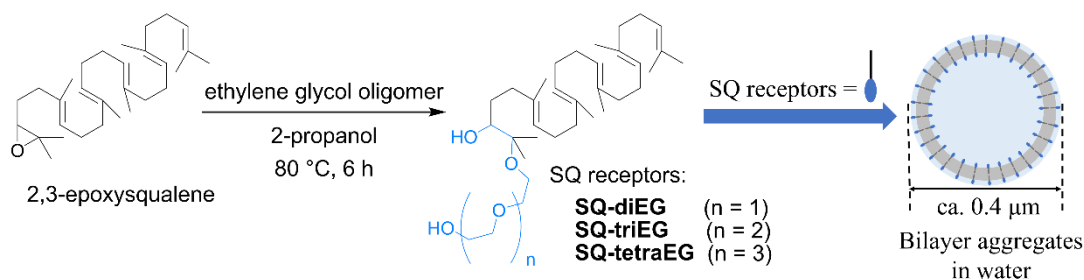
(産総研<sup>1</sup>・筑波大<sup>2</sup>) ○Tran Ngoc Linh<sup>1</sup>・有村 隆志<sup>1,2</sup>・富永 健一<sup>1,2</sup>・磯田 博子<sup>1,2</sup>・木越 英夫<sup>2</sup>

Syntheses and aggregation properties of squalene receptors bearing ethylene glycol moieties (<sup>1</sup> *National Institute of Advanced Industrial Science and Technology*, <sup>2</sup> *University of Tsukuba*)  
○Tran Ngoc Linh,<sup>1</sup> Takashi Arimura,<sup>1,2</sup> Tominaga Kenichi,<sup>1,2</sup> Hiroko Isoda,<sup>1,2</sup> Hideo Kigoshi,<sup>2</sup>

New squalene (SQ) receptors bearing open chain ethylene glycol (EG) oligomers (**SQ-diEG**, **SQ-triEG**, **SQ-tetraEG**) were synthesized by addition reaction of 2,3-epoxysqualene and the corresponding EG oligomers. We first determined stoichiometries and association constants of SQ receptors to metal ions in solution and revealed that EG oligomer moieties selectively associated to alkaline earth metal ions. Because SQ receptors have both hydrophobic SQ moieties and hydrophilic EG moieties, they could self-assemble into aggregates in water. So that, we also investigated their self-assembly behavior in water such as critical aggregation concentration and size and shape of the aggregates, using fluorescence spectral studies, laser diffraction particles size-based analyzes, scanning electron microscopy, and cryogenic transmission electron microscopy. SQ receptors showed interesting aggregation behavior and the presence of alkaline earth metal ions obviously affected to the aggregates.

**Keywords** : Squalene; Ethylene Glycol; Amphiphilic; Aggregation; Vesicle

スクアレンは、サメの肝油やオリーブオイルに含まれており、種々の生体機能が期待されている<sup>1)</sup>。本研究では、スクアレンを極性溶媒に可溶にするために、エチレングリコール基を有するスクアレンレセプター (**SQ-diEG**, **SQ-triEG**, **SQ-tetraEG**) を、2,3-エポキシスクアレン<sup>2)</sup>を出発原料として初めて合成した<sup>3)</sup>。水溶液中での会合挙動を調べたところ、直径凡そ 400 nm の球状の自己集合体を形成することをレーザ回折式粒径分布測定で明らかにした。さらに、電子顕微鏡観察により、スクアレンレセプターはミセルでなく、ラージベシクル構造の自己集合体を形成することを明らかにした。本講演では、自己組織化の特性、例えば、臨界集合濃度、さらにアルカリ土類金属イオンに応答して集合体の形状・サイズを変化させる現象についても説明する。



1) H. Gylling, T. A. Miettinen, *Atherosclerosis*, **1994**, 106, 169.

2) E. E. Van Tamelen, T. J. Curphey, *Tetrahedron Letters*, **1962**, 3, 121.

3) T. N. Linh, T. Arimura, et al., *Supramolecular Chemistry*, **2021**, DOI: 10.1080/10610278.2021.1970161

## [H201-2am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kouki Oka, Koji Harano

Thu. Mar 24, 2022 9:00 AM - 11:20 AM H201 (Online Meeting)

### [H201-2am-01] A strategy for obtaining supramolecular polymers dispersed in single molecular width

○Takuma Shimada<sup>1,2</sup>, Masayuki Takeuchi<sup>1</sup>, Kazunori Sugiyasu<sup>3</sup> (1. NIMS, 2. Kyushu Univ. Grad. Sch. Eng., 3. Kyoto Univ. Grad. Sch. Eng.)

9:00 AM - 9:20 AM

### [H201-2am-02] Dissecting Self-folding Process of Curved Supramolecular Polymers

○Atsushi Isobe<sup>1</sup>, Shiki Yagai<sup>2</sup> (1. Graduate School of Science and Engineering, Chiba University, 2. Institute for Global Prominent Research, Chiba University)

9:20 AM - 9:40 AM

### [H201-2am-03] Fabrication of a Large-Area and Highly-Uniform Proton-Conducting Nanofilm by Self-Assembly via Hydrogen-Bonding

○Hikaru Uchida<sup>1</sup>, Prince Ravat<sup>1</sup>, Ryosuke Sekine<sup>1</sup>, Ko Kamei<sup>1</sup>, Akihisa Yamamoto<sup>2</sup>, Oleg Konovalov<sup>3</sup>, Motomu Tanaka<sup>2,4</sup>, Teppei Yamada<sup>1</sup>, Koji Harano<sup>1</sup>, Eiichi Nakamura<sup>1</sup> (1. The University of Tokyo, 2. Kyoto University, 3. European Synchrotron Radiation Facility, 4. Heidelberg University)

9:40 AM - 10:00 AM

### [H201-2am-04] Construction of Core-Shell Block Co-Crystals Composed of Different Spin-Crossover Metal Complexes

○Tomoya Fukui<sup>1,2</sup>, Masahiro Tsuchiya<sup>1,2</sup>, Takanori Fukushima<sup>1,2</sup> (1. Lab. Chem. Life Sci., Tokyo Tech, 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

10:00 AM - 10:20 AM

### [H201-2am-05] Control of Aggregation Pathway and Self-Assembled Morphology by Partial Disabling of Hydrogen-bonding Group

○Takumi Aizawa<sup>1</sup>, Shiki Yagai<sup>2</sup> (1. Chiba University, 2. Chiba University IGPR)

10:20 AM - 10:40 AM

### [H201-2am-06] Creation of Highly Reactive Supramolecular Polymers Toward Hierarchical Self-assembly

○Chisako Kanzaki<sup>1</sup>, Yoshihiro Kikkawa<sup>2</sup>, Munenori Numata<sup>1</sup> (1. Grad. Sch. Life and Env. Sci., Kyoto Pref. Univ., 2. AIST)

10:40 AM - 11:00 AM

### [H201-2am-07] Multistep synthesis of supramolecular block concentric toroids

○Norihiko Sasaki<sup>1</sup>, Masayuki Takeuchi<sup>1</sup>, Kazunori Sugiyasu<sup>2</sup> (1. National Institute for Materials Science, 2. Grad. Sch. Eng., Kyoto Univ.)

11:00 AM - 11:20 AM

## A strategy for obtaining supramolecular polymers dispersed in single molecular width

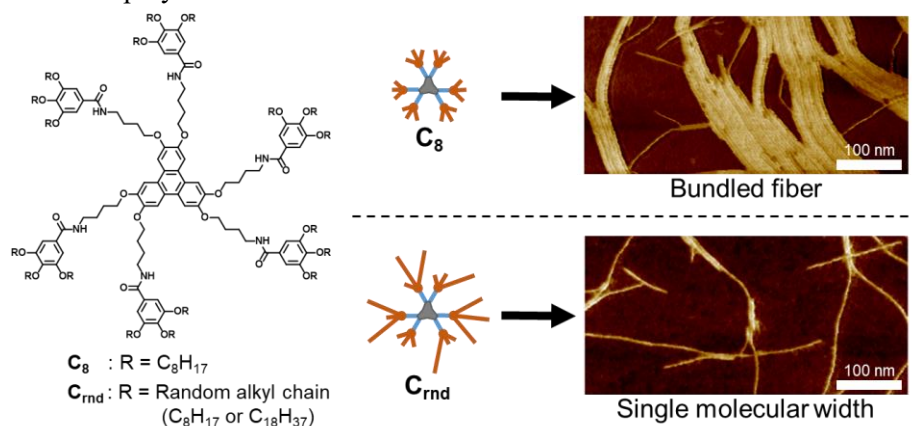
(1. NIMS, 2. Kyushu Univ. Grad. Sch. Eng., 3. Kyoto Univ. Grad. Sch. Eng.) ○Takuma Shimada<sup>1,2</sup>, Masayuki Takeuchi<sup>1</sup>, Kazunori Sugiyasu<sup>3</sup>

**Keywords:** Supramolecular polymer, Triphenylene, Self-assembly, Bundling

Although a rational monomer design for controlled supramolecular polymerization has been established,<sup>1</sup> and higher order nanostructures such as fibers, helices, toroids, spirals, nanosheets, etc. can nowadays be created,<sup>2</sup> it is still difficult to control interaction between these nanostructures. For example, even in the simplest case of the formation of one-dimensional (1D) supramolecular polymeric chains, interchain interaction cannot be controlled, often giving rise to a heavily bundled state. As a result, highly concentrated solution of supramolecular polymers results in gels and precipitates, which hinders to investigate long-term dynamics and rheological properties of a supramolecular polymer.

In this study, we designed and synthesized two triphenylene-based monomers bearing six amide groups and eighteen alkyl chains at the periphery of the triphenylene core. In one form of the monomers (compound **C<sub>8</sub>**), octyl chains were used as the alkyl chains, while in another form, octyl and octadecyl chains were randomly introduced to the eighteen positions (**C<sub>rnd</sub>**).

We investigated the bundling of supramolecular polymers in solutions. Atomic force microscopy (AFM) measurements immediately revealed that the supramolecular polymers of **C<sub>8</sub>** are bundled. In clear contrast, the bundling of supramolecular polymers of **C<sub>rnd</sub>** was obviously suppressed. We infer that randomly introduced longer octadecyl chains decreased cohesive energies between the supramolecular polymers and/or prevented secondary nucleation at the surface of the supramolecular polymers. In the presentation, we will discuss supramolecular polymerization mechanism, and the characterization and solution properties of the supramolecular polymers of **C<sub>8</sub>** and **C<sub>rnd</sub>**.



- 1) K. Sugiyasu, *Polym. J.*, **2021**, 53, 865.
- 2) S. Datta, S. Takahashi, S. Yagai, *Acc. Mater. Res.* **2022**, ASAP.

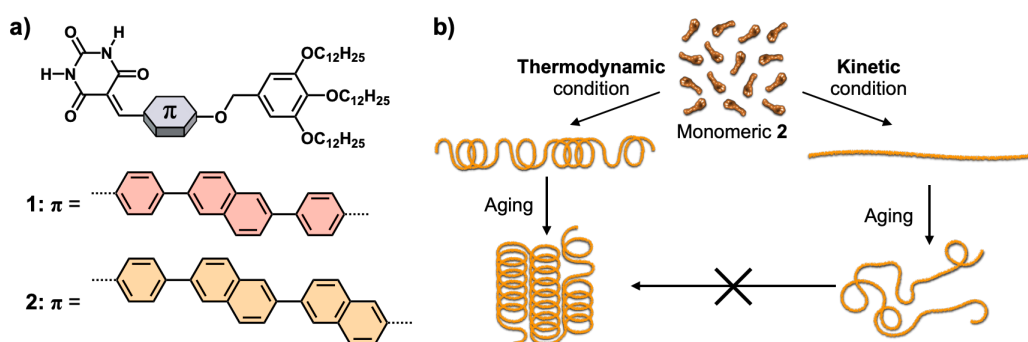
## Dissecting Self-folding Process of Curved Supramolecular Polymers

(<sup>1</sup>Graduate School of Science and Engineering, Chiba University, <sup>2</sup>Institute for Global Prominent Research (IGPR), Chiba University) ○Atsushi Isobe,<sup>1</sup> Shiki Yagai<sup>2</sup>

**Keywords:** Supramolecular polymer; Supramolecular polymerization; Folding; Kinetic control; High order structure

Intrachain folding of proteins enables their main chains to form specific high-order structures, which are essential for biological functions.<sup>1</sup> For supramolecular polymers (SPs), one-dimensional molecular assemblies formed through non-covalent bonds, replicating the folding remains challenging due to difficulty in embedding additional interaction sites that can guide folding the main chains.<sup>2</sup> Our group reported that barbituric acid-incorporated derivative **1** can form hydrogen-bonded macrocycles (rosettes), and the resultant rosettes stack via  $\pi$ - $\pi$  interaction to afford SPs with helically folded (helicoidal) and randomly coiled domains in a main chain. Interestingly, upon aging the SPs solution, highly folded helicoids can be obtained through self-folding process of randomly coiled domains by using helicoidal domains as template to result in highly folded helicoidal SPs.<sup>3</sup>

Based on the above study, we herein newly synthesized and explored self-assembly of compound **2** possessing two naphthalene rings (Figure 1a). Under thermodynamic condition achieved by temperature-controlled protocol, **2** formed highly folded helicoidal SPs through self-folding similarly to **1** (Figure 1b, left). On the other hand, kinetic condition by rapid solvent mixing protocol afforded linearly extended fibers (Figure 1b, right). Time-dependent AFM observations and spectroscopic measurements demonstrated that the linear fibers could partially self-fold to form curved domains but via a complex process. We discuss these two distinct self-folding processes of the SPs obtained from **2**.



**Figure 1.** a) Chemical structure of compound **1** and **2**. b) Schematic representation of folding processes of SPs obtained from **2**.

1) C. M. Dobson, *Nature* **2003**, 426, 884. 2) T. F. A. de Greef, E. W. Meijer et al., *Chem. Rev.*, **2009**, 109, 5687. 3) D. D. Prabhu, S. Yagai et al., *Sci. Adv.*, **2018**, 4, eaat8466.

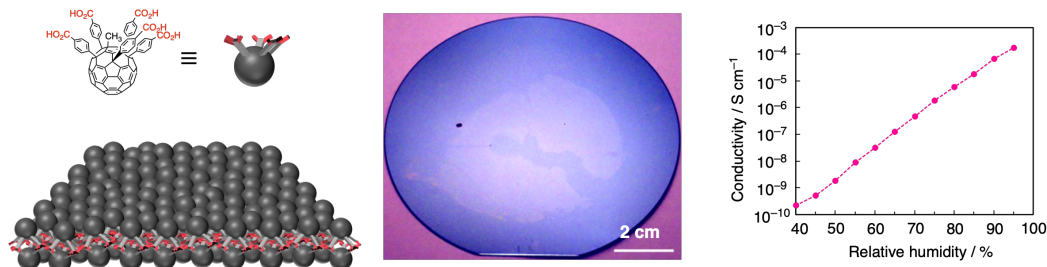
# Fabrication of a Large-Area and Highly-Uniform Proton-Conducting Nanofilm by Self-Assembly via Hydrogen-Bonding

(<sup>1</sup>Department of Chemistry, The University of Tokyo, <sup>2</sup>Institute for Advanced Study, Kyoto University, <sup>3</sup>European Synchrotron Radiation Facility, <sup>4</sup>Heidelberg University) ○Hikaru Uchida,<sup>1</sup> Prince Ravat,<sup>1</sup> Ryosuke Sekine,<sup>1</sup> Ko Kamei,<sup>1</sup> Akihisa Yamamoto<sup>2</sup>, Oleg Kononov<sup>3</sup>, Motomu Tanaka<sup>2,4</sup>, Teppei Yamada<sup>1</sup>, Koji Harano<sup>1</sup>, Eiichi Nakamura<sup>1</sup>

**Keywords:** 2D organic nanofilm, Hydrogen bond, Supramolecular polymer, Fullerene, Proton conduction

Two-dimensional (2D) nanofilms are of wide interest due to their specific structures and properties. For practical use of 2D materials, large-area synthesis, high uniformity, and precise thickness control are critical issues. However, the ideal synthetic design of nanofilms has been in a difficult situation. In this work, we designed an entangled hydrogen-bonding network to form a 2D reverse bilayer structure from a conical fullerene amphiphile (CFA)<sup>1</sup> with five carboxylic groups, which were capable of intermolecular hydrogen-bonding interaction. Herein, we report the fabrication of a self-assembled fullerene film (FF) with a large area and high uniformity by air/water interface synthesis, precise control of thickness, and 2D proton conduction.<sup>2</sup>

FF was fabricated from CFA solution (toluene/1-butanol = 3/1) by placing it on a water surface and by evaporating, and capable of being transferred onto various substrates. FF was obtained as a 3.0-nm thick nanofilm revealed by atomic force microscopy analysis. X-ray reflectivity analysis of FF on the water surface confirmed reversed bilayer structure, in which carboxylic groups face to the inside of the nanofilm, indicating the formation of bilayer structure via hydrogen-bonding interaction between CFA. Precise and facile control of the thickness of FF was also performed by changing concentration or by transferring one by one. FF was clearly visualized on SiO<sub>2</sub>/Si substrate, and the area was evaluated as ca. 30 cm<sup>2</sup>. Visible light reflection measurement at some points on FF was also performed to confirm high uniformity in a large area. In addition, relative humidity-dependent conduction measurement indicated high proton conduction via a 2D hydrogen-bonding network.



1) Y.-W. Zhong et al. *Org. Lett.* **2006**, 8, 1463. 2) P. Ravat et al. *Adv. Mater.* DOI:10.1002/adma.202106465.

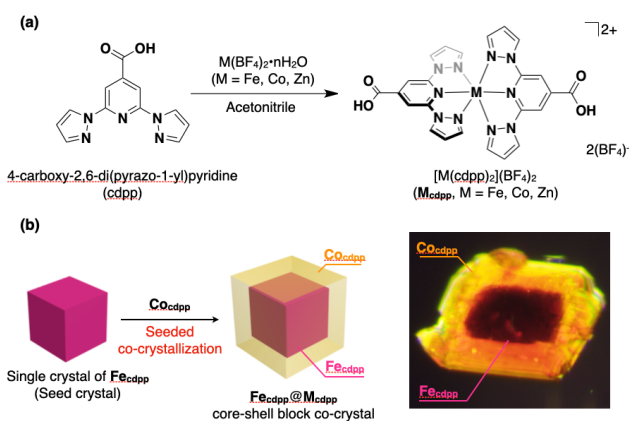
## 異種スピנקロスオーバー錯体からなるコアシェル型ブロック共結晶の構築

(東工大化生研<sup>1</sup>・東工大物質理工<sup>2</sup>) ○福井 智也<sup>1,2</sup>・土屋 雅弘<sup>1,2</sup>・福島 孝典<sup>1,2</sup>  
 Construction of Core-Shell Block Co-Crystals Composed of Different Spin-Crossover Metal Complexes (<sup>1</sup>Lab. Chem. Life Sci., Tokyo Tech., <sup>2</sup>Sch. Mater. and Chem. Tech., Tokyo Tech.)  
 ○Tomoya Fukui,<sup>1,2</sup> Masahiro Tsuchiya,<sup>1,2</sup> Takanori Fukushima<sup>1,2</sup>

As exemplified by block-co-polymers, block structures composed of different materials are expected to lead to synergic functions, which are not achieved by single-component systems. Here we focus the preparation of block co-crystals with two different compartments of spin-crossover metal complexes. For this purpose, here we chose spin crossover Fe(II) and Co(II) complexes with 2,6-dipyrazolylpyridine ligands and successfully obtained core-shell block co-crystals by selective growth of a crystalline segment of the Co(II) complex from a seed crystal of the Fe(II) complex.

**Keywords :** Block Structure; Core-Shell Block Co-Crystal; Seeded Crystallization; Spin Crossover; Hydrogen Bond

ブロックコポリマーに代表されるように、異種物質が連結されたブロック構造体は、単成分系では得られない相乗的な機能を発現することが期待されている。我々は、バルクなスケールの異種結晶をコンパートメントとして接合したブロック共結晶を構築し、各ブロック固有の性質がシナジーした新機能創出を目指す研究を展開している。今回我々は、温度や光といった外部刺激により低スピン状態と高スピン状態を可逆に変換可能なスピנקロスオーバー錯体を用い、異種金属錯体分子からなる結晶がヘテロ接合したブロック共結晶の作製について検討した。種々の検討の結果、Fe(II) 錯体の結晶を種として逐次的に Co(II) 錯体を結晶化することによって、Fe(II) 錯体結晶をコア、Co(II) 錯体結晶をシェルとする Fe(II)@Co(II) コアシェル型ブロック共結晶の作製に成功したので報告する。



図(a) 本研究に用いたスピנקロスオーバー錯体. (b) Fe(II)@Co(II) コアシェル型ブロック共結晶の作製と偏光顕微鏡像.



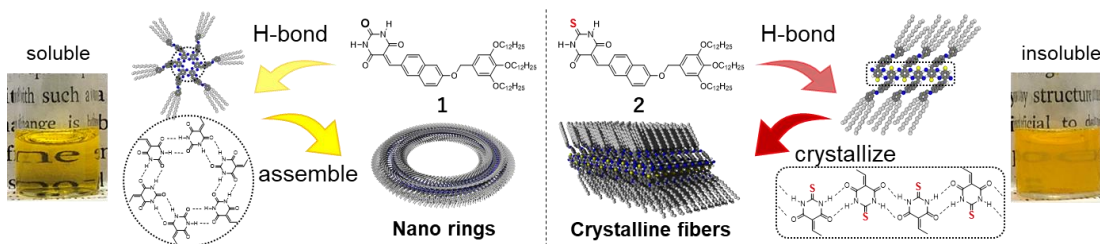
## Control of Aggregation Pathway and Self-Assembled Morphology by Partial Disabling of Hydrogen-bonding Group

(<sup>1</sup>Graduate School of Science and Engineering, Chiba University, <sup>2</sup>Institute for Global Prominent Research, Chiba University,) ○Takumi Aizawa,<sup>1</sup> Shiki Yagai<sup>2</sup>

**Keywords:** Hydrogen-bonding; Supramolecular Polymer; Self-assembly; Thiocarbonyl Group; Barbituric Acid

Hydrogen bond is one of the reliable noncovalent interactions to achieve controlled supramolecular assembly. However, for even those systems with highly directional multiple hydrogen bonding, polymorphism often results.<sup>1a</sup> A particular example is the crystalline polymorphism of barbiturate compounds showing characteristic hydrogen-bonded structures.<sup>1b</sup> In contrast, we have developed unique barbiturate supramolecular assemblies from barbituric acid-functionalized (barbiturated)  $\pi$ -conjugated molecules such as **1** (Figure 1, left) through hydrogen-bonded cyclic hexamers (rosettes).<sup>2</sup> The rosettes stack through  $\pi$ - $\pi$  interactions to provide supramolecular polymers with intrinsic curvature. The formation of the classical tape-like hydrogen-bonded motifs might be involved in the supramolecular polymerization process, but it is elusive due to strong aggregation trend of rosettes.<sup>3</sup> If the selective formation of tape-like hydrogen bonds is achieved by a structural modification of barbiturate units, we can make distinct materials from the same  $\pi$ -conjugated molecules. As the formation of rosette requires the hydrogen-bonding on C=O group at position 2 of barbiturate unit,<sup>4</sup> in this study we synthesized compound **2** as a 2-thiobarbituric acid analogue of **1** with the expectation that the weaker hydrogen-bonding ability of the C=S group at position 2 disable rosette formation.

Based on XRD and microscopic techniques, we show that **2** form crystalline fibers through the formation of the tapelike motif. (Figure. 2, right). We also applied computational approaches to explain selective formation of tapelike aggregates at the level of hydrogen-bonding.



**Figure 1.** Schematic illustrations of this study.

[1] (a) M. Wehner, F. Würthner et al., *J. Am. Chem. Soc.* **2019**, *141*, 6092–6107; (b) J. Bernstein, *Acta Crystallogr. Sect. B* **1991**, *47*, 1004 – 1010; [2] S. Yagai et al., *Acc. Chem., Res.* **2019**, *52*, 1325–1335; [3] A. Isobe, T. Aizawa, S. Yagai et al., *Chem. Eur. J.* **2020**, *26*, 8997–9004; [4] J. C. McDonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383–2420.

## 階層構造化がプログラムされた高活性な超分子ポリマーの創製

(京都府大院<sup>1</sup>・産総研<sup>2</sup>) ○神崎 千沙子<sup>1</sup>・吉川 佳広<sup>2</sup>・沼田 宗典<sup>1</sup>

Creation of Highly Reactive Supramolecular Polymers Toward Hierarchical Self-assembly

(<sup>1</sup>Graduate School of Life and Environmental Sciences, Kyoto Prefectural University,

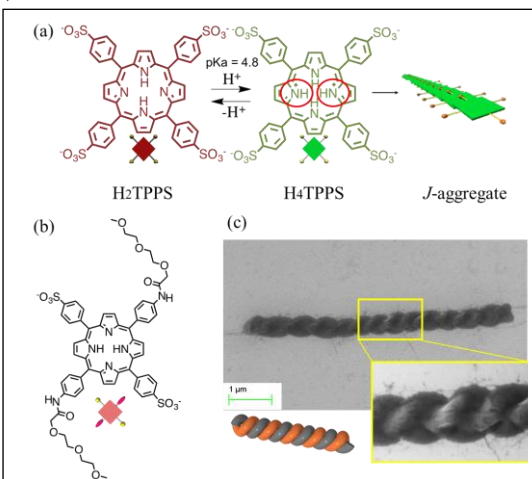
<sup>2</sup>National Institute of Advanced Industrial Science and Technology) ○Chisako Kanzaki,<sup>1</sup> Yoshihiro Kikkawa,<sup>2</sup> Munenori Numata<sup>1</sup>

In artificial supramolecular systems, molecular assemblies occur generally under thermodynamic processes and structural varieties of the resultant assemblies are restricted. Herein, we demonstrate that the use of microflow system to precisely regulate the self-assembling field enables control over the pathway for kinetic self-assembly processes. In the present study, we demonstrated that the porphyrin molecules spontaneously self-assembled in microflow space, thus leading to the creation of metastable supramolecular polymers.

**Keywords :** Supramolecular structures; Kinetic control; Supramolecular polymerization; Microflow; Non-equilibrium

複雑性と階層性を内在した超分子材料を創製するためには、階層を縦断した分子間力の数と位置の精密制御が必要である。我々はこの課題に挑戦するため、マイクロフロー空間を超分子反応場とすることで、分子間力を流れによって速度論的に制御できる独自の分子集積システムを確立してきた。これまでプロトン ( $H^+$ ) 化を鍵として超分子会合を引き起こす既知の Tetrakis(4-sulfonatophenyl)porphyrin (TPPS) をモデル分子とすることで、マイクロフロー空間における定常的な流れが速度論的な分子会合を引き起こすことを報告している (Fig. 1a)<sup>1)</sup>。本研究では、TPPS の4つのスルホン酸のうち、対角 (trans) に位置する2つをエチレングリコール部位に置き換えた新規 TPPS 誘導体 (trans- $H_2$ TPPS<sub>2</sub>-NH-EG<sub>2</sub>) の設計・合成を行い、その会合挙動を精査した (Fig. 1b)。trans- $H_2$ TPPS<sub>2</sub>-NH-EG<sub>2</sub> のメタノール溶液と HCl 水溶液をマイクロフロー空間で混合したところ、通常共会合し得ない非  $H^+$  体と  $H^+$  体が共会合した超分子ポリマーが得られた。マイクロフロー空間で起こる迅速かつ均質な溶液混合が  $H^+$  化と疎水相互作用を著しく促進した結果であると考えられる。さらに、この共会合超分子ポリマーは自発的に  $\mu m$  サイズの二重らせん構造へと組織化することが解った (Fig. 1c)。この高活性超分子ポリマーの創製とその階層化のメカニズムについて詳細に報告する。

1) C. Kanzaki, *et al*, *Bull. Chem. Soc. Jpn.*, **2021**, 94, 579-589.



**Fig. 1.** (a) Structure of TPPS. (b) Structure of trans- $H_2$ TPPS<sub>2</sub>-NH-EG<sub>2</sub>. (c) Scanning electron microscopy image of the resultant supramolecular double helix fiber.



## 超分子ブロック同心円トロイドの多段階合成

(物材機構<sup>1</sup>・京大院工<sup>2</sup>) ○佐々木 紀彦<sup>1</sup>・竹内 正之<sup>1</sup>・杉安 和憲<sup>2</sup>

Multistep synthesis of supramolecular block concentric toroids (<sup>1</sup>National Institute for Materials Science, <sup>2</sup> Graduate School of Engineering, Kyoto University) ○Norihiko Sasaki,<sup>1</sup> Masayuki Takeuchi,<sup>1</sup> Kazunori Sugiyasu<sup>2</sup>

Many unique supramolecular nanostructures formed by self-assembly have been reported<sup>1</sup>. The functions and properties of supramolecular polymers are closely related to the nanostructure<sup>2</sup>, so it is important to control the formation of the nanostructure; although it remains a significant challenge. Previously, we have synthesized supramolecular concentric toroids consisting of a zinc porphyrin **6FZn** which has fluorinated side chains through molecular self-assembly (Fig. a). Furthermore, it was possible to control the area of supramolecular concentric toroids<sup>3</sup>. In this study, we succeeded in creating the supramolecular block concentric toroids using a new copper porphyrin monomer **6FCu** (Fig. b).

**Keywords:** Self-assembly; Porphyrin; Supramolecular polymer; Concentric toroid; Supramolecular block copolymer

超分子集合体の機能や物性は、その形状、大きさ、組成などに依存するため、超分子集合体の精密合成は重要である<sup>1,2</sup>。しかしながら、分子間相互作用と超分子集合体の構造や形成メカニズムの相関は非常に複雑であり、超分子集合体の構造を自在に制御することは未だ難しい課題である。以前、我々はフルオロアルキル基を修飾した亜鉛ポルフィリン分子 **6FZn** を用いた超分子重合により、超分子同心円トロイドの精密合成を報告した(Fig. a)<sup>3</sup>。今回、新たに銅ポルフィリン分子 **6FCu** を合成し、各種分子を用いた多段階合成により、超分子ブロック同心円トロイドの精密合成を達成した(Fig. b)。本発表では多段階合成による超分子集合体の精密制御について報告する。

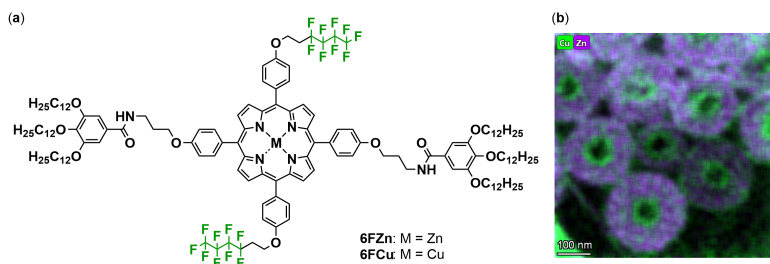


Figure (a) ポルフィリン誘導体の分子構造 (b) **6FZn** および **6FCu** からなる超分子ブロック同心円トロイドの TEM-EDS 元素マッピング像

1) T. Aida, E. W. Meijer, S. I. Stupp. *Science* **2012**, 335, 813. 2) A. K. Pearce, T. R. Wilks, M. C. Arno, R. K. O'Reilly. *Nat. Rev. Chem.* **2020**, 5, 21. 3) N. Sasaki *et al.* *Nat. Commun.* **2020**, 11, 3578.

## [K6-2am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Koichi Mitsudo, Toshiki Nokami

Thu. Mar 24, 2022 9:00 AM - 11:20 AM K6 (Online Meeting)

### [K6-2am-01] Synthesis and Electrochemical Properties of Pillar[6]quinone

○Tomoki Hirohata<sup>1</sup>, Naoki Shida<sup>2</sup>, Tomoki Ogoshi<sup>3</sup>, Ikuyoshi Tomita<sup>1</sup>, Shinsuke Inagi<sup>1,4</sup> (1. Tokyo Institute of Technology, 2. Yokohama National Univ., 3. Kyoto Univ., 4. JST PRESTO)  
9:00 AM - 9:20 AM

### [K6-2am-02] Electrochemical Post-functionalization of Poly(3-(2-ethylhexyl)thiophene) Facilitated by Forming the Ordered Structure

○Tomoyuki Kurioka<sup>1</sup>, Takahiro Komamura<sup>1</sup>, Naoki Shida<sup>2</sup>, Teruaki Hayakawa<sup>1</sup>, Ikuyoshi Tomita<sup>1</sup>, Shinsuke Inagi<sup>1,3</sup> (1. Sch. Mater. & Chem. Tech., Tokyo Tech., 2. Grad. Sch. Eng., Yokohama National University, 3. JST PRESTO)  
9:20 AM - 9:40 AM

### [K6-2am-03] Synthesis of Precursors of Chitin Oligosaccharides by Electrochemical Glycosylation Polymerization

○Azadur Md Rahman<sup>1</sup>, Kana Kuroda<sup>1</sup>, Tomoaki Hamada<sup>2</sup>, Hiraku Sakai<sup>2</sup>, Toshiki Nokami<sup>1</sup> (1. Tottori University, 2. Koganei Corporation)  
9:40 AM - 10:00 AM

### [K6-2am-04] Formation of Sterically Congested C-N bonds by Electrochemical Reductive Coupling of Amines and $\alpha$ -Bromo Carboxamides

○Titli Ghosh<sup>1</sup>, Hazuki Kaizawa<sup>1</sup>, Takashi Nishikata<sup>2</sup>, Toshiki Nokami<sup>1</sup> (1. Tottori University, 2. Yamaguchi University)  
10:00 AM - 10:20 AM

### [K6-2am-05] Electrosynthesis of hypervalent iodine using extended $\pi$ -system and its application to electrocatalysis

○Shohei Yoshinaga<sup>1</sup>, Naoki Shida<sup>1</sup>, Mahito Atobe<sup>1</sup> (1. Yokohama National University)  
10:20 AM - 10:40 AM

### [K6-2am-06] Diastereoselective Electrocatalytic Hydrogenation of Substituted Cyclohexanones in a PEM Reactor

○Yugo Shimizu<sup>1</sup>, Atsushi Fukazawa<sup>1</sup>, Naoki Shida<sup>1</sup>, Mahito Atobe<sup>1</sup> (1. Yokohama National University)  
10:40 AM - 11:00 AM

### [K6-2am-07] Hole-catalyzed selective C-C bond formation at benzylic position in lignin model materials by anodic oxidation

○Rumi Izumiya<sup>1</sup>, Naoki Shida<sup>1</sup>, Mahito Atobe<sup>1</sup> (1. Yokohama National University)  
11:00 AM - 11:20 AM

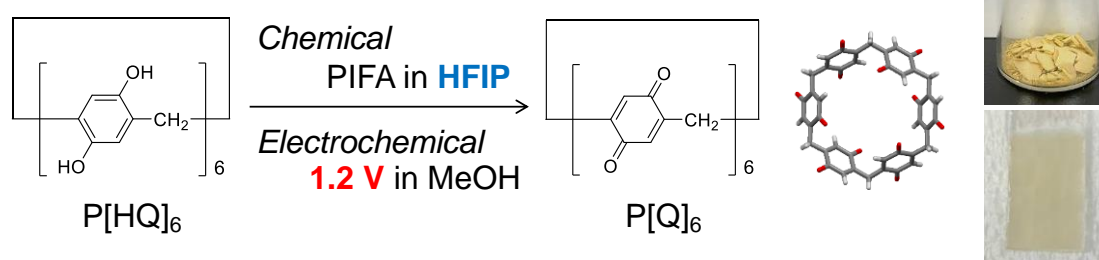
## Synthesis and Electrochemical Properties of Pillar[6]quinone

(<sup>1</sup>*School of Materials and Chemical Technology, Tokyo Institute of Technology*, <sup>2</sup>*Chemical Engineering and Life Science, Yokohama National University*, <sup>3</sup>*Graduate School of Engineering, Kyoto University* <sup>4</sup>*JST PRESTO*) ○Tomoki Hirohata,<sup>1</sup> Naoki Shida,<sup>2</sup> Tomoki Ogoshi,<sup>3</sup> Ikuyoshi Tomita,<sup>1</sup> Shinsuke Inagi,<sup>1,4</sup>

**Keywords:** Pillar[6]quinone; Macrocycles; Oxidation; DFT Calculation;

Pillar[n]arenes (n: number of units), macrocyclic *para*-arylene methylene molecules, have attracted attention owing to their symmetrical structures, host-guest properties, and original supramolecular assembly characteristics.<sup>1</sup> Similarly, their quinone counterparts, pillar[n]quinones (P[Q]<sub>n</sub>), are also fascinating macrocycles containing electron-deficient quinone units. A hexagonal molecule, pillar[6]quinone (P[Q]<sub>6</sub>), is expected to form densely packed structures and is a candidate for organic active material but the synthesis of P[Q]<sub>6</sub> still remains a challenge. We previously reported that the anodic oxidation (1.0 V vs. SCE) of 1,4-dihydroxypillar[6]arene (P[HQ]<sub>6</sub>) in methanol gave hexagonal cylinder structures on electrode surfaces which were composed of partially oxidized P[HQ]<sub>6-m</sub>[Q]<sub>m</sub> (composed of both hydroquinone and benzoquinone units) aggregating via quinhydrone formation.<sup>2</sup>

In this work, we successfully synthesized P[Q]<sub>6</sub> for the first time by oxidation of its hydroquinone precursor P[HQ]<sub>6</sub>. Electrochemical oxidation (1.2 V vs. SCE) of P[HQ]<sub>6</sub> in methanol gave the similar hexagonal cylindrical crystal of P[Q]<sub>6</sub> evidenced by single crystal X-ray diffraction, NMR and HRMS analyses.<sup>3</sup> In addition, we also found that scalable synthesis of P[Q]<sub>6</sub> was succeeded by chemical oxidation of P[HQ]<sub>6</sub> with phenyliodine(III)bis(trifluoroacetate) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Furthermore, the electrochemical properties and electron-transfer behavior of P[Q]<sub>6</sub> were revealed by various voltammetric studies.



**Fig.1** Chemical and electrochemical synthesis of pillar[6]quinone.

### References

1. T. Ogoshi, T. Yamagishi, Y. Nakamoto, *Chem. Rev.*, **2016**, *116*, 7937.
2. C. Tsuneishi, Y. Koizumi, R. Sueto, H. Nishiyama, K. Yasuhara, T. Yamagishi, T. Ogoshi, I. Tomita and S. Inagi, *Chem. Commun.*, **2017**, *53*, 7454.
3. T. Hirohata, N. Shida, H. Uekusa, N. Yasuda, H. Nishihara, T. Ogoshi, I. Tomita, S. Inagi, *Chem. Commun.*, **2021**, *57*, 6360.

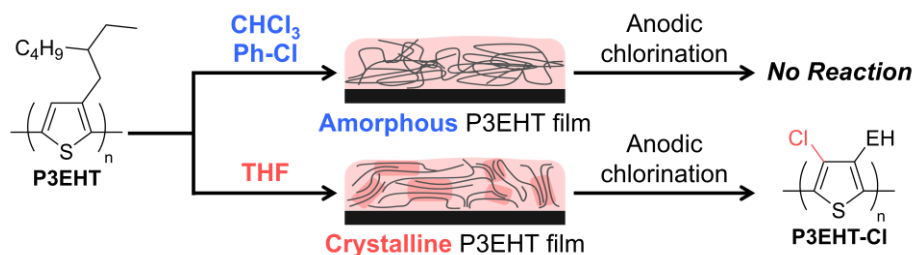
## Electrochemical Post-functionalization of Poly(3-(2-ethylhexyl)thiophene) Facilitated by Forming the Ordered Structure

(<sup>1</sup>*Sch. Mater. & Chem. Tech., Tokyo Tech.*, <sup>2</sup>*Grad. Sch. Eng., Yokohama National University*, <sup>3</sup>*JST PRESTO*) ○Tomoyuki Kurioka,<sup>1</sup> Takahiro Komamura,<sup>1</sup> Naoki Shida,<sup>2</sup> Teruaki Hayakawa,<sup>1</sup> Ikuyoshi Tomita,<sup>1</sup> Shinsuke Inagi<sup>1,3</sup>

**Keywords:**  $\pi$ -Conjugated polymer, Polythiophene, Anodic chlorination, *In situ* conductance measurements, Ordered structures

$\pi$ -Conjugated polymer films are promising materials for organic electronic devices due to their unique optoelectronic properties.<sup>[1]</sup> To improve the performance of these devices, huge number of efforts have been devoted to investigating the effects of the structures of  $\pi$ -conjugated polymer films on their optoelectronic properties. Recently, electron transfer-driven post-functionalization methods (e.g., electrochemical post-functionalization (ePF)) have been regarded as powerful approaches to impart various functionalities to  $\pi$ -conjugated polymer films.<sup>[2]</sup> In such methods, their structures should also serve as a crucial role for the efficacy of the reaction; however, the relationship between their structures and the electron transfer-driven post-functionalization has never been discussed.

Here, we clarified the relationship between the structures of  $\pi$ -conjugated polymer films and the efficacy of the electron transfer-driven post-functionalization by performing the ePF of poly(3-(2-ethylhexyl)thiophene) (P3EHT) films (Figure 1). Changing solvents to prepare P3EHT films resulted in providing P3EHT films with different structures (i.e., amorphous and crystalline structures). The amorphous P3EHT films were not electrochemically chlorinated, whereas P3EHT films possessing crystalline features were successfully chlorinated. *In situ* conductance measurements of P3EHT films concluded that the reactivity difference between both P3EHT films was because of their electrical conductivity.



**Figure 1.** Relationship between the structures of P3EHT films and the reactivity on anodic chlorination.

### References

- [1] X. Guo, M. Baumgarten, K. Müllen, *Prog. Polym. Sci.* **2013**, *38*, 1832–1908.
- [2] T. Kurioka, S. Inagi, *Chem. Rec.* **2021**, *21*, 2107–2119.

## Synthesis of Precursors of Chitin Oligosaccharides by Electrochemical Glycosylation Polymerization

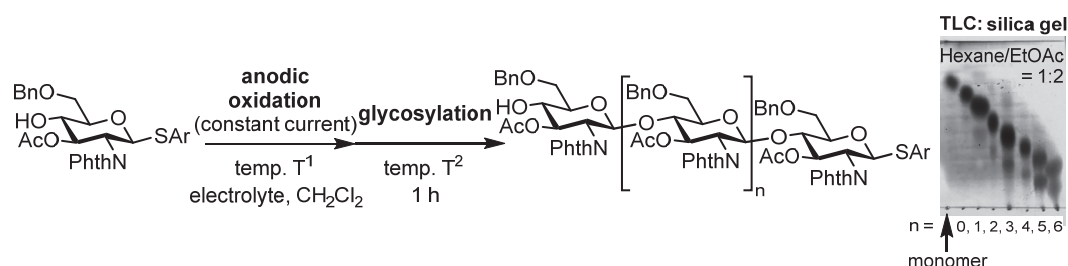
(<sup>1</sup>Department of Chemistry and Biotechnology, Tottori University, <sup>2</sup>Koganei Corporation)

○Md Azadur Rahman,<sup>1</sup> Kana Kuroda,<sup>1</sup> Tomoaki Hamada,<sup>2</sup> Hiraku Sakai,<sup>2</sup> Toshiki Nokami<sup>1</sup>

**Keywords:** Electrochemical Polymerization; Chitin Oligosaccharide; Thioglycoside

A convenient method to synthesize linear oligosaccharides using electrochemical glycosylation polymerization has been developed in this study. We have already reported automated electrochemical assembly for oligosaccharides synthesis.<sup>1,2</sup> This method is useful to prepare structurally well-defined oligosaccharides; however, this one-pot multiple-step synthesis is time-consuming and too sophisticated to prepare linear oligosaccharides with a single repeating unit. Therefore, we envisioned that glycosylation polymerization of a thioglycoside monomer under the electrochemical conditions might be an alternative method for oligosaccharide synthesis.

