

## 2024年3月20日(水)

アカデミックプログラム [B 講演] | 02. 理論化学・情報化学・計算化学：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 H937(9号館 [3階] 937)

## [H937-3am] 02. 理論化学・情報化学・計算化学

座長：杉山 佳奈美、石田 豊和

日本語

9:00 ~ 9:20

[H937-3am-01]

## 自己組織化マップと遷移状態モチーフによる有機化学反応の幾何学的分類

○松尾 勇二郎<sup>1</sup>、山口 徹<sup>1</sup>、船津 公人<sup>2</sup>、堀 憲次<sup>1,3,4</sup> (1. 株式会社TSテクノロジー、2. 奈良先端科学技術大学院大学、3. 国立開発研究法人産業総合技術研究所、4. 山口大学)

日本語

9:20 ~ 9:40

[H937-3am-02]

## 有限一次元分子集合系での一重項分裂過程と相関三重項対励起子の空間分布に関する理論研究

○宮本 孟<sup>1</sup>、岡田 健治<sup>1</sup>、岸 亮平<sup>1,2,3,4</sup>、北河 康隆<sup>1,2,3,4,5</sup> (1. 阪大院基礎工、2. 阪大QIQB、3. 阪大ICS-OTRI、4. 阪大RCSEC、5. 阪大CSRN)

日本語

9:40 ~ 10:00

[H937-3am-03]

## ジアリールエテン誘導体への光照射による溶解度変化

○中村 優斗<sup>1</sup>、沈 君偉<sup>1</sup>、深港 豪<sup>1</sup>、原田 祐希<sup>1</sup>、中村 振一郎<sup>1</sup>、渡邊 智<sup>1</sup>、大谷 涼真<sup>1</sup> (1. 熊本大学)

日本語

10:00 ~ 10:20

[H937-3am-04]

## 次元縮約法の選択に対する低次元反応空間構築の性能検証

○堤 拓朗<sup>1</sup>、小野 ゆり子<sup>2</sup>、武次 徹也<sup>1,2</sup> (1. 北大院理、2. 北大WPI-ICReDD)

日本語

10:30 ~ 10:50

[H937-3am-05]

## デジタルアニーラを活用したヘキサベンゾコロネンのハロゲン置換による特性最適化

○橋口 和弘<sup>1</sup>、丸尾 昭人<sup>1</sup>、添田 武志<sup>1</sup>、實宝 秀幸<sup>1</sup> (1. 富士通株式会社)

日本語

10:50 ~ 11:10

[H937-3am-06]

## 高圧氷における相転移の量子効果

○桑畑 和明<sup>1</sup>、立川 仁典<sup>1</sup> (1. 横浜市立大学)

日本語

11:10 ~ 11:30

[H937-3am-07]

## 酵素反応における基底状態不安定化仮説：バイオマス分解酵素 GH11-Xylanase の反応機構について

○石田 豊<sup>1</sup>、Jerry Parks<sup>2</sup>、Jeremy Smith<sup>2</sup> (1. 国立研究開発法人 産業技術総合研究所、2. オークリッジ国立研究所)

アカデミックプログラム [B 講演] | 03. 物理化学—構造：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 A1452(14号館 [5階] 1452)

## [A1452-3am] 03. 物理化学—構造

座長：恩田 健、米田 勇祐

英語

9:00 ~ 9:20

[A1452-3am-01]

強レーザー場フーリエ変換分光法によるsub-MHz精度の $\text{Kr}^+$ の超微細および微細構造の測定

○安藤 俊明<sup>1</sup>、山田 佳奈<sup>1</sup>、岩崎 純史<sup>1</sup>、山内 薫<sup>1</sup> (1. 東大)

日本語

9:20 ~ 9:40

[A1452-3am-02]

$\text{NO}_3 \times {}^2\text{A}_2'$  状態の  $\nu_2$  変角振動構造

○福島 勝<sup>1</sup> (1. 広島市立大学)

日本語

9:40 ~ 10:00

[A1452-3am-03]

時間分解赤外分光法による核酸塩基水溶液の超高速電子緩和過程の研究

○鈴木 俊法<sup>1</sup>、小原 祐樹<sup>1</sup>、Srijon Ghosh<sup>1</sup>、神柱 尚太<sup>1</sup> (1. 京都大学)

英語

10:00 ~ 10:20

[A1452-3am-04]

内向きプロトンポンプシゾロドプシン4における反応初期中間体の発色団構造の解明

○潤井 泰斗<sup>1</sup>、水野 操<sup>1</sup>、神取 秀樹<sup>2</sup>、水谷 泰久<sup>1</sup> (1. 阪大院理、2. 名工大院工)

日本語

10:30 ~ 10:50

[A1452-3am-05]

フェムト秒時間分解時間領域ラマン分光による非平衡な励起状態平面化ダイナミクスの観測

○米田 勇祐<sup>1,2</sup>、小西 智暉<sup>3</sup>、齊藤 尚平<sup>3</sup>、倉持 光<sup>1,2</sup> (1. 分子研、2. 総研大、3. 京大)

英語

10:50 ~ 11:10

[A1452-3am-06]

可視光領域での蛍光符号化低波数コヒーレントラマン分光法

○田村 徹<sup>1</sup>、Phillip McCann<sup>1</sup>、西山 諒<sup>1</sup>、平松 光太郎<sup>1,2</sup>、合田 圭介<sup>1,3,4</sup> (1. 東大、2. 九大、3. カリフォルニア大、4. 武漢大)

日本語

11:10 ~ 11:30

[A1452-3am-07]

細胞内水分子構造のラマン分光解析

○安田 充<sup>1</sup>、安井 正人<sup>1</sup> (1. 慶應大)



アカデミックプログラム [B講演] | 04. 物理化学—物性：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 A1441(14号館 [4階] 1441)

**[A1441-3vn] 04. 物理化学—物性**

座長：網島 亮

## ◆ 英語

15:55 ~ 16:15

[A1441-3vn-01]

**アルキルアミド置換ヘキサデヒドロトリベンゾ[12]アヌレン誘導体の形成する分子集合体の溶媒依存性**○笠原 遥太郎<sup>1</sup>、武田 貴志<sup>1,2</sup>、出倉 駿<sup>1</sup>、高井 淳朗<sup>3</sup>、姉帯 勇人<sup>3</sup>、久木 一朗<sup>4</sup>、竹内 正之<sup>3</sup>、芥川 智行<sup>1</sup> (1. 東北大、2. 信州大、3. 物質・材料機構、4. 阪大)

## ◆ 英語

16:15 ~ 16:35

[A1441-3vn-02]

**環境刺激による有機カチオンへの固相イオン交換と物性評価**○伊藤 みづき<sup>1</sup>、眞邊 潤<sup>1</sup>、市橋 克哉<sup>1</sup>、今野 大輔<sup>1</sup>、加藤 智佐都<sup>1</sup>、藤林 将<sup>2</sup>、Goulven Cosquer<sup>3,4</sup>、井上 克也<sup>1,3,4,5</sup>、平尾 岳大<sup>1</sup>、灰野 岳晴<sup>1,3,4</sup>、芥川 智行<sup>6</sup>、高橋 仁徳<sup>7</sup>、中村 貴義<sup>7</sup>、西原 禎文<sup>1,3,5,8</sup> (1. 広島大院先進理工、2. 宇部高専、3. 広島大CResCent、4. 広島大WPI-SKCM<sup>2</sup>、5. 広島大先進セ、6. 東北大多元研、7. 北大電子研、8. JST さきがけ)

## ◆ 英語

16:35 ~ 16:55

[A1441-3vn-03]

**多価金属イオンを導入した超分子カチオンを含むNi(dmit)<sub>2</sub>塩の作製と物性評価**○石川 大輔<sup>1</sup>、加藤 智佐都<sup>1</sup>、藤林 将<sup>2</sup>、Goulven Cosquer<sup>3,4</sup>、井上 克也<sup>1,3,4,5</sup>、芥川 智行<sup>6</sup>、高橋 仁徳<sup>7</sup>、中村 貴義<sup>7</sup>、西原 禎文<sup>1,3,5,8</sup> (1. 広島大院先進理工、2. 宇部高専、3. 広島大キラル国際研究拠点、4. 広島大キラルノット超物質拠点、5. 広島大先進機能物質研究センター、6. 東北大多元研、7. 北大電子研、8. JST さきがけ)

## ◆ 日本語

16:55 ~ 17:15

[A1441-3vn-04]

**4,4'-dinonyl-2,2'-bipyridineとdmit配位子をもつ非対称平面4配位型錯体を示すエレクトロクロミズムと熱的構造相転移**○久保 和也<sup>1</sup>、堀 葵<sup>1</sup>、キム ユナ<sup>2</sup>、田原 圭志朗<sup>3</sup>、梅谷 優太<sup>4</sup>、吾郷 友宏<sup>1</sup> (1. 兵庫県立大学大学院理学研究科、2. 宇都宮大学工学部、3. 香川大学創造工学部、4. 兵庫県立大学理学部)

アカデミックプログラム [B講演] | 05. 物理化学—反応：口頭B講演

2024年3月20日(水) 9:30 ~ 11:40 A1455(14号館 [5階] 1455)

**[A1455-3am] 05. 物理化学—反応**

座長：古部 昭広、村越 敬

## ◆ 英語

9:30 ~ 9:50

[A1455-3am-01]

ペロブスカイトナノ結晶とペリレンビスイミド誘導体からなるヘテロ構造の制御

○久保 直輝<sup>1</sup>、山内 光陽<sup>2</sup>、増尾 貞弘<sup>1</sup> (1. 関西学院大学、2. 京大化研)

## ◆ 日本語

9:50 ~ 10:10

[A1455-3am-02]

フェムト秒過渡吸収顕微鏡を用いたフィコシアニンたんぱく質結晶内におけるエネルギー移動反応観測

○片山 哲郎<sup>1</sup>、上田 柊斗<sup>1</sup>、梅名 泰史<sup>2</sup>、古部 昭広<sup>1</sup> (1. 徳島大学、2. 名古屋大学)

## ◆ 日本語

10:10 ~ 10:30

[A1455-3am-03]

マイクロ構造電極における酸素発生触媒能の動画観測評価

○芦澤 大輝<sup>1</sup>、福島 知宏<sup>2</sup>、村越 敬<sup>2</sup> (1. 北大院総化、2. 北大院理)

## ◆ 日本語

10:40 ~ 11:00

[A1455-3am-04]

真空中のポリオール添加水液滴の凍結過程：凍結時間の観測と分子動力学シミュレーションによる解析

○吉岡 拓哉<sup>1</sup>、荒川 雅<sup>1</sup>、秋山 良<sup>1</sup>、寺寄 亨<sup>1</sup> (1. 九大)

## ◆ 英語

11:00 ~ 11:20

[A1455-3am-05]

拮抗する二種類の酵素反応のカップリングに基づく自律的かつ再帰的なpH変化を示す系の設計と応用

○板谷 昌輝<sup>1</sup>、Paola Albanese<sup>2</sup>、Nadia Valletti<sup>2</sup>、Gábor Holló<sup>3</sup>、Sándor Kurunczi<sup>4</sup>、Robert Horvath<sup>4</sup>、Federico Rossi<sup>2</sup>、István Lagzi<sup>1</sup> (1. ブダペスト工科経済大学、2. シエナ大学、3. ローザンヌ大学、4. ハンガリーエネルギー研究所)

## ◆ 日本語

11:20 ~ 11:40

[A1455-3am-06]

酸化剤濃度に依存した運動・変形が発現する化学振動反応を内包した自己駆動液滴

○久世 雅和<sup>1</sup>、松尾 宗征<sup>2,3</sup>、白石 允梓<sup>1</sup>、中田 聡<sup>3</sup>、西森 拓<sup>1</sup> (1. 明治大学 先端数理科学インスティテュート、2. 東京大学大学院 総合文化研究科、3. 広島大学大学院 統合生命科学研究科)

アカデミックプログラム [B講演] | 06. 分析化学：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 会場 A1453(14号館 [5階] 1453)

**[A1453-3am] 06. 分析化学**

座長：火原 彰秀、南 豪

## ◆ 日本語

9:00 ~ 9:20

[A1453-3am-01]

UV吸収による環境中の鉛イオンの簡便な測定を目指したペプチド固定化マイクロビーズの開発

○吉田 秀平<sup>1</sup>、吉田 光輝<sup>1</sup>、鶴岡 孝章<sup>1</sup>、臼井 健二<sup>1</sup> (1. 甲南大学FIRST)

## ◆ 英語

9:20 ~ 9:40

[A1453-3am-02]

Development of quantitative barcode readout on microfluidic paper-based analytical devices (μPADs)

○Yanawut Manmana<sup>1</sup>, Yuki Hiruta<sup>1</sup>, Daniel Citterio<sup>1</sup> (1. Keio University)

## ◆ 英語

9:40 ~ 10:00

[A1453-3am-03]

Electrochemical detection of dopamine based on metal oxide/carbonaceous catalyst

○Alagan Jeevika<sup>1</sup>, Arinori Inagawa<sup>1</sup>, Yuna Kim<sup>1</sup>, Ken-ichi Iimura<sup>1</sup> (1. Utsunomiya University)

## ◆ 日本語

10:10 ~ 10:30

[A1453-3am-04]

吸収分光法に基づくマイクロ光ファイバーpHセンサーを用いた炭素作用電極および酸化チタン光触媒表面の局所pH変化のその場観測

○NGUYEN DUC QUANG<sup>1</sup>、宇佐美 久尚<sup>1</sup> (1. 信州大学)

## ◆ 英語

10:30 ~ 10:50

[A1453-3am-05]

塗布型導電性MOF薄膜デバイスによる多種アミンガス検出

○大代 晃平<sup>1</sup>、佐々木 由比<sup>1</sup>、本間 信孝<sup>2</sup>、中島 毅彦<sup>2</sup>、南 豪<sup>1</sup> (1. 東大生研、2. トヨタ自動車)

## ◆ 英語

10:50 ~ 11:10

[A1453-3am-06]

酸化アルミニウム生成in-situ観察による結晶多形現象の起源探究

○榊原 雅也<sup>1</sup>、中室 貴幸<sup>1</sup>、中村 栄一<sup>1</sup> (1. 東京大学)

## ◆ 日本語

11:10 ~ 11:30

[A1453-3am-07]

ガンマ線誘起陽電子消滅寿命測定による酸化セリウムの格子欠陥評価

○道志 智<sup>1</sup>、前田 和紀<sup>1</sup>、平 義隆<sup>2</sup>、渡邊 真太<sup>3</sup>、平出 哲也<sup>4</sup> (1. 大阪技術研、2. 分子研、3. AGC 先端基盤研究所、4. 原子力機構)

アカデミックプログラム [B講演] | 06. 分析化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 A1453(14号館 [5階] 1453)

**[A1453-3vn] 06. 分析化学**

座長：稲川 有徳、高貝 慶隆

## ◆ 日本語

15:55 ~ 16:15

[A1453-3vn-01]

凍結水溶液中に形成されたマイクロ構造を利用する粒子のサイズ分級法

○稲川 有徳<sup>1</sup>、君島 惇哉<sup>1</sup>、上原 伸夫<sup>1</sup> (1. 宇都宮大学)

## ◆ 日本語

16:15 ~ 16:35

[A1453-3vn-02]

相分離混相流を溶離液として使用するHPLCシステムの開発—緩衝液を使った三成分系溶離液のシリカカラム分離への影響—

○西村 亮哉<sup>1</sup>、居原田 健志<sup>1</sup>、塚越 一彦<sup>1</sup> (1. 同志社大学)

## ◆ 英語

16:35 ~ 16:55

[A1453-3vn-03]

リテンションインデックスプロット(RI-plot)を用いたWAX材料の構造評価

○海野 祐馬<sup>1,2</sup>、北浦 健大<sup>1</sup>、山田 宏明<sup>1</sup>、北川 慎也<sup>2</sup>、中村 清香<sup>3</sup>、渡邊 亮太<sup>3</sup>、佐藤 浩昭<sup>3</sup> (1. 住友ゴム工業、2. 名工大院工、3. 産総研機能化学)

## ◆ 英語

16:55 ~ 17:15

[A1453-3vn-04]

金ナノ粒子を用いた脂質混合物からの膜タンパク質特異的脂質のスクリーニング

○ワングアムマイボン スパコーン<sup>1</sup>、川井 隆之<sup>1</sup>、木下 祥尚<sup>1</sup>、松森 信明<sup>1</sup> (1. 九州大学)

アカデミックプログラム [B講演] | 07. 無機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:10 A1444(14号館 [4階] 1444)

**[A1444-3pm] 07. 無機化学**

座長：猿山 雅亮、後藤 真人

◆ 英語

13:00 ~ 13:20

[A1444-3pm-01]

## Trinuclear molecular complexes showing redox-switchable magnetic properties

○Aristide Maximilien Sacha Colin<sup>1,2</sup>, Yiting Wang, Nathalie Bridonneau<sup>2</sup>, François Lambert<sup>2</sup>, Zakaria Halime<sup>2</sup>, Nicolas Suaud<sup>3</sup>, Shin-ichi Ohkoshi<sup>1</sup>, Mohammed Bouammali<sup>3</sup>, Nathalie Guihéry<sup>3</sup>, Talal Mallah<sup>2</sup> (1. University of Tokyo - Graduate School of Science, 2. Université Paris-Saclay, ICMO, 3. Université de Toulouse Paul Sabatier, LCPQ)

◆ 英語

13:20 ~ 13:40

[A1444-3pm-02]

## イオン性ナノ結晶超格子のカチオン交換反応

○エン シャ<sup>1</sup>、雅亮 猿山<sup>2</sup>、利治 寺西<sup>2</sup> (1. 京都大学理学研究科、2. 京都大学化学研究所)

◆ 英語

13:40 ~ 14:00

[A1444-3pm-03]

## エトキシオリゴシロキサンから誘導されるポリシロキサンの性質およびそのシリカゲルへの変換

○佐藤 陽平<sup>1</sup>、速水 良平<sup>1</sup>、山本 一樹<sup>1</sup>、郡司 天博<sup>1</sup> (1. 東京理科大学)

◆ 英語

14:10 ~ 14:30

[A1444-3pm-04]

異常高原子価イオンを含むBaFeO<sub>3</sub>の酸素脱離・吸収

○渡邊 滯<sup>1</sup>、後藤 真人<sup>1</sup>、島川 祐一<sup>1</sup> (1. 京都大学)

◆ 日本語

14:30 ~ 14:50

[A1444-3pm-05]

ダブルペロブスカイトLn<sub>2</sub>LiFeO<sub>6</sub>のサイト置換効果

○後藤 真人<sup>1</sup>、島川 祐一<sup>1</sup> (1. 京都大学)

◆ 英語

14:50 ~ 15:10

[A1444-3pm-06]

ダブルペロブスカイト酸化物R<sub>2</sub>BaFe<sub>2</sub>O<sub>6</sub>における逐次相転移の希土類金属依存性

○飯星 真<sup>1</sup>、後藤 真人<sup>1</sup>、島川 祐一<sup>1</sup> (1. 京都大学)

アカデミックプログラム [B講演] | 08. 触媒：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 会場 A1457(14号館 [5階] 1457)

**[A1457-3am] 08. 触媒**

座長：大洞 康嗣、邨次 智

## ◆ 英語

9:00 ~ 9:20

[A1457-3am-01]

白金-ガドリニウム合金ナノ粒子電極触媒の調製と高耐久酸素還元活性

○森山 拓海<sup>1</sup>、邨次 智<sup>1</sup>、唯 美津木<sup>1,2</sup> (1. 名大院理、2. 名大物国セ)

## ◆ 日本語

9:20 ~ 9:40

[A1457-3am-02]

酸素発生反応電極触媒としてのハイエントロピースピネル酸化物ナノ粒子の開発とその反応メカニズムの解析

○岩瀬 和至<sup>1</sup>、加藤 涼雅<sup>1</sup>、筈居 高明<sup>1</sup>、本間 格<sup>1</sup> (1. 東北大学)

## ◆ 英語

9:40 ~ 10:00

[A1457-3am-03]

紫外可視拡散反射分光システムによる触媒水素化反応のその場観察

○Risheng Li<sup>1,2</sup>、川波 肇<sup>1,2</sup>、小平 哲也<sup>2</sup> (1. 筑波大学、2. 国立研究開発法人産業技術総合研究所)

## ◆ 英語

10:00 ~ 10:20

[A1457-3am-04]

1,3-ジエンの酸化的アミノ化反応におけるパラジウムナノクラスターの触媒ダイナミクス

○田原 一輝<sup>1</sup>、藤原 哲晶<sup>2</sup>、鳥居 一幸<sup>1</sup>、鈴木 健之<sup>3</sup>、長谷川 淳也<sup>4</sup>、大洞 康嗣<sup>1</sup> (1. 関西大化学生命工、2. 京大院工、3. 阪大産研、4. 北大触媒研)

## ◆ 英語

10:30 ~ 10:50

[A1457-3am-05]

POM-担持Agナノ粒子複合化触媒を用いたアルコールとアニリンの酸化的カップリングによるイミンの高選択的な合成

○福田 正次<sup>1</sup>、吉川 聡一<sup>1</sup>、山添 誠司<sup>1</sup> (1. 東京都立大学)

## ◆ 日本語

10:50 ~ 11:10

[A1457-3am-06]

層状複水酸化物-金属酸化物クラスター複合体の合成とその触媒応用

○高橋 浩輝<sup>1</sup>、吉川 聡一<sup>1</sup>、山添 誠司<sup>1</sup> (1. 東京都立大学)

## ◆ 英語

11:10 ~ 11:30

[A1457-3am-07]

Catalytic carboxylation and decarboxylation approach for the construction of bicyclic intermediates as core structural motifs in Natural products

○Sangita Karanjit<sup>1</sup>、Emiko Tanaka<sup>1</sup>、Rei Majima<sup>1</sup>、Ryota Sato<sup>1</sup>、Kosuke Namba<sup>1</sup> (1. Tokushima University)

アカデミックプログラム [B講演] | 08. 触媒：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 A1458(14号館 [5階] 1458)

**[A1458-3pm] 08. 触媒**

座長：影島 洋介、小寺 正徳

◆ 英語

13:00 ~ 13:20

[A1458-3pm-01]

窒素含有炭素材料の光触媒作用を利用した抗菌特性評価

○川口 雅之<sup>1</sup>、三宅 一樹<sup>1</sup>、村上 飛龍<sup>1</sup>、齊藤 安貴子<sup>1</sup>、森田 成昭<sup>1</sup> (1. 大阪電気通信大学)

◆ 英語

13:20 ~ 13:40

[A1458-3pm-02]