We investigated electrochemical glycosylation polymerization to synthesize chitin oligosaccharides containing  $\beta$ -1,4-glycosidic linkages of glucosamine as a model reaction. Various reaction parameters such as temperature, electrolyte, amount of electricity, current, anomeric leaving group, were optimized and oligosaccharides up to octasaccharide ( $n = 6$ ) have been detected by MALDI-TOF MS. Although higher conversion of a thioglycoside monomer was observed with more electricity and higher reaction temperature, the condition of excess amount of electricity ( $>0.6$  F/mol) was not appropriate to keep the anomeric thioaryl (SAr) leaving group and protecting groups of oligosaccharides intact. Oligosaccharides with different chain length and by-products such as hydroxy sugars can be easily separated by preparative GPC and silica gel column chromatography, respectively. We also examined synthesis of oligosaccharides longer than hexasaccharide ( $n = 4$ ) by repeating the same procedure in one pot. This method can be applicable to synthesis of other oligosaccharides containing glucose.



1) A. Shibuya, T. Nokami, *Chem. Rec.* **2021**, 21, 2389. 2) K. Yano, N. Sasaki, T. Itoh, T. Nokami, *J. Synth. Org. Chem. Jpn* **2021**, 79, 839.

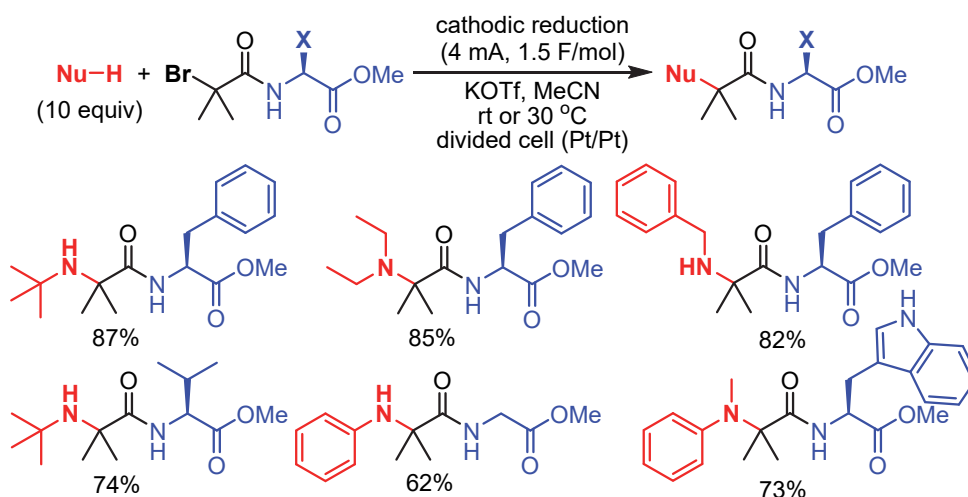
## Formation of Sterically Congested C-N bonds by Electrochemical Reductive Coupling of Amines and $\alpha$ -Bromo Carboxamides

(<sup>1</sup>Department of Chemistry and Biotechnology, Tottori University, <sup>2</sup>Department of Applied Chemistry, Yamaguchi University) ○Titli Ghosh,<sup>1</sup> Hazuki Kaizawa,<sup>1</sup> Takashi Nishikata,<sup>2</sup> Toshiki Nokami<sup>1</sup>

**Keywords:** Electrochemical Reduction; Amines;  $\alpha$ -Bromo Carboxamides; Formation of C-N bonds; Steric Congestion

Nucleophilic substitution of alkyl halides with amines is a conventional method to prepare alkyl amines; however, synthesis of congested bulky amines is still difficult. Copper-catalyzed amination reaction is a powerful method to construct hindered C–N bonds at room temperature from  $\alpha$ -bromo carboxamides.<sup>1</sup> Recently, cesium carbonate enabled formation of congested C–O bonds from  $\alpha$ -bromo carboxamides, and the hindered ethers were obtained under the electrochemical reductive conditions as well.<sup>2</sup>

Inspired by these previous works, we investigated electrochemical substitution of  $\alpha$ -bromo carboxamides with amines as nucleophiles to prepare sterically demanding amines at ambient temperature. After optimization of parameters of the electrochemical reaction a variety of  $\alpha$ -bromo carboxamides, which can be easily prepared by condensation with amino acids, coupled with primary and secondary amines to afford congested bulky amines in reasonable yields. In this oral presentation further scope and limitation of the method will be discussed in detail.



1) S. Ishida, K. Takeuchi, N. Taniyama, Y. Sunada, T. Nishikata, *Angew. Chem. Int. Ed.* **2017**, *56*, 11610. 2) G. Hirata, K. Takeuchi, Y. Shimoharai, M. Sumimoto, H. Kaizawa, T. Nokami, T. Koike, M. Abe, E. Shirakawa, T. Nishikata, *Angew. Chem. Int. Ed.* **2021**, *60*, 4329.

## π 拡張ヨードアレーンを用いた超原子価ヨウ素化合物の電解合成と触媒反応への応用

(横浜国立大学大学院<sup>1)</sup>) ○吉永 昌平<sup>1</sup>・信田 尚毅<sup>1</sup>・跡部 真人<sup>1</sup>

Electrosynthesis of hypervalent iodine compounds with extended π-system and their application to electrocatalysis

(<sup>1</sup>Yokohama National University) ○Shohei Yoshinaga,<sup>1</sup> Naoki Shida,<sup>1</sup> Mahito Atobe,<sup>1</sup>

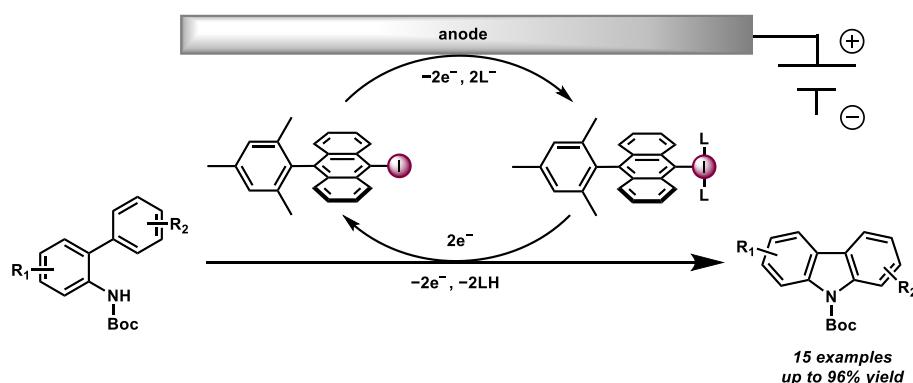
Although hypervalent iodine compounds are known to exhibit unique reactivity and thus regarded as a useful class of reagents, they have a significant environmental impact in their synthesis. In this study, we successfully synthesized novel hypervalent iodine compounds by electrochemical oxidation and applied to catalytic reactions. We demonstrate the electrochemical synthesis of hypervalent iodine compounds with π-extended structures and their application to C-N coupling reactions by controlling the donor properties of the electrolyte and selecting the structure of aromatic moieties of the iodine compounds.

**Keywords :** Electrosynthesis, Hypervalent iodine, extended π-system, Coordination chemistry, C-N coupling

超原子価ヨウ素は、多彩な反応性を示すことが知られている一方、これらの試薬は合成における環境負荷が大きいという課題がある。超原子価ヨウ素はヨードアレーンの電解酸化により合成することも可能であり、電極での酸化により合成した超原子価ヨウ素をその場で他の化合物と反応させ、触媒的に利用することができれば、超原子価ヨウ素独自の有用性の高い反応を廃棄物の少ない反応系で実現できる。<sup>1)</sup>

そこで本研究ではヨードアレーンのπ拡張による酸化電位の低下を利用した、電解酸化による超原子価ヨウ素合成と触媒反応への応用を目指した。電解液中の電解質のドナー性と芳香環部分の構造制御によりπ拡張構造を有する超原子価ヨウ素の電解合成とC-Nカップリング反応への応用を達成した。

実際に Boc 保護されたビフェニルアミンを反応基質として電解合成された超原子価ヨウ素と反応させることで、酸化的分子内 C-N カップリングが進行し、目的のカルバゾールが最大収率 97%で得られた。さらに電気化学測定により超原子価ヨウ素を用いた電極触媒過程の速度論的な解析にも初めて成功した。



1) M. Elsherbini, T. Wirth, *Chem. Eur. J.*, **2018**, 24, 13399–13407.



## PEM 型リアクター中における置換シクロヘキサノン類のジアステレオ選択的電解水素化反応

(横国大院理工) ○清水 勇吾・深澤 篤・信田 尚毅・跡部 真人

Diastereoselective Electrocatalytic Hydrogenation of Substituted Cyclohexanones in a PEM Reactor (*Graduate School of Engineering Science, Yokohama National University*) ○Yugo Shimizu, Atsushi Fukazawa, Naoki Shida, Mahito Atobe

Hydrogenated products of cyclic ketones are industrially important intermediates. However, most reactions for the hydrogenation of cyclic ketones require a catalyst and product separation process, which may have a significant impact on the environment. Under these backgrounds, we have focused on a PEM (Proton-Exchange Membrane) reactor, which is generally applied to a polymer electrolyte fuel cell, to develop a mild and clean method for organic synthesis.

In this work, the diastereoselective electrocatalytic hydrogenation of mono-substituted cyclohexanones was carried out using a PEM reactor. Especially, we examined influence of current density and electrocatalysts on the diastereoselective electrocatalytic hydrogenation. As a result, high *cis* or *trans* selectivity were achieved in this demonstration.

**Keywords :** *Electroorganic synthesis; PEM reactor; Electrocatalytic hydrogenation; Diastereoselective reaction; Cyclic ketones*

我々は環境に低負荷な反応プロセスの構築を目指し、固体高分子形燃料電池に採用されているPEM型リアクターを転用して有機電解反応を行っている。環状ケトンの水素化体である環状アルコールは工業的に有用な中間体であり、水素化体の立体配置が重要となる。そこで本研究では、PEM型リアクターを用いて一置換シクロヘキサノン類の電解水

素化を実施し、高選択的に片方のジアステレオマーを得ることを目的とした (Fig. 1)。電流密度とカソード電極触媒の検討を行い、環状アルコールのジアステレオ選択性への影響を精査した。4-*tert*-Butylcyclohexanone を基質として選定し、Rh 触媒を用いて電解水素化を行った結果、高電流効率 (93%)、および、高シス体選択率 (94%) で 4-*tert*-butylcyclohexanol を得た。また、ジアステレオ選択性を損なうことなく、グラムスケール電解 (5 g) が実施可能であることも明らかにした。

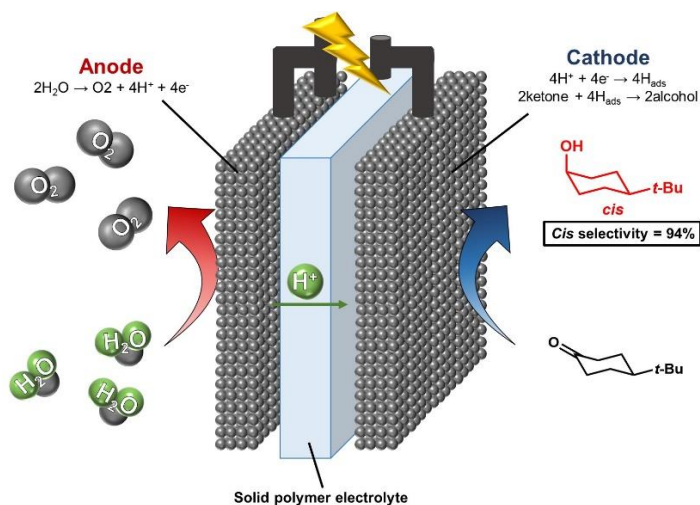


Figure 1. Schematic image of a PEM reactor.



## 陽極酸化によるリグニンモデル物質の正孔触媒型ベンジル位選択的 C-C 結合形成反応

(横国大院<sup>1)</sup>) ○泉谷 留美<sup>1</sup>・信田 尚毅<sup>1</sup>・跡部 真人<sup>1</sup>

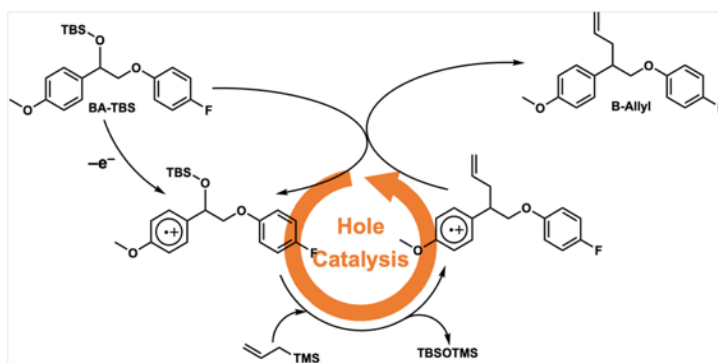
Hole-catalyzed selective C-C bond formation at benzylic position in lignin model materials by anodic oxidation (<sup>1</sup>*Graduate School of Science Engineering, Yokohama National University*)  
○Rumi Izumiya,<sup>1</sup> Naoki Shida,<sup>1</sup> Mahito Atohe<sup>1</sup>

Lignin is one of the main components of woody tissue. Lignin is regarded as a sustainable source of chemical materials because it is the most abundant aromatic polymer on earth. However, the use of lignin is still limited due to its complexity of the structure, thus the selective and reliable methodology for the modification of lignin is highly desirable. In this study, we investigated the electrochemical modification of benzylic C-O bonds to chemically robust C-C bonds lignin model compound, envisioning the establishment of an environmentally benign strategy for the modification of lignin. When a weakly-donating supporting electrolyte was used, an extremely efficient hole-catalyzed bond conversion reaction was achieved. Moreover, we clarify that the structure of the lignin model compound is suitable for this reaction from the perspective of the stability of the radical cation.

**Keywords :** *Electrosynthesis, Lignin valorization, Polymer reaction, Hole-catalysis*

近年、再生可能な資源である木質バイオマスの利用が重要視されている。その構成成分のうち、リグニンは唯一の含芳香族高分子であるため化成品の優れた原材料になると期待されており、選択的に改質する手法の開発が盛んに行われている<sup>1)</sup>。

本研究では、リグニンの環境調和型改質法の開発を目的とし、熱的・力学的耐性の向上を指向した陽極酸化による化学選択的な結合変換を検討した(Scheme 1)。1電子酸化をトリガーとする本反応は、全体的にレドックスニュートラルであることから正孔触媒的に進行し、中間体のラジカルカチオンの安定性を高める条件下において極めて高効率な反応の設計を達成した。



**Scheme 1.** Hole-catalyzed benzylic allylation of BA-TBS

発表では、低分子化合物をモデルとして用いた反応条件の最適化と反応機構考察に関する詳細に加え、高分子を用いた反応についても報告する。

1) B. M. Upton, A. M. Kasko, *Chem. Rev.* 2016, 116, 2275-2306.

## [K4-2pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Yuki Nagashima, Satoru Kuwano

Thu. Mar 24, 2022 1:00 PM - 3:40 PM K4 (Online Meeting)

### [K4-2pm-01] Cationic Rhodium(I)-Catalyzed Asymmetric [2+2+2] Cycloaddition of Homopropargyl Enamides with Alkynes

○Kohei Fujii<sup>1</sup>, Koji Masutomi<sup>1</sup>, Yuki Nagashima<sup>1</sup>, Ken Tanaka<sup>1</sup> (1. Tokyo Institute of Technology)

1:00 PM - 1:20 PM

### [K4-2pm-02] The Development of Stereoselective [2 + 3] Cycloaddition Reactions of Oxime Substituted Nitrile Oxides and Alkenes

○Nao Umemoto<sup>1</sup>, Ayumi Imayoshi<sup>1</sup>, Kazunori Tsubaki<sup>1</sup> (1. Kyoto Prefectural University)

1:20 PM - 1:40 PM

### [K4-2pm-03] Development of New Reactions by Quantum Chemical Calculations: the Synthesis of Unsymmetric DPPE via Difunctionalization of Ethylene

○Hideaki Takano<sup>1,2</sup>, Hitomi Katsuyama<sup>1,2</sup>, Hiroki Hayashi<sup>1,2</sup>, Wataru Kanna<sup>3</sup>, Yu Harabuchi<sup>1,2,3</sup>, Satoshi Maeda<sup>1,2,3</sup>, Tsuyoshi Mita<sup>1,2</sup> (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

1:40 PM - 2:00 PM

### [K4-2pm-04] Synthesis of Polycyclic Aromatic Amines via Benzannulation of Ynamine: $\pi$ -Extension Strategy for Optimization of Optical Properties

○Yasuhiro Okuda<sup>1</sup>, Mayo Fujimoto<sup>1</sup>, Kazuya Kiyohara<sup>1</sup>, Aina Kuwayama<sup>1</sup>, Akihiro Orita<sup>1</sup> (1. Fac. of Eng., Okayama Univ. of Sci.)

2:00 PM - 2:20 PM

### [K4-2pm-05] Synthesis and luminescence characteristics of disilane crosslinked DAD molecules

○Yoshinori Yamanoi<sup>1</sup>, Masaki Nishio<sup>1</sup>, Hiroto Miyabe<sup>1</sup>, Mizuha Ujita<sup>1</sup>, Shunya Matsushita<sup>1</sup>, Toyotaka Nakae<sup>1</sup>, Teppei Yamada<sup>1</sup> (1. The Univ of Tokyo)

2:20 PM - 2:40 PM

### [K4-2pm-06] Model Study on the Mechanism and Inhibition of Thyroid Hormone Activating Enzymes by Taking Advantage of a Cradled Selenopeptide

○Ryosuke Masuda<sup>1</sup>, Satoru Kuwano<sup>1</sup>, Shohei Sase<sup>1</sup>, Kei Goto<sup>1</sup> (1. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

### [K4-2pm-07] Catalytic hydroboration reaction of Lewis-base stabilized hydrostannylenes

○Kazuki Nakaya<sup>1</sup>, Yoshiki Kobayashi<sup>1</sup>, Norio Nakata<sup>1</sup>, Akihiko Ishii<sup>1</sup> (1. Saitama University)

3:00 PM - 3:20 PM

### [K4-2pm-08] Sulfonyl Pyrroles: Synthetic Linchpins for Late-Stage Functionalization of Primary Sulfonamides

Tomoya Ozaki<sup>1</sup>, Hideki Yorimitsu<sup>1</sup>, ○Gregory J. P. Perry<sup>1</sup> (1. Kyoto University)

3:20 PM - 3:40 PM



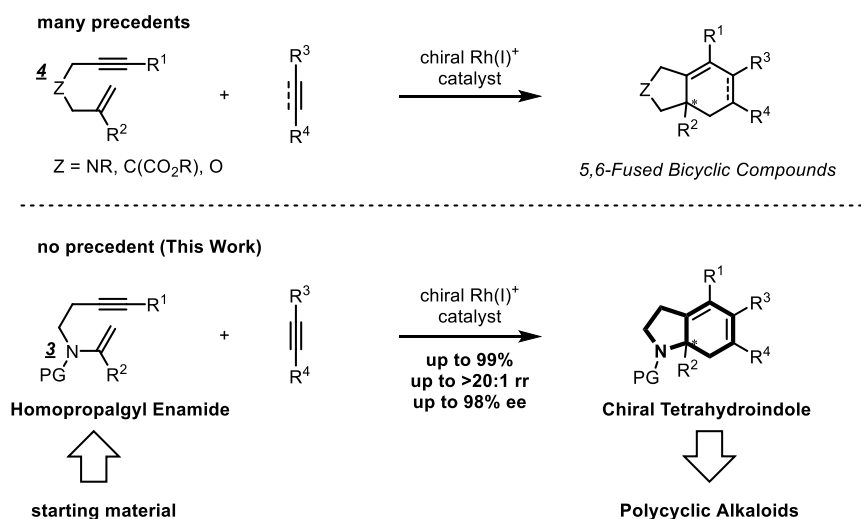
## Cationic Rhodium(I)-Catalyzed Asymmetric [2+2+2] Cycloaddition of Homopropargyl Enamides with Alkynes

(<sup>1</sup> Department of Chemical Science and Engineering, Tokyo Institute of Technology) ○ Kohei Fujii,<sup>1</sup> Koji Masutomi,<sup>1</sup> Yuki Nagashima,<sup>1</sup> Ken Tanaka<sup>1</sup>

**Keywords:** Asymmetric Catalysis; Cycloaddition; Enynes; Rhodium; Tetrahydroindoles

The transition-metal-catalyzed asymmetric [2+2+2] cycloaddition of 1,6-enynes with unsaturated compounds is a useful method for the construction of chiral bicyclic scaffolds in a highly efficient and atom-economical manner. For this transformation, cationic rhodium(I)/axially chiral biaryl bisphosphine complexes show high reactivity and selectivity. The asymmetric [2+2+2] cycloaddition reactions with alkynes or alkenes were reported by several groups.<sup>1</sup> However, these reports employed 4-position tethered 1,6-enynes that were easily synthesized.

In this research, we have achieved the unprecedented catalytic asymmetric [2+2+2] cycloaddition of homopropargyl enamides with alkynes. First, we synthesized homopropargyl enamides that possess enamide moieties as new 3-position tethered 1,6-enynes by efficient and general synthetic routes. The rhodium-catalyzed asymmetric [2+2+2] cycloaddition of the obtained homopropargyl enamides with alkynes produced tetrahydroindole derivatives with high yields and ee values. Additionally, for demonstration of the synthetic utility of this asymmetric [2+2+2] cycloaddition, we applied chiral tetrahydroindole to the total synthesis of polycyclic alkaloids.



1) a) Evans, P. A.; Lai, K. W.; Sawyer, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 12466–12467. b) Shibata, T.; Arai, Y.; Tahara, Y. *Org. Lett.* **2005**, *7*, 4955–4957. c) Masutomi, K.; Sakiyama, N.; Noguchi, K.; Tanaka, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 13031–13035.

## オキシム置換ニトリルオキシドとアルケンの立体選択的[2 + 3]環化付加反応の開発

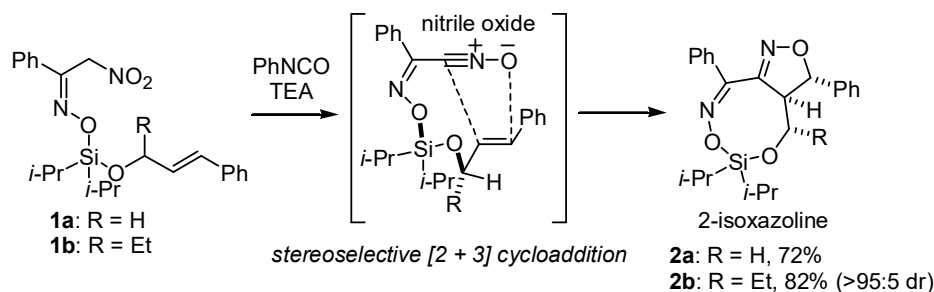
(京府大院生命環境) ○梅本 直・今吉 亜由美・椿 一典

Development of Stereoselective [2 + 3] Cycloaddition Reactions of Oxime Substituted Nitrile Oxides and Alkenes (*Graduate School of Life and Environmental Sciences, Kyoto Prefectural University*) Nao Umemoto, Ayumi Imayoshi, Kazunori Tsubaki

Nitrile Oxides afford 2-isoxazoline via [2 + 3] cycloaddition reactions with alkenes, which can be converted to various intermediates such as  $\beta$ -hydroxy ketones. However, nitrile oxides directly connected with a carbonyl group show low reactivity due to the decline of HOMO. In addition, in the case multi-substituted alkenes are used as substrates, controlling the regioselectivity is difficult task. Under the situation, we expected nitrile oxides remained high reactivity by converting carbonyl group with oxime and expected high regioselectivity using intramolecular reaction by binding oxime hydroxy group with alkenes. For this hypothesis we demonstrated intramolecular [2 + 3] cycloaddition reaction of **1a**. As a result, the desired cycloadduct **2a** was obtained with good yield. In addition, the cycloaddition reaction of **1b** afforded desired cycloadduct **2b** with high diastereoselectivity of >95:5.

**Keywords** : Nitrile Oxide; 2-Isloxazoline; Oxime; [2 + 3] Cycloaddition Reaction

ニトリルオキシドはアルケンとの [2+3] 環化付加反応により 2-イソオキサゾリンを与える。本生成物は  $\beta$ -ヒドロキシケトンを含む有機中間体へ誘導できる。しかし、ニトリルオキシドにカルボニルのような電子求引性基が置換すると HOMO の低下により反応性が大幅に低下する。さらに親双極子に多置換アルケンを用いた場合、その位置選択性を制御することは極めて難しい。我々はカルボニル基を弱電子求引性のオキシムに置き換えることによって、ニトリルオキシドの反応性を維持できると考えた<sup>1)</sup>。さらにオキシム水酸基にアルケンを連結することによって位置選択性を制御できると考えた。このような考えに基づき、オキシムとシンナミルアルコールをシリルで連結したニトロアルカン **1a** を調製し環化付加反応に付した。その結果、目的の付加体 **2a** を良好な収率、完全な位置選択性で得た。また、アルコール側に不斉点を導入したニトロアルカン **1b** の環化付加反応において付加体 **2b** を 95:5 以上の高いジアステレオ選択性で与え、面選択性を制御することにも成功した。



1) N. Umemoto, A. Imayoshi, K. Tsubaki, *Tetrahedron Lett.* **2020**, 61, 152213.

## 量子化学計算に基づく新規反応開発：エチレンのダブル官能基化反応による非対称 DPPE の合成

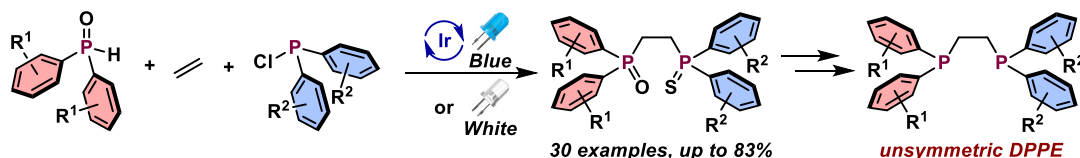
(北大 WPI-ICReDD<sup>1</sup>・JST-ERATO<sup>2</sup>・北大院理<sup>3</sup>) ○高野 秀明<sup>1,2</sup>・勝山 瞳<sup>1,2</sup>・林 裕樹<sup>1,2</sup>・神名 航<sup>3</sup>・原渕 祐<sup>1,2,3</sup>・前田 理<sup>1,2,3</sup>・美多 剛<sup>1,2</sup>

Development of New Reactions by Quantum Chemical Calculations: the Synthesis of Unsymmetric DPPE via Difunctionalization of Ethylene (<sup>1</sup>WPI-ICReDD, Hokkaido Univ., <sup>2</sup>JST-ERATO, <sup>3</sup>Fac. of Sci., Hokkaido Univ.) ○Hideaki Takano<sup>1,2</sup>, Hitomi Katsuyama<sup>1,2</sup>, Hiroki Hayashi<sup>1,2</sup>, Wataru Kanna<sup>3</sup>, Yu Harabuchi<sup>1,2,3</sup>, Satoshi Maeda<sup>1,2,3</sup>, Tsuyoshi Mita<sup>1,2</sup>

1,2-Bis(diphenylphosphino)ethane (DPPE) is an important bidentate ligand for transition-metal complexes which can promote various organic reactions in catalytic fashion. DPPE is generally synthesized by S<sub>N</sub>2 reaction of 1,2-dihaloethane with metal phosphide, or hydrophosphination for vinylphosphine. On the other hand, the synthesis of electronically and sterically unsymmetric DPPE derivatives (Ar<sup>1</sup>P-CH<sub>2</sub>-CH<sub>2</sub>-PAr<sup>2</sup>; Ar<sup>1</sup> ≠ Ar<sup>2</sup>), which is expected to control the catalytic activity by the choice of substituents on phosphine atoms, is much more difficult and complicated rather than the synthesis of symmetric DPPE. We first designed the facile synthesis of DPPE by artificial force induced reaction (AFIR) method-based backward reaction path search, and, after experimental investigations, we achieved the synthesis of unsymmetric DPPE derivatives by a three-component reaction of ethylene, phosphine oxide, and chlorophosphine under the irradiation of LED. Furthermore, we obtained unsymmetric DPPE ligands by the reductive treatment for obtained products.

**Keywords :** ethylene, quantum chemical calculation, photocatalyst, DPPE, three-component reaction

DPPE は遷移金属錯体の二座配位子として用いられる重要な化合物である。DPPE は一般に、金属ホスフィドとジハロエタンを用いた S<sub>N</sub>2 反応やビニルホスフィンに対するヒドロホスフィン化反応により合成される。一方、左右のリン原子上の置換基が電子的、立体的に異なる非対称 DPPE は置換基の選択により錯体の反応性を自在に制御可能な配位子であると期待されるが、対称な DPPE の合成に比べ、非対称 DPPE の合成は困難かつ煩雑であり、その報告例は限られている。今回我々は反応経路自動探索手法である人工力誘起反応(AFIR)法を用いることで、逆合成解析的な反応経路探索により、エチレンを出発原料とする DPPE の新規合成法を計算化学的に見出し、実験により具現化した。また更なる実験的な検討を行うことで、光照射下、エチレン、ホスフィンオキシド、クロロホスフィンを用いた三成分反応により、左右の電子的、立体的環境が異なる非対称 DPPE 誘導体の簡便合成を達成した。加えて、得られた非対称 DPPE 誘導体を還元処理することにより、非対称 DPPE 配位子の合成にも成功した。



• AFIR-based backward reaction path search • Three-component reaction of ethylene and phosphines

1) 美多 剛, 前田 理, 高野 秀明, エチレンを原料に用いた 1,2-ビス(ジフェニルホスフィノ)エタン(DPPE)誘導体の合成法, 特願 2021-131481 出願 (2021 年 8 月 11 日) 2) Takano, H.; Katsuyama, H.; Hayashi, H.; Kanna, W.; Harabuchi, Y.; Maeda, S.; Mita, T. *manuscript in preparation*.

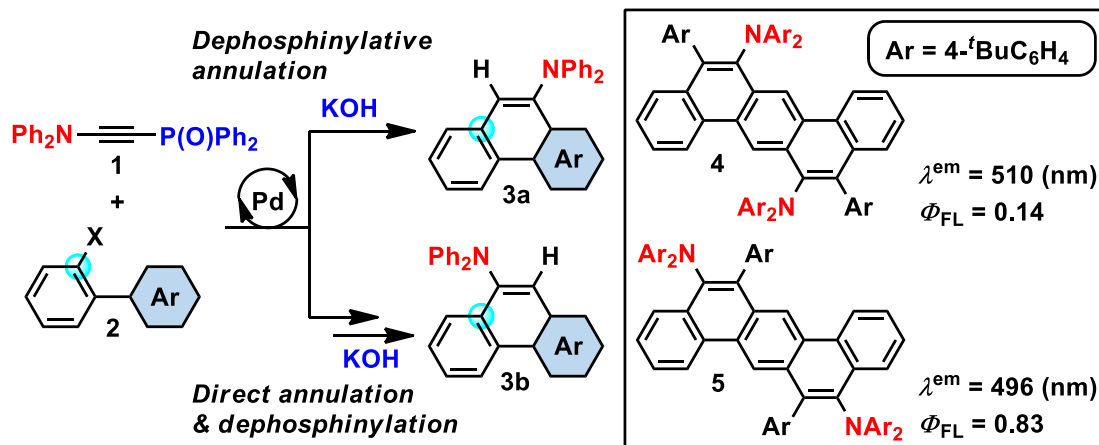
## イナミンの芳香環形成反応による多環芳香族アミンの合成：光学特性のチューニングを指向したパイ拡張戦略

(岡山理大工) ○奥田 靖浩・藤本 真世・清原 和也・桑山 愛菜・折田 明浩  
 Synthesis of Polycyclic Aromatic Amines via Benzannulation of Ynamine:  $\pi$ -Extension Strategy for Optimization of Optical Properties  
 (Fac. of Eng., Okayama Univ. of Sci.) ○Yasuhiro Okuda, Mayo Fujimoto, Kazuya Kiyohara, Aina Kuwayama, Akihiro Orita

Polycyclic aromatic amines (PAAs) have attracted our great attention as excellent light-emitting and hole-transporting materials due to their structural motif that an electron-donating amino group was conjugated to highly expanded  $\pi$ -system. Recently, we developed one-pot dephosphinylation [4 + 2] benzannulation using phosphinyl ynamine **1** as amino group-substituted C2 unit.<sup>1)</sup> In this presentation, we report a regioselective syntheses of dibenz[*a*, *h*]anthracene regioisomers **4** and **5** from the corresponding halides, and the comparison of their optical properties. We also show the consecutive synthesis of regioisomeric PAA **3b** via palladium-catalyzed [4 + 2] direct benzannulation of **2** with **1** and the subsequent KOH-promoted dephosphinylation.

**Keywords** : Polycyclic Aromatic Amines; Ynamine; Dephosphinylation; Benzannulation; Regiodivergent Synthesis

多環芳香族アミンは、電子供与基であるアミノ基が拡張パイ共役系に置換することから優れた発光や正孔輸送特性を示す。ごく最近、当研究室では炭素(sp)–窒素結合をもつイナミン **1** を C2 ユニットとして利用し、脱ホスフィニル化–環化という連続プロセスで多環芳香族アミン **3a** を合成した<sup>1)</sup>。本発表では、この環化反応によりアミノ基の置換位置の異なるジベンゾアントラセン誘導体 **4**, **5** を合成し、それらの光学特性を比較した結果を紹介する。また、ホスフィニル基を保持した直截環化と続く脱ホスフィニル化によりアミノ基の置換位置が異なる多環芳香族アミン **3b** も合成したので、この内容についても述べる。



1) Y. Okuda, M. Fujimoto, H. Akashi, A. Orita, *J. Org. Chem.* **2021**, 86, 17651.



## ジシラン架橋(DAD)分子の合成と発光特性

(東大院理) ○山野井慶徳・西尾正樹・宮部浩人・氏田瑞葉・松下峻也・中江豊崇・山田鉄兵

Synthesis and emission properties of disilane cross-linked (DAD) molecules (The University of Tokyo) ○Yoshinori Yamanoi, Masaki Nishio, Hiroto Miyabe, Mizuha Ujita, Shunya Matsushita, Toyotaka, Nakae, Teppei, Yamada

Molecules that connect an electron donor (D) and an electron acceptor (A) with a disilane bond (Si-Si) show intense photoluminescence in the solid state. In this work, we synthesized a novel D-Si-Si-A-Si-Si-D type molecule in which phenothiazine was introduced as an electron donor site. This compound exhibited mechanochromic and vapochromic emissions with response to external stimuli. The relationship between properties and structures was investigated using single crystal and powder X-ray diffraction measurements.

*Keywords : donor-acceptor, disilane*

電子ドナー(D)と電子アクセプター(A)をジシラン結合(Si-Si)でつないだ分子は結晶状態で特異な発光を示す。今回、メカノクロミック発光を示すことが知られているフェノチアジンを電子ドナー部位として導入した新規 D-Si-Si-A-Si-Si-D 型分子を合成し、その結晶構造と機械的刺激、溶媒蒸気への応答性を単結晶および粉末 X 線回折測定を利用して調査した。

合成したジシラン分子の単結晶について、Rigaku VariMax Dual を用いて単結晶 X 線回折測定を 93 K で行った。得られた測定データは Olex2 を用いて解析した。SHELXT プログラムを用いて位相決定を行い、SHELXL プログラムにて構造精密化を行った。また、結晶をすりつぶした試料、すりつぶした後に溶媒蒸気に暴露した試料、ジクロロメタン溶液から得られた試料に関して、キャピラリーに封入し、Rigaku SmartLab (K $\alpha$ 1)を用いて粉末 X 線回折測定を行った。

単結晶 X 線回折測定から、得られた新規ジシラン化合物は結晶状態において擬エクタトリアル型のフェノチアジンを有することが明らかになった。また粉末 X 線回折測定から、結晶性試料はすりつぶしによって非晶質に、溶媒蒸気への暴露によって再び結晶性になり、ジクロロメタン溶液からは非晶質試料が得られることが明らかになった。これらの X 線回折測定の結果と発光測定から、結晶状態からは青緑色、非晶質状態からは黄色に発光するメカノクロミック発光を示すことが明らかになった。得られた結晶構造を用いた量子化学計算の結果、これまでに知られているフェノチアジンのメカノクロミック発光の発現機構とは異なる新しい機構によるメカノクロミック発光であることが示唆された。

## Model Study on the Mechanism and Inhibition of Thyroid Hormone Activating Enzyme by Taking Advantage of a Cradled Selenopeptide

(School of Science, Tokyo Institute of Technology) ○ Ryosuke Masuda, Satoru Kuwano, Shohei Sase, Kei Goto

**Keywords:** Iodothyronine Deiodinases; Selenocysteines; Selenenyl Iodides; Molecular Cradles; Selenoproteins

Although selenocysteine selenenyl iodides (Sec-SeIs) have been proposed as important reaction intermediates in the catalytic cycle of iodothyronine deiodinases (Dios), even their trapping has never been reported due to their instability (Figure 1). Recently, we have succeeded in the first isolation of Sec-SeIs by utilizing selenocysteine and selenopeptide models bearing a cradled-type molecular framework.<sup>1</sup> Herein, we report the model study on the chemical processes in the catalytic cycle of Dios by taking advantage of these stable Sec-SeIs.

Sec-SeI **1** derived from a Sec-Gly-Gly tripeptide incorporated in the molecular cradle was successfully isolated as reddish-purple crystals. Its structure was established by X-ray diffraction analysis (Figure 2). As widely accepted mechanism shown in Figure 1, treatment of Sec-SeI **1** with a cysteine thiol afforded the corresponding selenenyl sulfide (Step B in Figure 1). The formation of a selenocysteine selenenic acid (Sec-SeOH) by the hydrolysis of a Sec-SeI was confirmed by the reaction of **1** with aqueous NaOH (Step D in Figure 1). The model study on the inhibition of Dios by propylthiouracil (PTU) was also examined by utilizing **1**.

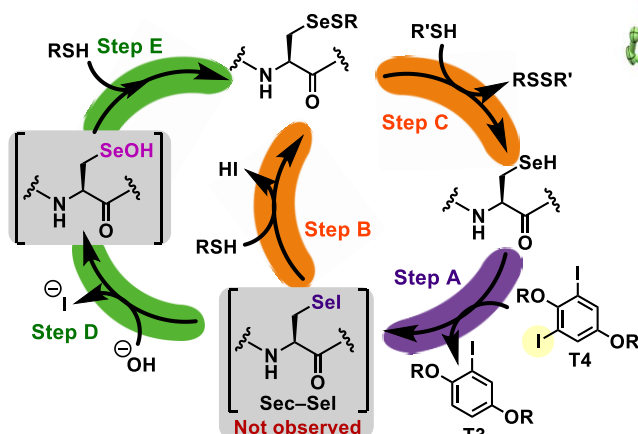


Figure 1. Proposed catalytic mechanism of Dios.

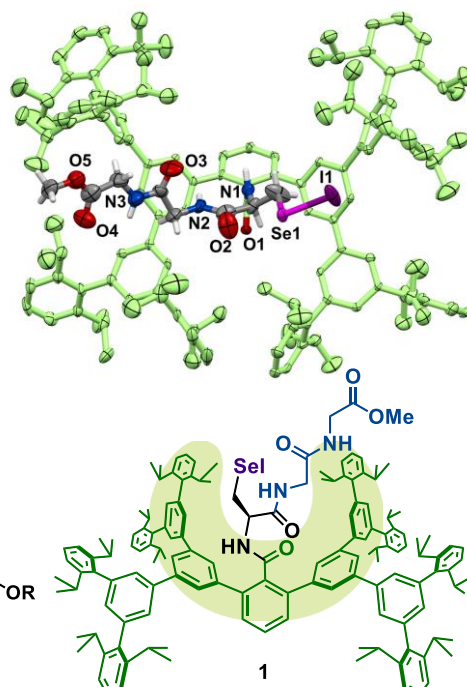


Figure 2. Molecular structure of Sec-SeI **1**.

1) R. Masuda, R. Kimura, T. Karasaki, S. Sase, K. Goto, *J. Am. Chem. Soc.*, **2021**, *143*, 6345.

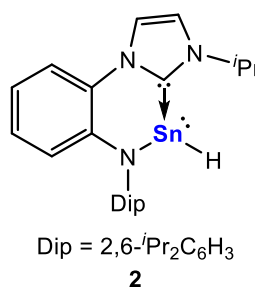
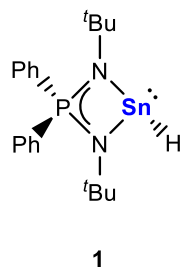
## Catalytic Hydroboration Reaction with Lewis-base Stabilized Hydrostannylenes

(Graduate School of Science and Engineering, Saitama University) ○Kazuki Nakaya, Yoshiki Kobayashi, Norio Nakata, Akihiko Ishii

**Keywords:** *Hydrostannylene; Iminophosphonamide Ligand; Intramolecular NHC Ligand; Hydroboration Reaction*

Currently, molecular transformations using low-valent p-block compounds have attracted much attention as alternative catalysts for transition metal compounds. Among them, much interest has been focused on the transformation of carbonyl compounds, which is one of the crucial processes in organic synthesis, using low-valent tin compounds. Meanwhile, hydrostannylenes, tin(II) hydrides are an intriguing class of organotin compounds because of their unusual structural behavior and as a key intermediate in the hydroboration reaction of carbonyl compounds<sup>1,2</sup>.

Recently, we are interested in the synthesis of a series of low-valent heavier group 14 element species stabilized by strong electron-donating Lewis bases. In this presentation, we will report on the synthesis of the Lewis-base stabilized hydrostannylenes **1**<sup>3</sup> and **2** by incorporating iminophosphonamide and amino-substituted *N*-heterocyclic carbene<sup>4</sup> ligands, respectively, and the catalytic hydroboration reactions of various carbonyl and imine compounds through them as key intermediates.



- 1) Hadlington, T.; Hermann, M.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2014**, *136*, 3028–3031.
- 2) Sharma, M. K.; Ansari, M.; Mahawar, P.; Rajaraman, G.; Nagendran, S. *Dalton Trans.* **2019**, *48*, 664–672.
- 3) Nakaya, K.; Takahashi, S.; Ishii, A.; Boonpalit, K.; Surawatanawong, P.; Nakata, N. *Dalton Trans.* **2021**, *50*, 14810–14819.
- 4) Cross, W. B.; Daly, C. G.; Ackerman, R. L.; George, I. R.; Singh, K. *Dalton Trans.* **2011**, *40*, 495–505.

## Sulfonyl Pyrroles: Synthetic Linchpins for Late-Stage Functionalization of Primary Sulfonamides

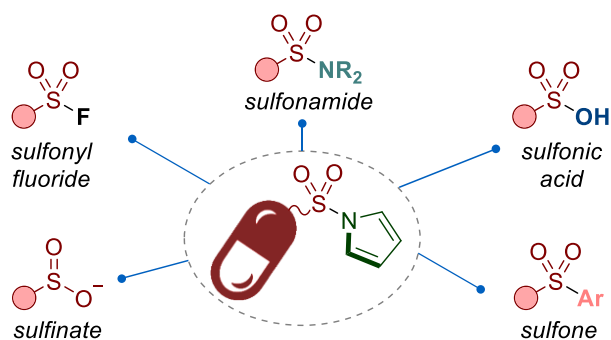
(<sup>1</sup>Department of Chemistry, Graduate School of Science, Kyoto University)

Tomoya Ozaki,<sup>1</sup> Hideki Yorimitsu,<sup>1</sup> ○Gregory J. P. Perry<sup>1</sup>

**Keywords:** organic chemistry/catalysis; late-stage functionalization; sulfonamide; sulfonyl pyrrole; photo-/electrochemistry

Late-stage functionalization is a useful strategy for the selective modification of complex molecules. Sulfonamides are prevalent in a variety of important compounds, most notably pharmaceuticals, however, ways to transform sulfonamides via S–N bond cleavage are rare. In particular, methods for the late-stage functionalization of complex sulfonamide-containing molecules are limited to a handful of recent reports.<sup>1,2,3</sup> Whereas the fields of C–N bond and amide activation have received much attention, the area of sulfonamide activation remains largely untouched. Thus, sulfonamide activation holds great potential in late-stage functionalization and the uncovering of new reactivities.

In this work, sulfonyl pyrroles are revealed as linchpins for primary sulfonamide functionalization.<sup>4</sup> These studies establish sulfonyl pyrroles, which were easily assembled from the corresponding primary sulfonamides via a Paal-Knorr/Clauson-Kaas-type reaction, as highly versatile reagents. This approach provides a variety of functional groups (e.g. sulfinates, sulfones, sulfonic acids, sulfonamides) using chemical, electrochemical or photochemical means. Furthermore, we demonstrate the utility of sulfonyl pyrroles for diversifying sulfonamide-containing drug molecules through late-stage functionalization. It is hoped these early findings highlight the untapped potential of sulfonyl pyrrole chemistry and encourage further investigations within the burgeoning field of sulfonamide activation.



1) P. S. Fier, K. M. Maloney, *J. Am. Chem. Soc.* **2019**, *141*, 1441. 2) A. Gómez-Palomino, J. Cornella, *Angew. Chem. Int. Ed.* **2019**, *58*, 18235. 3) Y. Luo, H. Ding, J.-S. Zhen, X. Du, X.-H. Xu, H. Yuan, Y.-H. Li, W.-Y. Qi, B.-Z. Liu, S.-M. Lu, C. Xue, Q. Ding, *Chem. Sci.* **2021**, *12*, 9556. 4) T. Ozaki, H. Yorimitsu, G. J. P. Perry, *Chem. Eur. J.* **2021**, *27*, 15387.

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Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B**[B104-2am] 16. Natural Products Chemistry, Chemical Biology**

Chair: Takuya Kaji, Ryo Tanifuji

Thu. Mar 24, 2022 9:00 AM - 11:40 AM B104 (Online Meeting)

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**[B104-2am-01] Discovery of New Aplaminone Derivatives from *Aplysia kurodai* and Elucidation of the Origin by Molecular Networking Analysis**

<sup>○</sup>Yusuke Hioki<sup>1</sup>, Ayuka Tochino<sup>2</sup>, Tatsuya Sato<sup>3</sup>, Toyoki Iwao<sup>4</sup>, Atsushi Kawamura<sup>5</sup>, Masaki Kita<sup>1</sup> (1. Graduate School of Bioagricultural Sciences, Nagoya University, 2. School of Agricultural Sciences, Nagoya University, 3. Zakko Club, 4. Toba Fisheries Science Center, 5. Interdisciplinary Cluster for Cutting Edge Research, Shinshu University)

9:00 AM - 9:20 AM

**[B104-2am-02] Structural Study of Actin-Aplyronine A-Tubulin Heterotrimeric Complex and Development of Actin-affinity Tags**

<sup>○</sup>Didik Huswo Utomo<sup>1</sup>, Akari Fujieda<sup>1</sup>, Atsunori Oshima<sup>2</sup>, Akihiro Narita<sup>3</sup>, Momoko Takahashi<sup>4</sup>, Hideo Kigoshi<sup>4</sup>, Masaki Kita<sup>1</sup> (1. Graduate School of Bioagricultural Sciences, Nagoya University, 2. Graduate School of Pharmaceutical Sciences, Nagoya University, 3. Graduate School of Sciences, Nagoya University, 4. Degree Programs of Pure and Applied Sciences, University of Tsukuba)

9:20 AM - 9:40 AM

**[B104-2am-03] Artificial throwback strategy of jasmonate perception by ancestral jasmonate ligand dn-iso-OPDA and *M. polymorpha* COI1 receptor**

<sup>○</sup>Takuya Kaji<sup>1</sup>, Haruka Sakurai<sup>1</sup>, Nobuki Kato<sup>1</sup>, Wang Jianxin<sup>1</sup>, Minoru Ueda<sup>1,2</sup> (1. Grad. Sch. of Science, Tohoku Univ., 2. Grad. Sch. of Life science, Tohoku Univ.)

9:40 AM - 10:00 AM

**[B104-2am-04] Synthetic Study on Mollenyne A**

<sup>○</sup>Nurcahyo Iman Prakoso<sup>1,2</sup>, Shi Quan<sup>1</sup>, Taiki Umezawa<sup>1</sup> (1. Hokkaido University, 2. Universitas Islam Indonesia)

10:00 AM - 10:20 AM

**[B104-2am-05] Generation of Mid-sized Alkaloidal Scaffolds Exhibiting Potent Anti-cancer Activities: Systematic Diversification of Macrocyclic Framework of Ecteinasidins**

<sup>○</sup>Ryo Tanifuji<sup>1</sup>, Erina Hosono<sup>2</sup>, Hiroki Oguri<sup>1</sup> (1. The University of Tokyo, 2. Tokyo University of Agriculture and Technology)

10:20 AM - 10:40 AM

**[B104-2am-06] Total Synthesis of Paclitaxel**

<sup>○</sup>Shota Iiyama<sup>1</sup>, Keisuke Fukaya<sup>1</sup>, Yu Yamaguchi<sup>1</sup>, Ami Watanabe<sup>1</sup>, Hiroaki Yamamoto<sup>1</sup>, Shota Mochizuki<sup>1</sup>, Ryosuke Saio<sup>1</sup>, Takashi Noguchi<sup>1</sup>, Takeshi Oishi<sup>2</sup>, Takaaki Sato<sup>1</sup>, Noritaka Chida<sup>1</sup> (1. Keio University, 2. School of Medicine, Keio University)

10:40 AM - 11:00 AM

**[B104-2am-07] Identification of intracellular proteases that degrade chimeric compounds**

<sup>○</sup>Kai Tahara<sup>1</sup>, Akinobu Nakamura<sup>1</sup>, Sachio Suzuki<sup>1</sup>, Yuki Ichihashi<sup>2</sup>, Yasuteru Urano<sup>2,3</sup>, Toru Komatsu<sup>2</sup>, Shinya Tsukiji<sup>1</sup> (1. Grad. Sch. of Eng., Nagoya Inst. of Tech., 2. Grad.

Sch. of Phar. Sci., The Univ. of Tokyo, 3. Grad. Sch. of Med., The Univ. of Tokyo)

11:00 AM - 11:20 AM

[B104-2am-08] A versatile inducible protein translocation tool for controlling  
plasma membrane signaling

<sup>○</sup>Sachio Suzuki<sup>1</sup>, Akinobu Nakamura<sup>2</sup>, Hatano Yuka<sup>1</sup>, Kazuhiro Aoki<sup>2</sup>, Shinya Tsukiji<sup>1</sup> (1.

Grad. Sch. of Eng., Nagoya Inst. of Tech., 2. ExCELLS, Natl. Inst. of Natural Sci.)

11:20 AM - 11:40 AM

## アメフラシ由来新規 aplaminone 誘導体の発見と分子ネットワーク解析によるその起源の解明

(名大院生命農<sup>1</sup>・名大農<sup>2</sup>・ざっこ Club<sup>3</sup>・鳥羽市水産研<sup>4</sup>・信大バイオメディカル研<sup>5</sup>) ○日置 裕介<sup>1</sup>・棚野 安友花<sup>2</sup>・佐藤 達也<sup>3</sup>・岩尾 豊紀<sup>4</sup>・河村 篤<sup>5</sup>・北 将樹<sup>1</sup>  
Discovery of New Aplaminone Derivatives from *Aplysia kurodai* and Elucidation of the Origin by Molecular Networking Analysis (<sup>1</sup>Graduate School of Bioagricultural Sciences and <sup>2</sup>School of Agricultural Sciences, Nagoya University, <sup>3</sup>Zakko Club, <sup>4</sup>Toba Fisheries Science Center, <sup>5</sup>Interdisciplinary Cluster for Cutting Edge Research, Shinshu University) ○Yusuke Hioki,<sup>1</sup> Ayuka Tochino,<sup>2</sup> Tatsuya Sato,<sup>3</sup> Toyoki Iwao,<sup>4</sup> Atsushi Kawamura,<sup>5</sup> Masaki Kita<sup>1</sup>

Many marine animals possess unique chemical compounds which are involved in defense, predation, and symbiosis, and a variety of bioactive compounds have been discovered so far. These marine natural products are seemed to be produced not by marine animals themselves, but by seaweeds and microorganisms in symbiosis or food chain relationships. However, the pathways have not been fully understood in many cases. In this study, we utilized molecular networking analysis<sup>1)</sup> to elucidate the origin of marine natural products including aplaminones<sup>2,3)</sup>.

We found five new aplaminone derivatives from the sea hare *Aplysia kurodai* and evaluated their cytotoxicity against HCT-116 human cancer cell line. We predicted that this herbivorous animal accumulated cytotoxic compounds from the feeds. Therefore, the secondary metabolites of 16 seaweed species were analyzed by molecular networking analysis, which were collected in the sea near Mie prefecture. As a result, aplaminones were detected in only one species of seaweed, indicating that they were accumulated in *A. kurodai* via the food chain.

**Keywords:** Marine Natural Products; Structure Elucidation; LC-MS/MS; Molecular Networking Analysis; Cytotoxicity

海洋生物には生体防御や捕食、共生に関わる特異な化学物質を持つものが多くみられ、これまでに様々な生物活性物質が発見されてきた。このような海洋天然物の多くは海洋生物自身ではなく、共生もしくは食物連鎖の関係にある海藻や微生物が生産しているとされるが、その獲得経路はほとんど理解が進んでいない。今回我々は、化合物を包括的に解析する分子ネットワーク解析<sup>1)</sup>を用い、海洋天然物 aplaminone<sup>2,3)</sup>の起源の解明を試みた。

これまでに、海洋軟体動物アメフラシ (*Aplysia kurodai*) の高極性画分から HCT-116 ヒトがん細胞の増殖抑制活性を示す新規 aplaminone 誘導体 5 種を単離し、それらの構造と生物活性を解明した。また、アメフラシはこれら化合物を餌の海藻から獲得していると推測し、アメフラシが生息する三重県近海の高極性画分について分子ネットワーク解析を行い、その二次代謝成分を包括的に解析した。その結果、ある 1 種の海藻から aplaminone 類が検出され、aplaminone 類が海藻から食物連鎖を介してアメフラシに蓄積されている可能性が示された。

1) L.-F. Nothias *et al.*, *Nat. Methods* **2020**, *17*, 905. 2) H. Kigoshi *et al.*, *Tetrahedron Lett.* **1990**, *31*, 4911. 3) H. Kigoshi *et al.*, *Tetrahedron Lett.* **1992**, *33*, 4195.

## Structural Study of Actin–Aplyronine A–Tubulin Heterotrimeric Complex and Development of Actin-affinity Tags

(<sup>1</sup>Graduate School of Bioagricultural Sciences, <sup>2</sup>Graduate School of Pharmaceutical Sciences, and <sup>3</sup>Graduate School of Science, Nagoya University, <sup>4</sup>Degree Program of Pure and Applied Sciences, University of Tsukuba)

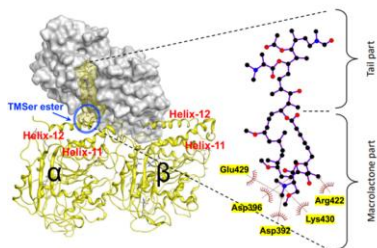
○Didik Huswo Utomo<sup>1</sup>, Akari Fujieda<sup>1</sup>, Atsunori Oshima<sup>2</sup>, Akihiro Narita<sup>3</sup>, Hideo Kigoshi<sup>4</sup>, Masaki Kita<sup>1</sup>

**Keywords:** aplyronine A, protein-protein interaction, actin, tubulin, cryo-EM

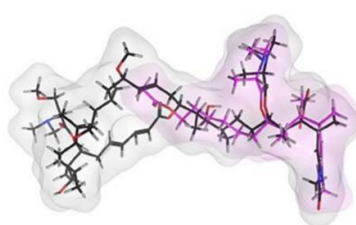
Aplyronine A (ApA) is a potent protein–protein interaction (PPI) inducer for actin and tubulin<sup>1</sup>. However, the binding position and antitumor molecular mechanism of ApA are still unclear. This study aimed to evaluate the heterotrimeric structure of “actin-ApA-tubulin” using cryo-electron microscopy (EM) and protein-protein docking approach. Initially, binding position analysis was performed by direct interaction between paclitaxel-stabilized microtubules (MTs) and actin-ApA. Negative staining-EM showed that MTs were rapidly disrupted by actin-ApA, but the binding position of actin-ApA on MT surface was unclear by cryo-EM analysis. To get heterotrimeric complex, single-particle analysis by cryo-EM was also examined, in which tubulin heterodimer and actin-ApA were directly mixed.

Next, protein-protein docking study was performed using molecular operating environment (MOE-2019) based on blind docking approach. 100 binding pose candidates were then screened based on the Gibbs free energy to get 10 heterotrimeric complexes. Further molecular dynamics simulation afforded a plausible heterotrimeric complex model, in which the C7 *N,N,O*-trimethylserine (TMSer) ester directly interacted with helix-11 and helix-12 of tubulin, being located at the outer surface of MT. These results suggested that the TMSer ester of ApA had an important role to stabilize the PPI between actin and tubulin heterodimer.

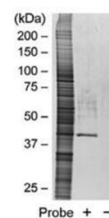
Inspired by ApA as a PPI inducer, we developed structurally-simplified C29–C34 side-chain analogs. The analogs possessing the C23 acyloxy group, the C29 *N,N*-dimethyl-L-alanine ester and the C34 *N*-methyl enamide selectively bound to actin and showed actin-depolymerizing activity, while reducing synthetic efforts.<sup>2</sup>



Heterotrimeric complex: actin-ApA-tubulin



Docking model of simplified analog and affinity purification



1) Kita, M. et al. *J. Am. Chem. Soc.* **2013**, *135*, 18089–18095; 2) Utomo, D. H. et al. *Chem. Commun.* **2021**, 57, 10540–10543.



## 始原植物ホルモン dn-iso-OPDA およびゼニゴケ COI1 受容体を用いたジャスモン酸認識の「人工的先祖返り」戦略

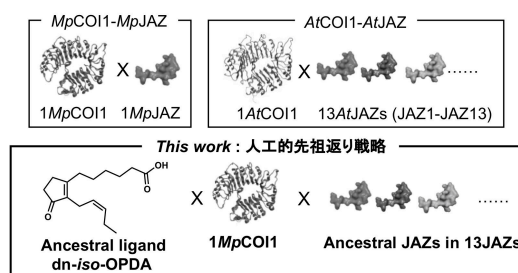
(東北大院理<sup>1</sup>・東北大院生命<sup>2</sup>) ○加治 拓哉<sup>1</sup>・櫻井 春香<sup>1</sup>・加藤 信樹<sup>1</sup>・Wang Jianxin<sup>1</sup>, 上田 実<sup>1,2</sup>

Artificial throwback strategy of jasmonate perception by ancestral jasmonate ligand dn-iso-OPDA and *M. polymorpha* COI1 receptor (<sup>1</sup>Graduate School of Science, Tohoku University, <sup>2</sup>Graduate School of Life Sciences, Tohoku University) ○Takuya Kaji,<sup>1</sup> Haruka Sakurai,<sup>1</sup> Nobuki Kato,<sup>1</sup> Wang Jianxin,<sup>1</sup> Minoru Ueda<sup>1,2</sup>

Dn-iso-OPDA was identified as an active ancestral jasmonate (JA) ligand in a bryophyte, *Marchantia polymorpha* L., whereas ordinary jasmonate ligand, 7-iso-JA-Ile cannot be perceived by *Mp*COI1-*Mp*JAZ co-receptor. Here we introduce an “artificial throwback” strategy to modify jasmonate perception of *A. thaliana* using dn-iso-OPDA and *Mp*COI1. By using this concept, endogenous JA ligand would not be perceived by *Mp*COI1 and JA response would be manually triggered by exogenous treatment of dn-iso-OPDA. In addition, ancestral receptor-ligand combination, *Mp*COI1-dn-iso-OPDA, would show selectivity against ancestral type of *At*JAZ subtypes. Herein, we will report the *in-vitro* evaluation of subtype selective binding activity of *Mp*COI1 and dn-iso-OPDA against *At*JAZ. As a result of pull-down assay, *At*JAZ3/9 selective binding activity was suggested.

**Keywords :** plant hormone; natural products chemistry; chemical biology; protein-protein interaction

ゼニゴケ(*M. polymorpha*)では dinor-iso-12-oxo-phytodienoic acid (dn-iso-OPDA)が始原植物ホルモンとして *Mp*COI1-*Mp*JAZ 共受容体に結合する一方、高等植物のジャスモン酸(JA)リガンドは結合しないことが近年報告された<sup>1</sup>。そこで我々はシロイヌナズナの COI1 を *Mp*COI1 で置き換える、始原植物ホルモンを用いたジャスモン酸認識の先祖返り戦略を立案した(図)。本戦略を用いると、*Mp*COI1 は高等植物の内因性 JA リガンドと結合しないことから、始原植物ホルモンの外部投与によって人為的に JA 応答が制御できると期待される。また、JA リガンドの COI1-JAZ 受容体との結合様式として、COI1 に JA リガンドが結合した後に JAZ とのタンパク質間相互作用が誘導されることが考えられている<sup>2</sup>。そこで、始原植物ホルモン受容体-リガンドである *Mp*COI1-dn-iso-OPDA に対し、13 種類存在する *At*JAZ の中でも原始的な JAZ サブタイプがより選択的に結合するものと予想し、実際に結合活性を評価した。その結果、*At*JAZ3/9 により選択的な結合活性が示唆されたので詳細を報告する。



1) Monte, I. *et al. Nat. Chem. Biol.* **2018**, *14*, 480. 2) Yan J. *et al. Mol. Plant* **2018**, *11*, 1237.

## Synthetic Study on Mollenyne A

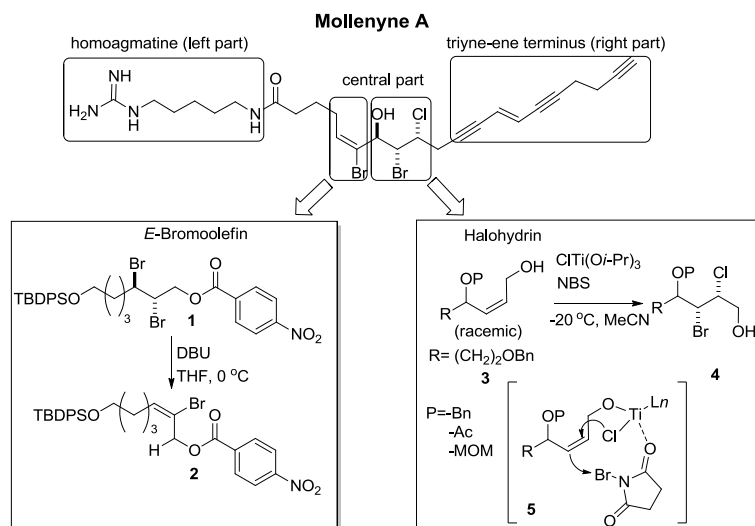
(<sup>1</sup>Graduate School of Environmental Science, Hokkaido University, <sup>2</sup>Chemistry Department, Universitas Islam Indonesia) ○Nurcahyo Iman Prakoso,<sup>1,2</sup> Shi Quan,<sup>1</sup> Taiki Umezawa,<sup>1</sup>

**Keywords:** Mollenyne A; Bromochlorination; Natural product; Halogen; Triyne-ene

Mollenyne A was isolated from the sponge *Spirastrella mollis* from Plana Cays, Bahamas by Molinski *et al.*, and has a biological activity as an anti-tumor potential in human colon tumor cells (HCT-116, with IC<sub>50</sub> = 1.3 µg/mL).<sup>1)</sup> Mollenyne A includes three important fragments, homoagmatine (left part), allylic alcohol flanked by halogenated carbons (central part) and triyne-ene terminus (right part). Due to the promising the biological activity as well as the intriguing chemical structure, the synthesis of Mollenyne A has been started for abundant supply.

The central part can be divided into two parts, the *E*-bromoolefin and halohydrin. The *E*-bromoolefin moiety was prepared with benzoate **1** via regio- and stereoselective *E*-elimination. *p*-Nitrobenzoyl group induced the desired elimination reaction through increase of the acidity of the hydrogen at the target position.<sup>2)</sup>

On the other hand, the halohydrin was also investigated with racemic model alcohol **3**. Based on a crucial findings by Burns, TiCl(O*i*-Pr)<sub>3</sub> as a Cl<sup>-</sup> source and NBS as a Br<sup>+</sup> source were used in the regioselective bromochlorination reaction to produce **4**.<sup>3)</sup> This reaction is rationalized by the complexed intermediate **5** which enables the regioselectivity of bromide and chloride. Effects of a substituent on hydroxy group toward diastereoselectivity are examined.



- 1) B.I. Morinaka, T.F. Molinski, *Org. Lett.*, **2011**, 13, 6338-6341
- 2) T. Ohgiya, S. Nishiyama, *Tetrahedron Lett.*, **2004**, 45, 8273-8275
- 3) D.X. Hu, F.J. Seidl, C. Bucher, N.Z. Burns, *J. Am. Chem. Soc.*, **2015**, 137, 3795-3798

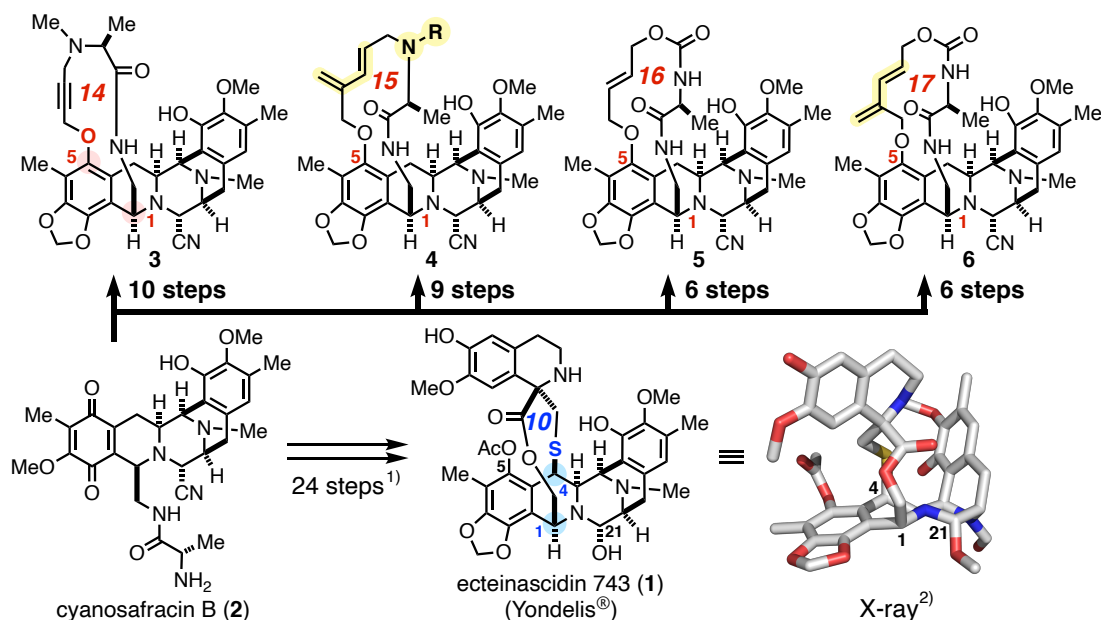
## Generation of Mid-sized Alkaloidal Scaffolds Exhibiting Potent Anti-Cancer Activities: Systematic Diversification of Macrocyclic Framework of Ecteinascidins

(<sup>1</sup>Graduate School of Science, The University of Tokyo, <sup>2</sup>Graduate School of Engineering, Tokyo University of Agriculture and Technology) ○Ryo Tanifuji,<sup>1</sup> Erina Hosono,<sup>2</sup> Hiroki Oguri<sup>1</sup>

**Keywords:** Tetrahydroisoquinoline Alkaloids; Macrocycle; Natural Products; Mid-sized Molecules; DNA Alkylation

Ecteinascidin 743 (**1**) exhibits potent anticancer activity and is clinically approved for the chemotherapy for sarcoma. The highly functionalized marine-derived alkaloid **1** has a 10-membered macrolactone ring bridged on the hexacyclic core scaffold at C1 and C4 positions. In this study, we conceived macrocycle formation at C5 in place of the C4 position to gain concise and flexible access to the novel alkaloidal scaffolds with DNA binding ability. We are developing a semi-synthetic process starting from cyanosafrafin B (**2**), allowing systematic diversification of the macrocyclic frameworks ranging from 14 to 17 membered rings.

Semi-synthesis of **3** bearing a 14-membered ring was achieved via Cu(I)-catalyzed three-component coupling reaction as a key step for macrocyclization. Then, 15- and 17-membered macrocycles (**4**, **6**) with a conjugated diene moiety were efficiently synthesized by employing ring-closing enyne metathesis reactions in 9 and 6 steps from **2**, respectively. The 16-membered macrocycle **5** with an olefinic double bond was also generated in 6 steps from **2** via a ring-closing metathesis reaction. DNA alkylating ability, potent growth inhibitory activity against various cancer cell lines, and further extension of semi-synthetic process will be presented.



1) Cuevas, C.; Francesch, A. *Nat. Prod. Rep.* **2009**, 26, 322–337.

2) Sakai, R.; Rinehart K. L.; Guan, Y.; Wang, A. H.-J. *Proc. Natl. Acad. Sci. USA*, **1992**, 89, 11456–11460.

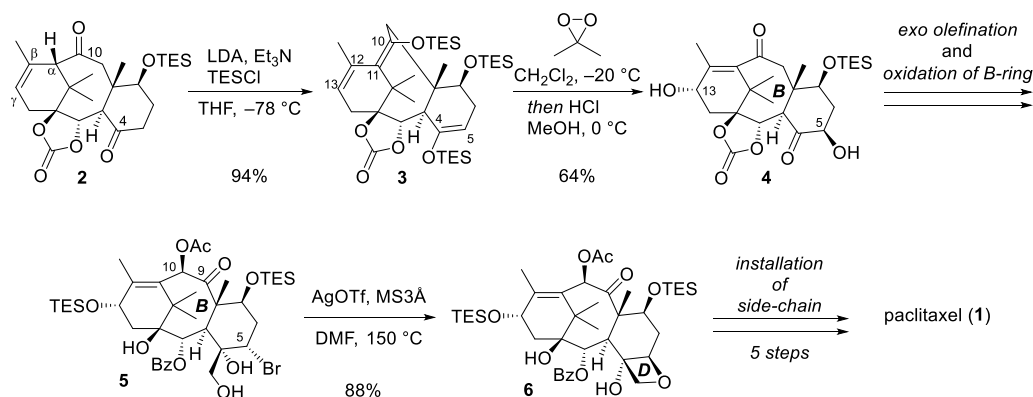
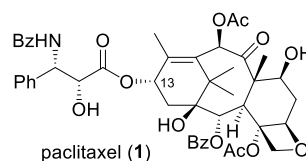
## Total Synthesis of Paclitaxel

(<sup>1</sup>*Faculty of Science and Technology, Keio University*, <sup>2</sup>*School of Medicine, Keio University*)

○ Shota Iiyama,<sup>1</sup> Keisuke Fukaya,<sup>1</sup> Yu Yamaguchi,<sup>1</sup> Ami Watanabe,<sup>1</sup> Hiroaki Yamamoto,<sup>1</sup> Shota Mochizuki,<sup>1</sup> Ryosuke Saio,<sup>1</sup> Takashi Noguchi,<sup>1</sup> Takeshi Oishi,<sup>2</sup> Takaaki Sato,<sup>1</sup> Noritaka Chida<sup>1</sup>

**Keywords:** paclitaxel; total synthesis; Rubottom oxidation; bridgehead olefin; oxetane

Paclitaxel (Taxol, **1**) is a well-known natural diterpenoid that has been efficacious as an anticancer drug. The structural features of **1** are bridgehead olefin and an oxetane ring which are embedded in highly oxidized tetracyclic framework. Moreover, **1** includes nine stereo centers including a quaternary carbon. In 2015, we achieved the formal synthesis of **1** via Takahashi's intermediate.<sup>1,2</sup> However, many steps were required for the installation of the bridgehead olefin, oxidation of the taxane framework, and formation of the oxetane-ring. To solve these problems, we investigated the 2nd generation synthesis of **1** (Scheme 1). Treatment of  $\beta,\gamma$ -unsaturated diketone **2** with TESCl and LDA gave bis(silyl enol ether) **3**. Epoxidation of **3** with DMDO and following acidic workup constructed a bridgehead olefin and two hydroxy groups at C-5 and C-13, simultaneously, through double Rubottom oxidation to generate diol **4**. Subsequently, **4** was transformed to oxetane precursor **5**. Treatment of **5** with AgOTf provided oxetane **6** in 88% yield. Finally, installing of a side-chain at C-13 and the removing of silly-group, we accomplished the total synthesis of paclitaxel (**1**) (47 steps, LLS from 3-methoxy toluene).<sup>3</sup>



Scheme 1. Synthesis of paclitaxel (**1**)

1) T. Takahashi *et al*, *Chem. Asian. J.* **2006**, *1*, 370–383. 2) N. Chida *et al*, *Org. Lett.* **2015**, *17*, 2570–2573; *Org. Lett.* **2015**, *17*, 2574–2577. 3) N. Chida *et al*, *Org. Lett.* **2021**, doi.org/10.1021/acs.orglett.1c03851

## キメラ化合物を分解する細胞内プロテアーゼの同定

(名工大院工<sup>1</sup>・東大院薬<sup>2</sup>・東大院医<sup>3</sup>) ○田原 海<sup>1</sup>・中村 彰伸<sup>1</sup>・鈴木 祥央<sup>1</sup>・市橋 祐樹<sup>2</sup>・浦野 泰照<sup>2,3</sup>・小松 徹<sup>2</sup>・築地 真也<sup>1</sup>

Identification of intracellular proteases that degrade chimeric compounds (<sup>1</sup>*Graduate School of Engineering, Nagoya Institute of Technology*, <sup>2</sup>*Graduate School of Pharmaceutical Sciences, The University of Tokyo*, <sup>3</sup>*Graduate School of Medicine, The University of Tokyo*) ○Kai Tahara,<sup>1</sup> Akinobu Nakamura,<sup>1</sup> Sachio Suzuki,<sup>1</sup> Yuki Ichihashi<sup>2</sup>, Yasuteru Urano<sup>2,3</sup>, Toru Komatsu<sup>2</sup>, Shinya Tsukiji<sup>1</sup>

In chemical biology, various chimeric compounds, such as chemical inducers of dimerization, PROTACs, and self-localizing ligands, have been generated by connecting two functional molecules (e.g. ligands) via a linker with amide bonds. Such chimeric compounds have been considered to be stable in cells. However, we recently found that mgcTMP, a chimeric molecule consisting of trimethoprim and the myristoyl-Gly-Cys motif, undergoes degradation of the amide bond C-terminal to the Cys residue in cells. In this work, we identified proteases responsible for the mgcTMP degradation. We also tested several other amide-containing chimeric compounds for possible cellular degradation, revealing that even a simple lipid-tethered small molecule without any amino acid is susceptible to proteolytic degradation.

**Keywords:** *chimeric compound; self-localizing ligand; intracellular degradation; protease*

小分子リガンドなどの機能性分子を複数連結したキメラ化合物は、生命現象の解明や制御のための強力なツールとして注目されている。例えば、「化学二量化剤」、「PROTACs」、「局在性リガンド」などがキメラ化合物の代表例として挙げられる。これらキメラ化合物の設計では、2つの機能性分子をスパーサーを介してアミド結合で連結する場合が多く、これらは細胞内で安定であるという前提で使用する。本発表では、アミド結合を持つキメラ化合物は必ずしも細胞内で安定ではなく、構造によっては細胞内で分解されうることが報告する。

当研究室では以前に、大腸菌ジヒドロ葉酸還元酵素 (eDHFR) に対する小分子リガンドトリメトプリム (TMP) に、ミリスチン酸-グリシン-システインを連結した化合物「mgcTMP」を開発した<sup>1)</sup>。mgcTMPは動物細胞内に発現させた eDHFR 融合タンパク質を細胞質から細胞膜内膜へ移行させることができる。しかし、想定外なことに、その局在移行は一過的であり、その原因は mgcTMP 中のアミド結合の細胞内分解に起因することを見出した<sup>2)</sup>。このようなキメラ化合物の細胞内分解はほとんど研究されておらず、どのような酵素が分解に関与し、どのような構造のキメラ化合物が分解を受けやすいのかといった知見はほとんどない。そこで本研究ではまず、mgcTMPの分解酵素を Diced Electrophoresis Gel (DEG) 法<sup>3)</sup>、阻害剤アッセイ、ノックアウト細胞を用いた実験により同定した。さらに、mgcTMP以外の化合物についても評価することで、アミド結合連結型キメラ化合物の細胞内分解の一般性について評価した。

1) M. Ishida et al. *J. Am. Chem. Soc.*, **2013**, *135*, 12684–12689. 2) A. Nakamura et al. *ACS Chem. Biol.*, **2020**, *15*, 837–843. 3) T. Komatsu et al. *J. Am. Chem. Soc.*, **2013**, *135*, 6002–6005.

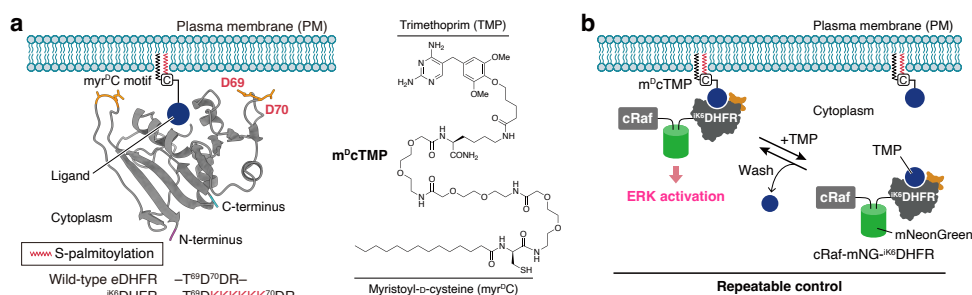
## A versatile inducible protein translocation tool for controlling plasma membrane signaling

(<sup>1</sup>Graduate School of Engineering, Nagoya Institute of Technology, <sup>2</sup>Exploratory Research Center on Life and Living Systems, National Institutes of Natural Sciences) ○Sachio Suzuki,<sup>1</sup> Akinobu Nakamura,<sup>2</sup> Yuka Hatano,<sup>1</sup> Kazuhiro Aoki,<sup>2</sup> Shinya Tsukiji<sup>1</sup>

**Keywords:** chemogenetics; protein translocation; self-localizing ligand; plasma membrane; signal oscillation

The inner leaflet of the plasma membrane (iPM) serves as a platform for intracellular signaling networks. Therefore, the ability to rapidly recruit signaling proteins to the iPM is a powerful approach for cell signaling research. For this purpose, several methods based on chemically induced dimerization (CID) have been developed. However, most of the CID tools require the expression of two protein components to control a single target protein and are ill-suited for controlling proteins reversibly and repeatedly.

The SLIPT (self-localizing ligand-induced protein translocation) system developed by us is a methodology to control protein translocation.<sup>1,2</sup> In SLIPT, a small-molecule hybrid ligand with an organelle/membrane localization ability is used to recruit its binding protein from the cytoplasm to the target site. Here, we present a versatile chemogenetic SLIPT system for iPM-specific protein recruitment. We created an engineered SLIPT tag, termed <sup>iK6</sup>DHFR (**Fig. a**), by inserting a hexalysine (K6) sequence into the loop region of *Escherichia coli* dihydrofolate reductase (eDHFR).<sup>3</sup> The <sup>iK6</sup>DHFR-fused proteins can be recruited specifically from the cytoplasm to the iPM within a few minutes with the myristoyl-D-Cys-tethered trimethoprim ligand (m<sup>D</sup>cTMP).<sup>2</sup> The <sup>iK6</sup>DHFR/m<sup>D</sup>cTMP system is applicable to control various signal processes, such as Raf/ERK activation, Ca<sup>2+</sup> signaling, and cAMP generation. We also succeeded in manipulating the localization and activity of signaling proteins repeatedly by using two chemicals, m<sup>D</sup>cTMP and TMP (**Fig. b**). In this presentation, we will report the details and applications of the <sup>iK6</sup>DHFR/m<sup>D</sup>cTMP platform.



**Fig. (a)** Design of <sup>iK6</sup>DHFR and structure of m<sup>D</sup>cTMP. **(b)** Synthetic chemical oscillation of ERK.

1) M. Ishida *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 12684. 2) A. Nakamura *et al.*, *ACS Chem. Biol.* **2020**, *15*, 1004. 3) Y. Hatano *et al.*, *bioRxiv* DOI: 10.1101/2021.03.16.435568.

**[G101-2am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Tamaki Endoh, Hiromu Kashida

Thu. Mar 24, 2022 9:00 AM - 11:40 AM G101 (Online Meeting)

**[G101-2am-01] Photocaged chemically modified PCR primer aiming accurate and efficient DNA assembly**

○Fumitaka Hashiya<sup>1</sup>, Kaoru Onda<sup>2</sup>, Kohei Nomura<sup>2</sup>, Gao Yuino<sup>2</sup>, Hirotaka Murase<sup>2</sup>, Kosuke Nakamoto<sup>2</sup>, Masahito Inagaki<sup>2</sup>, Haruka Hiraoka<sup>2</sup>, Naoko Abe<sup>2</sup>, Yasuaki Kimura<sup>2</sup>, Natsuhisa Oka<sup>3,4,6</sup>, Goro Terai<sup>5,6</sup>, Kiyoshi Asai<sup>5,6</sup>, Hiroshi Abe<sup>1,2,6,7</sup> (1. Research Center for Material Science, Nagoya University, 2. Graduate School of Science, Nagoya University, 3. Department of Chemistry and Biomolecular Science, Gifu University, 4. Institute for Glyco-core Research (iGCORE), Gifu University, 5. Department of Computational Biology and Medical Sciences, University of Tokyo, 6. CREST, Japan Science and Technology Agency, 7. Institute for Glyco-core Research (iGCORE), Nagoya University)

9:00 AM - 9:20 AM

**[G101-2am-02] Orthogonal signal amplification circuit composed of acyclic nucleic acid for RNA visualization**

○Yanglingzhi Chen<sup>1</sup>, Keiji Murayama<sup>1</sup>, Hiroyuki Asanuma<sup>1</sup> (1. The Univ. of Nagoya)

9:20 AM - 9:40 AM

**[G101-2am-03] Improvement of inhibitory activity of SNA-based anti-miRNA-21 by introduction of pseudocomplementary bases**

○Fuminori Sato<sup>1</sup>, Keiji Murayama<sup>1</sup>, Yukiko Kamiya<sup>1</sup>, Hiroyuki Asanuma<sup>1</sup> (1. The Univ. of Nagoya)

9:40 AM - 10:00 AM

**[G101-2am-04] Staple oligomer hijacks protein translation machinery based on the conformational changes of mRNA structure**

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

10:00 AM - 10:20 AM

**[G101-2am-05] Imidazolium-modified supports as nucleic acid adsorbents and its application to DNA amplification testing**

○Yasuaki Kakikura<sup>1</sup> (1. Osaka Research Institute of Industrial Science and Technology)

10:20 AM - 10:40 AM

**[G101-2am-06] Photo-oxidation properties of guanosine in the duplex by a small, efficient photosensitizer**

○Takashi Kanamori<sup>1</sup>, Shota Kaneko<sup>1</sup>, Kohji Hanamoto<sup>1</sup>, Chao Wang<sup>1</sup>, Ruoyu Li<sup>1</sup>, Hideya Yuasa<sup>1</sup> (1. Tokyo Institute of Technology)

10:40 AM - 11:00 AM

[G101-2am-07] Evaluation of side-products in chemically synthesized DNA by next-generation sequencing

○Yoshiaki Masaki<sup>1,2</sup>, Taichi Yagata<sup>1</sup>, Kohji Seio<sup>1</sup> (1. Tokyo Tech, 2. JST PRESTO)

11:00 AM - 11:20 AM

[G101-2am-08] Effect of the ordered hydration layer for the enzymatic reactions on DNA scaffold

○Peng Lin<sup>1</sup>, Huyen Dinh<sup>1</sup>, Eiji Nakata<sup>1</sup>, Takashi Morii<sup>1</sup> (1. Institute of Advanced Energy, Kyoto University)

11:20 AM - 11:40 AM



## 高精度かつ高効率な DNA 連結を実現する光保護化学修飾プライマー

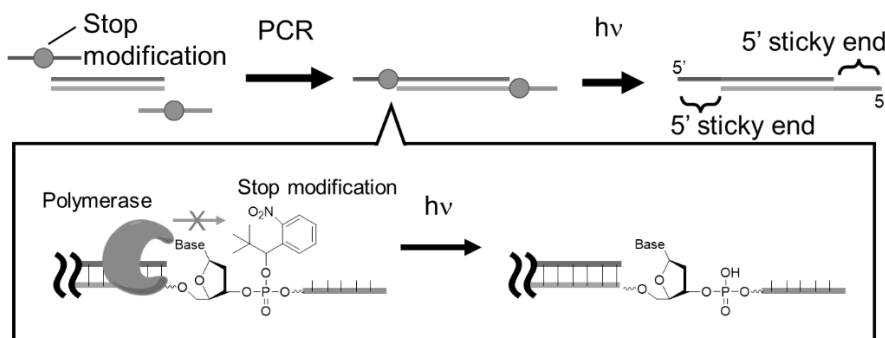
(名大 物国センター<sup>1</sup>・名大 院理<sup>2</sup>・岐大 院工<sup>3</sup>・岐大 糖鎖コア<sup>4</sup>・東大 創域<sup>5</sup>・JST CREST<sup>6</sup>・名大 糖鎖コア<sup>7</sup>) ○橋谷 文貴<sup>1</sup>・恩田 馨<sup>2</sup>・野村 浩平<sup>2</sup>・Gao Yiuno<sup>2</sup>・村瀬 裕貴<sup>2</sup>・中本 航介<sup>2</sup>・稲垣 雅仁<sup>2</sup>・平岡 陽花<sup>2</sup>・阿部 奈保子<sup>2</sup>・木村 康明<sup>2</sup>・岡 夏央<sup>3,4,6</sup>・寺井 悟朗<sup>5,6</sup>・浅井 潔<sup>5,6</sup>・阿部 洋<sup>1,2,6,7</sup>

Photocaged chemically modified PCR primer aiming accurate and efficient DNA assembly (<sup>1</sup>Research Center for Material Science, Nagoya University, <sup>2</sup>Graduate School of Science, Nagoya University, <sup>3</sup>Department of Chemistry and Biomolecular Science, Gifu University, <sup>4</sup>Institute for Glyco-core Research (iGCORE), Gifu University, <sup>5</sup>Department of Computational Biology and Medical Sciences, University of Tokyo, <sup>6</sup>CREST, Japan Science and Technology Agency, <sup>7</sup>Institute for Glyco-core Research (iGCORE), Nagoya University) ○Fumitaka Hashiya,<sup>1</sup> Kaoru Onda,<sup>2</sup> Kohei Nomura,<sup>2</sup> Gao Yuino,<sup>2</sup> Hiroataka Murase,<sup>2</sup> Kosuke Nakamoto,<sup>2</sup> Masahito Inagaki,<sup>2</sup> Haruka Hiraoka,<sup>2</sup> Naoko Abe,<sup>2</sup> Yasuaki Kimura,<sup>2</sup> Natsuhisa Oka,<sup>3,4,6</sup> Goro Terai,<sup>5,6</sup> Kiyoshi Asai,<sup>5,6</sup> Hiroshi Abe,<sup>1,2,6,7</sup>

In DNA assembly, each DNA fragments need to be concatenated through sticky-end generated on the end of fragments. Conventional methods generate it by enzymatic digestion. However, the method requires specific sequence, and the generated sticky-end is not enough long to ensure accuracy and fidelity. In the present study, we have synthesized DNA primer containing stop modification to generate any length and sequence sticky-end. PCR with the primer effectively generated sticky-ends and achieved accurate and efficient DNA assembly. Furthermore, it was an attractive method to perform genome scale DNA build up.