大面積化に向けた反応器による過酸化水素の人工光合成

○潘 振華<sup>1</sup>、片山 建二<sup>1</sup>、Shu Hu<sup>2</sup>、Chiheng Chu<sup>3</sup> (1. 中央大学、2. イェール大学、3. 浙江大学)

◆ 日本語

13:40 ~ 14:00

[A1458-3pm-03]

メタン存在下における光触媒水分解反応の特異的な促進

○斎藤 晃<sup>1</sup>、佐藤 宏祐<sup>1</sup>、東 泰佑<sup>1</sup>、杉本 敏樹<sup>1,2</sup> (1. 分子科学研究所、2. 総合研究大学院大学)

◆ 英語

14:00 ~ 14:20

[A1458-3pm-04]

アルカン酸化と水素生成を同時駆動する光レドックスカスケード触媒系の構築

○小林 厚志<sup>1</sup> (1. 北海道大学)

◆ 英語

14:30 ~ 14:50

[A1458-3pm-05]

非混和性二相溶液間を自発的に移動する電子伝達体により水の酸化と統合された新規光触媒反応系の開発

○板垣 廉<sup>1,2</sup>、中田 明伸<sup>1,3</sup>、鈴木 肇<sup>1</sup>、富田 修<sup>1</sup>、張 浩徹<sup>4</sup>、阿部 竜<sup>1</sup> (1. 京大院工、2. 学振DC1、3. JSTさきがけ、4. 中大理工)

◆ 英語

14:50 ~ 15:10

[A1458-3pm-06]

Scalable and efficient water-splitting photocatalyst sheets based on carbon-based conductors

○Chen Gu<sup>1</sup>, Yi-Wen Ma<sup>1</sup>, Tsuyoshi Takata<sup>1</sup>, Takashi Hisatomi<sup>1</sup>, Yuta Nishina<sup>3</sup>, Nobuyuki Zettsu<sup>1</sup>, Kazunari Domen<sup>1,2</sup> (1. Shinshu University, 2. The University of Tokyo, 3. Okayama University)

◆ 英語

15:10 ~ 15:30

[A1458-3pm-07]

Development of charge carrier-selective heterodyne transient grating spectroscopic technique and its application in the distinction of surface trap states in hematite

○Woon Yong Sohn<sup>1</sup> (1. Chungbuk National University)

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 F1231(12号館 [3階] 1231)

**[F1231-3vn] 09. 錯体化学・有機金属化学**

座長：近藤 美欧、畑中 翼

## ◆ 英語

15:55 ~ 16:15

[F1231-3vn-01]

配位高分子融液のCO<sub>2</sub>に対する反応性○西口 大智<sup>1</sup>、門田 健太郎<sup>1</sup>、堀毛 悟史<sup>1</sup> (1. 京都大学)

## ◆ 日本語

16:15 ~ 16:35

[F1231-3vn-02]

TADF有機分子を光増感剤 Mn(II)錯体を触媒として用いたCO<sub>2</sub>還元光触媒反応○井上 麗<sup>1</sup>、Elena Bassan<sup>2</sup>、Francesco Calogero<sup>2</sup>、Simone Potenti<sup>2</sup>、Andrea Gualandi<sup>2</sup>、Pier Cozzi<sup>2</sup>、Paola Ceroni<sup>2</sup>、玉置 悠祐<sup>3</sup>、石谷 治<sup>1,4</sup> (1. 東京工業大学、2. ボローニャ大学、3. 産業技術総合研究所、4. 広島大学)

## ◆ 英語

16:35 ~ 16:55

[F1231-3vn-03]

水溶性ロジウム触媒によるCO<sub>2</sub>光還元における選択的ギ酸生成のメカニズム○イドンソブ<sup>1</sup>、山内 幸正<sup>1</sup>、酒井 健<sup>1</sup> (1. 九大院理)

## ◆ 英語

16:55 ~ 17:15

[F1231-3vn-04]

## 分子内電子移動を活用した光還元種生成量子収率の向上とその原理

○細川 直輝<sup>1</sup>、石谷 治<sup>1,2</sup> (1. 東京工業大学、2. 広島大学)



アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 F1232(12号館 [3階] 1232)

**[F1232-3vn] 09. 錯体化学・有機金属化学**

座長：大木 靖弘、劔 隼人

## ◆ 日本語

15:55 ~ 16:15

[F1232-3vn-01]

パックマン型ポルフィリン配位子を有する二核Cu, Zn錯体の酸化還元挙動とCO<sub>2</sub>還元反応メカニズム○竹山 知志<sup>1</sup>、檜垣 達也<sup>2</sup>、大木 靖弘<sup>2</sup>、太田 雄大<sup>1</sup> (1. 山陽小野田市立山口東京理科大学、2. 京都大学)

## ◆ 英語

16:15 ~ 16:35

[F1232-3vn-02]

固液界面でのCu(phen)錯体の2核化およびアルコール空気酸化促進

○久米 晶子<sup>1</sup>、安倍 大貴<sup>1</sup> (1. 広島大学大学院先進理工系科学研究科)

## ◆ 英語

16:35 ~ 16:55

[F1232-3vn-03]

多核銅錯体を触媒とするH<sub>2</sub>O<sub>2</sub>によるメタン酸化の合理化：μ-O•活性種とH<sub>2</sub>O<sub>2</sub>効率○藤川 恭祐<sup>1</sup>、亀谷 陽平<sup>2</sup>、田中 皐晴<sup>1</sup>、四宮 聖菜<sup>1</sup>、塩田 淑仁<sup>2</sup>、吉澤 一成<sup>2</sup>、小寺 政人<sup>1</sup> (1. 同志社大学大学院、2. 九州大学)

## ◆ 英語

16:55 ~ 17:15

[F1232-3vn-04]

シクロペンタジエニルフェノキシ配位子を有する新規サマリウム錯体の合成と窒素固定に対する反応性

○光本 泰知<sup>1</sup>、西林 仁昭<sup>1</sup> (1. 東大院工)

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 F1233(12号館 [3階] 1233)

**[F1233-3vn] 09. 錯体化学・有機金属化学**

座長：伊藤 亮孝、小林 厚志

◆ 英語

15:55 ~ 16:15

[F1233-3vn-01]

抗酸化物質検出を指向したニトロキシドラジカル結合型室温燐光性Irポルフィリンの開発

○楊川 博久<sup>1</sup>、村田 慧<sup>1</sup>、石井 和之<sup>1</sup> (1. 東大生研)

◆ 英語

16:15 ~ 16:35

[F1233-3vn-02]

Vaulted-structure induced efficient solid-state phosphorescence in *trans*-bis(iminomethylpyrrolato)platinum(II) complexes○Shufang HUANG<sup>1</sup>, Soichiro Kawamorita<sup>1</sup>, Takeshi Naota<sup>1</sup> (1. Osaka University)

◆ 日本語

16:35 ~ 16:55

[F1233-3vn-03]

マンガン(II)錯体を示すマグネトルミネッセンス

○壬生 託人<sup>1</sup>、松岡 亮太<sup>1</sup>、草本 哲郎<sup>1,2</sup> (1. 大阪大学、2. JST さきがけ)

◆ 日本語

16:55 ~ 17:15

[F1233-3vn-04]

室温で長寿命な可視光発光を示す亜鉛錯体の合成および光物性評価

○岩本 秀光<sup>1</sup>、和田 啓幹<sup>1,2</sup>、砂田 祐輔<sup>1,2,3</sup> (1. 東大院工、2. 東大生研、3. JST さきがけ)

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 F1234(12号館 [3階] 1234)

**[F1234-3vn] 09. 錯体化学・有機金属化学**

座長：大竹 研一、芳野 遼

英語

15:55 ~ 16:15

[F1234-3vn-01]

波打ち構造を持つ二次元MOFsの機械的性質

○大谷 亮<sup>1</sup>、大場 正昭<sup>1</sup> (1. 九州大学)

英語

16:15 ~ 16:35

[F1234-3vn-02]

Glassy nonporous Zn coordination polymer for gas separation

○Xin Zheng<sup>1</sup>, Shin-ichiro Noro<sup>1</sup> (1. Fac. of Env. Earth Sci., Hokkaido Univ.)

英語

16:35 ~ 16:55

[F1234-3vn-03]

配位高分子二元系の共融現象

○田部 博康<sup>1</sup>、Karnjana Atthawilai<sup>2</sup>、堀毛 悟史<sup>1,2</sup> (1. 京大、2. タイ王国ウィタヤシリメティー科学技術大学院大学)

日本語

16:55 ~ 17:15

[F1234-3vn-04]

有機金属構造体の合成後修飾による二次配位部位に基づく不均一系触媒の設計

○相本 美咲<sup>1</sup>、Pavel Usov<sup>1</sup>、和田 雄貴<sup>1</sup>、松本 隆也<sup>1,2</sup>、河野 正規<sup>1</sup> (1. 国立大学法人東京工業大学、2. ENEOS株式会社)

アカデミックプログラム [B講演] | 11. 有機化学—構造有機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 E1113(11号館 [1階] 1113)

**[E1113-3pm] 11. 有機化学—構造有機化学**

座長：若宮 淳志、川畑 公輔

## ◆ 英語

13:00 ~ 13:20

[E1113-3pm-01]

 **$\pi$ 共役系骨格内における様々な酸化状態の超原子価アンチモン化合物の合成と光学特性**○谷村 和哉<sup>1</sup>、権 正行<sup>1</sup>、田中 一生<sup>1</sup> (1. 京大院工)

## ◆ 日本語

13:20 ~ 13:40

[E1113-3pm-02]

**ポルフィリン修飾ポリチオフェンによるキラル増幅を利用したセンシング**○本告 潤之介<sup>1</sup>、福原 学<sup>1</sup> (1. 東京工業大学)

## ◆ 英語

13:40 ~ 14:00

[E1113-3pm-03]

**超原子価スズ化合物の7配位化による光学特性と刺激応答性の評価**○権 正行<sup>1</sup>、森崎 祐介<sup>1</sup>、田中 一生<sup>1</sup> (1. 京大院工)

## ◆ 日本語

14:00 ~ 14:20

[E1113-3pm-04]

**スピロフルオレンを導入したシクロペンタチオフェンを $\pi$ 共役リンカーとする非縮環型電子受容性分子の開発と波長選択型有機太陽電池への応用**○陣内 青萌<sup>1</sup>、家 裕隆<sup>1</sup> (1. 大阪大学)

## ◆ 英語

14:30 ~ 14:50

[E1113-3pm-05]

**キノイド構造を有する超電子供与性分子の合成と応用**○松尾 崇也<sup>1,2</sup>、川畑 公輔<sup>1,2</sup>、瀧宮 和男<sup>1,2,3</sup> (1. 東北大院理、2. 理研CEMS、3. 東北大WPI-AIMR)

## ◆ 英語

14:50 ~ 15:10

[E1113-3pm-06]

**カルコゲン相互作用に基づく超分子的有機半導体の分子集積と電荷輸送**○田中 優成<sup>1</sup>、森 達哉<sup>1</sup>、小路口 由佳<sup>1</sup>、ヤン ユソク<sup>1</sup>、安田 琢磨<sup>1,2</sup> (1. 九大院工、2. 九大高等研)

## ◆ 英語

15:10 ~ 15:30

[E1113-3pm-07]

**含窒素芳香族化合物の部分的に分離したフロンティア軌道を利用した光機能性ホウ素錯体の創出**○伊藤 峻一郎<sup>1</sup>、高橋 宏昌<sup>1</sup>、田中 一生<sup>1</sup> (1. 京大院工)

アカデミックプログラム [B講演] | 11. 有機化学—構造有機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 E1121(11号館 [2階] 1121)

**[E1121-3pm] 11. 有機化学—構造有機化学**

座長：庄子 良晃、石垣 侑祐

◆ 英語

13:00 ~ 13:20

[E1121-3pm-01]

アミド埋込型 $\pi$ 共役系分子の機能開拓○森下 大輝<sup>1</sup>、伊藤 喜光<sup>1,2</sup> (1. 東大院工、2. JSTさきがけ)

◆ 英語

13:20 ~ 13:40

[E1121-3pm-02]

アセン類のL-regionをジフェニレン縮環によって $\pi$ 拡張した含七員環PAHの合成と物性○久田 雅人<sup>1</sup>、清水 大貴<sup>1</sup>、松田 建児<sup>1,2</sup> (1. 京大院工、2. 京大福井セ)

◆ 英語

13:40 ~ 14:00

[E1121-3pm-03]

チオフェン縮環ナノベルトの合成と性質

○周戸 大季<sup>1</sup>、Philipp Wiesener<sup>2</sup>、Elena Kolodzeiski<sup>2</sup>、水上 輝市<sup>3</sup>、Harry Mönig<sup>2</sup>、Saeed Amirjalayer<sup>2</sup>、Henning Klaasen<sup>2</sup>、Bart Jan Ravoo<sup>2</sup>、君塚 信夫<sup>3</sup>、八木 亜樹子<sup>1</sup>、伊丹 健一郎<sup>1</sup> (1. 名古屋大学、2. ミュンスター大学、3. 九州大学)

◆ 英語

14:00 ~ 14:20

[E1121-3pm-04]

ジチンビスキノジメタンの配座変化を鍵とするドミノ酸化還元反応の実証

○張本 尚<sup>1</sup>、田所 朋樹<sup>1</sup>、杉山 聡一郎<sup>1</sup>、鈴木 孝紀<sup>1</sup>、石垣 侑祐<sup>1</sup> (1. 北大院理)

◆ 英語

14:30 ~ 14:50

[E1121-3pm-05]

亜鉛を用いたカルボアニオン型環化反応による新規スピロ共役分子のダイバジェント合成

○福間 翔太<sup>1</sup>、Rui Shang<sup>1</sup>、中村 栄一<sup>1</sup> (1. 東京大学)

◆ 日本語

14:50 ~ 15:10

[E1121-3pm-06]

弓形構造を構成単位とするオリゴチオフェン2次元シートの光・電子物性と階層構造制御

○名倉 和彦<sup>1</sup>、町田 崇<sup>1</sup>、中西 尚志<sup>1</sup> (1. 物質・材料研究機構)

◆ 日本語

15:10 ~ 15:30

[E1121-3pm-07]

実在反芳香族分子の近接積層 $\pi$ 二量体に対する量子化学計算に基づくエネルギー分割解析○杉森 亮太<sup>1</sup>、岸 亮平<sup>1,2,3,4</sup>、北河 康隆<sup>1,2,3,4,5</sup> (1. 阪大院基礎工、2. 阪大RCSEC、3. 阪大QIQB、4. 阪大ICS-OTRI、5. 阪大CSRN)

アカデミックプログラム [B講演] | 11. 有機化学—構造有機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:00 皿 E1122(11号館 [2階] 1122)

**[E1122-3pm] 11. 有機化学—構造有機化学**

座長：長谷川 真士、八木 亜樹子

## ◆ 英語

13:00 ~ 13:20

[E1122-3pm-01]

ヘテロ原子を導入した混み合った $\pi$ 共役アルケンのメカノクロミズム特性○山田 航平<sup>1</sup>、安達 洋平<sup>1</sup>、大下 浄治<sup>1</sup> (1. 広島大)

## ◆ 日本語

13:20 ~ 13:40

[E1122-3pm-02]

赤色・近赤外領域で強発光特性を示すアルミニウム二核三重螺旋錯体の合成

○小西 悠斗<sup>1</sup>、星野 友<sup>1,2</sup>、小野 利和<sup>1,2</sup> (1. 九大院工、2. 九大CMS)

## ◆ 日本語

13:40 ~ 14:00

[E1122-3pm-03]

ヒドリンダセン骨格を含む水溶性シクロパラフェニレン：水中でのアクリジニウム塩の包接と可視光フォトレドックス触媒への展開

○土戸 良高<sup>1</sup>、森戸 良<sup>1</sup>、小坂田 耕太郎<sup>2</sup>、井手 智仁<sup>3</sup>、河合 英敏<sup>1</sup> (1. 東理大理、2. 東工大化生研、3. 東京高専物質工)

## ◆ 英語

14:00 ~ 14:20

[E1122-3pm-04]

末端 $\pi$ 拡張型[7]ヘリセン誘導体の非線形分子ばね特性○胡 維哲<sup>1</sup>、村田 靖次郎<sup>1</sup>、廣瀬 崇至<sup>1</sup> (1. 京都大学化学研究所)

## ◆ 日本語

14:20 ~ 14:40

[E1122-3pm-05]

1,1'-ビアズレン骨格で構成される不斉ヘリセン化合物とそのカチオンラジカルの構造と性質

青山 大樹<sup>1</sup>、成田 昌弘<sup>1</sup>、五島 健太<sup>1</sup>、村藤 俊宏<sup>2</sup>、井川 和宣<sup>3</sup>、河崎 悠也<sup>1</sup>、友岡 克彦<sup>1</sup>、○谷 文都<sup>1</sup> (1. 九州大学、2. 山口大学大学院、3. 熊本大学大学院)

## ◆ 英語

14:40 ~ 15:00

[E1122-3pm-06]

末端2,1,3-チアジアゾール基を持つヘテロ[n]ヘリセンのホモキラル結晶におけるらせん状カラム配列

○張 政<sup>1</sup>、村田 靖次郎<sup>1</sup>、廣瀬 崇至<sup>1</sup> (1. 京都大学化学研究所)

アカデミックプログラム [B講演] | 12. 有機化学—有機結晶・超分子化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 E1123(11号館 [2階] 1123)

**[E1123-3vn] 12. 有機化学—有機結晶・超分子化学**

座長：越智 里香、大城 宗一郎

## ◆ 日本語

15:55 ~ 16:15

[E1123-3vn-01]

ペプチド型超分子ファイバーと界面活性剤ミセルの複合化による動的不安定性の創発

○窪田 亮<sup>1</sup>、鳥越 祥吾<sup>1</sup>、濱中 佑也<sup>1</sup>、長尾 和俊<sup>1</sup>、浜地 格<sup>1,2</sup> (1. 京大院工、2. JST ERATO)

## ◆ 英語

16:15 ~ 16:35

[E1123-3vn-02]

リングからファイバーへの構造転移を示す自己集合性アゾベンゼン二量体

○須田 奈月<sup>1</sup>、花山 博紀<sup>2</sup>、矢貝 史樹<sup>3</sup> (1. 千葉大院融合理工、2. 千葉大院工、3. 千葉大IAAR)

## ◆ 英語

16:35 ~ 16:55

[E1123-3vn-03]

高速AFMを利用した光誘起超分子構造変換のリアルタイム観察

○玉木 健太<sup>1</sup>、花山 博紀<sup>2</sup>、矢貝 史樹<sup>3</sup> (1. 千葉大院融合理工、2. 千葉大工学研究院、3. 千葉大IAAR)

## ◆ 日本語

16:55 ~ 17:15

[E1123-3vn-04]

短いアルコキシ修飾でフィルムを与えるフルオランテン縮環プロペラン

○加藤 研一<sup>1</sup>、内田 雄太<sup>1</sup>、金田 知也<sup>1</sup>、橘 智紀<sup>1</sup>、大谷 俊介<sup>1</sup>、生越 友樹<sup>1,2</sup> (1. 京大、2. 金沢大)

アカデミックプログラム [B講演] | 12. 有機化学—有機結晶・超分子化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 E1131(11号館 [3階] 1131)

**[E1131-3vn] 12. 有機化学—有機結晶・超分子化学**

座長：伊藤 傑、北川 大地

日本語

15:55 ~ 16:15

[E1131-3vn-01]

アルキル置換シクロヘキシル基を持つn型有機半導体のレンガ型結晶構造と電荷輸送特性

○熊谷 翔平<sup>1</sup>、荒井 勇太郎<sup>1</sup>、渡辺 豪<sup>2,3</sup>、石井 宏幸<sup>4</sup>、佐藤 寛泰<sup>5</sup>、竹谷 純一<sup>6,7</sup>、岡本 敏宏<sup>1,7</sup> (1. 東工大、2. 北里大、3. 神奈川県産総研、4. 筑波大、5. (株) リガク、6. 東大、7. CREST (JST))

日本語

16:15 ~ 16:35

[E1131-3vn-02]

強アクセプター性ナフタレンを基盤とした棒状分子の合成と固体構造

○田中 彩樹<sup>1</sup>、松尾 匠、林 正太郎 (1. 高知工科大学)

日本語

16:35 ~ 16:55

[E1131-3vn-03]

*tert*-Butyl修飾による発光性分子の結晶構造制御：光物性からレーザー発振まで○東 蒼一朗<sup>1</sup>、松尾 匠<sup>1</sup>、林 正太郎<sup>1</sup> (1. 高知工大)

日本語

16:55 ~ 17:15

[E1131-3vn-04]

フッ素化π共役系分子からなる発光性柔軟性分子結晶の創成と光機能

○中林 真宏<sup>1</sup>、松尾 匠<sup>1</sup>、林 正太郎<sup>1</sup> (1. 高知工科大学)



アカデミックプログラム [B講演] | 13. 有機化学—反応機構・光化学・電気化学：口頭B講演

2024年3月20日(水) 15:55 ~ 16:55 会場 E1132(11号館 [3階] 1132)

**[E1132-3vn] 13. 有機化学—反応機構・光化学・電気化学**

座長：佐藤 英祐、松本 浩一

## ◆ 日本語

15:55 ~ 16:15

[E1132-3vn-01]

レドックス活性イオン液体を触媒、電解質および反応メディアとする電解水素発生系の開発

○佐藤 綾<sup>1</sup>、星野 友<sup>1</sup>、鳶越 恒<sup>1</sup> (1. 九大院工)

## ◆ 英語

16:15 ~ 16:35

[E1132-3vn-02]

流動電位を用いる電解重合法の開発

○岩井 優<sup>1</sup>、佐藤 宏亮<sup>1</sup>、長谷川 丈二<sup>2</sup>、石塚 紀生<sup>3</sup>、松川 公洋<sup>4</sup>、富田 育義<sup>1</sup>、稲木 信介<sup>1</sup> (1. 東京工業大学、2. 名古屋大学、3. エマオス京都、4. 京都工芸繊維大学)

## ◆ 日本語

16:35 ~ 16:55

[E1132-3vn-03]

電気化学的炭素挿入に基づく多置換芳香環の構築

○信田 尚毅<sup>1</sup>、森本 達也<sup>1</sup>、今野 祐希<sup>1</sup>、跡部 真人<sup>1</sup> (1. 横浜国立大学)

アカデミックプログラム [B講演] | 14. 有機化学—芳香族・複素環・ヘテロ原子化合物：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 E1133(11号館 [3階] 1133)

**[E1133-3vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物**

座長：井本 裕顕、北村 充

◆ 英語

15:55 ~ 16:15

[E1133-3vn-01]