**Keywords :** Chemical biology, Synthetic biology, DNA assembly, Genome DNA build-up, Photocaged nucleotide

DNA 断片の連結では突出末端を形成し、断片同士を近接する必要がある。従来法では酵素消化によって突出末端を形成するが利用できる DNA 配列に制限があり、生じる突出部分が短いため正確性と効率の担保が困難となっている。本研究では光保護化学修飾を DNA に導入することで PCR を停止する stop プライマーの開発に成功した。このプライマーを用いることで任意の長さ、配列の突出末端形成を実現した。加えて高精度かつ高効率な DNA 連結、およびゲノムスケール DNA の合成も達成したので併せて発表する。



## Orthogonal signal amplification circuit composed of acyclic nucleic acid for RNA visualization

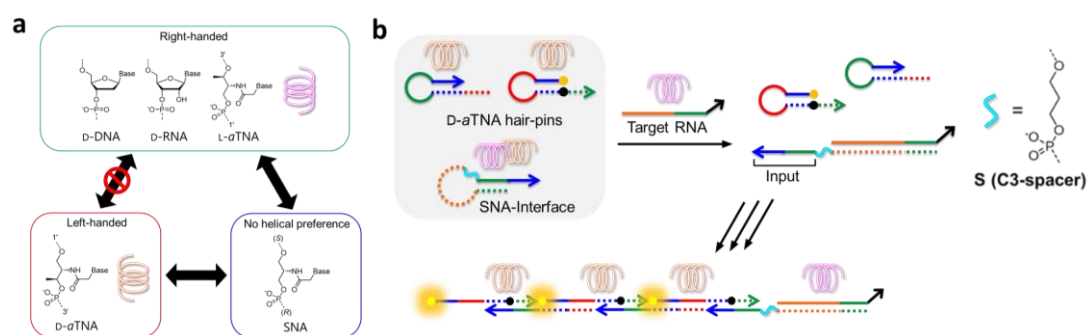
(<sup>1</sup>Graduate School of Engineering, Nagoya University) ○ Yanglingzhi Chen,<sup>1</sup> Keiji Murayama,<sup>1</sup> Hiroyuki Asanuma<sup>1</sup>

**Keywords:** Hybridization chain reaction; Orthogonality; RNA detection

By utilizing a simple concept of toehold-mediated strand displacement, hybridization chain reaction (HCR) circuit enables signal amplification targeting nucleic acids. However, application of DNA-HCR *in vivo* is limited due to unintended cross-hybridization and degradation by nuclease.

Previously, our group has demonstrated high orthogonality of left-handed *acyclic* D-threoninol nucleic acid (D-*a*TNA) against D-DNA and D-RNA.<sup>[1]</sup> Serinol nucleic acid (SNA), composed symmetric linker with no helical preference, could act as interface that enabled activation of D-*a*TNA circuit by D-RNA (figure 1a).<sup>[2]</sup>

We report a novel HCR circuit composed of D-*a*TNA. Since D-threoninol cannot be recognized by nuclease, high enzymatic resistance has been confirmed. Because of strong base-pairing interaction, *a*TNA hairpin with short stem (7-mer) ensured clear ON-OFF control of the HCR circuit. Right-handed *acyclic* L-threoninol nucleic acid (L-*a*TNA) HCR circuit was also designed, and high orthogonality between D- and L-*a*TNA HCRs was confirmed by activation of each *a*TNA HCR via corresponding input strand. Finally, D-*a*TNA HCR was applied to RNA-dependent signal amplification system via SNA-interface (figure 1b). Incorporation of C3-spacer into SNA-interface solved inhibition of activating D-*a*TNA HCR by a propagation of helicity, achieving fast signal amplification (data not shown). This work represents the first example for conducting heterochiral HCR circuits, which is potential for direct visualization of RNA *in vivo*.



**Figure 1** (a) Chemical structures, helicities, and hybridization compatibilities of DNA, RNA and acyclic XNAs. (b) Schematic illustration of SNA-mediated D-*a*TNA HCR triggered by RNA.

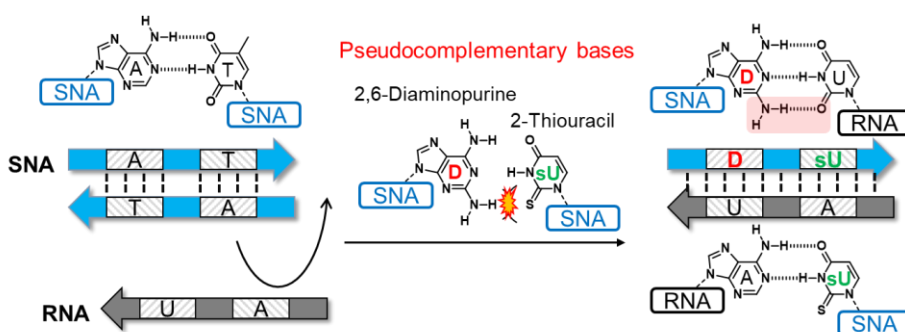
1) Murayama, K.; Kashida, H.; Asanuma, H. *Chem. Commun.* **2015**, 51, 6500-6503. 2) Murayama, K.; Nagao, R.; Asanuma, H. *ChemistrySelect* **2017**, 2, 5624–5627.

## Improvement of inhibitory activity of SNA-based anti-miRNA-21 by introduction of pseudocomplementary bases

(Graduate School of Engineering, Nagoya University) ○Fuminori Sato, Keiji Murayama, Yukiko Kamiya, Hiroyuki Asanuma

**Keywords:** SNA; Pseudocomplementary bases; Anti-miRNA oligonucleotides

Artificial nucleic acids that have high nuclease resistance and affinity to natural oligonucleotides are promising for use in nucleic acid drugs. We have developed an acyclic artificial nucleic acid, SNA that can stably hybridize with natural oligonucleotides and have remarkably high nuclease resistance. Using SNA we have attempted to develop anti-miRNA oligonucleotides (SNA-AMOs) for inhibition of disease-related miRNA. Previously we reported improvement of the antisense activity of SNA-AMO against miR-21 by replacing of adenines with 2,6-diaminopurines (D).<sup>2</sup> However we also found that multiple introductions of D promote self-association of SNA-AMO, resulting in reduction of its anti-miRNA activity. To solve this issue, we focused on D and 2-thiouracil (sU) known as “Pseudocomplementary bases”.<sup>3</sup> The sulfur atom on sU causes steric hindrance that prevents pairing with D, whereas D can recognize uracil much stronger than adenine through three hydrogen bonds. Therefore, we introduced multiple sU residues at the base-pairing position of D residue in the complementary region of SNA-AMO. We conducted  $T_m$  measurements and Native-PAGE analyses to investigate effect of D-sU incorporations into SNA-AMOs on SNA-SNA or SNA-RNA interactions. We succeeded in decrease of SNA-SNA interaction and increase of affinity to miR-21 simultaneously upon substitution with D-sU pairs. Significant improvement of the antisense activity against miR-21 by introducing of D-sU pairs into SNA-AMO was also clearly demonstrated.



1) (a) H. Kashida *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 1285, (b) K. Murayama *et al.*, *Chem. Eur. J.* **2013**, 19, 14151.

2) Y. Kamiya, *et al.*, *ChemBioChem*, **2017**, 18, 1917.

3) Y. Kamiya, F. Sato, *et al.*, *Chem. Asian J.*, **2020**, 15, 1266.

## Staple oligomer hijacks protein translation machinery based on the conformational changes of mRNA structure

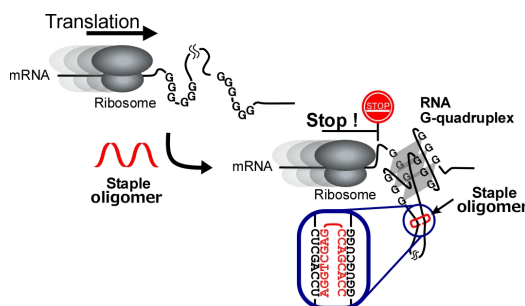
(<sup>1</sup>Faculty of Advanced Science and Technology, Kumamoto University, <sup>2</sup>Department of Medical Information Sciences and Administration Planning, Kumamoto University Hospital, <sup>3</sup>Department of Cardiovascular Medicine, Faculty of Life Sciences, Kumamoto University, <sup>4</sup>Faculty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

**Keywords:** RNA G-quadruplex; Staple oligomer; Suppression of gene expression; Off-target effect; Next generation nucleic acid medicine

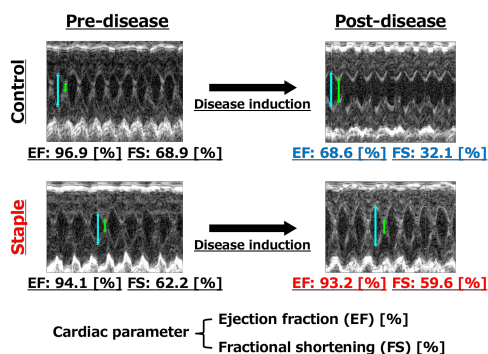
Nucleic acid-based technologies such as antisense oligonucleotide (ASO) and small interfering RNA (siRNA) are effective strategies to inhibit the expression of disease-causing genes with sequence complementarity. The technologies often exhibit off-target effects emerging from the mis-hybridization to unintended genes. This is one of the challenges in the development of nucleic acid medicines. Although various ASO and siRNA design platforms have been developed to address this problem, there are still some genes that are difficult to target due to the limited number of potential sequences for high suppression efficiency and low off target effects.

Here, we developed an alternative method to suppress gene expression through induction of G-quadruplex structure in the target mRNA using single strand DNA or RNA named staple oligomer (**Fig. 1**). RNA G-quadruplex structure is known to inhibit protein translation by blocking the progression of ribosomes. The staple induced G-quadruplex structure on 5'UTR of mRNA and its expression level was significantly decreased both in vitro and in vivo. Furthermore, we succeeded in inhibiting the progression of the disease by suppressing responsible gene expression using the staple in disease-model mouse (**Fig. 2**).

The staple system would be a promising technique as a research tool in life sciences and new class of nucleic acid medicines.



**Fig. 1** The suppression of target gene expression by staple-induced G-quadruplex



**Fig. 2** Evaluation of the effect of the staple on the disease progression.

## イミダゾリウム修飾担体の DNA 吸着特性と核酸増幅法への適用

(地方独立行政法人大阪産業技術研究所) ○柿倉 泰明

Imidazolium-modified supports as nucleic acid adsorbents and its application to DNA amplification testing (*Osaka Research Institute of Industrial Science and Technology*)

○Yasuaki Kakikura

Imidazolium modified silica (IMS) was prepared toward facile DNA extraction without multiple instrument steps and organic solvent treatment. The results indicated that the IMS was capable for specifically adsorbing DNA by electrostatic interactions with the imidazolium. The adsorbed DNA on the IMS was effectively eluted by means of high concentration buffer. The developed method could be employ for nucleic acid testings such as PCR.

*Keywords : DNA Extraction; Imidazolium; Nucleic Acid Testing*

核酸検査は、病原体などの標的に由来する核酸を増幅して検出する手法であり、微量の標的を高感度検出できる。そのため、医療や農畜産などの分野で広く活用されている。近年では特定の検査室の外でも使えるポータブルな核酸増幅反応用の装置が上市され<sup>1)</sup>、検体を採取した現場での核酸検出を可能にしている。一方で、その前処理工程である核酸抽出に着目すると、遠心操作や有機溶媒処理など、煩雑な操作を要する手法が標準的に用いられているのが現状である。そこで、簡便な核酸抽出の手法の開発に向けて、シリカゲル表面にイミダゾリウムを修飾した核酸吸着体(Imidazolium modified silica, IMS)を作製した。本発表では IMS への静電的相互作用による核酸の吸着、溶出方法の検討、および溶出液の核酸増幅への適用結果について報告する。

アルコキシシランを原料として、ゾルーゲル法によりチオール基を有するシリカゲルを作製した。このシリカゲル表面に、ene-thiol 反応によってビニルイミダゾリウムを修飾して、IMS を得た。これをピペットチップに装填し、大腸菌を熱破砕した液を通過させた。続いて、IMS を水で通液洗浄し、高濃度の緩衝液をピペッティングすることで溶出操作を行った。IMS への DNA の吸着および溶出は、16S rRNA 遺伝子を検出対象としたリアルタイム PCR により行った。その結果、IMS に DNA が特異的に吸着され、ピペッティングによる溶出操作により DNA が回収可能であることを確認した。当日は、等温核酸増幅法による検出への適用についても併せて報告する。

1) S. Zidovec Lepej, M. Poljak, *Clin. Microbiol. Infect.* **2020**, 26, 411.

## 小型高効率光増感剤による二重鎖中のグアノシンの光酸化特性

(東工大生命理工) ○金森功吏・金子翔太・浜本航治・汪潮・李若瑜・湯浅英哉  
Photo-oxidation properties of guanosine in the duplex by a small, efficient photosensitizer  
(*School of life science and technology, Tokyo institute of technology*) ○Takshi Kanamaori,  
Shota Kaneko, Kohji Hamamoto, Chao Wang, Louyu Li, Hideya Yuasa

Guanine base, one of the components of nucleic acid, tends to be relatively easily oxidized by reactive oxygen species (ROS) compared to other nucleobases. As a result of oxidation, guanine changes to 8-oxo-guanosine (8-oxo-G) or further oxidized derivatives. This oxidation reaction also occurred by  $^1\text{O}_2$  which is generated by photoirradiation of photosensitizers. Therefore, in this study, we tried to develop photosensitizer-oligonucleotide conjugates to develop a methodology that enables spatiotemporal gene control by photoirradiation.

Photo oxidation by photosensitizer is categorized into one electron oxidation mechanism and  $^1\text{O}_2$  mediated oxidation mechanism. In the case of photo oxidation of duplex by one electron oxidation mechanism, site selectivity is decreased because of the hole transfer. On the other hand, in the case of  $^1\text{O}_2$  mediated photo oxidation, there have been several reports which utilized porphyrin derivatives. However, they have disadvantages such as low target guanosine selectivity possibly due to the large size of photosensitizer and concern about off target oxidation of nearby biomolecules. We tried to overcome these problems by introducing our small, efficient photosensitizer ( $^1\text{O}_2$  quantum yield  $\Phi$  0.93,  $\lambda_{\text{ex}}$  405 nm) onto the major groove to oxidize nearby target guanosine. We will present our recent study on model oligo duplexes.

**Keywords :** *Photosensitizer; 8-oxo-guanosine; optical gene regulation; photodynamic therapy*

核酸を構成する塩基の一つであるグアニン塩基は、種々の活性酸素種によって酸化されやすく、8-オキソグアニン (8-oxo-G) を始め種々の酸化損傷塩基へと酸化される。このような酸化は、光増感剤を用いた酸化反応によっても生じる。そこで本研究では、光をもちいた時空間制御可能な遺伝子制御法の開発を目指し、光増感剤修飾オリゴ核酸を用い、グアノシン(G)を 8-oxoG 等の酸化体へ光酸化して DNA への変異導入や mRNA の翻訳制御を目指した。

光増感剤による酸化は、一電子酸化型と  $^1\text{O}_2$  酸化型の2つに大別される。核酸二重鎖の一電子酸化では、光増感剤近傍の酸化位置からホール移動を伴って遠位で酸化が生じるため位置選択性の低下が懸念される。一方、 $^1\text{O}_2$  酸化型の光増感反応について、これまでも他の研究グループにおいて、オリゴ核酸にポルフィリン類縁体などの光増感剤を結合させた報告はあるが、光増感剤としては分子サイズが大きく、リンカーを介して二重鎖から比較的離れた位置に導入されており、配列選択性の低さや二重鎖周囲の分子を広範囲に酸化する副反応の懸念があった。そこで本研究では、 $^1\text{O}_2$  酸化型の小型光増感剤を二重らせんの主溝に配置し、標的グアノシンの酸化の位置選択性を詳細に調べた。光増感剤としては、らせんの主溝に配置するのに十分に小型で、高い増感能を有する我々が開発したビフェニル型増感剤を採用した ( $^1\text{O}_2$  生成量子収率  $\Phi$  0.93,  $\lambda_{\text{ex}}$  405 nm)。本発表では、これらのグアニン光酸化特性について発表する。

## 次世代シーケンサーをもちいた化学合成 DNA の副生成物解析

(東京工業大学<sup>1</sup>・JST、さがけ<sup>2</sup>)

○正木 慶昭<sup>1,2</sup>、矢形 太一<sup>1</sup>、清尾 康志<sup>1</sup>

Evaluation of side-products in chemically synthesized DNA by next-generation sequencing

(<sup>1</sup>*Tokyo Institute of Technology*, <sup>2</sup>*JST, PRESTO*)

○Yoshiaki Masaki<sup>1,2</sup>, Taichi Yagata<sup>1</sup>, Koji Seio<sup>1</sup>

Synthesis of long DNAs is an emerging field for the application of de novo synthesis of designed genes and genomes, as well as for DNA digital data storage. One of the technological challenges is the fidelity of chemically synthesized DNA sequences. The chemical synthesis of DNA is known to produce tiny amounts of side-products in each synthetic cycle. These side-products could cause mutation, deletion, and insertion (synthetic errors) in long DNAs. Thus, it is urgent to develop the quantification method of synthetic errors, due to the DNA chemical synthesis.

In this study, we applied a next-generation sequencer for quantification of the synthetic errors due to the side-products in chemical synthesis. The detail will be discussed.

*Keywords : DNA synthesis; Phosphoramidite chemistry; Synthetic errors*

長鎖 DNA 合成は、設計された新規遺伝子やゲノム配列の de novo 合成や DNA ストレージへの応用などへの応用が期待されている。そのような応用において問題となる点の一つに、合成した DNA 配列の信頼性が挙げられる。DNA の化学合成では、合成サイクル毎にごく微量の副生成物を生成することが知られている。これらの副生成物は、変異、欠失、挿入といった配列エラーを引き起こす原因となりうる。そのため、化学合成によるエラーを定量的に評価し、合成サイクルを最適化していく必要があると言える。

本研究では、次世代シーケンサーを利用し、化学合成による副生成物由来の合成エラーの定量を行なった。化学合成条件に依存した合成エラーの定量から、メカニズムの推定や回避する方法論の開発を行なった。その詳細について報告する。

## Effect of the ordered hydration layer for the enzymatic reactions on DNA scaffold

(<sup>1</sup>*Institute of Advanced Energy, Kyoto University*) ○Peng Lin,<sup>1</sup> Huyen Dinh,<sup>1</sup> Eiji Nakata,<sup>1</sup> Takashi Morii<sup>1</sup>

**Keywords:** Scaffolding Effect; Enzyme Reactions; Catalytic Enhancement; Hydration Layer

The catalytic enhancement of DNA scaffolded enzymes have been attributed to the reduced adsorption,<sup>1</sup> lower local pH<sup>2</sup> or ordered hydration layer on the DNA scaffold surface,<sup>3</sup> however, the exact working mechanisms remain unclear. In this study, xylose reductase (XR) and xylitol dehydrogenase (XDH), with the optimal activity at pH 6 or 8 equally displayed significant catalytic enhancements on the DNA scaffold. By using a pH sensor, a lower local pH shift of 0.8 was observed near the DNA scaffold. The postulated local pH change near the DNA scaffold surface unlikely plays a general role in enhancing the activity of scaffolded enzymes. Instead, the ordered hydration layer attracted by the negatively charged DNA scaffold surface is a plausible candidate for the general factor for the catalytic enhancement.<sup>4</sup>

Here, we hypothesized that the ordered hydration layer enhanced the activity of DNA scaffolded enzymes by increasing the local concentration of hydrophilic substrates. This hypothesis was tested by the hydrophilic or hydrophobic substrates of XR, and the of salts (NaCl or CsCl) in a high concentration that disrupted the ordered hydration layer. To further tested this hypothesis, the enzyme reactions of carbonic anhydrase (CA) in free and DNA scaffolded form were investigated with different hydrophobic substrates. This study gives the new insight into the origins of the catalytic enhancement of enzymes assembled on the DNA scaffold.

1) C. Timm, C. M. Niemeyer, *Angew. Chem., Int. Ed.* **2015**, 54, 6745. 2) Y. Zhang, S. Tsitkov and H. Hess, *Nat. Commun.* **2016**, 7, 1-9. 3) Z. Zhao, J. Fu, S. Dhakal, A. Johnson-Buck, M. Liu, T. Zhang, N. W. Woodbury, Y. Liu, N. G. Walter and H. Yan, *Nat. Commun.* **2016**, 7, 1-9. 4) P. Lin, H. Dinh, E. Nakata, T. Morii, *Chem. Commun.* **2021**, 57, 3925.



**[G202-2am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Hideki Mori, Kazunori Shimizu

Thu. Mar 24, 2022 9:00 AM - 11:40 AM G202 (Online Meeting)

**[G202-2am-01] Autonomous Arrangement of Micro-Droplets Entrapping DNA and Living Cells Generated through Micro Phase-Separation**

○Mayu Shono<sup>1</sup>, Ritsuki Ito<sup>2</sup>, Fumika Fujita<sup>2</sup>, Hiroki Sakuta<sup>2</sup>, Akihisa Shioi<sup>1</sup>, Kenichi Yoshikawa<sup>2</sup> (1. Department of Chemical Engineering and Materials Science, Doshisha Univ., 2. Faculty of Life and Medical Sciences, Doshisha Univ.)

9:00 AM - 9:20 AM

**[G202-2am-02] Effect of polyunsaturated docosahexaenoic acid on the lipid-raft mimetic ordered/disordered phase separated membranes**

○Masanao Kinoshita<sup>1</sup>, Akira Sorada<sup>1</sup>, Yutaro Tajima<sup>1</sup>, Nobuaki Matsumori<sup>1</sup> (1. Kyushu University)

9:20 AM - 9:40 AM

**[G202-2am-03] Detection of biological molecule using  $\beta$ -barrel nanopore protein by changing number of  $\beta$ -strands**

○Toshiyuki Tosaka<sup>1</sup>, Koki Kamiya<sup>1</sup> (1. Gunma Univ.)

9:40 AM - 10:00 AM

**[G202-2am-04] Analysis of the Akt isoform-specific signaling pathway regulation using optogenetics and mathematical modeling**

○Yuka Sekine<sup>1</sup>, Genki Kawamura<sup>1</sup>, Takeaki Ozawa<sup>1</sup> (1. The University of Tokyo)

10:00 AM - 10:20 AM

**[G202-2am-05] Optical control of Akt to analyze cellular metabolic signalling pathways**

○Genki Kawamura<sup>1</sup>, Takeaki Ozawa<sup>1</sup> (1. The Univ. of Tokyo)

10:20 AM - 10:40 AM

**[G202-2am-06] Development of an evaluation system for contractility of cultured muscle tissues and its application to the screening for anti-atrophic peptides**

○Kazunori Shimizu<sup>1</sup>, Kazuki Yamamoto<sup>1</sup>, Saki Ohsumi<sup>1</sup>, Takunori Nagashima<sup>1</sup>, Hirokazu Akiyama<sup>1</sup>, Hiroyuki Honda<sup>1</sup> (1. Nagoya University)

10:40 AM - 11:00 AM

**[G202-2am-07] Single-cell analysis of immune cell cytotoxicity using a photo-reactive surface**

○Takahiro Kosaka<sup>1</sup>, Satoshi Yamaguchi<sup>2</sup>, Shinya Yamahira<sup>3</sup>, Akimitsu Okamoto<sup>1,2</sup> (1. School of Engineering, The University of Tokyo, 2. Research Center for Advanced Science and Technology, The University of Tokyo, 3. St. Luke's International University)

11:00 AM - 11:20 AM

**[G202-2am-08] Nylon mesh scaffolds for the adherent culture of neural stem/progenitor cells**

○Masayuki Hara Hara<sup>1</sup>, Hideki Mori<sup>1</sup> (1. Osaka Prefecture University)

11:20 AM - 11:40 AM



## Autonomous Arrangement of Micro-Droplets Entrapping DNA and Living Cells Generated through Micro Phase-Separation

(<sup>1</sup>Department of Chemical Engineering and Materials Science, Doshisha University, <sup>2</sup>Faculty of Life and Medical Sciences, Doshisha University) ○Mayu Shono,<sup>1</sup> Ritsuki Ito,<sup>2</sup> Fumika Fujita,<sup>2</sup> Hiroki Sakuta,<sup>2</sup> Akihisa Shioi,<sup>1</sup> Kenichi Yoshikawa<sup>2</sup>

**Keywords:** Water/Water Micro Phase-Separation; Proto Cell; Spontaneous Arrangement of Droplets

Cell-sized micro-droplets are focused on as a proto cell with a polymer-crowded environment like living cells. These droplets can be generated through the water/water micro phase-separation of a binary polymer solution (PEG/DEX). Recently, a proto cell structure that can be created by utilizing these micro-droplets has attracted great interest.<sup>1, 2</sup>

Figure 1 shows linear arrangement of the micro-droplets generated in an autonomous manner along a glass capillary (inner diameter: 140  $\mu\text{m}$ ), which was generated from an aqueous solution of PEG/DEX. It is noted that these droplets are entrapping DNA and living cells spontaneously. Dashed lines indicate the inner glass wall. Figure 2 (right panel) shows snapshots of the micro-droplets arranged by introducing PEG/DEX aqueous solution, where the green region corresponds to DEX-rich solution. The spatio-temporal plot on the left panel shows the generated droplets are linearly arranged with almost the same size and stable over 30 min, at least. Time indicates the duration after the start of the microscopic observation, which is 2 min after the timing of mechanical mixing. The mechanism of our novel observations will be discussed with the help of theoretical analysis by using Cahn-Hilliard-type partial differential equation.

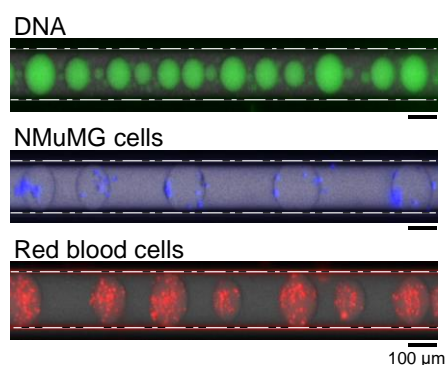


Fig. 1 Linearly arranged w/w droplets entrapping DNA and living cells in a self-organized manner.<sup>3</sup> Dashed lines indicate the inner glass wall.

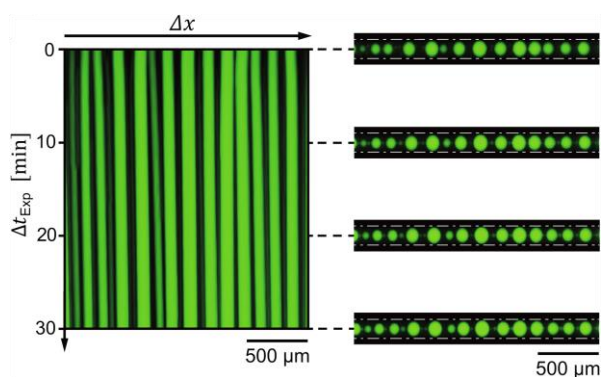


Fig. 2 Stability of the arranged droplets. Left: Spatio-temporal plot, Right: Snapshots of the capillary at different times.<sup>3</sup>  $\Delta t_{\text{EXP}}$  is the time that starts at 2 min after the mechanical mixing.

1) N. Nakatani, *et al.*, *ChemBioChem* **2018**, 19, 1370. 2) H. Sakuta, *et al.*, *ChemBioChem* **2020**, 21, 3323. 3) M. Shono, *et al.*, *Sci. Rep.* **2021**, 11, 23570.

## 高度不飽和脂肪酸ドコサヘキサエン酸がラフトを模倣した秩序/無秩序相分離膜に及ぼす影響

Effect of polyunsaturated docosahexaenoic acid on the lipid-raft mimetic ordered/disordered phase separated membranes. (*Graduate School of Science, Kyushu University*)

○Masanao Kinoshita, Akira Sorada, Yutaro Tajima, Nobuaki Matsumori

Docosahexaenoic acid (DHA; C22:6) is a representative  $\omega$ -3 poly-unsaturated fatty acid and widely marketed as a dietary supplement for the brain health. Recently, it was reported that DHA is essential for the activation of the membrane proteins, which are related to neuroprotection and cell growth. Considering that these proteins are abundantly found in the functional membrane domains called lipid rafts<sup>1)</sup>, we speculated that DHA regulates physicochemical and structural properties of lipid rafts. Here, we examined effect of free- and esterified-DHAs (inclusively termed DHAs) on lipid rafts using the raft-like ordered (Lo)/non-raft-like disordered (Ld) phase separated membranes. We newly prepared fluorescent DHA analogs and observed their distribution in the Lo/Ld phase separated membranes. As a result, DHAs largely distribute in the Ld phase but partly bind to the Lo phase; 25% and 10% for free- and esterified-DHAs, respectively. Moreover, x-ray experiments and fluorescent correlation spectroscopy showed that DHAs perturb chain packing of the lipids and, thus, increase fluidity of the Lo phase. We speculated that the membrane perturbation enhance the recruitment membrane proteins in lipid rafts.

**Keywords :** *lipid rafts, polyunsaturated fatty acid, fluorescent lipid analog, model membrane*

ドコサヘキサエン酸(DHA; C22:6)は脳に居在する代表的  $\omega$ -3 不飽和脂肪酸であり、神経保護や細胞成長などの生体機能に必須の脂肪酸である。それゆえ、DHA は脳機能維持を謳うサプリメントとして巷のドラッグストアで販売されている。近年、DHA が標的とする膜タンパク質の幾つかが、細胞膜に存在する秩序的膜領域「脂質ラフト」に局在することが報告された<sup>1)</sup>。そこで、我々は DHA が脂質ラフトの構造や物性を調節しているのではないかと考えた。本研究ではラフト様秩序相(Lo 相)と周囲の流動相(Ld 相)が相分離した膜を用いて、遊離 DHA と脂質疎水部に結合したエステル型 DHA(DHAs と総称する)がラフトに及ぼす影響を調査した。まず、我々は新たに蛍光 DHAs 類似体を合成し、Lo/Ld 相分離膜における DHAs の分布を可視化した。その結果、DHAs の大部分は Ld 相に分布したが、一部の DHA(遊離 DHA; 25%, エステル型 DHA; 10%)は Lo 相に取り込まれた。次に、X 線散乱や蛍光相関分光法により DHAs は脂質炭素鎖の充填を乱し、Lo 相の流動性を増加させることが分かった。そのような膜の流動性の変化が、ラフトに対するタンパク質のへの取り込みを促進するのではないかと考えている。

1) Javanainen *et al.*, 2019. *PLoS Comput. Biol.* 15 (5) e1007033.

## β ストランド数変化による β バレルナノポアタンパク質のポアサイズ変換と生体分子の検出

(群馬大院理工<sup>1</sup>) ○登坂 俊行<sup>1</sup>・神谷 厚輝<sup>1</sup>

Detection of biological molecule using β-barrel nanopore protein by changing number of β-strands ( <sup>1</sup>*Graduate School of Science and Technology, Gunma University*) ○Toshiyuki Tosaka,<sup>1</sup> Koki Kamiya<sup>1</sup>

Nanopore proteins have been applied as single-molecule detections. α-Hemolysin (α-HL), which is most commonly used for a single molecule detection, forms a nanopore assembled by heptamer or hexamer. Therefore, the nanopores of α-HL have two different diameters with each form. On the other hands, outer membrane protein G (OmpG) has β-barrel structure with 14 β-strand and forms a stable nanopore from monomer. In this study, to detect various types of biological molecule, we create mutants of OmpG by changing number of β-strands. The ion permeability and pore size of mutant of OmpG were investigated using a patch clamp method with nonelectrolyte martials at different molecular weights. In addition, we demonstrated the detection of various structures of DNA depending on the nanopore sizes using the OmpG WT or mutated OmpG.

**Keywords :** nanopore protein; nanopore sensing; patch clamp method

ナノポアタンパク質は物質を一分子レベルで検出できる生体分子として利用されている<sup>1)</sup>。DNA シーケンサーとして研究されている α-ヘモリシンは細胞膜上で多量体を形成することでナノポアを形成する。α-ヘモリシンの安定構造に 6 量体と 7 量体が存在し、それぞれポアサイズが異なる<sup>2)</sup>。対して、グラム陰性菌の外膜に存在する Outer membrane protein G (OmpG)は 14 本の β ストランドからなる β バレル構造をもち、単量体で安定的なナノポアを形成する<sup>3)</sup>。本研究では様々な大きさの生体分子の検出を目指し、OmpG の β ストランド数を増減させることによりポアサイズの異なる変異型 OmpG を作製した。まず野生型 OmpG と変異型 OmpG のイオン透過性やポアサイズの違いを種々の大きさの非電解質物質を用いた人工膜パッチクランプ法<sup>4)</sup>により検討した。また、ポアサイズ変化により異なる形状の生体分子が検出可能かを、種々の形状の DNA を用いて検討した。

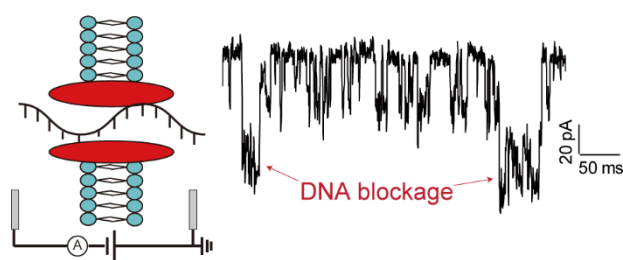


図 1. OmpG による一本鎖 DNA の検出

1) Ana Crnkovic et al. *Life*, 2021, 11, 27.

2) Simone Furini et al. *Biophysical Journal*, 2008, 95, 2265-2274.

3) Gowtham V. Subbarao et al. *Journal of Molecular Biology*, 2006, 360, 750-759.

4) Koki Kamiya, et al. *Scientific Reports*, 2018, 8, 17498.

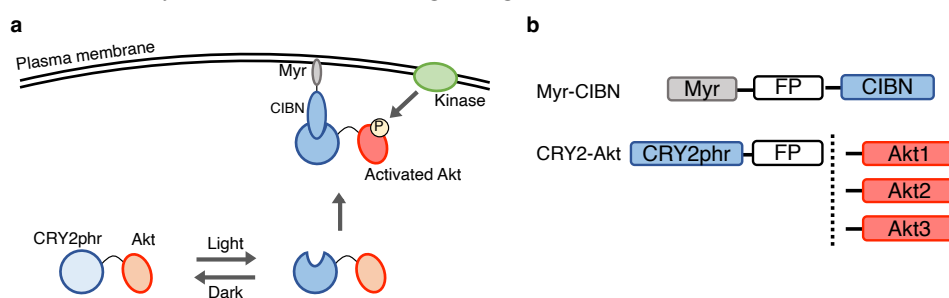
## Analysis of the Akt isoform-specific signaling pathway regulation using optogenetics and mathematical modeling

(<sup>1</sup>*School of Science, The University of Tokyo*) ○Yuka Sekine,<sup>1</sup> Genki Kawamura,<sup>1</sup> Takeaki Ozawa<sup>1</sup>

**Keywords:** Optogenetics, mathematical model, signal transduction, Akt, isoform

A Ser/Thr kinase, Akt, plays a pivotal role in various protein signal transductions in live cells. There are three Akt isoforms, Akt1, Akt2, and Akt3, of which functional differences in signaling pathways have been investigated. However, the temporal activation patterns of the Akt isoforms is unclear. Additionally, the relationship between the isoforms' temporal activation patterns and their regulation mechanisms of downstream signal transduction remains elusive. The purpose of this research is to examine the differences in the temporal aspects of the Akt isoforms' signal transduction. Previously, we developed an optogenetic method named photoactivatable Akt (PA-Akt) system for controlling the activity of Akt1<sup>1</sup>. The PA-Akt system enables us to artificially activate Akt by utilizing a light-induced dimerization of a photoreceptor CRY2 with CIBN (Fig. 1a). In this research, we newly applied this system to Akt2 and Akt3 (Fig. 1b). By using the PA-Akt systems for the three Akt isoforms, we enable individual manipulation of the activation pattern of each Akt isoform with high temporal resolution. We have confirmed that all the PA-Akt systems activated CRY2-Akt upon light stimulation by observing CRY2-Akt translocation to the plasma membrane and detecting the phosphorylated CRY2-Akt.

To quantitatively analyze the temporal activation patterns of the Akt isoforms, the combination of the PA-Akt system and a mathematical model is effective. For the construction of a mathematical model, we quantified the CRY2-Akt phosphorylation levels using western blotting. By constructing the mathematical model, the factors contributing to the differences among the isoforms' temporal phosphorylation level changes would be revealed. We aim to individually manipulate the Akt isoforms' activity and investigate the isoforms' selectivity to the downstream signaling.



**Fig 1.** PA-Akt system. (Created based on [1])

1) Y. Katsura, H. Kubota, K. Kunida, A. Kanno, S. Kuroda, T. Ozawa. *Sci. Rep.* **2015**, 5, 1–10.

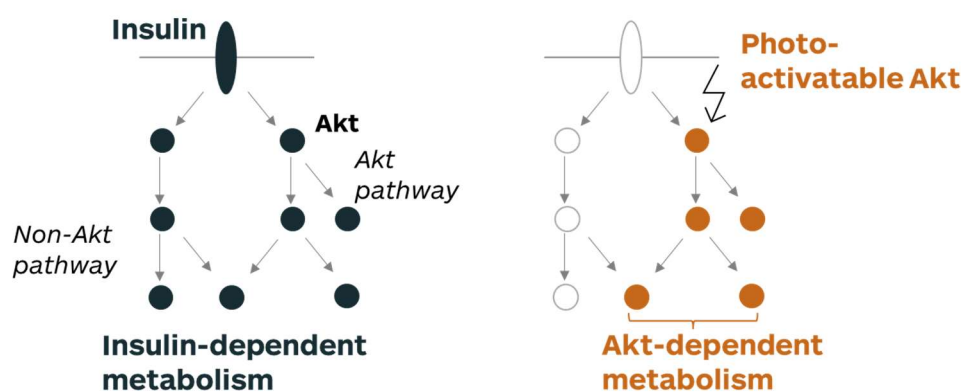
## Optical control of Akt to analyze cellular metabolic signalling pathways

(Graduate School of Science, The University of Tokyo) ○Genki Kawamura, Takeaki Ozawa

**Keywords:** Optogenetics, Insulin signaling, Akt, Omics analysis, Cellular metabolism

Insulin is a hormone secreted during feeding that promotes cellular metabolism. Insulin initiates cellular metabolism by activating intracellular signaling pathways, including the kinase Akt. Previous studies have shown that different temporal pattern of insulin concentration leads to selective metabolic pathway activation accompanied by the phosphorylation of Akt.<sup>1,2</sup> However, the link between Akt activity and metabolic pathway regulation remains elusive. Here, we aimed to identify the role of Akt in metabolic signaling pathways by specifically activating Akt with an optogenetic tool, the photoactivated Akt system.<sup>3</sup>

Regulation of metabolic processes involves a variety of reactions, including post-translational modification of metabolic enzymes, changes in metabolic enzyme abundance through transcriptional regulation, and allosteric regulation of metabolic enzyme. Thus, a comprehensive analysis of biomolecules is necessary to elucidate Akt-dependent cellular metabolism. In this study, we collected large-scale data for three types of molecules by RNA-seq, LC-MS, and Western blotting, upon stimulation. The collected omics data were integrated to construct a signaling network corresponding to Akt-specific activation. From the constructed network, we revealed the metabolic signaling that is attributed to Akt activation. We found distinctive regulation in the selectivity of metabolic pathways between Akt-specific activation and insulin stimulation: the glycolytic pathway was not regulated by Akt-specific activation, and nucleotide metabolism was regulated in a similar pattern to insulin stimulation. Taken together, our findings reveal the mechanism of metabolic pathway regulation that is dependent on Akt activation.



References: 1) Kubota et al., *Mol. Cell*, 46, 820 (2012). 2) Kubota et al. *Cell Systems*, 7, 118–128 (2018). 3) Katsura et al. *Sci. Rep.*, 5, 14589 (2015).

## 培養筋組織収縮力評価系の開発と抗筋萎縮ペプチド探索への応用

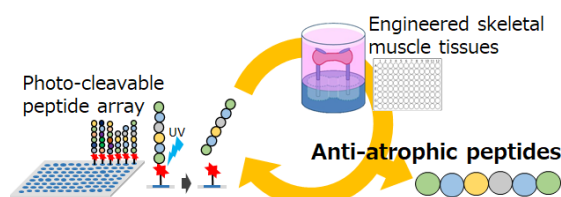
(名大院工<sup>1</sup>) ○清水 一憲<sup>1</sup>・山本 一貴<sup>1</sup>・大隅 早紀<sup>1</sup>・長島 拓則<sup>1</sup>・秋山 裕和<sup>1</sup>・本多 裕之<sup>1</sup>

Development of an evaluation system for contractility of cultured muscle tissues and its application to the screening for anti-atrophic peptides (<sup>1</sup>*Graduate School of Engineering, Nagoya University*) ○Kazunori Shimizu,<sup>1</sup> Kazuki Yamamoto,<sup>1</sup> Saki Ohsumi,<sup>1</sup> Takunori Nagashima,<sup>1</sup> Hirokazu Akiyama,<sup>1</sup> Hiroyuki Honda<sup>1</sup>

As skeletal muscle atrophy worsens the quality of life, the development of anti-atrophic substances is desirable. Here, we demonstrated a screening process for anti-atrophic peptides using photo-cleavable peptide array technology<sup>1)</sup> and 96-well scale human contractile atrophic muscle models. Dexamethasone-induced human atrophic tissue was constructed on the microdevices for contractile force measurement. Eight peptides were selected from the literature and used for the screening of peptides for preventing the decrease of the contractile forces of tissues. The peptide QIGFIW<sup>2)</sup>, which showed preventive activity, was selected as the seed sequence. As a result of amino acid substitution, we obtained QIGFIQ as a peptide with higher anti-atrophic activity. These results indicate that the combinatorial use of the photo-cleavable peptide array technology and 96-well screening system could comprise a powerful approach to obtaining anti-atrophic peptides.

**Keywords:** Phenotypic screening; Organ-on-a-chip; Tissue engineering; Peptides

骨格筋の萎縮は生活の質を低下させるため、抗萎縮物質の開発が望まれている。本研究では、光分解ペプチドアレイ技術<sup>1)</sup>と 96 ウェルサイズのヒト萎縮筋モデルを用いて、抗筋萎縮ペプチドのスクリーニングプロセスを実証した。デキサメタゾン誘導によるヒト萎縮筋組織を収縮力測定マイクロデバイス上に構築した。文献から 8 つのペプチドを選び、培養筋組織の収縮力低下を防ぐ活性のあるペプチドのスクリーニングを行った。その結果、収縮力低下を抑制するペプチド QIGFIW<sup>2)</sup>をシード配列として選択した。アミノ酸を置換した結果、より高い活性を持つペプチドとして QIGFIQ を得た。以上、光分解性ペプチドアレイ技術と 96 ウェルスクリーニングシステムを組み合わせは、抗筋萎縮性ペプチドを得るための強力なアプローチとなると期待される。



1) Screening of an  $\alpha$ -amylase inhibitor peptide by photolinker-peptide array. T. Ochiai, T. Sugita, R. Kato, M. Okochi, H. Honda, *Biosci. Biotechnol. Biochem.*, **2012**, 76, 819.