機械学習を活用したMayr反応性パラメータの予測と含窒素複素芳香族分子のマンニッヒ型反応における新規求核剤の探索

○大石 峻也<sup>1,2</sup>、大塚 尚哉<sup>1,2</sup>、丸山 莉央<sup>1</sup>、鈴木 敏泰<sup>1</sup>、楳山 儀恵<sup>1,2</sup> (1. 分子研、2. 総研大)

◆ 英語

16:15 ~ 16:35

[E1133-3vn-02]

新規キノリン系大環状化合物の開発

○シュウエイ<sup>1</sup>、木原 和輝<sup>1</sup>、野仲 はる<sup>1</sup>、八神 諒汰<sup>1</sup>、武田 彩海<sup>1</sup>、田代 奨吾<sup>1</sup>、熊谷 直哉<sup>1,2</sup> (1. 慶大院薬、2. 微化研)

◆ 英語

16:35 ~ 16:55

[E1133-3vn-03]

キノリン/インドール環状4量体 (Q<sub>2</sub>In<sub>2</sub>) の誘導体合成および機能探索○木原 和輝<sup>1</sup>、小林 透威<sup>1</sup>、木村 美玲<sup>1</sup>、Wei Xu<sup>1</sup>、熊谷 直哉<sup>1,2</sup> (1. 慶大院薬、2. 微化研)

◆ 日本語

16:55 ~ 17:15

[E1133-3vn-04]

環状ジケトン類の結合切断戦略によるメタルフリー型ヘテロ環合成

○要藤 友佑<sup>1</sup>、知名 秀泰<sup>2</sup>、宮尾 優希<sup>1</sup>、佐々 裕隆<sup>1</sup>、菊嶋 孝太郎<sup>1</sup>、土肥 寿文<sup>1</sup> (1. 立命館大薬、2. 長浜バイオ大バイオ)

アカデミックプログラム [B講演] | 15. 有機化学—脂肪族・脂環式化合物, 新反応技術: 口頭B講演

2024年3月20日(水) 13:00 ~ 15:40 E1142(11号館 [4階] 1142)

**[E1142-3pm] 15. 有機化学—脂肪族・脂環式化合物, 新反応技術**

座長: 吉野 達彦、矢島 知子

英語

13:00 ~ 13:20

[E1142-3pm-01]

外輪型キラル二核ルテニウム触媒による分子間不斉ナイトレン移動型反応の開発

○牧野 思子<sup>1</sup>、桐生 昇一<sup>1</sup>、森 康平<sup>1</sup>、宮澤 拓<sup>1</sup>、熊谷 悠平<sup>1</sup>、東田 皓介<sup>2</sup>、小島 正寛<sup>1</sup>、吉野 達彦<sup>1</sup>、松永 茂樹<sup>1,2</sup> (1. 北大院薬、2. 京大院理)

英語

13:20 ~ 13:40

[E1142-3pm-02]

キラルπ-銅(II)錯体触媒によるイソキノリニウムイリドとα,β-エナミド及びα,β,γ,δ-ジエナミドの位置、配向、化学、エキソ及びエナンチオ選択的脱芳香族[3+2]環化付加反応

○郭 威威<sup>1</sup>、石原 一彰<sup>1</sup> (1. 名古屋大学)

英語

13:40 ~ 14:00

[E1142-3pm-03]

キラルスルフィド触媒によるプロモラクトン化を介したα位にアリル基とプロパルギル基を有するカルボン酸の速度論的光学分割

○奥野 研<sup>1</sup>、Bun Chan<sup>1</sup>、白川 誠司<sup>1</sup> (1. 長崎大学)

英語

14:10 ~ 14:30

[E1142-3pm-04]

10-Phenylphenothiazine-Catalyzed Bromo-Perfluoroalkylation of Unactivated Olefins

○Koto Tagami<sup>1,2</sup>, Dominique Cahard<sup>2</sup>, Tomoko Yajima<sup>1</sup> (1. Ochanomizu University, Japan, 2. CNRS, University of Rouen Normandy, France)

英語

14:30 ~ 14:50

[E1142-3pm-05]

N-ヘテロ環カルベン触媒によるラジカル-ラジカルカップリングを介したβ-アミドケトンのジアステレオ選択的合成

○佐藤 由季也<sup>1</sup>、隅田 有人<sup>2</sup>、大宮 寛久<sup>1</sup> (1. 京大化研、2. 医科歯科大生材研)

英語

15:00 ~ 15:20

[E1142-3pm-06]

亜硝酸エステルを用いる芳香族ニトロソ化反応とジアゾ化合物への誘導

○橋床 亜伊瑠<sup>1</sup>、中尾 優希<sup>1</sup>、北之園 拓<sup>1</sup>、山下 恭弘<sup>1</sup>、小林 修<sup>1</sup> (1. 東京大学)

英語

15:20 ~ 15:40

[E1142-3pm-07]

Development of biocompatible chiral scandium catalyst

○Watchara Srimontree<sup>1</sup>, Taku Kitanosono<sup>1</sup>, Yasuhiro Yamashita<sup>1</sup>, Shū Kobayashi<sup>1</sup> (1. Graduate School of Science, The University of Tokyo)

アカデミックプログラム [B 講演] | 15. 有機化学—脂肪族・脂環式化合物, 新反応技術: 口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 E1143(11号館 [4階] 1143)

## [E1143-3vn] 15. 有機化学—脂肪族・脂環式化合物, 新反応技術

座長: 山下 恭弘、野上 敏材

英語

15:55 ~ 16:15

[E1143-3vn-01]

### マイクロフロー装置によるビニルモノマーのシークエンスオリゴマー合成

○ユドウン<sup>1</sup>、岡本 和紘<sup>1</sup>、吉岡 里佳子<sup>1</sup>、中里 遼平<sup>1</sup>、芦刈 洋祐<sup>1</sup>、永木 愛一郎<sup>1</sup> (1. 北海道大学)

英語

16:15 ~ 16:35

[E1143-3vn-02]

### 三成分連結反応を基盤とするペプチド鎖高速伸長法の開発

○杉澤 直斗<sup>1</sup>、安東 章<sup>1</sup>、布施 新一郎<sup>1</sup> (1. 名大院創薬)

英語

16:35 ~ 16:55

[E1143-3vn-03]

### 不均一系酸触媒を用いる連続フローエポキシド・アジリジン開環反応

○西澤 健<sup>1</sup>、齋藤 由樹<sup>1</sup>、小林 修<sup>1</sup> (1. 東京大学)

英語

16:55 ~ 17:15

[E1143-3vn-04]

### マイクロフローリアクター中でのアシルアンモニウム/ピリジニウムイオンによるH-ホスホネートの化学選択的アシル化反応の開発

○北村 宙士<sup>1</sup>、布施 新一郎<sup>1</sup> (1. 名大院創薬)

アカデミックプログラム [B講演] | 16. 天然物化学・ケミカルバイオロジー：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 H933(9号館 [3階] 933)

**[H933-3vn] 16. 天然物化学・ケミカルバイオロジー**

座長：深谷 圭介、西川 慶祐

## ◆ 英語

15:55 ~ 16:15

[H933-3vn-01]

## 生合成模倣渡環反応によるマンザミンアルカロイド型骨格の合成

○和山 稔明<sup>1</sup>、大栗 博毅<sup>1</sup> (1. 東京大学)

## ◆ 英語

16:15 ~ 16:35

[H933-3vn-02]

## Keramaphidin BとIngenamineの全合成

○栗原 悠熙<sup>1</sup>、八木 みのり<sup>1</sup>、野口 嵩史<sup>1</sup>、安福 悠<sup>1</sup>、沖田 采音<sup>1</sup>、深谷 圭介<sup>2</sup>、占部 大介<sup>2</sup>、大石 毅<sup>3</sup>、千田 憲孝<sup>1</sup>、岡村 俊孝<sup>1</sup>、佐藤 隆章<sup>1</sup> (1. 慶大理工、2. 富山県大工、生医工研セ、3. 慶大医)

## ◆ 英語

16:35 ~ 16:55

[H933-3vn-03]

## セコドラスタン型ジテルペン Isolinearol の合成研究

○鶴田 智暉<sup>1</sup>、吉野 優季花<sup>1</sup>、西川 慶祐<sup>1</sup>、森本 善樹<sup>1</sup> (1. 大阪公立大学)

## ◆ 日本語

16:55 ~ 17:15

[H933-3vn-04]

## 炭素連結型シアロ糖鎖の統一的合成を志向したC-グリコシル化反応の検討

○竹田 大樹<sup>1</sup>、寄立 麻琴<sup>1</sup>、的場 博亮<sup>1</sup>、平井 剛<sup>1</sup> (1. 九州大学大学院)

アカデミックプログラム [B講演] | 16. 天然物化学・ケミカルバイオロジー：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 H935(9号館 [3階] 935)

**[H935-3vn] 16. 天然物化学・ケミカルバイオロジー**

座長：小椋 章弘、松丸 尊紀

## ◆ 日本語

15:55 ~ 16:15

[H935-3vn-01]

## システムホルミル化による標的タンパク質選択的切断法の開発と機能制御応用

○善明 直輝<sup>1</sup>、松本 侑也<sup>1</sup>、安田 斉弘<sup>1</sup>、内之宮 祥平<sup>1</sup>、進藤 直哉<sup>1</sup>、田畑 香織<sup>1</sup>、王子田 彰夫<sup>1</sup> (1. 九大院・薬)

## ◆ 英語

16:15 ~ 16:35

[H935-3vn-02]

## 多機能ナノ材料合成のためのクリッカブルな二反応性小型金ナノクラスター

○渡邊 賢司<sup>1</sup>、Mao Qiyue<sup>2</sup>、Zhang Zhouen<sup>1</sup>、畑 真知<sup>2</sup>、小寺 政人<sup>2</sup>、北岸 宏亮<sup>2</sup>、丹羽 節<sup>1,3,4</sup>、細谷 孝充<sup>1,4</sup> (1. 理化学研究所、2. 同志社大学、3. 九州大学、4. 東京医科歯科大学)

## ◆ 日本語

16:35 ~ 16:55

[H935-3vn-03]

ホスフィン酸リガンドに基づく低親和性  $\text{Ca}^{2+}$  蛍光プローブの開発と細胞内  $\text{Ca}^{2+}$  イメージングへの応用○坂間 亮浩<sup>1</sup>、熊田 怜<sup>1</sup>、新藤 豊<sup>2,3</sup>、黒沼 柚花<sup>1</sup>、岩澤 尚子<sup>1</sup>、チッテリオ ダニエル<sup>1</sup>、岡 浩太郎<sup>2,3,4,5</sup>、蛭田 勇樹<sup>1</sup> (1. 慶大理工・応化、2. 慶大理工・生命情報、3. 北里大未来工、4. 早大理工総研、5. 高雄医大・医)

## ◆ 英語

16:55 ~ 17:15

[H935-3vn-04]

## Th2型バイアス型の糖脂質抗原の合成とCD1d-糖脂質複合体の機能解析

○末吉 耕大<sup>1</sup>、岸 惇一郎<sup>1</sup>、井貫 晋輔<sup>1,2</sup>、松丸 尊紀<sup>1</sup>、藤本 ゆかり<sup>1</sup> (1. 慶應義塾大学理工学部、2. 京都大学大学院薬学研究科)

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 H932(9号館 [3階] 932)

**[H932-3am] 17. 生体機能関連化学・バイオテクノロジー**

座長：平山 祐、野中 洋

◆ 英語

9:00 ~ 9:20

[H932-3am-01]