2) Bigbelly seahorse (*Hippocampus abdominalis*)-derived peptides enhance skeletal muscle differentiation and endurance performance via activated P38MAPK/AKT signalling pathway: An in vitro and in vivo analysis. K. Muthuramalingam, S. Y. Kim, Y. Kim, H. S. Kim, Y. J. Jeon, M. Cho, *J. Funct. Foods*, **2019**, 52, 147



## Single-cell analysis of immune cell cytotoxicity using a photo-reactive surface

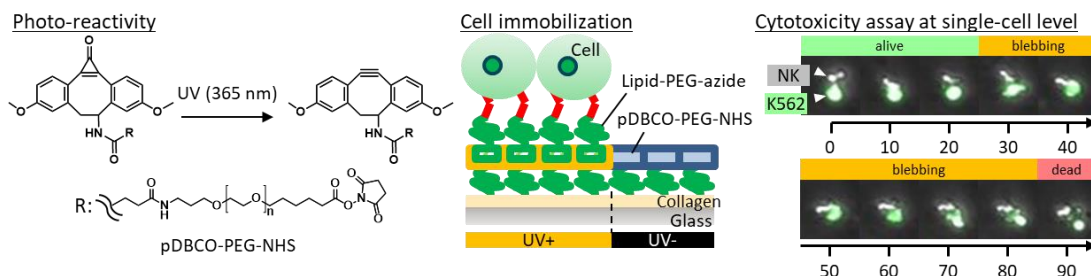
(<sup>1</sup>*School of Engineering, The University of Tokyo*, <sup>2</sup>*Research Center for Advanced Science and Technology, The University of Tokyo*, <sup>3</sup>*St. Luke's International University*) ○ Takahiro Kosaka,<sup>1</sup> Satoshi Yamaguchi,<sup>2</sup> Shinya Yamahira,<sup>3</sup> Akimitsu Okamoto,<sup>1,2</sup>

**Keywords:** Photo-reactive; Click reaction; Single-cell analysis; Cell immobilization; Cancer immunology

Cancer immunotherapy is one of the promising medical treatments, which harnesses the cytotoxic interaction of immune cells to cancer cells. It shows high therapeutic effects on some patients, but there are some remaining problems such as non-responders and severe side effects. Considering the heterogeneity of immunocytes and cancer cells, it is critical to analyze their interactions at the single-cell level for the prediction of therapeutic response and the screening of therapeutic cells. However, there are only a few reports for analysis of intercellular communication at the single-cell level. In this research, we aimed to develop the method to create pairs of cells on a substrate, and observe the interaction between immune cells and cancer cells at the single-cell level.

To create the area for cell immobilization by light irradiation, a precursor of dibenzocyclooctyne (DBCO) was employed for light-guided modification of cell-attaching molecules. This moiety is converted to DBCO by UV light irradiation at 365 nm.<sup>1</sup> A compound that has a DBCO precursor at the end of polyethylene glycol (PEG) was designed and modified on a collagen-coated glass substrate. As a cell-attaching molecule, PEG-Lipid was employed and azidated to react with DBCO. It was confirmed that heterogenous cells were patterned at the single-cell level in a light-guided manner by using the photo-reactive substrate and azidated PEG-Lipid (Lipid-PEG-azide).

We fabricated single-cell pairs of NK cells and K562 cells with this system and observed the cytotoxicity of NK cells at the single-cell level. The NK cells caused the different types of target cell death; apoptotic and necrotic cell death, and it was confirmed that this system enabled to observe the cytotoxicity at the single-cell level.



1) Poloukhine, A. A.; Mbua, N. E.; Wolfert, M. A.; Boons, G.-J.; Popik, V. V. *J. Am. Chem. Soc.* **2009**, *131*, 15769–15776.

## 神経幹前駆細胞の接着培養に用いるナイロン網目を用いた培養基材の開発

(阪府大院理) ○原 正之・森 英樹

Nylon Mesh Scaffolds for The Adherent Culture of Neural Stem/Progenitor Cells (*Graduate School of Science, Osaka Prefecture University*) ○Masayuki Hara, Hideki Mori

Neural stem/progenitor cells (NSPCs) can be amplified by suspension culture of spherical cell clusters called neurosphere. NSPCs are useful stem cells in regenerative medicine because they can give rise to both neurons and glial cells. Suitable scaffolds for adherent culture of NSPCs have been searched.

We prepared polyacrylic acid-grafted nylon mesh (PAA-NM) by graft polymerization method using gamma-irradiation. Matrigel, which is a mixture of extracellular matrix in basal lamina, was covalently immobilized to prepare the Matrigel-immobilized PAA-grafted nylon mesh (M-PAA-NM) using 1-ethyl-3-(3-dimethylamino propyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS), as cross-linking reagents.

Cell adhesion property of NSPCs between the NM, PAA-NM, and M-PAA-NM was different from each other. The neurosphere-like clusters of NSPCs were weakly bound to NM and PAA-NM without spreading. The NSPCs were firmly adhered to, spread, and covered the surface of M-PAA-NM. We evaluated the state of differentiation by qRT-PCR and immunocytochemistry. NSPCs were not differentiated on the M-PAA-NM. We concluded that the M-PAA-NM scaffold efficiently enables the adherent culture of immature NSPCs.

**Keywords :** Nylon; Polyacrylic acid; Graft polymerization; Matrigel; Neural stem cell; Scaffold

神経幹/前駆細胞は、ニューロスフィアと呼ばれる球状細胞集塊の懸濁培養で増やすことが可能である。神経細胞とグリア細胞に分化できるので、再生医療に有用な細胞である。この細胞の培養に適した接着培養基材が求められてきた。

我々はナイロン網目 (NM) の表面に、ポリアクリル酸をガンマ線グラフト重合し (PAA-NM)、さらに、基底膜細胞外マトリクス成分混合物のマトリゲル(Matrigel)を、EDC/NHS 架橋試薬を用いて共有結合固定化した(M-PAA-NM)を作り、マウス神経幹前駆細胞 (NSPC) を培養して細胞接着性を調べた。

これらの基材間で細胞接着性が大きく異なり、NM と PAA-NM には neurosphere 状の細胞の球状集塊が接着したのに対して、M-PAA-NM の表面を細胞が覆って接着し、増殖した。細胞分化マーカーの遺伝子発現を定量的 RT-PCR と免疫組織化学的手法により調べると未分化な状態を維持していた。M-PAA-NM は NSPC の接着培養に適した基材であると結論した。

1) Nylon mesh-based 3D scaffolds for the adherent culture of neural stem/progenitor cells. H. Mori, R. Naka, M. Fujita, M. Hara, *J. Biosci. Bioeng.* **2021**, 113(4), 442-452.

**[G301-2am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Takafumi Ueno, Norifumi Kawakami

Thu. Mar 24, 2022 9:00 AM - 11:40 AM G301 (Online Meeting)

**[G301-2am-01] Design of the heteroepitaxial vertical assembly of asymmetric protein needles**○Kosuke Kikuchi<sup>1</sup>, Takafumi Ueno<sup>1</sup> (1. Tokyo Institute of Technology)

9:00 AM - 9:20 AM

**[G301-2am-02] Enrichment of hierarchical supramolecular polymers into droplets and effect on protein functions under liquid-liquid phase separation environment**○Hiroki Obayashi<sup>1</sup>, Rie Wakabayashi<sup>1</sup>, Masahiro Goto<sup>1,2</sup>, Noriho Kamiya<sup>1,2</sup> (1. Graduate School of Engineering, Kyusyu University, 2. Center for Future Chemistry, Kyushu University)

9:20 AM - 9:40 AM

**[G301-2am-03] Development of enzyme-mimetic oxidative protein folding promoters**○Shunsuke Okada<sup>1</sup>, Masaki Okumura<sup>2</sup>, Takahiro Muraoka<sup>1,3</sup> (1. Tokyo Univ. of Agr. and Tech., 2. Tohoku Univ., 3. KISTEC)

9:40 AM - 10:00 AM

**[G301-2am-04] Construction of Functional Protein Needle Encapsulated in In-cell Protein Crystal**○THUC TOAN PHAM<sup>1</sup>, Satoshi Abe<sup>1</sup>, Kazuhiko Katayama<sup>2</sup>, Takafumi Ueno<sup>1</sup> (1. Tokyo Institute of Technology, 2. Kitasato University, Omura Satoshi Memorial Institute)

10:00 AM - 10:20 AM

**[G301-2am-05] Functionalization of amyloid beta peptide into ferritin cage and observation of the cage disassembly.**○Basudev Maity<sup>1</sup>, Shiori Kameyama<sup>1</sup>, Satoshi Abe<sup>1</sup>, Takafumi Ueno<sup>1</sup> (1. TOKYO INSTITUTE OF TECHNOLOGY)

10:20 AM - 10:40 AM

**[G301-2am-06] Encapsulation of heterologous proteins in an inner space of an artificial protein nanocage TIP60**○Norifumi Kawakami<sup>1</sup>, Keiichi Hayashi<sup>1</sup>, Mao Kitamura<sup>1</sup>, Kenji Miyamoto<sup>1</sup> (1. Keio University)

10:40 AM - 11:00 AM

**[G301-2am-07] Catalytic activity of enzymes immobilized with ionic metal-organic cages**○Benjamin LE OUAY<sup>1</sup>, Ryosuke Minami<sup>1</sup>, Ryo Ohtani<sup>1</sup>, Masaaki Ohba<sup>1</sup> (1. Kyushu University)

11:00 AM - 11:20 AM

**[G301-2am-08] Analysis of Dynamic Behavior of Aromatic Interactions using Protein Cages**○Yuki Hishikawa<sup>1</sup>, Asuka Asanuma<sup>1</sup>, Basudev Maity<sup>1</sup>, Satoru Nagatoishi<sup>2</sup>, KouheiTsumoto<sup>2,3</sup>, Satoshi Abe<sup>1</sup>, Takafumi Ueno<sup>1</sup> (1. Sch. of Life Sci. & Technol., Tokyo Inst. of

Technol., 2. The Inst. of Med. Sci., The Univ. of Tokyo, 3. Sch. of Eng., The Univ. of Tokyo)

11:20 AM - 11:40 AM

## Design of the heteroepitaxial vertical assembly of asymmetric protein needles

(<sup>1</sup>*School of Life Science and Technology, Tokyo Institute of Technology*)

○Kosuke Kikuchi,<sup>1</sup> Takafumi Ueno<sup>1</sup>

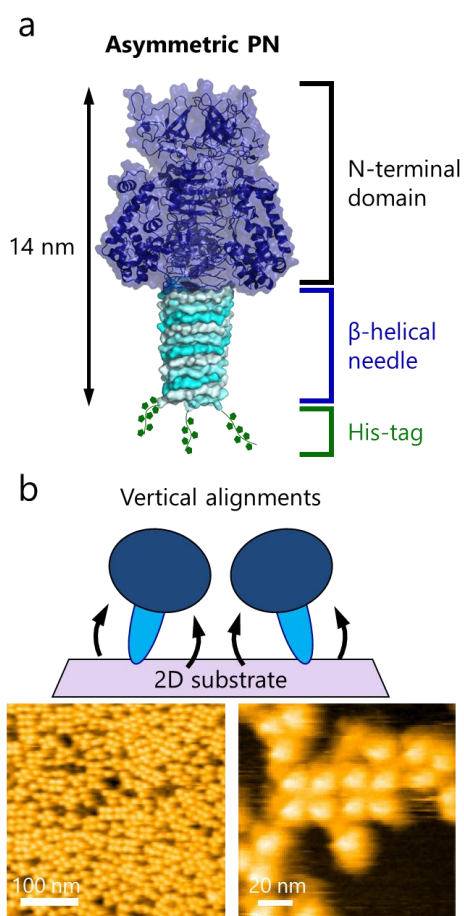
**Keywords:** protein assembly;  $\beta$ -helical protein needle; asymmetry; high-speed atomic force microscopy

Proteins assemble into oligomers then form highly ordered one-, two-, or three-dimensional nanostructures. Due to their biocompatibility, spontaneous organization, and spatial periodicity, protein assemblies have attracted significant attention for developing bio-nanomaterials.<sup>1</sup> The functionality of assemblies is deeply associated with the alignments of protein units. However, it is still challenging to manipulate the alignments of each protein unit in assembly structures because of the complexity and asymmetry of protein-protein interactions.

Recently, we reported the modulation of two-dimensional assembly patterns of protein needles (PNs).<sup>2</sup> PN is a robust trimer-dimer protein with an end-to-end symmetry.<sup>3</sup> By engineering the distal ends of PNs, we changed their alignments in the horizontal plane and constructed different two-dimensional patterns. In this study, we construct the vertical assembly of protein needles on a substrate. We designed asymmetric PNs so that PNs stand on a substrate with one end is immobilized on a surface while the other end faces upward (**Figure 1a**). The high-speed atomic force microscopy (HS-AFM) observations revealed that the designed asymmetric PNs vertically stood on mica and formed tetrameric assembly despite its unfavorable aspect ratio (**Figure 1b**).

Currently, we are investigating the protein-protein interactions and the driving force of the vertical conformations.

1) J. Zhu, *et al.*, *Chem Rev* **2021**, *121*, 13701. 2) K. Kikuchi, *et al.*, *Small* (in press). 3) N. Yokoi, *et al.*, *Small* **2010**, *6*, 1873-1879.



**Figure 1** | The structure of the asymmetric PN (a) and the results of HS-AFM observations (b).

## 液液相分離環境下の超分子構造体の濃縮とタンパク質機能への影響

(九大院工<sup>1</sup>・九大未来化セ<sup>2</sup>) ○大林 洋貴<sup>1</sup>・若林 里衣<sup>1</sup>・後藤 雅宏<sup>1,2</sup>・神谷 典穂<sup>1,2</sup>

Enrichment of hierarchical supramolecular polymers into droplets and effect on protein functions under liquid-liquid phase separation environment (<sup>1</sup>*Graduate School of Engineering, Kyushu University*, <sup>2</sup>*Center for Future Chemistry, Kyushu University*) ○Hiroki Obayashi,<sup>1</sup> Rie Wakabayashi,<sup>1</sup> Masahiro Goto,<sup>1,2</sup> Noriho Kamiya<sup>1,2</sup>

Droplets formed through liquid-liquid phase separation (LLPS) work in cells as compartmentalized places that influence the localization or organization of biomolecules and regulate various reactions [1]. To reveal our hypothesis that artificial supramolecular polymers may also show a similar phase selectivity, we used our recently reported co-assembly system composed of complementary interacting molecular pair, cyanuric acid (Cya)-introduced peptide amphiphiles (Cya-PA) and melamine (Mel)-introduced nitrobenzofurazan (Mel-NBD) [2]. The Cya-PA/Mel-NBD supramolecular polymers showed the phase-selectivity depending on their structures. Moreover, the supramolecular polymers enabled the accumulation of enzymes on their structures and the control of the sequential enzymatic reactions (Fig. 1).

**Keywords:** Peptide amphiphile; liquid-liquid phase separation; enzymatic reaction; co-assembly

液液相分離 (liquid-liquid phase separation, LLPS) を通して形成される液滴 (ドロップレット) は、細胞内の生体分子の局在や組織化に影響を与え、様々な反応を制御する区画化された場として重要な役割を果たしている [1]。我々は LLPS 環境が人工超分子ポリマーの局在にも影響を与えるのではないかと考え、両親媒性ペプチド (Peptide amphiphiles: PA) と蛍光小分子 (ニトロベンゾフラザン: NBD) からなる共集合システム [2] を用いて調査した。相補的な水素結合ペアであるシアヌル酸 (Cya) とメラミン (Mel) を有する Cya-PA と Mel-NBD は水中で自発的に共集合化し、その集合状態に応じた相選択性を示した。さらに、本共集合超分子がタンパク質を非特異的に吸着する性質を利用し、超分子上への酵素集積化と連続酵素反応の制御を試みた結果についても報告する (Fig. 1)。

[1] M. K. Rosen *et al.*, *Nat. Rev. Mol. Cell Biol.*, **18**, 285–298 (2017) [2] R. Wakabayashi *et al.*, *Chem. Commun.*, **55**, 6997–7000 (2019).

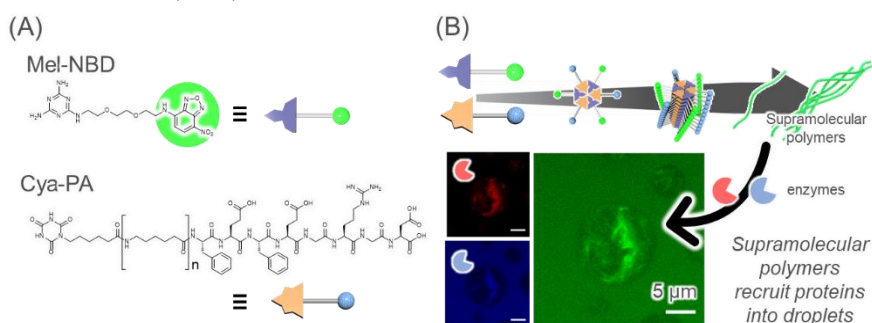


Fig. 1 (A) Molecular Structure, (B) Schematic illustration of

## 生体酵素模倣を指向したタンパク質酸化的フォールディング促進剤の開発

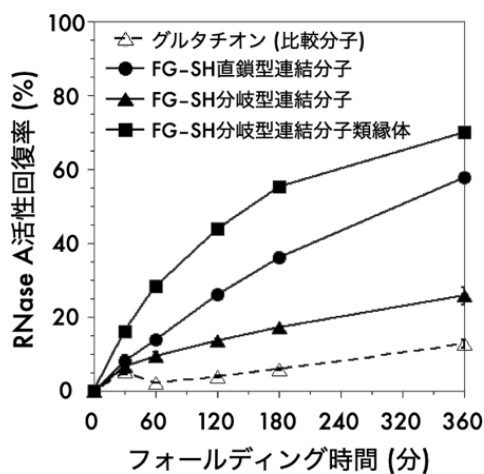
(東京農工大<sup>1</sup>・東北大<sup>2</sup>・KISTEC<sup>3</sup>) ○岡田 隼輔<sup>1</sup>・奥村 正樹<sup>2</sup>・村岡 貴博<sup>1,3</sup>

Development of enzyme-mimetic oxidative protein folding promoters (<sup>1</sup>Tokyo Univ. of Agr. and Tech., <sup>2</sup>Tohoku Univ., <sup>3</sup>KISTEC) ○Shunsuke Okada,<sup>1</sup> Masaki Okumura,<sup>2</sup> Takahiro Muraoka<sup>1,3</sup>

Proteins are functional molecules for materials science and pharmaceutical applications. They form the native conformations by folding of the polypeptide chains, which allows performing their inherent functions. In the case of protein synthesis using *E. coli*, misfolding and the following precipitation is one of the critical technical problems that lower the yield of the target protein in the active form, thus promotion of protein folding is an important technique for biological study and applications. To design synthetic folding promoters, we focused on the formation of disulfide bonds that closely relate to oxidative protein folding. In the folding process in our body, A polypeptide chain synthesized from ribosome is folded via disulfide bonds formation, and the folding process is assisted by multiple enzymes, such as protein disulfide isomerase (PDI) to furnish the native proteins efficiently. In this study, we developed novel synthetic folding promoters as PDI mimics for the promotion of folding. The developed molecules consist of a thiol group and multiple functional groups and found that their molecular structures largely influence the efficiencies of oxidative protein folding.

**Keywords :** Oxidative Protein Folding; Thiol; Disulfide-bond Exchange Reaction; Native Conformation

タンパク質は、機能性材料や薬剤などとして近年注目を集める重要な物質群である。その生物学的機能や薬効の発現には、天然構造へのフォールディングが不可欠である。大腸菌などを用いて、ある目的タンパク質を発現する際、可用性画分に天然構造として得られる収率は必ずしも高くない。従って、目的タンパク質を効率的に天然構造へ折り畳むことは、タンパク質の応用上、重要な技術である。生体において、翻訳された新生タンパク質は、ジスルフィド結合形成を伴い、折り畳まれる(酸化的フォールディング)。複数種の酵素がこのプロセスを触媒し、タンパク質の品質が高水準で保たれている。この点に着目し、本研究では、触媒酵素の化学的性質を模倣したフォールディング促進分子を開発した。機能性官能基(FG)とチオール(SH)基を連結した分子が生体酵素に類似する促進パフォーマンスを示し、さらに、その連結形体の違いが、フォールディング促進効果に大きく影響を及ぼすことを見出した。得られた促進効果について、SH基の化学的性質から議論する。



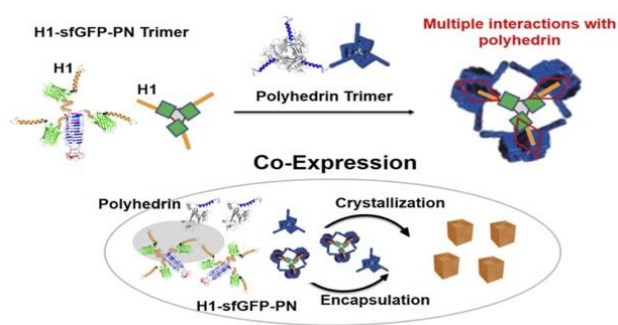
## Construction of Functional Protein Needle Materials Encapsulated in In-cell Protein Crystal

(<sup>1</sup>School of Life Science and Technology, Tokyo Institute of Technology, <sup>2</sup>Kitasato University, Omura Satoshi Memorial Institute) ○Thuc Toan PHAM<sup>1</sup>, Satoshi Abe<sup>1</sup>, Kazuhiko Katayama<sup>2</sup>, Takafumi Ueno<sup>1</sup>

**Keywords:** Protein Needle, Polyhedra crystal, In-cell encapsulation, Multiple protein interface.

In-cell protein crystals such as polyhedra (PhC) provide an advantage in the construction of solid biomaterials because they have high stability against a wide range of pH, organic solvents, and physical stresses.<sup>1,2</sup> Immobilization of proteins and enzymes into in-cell crystals is a unique method for the synthesis of functional materials used as solid-state catalysts. However, such techniques based on electrostatic interactions and genetic fusions between a target protein and in-cell crystal protein are still challenging to apply to protein assemblies.

In this work, we used the polyhedra crystal (PhC) as the scaffold to develop a new strategy to immobilize various proteins with a high encapsulation yield. Here, a protein needle (PN), a protein assembly, was used as the platform to be immobilized into the PhC. The feature of PN is to form symmetry assembly structures ( trimer or trimer-dimer) even when fused with foreign proteins. Therefore, we expect the foreign protein connected to PN to be efficiently encapsulated by multiple interactions with PhC. To demonstrate this strategy, we designed GFP-PN fusion proteins. In addition, to immobilize GFP-PN into PhCs, the H1-helix derived from polyhedrin monomer (PhM) was fused to the N-terminus of GFP-PN. When H1-GFP-PN and PhM were co-expressed in the living cells, the hybrid crystals encapsulating H1-GFP-PN were constructed. This design provided a much higher encapsulation of GFP into PhC than H1-GFP. In addition, PN-based material provides cellular penetration and immunological response.<sup>4</sup> Therefore, this new technique opens a promising future for construction materials for biological applications such as oral vaccines or drug deliveries.



**Figure 1** Construction of PN materials encapsulated in PhC using in-cell crystallization

1. Abe, S. et al., *Adv Mater* **2015**, 27 (48), 7951-6.
2. Coulibaly, F. et al., *Nature* **2007**, 446 (7131), 97-101.
3. Yang, Z.; et al., *Biomaterials* **2021**, 271, 120759.
4. Sanghamitra, N. J.; et al., *Mol Biosyst* **2014**, 10 (10), 2677-83.



## Functionalization of Amyloid Beta Peptide into Ferritin Cage and Observation of the Cage Disassembly

(<sup>1</sup>*School of Life Science and Technology, Tokyo Institute of Technology*) ○Basudev Maity,<sup>1</sup> Shiori Kameyama,<sup>1</sup> Satoshi Abe,<sup>1</sup> Takafumi Ueno.<sup>1</sup>

**Keywords:** Ferritin cage; Amyloid beta peptide; Cage disassembly; High-speed AFM.

The intrinsically disordered, amyloid beta (A $\beta$ ) peptides are known to be linked with the Alzheimer's disease.<sup>1</sup> The toxic A $\beta$  oligomers aggregate to form fibrillar structure and deposited into brain.<sup>1</sup> To develop oligomer specific drug, understanding their role in the disease and the formation process of A $\beta$  fibrils, it is important to know the details of an oligomeric state. However, due to frequent aggregation, transient nature, heterogeneity etc., it is difficult to isolate and characterize a precise oligomeric state. In this work, we aimed to encapsulate a defined number of A $\beta$  peptides into the confined environment of a ferritin cage (Figure 1). 24 A $\beta$  peptides were genetically fused at the C-terminal of ferritin cage which is located inside the cage. In vivo assembly will incorporate the A $\beta$  peptides into the cage. Since ferritin cage is known to show reversible disassembly in solution, the encapsulated amyloid core can be exposed by cage disassembly.<sup>2</sup> This presentation will describe the process of A $\beta$  peptides encapsulation into the ferritin cage, detailed characterization, and study of the amyloid dynamics by high-speed AFM measurement.



Figure 1: Schematic representation of the encapsulation of A $\beta$  oligomer into ferritin cage.

1) S. J. C. Lee, E. Nam, H. J. Lee, M. G. Savelieff, M. H. Lim, *Chem. Soc. Rev.* **2017**, 46, 310.

2) B. Maity, Z. Li, K. Niwase, C. Ganser, T. Furuta, T. Uchihashi, D. Lu, T. Ueno, *Phys. Chem. Chem. Phys.*, **2020**, 22, 18562.

## 人工タンパク質ナノケージ TIP60 への異種タンパク質の内包

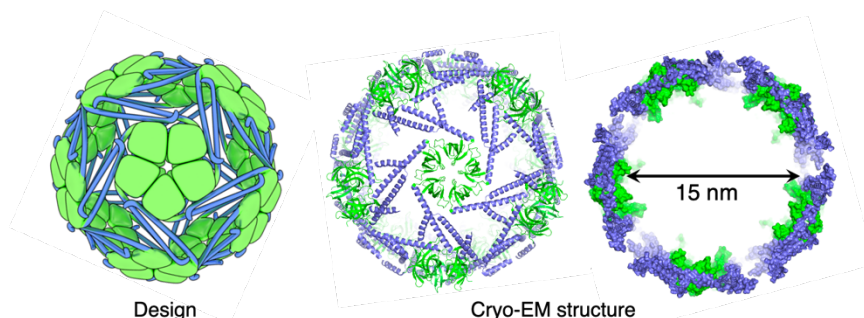
(慶應義塾大学<sup>1)</sup>) ○川上 了史・林 慶一・北村 真緒・宮本 憲二

Encapsulation of heterologous proteins in an inner space of an artificial protein nanocage TIP60 (Keio University)○Norifumi Kawakami, Keiichi Hayashi, Mao Kitamura, Kenji Miyamoto

We have recently produced protein nanocage TIP60. In this study, we have developed an approach to introduce heterologous proteins in the inner space of TIP60. The TIP60 was co-expressed with the proteins of interest in *E. coli* cells. Four different proteins are used for encapsulation: glutathione S-transferase, trigger factor, and two alcohol dehydrogenases from *thermoanaerobacter brockii* (TbADH) and human (hADH). As a result, all four are incorporated in the inner space of TIP60 confirmed by size excluded column chromatography. We also monitored the catalytic activities of TbADH and hADH. Although the encapsulated TbADH showed catalytic activity, the hADH did not. This indicates that at least TbADH kept their natural structure even after encapsulation

**Keywords :** Protein; nanocage; Molecular encapsulation; TIP60

これまでに中空サッカーボール型タンパク質ナノケージ、TIP60 の設計と構築を行った<sup>1)</sup>。クライオ電子顕微鏡による構造解析からもほとんど設計通りの構造が得られていることが明らかになった<sup>2)</sup>。また、その内部空間は 15 nm という比較的大きな空間があることも突き止められている(図)。この大きさは、多くの可溶性タンパク質を内包するのに適していると考え、異種タンパク質の内包技術の開発を検討してきた。手法は単純な共発現を採用した。用いたタンパク質は glutathione S-transferase、trigger factor、および *thermoanaerobacter brockii* 由来のアルコール脱水素酵素(TbADH) とヒト由来のアルコール脱水素酵素(hADH)である。その結果、いずれのタンパク質についても内包が認められた。特に、ADH については、内包状態での酵素活性についても評価を行った。TbADH については活性が認められたものの、hADH については現時点では明瞭な活性が認められなかった。この原因は不明であるが、少なくとも TbADH については、天然構造に近い構造を維持したまま内包できていることが示唆された。



- 1) Kawakami, N., et al. *Angew. Chemie. Int. Ed.* **2018**, 57, 12400.
- 2) Obata, J., et al. *Chem. Commun.* **2021**, 57, 10226.

## Catalytic activity of enzymes immobilized with ionic metal-organic cages

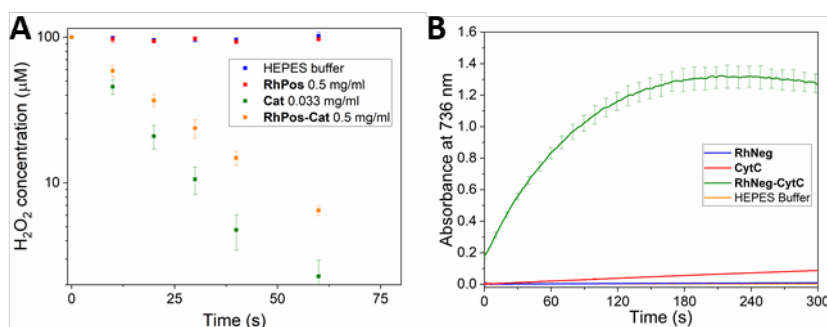
(<sup>1</sup>Graduate School of Science, Kyushu University) ○Benjamin Le Ouay,<sup>1</sup> Ryosuke Minami,<sup>1</sup> Ryo Ohtani,<sup>1</sup> Masaaki Ohba,<sup>1</sup>

**Keywords:** *Metal-organic cage, Enzyme immobilization, Catalase, Peroxidase*

Enzyme immobilization is a powerful strategy to harness their high catalytic activity and exquisite selectivity while allowing to work with a solid-state material that can easily be manipulated, increasing greatly stability and recyclability. We recently developed a new strategy for immobilization for proteins, relying on their charge-driven co-assembly with ionic metal-organic cages (MOCs).<sup>1</sup> This technique allows a very mild immobilization, at neutral pH and without chemical modification needed. Furthermore, the intrinsic porosity of the cages, acting as spacers, is expected to greatly help the mass transport within the MOC-enzyme composite. While the principles of immobilization are discussed in another presentation for the archetypal protein **BSA** (non-enzymatic), we discuss here the maintenance of a catalytic activity for enzymes when immobilized with MOCs.

We first consider the activity of bovine liver catalase (**Cat**), catalyzing the disproportionation of  $\text{H}_2\text{O}_2$  into  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The composite formed spontaneously by mixing cages and **Cat**, and with a mass ratio of MOC to **Cat** of 20:80. **Cat** maintained a significant fraction activity of its activity when immobilized, with only a decrease by a factor 12 (Figure 1A). Furthermore, the composite could be recycled several times, with only minimal loss of catalytic activity.

In addition, we demonstrated the maintenance of catalytic activity for Horse heart cytochrome C (**CytC**), acting as a peroxidase. In this case, the MOC to **CytC** mass ratio in the composite was 24:75. Activity was evaluated by following the oxidation of ABTS by  $\text{H}_2\text{O}_2$ . Remarkably, the activity of **CytC** was not only maintained, but even increased by a factor 40 upon immobilization with MOCs (Figure 1B). A likely reason for this effect is the distortion of the active site of the enzyme when placed in a strongly ionic environment.



**Figure 1.** Catalytic activity of **Cat** (A) and **CytC** (B).

1) Submitted

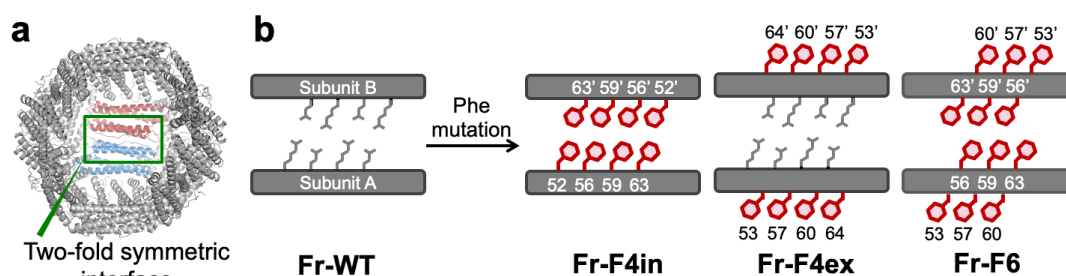
## Analysis of Dynamic Behavior of Aromatic Interactions using Protein Cages

(<sup>1</sup>*School of Life Science & Technology, Tokyo Institute of Technology*, <sup>2</sup>*The Institute of Medical Science, The University of Tokyo*, <sup>3</sup>*School of Engineering, The University of Tokyo*) ○Yuki Hishikawai,<sup>1</sup> Asuka Asanuma,<sup>1</sup> Basudev Maity,<sup>1</sup> Satoru Nagatoishi,<sup>2</sup> Kouhei Tsumoto,<sup>2,3</sup> Satoshi Abe,<sup>1</sup> Takafumi Ueno<sup>1</sup>

**Keywords:** *Protein cage; Aromatic cluster; X-ray crystallography; Molecular dynamics simulation; Thermal unfolding*

Aromatic clusters formed by multiple aromatic residues are important in biological systems such as folding and channel gating.<sup>1</sup> Recent spectroscopic studies have implied that aromatic residues exhibit cooperative dynamic behavior when clustered;<sup>2</sup> however, it is still difficult to assess physical properties of aromatic clusters and relevance to their structural correlation at the atomic level. To address these issues, we performed a) systematic construction and structural determination of aromatic clusters using protein cages, and b) analysis of aromatic interactions during the unfolding process from a dynamic perspective.

Aromatic ferritin cages (**Fr-F4in**, **Fr-F4ex** and **Fr-F6**) were designed by introducing phenylalanine residues at the two-fold symmetric interface of the cage (Fig 1) by following our previous design.<sup>3</sup> The X-ray crystal structural analysis showed aromatic cluster formation at inter and intra-subunit. The results of Circular Dichroism (CD) and Differential Scanning Calorimetry (DSC) showed that **Fr-F4ex** has lower thermal stability than **Fr-F4in**, which highlights the influence of geometry and location of the aromatic clusters. Furthermore, the thermal measurements suggested that the thermal disassembly and unfolding process of the ferritin cages undergoes multiple transient states. This study would provide insights into the unique physical properties of aromatic interactions and guidelines for designing aromatic interactions in a protein cage.



**Fig 1.** (a) The structure of a ferritin cage and the two-fold symmetric interface (PDB ID: 1DAT). (b) Design of aromatic ferritin mutants by introducing phenylalanine residues.

1) K. M. Makwana *et al.*, *Protein Sci.*, **2015**, 24, 1920. 2) M. Dreydoppel *et al.*, *J Biomol NMR* **2020**, 74, 183. 3) Y. Hishikawa *et al.*, *Chem. Lett.*, **2020**, 49, 840.

**[G201-2am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Hiroshi Nonaka, Yusuke Yonamine

Thu. Mar 24, 2022 9:00 AM - 11:40 AM G201 (Online Meeting)

**[G201-2am-01] Probing the biogenesis of storage organelles in algal cells via Raman imaging with stable isotope labeling**

○Yusuke Yonamine<sup>1</sup>, Takuro Ito<sup>2</sup>, Yasuyuki Ozeki<sup>3</sup>, Yu Hoshino<sup>4</sup>, Hideyuki Mitomo<sup>1</sup>, Kuniharu Ijro<sup>1</sup> (1. RIES, Hokkaido Univ., 2. NIT, Tsuruoka Col., 3. Grad. Sch. of Eng., The Univ. of Tokyo, 4. Grad. Sch. of Eng., Kyushu Univ.)

9:00 AM - 9:20 AM

**[G201-2am-02] Ligand directed chemistry in live mouse brain (1): Labeling and imaging of AMPA-type glutamate receptor**

○Kazuki Shiraiwa<sup>1</sup>, Seiji sakamoto<sup>1</sup>, Hiroshi Nonaka<sup>1,2</sup>, Shigeki Kiyonaka<sup>2,3</sup>, Itaru Hamachi<sup>1,2</sup> (1. Graduate school of Engineering, Kyoto University, 2. JST ERATO, 3. Graduate school of Engineering, Nagoya University)

9:20 AM - 9:40 AM

**[G201-2am-03] Ligand directed chemistry in live mouse brain (2): Application to other endogenous neurotransmitter receptors and their life-time analysis.**

○Seiji Sakamoto<sup>1</sup>, Kazuki Shiraiwa<sup>1</sup>, Shigeki Kiyonaka<sup>2</sup>, Nonaka Hiroshi<sup>1,3</sup>, Itaru Hamachi<sup>1,3</sup> (1. Kyoto University, 2. Nagoya University, 3. JST ERATO)

9:40 AM - 10:00 AM

**[G201-2am-04] Ligand directed chemistry in live mouse brain (3): Pulse-chase analysis of AMPA receptors in the brain during postnatal development**

○Hiroshi Nonaka<sup>1,2</sup>, Kazuki Shiraiwa<sup>1</sup>, Seiji Sakamoto<sup>1</sup>, Shigeki Kiyonaka<sup>2,3</sup>, Itaru Hamachi<sup>1,2</sup> (1. Graduate School of Engineering, Kyoto Univ, 2. ERATO, JST, 3. Graduate School of Engineering, Nagoya Univ)

10:00 AM - 10:20 AM

**[G201-2am-05] Optical regulation of protein translocation using a photo-reversible protein labeling system**

○Takato Mashita<sup>1</sup>, Toshiyuki Kowada<sup>1,2</sup>, Toshitaka Matsui<sup>1,2</sup>, Shin Mizukami<sup>1,2</sup> (1. Graduate School of Science, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

10:20 AM - 10:40 AM

**[G201-2am-06] Development of fluorescent probes for visualizing membrane contact sites in living cells**

○Moeka Ajiki<sup>1</sup>, Masaru Yoshikawa<sup>2</sup>, Keita Tsutsui<sup>2</sup>, Fubito Nakatsu<sup>3</sup>, Shinya Tsukiji<sup>1,2</sup> (1. Fac. of Eng., Nagoya Inst. of Tech., 2. Grad. Sch. of Eng., Nagoya Inst. of Tech., 3. Grad. Sch. of Med. and Dent. Sci., Niigata Univ.)

10:40 AM - 11:00 AM

**[G201-2am-07] Development of chemical tools for manipulating membrane contacts in living cells**

○Masaru Yoshikawa<sup>1</sup>, Moeka Ajiki<sup>2</sup>, Keita Tsutsui<sup>1</sup>, Fubito Nakatsu<sup>3</sup>, Shinya Tsukiji<sup>1</sup> (1.

Grad. Sch. of Eng., Nagoya Inst. of Tech., 2. Fac. of Eng., Nagoya Inst. of Tech., 3. Grad.  
School of Niigata Univ.)

11:00 AM - 11:20 AM

[G201-2am-08] Fluorescence lifetime mapping of lipid compositions using an  
environment-responsive lipid droplet probe

○Keiji Kajiwara<sup>1</sup>, Yuki Ohsaki<sup>2</sup>, Masayasu Taki<sup>1</sup>, Shigehiro Yamaguchi<sup>1</sup> (1. Nagoya Univ.,  
2. Sapporo Medical Univ.)

11:20 AM - 11:40 AM

## 安定同位体標識を用いたラマンイメージングによる藻類細胞の貯蔵オルガネラ新生の追跡

(北大電子研<sup>1</sup>・鶴岡高専<sup>2</sup>・東大院工<sup>3</sup>・九大院工<sup>4</sup>) ○与那嶺雄介<sup>1</sup>・伊藤卓朗<sup>2</sup>・小関 泰之<sup>3</sup>・星野友<sup>4</sup>・三友秀之<sup>1</sup>・居城邦治<sup>1</sup>

Probing the Biogenesis of Storage Organelles in Algal Cells via Raman Imaging with Stable Isotope Labeling (<sup>1</sup>Research Institute for Electronic Science, Hokkaido University, <sup>2</sup>National Institute of Technology, Tsuruoka College, <sup>3</sup>Graduate School of Engineering, The University of Tokyo, <sup>4</sup>Faculty of Engineering, Kyushu University) ○Yusuke Yonamine,<sup>1</sup> Takuro Ito,<sup>2</sup> Yasuyuki Ozeki,<sup>3</sup> Yu Hoshino,<sup>4</sup> Hideyuki Mitomo,<sup>1</sup> Kuniharu Ijro<sup>1</sup>

In this presentation, the biosynthesis of polysaccharide granules (paramylons) accumulated in a unicellular photosynthetic alga, *Euglena gracilis*, was spatiotemporally probed via stimulated Raman scattering (SRS) microscopy using a stable isotope (<sup>13</sup>C) as the tracking probe. The carbon source of the culture medium was switched from <sup>12</sup>CO<sub>2</sub> to <sup>13</sup>CO<sub>2</sub> during the production of the paramylon granules; this resulted in the distribution of the <sup>12</sup>C and <sup>13</sup>C constituents in the granules so that the biosynthetic process could be tracked. Taking advantage of high-resolution SRS imaging and label switching, the localization of the <sup>12</sup>C and <sup>13</sup>C constituents inside a single paramylon granule could be visualized in three dimensions, thus revealing the growth process of paramylon granules.

**Keywords :** Raman Imaging; Microalgae; Stable Isotope; Metabolism

微細藻類のユーグレナは、光合成を行いパラミロンと呼ばれる多糖 (β-1,3 グルカン) の顆粒を貯蔵する。パラミロンは、バイオ燃料として利用できる油脂成分に変換されたため、パラミロンの新生機構を解明することで、その生産性を向上できる可能性がある。ラマン分光法では化合物を安定同位体 (SI) で置換すると、分子振動の変化に起因するラマンスペクトルのシフトが起こる。この現象を利用して、SI 標識した基質を細胞に代謝させ、標的生成物のスペクトル変化を追うことで、その代謝プロセスを追跡できる。本研究では <sup>13</sup>CO<sub>2</sub> を代謝追跡プローブとして用い、ユーグレナ細胞の光合成による <sup>13</sup>C のパラミロンへの取り込みを誘導ラマン散乱 (SRS) 顕微鏡により時空間的に追跡した (Figure 1)。<sup>12</sup>C 含有培地から <sup>13</sup>C 含有培地へ切替えてパラミロンを誘導したところ、顆粒の外縁に <sup>13</sup>C 成分が局在していた。さらに 3 次元 SRS 画像を断面解析した結果、中心が <sup>12</sup>C で外殻が <sup>13</sup>C のコアシェル構造が確認された。これらの結果からパラミロン顆粒は新生した成分が表面に蓄積して成長するモデルが示された。

### 【参考文献】

Y. Yonamine et al., *Anal. Chem.*, **93**, 16796-16803 (2021).

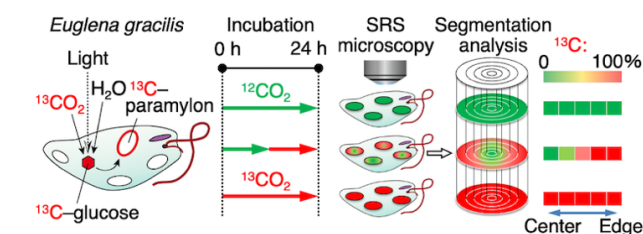


Figure 1. The biogenesis of paramylon granules in an algal cell was investigated via SRS microscopy employing <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub> substrates that were exposed to different conditions and subsequent segmentation analysis of each granule.

## Ligand directed chemistry in live mouse brain (1): AMPA 型グルタミン酸受容体のラベル化とイメージング

(京大院工<sup>1</sup>・JST ERATO<sup>2</sup>・名大院工<sup>3</sup>) ○白岩 和樹<sup>1</sup>・坂本 清志<sup>1</sup>・野中 洋<sup>1,2</sup>・清中 茂樹<sup>2,3</sup>・浜地 格<sup>1,2</sup>

Ligand directed chemistry in live mouse brain (1): Labeling and imaging of AMPA-type glutamate receptor (<sup>1</sup>Graduate school of Engineering, Kyoto University, <sup>2</sup>JST ERATO, <sup>3</sup>Graduate school of Engineering, Nagoya University) ○Kazuki Shiraiwa<sup>1</sup>, Seiji Sakamoto<sup>1</sup>, Hiroshi Nonaka<sup>1,2</sup>, Shigeki Kiyonaka<sup>2,3</sup>, Itaru Hamachi<sup>1,2</sup>

The complex neural network is founded on the release and reception of neurotransmitters at synapses, and are responsible for higher functions of the brain such as memory, learning, and movement. The homeostasis of these complex neural systems is maintained only in a living brain, and even now it is difficult to reproduce artificially. Therefore, there is a need for a method to analyze neurotransmitter receptor functions while maintaining the original environment of the brain.

We have successfully developed ligand-directed acyl imidazole (LDAI) chemistry, a selective chemical modification of endogenous proteins in cultured cells.<sup>1,2</sup> In this study, we attempted to label AMPA-type glutamate receptors (AMPA-Rs) in living mouse brain by using LDAI chemistry. Western blot and fluorescence imaging analysis revealed that endogenous AMPARs were selectively labeled and visualized in the live mouse brain. In combination with tissue clearing technology, we have succeeded in visualizing three-dimensional localization of endogenous AMPARs in the live brain. In this talk, we will report the details.

**Keywords :** Chemical label; Glutamate receptor; In live brain; Endogenous protein; Ligand directed chemistry

複雑な神経ネットワークは、シナプスにおける神経伝達物質の放出と受容を起点として形成され、記憶・学習・運動などの脳の高次機能を担う。このような複雑な脳神経系は、3次元階層を持った生体脳でこそ恒常性が維持されており、人工的な再現は現在でも難しい。そのため、脳そのまゝの環境を維持した状態で、神経伝達物質受容体機能を解析できる手法が求められている。

当研究室では、これまでに培養細胞における内在性タンパク質の選択的化学修飾法であるリガンド指向性アシルイミダゾール(LDAI)化学の開発に成功している<sup>1,2</sup>。今回我々は、LDAI化学を用いて、生きたマウス脳内の内在性 AMPA 型グルタミン酸受容体 (AMPA-R) のラベル化を試みた。ウェスタンブロットや蛍光イメージング等の解析の結果、生きたマウスの脳内で内在性 AMPAR の選択的ラベル化および可視化が可能であった。さらに組織透明化技術と組み合わせることで、全脳レベルで AMPAR の3次元分布を可視化することにも成功した。本講演では、その詳細に関して報告する。

1) S. Fujishima *et al.*, *J. Am. Chem. Soc.*, **134**, 3961 (2012)

2) S. Wakayama *et al.*, *Nat. Commun.*, **8**, 14850 (2017)



## Ligand directed chemistry in live mouse brain (2): 様々な神経伝達物質受容体への拡張と寿命解析

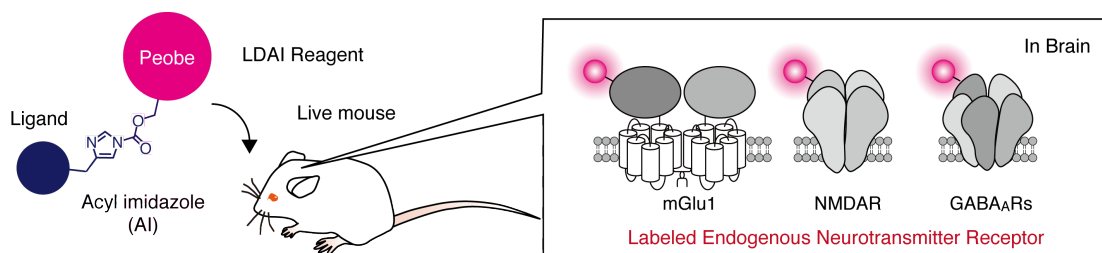
(京大院工<sup>1</sup>・名大院工<sup>2</sup>・JST ERATO<sup>3</sup>) ○坂本 清志<sup>1,3</sup>・白岩 和樹<sup>1</sup>・清中 茂樹<sup>2,3</sup>・野中 洋<sup>1,3</sup>・浜地 格<sup>1,3</sup>

Ligand directed chemistry in live mouse brain (2): Application to other endogenous receptors and their life-time analysis. (<sup>1</sup>*Graduate School of Engineering, Kyoto University*, <sup>2</sup>*Graduate School of Engineering, Nagoya University*, <sup>3</sup>*JST ERATO*) ○Seiji Sakamoto,<sup>1,3</sup> Kazuki Shiraiwa,<sup>1</sup> Shigeki Kiyonaka,<sup>2,3</sup> Hiroshi Nonaka,<sup>1,3</sup> Itaru Hamachi<sup>1,3</sup>

Ligand-directed acyl imidazole (LDAI) chemistry developed by Hamachi and co-workers allows the chemical labeling of endogenous proteins in a ligand recognition manner. By employing the LDAI method, we have succeeded in the chemical labeling of endogenous AMPA receptors in live mouse brain. Given the modular feature of the acyl transfer reagent, we further applied the LDAI chemistry for other endogenous receptors by replacing the ligand part with an appropriate small molecule to each target, that is two other glutamate receptors (mGlu1 and NMDAR) or an ionotropic GABA receptor (GABA<sub>A</sub>R). Western blot analysis and CLSM imaging confirmed the selective labeling of target receptor was achieved in mouse brain. Moreover, in gel fluorescence analysis of brain tissue lysates provided the kinetic parameters for acyl transfer reaction and degradation of labeled receptors.

**Keywords :** Chemical Labeling of Protein; Neurotransmitter Receptor; Ligand-directed Chemistry; Acyl Transfer Reaction; Endogenous Proteins

リガンド指向性アシルイミダゾール (LDAI) 化学は、リガンド認識駆動に基づき内在性タンパク質のケミカルラベルを可能とする。先の講演で報告したように、LDAI 化学を用いて、生きたマウス脳内における内在性 AMPA 型グルタミン酸受容体 (AMPA) のラベル化とイメージングに成功している。本研究では、LDAI 化学の様々な神経伝達物質受容体への拡張とマウス脳内における受容体の寿命解析への応用を試みた。具体的には、LDAI 試薬のリガンド部分を適切な小分子に置換することで、AMPA とは異なる二種類のグルタミン酸受容体 (mGlu1 および NMDAR) ならびに抑制性 GABA 受容体 (GABA<sub>A</sub>R) の生きたマウス脳内におけるラベル化を行った。さらに、LDAI 試薬投与後の時間経過に伴うラベル化受容体量の変化を調べることで、マウス脳内における受容体寿命解析にも成功したのでその詳細を報告する。



## Ligand directed chemistry in live mouse brain (3): 生後発達期の脳内 AMPA 受容体の動態解析

(京大院工<sup>1</sup>・JSTERATO<sup>2</sup>・名大院工<sup>3</sup>) ○野中 洋<sup>1,2</sup>・白岩 和樹<sup>1</sup>・坂本 清志<sup>1</sup>・清中 茂樹<sup>2,3</sup>・浜地 格<sup>1,2</sup>

Ligand directed chemistry in live mouse brain (3): Pulse-chase analysis of AMPA receptors in the brain during postnatal development (<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>JST, ERATO, <sup>3</sup>Graduate School of Engineering, Nagoya University) ○Hiroshi Nonaka,<sup>1,2</sup> Kazuki Shiraiwa,<sup>1</sup> Seiji Sakamoto,<sup>1</sup> Shigeki Kiyonaka,<sup>2,3</sup> Itaru Hamachi<sup>1,2</sup>

In the postnatal development, the nervous system undergoes dramatic changes in brain size and component/localization of cells, during which synapses are scrapped and built to form mature neural circuits. This is one of the essential processes for creating functional and lean neural circuits.

Taking advantage of the features of ligand-directed acyl imidazole (LDAI) chemistry, *e.g.* labeling in live mice and labeling time of a few hours, we attempted to conduct pulse-chase analysis of AMPA-type glutamate receptors (AMPA receptors) in the postnatal mouse brain. Fluorescence imaging and western blot analysis revealed that AMPARs can be selectively labeled in the postnatal mouse brain. Furthermore, we performed pulse-chase analysis using LDAI chemistry to analyze the dynamics of AMPARs during postnatal cerebellar development. We found for the first time that labeled AMPARs, which were present in early synapses at the time of labeling, migrate to new synapses. In this talk, we will report on the details.

**Keywords :** *Ligand directed chemistry; Chemical labeling; Neurotransmitter receptor; Pulse-chase analysis*

生後発達期の脳神経系では、脳の大きさや細胞の構成要素/局在が劇的に変化し、シナプスのスクラップ&ビルドがなされ、成熟した神経回路が形成される。<sup>1</sup> この現象は、機能的で無駄のない神経回路を作るための必須なプロセスの一つである。この動的な変化の中で、シナプスに存在する神経伝達物質受容体がどのような挙動をとるのか未だ不明な点が多い。

前講演までで新たに明らかになったリガンド指向性アシルイミダゾール (LDAI) 化学の特徴 (生きたマウス中でのラベル化が可能、ラベル化時間は数時間程度) を活用して、生後発達期マウス脳内の AMPA 型グルタミン酸受容体 (AMPA) の動態解析を試みた。蛍光イメージングやウエスタンブロット等の解析の結果、生後発達期マウス脳内で AMPAR を選択的にケミカルラベルできていることが明らかになった。さらに、生後発達期小脳の発達に伴う AMPAR の動態解析を志向して、LDAI 化学を用いたパルスチェイス解析を実施した。その結果、ラベル化した時点で初期のシナプスに存在したラベル化 AMPAR が、成長に伴い新生された別のシナプスに移行することを世界で初めて明らかにした。本講演では、その詳細に関して報告する。

1) M. Kano *et al.*, *F1000Res.*, **8**, 1191 (2019).

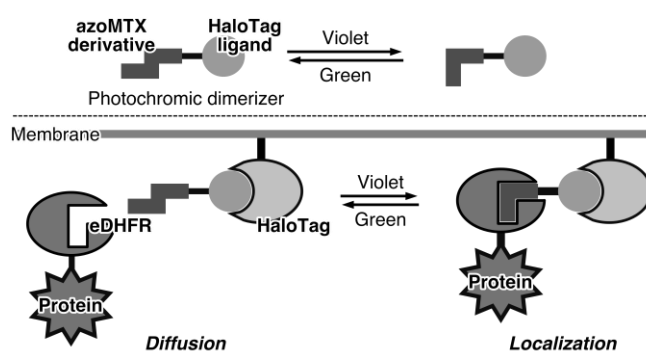
## Optical regulation of protein translocation using a photo-reversible protein labeling system

(<sup>1</sup>Graduate School of Science, Tohoku University, <sup>2</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University) ○Takato Mashita<sup>1</sup>, Toshiyuki Kowada<sup>1,2</sup>, Toshitaka Matsui<sup>1,2</sup>, Shin Mizukami<sup>1,2</sup>

**Keywords:** Protein labeling system, Optical regulation, Photochromism, Protein translocation

Artificial control of the dynamics of proteins with high precision provides valuable insight into complicated biological networks. Optogenetics and photo-responsive chemically induced dimerization (CID) are famous methods for spatiotemporal regulation of protein dynamics. However, both methods leave significant challenges for the fine-tuning at precise time and locations or cycle of repetition. In this study, we aimed at developing a novel chemical tool that allows photo-reversible control of subcellular protein localization, focusing on a photochromic compound. We previously developed a photochromic ligand, azoMTX, which binds to *Escherichia coli* dihydrofolate reductase (eDHFR) in a light-wavelength-dependent manner.<sup>1</sup> We thus designed a photochromic ligand for eDHFR conjugated with a HaloTag ligand to establish a photochromic CID system (**Figure 1**).

The designed photochromic dimerizer isomerized from *E* to *Z* isomer upon violet light irradiation and from *Z* to *E* isomer upon green light irradiation. The binding assay showed that the photochromic dimerizer had a higher affinity to eDHFR under violet light irradiation than dark conditions. HeLa cells co-expressing an organelle-targeted HaloTag and an eDHFR-fused fluorescent protein (FP) were treated with the photochromic dimerizer. When the cells were illuminated with violet and green light alternately, subcellular localization of the eDHFR-fused FP was photo-reversibly regulated.



**Figure 1.** Schematic illustration of photochromism-based protein translocation.

- 1) Mashita, T.; Kowada, T.; Takahashi, H.; Matsui, T.; Mizukami, S. *ChemBioChem* **2019**, *20*, 1382–1386.

## 生細胞内メンブレンコンタクトを可視化する蛍光プローブの開発

(名工大工<sup>1</sup>・名工大院工<sup>2</sup>・新潟大院医歯<sup>3</sup>) ○阿喰 萌香<sup>1</sup>・吉川 優<sup>2</sup>・筒井 啓太<sup>2</sup>・中津 史<sup>3</sup>・築地 真也<sup>1,2</sup>

Development of fluorescent probes for visualizing membrane contact sites in living cells (<sup>1</sup>Faculty of Engineering, Nagoya Institute of Technology, <sup>2</sup>Graduate School of Engineering, Nagoya Institute of Technology, <sup>3</sup>Graduate School of Medical and Dental Sciences, Niigata University) ○Moeka Ajiki,<sup>1</sup> Masaru Yoshikawa,<sup>2</sup> Keita Tsutsui,<sup>2</sup> Fubito Nakatsu,<sup>3</sup> Shinya Tsukiji,<sup>1,2</sup>

Eukaryotic cells contain various membrane-bound organelles such as the nucleus, mitochondria, and endoplasmic reticulum (ER). It has been recognized that these organelles are physically separated from each other. However, in recent years, a growing number of evidence has revealed that the ER communicates with other organelles and the plasma membrane (PM) by forming close contacts, often called “membrane contact sites” (MCSs). MCSs play various important roles in cell physiology. However, the spatiotemporal dynamics of MCSs in living cells remains poorly understood due to the lack of methods suitable for MCS visualization. In this work, we aimed to develop a method that allows specific visualization of MCS dynamics in living cells. For this purpose, we focused on splitFAST, a reversible fluorescence complementation system that allows monitoring of association and dissociation of an N-FAST/C-FAST fragment assembly in the presence of a fluorogenic dye, HBR. We will show that ORP5-mediated ER-PM contact sites can be visualized in living cells by using PM-targeted N-FAST and C-FAST-fused ORP5 constructs.

**Keywords:** *membrane contact; fluorescent probe; split protein; plasma membrane; endoplasmic reticulum*

真核細胞には、核、ミトコンドリア、小胞体（ER）などに代表される「オルガネラ」が存在する。長年、これらのオルガネラはそれぞれが物理的・空間的に離れて存在していると考えられてきた。しかし近年、ERが細胞膜（PM）や他のオルガネラと距離的に近接し、膜と膜がタンパク質によって係留されたメンブレンコンタクト（以下、コンタクト）を形成することが明らかになってきた<sup>1)</sup>。コンタクトは、脂質交換をはじめとする様々な細胞生理機能を制御していると考えられている。しかし、コンタクトの形成や解消などの時空間動態を解析できる可視化技術の開発が遅れているため、コンタクトの機能や制御機構については未だ不明な点が多い。そこで本研究では、生細胞内のコンタクト動態を特異的かつ可逆的に検出できる蛍光プローブの開発を目指した。

本研究では、コンタクト検出のための汎用的手法を確立するため、脂質交換輸送に関わるタンパク質 ORP5 による ER-PM コンタクトの蛍光検出から着手した。我々の戦略では、FAST と呼ばれるタンパク質を分割した splitFAST（N-FAST フラグメントと C-FAST フラグメントのペア）を利用する。FAST は本来、HBR という小分子化合物と結合することで蛍光を発するが、FAST を分割した N-FAST と C-FAST は HBR 存在下でも蛍光を発さない。一方、これらのフラグメントが近接すると両断片が結合して再構成し、HBR と結合して蛍光を発するようになる<sup>2)</sup>。そこで我々は、膜と膜が近接したコンタクト領域で splitFAST の再構成を引き起こすことでコンタクト領域を特異的に HBR 蛍光で可視化できるものと考えた。そこで、N-FAST を PM 上に、ORP5 に C-FAST を融合したものを ER 上に発現させたところ、ER 上の ORP5 が PM に接触した領域で splitFAST の再構成が起こり、ORP5 による ER-PM コンタクトを特異的に可視化することに成功した。本発表では、splitFAST によるコンタクト検出法と応用について報告する。

1) W. A. Prinz, A. Toulmay, T. Balla, *Nat. Rev. Mol. Cell Biol.* **21**, 7–24 (2020).

2) A. G. Tebo, A. Gautier, *Nat. Commun.* **10**, 2822 (2019).

## 生細胞内メンブレンコンタクトを操作する化学ツールの開発

(名工大院工<sup>1</sup>・名工大工<sup>2</sup>・新潟大院医歯<sup>3</sup>) ○吉川 優<sup>1</sup>・阿喰 萌香<sup>2</sup>・筒井 啓太<sup>1</sup>・中津 史<sup>3</sup>・築地 真也<sup>1,2</sup>

Development of chemical tools for manipulating membrane contacts in living cells (<sup>1</sup>*Graduate School of Engineering, Nagoya Institute of Technology*, <sup>2</sup>*Faculty of Engineering, Nagoya Institute of Technology*, <sup>3</sup>*Graduate School of Medical and Dental Science, Niigata University*)  
○Masaru Yoshikawa,<sup>1</sup> Moeka Ajiki,<sup>2</sup> Keita Tsutsui,<sup>1</sup> Fubito Nakatsu,<sup>3</sup> Shinya Tsukiji<sup>1,2</sup>

Membrane contact sites (MCSs) are formed by the proximity of two organelle membranes and associated with various cellular functions such as lipid metabolism and signal transduction. To investigate physiological roles and formation mechanism of MCSs, experimental methods that enable conditional and reversible control of MCS formation between intended organelles are highly needed. Here we report a chemogenetic system for inducing MCS formation between the endoplasmic reticulum (ER) and the plasma membrane (PM) in living cells. In this system, an ER-spanning protein is expressed as a fusion with a tag protein and is chemically tethered to the PM by using a lipid-conjugated small-molecule ligand (i.e., self-localizing ligand) for the protein tag. This ER-PM crosslink generates ER-PM contact, and this synthetic contact can be reverted by the addition of a free (unmodified) ligand. With this approach, ER-PM contact formation and associated physiological functions were successfully controlled in living cells.

**Keywords:** *membrane contact; self-localizing ligand; endoplasmic reticulum; lipid; plasma membrane*

オルガネラ膜同士の近接により形成されるメンブレンコンタクト（以下、コンタクト）は、細胞内の脂質代謝やシグナル伝達において重要な役割を果たしている。しかし、その生理的役割や形成メカニズムには未解明の部分が多く残されており、それらの解明には生きた細胞内の任意のオルガネラ膜間のコンタクトを人工的に誘導可能なツールの開発が不可欠である。コンタクト形成を誘導する既存法として、Rapamycin による FKBP と FRB の化学誘導二量化を利用するものがあるが、可逆性がないためコンタクト解消後の細胞動態の追跡やコンタクト形成の繰り返し制御には不向きであった。そのため、コンタクト形成の可逆制御が可能なツールの開発が望まれている。

今回我々は、小胞体と細胞膜（ER-PM）間のコンタクト形成を制御している ER 局在タンパク質 ORP5 に着目し、これを基に ER-PM コンタクトの形成を可逆操作する化学ツールを設計した。具体的には、ORP5 の PM 結合ドメインをタグタンパク質に置き換え、そこに PM に結合する脂質化修飾リガンド（局在性リガンド）を添加することで ER-PM 間を架橋させる。本ツールを用いることで、局在性リガンドの添加によって ER-PM コンタクトを誘導でき、さらに未修飾リガンドの添加によってコンタクトを解消することができた。また、コンタクト形成に伴う生理的機能（ER-PM 間の脂質交換輸送）の誘導や、光応答的なコンタクト制御システムの開発にも成功した。本発表では、生細胞内の ER-PM コンタクトを操作する新規化学ツールの詳細と、その展望について報告する。

## Fluorescence lifetime mapping of lipid compositions using an environment-responsive lipid droplet probe

(<sup>1</sup>Graduate School of Science, Nagoya University, <sup>2</sup>School of Medicine, Sapporo Medical University, <sup>3</sup>Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University)

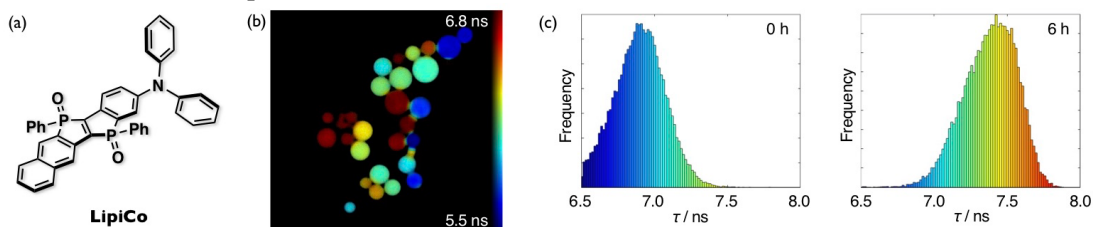
○Keiji Kajiwar, <sup>1</sup>Yuki Ohsaki, <sup>2</sup>Masayasu Taki, <sup>3</sup>Shigehiro Yamaguchi<sup>1,3</sup>

**Keywords:** Fluorescence lifetime imaging; Lipid droplet; Fluorescent probe; Lipid compositions; Live-cell imaging

Lipid droplet (LD) is an essential organelle, which consists of lipid esters core covered with a phospholipid monolayer. Much attention has recently been paid to the effect of the composition of neutral lipids, especially a ratio of triacylglycerol (TAG) and cholesterol ester (CE), in LDs on cell functions. However, although many fluorescent probes for LDs have been developed to date, none of them can evaluate lipid composition. Therefore, it is a challenge to develop a new fluorescent probe that has high LD selectivity as well as high environmental sensitivity that can discriminate between TAG-rich and CE-rich LDs. Herein, we report a phosphole-oxide-based LD probe, **LipiCo** (Figure 1a) and its practical applications to the LDs imaging by fluorescence lifetime imaging microscopy (FLIM).

The fluorescence lifetime ( $\tau$ ) of **LipiCo** is very sensitive to the solvent polarity, which allows us to distinguish even a slight difference in polarity between toluene and  $\text{CH}_2\text{Cl}_2$  with the  $\tau$  values of 7.7 ns and 6.8 ns, respectively. Because its fluorescence is significantly quenched in more polar solvents such as DMSO, non-polar LDs is clearly visualized using **LipiCo** with high signal-to-noise ratio, even at ultra-small sizes. Indeed, LDs were selectively detected with **LipiCo** in a variety of cell types.

First, using FLIM, we measured the fluorescence lifetime of **LipiCo** in artificial LDs consisting of triolein and cholesterol oleate. The  $\tau$  values increase with increasing a ratio of cholesterol oleate, indicating that **LipiCo** enables the evaluation of lipid composition in cells. We then stained HuH-7 cells and recorded the LDs by FLIM. Importantly, even in a single cell, the fluorescence lifetime of each LD showed a heterogeneous distribution in the range of 5.5 ns to 6.8 ns (Figure 1b). Taking advantage of these unique properties of **LipiCo**, we monitored the metabolic accumulation process of cholesterol into the LDs in hepatocytes. Upon the addition of cholesterol, longer  $\tau$  values were observed, as the incubation time was increased (Figure 1c). The wide distribution of  $\tau$  values in this case suggest that cholesterol is not taken up uniformly by all LDs and each LD plays a different role in the metabolic process.



**Figure 1.** (a) A molecular structure of **LipiCo**. (b) A FLIM image of LDs in one HuH-7 cell stained with **LipiCo**. (c) Distributions of fluorescence lifetime in LDs of HuH-7 cells 0 h (left) and 6 h (right) after the addition of cholesterol.

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Academic Program [Oral B] | 18. Polymer | Oral B**[C203-2am] 18. Polymer**

Chair: Masayuki Gon, Kenichi Oyaizu

Thu. Mar 24, 2022 9:00 AM - 11:40 AM C203 (Online Meeting)

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**[C203-2am-01] Topology Transformation toward Cyclic, Figure-Eight-Shaped, and Cross-Linked Polymers via Dynamic Covalent Chemistry**○Hirogi Yokochi<sup>1</sup>, Daisuke Aoki<sup>1,2</sup>, Hideyuki Otsuka<sup>1</sup> (1. Tokyo Institute of Technology, 2. JST PRESTO)

9:00 AM - 9:20 AM

**[C203-2am-02] Synthesis, Reactions, and DFT Study of Radical-type Mechanophores with Bisarylfluorene Skeletons**○Hajime Sugita<sup>1,2</sup>, Yi Lu<sup>2</sup>, Koichiro Mikami<sup>1</sup>, Daisuke Aoki<sup>2</sup>, Hideyuki Otsuka<sup>2</sup> (1. Sagami Chemical Research Institute, 2. Tokyo Institute of Technology)

9:20 AM - 9:40 AM

**[C203-2am-03] Synthesis and Functionalities of Luminescent Conjugated Polymers Based on Dialdiminate Boron Complexes**○Shunichiro Ito<sup>1</sup>, Yuki Sakai<sup>1</sup>, Miyako Hashizume<sup>1</sup>, Kazuo Tanaka<sup>1</sup>, Yoshiki Chujo<sup>1</sup> (1. Kyoto University)

9:40 AM - 10:00 AM

**[C203-2am-04] Synthesis of functional peroxide mechanophores and their application to mechanoresponsive polymer networks that release fluorescent molecules**○Yi Lu<sup>1</sup>, Hajime Sugita<sup>2</sup>, Koichiro Mikami<sup>2</sup>, Daisuke Aoki<sup>1</sup>, Hideyuki Otsuka<sup>1</sup> (1. Tokyo Institute of Technology, 2. Sagami Chemical Research Institute)

10:00 AM - 10:20 AM

**[C203-2am-05] A cyclophane-based supramolecular mechanophore that shows ratiometric change in emission between monomer and exciplex**○Shakkeeb Thazhathethil<sup>1</sup>, Nobuyuki Tamaoki<sup>1</sup>, Yoshimitsu Sagara<sup>2</sup> (1. Hokkaido University, 2. Tokyo Institute of Technology)

10:20 AM - 10:40 AM

**[C203-2am-06] A Photostable Gel that Degrades by Simultaneous Treatment with Acid and UV Light for Phototuning of Optical Functionalities**○Go Martin Russell<sup>1</sup>, Takashi Kaneko<sup>1</sup>, Hiroshi Masai<sup>1</sup>, Jun Terao<sup>1</sup> (1. The Univ. of Tokyo)

10:40 AM - 11:00 AM

**[C203-2am-07] Poly(para-phenylene) ionomer membranes containing methyl or trifluoromethyl substituents**○FANGHUA LIU<sup>1</sup>, Kenji Miyatake<sup>1,2</sup> (1. Univ. Yamanashi, 2. Waseda Univ.)

11:00 AM - 11:20 AM

**[C203-2am-08] Revealing the relationships between processes, structures, and properties of poly(phenylene ether)-based solid-state electrolytes by materials informatics**○Kan Hatakeyama-Sato<sup>1</sup>, Momoka Umeki<sup>1</sup>, Hiroki Adachi<sup>1</sup>, Kenichi Oyaizu<sup>1</sup> (1. Waseda University)

11:20 AM - 11:40 AM



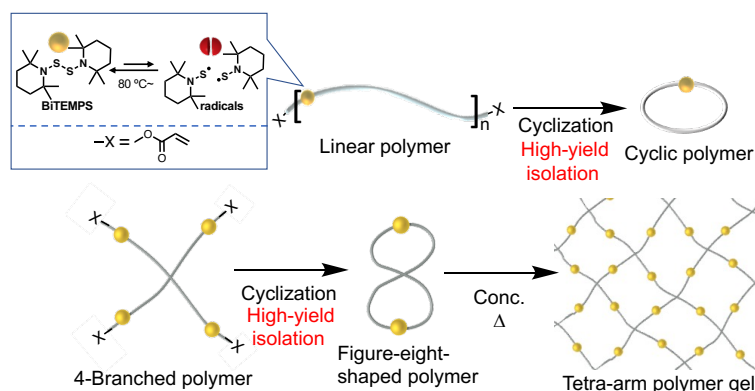
## Topology Transformation toward Cyclic, Figure-Eight-Shaped, and Cross-Linked Polymers via Dynamic Covalent Chemistry

(<sup>1</sup>*School of Materials and Chemical Technology, Tokyo Institute of Technology*, <sup>2</sup>*JST-PRESTO*)

○Hirogi Yokochi,<sup>1</sup> Daisuke Aoki,<sup>1,2</sup> Hideyuki Otsuka<sup>1</sup>

**Keywords:** Topology; Cyclic Polymers; Figure-eight-shaped Polymers; 4-Branched Polymers; Dynamic Covalent Chemistry

Topological transformations of polymer architectures via dynamic covalent chemistry have attracted considerable attention in recent decades, as they change the primary structure of the polymer architecture and thus the polymer properties. However, topological transformations to produce cyclic topologies remain challenging. In this study, cyclic and figure-eight-shaped polymers were synthesized based on the dynamic behavior of the bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) linkage.<sup>1</sup> Linear and 4-branched polymers were transformed into cyclic polymers and figure-eight-shaped polymers, using the following sequence: 1) A thiol–ene reaction was used to introduce BiTEMPS units into the terminal structures of the polymers to be cyclized; 2) an entropy-driven transformation to give the desired cyclic topology through the exchange reaction of the BiTEMPS units was induced by dilution and heating; 3) acyclic impurities with reactive groups were selectively removed via a thiol–ene click reaction with polystyrene particles that contain dangling thiol groups on their surface and subsequent simple filtration. The radicals generated by BiTEMPS upon heating are highly tolerant toward a variety of chemical species, including oxygen and olefins, and exhibit high reactivity in exchange reactions, making them applicable for various skeletons. The simplicity and substrate versatility of this procedure are demonstrated via the highly efficient gram-scale synthesis of cyclic and figure-eight-shaped polymers. Moreover, we describe the topological transformation of the obtained cyclic and/or figure-eight-shaped polymers into cross-linked polymers with precisely controlled physical properties by using their cyclic or figure-eight topology and the dynamic nature of the BiTEMPS units in their structures.



1) H. Yokochi, D. Aoki, H. Otsuka *et al.*, *Macromolecules*. **2021**, 54, 9992.

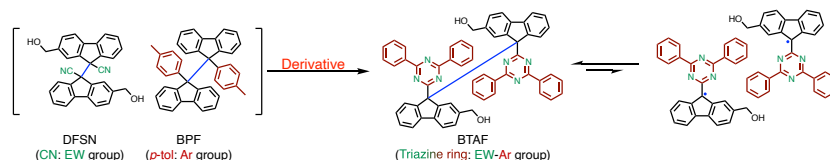
## ビスアリールフルオレン骨格を有するラジカル系メカノフォアの合成、反応、および DFT 計算

(相模中央化学研究所<sup>1</sup>・東京工業大学<sup>2</sup>・) ○杉田 一<sup>1,2</sup>・Yi Lu<sup>2</sup>・已上 幸一郎<sup>1</sup>・青木 大輔<sup>2</sup>・大塚 英幸<sup>2</sup>

Synthesis, Reactions, and DFT Study of Radical-type Mechanophores with Bisarylfluorene Skeletons (<sup>1</sup>Sagami Chemical Research Institute, <sup>2</sup>Department of Chemical Science and Engineering, Dept. of Chem. Sci. and Eng., Tokyo Tech.) ○Hajime Sugita,<sup>1,2</sup> Yi Lu,<sup>2</sup> Koichiro Mikami,<sup>1</sup> Daisuke Aoki,<sup>2</sup> Hideyuki Otsuka<sup>2</sup>

Radical-type mechanophores (RMs) are expected for self-healing and visualization of damaged parts or mechanical stress in polymeric materials via homolysis of their central C–C bonds. They showed different oxygen- or thermo-stabilities, and they are important factors to keep RM properties in polymer processing. To understand the relationship between the structure of RMs and both stabilities, we synthesized bistriazinefluorene (BTAF) as a derivative of bisphenylfluorene (BPF) and difluorenylsuccinonitrile (DFSN). Variable temperature electron paramagnetic resonance (EPR) measurements revealed that ground polymer with a BTAF generated radical species.  $\Delta E$  in C–C bond dissociation reaction which was evaluated by density functional theory (DFT) calculation of DFSN, BPF, and BTAF are 15.9 kcal/mol, 2.8 kcal/mol, and 9.1 kcal/mol, respectively, and these results were consistent with thermo-stability. **Keywords** : *Mechanochemistry; Mechanoradical; Electron paramagnetic resonance; Density functional theory calculation*

ラジカルメカノフォア (RM) は自己修復性、損傷部位や応力検知といった材料に期待されており<sup>1,2)</sup>、それらの特性は RM の中心炭素炭素結合のホモリシスによって発現される。しかし RM の熱安定性や酸素安定性は骨格によって大きく異なるため、高分子材料の加工過程においてメカノフォアの機能を損なう場合がある。そこで本研究では DFSN<sup>3)</sup> や BPF<sup>4,5)</sup> の誘導体である BTAF を合成し、分子骨格による熱安定性、酸素安定性の影響を調査した。BTAF の温度可変 電子スピン共鳴 (ESR) 測定や BTAF が導入された高分子試料破碎後のサンプルの ESR 測定はどちらもラジカル種の生成を示した。DFT 計算より見積もられた DFSN、BPF、BTAF の開裂反応における原系と生成系のエネルギー差はそれぞれ 15.9 kcal/mol、2.8 kcal/mol、9.1 kcal/mol と実験事実より考えられる熱安定性と良い一致を示した。



1) H. Otsuka et al., *Angew. Chem. Int. Ed.*, **2012**, *51*, 1138; 2) H. Otsuka et al., *Chem. Commun.*, **2016**, *52*, 10482; 3) H. Otsuka et al., *ACS Macro Lett.*, **2018**, *7*, 1359; 4) J. C. Scaiano et al., *Org. Lett.*, **2004**, *6*, 2579; 5) H. Otsuka et al., *J. Am. Chem. Soc.*, **2021**, *143*, 17744.

## Synthesis and Functionalities of Luminescent Conjugated Polymers Based on Daldiminate Boron Complexes

(Graduate School of Engineering, Kyoto University) ○Shunichiro Ito, Yuki Sakai, Miyako Hashizume, Kazuo Tanaka, Yoshiki Chujo

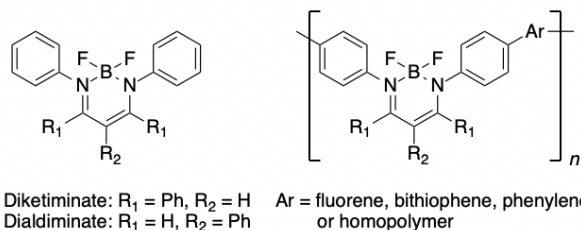
**Keywords:** Solid-State Emission; Conjugated Polymer; Boron Complex; Group 13 Elements

### Abstract

Solid-state luminescent molecules are essential for the development of advanced optical materials and devices, such as organic light-emitting diodes, chemical sensors, and organic lasers. Luminescent boron complexes have attracted attention because of their electron-accepting character and stimuli-responsive properties. We have developed solid-state emissive materials based on group 13 elements  $\beta$ -diiminate complexes with crystallization-induced emission.<sup>1</sup> Herein, we synthesized  $\beta$ -diiminate boron complexes and their polymers with highly efficient luminescence both in the solutions and solids. Moreover, a series of conjugated polymers composed of the complex were obtained by coupling reactions. We will describe their molecular design, syntheses, and luminescent properties.

### Results and Discussion

We synthesized boron complexes with aromatic groups at different positions as shown in Figure 1. The compounds with aromatic rings at  $R_1$  position are named as diketiminates, while daldiminates possess hydrogen atoms at  $R_1$  position. Conjugated polymers



**Figure 1.** Chemical structures of synthesized complexes and polymers.

composed of these complexes were obtained by using metal-catalyzed copolymerization with fluorene, bithiophene, or phenylene comonomers. Furthermore, homopolymers were synthesized by nickel-mediated Yamamoto coupling with dibrominated boron complexes.

Diketimate complexes showed fluorescence at the crystalline state, meanwhile they were not emissive in their solutions. On the other hand, daldimate complexes showed not only at the crystalline state but also in the solutions. It was suggested that non-radiative quenching processes would be accelerated by the aromatic substituents at  $R_1$  positions.

The polymers of diketiminates exhibited solid-state emission, but their solutions hardly emitted light. On the other hand, the polymers of daldiminates were luminescent at both solid and solution states as well as the corresponding daldimate small molecules. Furthermore, the homopolymers of daldiminates showed solvent-dependent change in emission color and intensity, which was not observed from the small molecules.

### Reference

[1] Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2014**, *136*, 18131.

## Synthesis of Functional Peroxide Mechanophores and Their Application to Mechanoresponsive Polymer Networks That Release Fluorescent Molecules

(<sup>1</sup>Department of Chemical Science and Engineering, Tokyo Institute of Technology, <sup>2</sup>Sagami Chemical Research Institute) ○Yi Lu,<sup>1</sup> Hajime Sugita,<sup>2</sup> Koichiro Mikami,<sup>2</sup> Daisuke Aoki,<sup>1</sup> Hideyuki Otsuka<sup>1</sup>

**Keywords:** Mechanochemistry, Mechanochromism, Peroxides, Polymer Networks, Functional molecule Releasing

For a long time, organic peroxides have been considered as unstable species and applied as radical generators or bleaching agents. Nevertheless, we found that bis(9-methyl-9-fluorenyl) peroxide derivatives (**BMPF**) were a class of stable compounds at room and even elevated temperatures. Furthermore, **BMPF** underwent chemical reactions in response to mechanical force and thus exhibited mechanochromic properties. Study on the model compound revealed the mechanism of the mechanochemical reaction in which 9-fluorenone, a fluorescent molecule, was released via the homolytic cleavage of peroxide bond, followed by  $\beta$ -scission<sup>1</sup> of the resulting oxygen radical. Since the mechanochemical properties of organic peroxide have rarely been documented hitherto, herein, we report our findings in exploring the mechanochemical properties of **BMPF**.<sup>2</sup>

Namely, **BMPF** was introduced as cross-linking units into both glassy and elastomeric network polymers. Grinding test to the glassy network polymer resulted in mechanochromic phenomena (Fig. 1B, upper) derived from the releasing of 9-fluorenone from the network polymer (Fig. 1A), which was consistent with the proposed mechanism in the model study. On the other hand, the elastomeric network showed mechanochromic behaviors under compressive force. A well-controlled fluorescent pattern could be printed by compressing the elastomer with an H-shaped metal stamp (Fig. 1B, lower). Besides, the network polymer exhibited satisfying stability at elevated temperatures up to 100 °C without stress relaxation or optical change. These results suggested that **BMPF** is a potential candidate as a novel peroxide-based mechanochromophore.

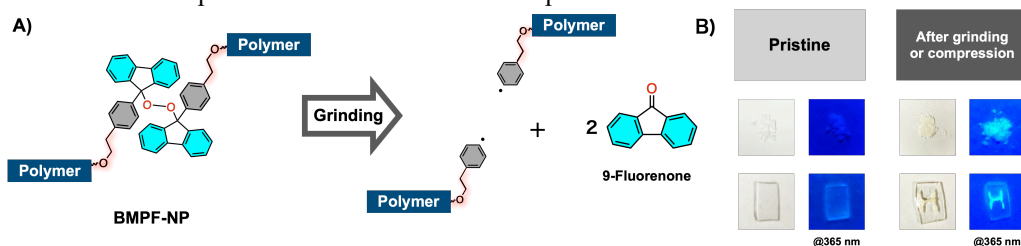


Fig. 1 (A) Releasing of 9-fluorenone from network polymer cross-linked by BMPF units, (B) Mechanochromic phenomena of BMPF cross-linked polymers.

1) P. G. Mekarbane and B. J. Tabner, *Macromolecules*, 1999, **32**, 3620–3625.

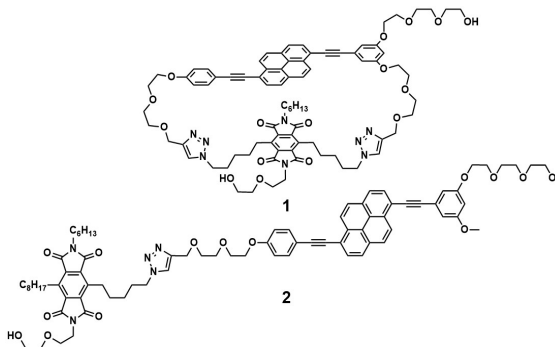
2) Y. Lu, H. Sugita, K. Mikami, D. Aoki, H. Otsuka, *J. Am. Chem. Soc.*, 2021, **143**, 17744–17750.

## A Cyclophane-based Supramolecular Mechanophore that Shows Ratiometric Change in Emission Between Monomer and Exciplex

(<sup>1</sup>Research Institute for Electronic Science, Hokkaido University, <sup>2</sup>School of Materials and Chemical technology, Tokyo Institute of Technology) ○ Shakkeeb Thazhathethil,<sup>1,2</sup> Nobuyuki Tamaoki,<sup>1</sup> Yoshimitsu Sagara<sup>2</sup>

**Keywords:** Supramolecular mechanophore; Cyclophane; Exciplex; Mechanochromic luminescence; Elastomer

The mechanophores are the molecular units that show various responses when an external mechanical force is applied.<sup>1</sup> The number of supramolecular mechanophores, in which the activation does not require covalent bond scission, is still limited.<sup>2–4</sup> Here, we report a cyclophane-based supramolecular mechanophore **1** featuring a 1,6-bis(phenylethynyl)pyrene luminophore and a pyromellitic diimide quencher. A linear reference compound **2** having the same luminophore and quencher was also synthesized. The monomer emission of the luminophore in cyclophane **1** is almost completely quenched in chloroform and toluene. In contrast, compound **2** shows partial quenching of the monomer emission from the luminophore. The cyclophane exhibits clear exciplex emission in toluene. Both the exciplex formation and effective quenching of the monomer emission in cyclophane are ascribed to the intramolecular charge-transfer interactions of the luminophore and quencher due to their close vicinity in the cyclic structure. Cyclophane **1** was covalently integrated into a linear segmented polyurethane to acquire **1-PU**. The **1-PU** films which were obtained through solvent casting exhibit exciplex-dominated orange emission. The deformation of the films results in changes of emission intensity ratio between monomer to exciplex, which is attributed to the spatial separation of the luminophore and the quencher. The changes in the emission intensity ratio show a correlation with the applied stress to the polymer film. The mechanochromic luminescence properties of the **1-PU** films is instantly reversible.



**Fig. 1.** Molecular structures of cyclophane **1** and linear reference compound **2**.

1) Y. Chen, G. Mellot, D. V. Luijk, C. Creton, R. P. Sijbesma, *Chem. Soc. Rev.* **2021**, *50*, 4100. 2) Y. Sagara, M. Karman, E. Verde-Sesto, K. Matsuo, Y. Kim, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2018**, *140*, 1584. 3) T. Muramatsu, Y. Okado, H. Traeger, S. Schrettl, N. Tamaoki, C. Weder, Y. Sagara, *J. Am. Chem. Soc.* **2021**, *143*, 9884. 4) Y. Sagara, H. Traeger, J. Li, Y. Okado, S. Schrettl, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2021**, *143*, 5519.

## A Photostable Gel that Degrades by Simultaneous Treatment with Acid and UV Light for Phototuning of Optical Functionalities

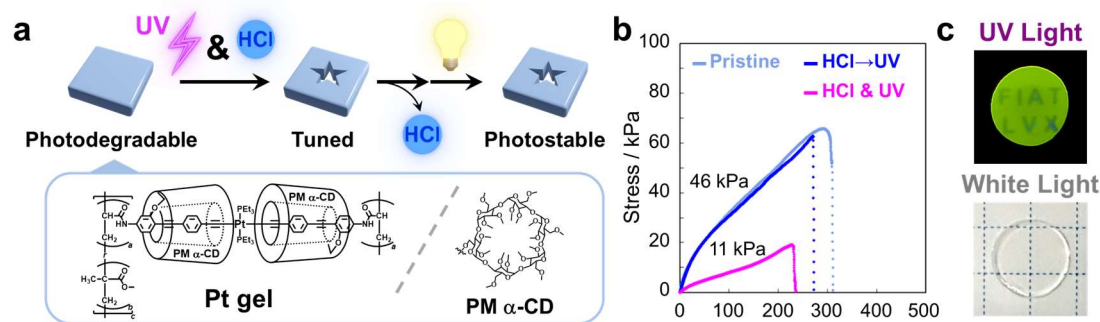
(<sup>1</sup>Graduate School of Arts and Sciences, The University of Tokyo) ○Go M. Russell, Takashi Kaneko, Hiroshi Masai, Jun Terao

**Keywords:** Photostability; Photoprocessability; Gels; Cross-linkers; Photoluminescence

Photodegradable materials exhibit on-demand phototunability with high spatiotemporal resolution and have gained importance in various applications.<sup>1</sup> However, due to their photoinstability, they can only be used transiently in most environments. Namely, the trade-off between photodegradability and photostability has limited the potential applications of photodegradable materials in naturally lit environments.