近赤外蛍光性金属ナノプローブの開発と生体イメージングへの応用

○田中 慎一<sup>1</sup>、和達 大樹<sup>2</sup>、新岡 宏彦<sup>3</sup> (1. 呉工業高等専門学校、2. 兵庫県立大学、3. 大阪大学)

◆ 英語

9:20 ~ 9:40

[H932-3am-02]

腫瘍セラノスティクスを指向した抗がん剤複合化ガドリニウム酸化物ナノ粒子の合成

○王 星辰<sup>1</sup>、木村 祐<sup>1</sup>、今井 悠太<sup>1</sup>、三浦 理紗子<sup>1</sup>、今井 宏彦<sup>2</sup>、近藤 輝幸<sup>1</sup> (1. 京大院工、2. 京大院情報)

◆ 日本語

9:40 ~ 10:00

[H932-3am-03]

脳内リガンド指向性化学とクリックケミストリーの組み合わせによるグルタミン酸受容体の高速ラベル化戦略

○坂本 清志<sup>1,2</sup>、白岩 和樹<sup>1</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup> (1. 京大院工、2. JST ERATO)

◆ 日本語

10:00 ~ 10:20

[H932-3am-04]

生きたマウス脳内でのミクログリア選択的化学標識と機能解析への展開

○王 萌初<sup>1</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup> (1. 京都大学大学院工学研究科、2. JST ERATO)

◆ 英語

10:30 ~ 10:50

[H932-3am-05]

特定の酵素活性を持つ細胞選択的にclick to release 反応を起こす新規ケミカルツールの開発

○伊藤 廉<sup>1</sup>、神谷 真子<sup>2,3</sup>、浦野 泰照<sup>1,4</sup> (1. 東大院薬、2. 東工大院生命理工、3. 東京工業大学国際先駆研究機構、4. 東大院医)

◆ 英語

10:50 ~ 11:10

[H932-3am-06]

精密に設計された超偏極分子プローブ群を用いる複数のアミノペプチダーゼ活性の生体内同時検出

○谷田部 浩行<sup>1</sup>、斎藤 雄太朗<sup>1</sup>、高草木 洋一<sup>2,3</sup>、斎藤 圭太<sup>2</sup>、山本 和俊<sup>4</sup>、Murali Krishna<sup>4</sup>、山東 信介<sup>1</sup> (1. 東大院工、2. 量子科学技術研究開発機構、3. 千葉大院融合理工、4. 米国国立衛生研究所)

◆ 英語

11:10 ~ 11:30

[H932-3am-07]

ラマン分光法を用いた nectriatide の細胞内動態解析

○三宅 良介<sup>1</sup>、安藤 正浩<sup>2</sup>、小林 啓介<sup>3</sup>、供田 洋<sup>3</sup>、大城 太一<sup>3</sup>、竹山 春子<sup>1,2,4,5</sup> (1. 早大院・先進理工、2. 早大・ナノライフ創新研、3. 北里大院・薬、4. 産総研・早大CBBDOIL、5. 早大・生命動態研)

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 会場 H936(9号館 [3階] 936)

**[H936-3am] 17. 生体機能関連化学・バイオテクノロジー**

座長：稲葉 央、金原 数

◆ 英語

9:00 ~ 9:20

[H936-3am-01]

**Development of Artificial Metalloproteins from Hemophore of *Acinetobacter baumannii* for Antibacterial Applications**○Viet Quoc Nguyen<sup>1</sup>, Shinya Ariyasu<sup>1</sup>, Yuichiro Aiba<sup>1</sup>, Hiroshi Sugimoto<sup>2</sup>, Osami Shoji<sup>1</sup> (1. Grad. Sch. of Sci., Nagoya Univ., 2. RIKEN SPring-8)

◆ 英語

9:20 ~ 9:40

[H936-3am-02]

**Artificial Vesicular and Fibrous Assembly of Amphiphilic Peptide WR9 in Living Cells**○Qinxuan Yang<sup>1</sup>, Takuzo Aida<sup>1</sup>, Takayuki Miki<sup>1</sup> (1. The Univ. of Tokyo)

◆ 英語

9:40 ~ 10:00

[H936-3am-03]

**Analytical chromatography for insulin fibrillation monitoring**○ティラサラ ピトワラカンカナマゲ<sup>1</sup>, Wijak Yospanya<sup>1</sup>, Kazushi Kinbara<sup>1</sup> (1. 東京工業大学)

◆ 英語

10:00 ~ 10:20

[H936-3am-04]

**ATP responsive 2-dimensional scaffold from biomolecular machines exhibiting enhanced catalytic activity**○Tonmoy Ray<sup>1</sup>, Takuzo Aida<sup>1,2</sup>, Hideki Taguchi<sup>3</sup>, Tatsuya Niwa<sup>3</sup> (1. The University of Tokyo, 2. Center for Emergent Matter Science, RIKEN, 3. Tokyo Institute of Technology (TITECH))

◆ 日本語

10:30 ~ 10:50

[H936-3am-05]

**スピロピラン修飾Tau由来ペプチドによる微小管構造の可逆的光操作**○稲葉 央<sup>1</sup>、阪口 みなも<sup>1</sup>、渡 宗英<sup>1</sup>、角五 彰<sup>2</sup>、松浦 和則<sup>1</sup> (1. 鳥取大院工、2. 京大院理)

◆ 英語

10:50 ~ 11:10

[H936-3am-06]

**人工触媒反応による転写活性化を介した新規抗がん戦略の開発**○山梨 祐輝<sup>1</sup>、高丸 慎平<sup>1</sup>、東屋 勇都<sup>1</sup>、上村 祐悟<sup>1</sup>、岡部 篤史<sup>2</sup>、海渡 智史<sup>3</sup>、鯨井 智也<sup>4</sup>、胡桃坂 仁志<sup>4</sup>、岩間 厚志<sup>3</sup>、金田 篤志<sup>2</sup>、山次 健三<sup>1</sup>、川島 茂裕<sup>1</sup>、金井 求<sup>1</sup> (1. 東大院薬、2. 千葉大院医、3. 東大医科研、4. 東大定量研)

◆ 日本語

11:10 ~ 11:30

[H936-3am-07]

**抗原タンパク質修飾ペプチドファイバーの細胞内取り込み制御**○若林 里衣<sup>1</sup>、樋口 亜也斗<sup>1</sup>、難波江 友紀<sup>1</sup>、神谷 典穂<sup>1</sup>、後藤 雅宏<sup>1</sup> (1. 九州大学)



アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 H931(9号館 [3階] 931)

**[H931-3pm] 17. 生体機能関連化学・バイオテクノロジー**

座長：真鍋 良幸、田村 朋則

◆ 英語

13:00 ~ 13:20

[H931-3pm-01]

過酸化亜硝酸塩 (ONOO<sup>-</sup>) 応答性タンパク質ラベリングの開発○朱 浩<sup>1</sup>、宇野 寛彬<sup>1</sup>、松葉 恭一<sup>1</sup>、浜地 格<sup>1,2</sup> (1. 京都大学、2. JST ERATO)

◆ 英語

13:20 ~ 13:40

[H931-3pm-02]

チロシナーゼを用いた生細胞と*in vivo*での近傍ラベル化法○松田 侑奈<sup>1</sup>、朱 浩<sup>1</sup>、Jae Hoon Oh<sup>2</sup>、美野 丈晴<sup>1</sup>、石川 守<sup>2</sup>、中村 秀樹<sup>1,3</sup>、辻川 宗男<sup>2</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup> (1. 京大院工、2. JST ERATO、3. 京大白眉センター)

◆ 英語

13:40 ~ 14:00

[H931-3pm-03]

## 疾患バイオマーカーを検出して光るシンセティックセルのボトムアップ構築

○筒井 啓太<sup>1</sup>、吉川 優<sup>1</sup>、松浦 友亮<sup>2</sup>、築地 真也<sup>1</sup> (1. 名工大院工、2. 東工大地球生命研)

◆ 日本語

14:00 ~ 14:20

[H931-3pm-04]

## メンブレンコンタクト動態を可視化する分割型蛍光プローブの開発

阿喰 萌香<sup>1</sup>、○吉川 優<sup>1</sup>、筒井 啓太<sup>1</sup>、中津 史<sup>2</sup>、築地 真也<sup>1</sup> (1. 名工大院工、2. 新潟大院医歯)

◆ 日本語

14:30 ~ 14:50

[H931-3pm-05]

## SLIPTによるマウス内シグナル操作

○田原 海<sup>1</sup>、吉川 優<sup>1</sup>、高倉 加奈子<sup>2</sup>、寺井 健太<sup>3</sup>、松田 道行<sup>2,3</sup>、築地 真也<sup>1</sup> (1. 名工大院工、2. 京大院生命、3. 京大院医)

◆ 英語

14:50 ~ 15:10

[H931-3pm-06]

## 環状ペプチドヘテロダイマーリガンド探索系の構築

○大野 湧仁<sup>1</sup>、Alexander Vinogradov<sup>1</sup>、菅 裕明<sup>1</sup> (1. 東京大学)

◆ 英語

15:10 ~ 15:30

[H931-3pm-07]

## 人工ヘムタンパク質モデル錯体による水中での硫化水素の捕捉および硫化水素中毒解毒剤としての応用

○中上 敦貴<sup>1</sup>、堀谷 正樹<sup>2</sup>、北岸 宏亮<sup>1</sup> (1. 同志社大学、2. 佐賀大学)

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 H934(9号館 [3階] 934)

**[H934-3pm] 17. 生体機能関連化学・バイオテクノロジー**

座長：梶原 康宏、珠玖 仁

## ◆ 英語

13:00 ~ 13:20

[H934-3pm-01]

## 抗体修飾による小児髄髄芽腫を対象とした薬物輸送システムの開発

○渡邊 隆義<sup>1</sup>、水野 隼斗<sup>2</sup>、乗松 純平<sup>1</sup>、Cabral Horacio<sup>1</sup>、川内 大輔<sup>2</sup>、安楽 泰孝<sup>3</sup> (1. 東京大学、2. 国立精神・神経医療研究センター、3. 東京工業大学)

## ◆ 英語

13:20 ~ 13:40

[H934-3pm-02]

## Synthesis of Shortwave-Infrared (SWIR) Organic Fluorescent Probes for Deep Tissue Molecular Imaging of Breast Cancer.

○Mahadeva Swamy Makanahalli Madegowda<sup>1</sup>, Yuta Murai<sup>1</sup>, Setsuko Tsuboi<sup>2</sup>, Aravind Kanda Swamy<sup>1</sup>, Takashi Jin<sup>2</sup>, Kenji Monde<sup>1</sup> (1. Faculty of Advanced Life Science, Hokkaido University, 2. Center for Biosystems Dynamics Research, RIKEN)

## ◆ 日本語

13:40 ~ 14:00

[H934-3pm-03]

## 表皮再生促進効果を期待した薬剤ラッピング高接着性ナノシートの創製と機能評価

○芝 耀汰<sup>1</sup>、谷神 絃太<sup>1</sup>、布山 忠裕<sup>1</sup>、住吉 秀明<sup>2</sup>、稲垣 豊<sup>2</sup>、岡村 陽介<sup>1,3</sup> (1. 東海大院工、2. 東海大医、3. 東海大マイクロ・ナノ研)

## ◆ 英語

14:00 ~ 14:20

[H934-3pm-04]