To realize a material that is both photostable and photodegradable, it is desirable for the material to be switched from photostable to photodegradable states in the presence of a particular chemical additive. In our previous study, we found that the photostable platinum-acetylide conjugated polymers cleaves by a combination of HCl and UV light.<sup>2</sup> In this study, we applied the reactivity of platinum-acetylide complex to polymer network materials to realize a photostable gel that can be converted into a photodegradable state by the addition of an acid, and into a photostable state by the removal of the acid (Fig. 1a).

**Pt gel**, a gel incorporating a platinum-acetylide cross-linker encapsulated by permethylated  $\alpha$ -cyclodextrin (PM  $\alpha$ -CD) was synthesized. When exposed to UV light under HCl solution, **Pt gel** underwent significant softening by the cleavage of the platinum-acetylide cross-linker (Fig. 1b). Conversely, when the acid was removed from the gel, its photostability was restored. By utilizing luminescence changes caused by decrosslinking, sub-millimeter-sized luminescent characters were photopatterned on the transparent gel (Fig. 1c). The characters were readily visualized without degradation under UV light while remained invisible under white light. Therefore, this technology expands the scope of photoprocessing applications for utilization under illumination.



**Figure 1.** a) Behavior and structure of the synthesized material in this work. b) Stress-strain curves of **Pt gel** before and after exposure to stimuli either sequentially or simultaneously. c) Photographs of photopatterned **Pt gel** under (top) 365 nm excitation and (bottom) white light.

1) L. Li, *et al. Adv. Mater.* **2019**, *31*, 1807333. 2) J. Terao, *et al. Polymers* **2020**, *12*, 244.

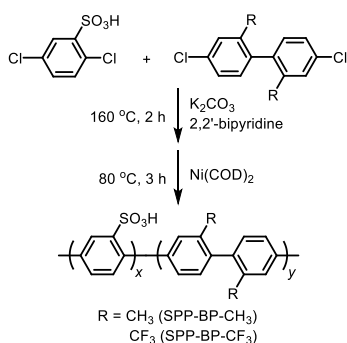


## Poly(*para*-phenylene) ionomer membranes containing methyl or trifluoromethyl substituents

(<sup>1</sup>Integrated Graduate School of Medical, Industrial and Agricultural Sciences, University of Yamanashi, <sup>2</sup>Clean Energy Research Center, University of Yamanashi, <sup>3</sup>Fuel Cell Nanomaterials Center, University of Yamanashi, <sup>4</sup>Department of Applied Chemistry, and Research Institute for Science and Engineering, Waseda University) ○Fanghua Liu,<sup>1</sup> Kenji Miyatake,<sup>2,3,4</sup>

**Keywords:** Poly(*para*-phenylene); Proton conductive polymers; sulfonated polymers

Sulfonated poly(*para*-phenylene)s with high molecular weight and membrane forming capability were obtained by using methyl and trifluoromethyl substituents. The linearity of the polymer main chain decreased by introducing these substituents; the persistence length ( $l_p$ , index of linearity, distance required for a polymer chain to bend by 90° on average) of homopolymers for 2,2'-dimethyl-1,1'-biphenyl (BP-CH<sub>3</sub>) and 2,2'-bis(trifluoromethyl)-1,1'-biphenyl (BP-CF<sub>3</sub>) was ca.350.6 and 87.7 nm, respectively, estimated by numerically averaging backbone conformations. Copolymers with sulfo-*para*-phenylene groups, SPP-BP-CH<sub>3</sub> and SPP-BP-CF<sub>3</sub>, were obtained as high molecular weight (Mn = 28–30 kDa and Mw = 88–100 kDa for SPP-BP-CH<sub>3</sub> and Mn = 49–149 kDa and Mw = 161–316 kDa for SPP-BP-CF<sub>3</sub>, respectively) to provide flexible membranes by casting from the solution. Despite more hydrophobic nature of the substituents, SPP-BP-CF<sub>3</sub> membranes showed higher water uptake and proton conductivity than those of SPP-BP-CH<sub>3</sub> membranes with comparable ion exchange capacity (IEC). SPP-BP-CF<sub>3</sub> membranes showed slightly higher maximum strain (2.9–5.2%) than SPP-BP-CH<sub>3</sub> membranes (1.1–2.1%), leading to higher rupture energy as expected from the smaller persistence length of BP-CF<sub>3</sub> homopolymers. While SPP-BP-CH<sub>3</sub> decomposed under harsh oxidative conditions, SPP-BP-CF<sub>3</sub> was more oxidatively stable and exhibited negligible changes in the weight, molecular weight, molecular structure and membrane properties (proton conductivity, mechanical properties, etc.)



Scheme 1. Synthesis of SPP-BP-CH<sub>3</sub> and CF<sub>3</sub>.

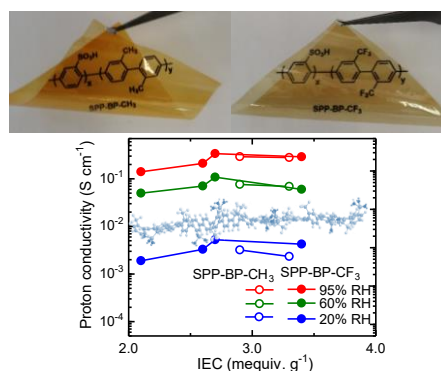


Figure 1. IEC dependence of proton conductivity of SPP-BP-CH<sub>3</sub> and -CF<sub>3</sub> at 80 °C.

## マテリアルズ・インフォマティクスを活用したポリフェニレンエーテル系固体電解質の製法・構造・物性の相関解明

(早大理工) ○畠山 歓・梅木 桃花・足立 裕樹・小柳津 研一 Revealing the relationships between processes, structures, and properties of poly(phenylene ether)-based solid-state electrolytes by materials informatics (*Dept. of Applied Chem., Waseda Univ.*)

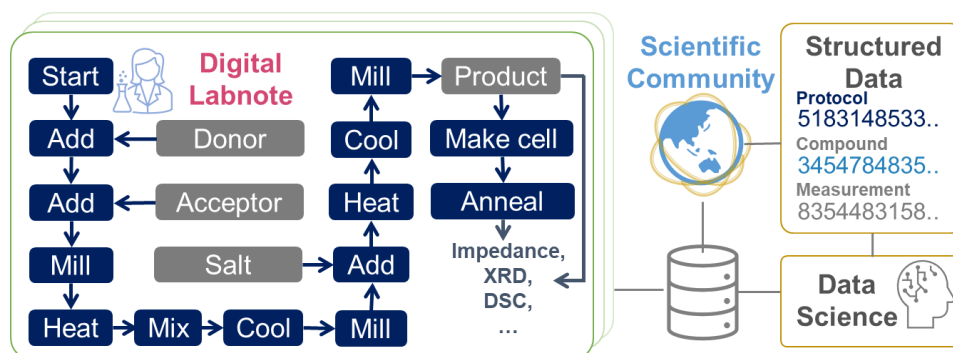
○Kan Hatakeyama-Sato, Momoka Umeki, Hiroki Adachi, Kenichi Oyaizu

We developed a new, flowchart-based materials informatics system that can analyze various process and material data of experiments. New glassy aromatic electrolytes were explored using the system. Data science-assisted analyses of the materials' processes, structures, and properties helped us reveal the optimal strategy of highly conductive electrolytes with  $\sigma_{\text{Li}} \cong 10^{-4}$  S/cm at room temperature and understand their mechanisms.

**Keywords :** Materials informatics; Polymer electrolyte; Solid-state lithium-ion battery

マテリアルズ・インフォマティクス<sup>1</sup>はデータ主導の研究手法として注目を集めているが、実際の運用にあたっては、複雑な製法・材料データの記録や解析等に困難を伴うことが多い。本研究では、フローチャート形式で記録された操作と実験結果の関係性をグラフ構造として明示的に記録し、自動解析するシステムを設計した(**Figure 1**)。

例題として、ポリフェニレンエーテルのような芳香族系ポリマーからなるガラス状電解質<sup>2</sup>の合成過程とイオン伝導度等の解析結果を記録した。研究中に得た 500 件以上の製法・構造・物性(インピーダンス・NMR・DSC・XRD 等)のデータを機械学習の手法で解析しながら研究を推進することで、室温で  $10^{-4}$  S/cm 程度の  $\text{Li}^+$ 伝導性を示す固体電解質の作製法や伝導メカニズムの解明が可能になった<sup>3</sup>。



**Figure 1** Data processing scheme by the system.

- 1 R. Ramprasad, R. Batra, G. Pilania, A. Mannodi-Kanakkithodi, C. Kim, *Npj Comput. Mater.* **2017**, 3, 54.
- 2 K. Hatakeyama-Sato, T. Tezuka, M. Umeki, K. Oyaizu, *J. Am. Chem. Soc.* **2020**, 142, 3301.
- 3 Manuscript in preparation.



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Academic Program [Oral B] | 18. Polymer | Oral B**[C202-2am] 18. Polymer**

Chair: Nobuhiko Hosono, Fumitaka Ishiwari

Thu. Mar 24, 2022 9:00 AM - 11:00 AM C202 (Online Meeting)

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**[C202-2am-01] Threading ultra-long polymers into MOF: Formation of a new penetration complex**○Tomoya Iizuka<sup>1</sup>, Hiroyuki Sano<sup>2</sup>, Nobuhiko Hosono<sup>2</sup>, Takashi Uemura<sup>2</sup> (1. Univ. of Tokyo, Grad. Sch. of Front. Sci., 2. Univ. of Tokyo, Grad. Sch. of Eng.)

9:00 AM - 9:20 AM

**[C202-2am-02] Synthesis, Properties, and Conformational Dynamics of Ladder Polymers Containing *N,N'*-Diacylated Diazacyclooctane Units in their Main Chains**○Keiki Inoue<sup>1,2</sup>, Fumitaka Ishiwari<sup>3</sup>, Takanori Fukushima<sup>1,2</sup> (1. Sch. of Mat. and Chem. Tech., Tokyo Tech, 2. CLS, Tokyo Tech, 3. Grad. Sch. of Eng., Osaka Univ.)

9:20 AM - 9:40 AM

**[C202-2am-03] Solid-state supramolecular polymers with ordered nanostructures**○Zebin Su<sup>1</sup> (1. Riken)

9:40 AM - 10:00 AM

**[C202-2am-04] In situ observation of polymeric vesicle formation by time-resolved ultra small-angle X-ray scattering**○Rintaro Takahashi<sup>1</sup>, Theyencheri Narayanan<sup>2</sup>, Shin-ichi Yusa<sup>4</sup>, Takahiro Sato<sup>3</sup> (1. Nagoya University, 2. ESRF-The European Synchrotron, 3. Osaka University, 4. University of Hyogo)

10:00 AM - 10:20 AM

**[C202-2am-05] Thermal degradation of a poly (ethylene-co-methacrylic acid) ionomer investigated by solid-state <sup>13</sup>C NMR and ESR**○Shohei Mikage<sup>1</sup>, Atsushi Asano<sup>1</sup> (1. National Defense Academy of Japan)

10:20 AM - 10:40 AM

**[C202-2am-06] Design of Stabilizer Formulations for Yellowing Inhibition of Polymeric Materials based on High-Throughput Experiments and Genetic Algorithm**○Ken Takimoto<sup>1</sup>, Toshiaki Taniike<sup>1</sup> (1. Japan Advanced Institute of Science and Technology)

10:40 AM - 11:00 AM

## MOF への超長鎖高分子の挿入：新規貫通複合体の合成

(東大院新領域<sup>1</sup>・東大院工<sup>2</sup>) ○飯塚 知也<sup>1</sup>・佐野 鴻之<sup>2</sup>・細野 暢彦<sup>2</sup>・植村 卓史<sup>2</sup>  
 Threading ultra-long polymers into MOF: Formation of a new penetration complex (<sup>1</sup>*Graduate School of Frontier Sciences., The Univ. of Tokyo*, <sup>2</sup>*Graduate School of Engineering, The Univ. of Tokyo*) ○Tomoya Iizuka,<sup>1</sup> Hiroyuki Sano,<sup>2</sup> Nobuhiko Hosono,<sup>2</sup> Takashi Uemura<sup>2</sup>

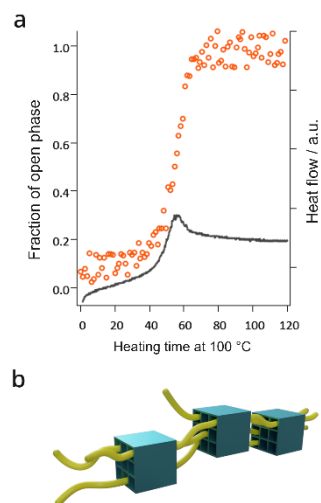
Penetrating complexes, such as rotaxanes, are molecular elements that have attracted attention because of their unique bonding mode based on topological constraints between rotor and axle. In this study, we have synthesized a new type of penetrating complex by threading ultra-long polymer chain on metal-organic framework (MOF) microcrystals. Ultra-long PEO with a molecular weight of 4,000,000 (**PEO4M**, contour length: ~30  $\mu\text{m}$ ) was inserted into a flexible MOF  $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]_n$  (**1**, bdc = 1,4-benzenedicarboxylate, bpy = 4,4'-bipyridyl). In the in-situ PXRD-DSC measurements, dynamic structure change of the flexible MOF and simultaneous heat generation due to the interaction between **1** and PEO were observed (Fig. 1a), indicating the insertion of such a very long-chain into the MOF pores. Detailed investigations suggested that the resultant complexes have a unique structure in which a single polymer chain penetrates multiple MOF particles (Fig. 1b).

**Keywords** : Ultra-long polymer; Metal-organic framework; Penetration complex

ロタキサンに代表される貫通型分子複合体は、分子同士のトポロジカルな拘束に基づいた結合様式を有し、力学物性などにおいて古くから注目されている分子素子である。本研究では、この概念をより大きなスケールへと拡張した新しい貫通複合体を合成した。以前より、我々のグループは分子量数百から一万程度の高分子が多孔性金属錯体 (Metal-organic framework, MOF) の細孔へと自発的に浸入することを報告している<sup>1)</sup>。本研究では従来に比べて極めて長い超長鎖高分子を MOF 微結晶へと挿入することで、新しい貫通複合体の合成を試みた。

分子量 4,000,000 (伸び切り鎖長: ~30  $\mu\text{m}$ ) の PEO (**PEO4M**) と柔軟性 MOF  $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]_n$  (**1**, bdc = 1,4-benzenedicarboxylate, bpy = 4,4'-bipyridyl)<sup>2)</sup>を混合し、100  $^{\circ}\text{C}$ に加熱して粉末 X 線回折測定を行ったところ、明確な **1** の構造変形 (closed 構造 **1-cp** から open 構造 **1-op**) が観測された (Fig. 1a)。一般にこの構造変形は MOF 細孔へのゲスト分子の包接に対応するため<sup>2)</sup>、本現象は超長鎖 **PEO4M** の包接を示唆している。さらに、MOF の構造変形と同時に **1** と PEO の相互作用に由来する発熱が観測されたことから (Fig. 1a)、**PEO4M** の挿入が自発的に起こることが裏付けられた。詳細な検討から、得られた複合体では高分子鎖が MOF 粒子を貫通し、複数の粒子にまたがって挿入された特殊な構造をとっていることが示唆された (Fig.1b)。

1) T. Uemura *et al.*, *Nat. Commun.* **2010**, *1*, 83. 2) Y. Sakata *et al.*, *Science*, **2013**, *339*, 193.



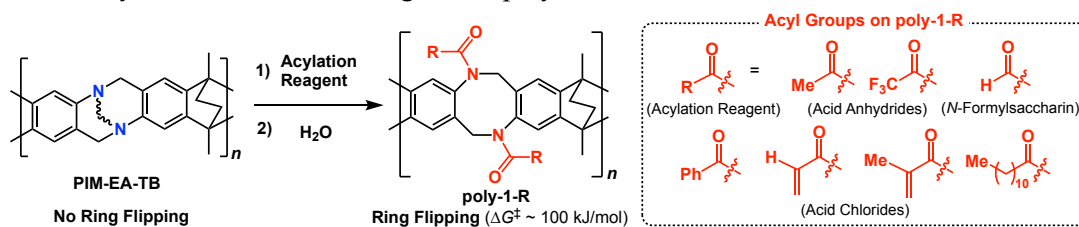
**Fig. 1.** (a) Time evolution plot of the fraction of **1-op** in contact with **PEO4M** at 100  $^{\circ}\text{C}$  (circles) and DSC heating curve (solid line). (b) A schematic image of the insertion of ultra-long polymers into MOF.

## Synthesis, Properties, and Conformational Dynamics of Ladder Polymers Containing *N,N'*-Diacylated Diazacyclooctane Units in their Main Chains

(<sup>1</sup>*School of Materials and Chemical Technology, Tokyo Tech*, <sup>2</sup>*Chemistry and Life Science, Tokyo Tech*, <sup>3</sup>*Graduate School of Engineering, Osaka University*) ○ Keiki Inoue,<sup>1,2</sup> Fumitaka Ishiwari,<sup>3</sup> Takanori Fukushima<sup>1,2</sup>

**Keywords:** Ladder polymer; Post-polymerization modification; Diazacyclooctane; Porous material; Conformational dynamics

Ladder polymers are an interesting class of polymers having two or more than two bonds in their main chains and potentially exhibit superb properties, such as microporosity<sup>1</sup>, over conventional non-ladder-type polymers. Although every previously reported ladder polymer consists of a rigid main chain, we recently reported the synthesis of conformationally flexible *N,N'*-dialkylated diazacyclooctane (DACO)-containing ladder polymers<sup>2-4</sup> by multi-step sequential post-polymerization reactions of a Tröger's base (TB)-containing ladder polymer (PIM-EA-TB). In this work, we report a facile one-pot synthesis of *N,N'*-diacylated DACO-containing ladder polymers (poly-1-R) from PIM-EA-TB and their properties including the conformational dynamics and microporosity in the solid state. The reactions between PIM-EA-TB and acylation reagents, such as acid anhydrides, acid halides, and *N*-formylsaccharin, followed by addition of H<sub>2</sub>O, successfully afforded *N,N'*-diacylated DACO-containing ladder polymers (poly-1-R) in quantitative conversions. The DFT calculations of the corresponding DACO monomer unit and the analysis of <sup>1</sup>H NMR spectra of the model compounds and polymers revealed that the *N,N'*-diacylated DACO ring undergoes ring flipping with an activation energy of ca. 100 kJ/mol in solution. Interestingly, despite their conformational flexibility, N<sub>2</sub> gas adsorption measurements at 77 K of the polymers showed that most of the *N,N'*-diacylated DACO-containing ladder polymers have microporosity in the solid state except for the polymers with phenyl groups or undecyl groups. In the presentation, we will detail the synthesis, properties, conformational dynamics, and gas adsorption properties of the *N,N'*-diacylated DACO-containing ladder polymers.



1) N. B. McKeown, *et al.*, *Science* **2013**, 339, 303. 2) F. Ishiwari, N. Takeuchi, T. Sato, H. Yamazaki, R. Osuga, J. N. Kondo, T. Fukushima, *ACS Macro Lett.* **2017**, 6, 775. 3) K. Inoue, R. Selyanchyn, S. Fujikawa, F. Ishiwari, T. Fukushima, *ChemNanoMat* **2021**, 7, 824. 4) K. Inoue, F. Ishiwari, T. Fukushima, *Polym. Chem.* **2020**, 11, 3690.

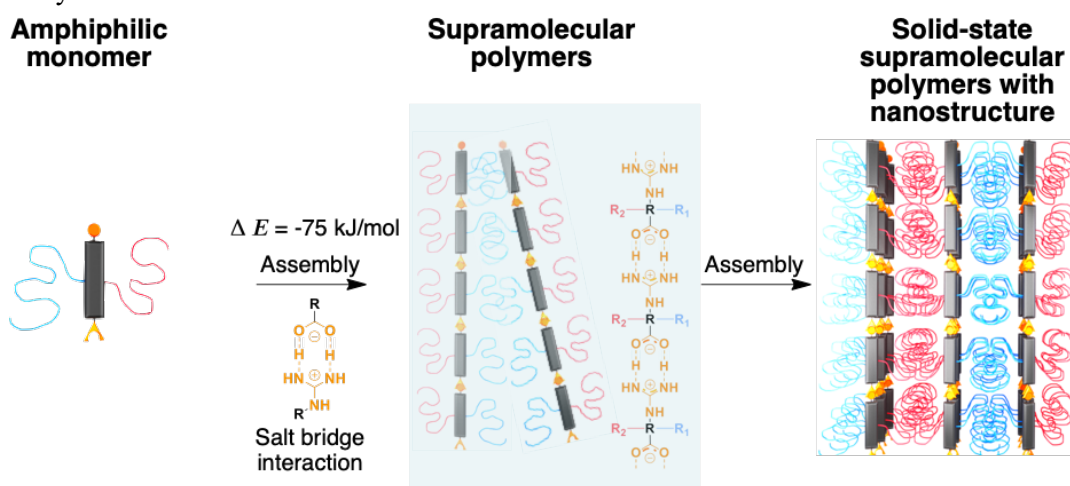
## Solid-State Supramolecular Polymers with Ordered Nanostructure

○Zebin Su,<sup>1</sup> Hubiao Huang,<sup>1</sup> Takuzo Aida<sup>1,2</sup> (<sup>1</sup>*RIKEN Center for Emergent Matter Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.* <sup>2</sup>*Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*)

Tel: +81-70-8430-3966, E-mail: zebin.su@riken.jp

**Keywords:** Supramolecular Polymer, Ordered Nanostructure, Self-Assembly, Microphase Separation

Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solutions.<sup>1</sup> Through the years, the research field of supramolecular polymers and their materials have grown to a new discipline in polymer science especially since novel functionalities were incorporated into these supramolecular polymers.<sup>2,3</sup> However, the solid-state behaviors of supramolecular polymers have been rarely explored. Here, I designed and synthesized a library of novel molecules (or monomers), which are attached with thermodynamically incompatible side chains. These monomers polymerized into supramolecular polymers via noncovalent salt-bridge interaction. These supramolecular polymers further self-assemble into various ordered nanostructures by microphase separation due to the thermodynamically incompatible side chains. The ordered nanostructures are unambiguously characterized by SAXS in reciprocal space and TEM in real space. This project makes significant progress in understanding the behaviors of solid-state supramolecular polymers, which shall be a crucial step toward using them as next-generation environmentally friendly materials.



### References

- [1]. T. Aida, *Isr. J. Chem.* **2020**, 60, 33-47.
- [2]. J. Kang, *Science* **2015**, 347, 646-651.
- [3]. P. K. Hashim, *Prog. Polym. Sci.* **2020**, 105, 101250.

## 時間分解超小角 X 線散乱による高分子ベシクルの形成過程のその場観察<sup>1)</sup>

(名大院工<sup>1</sup>・ESRF<sup>2</sup>・阪大院理<sup>3</sup>・兵庫県立大院工)

○高橋 倫太郎<sup>1</sup>・Theyencheri NARAYANAN<sup>2</sup>・遊佐 真一<sup>4</sup>・佐藤 尚弘<sup>3</sup>

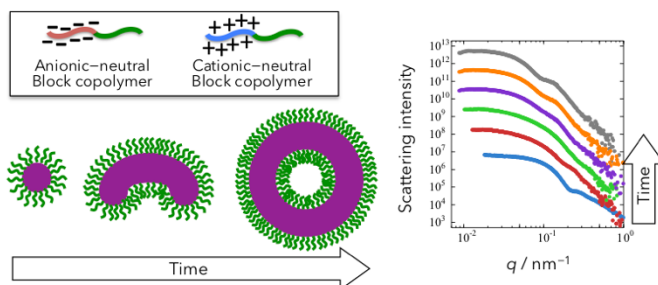
*In situ* observation of polymeric vesicle formation by time-resolved ultra small-angle X-ray scattering (<sup>1</sup>Graduate School of Engineering, Nagoya University, <sup>2</sup>ESRF, <sup>3</sup>Graduate School of Science, Osaka University, <sup>4</sup>Graduate School of Engineering, University of Hyogo) ○Rintaro Takahashi,<sup>1</sup> Theyencheri Narayanan,<sup>2</sup> Shin-ichi Yusa,<sup>4</sup> Takahiro Sato<sup>3</sup>

Polymer vesicles have grabbed considerable attention over the last several decades, but little has been known about the kinetics of the formation process, in spite of their importance both scientifically and in practical applications. Here, we report the self-assembly kinetics of polymer vesicles in aqueous NaCl solutions of anionic-neutral and cationic-neutral block copolymers when they transform from micelles. The vesicle formation from spherical or cylindrical micelles was initiated by fast mixing with a stopped-flow device, followed by employing time-resolved ultra-small-angle X-ray scattering with millisecond resolution. This technique enabled monitoring the kinetic process of the vesicle formation. This is the first study on the self-assembly kinetics of polymer vesicles using time-resolved small-angle scattering.

**Keywords :** Polymer vesicle; Time-resolved ultra-small-angle X-ray scattering; Self-assembly kinetics; Stopped-flow device

高分子ベシクルは多くの関心を集めている。しかしながら、その形成過程の動力学に関する実験の報告例はほとんどない。その要因は、単に水に高分子を溶解させただけで高分子ベシクルを形成する系が限られているため、また、形成過程が速すぎて直接的な手法で観測することが困難であるためだと思われる。高分子ベシクルの形成過程の動力学は、形成されるベシクルのサイズや、薬剤を内包させる場合の内包率と密接に関わることから応用上も重要な課題である。本研究では、カチオン性ブロック鎖と電気的中性ブロック鎖から成るブロック共重合体と、カチオン性ブロック鎖と電気的中性ブロック鎖から成るブロック共重合の塩化ナトリウム水溶液中におけるベシクルを対象とする。これらの高分子は、水溶液中で自発的にベシクルを形成することが知られている。この高分子溶液系において、ストップフロー装置を用いてミセルからベシクルへの形態転移を誘起させ、その直後から時間分解超小角 X 線散乱測定を行い、ベシクルの形成過程を観察した。その結果、ミセルがディスク状に成長し、その後ディスク状ミセルが湾曲してベシクルを形成することがわかった (Figure 1)。

1) R. Takahashi, T. Narayanan, S. Yusa, T. Sato, *Macromolecules* in press.



**Figure 1.** Illustrations of block copolymers and the formation process of the polymer vesicles (left). Time-evolution of the scattering profile during the vesicle formation (right).

## Thermal degradation of a poly (ethylene-co-methacrylic acid) ionomer investigated by solid-state $^{13}\text{C}$ NMR and ESR

(Department of Applied Chemistry, National Defense Academy of Japan) ○Shohei Mikage, Atsushi Asano

**Keywords:** poly (ethylene-co-methacrylic acid); thermal degradation; ESR; solid-state  $^{13}\text{C}$  NMR

Poly (ethylene-co-methacrylic acid) (EMAA) ionomers, which carboxy groups are neutralized with  $\text{Na}^+$  cations, are well known to show the excellent physical and chemical properties, such as strong toughness and good fabricability.<sup>1</sup> EMAA ionomers have been used as engineering and commercial materials for a long time and their structure and dynamics have been investigated by NMR and ESR measurements.<sup>2,3</sup> It is also very important and interesting how the thermal degradation is affected by the existence of the ionic clusters. In this study, we examined EMAA and EMAA ionomers (EMAA-30Na and -54Na: the number represents the degree of neutralization) heat-treated at  $200^\circ\text{C}$  to reveal the structural change occurring during the thermal degradation using the solid-state  $^{13}\text{C}$  NMR and ESR.

The radicals created after heat treatment were measured as a spin quantity with heating period by ESR (Fig. 1). It is obvious that the amount of radicals increases in two stages, and the quantity for EMAA-54Na became about twice and seven folds as compared to that for EMAA-30Na and for EMAA, respectively at 3000 min. However, the newly observed NMR peaks, which are attributed to the cross-linking structures produced with the radical residues, were much intense for EMAA rather than those for EMAA ionomers. The main product was a  $\sim\text{CH}_2\text{-COO-CH}_2\sim$  bond created from  $\text{-COOH}$  and  $\cdot\text{OCH}_2\text{-}$  functional groups which are resonated around 175 ppm (Fig. 2). The other reaction processes during thermal degradation will be discussed in detail.

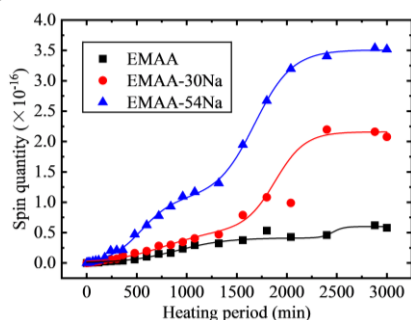


Fig. 1 Spin quantity vs. heating period.

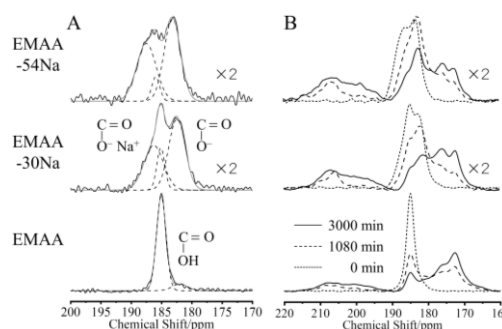


Fig. 2 Expanded  $^{13}\text{C}$  CPMAS NMR spectra for C=O region; (A) before and (B) after heat treatment.

- 1) S. Yano, E. Hirasawa, Development of ionomer and ion containing polymer, CMC publishing, 2009.
- 2) H. Yoshimizu, Y. Tsujita, *Ann. Rep. NMR Spect.*, **2001**, 44, 1-22.
- 3) Y. Miwa, T. Kondo, S. Kutsumizu, *Macromolecules*, **2013**, 46, 5232-5237.



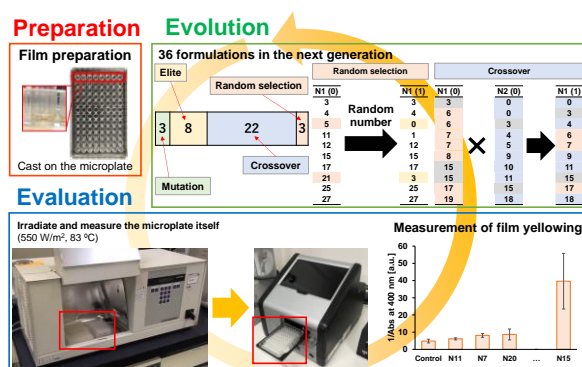
## Design of Stabilizer Formulations for Yellowing Inhibition of Polymeric Materials based on High-Throughput Experiments and Genetic Algorithm

(<sup>1</sup>Graduate School of Japan Advanced Institute of Science and Technology) ○Ken Takimoto,<sup>1</sup> Toshiaki Taniike<sup>1</sup>

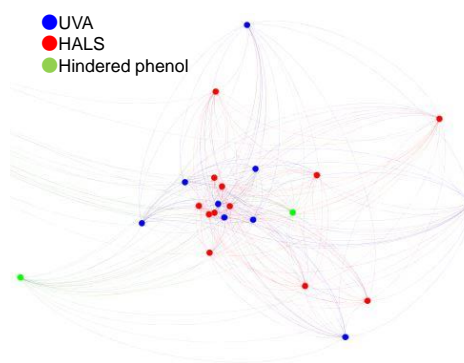
**Keywords:** Photo degradation; Synergism; Microplate method; Genetic algorithm; Combinatorial rules

Transparent plastics are used as alternatives to inorganic glass due to their advantages of transparency, processability, light weight, and low cost. On the other hand, their weaknesses are low scratch resistance and heat resistance, as well as their susceptibility to yellowing. In particular, yellowing due to outdoor exposure directly damages the high transparency, so its inhibition for a long term is highly desired. This problem is exclusively addressed by the addition of stabilizers. Although the basic strategy is to add a larger amount of stabilizers it with higher efficacy, there are limitations to increase the amount of the addition, so the development of synergistic formulations is essential.<sup>1</sup>

In this study, we developed a high-throughput experimental protocol, in order to efficiently explore stabilizer formulations regarding yellowing inhibition. By combining with a genetic algorithm, we conducted non-empirical exploration of stabilizer formulations that can inhibit yellowing of atactic polystyrene without increasing the addition amount. Cast films containing different formulations are prepared on 96 well-microplates, and the microplates were directly subjected to photo irradiation, which enabled simultaneous photo aging of 288 samples (3 microplates). Then, the yellowing of films was rapidly determined by subjecting the microplates after the irradiation to a microplate reader. Furthermore, the obtained big data corresponding to the 7 years of photo aging was analyzed in order to understand common features of high-performing formulations as well as rules of making synergistic combinations.



Stabilizer formulations exploration



Visualization of binary interactions

1) T. Taniike, T. Kitamura, K. Nakayama, K. Takimoto, N. Aratani, T. Wada, A. Thakur, P. Chammingkwan, *ACS Appl. Polym. Mater.*, **2020**, 2, 8, 3319–3326.

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Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B**[C205-2pm] 20. Materials Chemistry -Basic and Application-**

Chair: Ryota Sato, Kazuki Yamamoto

Thu. Mar 24, 2022 1:40 PM - 3:40 PM C205 (Online Meeting)

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**[C205-2pm-01] Synthesis and Properties of Diethoxysiloxane Derivatives**○Yohei Sato<sup>1</sup>, Ryohei Hayami<sup>2</sup>, Kazuki Yamamoto<sup>1</sup>, Takahiro Gunji<sup>1</sup> (1. Tokyo University of Science, 2. Zoom LLC)

1:40 PM - 2:00 PM

**[C205-2pm-02] Synthesis and Properties of Polysiloxanes from Monomers Consisting of Different Silicon Units**○Kazuki Yamamoto<sup>1</sup>, Tomoya Shimoda<sup>1</sup>, Takahiro Gunji<sup>1</sup> (1. Tokyo University of Science)

2:00 PM - 2:20 PM

**[C205-2pm-03] The substitution pattern effect on thermal, liquid-physical and optical properties of alkylated distyrylbenzene liquids.**○Xiao Zheng<sup>1,2</sup>, Kazuhiko Nagura<sup>2</sup>, Takashi Nakanishi<sup>1,2</sup> (1. Division of Soft Matter, Graduate School of Life Science, Hokkaido University, 2. International Center for Materials Nanoarchitectonics, National Institute for Materials Science)

2:20 PM - 2:40 PM

**[C205-2pm-04] Diffusion process of Fe immiscible with In into Pd-In alloy nanoparticles**○Kenshi Matsumoto<sup>1</sup>, Ryo Takahata<sup>1</sup>, Ryota Sato<sup>1</sup>, Toshiharu Teranishi<sup>1</sup> (1. Kyoto University)

2:40 PM - 3:00 PM

**[C205-2pm-05] Unusual cationic coordination network based on boron-bridged structure**○Takeshi Kato<sup>1</sup>, Masataka Ohtani<sup>1</sup> (1. Kochi University of Technology)

3:00 PM - 3:20 PM

**[C205-2pm-06] Site-selective formation of coordination polymer consisting of Cu-thiolate ligands using metal ion-doped polymer substrate**○Takaaki Tsuruoka<sup>1</sup>, Yuri Miyashita<sup>1</sup>, Ryuki Yoshino<sup>1</sup>, Myu Fukuoka<sup>1</sup>, Yohei Takashima<sup>1</sup>, Kensuke Akamatsu<sup>1</sup> (1. Konan University)

3:20 PM - 3:40 PM



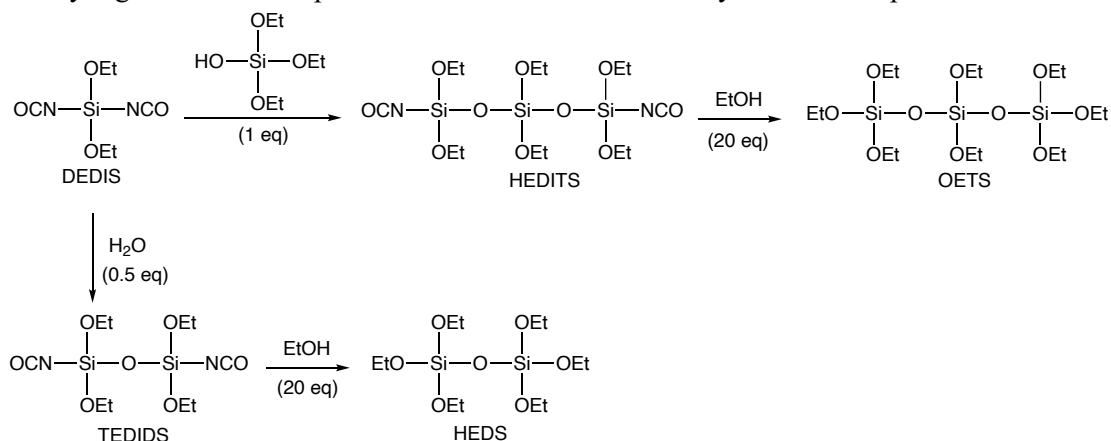
## Synthesis and Properties of Diethoxysiloxane Derivatives

(<sup>1</sup>Tokyo University of Science, <sup>2</sup>Zoome LLC) ○ Yohei Sato,<sup>1</sup> Ryohei Hayami,<sup>2</sup> Kazuki Yamamoto,<sup>1</sup> Takahiro Gunji<sup>1</sup>

**Keywords:** Polysiloxane, Alkoxysilane, Sol-gel reaction, Oligosiloxane, Silicone

Sol-gel reaction of alkoxysilane is widely used for the synthesis of polysiloxane materials such as silica and silicones. In particular, acid catalyzed sol-gel reaction of alkoxysilane has been expected to form linear alkoxypolysiloxanes. The initial products of sol-gel reaction also have been estimated to generate linear ethoxypolysiloxanes from gas chromatograph/ mass spectrometry. From that point of view, knowledge of linear ethoxypolysiloxanes is considered to be important. However, there have been few reports on the isolation and identification of linear ethoxysiloxanes. In this study, we will report the synthesis and properties of diethoxysiloxane derivatives.

The reactivity of the sila-functional silanes is reported to be in the order  $\text{OEt} < \text{NCO} < \text{Cl}$ . Isocyanatosilane is attracting attention as a precursor for a selective synthesis of oligosiloxane. Ethoxy(isocyanato)silanes as a starting compound were selected to have difference of reactivity between functional groups. Diethoxy(diisocyanato)silane (DEDIS) was synthesized according to the previous literature<sup>1</sup>. Tetraethoxy(diisocyanato)disiloxane (TEDIDS) was obtained in 32 % yield by the hydrolysis of DEDIS. Hexaethoxy(diisocyanato)trisiloxane (HEDITS) was obtained in 44 % yield by the condensation between DEDIS and triethoxysilanol. Hexaethoxydisiloxane (HEDS) and octaethoxytrisiloxane (OETS) were obtained in 12 % and 42 % yield, respectively, by ethanolation of TEDIDS and HEDITS. Mass spectroscopic studies of the hydrolysis products of linear ethoxypolysiloxanes was performed to estimate the reactivity of these compounds.



1) Y. Abe, K. Motoyama, T. Kobayashi, T. Iwasaki, T. Gunji, *Nippon Kagaku Kaishi*, 969-974 (1996).

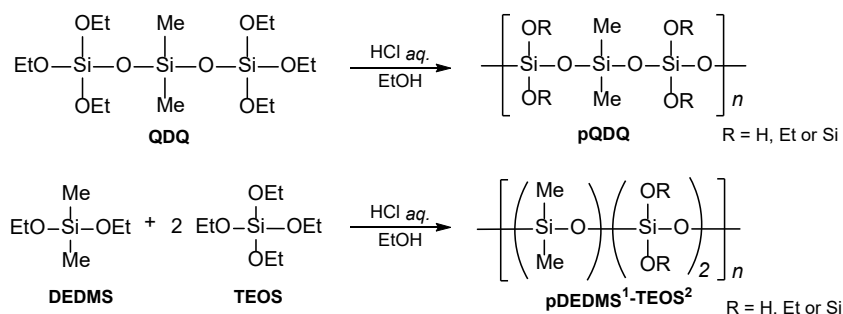
## Synthesis and Properties of Polysiloxanes from Monomers Consisting of Different Silicon Units

(<sup>1</sup>Faculty of Science and Technology, Tokyo University of Science) ○Kazuki Yamamoto,<sup>1</sup> Tomoya Shimoda,<sup>1</sup> Takahiro Gunji,<sup>1</sup>

**Keywords:** Polysiloxanes, Sol-Gel process, Inorganic polymers, Films

Polysiloxanes have attracted much attention because of their unique properties such as transparency, thermal stability, and mechanical strength. Although material properties of polysiloxanes can be changed by the unit structure of silicon atoms with the chemical structural formulae of  $[R_{(4-n)}SiO_{0.5}]_n$  M ( $n=1$ ), D ( $n=2$ ), T ( $n=3$ ), and Q ( $n=4$ )<sup>1)</sup>, there are few reports on the synthesis of oligomers consisting of multiple components and their polymerization. In this study, we synthesized alkoxytrisiloxane monomers with QDQ and TDT structures, prepared polymer and gel films by sol-gel process, and measured them by GPC, NMR, IR, UV-Vis, TGA, and tensile strength test.

The polymers, pQDQ, pTDT, an equivalent of diethoxy(dimethyl)silane (DEDMS) and two equivalents of tetraethoxysilane (TEOS) polymer pDEDMS<sup>1</sup>-TEOS<sup>2</sup>, and an equivalent of DEDMS and two equivalents of tetraethoxysilane (TEOS) polymer pDEDMS<sup>1</sup>-TEOS<sup>2</sup>, were prepared respectively. The polymers with approximately  $M_w$  10,000 were obtained. Transparent gel films were obtained from pQDQ, pDEDMS<sup>1</sup>-TEOS<sup>2</sup>, and pTDT, although pDEDMS<sup>1</sup>-MTES<sup>2</sup> could not be obtained because pDEDMS<sup>1</sup>-MTES<sup>2</sup> could not solidify. The gel films between pQDQ and pDEDMS<sup>1</sup>-TEOS<sup>2</sup> showed similar structure and properties except for tensile strength; pQDQ film showed higher young's modulus and breaking stress than those of pDEDMS<sup>1</sup>-TEOS<sup>2</sup> film, which suggesting that arrangement of Q and D units affect mechanical strength of the gel films. pTDT had weaker mechanical strength than that of pQDQ, which is due to the lower cross-linking point of the ethoxy group in pTDT.



1) R. Hayami, I. Nishikawa, T. Hisa, H. Nakashima, Y. Sato, Y. Ideno, T. Sagawa, S. Tsukada, K. Yamamoto, T. Gunji *J. Sol-Gel Sci. Technol.* **2018**, 88, 660–670.

## Alkylated distyrylbenzene as a model to clarify substitution pattern effect on liquid properties

(<sup>1</sup>Graduate School of Life Science, Hokkaido University, <sup>2</sup>International Center for Materials Nanoarchitectonics, National Institute for Materials Science) ○Xiao Zheng,<sup>1,2</sup> Kazuhiko Nagura,<sup>2</sup> Takashi Nakanishi<sup>1,2</sup>

**Keywords:** Functional molecular liquids; Viscosity; Distyrylbenzene; Substitution pattern

Alkyl- $\pi$  functional molecular liquids (FMLs) constructed by attaching bulky yet flexible alkyl chains to the functional  $\pi$ -conjugated core unit are a new kind of soft matter.<sup>1</sup> Richer optoelectronic properties from larger  $\pi$ -conjugated moiety is in trade-off relationship with lower viscosity of alky- $\pi$  FMLs. For instance, liquid porphyrins possessing electret properties exhibit relatively high viscosity in the range of 15.7-75.1 Pa·s, which might cause limitations when fabricating into devices.<sup>2</sup> Therefore, establishment of rational molecular design strategy for predictable creation of alkyl- $\pi$  FMLs with richer optoelectronic property as well as lower viscosity is particularly essential.

In order to clarify the relationship between the molecular structure of alkyl- $\pi$  FMLs and its thermal, optical and liquid-physical properties, we have investigated substitution pattern effect on distyrylbenzene (DSB) model system. That is attaching 2-octyldodecyl ( $C_8C_{12}$ ) chains at 3,5-, 2,4-, 2,5- and 2,6-substituted position of the both terminal phenyl units, and another is various length of alkyl chains including 2-hexyldecyl ( $C_6C_{10}$ ), 2-decyltetradecyl ( $C_{10}C_{14}$ ), 2-dodecylhexadecyl ( $C_{12}C_{16}$ ) at 2,5-substituted positions. A 2,5-substituted derivative with  $C_{10}C_{14}$  chains exhibits the lowest viscosity as kinetically-stable liquid. Moreover, we have confirmed the applicability of 2,5- $C_{10}C_{14}$  substitution pattern on dicyanostyrylbenzene (DCS). Although a bare DCS moiety aggregates easily, 2,5- $C_{10}C_{14}$ -DCS shows comparable low viscosity as 2,5- $C_{10}C_{14}$ -DSB and retaining its intrinsic optical property. In this presentation, the liquid properties of alkylated DSB and DCS derivatives will be discussed further.

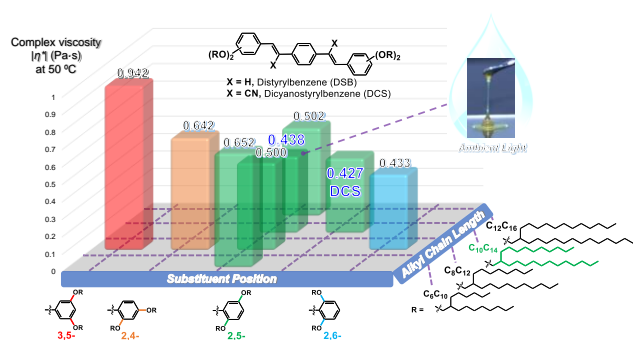


Figure 1. Complex viscosity  $|\eta^*|$  of alkylated DSB and DCS derivatives at 50 °C.

- 1) T. Nakanishi, ed., Functional Organic Liquids. **2019**, Wiley-VCH Verlag GmbH & Co. KGaA. 2)
- A. Ghosh, et al, *Nat. Commun.*, **2019**, 10, 1042.

## In と固溶できない Fe の Pd-In 合金ナノ粒子内への拡散過程

(京大化研<sup>1</sup>) ○松本 憲志<sup>1</sup>・高畑 遼<sup>1</sup>・佐藤 良太<sup>1</sup>・寺西 利治<sup>1</sup>

Diffusion process of Fe immiscible with In into Pd-In alloy nanoparticles (<sup>1</sup>*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.*) ○Kenshi Matsumoto<sup>1</sup>, Ryo Takahata<sup>1</sup>, Ryota Sato<sup>1</sup>, Toshiharu Teranishi<sup>1</sup>

It has been recently reported that the inter-element miscibility or affinity is one of crucial factors for building a framework in a ternary alloy<sup>[1, 2]</sup>. As one example<sup>[2]</sup>, we experimentally showed the first example of Z3-type Fe(Pd,In)<sub>3</sub> alloy nanoparticles composed of L1<sub>0</sub>-type PdFePd trilayer and Pd-In alloy monolayer, where first-principles calculations strongly supported that the inter-element miscibility of In, which was miscible with Pd but immiscible with Fe, worked as the stabilizer of Z3-type structure. However, there is the possibility that the diffusion of Fe into Pd-In alloy might form Fe-Pd-In solid-solution alloy until forming Z3-type structure regardless of the inter-element miscibility. Then, we investigated the atomic diffusion process from Pd-In@FeO<sub>x</sub> core@shell to Z3-type Fe(Pd,In)<sub>3</sub> nanoparticles, which showed that the immiscibility of In with Fe was reflected during the diffusion process.

**Keywords :** Inter-Element Miscibility, Atomic Diffusion, Pseudo Binary Alloy, Nanoparticles, Z3-type Fe(Pd,In)<sub>3</sub> phase

二元系相図上の元素間の固溶可能・不可能といった特徴（以下、元素間固溶性）や元素間の親和性が三元合金の骨格を決める重要な因子になることが最近分かってきた<sup>[1, 2]</sup>。その一例として、我々は In の元素間固溶性（Pd と固溶でき、Fe と固溶できない）を駆動力として、すべての合金相を含めても初となる Z3 型構造（L1<sub>0</sub>-FePd 1 層と Pd-In 合金 1 層の積層構造）の安定化に成功した<sup>[2]</sup>。ところが、還元熱処理下での Pd-In@FeO<sub>x</sub> から Z3 型構造に至る過程、つまり非平衡過程においても Fe-In 間の元素間固溶性を反映した相が形成されるかは自明ではない。そこで、本研究では Z3 型構造に至る拡散経路について調査した。

Pd-In@FeO<sub>x</sub> コア@シェルナノ粒子に対して種々の熱処理条件で還元拡散を行い、粉末 XRD 測定、HADDF-STEM 像観察、および EDX 元素マッピングにより相同定を行った。昇温過程で 500 °C に到達すると FeO<sub>x</sub> が Fe に還元され、500 °C で 3 時間維持すると Pd-In@Z3-Fe(Pd,In)<sub>3</sub>@L1<sub>0</sub>-FePd ナノ粒子が形成され、さらに 800 °C まで昇温することで Z3-Fe(Pd,In)<sub>3</sub> 相が単相で得られた。以上より、Pd-In 合金内への Fe 原子

拡散では Fe-Pd-In 三元合金は逐次的に形成されず、一度 Fe-Pd/Pd-In 相分離構造を経由し、その界面から Z3 型構造が形成されることが明らかとなった（図 1）。

[1] S. Goto *et al.*, *Sci. Rep.* **2017**, 7, 13216. [2] K. Matsumoto *et al.*, accepted.

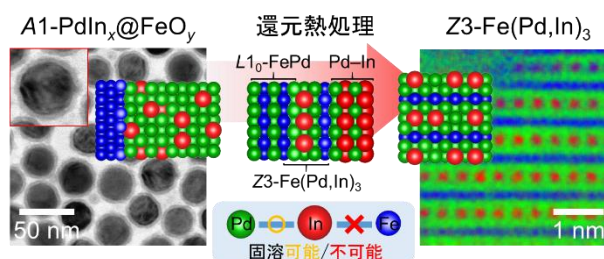


図1. 拡散前後のTEM像とEDXマップ図、およびその拡散過程

## ホウ素架橋構造が示す特異なカチオン性配位空間

(高知工大院<sup>1</sup>・高知工大<sup>2</sup>) ○加藤 健史<sup>1</sup>・大谷 政孝<sup>2</sup>

Unusual cationic coordination network based on boron-bridged structure

(Kochi University of Technology) ○Takeshi Kato, Masataka Ohtani

A metal-organic framework composed of imidazolate ligands with a boron-bridged structure (BIF) has attracted attention as a new porous crystal. While having a coordination space structure like that of the conventional metal-organic framework, they have been reported to exhibit unique gas adsorption properties, especially a high adsorption capacity for CO<sub>2</sub>. However, there are unclear points about the properties of porous coordination networks due to the boron-bridged structure. In this study, we conduct systematic studies about structure and properties of BIF crystals obtained by various experimental conditions.

As a result of screening various experimental conditions, we successfully synthesized copper-BIF crystals by heating and room-temperature synthesis (Fig. 1a). According to the gas adsorption measurements, the N<sub>2</sub> adsorption capacity of the obtained BIF crystals was significantly different (Fig. 1b). Considering the results of various spectroscopic analyses, we demonstrate that the porous coordination space exhibits a cationic network to encapsulate counter anions due to the valence state of the metal center in BIF crystals, resulting in the enhancement of gas adsorption properties.

**Keywords :** Metal-organic framework, Gas adsorption, Boron-bridged structure

ホウ素架橋構造によって連結されたイミダゾレートからなる金属有機構造体(BIF)は、新たな多孔性結晶として注目されている。特に、従来の金属有機構造体と類似した配位空間構造を有する一方で、異なるガス吸着特性を示し、特にCO<sub>2</sub>に対して高い吸着能を示すことが報告されている。しかしながら、ホウ素架橋構造が配位空間の性質に与える影響は未解明な点が多い。本研究では、様々な条件で得られるBIF結晶の構造と性質を詳細に調べた。

様々な合成条件検討の結果、加熱合成と室温合成によってBIF結晶の合成に成功した(Fig. 1a)。また、得られたBIF結晶のN<sub>2</sub>吸着能に大きな違いが見られた(Fig. 2b)。種々の分析により、BIF結晶中に含まれる金属イオンの価数によって、配位空間はカウンターアニオンを取り込むカチオン性ネットワークとなり、ガス吸着特性が変化することを示唆した。

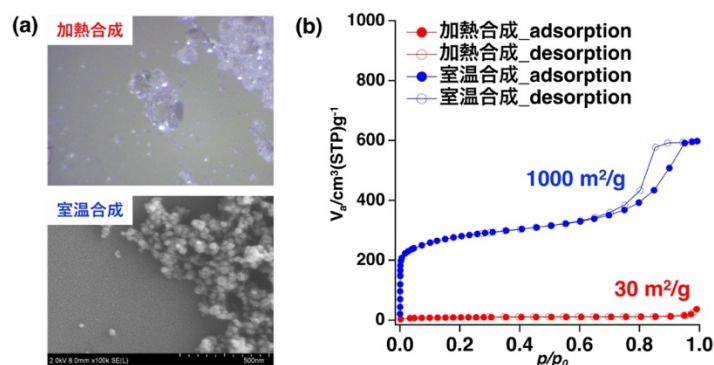


Figure 1. (a) Optical microscope image (upper), SEM image (lower), and (b) N<sub>2</sub> adsorption-desorption isotherms of copper-BIF crystals obtained by heating and room-temperature synthesis.

## Site-Selective Formation of Coordination Polymer consisting of Cu-Thiolate Ligands using Metal Ion-Doped Polymer Substrate

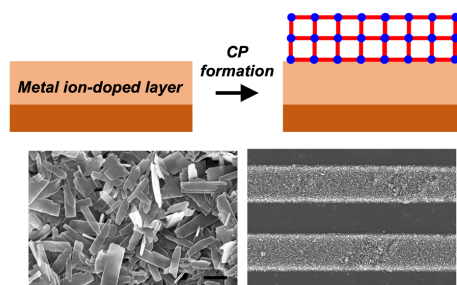
(*Frontiers of Innovative Research in Science and Technology (FIRST)*, Konan University)

○Takaaki Tsuruoka, Yuri Miyashita, Ryuki Yoshino, Myu Fukuoka, Yohei Takashima, Kensuke Akamatsu

**Keywords:** Coordination Polymer; Thin Film; Patterning

A variety of flexible, lightweight, and portable solid-state optoelectronic devices consisting of coordination polymers (CPs) have been proposed owing to the ease of synthesis of CPs with high crystallinity as well as their unique photoluminescence properties. However, the significant challenges in CP-based thin films should be addressed to realize CP optoelectronics by device integration. The poor processability of CPs considerably limits their applicability, as CP materials exhibit intrinsic instability against a range of process parameters to form the desired shapes and patterns. Therefore, facile synthetic approaches to fabricate thin films of CPs on flexible substrates are in significant demand, such as the in situ one-pot synthesis of CPs on substrates under mild reaction conditions.<sup>1</sup>

Herein, we demonstrate an interfacial synthetic approach for fabricating CPs comprising  $d^{10}$  coinage metals and thiolates on polymer substrates.<sup>2</sup> In this study, we selected a  $[\text{Cu}(p\text{-SPhCOOH})]_n$ ,  $[\text{Ag}(p\text{-SPhCOOH})]_n$  and mixed-metal  $[\text{Cu}_x\text{Ag}_{1-x}(p\text{-SPhCOOH})]_n$  CPs. We employed the polyimide substrate bearing cation-exchangeable group by hydrolyzing alkali solutions for precursors and template for CP-based films. The metal ion-doped polymer substrate led to the selective formation of CPs on the surface and the construction of mixed-metal CPs. In addition, a pattern of polymethyl methacrylate (PMMA) photoresist on a metal ion-doped polymer substrate was fabricated in a positive-type with vacuum ultraviolet (VUV) light illumination, enabling the formation of CP thin films with the desired patterns.



**Figure.** Schematic illustration of the developed interfacial approach for formation of CPs on a substrate. SEM images of the obtained sample (scale bar: 1  $\mu\text{m}$ ).

1) T. Tsuruoka et al., *Cryst. Growth Des.* **2020**, *20*, 1961. 2) T. Tsuruoka, et al., *submitted*

## [D103-2pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Tatsuya Kameyama, Kazuhide Kamiya

Thu. Mar 24, 2022 1:00 PM - 3:40 PM D103 (Online Meeting)

### [D103-2pm-01] Carbon nanotube-based novel non-precious metal electrode catalyst with high performance

○Naotoshi Nakashima<sup>1</sup>, Ganesan Pandian<sup>1</sup>, Chearin Kim<sup>1</sup>, Jin Nishida<sup>1</sup>, Hiroki Shu<sup>2</sup>, Mitsugu Uejima<sup>2</sup>, Aleksandar Staykov<sup>1</sup> (1. Kyushu University, 2. Zeon Co.)

1:00 PM - 1:20 PM

### [D103-2pm-02] Synthesis of double-layer platinum nanosheets and electrocatalytic reaction

○Daisuke Takimoto<sup>1</sup>, Shino Toma<sup>1</sup>, Yuya Suda<sup>2</sup>, Masashi Matsumoto<sup>3</sup>, Hideto Imai<sup>3</sup>, Wataru Sugimoto<sup>2</sup> (1. University of the Ryukyus, 2. Shinshu University, 3. NISSAN ARC LTD.)

1:20 PM - 1:40 PM

### [D103-2pm-03] Bimetal oxide nanoparticles embedded in rGO as catalyst for rechargeable Zn-air batteries

○Mai Thanh Nguyen<sup>1</sup>, Wei Jian Sim<sup>1</sup>, Zixuan Huang<sup>1</sup>, Masayuki Takahashi<sup>1</sup>, Tetsu Yonezawa<sup>1</sup> (1. Hokkaido University)

1:40 PM - 2:00 PM

### [D103-2pm-04] Catalytic synergies in multimetallic nano and subnanoparticles for hydrogen evolution reaction (HER)

○Quan ZOU<sup>1</sup>, Yuji Akada<sup>1</sup>, Akiyoshi Kuzume<sup>2,3</sup>, Takane Imaoka<sup>1,2</sup>, Kimihisa Yamamoto<sup>1,2</sup> (1. Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, 2. JST-ERATO, 3. University of Yamanashi )

2:00 PM - 2:20 PM

### [D103-2pm-05] Co-sintering Process of LiCoO<sub>2</sub> Cathodes and NASICON-type LATP Solid Electrolytes Studied by X-ray Absorption Fine Structure and X-ray Diffraction

○Fumihiko Ichihara<sup>1</sup>, Shogo Miyoshi<sup>1</sup>, Takuya Masuda<sup>1</sup> (1. National Institute for Materials Science )

2:20 PM - 2:40 PM

### [D103-2pm-06] Feasibility Studies of Graphite as a Negative Electrode Material for Mg-Ion Batteries

○Masahiro SHIMIZU<sup>1</sup>, Susumu Arai<sup>1</sup> (1. Shinshu University)

2:40 PM - 3:00 PM

### [D103-2pm-07] Effect of thermal maturation on the evaluation indicator for source organic matter of crude oil using naphthalene composition

○Kenta Asahina<sup>1</sup>, Koji U. Takahashi<sup>1</sup>, Kazuya Morimoto<sup>1</sup>, Takeshi Nakajima<sup>1</sup>, Yuichiro Suzuki<sup>1</sup> (1. National Institute of Advanced Industrial Science and Technology)

3:00 PM - 3:20 PM

### [D103-2pm-08] Electricity generation by radiolysis of water in the presence of iron oxide particles

○ Momoko Shimaoka<sup>1</sup>, Sakyo Ueno<sup>1</sup>, Sana Itakura<sup>1</sup>, Sota Goto<sup>1</sup>, Shin-ichi Hashimoto<sup>1</sup>,  
Yusa Muroya<sup>2</sup>, Kaname Tsutsumiuchi<sup>1</sup> (1. Chubu Univ., 2. SANKEN, Osaka U.)

3:20 PM - 3:40 PM



## Carbon nanotube-based novel non-precious metal electrode catalyst with high performance

カーボンナノチューブを素材とした貴金属を使わない新しい高性能電池触媒デザイン

Pandian Ganesan,<sup>1</sup> Chaerin Kim,<sup>1</sup> Jin Nishida,<sup>1</sup> Aleksandar Staykov,<sup>1</sup> Hiroki Shu,<sup>2</sup>  
Mitsugu Uejima,<sup>2</sup> and Naotoshi Nakashima<sup>1</sup> (Kyushu Univ.,<sup>1</sup> Nihon Zeon Co.<sup>2</sup>)

**Keywords:** Carbon nanotubes; non-precious metal electrode; oxygen reduction reaction; oxygen evolution reaction; Zn-air electrode

The development of Pt-free metal electrocatalysts for fuel cells, water splitting and batteries with high performance, durability, and scalability is a strong social demand for the next-generation eco-friendly energy society[1]. Recently, we have already reported that i) nanocarbons/iron phthalocyanine (II) hybrids with well-defined nanostructures show excellent efficiency for oxygen reduction reaction (ORR)[2,3], ii) decorating unoxidized-carbon nanotubes with homogeneous Ni-Co-spinel nanocrystals that show superior performance for oxygen evolution (OER) and ORR[4] and iii) Fe<sup>III</sup>-doped nickel sulfides/carbon nanotube hybrid catalyst for alkaline electrolyte membrane water electrolyzer and enhanced Zn-air battery performance[5].

Here we report the design and synthesis of a less-expensive metal-coordinated poly(thiourea-formaldehyde) polymer/nanocarbon (Vulcan, porous carbon, 2-different multi-walled carbon nanotubes, or single-walled carbon nanotubes) hybrid catalysts. The catalysts were found to show high oxygen electrode performance with ORR:  $E_{1/2}$ : 0.81 V vs. RHE, and OER: 1.57 V vs. RHE at 10 mA/cm<sup>2</sup>. The catalyst also showed an efficient and durable cathode for a rechargeable Zn-air battery (charge-discharge overpotential gap of 0.45 V). Such a study is of importance in the development of advanced energy materials in batteries and molecular catalyst.

## References

- [1] N. Nakashima (Editor), "Nanocarbons for Energy Conversion-Supramolecular Approach-", Springer, **2018**, pp. 1-564.
- [2] J. Yang, J. Tao, T. Isomura, H. Yanagi, I. Moriguchi, N. Nakashima, *Carbon*, **2019**, *145*, 565-571.
- [3] J. Yang, F. Toshimitsu, T. Fujigaya, N. Nakashima, *J. Mater. Chem. A*, **2017**, *5*, 1184-1191
- [4] J. Yang, T. Fujigaya, N. Nakashima, *Sci. Rep.*, **2017**, *7*, art.no.45384.
- [5] P. Ganesan, A. Staykov, H. Shu, M. Uejima, N. Nakashima, *ACS Appl. Energy Mater.* **2020**, *3*, 10961-10975.

## 全原子が露出した Pt ナノシートの創製と電極触媒への応用

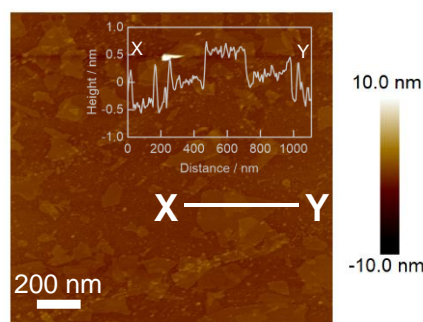
(琉大理<sup>1</sup>・信大繊維<sup>2</sup>・日産アーク<sup>3</sup>) ○滝本 大裕<sup>1</sup>・當間 志乃<sup>1</sup>・須田 祐矢<sup>2</sup>・松本 匡史<sup>3</sup>・今井 英人<sup>3</sup>・杉本 渉<sup>2</sup>

Synthesis of double-layer platinum nanosheets and electrocatalytic reaction (<sup>1</sup>*Faculty of Science, University of the Ryukyus*, <sup>2</sup>*Faculty of Textile Science and Technology, Shinshu University*, <sup>3</sup>*Device-functional analysis department, NISSAN ARC LTD.*) ○ Daisuke Takimoto<sup>1</sup>, Shino Toma<sup>1</sup>, Yuya Suda<sup>2</sup>, Masashi Matsumoto<sup>3</sup>, Hideto Imai<sup>3</sup>, Wataru Sugimoto<sup>2</sup>

Pt nanoparticles are widely used as a (electro)catalysts. However, the internal Pt atoms do not contribute to the (electro)catalytic reaction, low Pt efficiency. We have shown that the metal nanosheets possesses a high catalytic activity and durability against electrochemical reactions<sup>1-3</sup>. In this study, we report the synthesis of double-layer platinum nanosheets via exfoliation of layered platinum acid and its electrochemical properties. The electrochemically active surface area of Pt nanosheets was found to be 124 m<sup>2</sup> (g-Pt)<sup>-1</sup>, which is 1.6 times larger than that of the 3 nm Pt nanoparticles. The oxygen reduction reaction activity of the Pt nanosheets was also 1.5 times higher than that of the nanoparticles. These results indicate that the high activity of the Pt nanosheets is attributed to the large electrochemically active surface area. The durability of the Pt nanosheets was 3 times higher than that of the nanoparticles.

**Keywords :** Platinum; Nanosheets; Double layer; Oxygen Reduction Reaction

Pt ナノ粒子は広範に使用されている触媒であり、一般的な触媒形態である。しかし、内部 Pt 原子は触媒反応に寄与しない。我々は、金属ナノシートが種々の電気化学反応に対して高い触媒活性と安定性を有することを明らかにしてきた<sup>1-3</sup>。本研究では、層状白金酸の剥離により得られる白金酸ナノシートの合成、および白金酸ナノシートのトポタクティック反応により得られる二原子層厚の白金ナノシートの合成と電極触媒特性について報告する。得られた白金ナノシートの厚みは  $0.6 \pm 0.1$  nm であった(下図)。XAFS 測定より、白金ナノシートの平均配位数が  $10.6 \pm 0.4$  であったことから、二原子層厚(部分的に三原子層)で構成されていることがわかった。白金ナノシートの電気化学的活性表面積は  $124 \text{ m}^2 (\text{g-Pt})^{-1}$  であり、標準触媒の 3 nm Pt ナノ粒子より 1.6 倍大きいことがわかった。また、白金ナノシートの酸素還元反応活性も 1.5 倍大きかった。この結果から、白金ナノシートの高活性化は、大きな電気化学的活性表面積に由来することがわかった。耐久性に関しては、白金ナノシートは、ナノ粒子より約 3 倍高いことがわかった。



- 1) D. Takimoto, T. Ohnishi, J. Nutariya, Z. Shen, Y. Ayato, D. Mochizuki, A. Demortière, A. Boulineau, W. Sugimoto, *J. Catal.* **2017**, 345, 207.
- 2) D. Takimoto, W. Sugimoto, Q. Yuan, N. Takao, T. Itoh, T. V. T. Duy, T. Ohwaki, H. Imai, *ACS Appl. Nano Mater.* **2019**, 2, 5743.
- 3) W. Sugimoto, D. Takimoto, *Chem. Lett.* **2021**, 50, 1304.

## Bimetal Oxide Nanoparticles Embedded in rGO as Catalyst for Rechargeable Zinc-Air Battery

(Faculty of Engineering, Hokkaido University) ○Mai Thanh Nguyen, Wei Jian Sim, Zixuan Huang, Masayuki Takahashi, Tetsu Yonezawa

**Keywords:** Rechargeable Zinc-Air Batteries; ORR/OER; Bifunctional Catalysts; Bimetallic Oxides; High Current Density

Rechargeable zinc-air batteries (ZAB) are promising for energy storage thanks to their environmental friendliness, abundant zinc reserves, high capacity, and safe operation.<sup>1</sup> One of their current limitations relates to low oxygen reduction reaction (ORR) in discharging and high overpotential of oxygen evolution reaction (OER) in charging at the air cathode. Catalysts are, thus, indispensable for high-rate performance.<sup>2</sup> Earth-abundant binary transition metal oxides have been emerging as potential catalysts for both ORR and OER to substitute the expensive and scarce ones (noble Pt and IrO<sub>2</sub>).<sup>2</sup> Recent findings reveal the synergetic catalytic activities of bimetal oxides compared with the monometallic oxide counterparts.<sup>3</sup> When the binary oxide catalysts were applied to rechargeable ZAB, however, the cycle stability and power density have been reported only for low current densities ( $\leq 30$  mA cm<sup>-2</sup>) in short time per cycle.<sup>4</sup> Stable performance of ZAB at high current densities is significant for high-rate and large-scale harvesting renewable energies and grid application. Therefore, we developed binary metal oxides of Fe, Co, and Ni embedded on reduced graphene oxide (rGO), i.e., FeCo/rGO and CoNi/rGO, as ORR/OER bifunctional catalysts. For the first time, we evaluated them in ZAB at high current density (100 mA cm<sup>-2</sup>) for 1 h each charge and discharge and set light on the structure-performance relation and issues associated with high-rate ZAB.

Our results revealed that the ORR/OER catalytic activities depended on the metal feeding ratio and metal loadings. The equimolar metal feedings resulted in the synergistic ORR catalytic effect. This ratio was found to enable the most abundant and the highest Co-rich bimetallic oxide nanocrystals in CoNi/rGO, which delivered high ORR activities. The lowest charging voltage of ZAB over cycles also belonged to the catalyst of equimolar metal feeding, suggesting the synergistic OER performance at high current density. At equimolar metal ratios, the loading of bimetallic oxide on rGO was found important for uniformly dispersing oxide catalyst on the conductive rGO substrate. Medium catalyst loading levels correlated with stable charging performance of ZAB by lowering the cathode corrosion using both FeCo/rGO and CoNi/rGO compared with only rGO and only metal oxides. The loading level was found to vary not only the dispersion but also the crystal structure of the bimetal oxides. The best cycle stability was more than 40 cycles for consecutive 80 h at 100 mA cm<sup>-2</sup> while maintaining 90 % discharge capacity.

1) P. Gu, *J. Mater. Chem. A* **2017**, 5, 7651. 2) S. Ren, *J. Mater. Chem. A* **2020**, 8, 6144. 3) L. Wei, *Adv. Mater.* **2017**, 29, 1701410. 4) N. Radenahmad, *J. Alloys Compd.* **2021**, 883, 160935.

## Catalytic synergies in multimetallic nano and subnanoparticles for hydrogen evolution reaction (HER)

(<sup>1</sup>Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, <sup>2</sup>JST-ERATO)

○Quan Zou<sup>1</sup>, Yuji Akada<sup>1</sup>, Akiyoshi Kuzume<sup>2</sup>, Takane Imaoka<sup>1,2</sup>, Kimihisa Yamamoto<sup>1,2</sup>

**Key words:** Multimetallic, subnanoparticles, hydrogen evolution reaction

Many unexpected catalytic performances between nanoparticles (NPs) and subnanoparticles (SNPs) were found in recent years. It was prospected to discover other unique catalytic performance of SNPs<sup>1,2</sup>. Moreover, it is desired to systematically investigate the differences between NPs and SNPs. HER, due to its simple reaction mechanism, was selected as the probe reaction for investigating intrinsic properties of catalysts. Metals can be categorized into oxyphilic metals and oxyphobic metals, at nanoscale the mixing of bimetals tend to form segregated phase, while phase segregation can be avoided at subnanoscale. If we mix oxyphobic metals and oxyphyic metals that never mix at nanoscale, it is possible we acquire fully alloyed metal and metal oxides with enhanced catalytic performance.

In this work, PtZr SNPs and NPs were prepared. XPS confirmed the existence of Pt and Zr oxides. Combine with STEM images, we determined the successful preparation of fully alloyed PtZr SNPs and phase segregated PtZr NPs and the enhanced catalytic activity of PtZr SNPs were observed. To test the university of this discovery, we systematically investigated a series of multimetallic SNPs and NPs. To find the rules in all the combinations, we established a hydrogen synergistic effects index(HSI) for evaluating the synergistic effects between different elements. It demonstrated that SNPs can be a series of more potential material for HER than NPs. Among bimetallic combinations, we found that some rules were found when we regulated the HSI of different combinations according to periodic table.

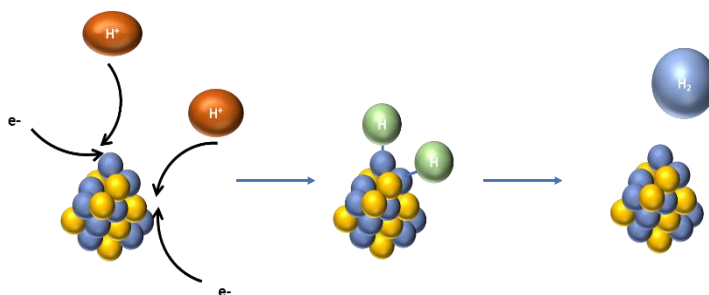


Fig 1. Hydrogen evolution process on bimetallic SNPs.

1)Moriai,T. *Angwandte Chemie*(2020)doi:10.1002/ange.20201019.2)Sonobe,K. *ACS Nano***14**,1804-1810(2020)3) 3)Zhu,J. *Chemical reviews* **120**,851-981(2020).

## X線吸収微細構造法とX線回折法によるLiCoO<sub>2</sub>正極とNASICON型LATP固体電解質の共焼結過程の解明

(物質・材料研究機構<sup>1</sup>) ○市原 文彦<sup>1</sup>・三好 正悟<sup>1</sup>・増田 卓也<sup>1</sup>

Co-sintering Process of LiCoO<sub>2</sub> Cathodes and NASICON-type LATP Solid Electrolytes Studied by X-ray Absorption Fine Structure and X-ray Diffraction (<sup>1</sup>National Institute for Materials Science) ○Fumihiko Ichihara,<sup>1</sup> Shogo Miyoshi,<sup>1</sup> Takuya Masuda<sup>1</sup>

The electrode material/solid electrolyte interface for oxide-based all-solid-state batteries is formed by co-sintering process. Na<sup>+</sup> superionic conductor (NASICON)-type solid electrolyte, Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) and a high-capacity cathode material, LiCoO<sub>2</sub> (LCO) are stable compounds when sintered independently. However, co-sintering of LCO and LATP inevitably produce undesired side reactions instead of the formation of a well-defined interface. In this study, we sintered composites of LCO and LATP at a volume ratio of 3:7 sintered at various temperatures and quantitatively analyzed the chemical species including crystalline phases with long range order and amorphous phases by Rietveld analysis of XRD and linear combination fitting of XANES to discuss the reaction mechanism. LCO and LATP reacted with each other to form Co<sub>3</sub>O<sub>4</sub> and Li<sub>3</sub>PO<sub>4</sub> in the temperature range of 300-500°C and those species further reacted with each other to form LiCoPO<sub>4</sub>, TiO<sub>2</sub>, and CoTiO<sub>3</sub> in the temperature range higher than 500°C.

**Keywords :** Batteries; Co-Sintering; X-Ray Diffraction; X-Ray Absorption Fine Structure

酸化物系全固体電池のための電極活物質/固体電解質界面は共焼結によって形成される。リチウムイオン電池の正極材料のLiCoO<sub>2</sub>と酸化物系固体電解質のLi<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub>はそれぞれ単独では熱的に安定だが、共焼結時にLCOとLATPが予期せぬ副反応を起こしイオン伝導性に優れた界面を形成することができない。本研究ではLCOとLATPを体積比3:7で混合した粉末を様々な温度で共焼結し、XRDとXAESを駆使することによって、長周期構造を持つ結晶相のみならず長周期構造を持たない非晶質相を含む化学種を同定・定量し、反応機構の解明を試みた。300°Cから500°Cまでの低温域ではLCOとLATPが反応してCo<sub>3</sub>O<sub>4</sub>、Li<sub>3</sub>PO<sub>4</sub>相の生成が観測された。さらに500°C以上の高温側ではLiCoPO<sub>4</sub>やTiO<sub>2</sub>、CoTiO<sub>3</sub>の生成が観測された。

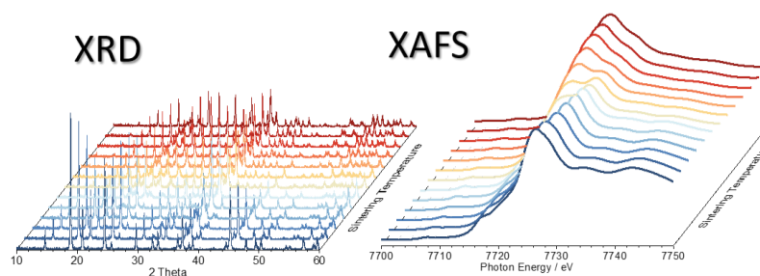


Fig.1 各温度で焼結した試料の回折パターン（左）とXANESスペクトル（右）

## マグネシウム二次電池負極としての黒鉛の可能性に関する検討

(信州大) ○清水 雅裕・新井 進

Potential of Graphite as a Negative Material for Magnesium-Ion Rechargeable Batteries  
(Department of Materials Chemistry, Faculty of Engineering, Shinshu University)

○Masahiro Shimizu, Susumu Arai

Rechargeable Mg-ion batteries which are independent of Li have attractive much attention as a next-generation energy device. This is motivated by the high theoretical capacity and the element abundance of Mg ( $2205 \text{ mA h g}^{-1}/3832 \text{ mA h cm}^{-3}$ ). There are few reports on the use of graphite as a negative electrode material even when its scope is expanded to include not binary but ternary Mg-graphite intercalation compounds (GICs). In the previously our report, we studied the electrochemical formation of Mg-GICs in DMF-based electrolytes to achieve a capacity of  $180 \text{ mA h g}^{-1}$  by reversible intercalation/deintercalation of solvated  $\text{Mg}^{2+}$ . In this study, we focused on size and donor number of solvent and investigated the solvent effect on the formation of ternary Mg-GICs. **Keywords** : Mg-ion batteries; Intercalation; Graphite

Li 資源に依存しない次世代蓄電池として、Mg 二次電池に高い関心が寄せられている。その負極材料として、Mg 金属が盛んに研究されているものの、その金属表面に形成される不動態被膜により可逆的な析出－溶解反応を長期にわたって実現することが課題とされている。他方、Li 二次電池の負極として使用されている黒鉛において、その層間への  $\text{Mg}^{2+}$  の挿入反応に関する報告例はほとんどない。これまでに我々は、単独ではなく溶媒和  $\text{Mg}^{2+}$  の状態ではあるものの黒鉛層間への可逆的な挿入－脱離反応を達成し、 $180 \text{ mA h g}^{-1}$  の充放電容量を得ることに成功している。溶媒和イオンを含む三元系黒鉛層間化合物の形成においては、その溶媒のサイズなどが大きく関与するものと推察される。そこで本研究では、黒鉛層間への  $\text{Mg}^{2+}$  の挿入反応において、溶媒がおよぼす影響について調査した (Fig. 1)。Li 二次電池において使用されている EC:DEC や 2-MeTHF では酸化応答が認められず、環状を示す嵩高い溶媒を含む系では共挿入反応が進行しにくいものと推察される。他方、DMSO および DMF の系では酸化電流が明瞭に現れた。これらの系において、電流密度： $74.4 \text{ mA g}^{-1}$  の条件で  $-2.65 \text{ V vs. Ag/Ag}^+$  の電位に到達した段階で X 線回折測定を実施した。DME, DMSO の系では三元系黒鉛層間化合物の形成が認められ、層間距離は溶媒サイズの大きい DMF の方がより拡張することが分かった。DME の系においては、002 回折のピークの強度が減少したものの、ピークシフトは見られなかった。ただし、黒鉛電極の色味が著しく変化し GIC の形成が示唆された。XRD で検出できなかったのは、不安定な二元 Mg-GIC が形成され、XRD 測定に至るまでに分解したためと予想される。

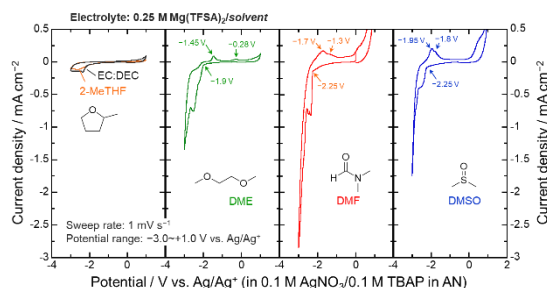


Fig. 1 Cyclic voltammograms of graphite composite electrodes in several electrolytes (0.25 M). The solvents used in this study is EC:DEC, 2-MeTHF, DME, DMSO, and DMF.

## ナフタレン組成を用いた原油の起源有機物指標の熱熟成による影響

(産業技術総合研究所 地質調査総合センター<sup>1</sup>) ○朝比奈健太<sup>1</sup>・高橋幸士<sup>1</sup>・森本和也<sup>1</sup>・中嶋健<sup>1</sup>・鈴木祐一郎<sup>1</sup>

Effect of thermal maturation on the evaluation indicator for source organic matter of crude oil using naphthalene composition (<sup>1</sup>*Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology*) ○Kenta Asahina,<sup>1</sup> Koji U. Takahashi,<sup>1</sup> Kazuya Morimoto,<sup>1</sup> Takeshi Nakajima<sup>1</sup>, Yuichiro Suzuki<sup>1</sup>

The composition of organic matter in crude oil has been used to estimate the source organic matter. Our previous study proposed an indicator for evaluation of source organic matter using methylated naphthalene composition in crude oil. However, this indicator may not be applicable to matured crude oil because methyl naphthalenes are isomerized as thermal maturation. This presentation will report the factors that affect the isomerization of naphthalene and the application range of the evaluation indicator based on the results of pyrolysis experiments of each naphthalene and coal.

**Keywords :** *Naphthalene, Crude oil, Source organic matter, Thermal maturation, Clay catalyst*

原油の起源有機物 (陸源 or 海成有機物) の推定は、それらを生成・排出した堆積岩 (石油根源岩) の特定につながるため、石油探鉱における検討項目のひとつである。これまで原油中の有機物組成による原油の起源有機物の推定が行われてきたが、熱分解や微生物分解を受けた原油では、その組成が変わるため利用できない。先に我々は、これらの分解作用に耐性を持つ原油中のジメチルナフタレン(DMN)の組成比を用いた起源有機物の推定指標(DMR)を提案した<sup>1)</sup>。

$$DMR = \frac{[1,5 - DMN + 1,6 - DMN]}{[1,3 - DMN + 1,7 - DMN]}$$

陸源有機物由来の原油の DMR は、1.0 以上、海成有機物由来の原油は、1.0 以下を示す<sup>1)</sup>。

一方、メチルナフタレン類は、熱熟成の進行に伴い異性化するため<sup>2)</sup>、原油の起源推定指標として適用できる熟成度の上限を明らかにする必要がある<sup>3)</sup>。本講演は、DMR の適用可能な熟成度の上限と、異性化を促進する粘土鉱物の触媒作用を明らかにするために、各種ナフタレン類と石炭の熱分解実験を行った<sup>2,3)</sup>。実験の結果、粘土鉱物の比表面積とプロトン付加能力が、メチル化ナフタレンの異性化に寄与することが明らかとなった。DMR は、ビトリナイト反射率 (熱熟成指標) 1.3-1.4%までは、1.0 以上を保ったことから、軽質油のような高い熱熟成度の原油にも適用できることを明らかにした(Fig)。

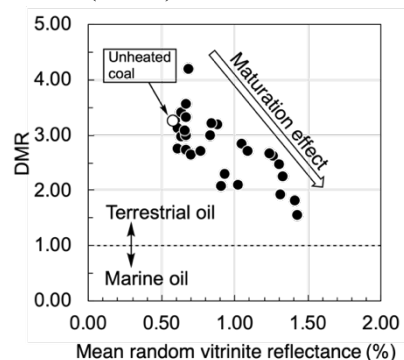


Fig. Plots of DMR values in heating experiments of immature coal against thermal maturity indicator.

1) K. Asahina, N. Suzuki, *Org. Geochem.* **2018**, 124, 46.

2) K. Asahina, T. Nakajima, K. Morimoto, Y. Hanamura, M. Kobayashi, *Chem. Lett.* **2020**, 49, 728.

3) K. Asahina, K. U. Takahashi, Y. Suzuki, T. Nakajima, M. Kobayashi, *Chem. Lett.* **2021**, 50, 1718.



## 酸化鉄微粒子存在下の水の放射線分解による発電

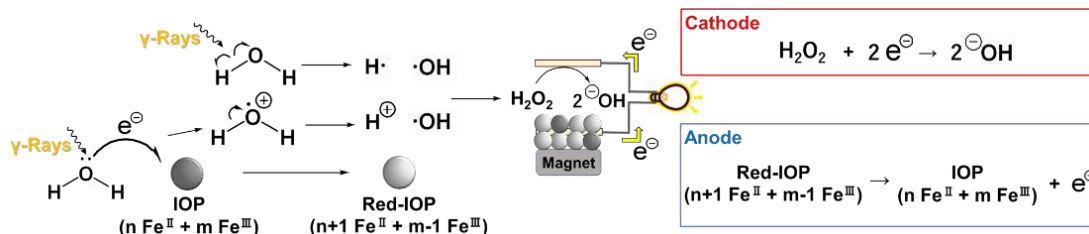
(中部大応生<sup>1</sup>・中部大工<sup>2</sup>・阪大産研<sup>3</sup>) ○島岡 桃子<sup>1</sup>・上野 左京<sup>1</sup>・板倉 左奈<sup>1</sup>・後藤 颯太<sup>1</sup>・橋本 真一<sup>2</sup>・室屋 裕佐<sup>3</sup>・堤内 要<sup>1</sup>

Electricity generation by radiolysis of water in the presence of iron oxide particles (<sup>1</sup>*College of Bioscience and Biotechnology, Chubu University*, <sup>2</sup>*College of Engineering, Chubu University*, <sup>3</sup>*Institute of Scientific and Industrial Research, Osaka University*) ○Momoko Shimaoka,<sup>1</sup> Sakyo Ueno,<sup>1</sup> Sana Itakura,<sup>1</sup> Sota Goto,<sup>1</sup> Shin-ichi Hashimoto,<sup>2</sup> Yusa Muroya,<sup>3</sup> Kaname Tsutsumiuchi<sup>1</sup>

Most of spent nuclear fuel is stored without reusing due to the high cost required for reprocessing. Especially,  $\gamma$ -rays of the radioactive waste are harmful and difficult to shield, but they have enormous energy. Therefore, we focused to develop electricity generation technology from  $\gamma$ -rays. In a previous study,  $\text{Al}_2\text{O}_3$  particles were used to promote hydrogen production from water with  $^{60}\text{Co}$   $\gamma$ -rays<sup>1</sup>. We expected that iron oxide particles (IOPs) also contributed to  $\text{H}_2$  production; however, IOPs preferred reduction of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  under high concentration of IOPs in water. We considered that the IOPs trapped some electrons produced from radiolysis of water. The  $\gamma$ -rays-irradiated IOPs were applied for electricity generation. We could detect electric power when the IOPs were attracted to an electrode side by magnet in the dispersion with two electrodes.

**Keywords :** gamma-rays; iron oxide; radiolysis; electricity generation; radiation

使用済み核燃料は再処理に高いコストがかかることから、そのほとんどが再利用されることなく貯蔵されている。特に  $\gamma$  線は有害で遮蔽も難しいが、高いエネルギーを有している。そこで我々は  $\gamma$  線からの発電技術の開発に取り組んだ。先行研究としてアルミナ微粒子分散液に  $^{60}\text{Co}$  の  $\gamma$  線を照射した実験がある<sup>1</sup>。アルミナでは水の放射線分解による水素生成が促進されたことから、酸化鉄微粒子 (IOPs) でも同様の効果が期待できると考え、実験を試みた。その結果、IOPs では水素生成より 3 価鉄の還元反応が進行していた。高濃度の IOPs 分散液では、水の放射線分解で生成する電子が IOPs に取り込まれたのであろう。そこで我々はこの現象を水素生成ではなく、発電に利用することとした。 $\gamma$  線照射した IOPs 分散液に 2 つの電極を導入し、一方の電極に IOPs を磁石で引き寄せ、電気化学セルを放電したところ、 $\mu\text{W}$  オーダーの出力が確認された。



<sup>1</sup> T. Yoshida *et al.*, *J. Radioanal. Nucl. Chem.*, **272**, 471 (2007).