## アレルギーの根本治療を目指した鼻粘膜へのリポソームDDSの開発

○佳月 李<sup>1</sup>、森田 直樹<sup>2</sup>、三浦 理紗子<sup>1</sup>、木村 祐<sup>1</sup>、新藏 礼子<sup>2</sup>、近藤 輝幸<sup>1</sup> (1. 京大院工、2. 東大定量生命科学研究所)

## ◆ 英語

14:30 ~ 14:50

[H934-3pm-05]

## 新規サンプリング法を用いた核磁気共鳴法による糖と水の相互作用解析

○森口 達也<sup>1</sup>、真木 勇太<sup>1,2</sup>、岡本 亮<sup>1,2</sup>、梶原 康宏<sup>1,2</sup> (1. 阪大院理、2. 阪大院理フォアフロント研究センター)

## ◆ 日本語

14:50 ~ 15:10

[H934-3pm-06]

## 生体模倣システムのための多孔膜電極デバイス

○伊野 浩介<sup>1</sup>、宇田川 喜信<sup>1</sup>、阿部 博弥<sup>1</sup>、珠玖 仁<sup>1</sup> (1. 東北大学)

## ◆ 英語

15:10 ~ 15:30

[H934-3pm-07]

## 出芽酵母の画像活性分取におけるAI画像解析法の有効性評価

林 実加<sup>1</sup>、大貫 慎輔<sup>1</sup>、Yating Tsai<sup>1</sup>、〇丁 天本<sup>1</sup>、磯崎 瑛宏<sup>2,1</sup>、大矢 禎一<sup>1</sup>、合田 圭介<sup>1,3,4,5</sup> (1. 東京大学、2. 立命館大学、3. カリフォルニア大学ロサンゼルス校、4. 武漢大学、5. CYBO)

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 H936(9号館 [3階] 936)

## [H936-3vn] 17. 生体機能関連化学・バイオテクノロジー

座長：小野田 晃、神谷 典穂

英語

15:55 ~ 16:15

[H936-3vn-01]

### Immobilization of Proteins on Triazolecarbaldehyde-linked Polymer Resin

〇Shiyu Wang<sup>1</sup>, Akira Onoda<sup>1,2</sup> (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

英語

16:15 ~ 16:35

[H936-3vn-02]

### Enhancing Enzymatic Breakdown of Polyethylene Terephthalate by Cutinase Tethering Hydrophobic Moiety at N-terminus

〇Md Sadikur Rahman Shuvo<sup>1</sup>, Joel Muyomba<sup>1</sup>, Akira Onoda<sup>1,2</sup> (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

英語

16:35 ~ 16:55

[H936-3vn-03]

### Expanding the Substrate Specificity of Alcohol Dehydrogenase from *Geotrichum candidum* NBRC 4597 toward Diaryl Ketones by Site-directed Mutagenesis

〇Zhongyao Tang<sup>1</sup>, Yuuki Takagi<sup>1</sup>, Afifa Ayu Koesoema<sup>1</sup>, Tomoko Matsuda<sup>1</sup> (1. Tokyo Institute of Technology)

英語

16:55 ~ 17:15

[H936-3vn-04]

### キチン粉末を利用したアフィニティ精製手法の開発：立体選択的シクロプロパン化反応の触媒として働くヘムタンパク質探索への応用

〇竹内 康基<sup>1</sup>、岩木 元直<sup>1</sup>、加藤 俊介<sup>1</sup>、林 高史<sup>1</sup> (1. 大阪大学)

アカデミックプログラム [B講演] | 18. 高分子：口頭B講演

2024年3月20日(水) 9:00 ~ 11:10 D342(3号館 [4階] 342)

**[D342-3am] 18. 高分子**

座長：小林 裕一郎、廣瀬 大祐

## ◆ 日本語

9:00 ~ 9:20

[D342-3am-01]

スルホニルホスホロアミド酸構造を側鎖に有する脂溶性らせん状ポリ(フェニルアセチレン)のらせん誘起と静的記憶

○西川 裕基<sup>1</sup>、惣名 翔大<sup>1</sup>、廣瀬 大祐<sup>2</sup>、前田 勝浩<sup>2,3</sup> (1. 金沢大院新学術、2. 金沢大院自然、3. 金沢大WPI-NanoLSI)

## ◆ 日本語

9:20 ~ 9:40

[D342-3am-02]

超分子硫黄含有ポリマーの合成とその特性

○小林 裕一郎<sup>1,2,3</sup>、山岸 佑輝<sup>1</sup>、北野 大輝<sup>1</sup>、堀口 顕義<sup>1</sup>、西村 龍人<sup>1</sup>、橋本 駿<sup>1</sup>、神岡 龍之介<sup>1</sup>、山口 浩靖<sup>1</sup> (1. 阪大院理、2. ICS-OTRI、3. 阪大FRC)

## ◆ 英語

9:40 ~ 10:00

[D342-3am-03]

高効率環状ポリマー合成—シクロデキストリン誘導体との擬ポリロタキサン形成に基づくによる高濃度ポリエチレングリコールの環化反応—

○シャオ チュンリン<sup>1</sup>、辻 佳弘<sup>1</sup>、小林 裕一郎<sup>1</sup>、原田 明<sup>1</sup>、山口 浩靖<sup>1</sup> (1. 阪大)

## ◆ 日本語

10:10 ~ 10:30

[D342-3am-04]

金属酵素の活性制御を利用した環境適応性人工細胞の創製

○東 小百合<sup>1</sup>、Taniya Chakraborty<sup>2</sup>、Yanjun Zheng<sup>3</sup>、Azadeh Alavizargar<sup>3</sup>、Andreas Heuer<sup>3</sup>、Seraphine Wegner<sup>3</sup> (1. 岐阜大学、2. マックスプランク医学研究所、3. ミュンスター大学)

## ◆ 英語

10:30 ~ 10:50

[D342-3am-05]

Fabrication of chitosan nanofiber-based sponge materials using freeze-thaw method

○H.P.M. PANCHABASHINI<sup>1</sup>、Akihide Sugawara<sup>1</sup>、Hiroshi Uyama<sup>1</sup> (1. Osaka University)

## ◆ 英語

10:50 ~ 11:10

[D342-3am-06]

Application of Hierarchically Porous Chitosan Monolith on Enzyme Immobilization

○HAJILI EMIL<sup>1</sup> (1. Osaka University)

アカデミックプログラム [B講演] | 18. 高分子：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 D342(3号館 [4階] 342)

**[D342-3pm] 18. 高分子**

座長：Li Feng、西川 剛

## ◆ 英語

13:00 ~ 13:20

[D342-3pm-01]

イソプロペニルボロン酸エステルの制御ラジカル重合と解重合

○金澤 共晃<sup>1</sup>、西川 剛<sup>1</sup>、大内 誠<sup>1</sup> (1. 京都大学大学院)

## ◆ 英語

13:20 ~ 13:40

[D342-3pm-02]

活性化エステルを側鎖に有するアクリレートとジエンのラジカル交互共重合と後反応による光分解性高分子の精密合成

○黒田 啓太<sup>1</sup>、大内 誠<sup>1</sup> (1. 京都大学)

## ◆ 日本語

13:40 ~ 14:00

[D342-3pm-03]

ラジカル共重合反応の電子スピン共鳴分光(ESR)法による詳細な観測

○梶原 篤<sup>1</sup> (1. 奈良教育大学)

## ◆ 日本語

14:00 ~ 14:20

[D342-3pm-04]

MOFの一次元ナノ細孔での非対称二重鎖高分子の合成

○亀谷 優樹<sup>1</sup>、山口 麟太郎<sup>1</sup>、植村 卓史<sup>1</sup> (1. 東京大学)

## ◆ 日本語

14:30 ~ 14:50

[D342-3pm-05]

重合度が規定された精密アクリルオリゴマーの合成と側鎖変換反応

○辻 爽太郎<sup>1</sup>、永井 薫子<sup>1</sup>、小野 利和<sup>1,2</sup>、嵐越 恒<sup>1</sup>、星野 友<sup>1,2</sup> (1. 九大院工、2. 九大分子システムセ)

## ◆ 英語

14:50 ~ 15:10

[D342-3pm-06]

種々の置換基を導入した3-メチレンフタリド誘導体の重合と分解、モノマー再生

○千葉 耀太<sup>1</sup>、高坂 泰弘<sup>1,2,3</sup> (1. 信州大学繊維学部、2. 信州大学先鋭材料研究所、3. JSTさきがけ)

## ◆ 日本語

15:10 ~ 15:30

[D342-3pm-07]

植物原料由来のケミカルリサイクル可能な非天然型高分子多糖類の合成

○リ ホウ<sup>1</sup>、水上 湧太<sup>2</sup>、箕 祐人<sup>2</sup>、田島 健次<sup>1</sup>、山本 拓矢<sup>1</sup>、磯野 拓也<sup>1</sup>、佐藤 敏文<sup>1,3</sup> (1. 北海道大学・工学研究院、2. 北海道大学・総合化学院、3. 北海道大学・ICReDD List-PF)

アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 会場 A1442(14号館 [4階] 1442)

**[A1442-3am] 19. コロイド・界面化学**

座長：三友 秀之、石田 拓也

◆ 日本語

9:00 ~ 9:20

[A1442-3am-01]

## 金属間化合物ナノ粒子の局在表面プラズモン共鳴

○竹熊 晴香<sup>1</sup>、佐藤 良太<sup>1</sup>、飯田 健二<sup>2</sup>、川脇 徳久<sup>3</sup>、治田 充貴<sup>1</sup>、寺西 利治<sup>1</sup> (1. 京大、2. 北大、3. 東理大)

◆ 日本語

9:20 ~ 9:40

[A1442-3am-02]

## プラズモニック規則合金ナノ粒子群の創製

○佐藤 良太<sup>1</sup>、竹熊 晴香<sup>1</sup>、飯田 健二<sup>2</sup>、川脇 徳久<sup>3</sup>、治田 充貴<sup>1</sup>、寺西 利治<sup>1</sup> (1. 京大化研、2. 北大触媒研、3. 東理大理)

◆ 日本語

9:40 ~ 10:00

[A1442-3am-03]

## 反応性粗視化分子動力学法およびトポロジカルデータ解析を用いたシリカ凝集過程の検討

○笹原 茂生<sup>1</sup>、上條 由人<sup>1</sup>、尾関 寿美男<sup>2</sup> (1. 富士化学株式会社、2. 信州大学)

◆ 日本語

10:00 ~ 10:20

[A1442-3am-04]

## ケイ酸ソーダ水溶液のゲル化にともなうシリカ骨格構造の形成過程

○上條 由人<sup>1</sup>、尾関 寿美男<sup>2</sup>、笹原 茂生<sup>1</sup> (1. 富士化学(株)、2. 信州大)

◆ 日本語

10:30 ~ 10:50

[A1442-3am-05]

## インジウムアンチモン量子ドットの湿式合成と短波長赤外フォトダイオードへの応用

○白幡 直人<sup>1,2,3</sup>、Subhashri Chatterjee<sup>1,2</sup> (1. 物質・材料研究機構、2. 北大、3. 中大)

◆ 日本語

10:50 ~ 11:10

[A1442-3am-06]

## サイズに依存したCdTeナノ粒子の発光性能への欠陥の影響

○高畑 遼<sup>1,2</sup>、猿山 雅亮<sup>1</sup>、山添 誠司<sup>3</sup>、寺西 利治<sup>1,2</sup> (1. 京大化研、2. 京大院理、3. 都立大院理)

◆ 英語

11:10 ~ 11:30

[A1442-3am-07]

## Au ナノ粒子および量子ドットをコアとした有機無機ハイブリッドデンドリマーによる交互積層超格子

○佐藤 梨奈<sup>1</sup>、谷地 昶拓<sup>1</sup>、松原 正樹<sup>2,3</sup>、陶山 めぐみ<sup>1</sup>、三友 秀之<sup>4</sup>、玉田 薫<sup>5</sup>、村松 淳司<sup>1,2</sup>、蟹江 澄志<sup>1,2</sup> (1. 東北大多元研、2. 東北大SRIS、3. 仙台高専、4. 北大電子研、5. 九大先導研)

アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2024年3月20日(水) 9:30 ~ 11:20 会場 A1443(14号館 [4階] 1443)

**[A1443-3am] 19. コロイド・界面化学**

座長：上田 貴洋、二村 竜祐

日本語

9:30 ~ 9:50

[A1443-3am-01]

## 水素発生反応ナノ構造触媒電極の活性評価

○佐藤 大樹<sup>1</sup>、田尾 和花子<sup>2</sup>、福島 知宏<sup>3</sup>、村越 敬<sup>3</sup> (1. 北大院総化、2. 北大理、3. 北大院理)

日本語

9:50 ~ 10:10

[A1443-3am-02]

## 電子移動反応速度における強結合状態形成の影響

林 峻大<sup>1</sup>、○福島 知宏<sup>2</sup>、村越 敬<sup>2</sup> (1. 北大院総化、2. 北大院理)

英語

10:10 ~ 10:30

[A1443-3am-03]

## Fabrication of Titanium Dioxide Nanocatalyst within Carbon nanotubes for High Thermal Stability and UV/Visible light Photocatalytic Activity

○Smita Dnyandeo Takawane<sup>1</sup>, Masatoshi Miyamoto<sup>1</sup>, Takumi Watanabe<sup>1</sup>, Tomonori Ohba<sup>1</sup> (1. Chiba University)

日本語

10:40 ~ 11:00

[A1443-3am-04]

## 匂い分子のリン脂質膜への吸着脱離に基づく動的応答

○四元 まい<sup>1</sup>、松尾 宗征<sup>2,1</sup>、中田 聡<sup>1</sup> (1. 広島大学、2. 東京大学)

日本語

11:00 ~ 11:20

[A1443-3am-05]

単層カーボンナノチューブによる皮膚からのCO<sub>2</sub>の非侵襲・選択的検出Preety Ahuja<sup>1</sup>、Sanjeev Ujjain<sup>1</sup>、瓜田 幸幾<sup>2</sup>、森口 勇<sup>2</sup>、古瀬 あゆみ<sup>1</sup>、○金子 克美<sup>1</sup> (1. 信州大学先鋭材料研究所、2. 長崎大学工学部)

アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 A1442(14号館 [4階] 1442)

**[A1442-3pm] 19. コロイド・界面化学**

座長：今岡 享稔、佐藤 良太

## ◆ 英語

13:00 ~ 13:20

[A1442-3pm-01]

Enhancing Photoluminescence of  $\text{Ag}_8\text{GeS}_6$  Quantum Dots through Controlled ZnS Shell Thickness for Near-IR *In Vivo* Bioimaging

○Nurmanita Rismaningsih<sup>1</sup>, Junya Kubo<sup>1</sup>, Tatsuya Kameyama<sup>1</sup>, Norikazu Fujihira<sup>2</sup>, Hiroshi Yukawa<sup>1</sup>, Yoshinobu Baba<sup>1</sup>, Tsukasa Torimoto<sup>1</sup> (1. Graduate School of Engineering, Nagoya University, 2. Murata Manufacturing Co., Ltd.)

## ◆ 日本語

13:20 ~ 13:40

[A1442-3pm-02]

高分子コーティングをテンプレートした $\text{CeO}_2$ 粒子を用いた球状のコロイド結晶の作製及び評価

○姜 楊楠<sup>1</sup>、竹岡 敬和<sup>1</sup>、大貫 良輔<sup>2</sup>、吉岡 伸也<sup>2</sup>、白井 綾野<sup>3</sup>、桑折 道清<sup>3</sup> (1. 名古屋大学大学院工学研究科、2. 東京理科大学創域理工学研究科、3. 千葉大学大学院工学研究院)

## ◆ 日本語

13:40 ~ 14:00

[A1442-3pm-03]

## 微粒子界面における核酸塩基光反応を利用した刺激応答性カプセルの合成

○北山 雄己哉<sup>1</sup>、堂阪 あかり<sup>1</sup>、芝 向日葵<sup>1</sup>、弓場 英司<sup>1</sup>、原田 敦史<sup>1</sup> (1. 阪公大)

## ◆ 日本語

14:10 ~ 14:30

[A1442-3pm-04]

## 裁断化ナノファイバーからなる新規異方性分散体の創製と凝集比濁用担体への応用

○横瀬 颯人<sup>1</sup>、市原 直弥、岡村 陽介<sup>1,2</sup> (1. 東海大院工、2. 東海大マイクロ・ナノ研)

## ◆ 日本語

14:30 ~ 14:50

[A1442-3pm-05]

## 無機ナノシートの自発的集合による超分子的ポリマーの作製と機能探索

上野 夏子<sup>1</sup>、海老名 保男<sup>2</sup>、佐々木 高義<sup>2</sup>、○佐野 航季<sup>1,3</sup> (1. 信州大、2. 物材機構、3. JSTさきがけ)

## ◆ 日本語

14:50 ~ 15:10

[A1442-3pm-06]

## 一次元ナノコロイドの配向・自己組織化による無機超分子ナノシート

○小川 大輔<sup>1</sup>、佐野 航季<sup>1,2</sup> (1. 信州大、2. JSTさきがけ)

## ◆ 日本語

15:10 ~ 15:30

[A1442-3pm-07]

## コロイド結晶をモデルとしたエントロピー生成最大原理の実験的検証

○對馬 琴梨<sup>1</sup>、伴 貴彦<sup>2</sup>、並河 英紀<sup>3</sup> (1. 山大院理工、2. 阪大院理工、3. 山形大理)



アカデミックプログラム [B講演] | 20. 材料化学—基礎と応用：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 C443(4号館 [4階] 443)

**[C443-3am] 20. 材料化学—基礎と応用**

座長：竹谷 純一、齋藤 健一

## 日本語

9:00 ~ 9:20

[C443-3am-01]

難燃剤の組合せ効果解析法及びそれを用いた難燃性高分子設計法

○倉地 育夫<sup>1</sup> (1. 株式会社ケンシュウ)

## 英語

9:20 ~ 9:40

[C443-3am-02]

Establishment of a universal functional tuning strategy via homogeneous alkyl- $\pi$  liquid blending○Zhenfeng Guo<sup>1,2</sup>, Chengjun Pan<sup>3</sup>, Akira Shinohara<sup>2</sup>, Takashi Nakanishi<sup>1,2</sup> (1. Hokkaido University, 2. National Institute for Materials Science (NIMS), 3. Shenzhen University)

## 英語

9:40 ~ 10:00

[C443-3am-03]

プロトン共役電子移動を用いた有機半導体キャリア密度の精密制御

○石井 政輝<sup>1,2</sup>、山下 侑<sup>2,3</sup>、渡邊 峻一郎<sup>3</sup>、竹谷 純一<sup>2,3</sup>、有賀 克彦<sup>1,2,3</sup> (1. 東理大、2. 物材研究機構、3. 東大)

## 英語

10:00 ~ 10:20

[C443-3am-04]

Temporarily Controllable Dual-Emission from Gold(I)-NHC Complex with Flexible Alkoxy Chain.

○Arushi Rawat<sup>1</sup>, Siddhant Kumar<sup>1</sup>, Kohsuke Matsumoto<sup>1</sup>, Ganesan Prabusankar<sup>2</sup>, Osamu Tsutsumi<sup>1</sup> (1. Ritsumeikan University, 2. Indian Institute of Technology Hyderabad)

## 日本語

10:30 ~ 10:50

[C443-3am-05]

キラル側鎖を有するドナー・アクセプター連結分子の機能評価

○関 淳志<sup>1,2</sup>、土井 早雲<sup>2</sup>、青木 健一<sup>1,2</sup> (1. 東理大、2. 東理大院)

## 英語

10:50 ~ 11:10

[C443-3am-06]

色素ドープ液晶の非線形分子配向変化：液晶分子構造に依存した高感度光応答

○横田 純輝<sup>1</sup>、相沢 美帆<sup>1,2</sup>、久野 恭平<sup>1</sup>、久保 祥一<sup>1</sup>、山口 留美子<sup>3</sup>、穴戸 厚<sup>1</sup> (1. 東工大化生研、2. JSTさきがけ、3. 秋田大院理工)

## 日本語

11:10 ~ 11:30

[C443-3am-07]

SOFT法によるDonor-Acceptor型共役系ポリマーの配向膜作製：*in-situ*時間分解分光による配向ダイナミクス

○廣田 天丸<sup>1</sup>、坂田 俊樹<sup>2</sup>、齋藤 健一<sup>1,2,3</sup> (1. 広島大院先進理工、2. 広島大院理、3. 広島大自然セ)

アカデミックプログラム [B 講演] | 20. 材料化学—基礎と応用：口頭B講演

2024年3月20日(水) 13:00 ~ 14:40 C442(4号館 [4階] 442)

## [C442-3pm] 20. 材料化学—基礎と応用

座長：深津 亜里紗、速水 真也

英語

13:00 ~ 13:20

[C442-3pm-01]

液晶性コロイド前駆体を用いた自立性酸化亜鉛材料のナノ構造制御

○三上 喬弘<sup>1</sup>、加藤 利喜<sup>1</sup>、細川 済弘<sup>1</sup>、宮元 展義<sup>2</sup>、加藤 隆史<sup>1</sup> (1. 東大院工、2. 福岡工大)

英語

13:20 ~ 13:40

[C442-3pm-02]

原グラフェン酸化物負荷三元過渡金属硫化物量子ドットとしての新規デュアルバンド電磁波吸収体

○Cai Ze<sup>1</sup>、真也 速水<sup>1</sup>、Md. Saidul Islam<sup>1</sup> (1. 熊本大学)

日本語

13:40 ~ 14:00

[C442-3pm-03]

対カチオン制御による温度応答性酸化グラフェンの作製とその転移温度制御

○近藤 翔麻<sup>1</sup>、西村 智貴<sup>1</sup>、仁科 勇太<sup>2</sup>、佐野 航季<sup>1,3</sup> (1. 信州大、2. 岡山大、3. JSTさきがけ)

英語

14:00 ~ 14:20

[C442-3pm-04]

機械刺激応答特性を示す発光性分子材料の結晶学および力学パラメーター

○平井 悠一<sup>1</sup>、中西 貴之<sup>1</sup>、武田 隆史<sup>1</sup>、大村 孝仁<sup>1</sup> (1. 物質・材料研究機構 (NIMS))

日本語

14:20 ~ 14:40

[C442-3pm-05]

天然由来DNAと各種金属イオンの特異的な相互作用により架橋された多機能性ハイドロゲルの構造解析

○深津 亜里紗<sup>1</sup>、栗栖 沙理<sup>2</sup>、倉本 七夏海<sup>1</sup>、吉田 和加<sup>1</sup>、安井 伊吹<sup>1</sup>、野村 佳澄<sup>2</sup>、藤原 照巳<sup>2</sup>、岡田 健司<sup>1</sup>、高橋 雅英<sup>1</sup> (1. 大阪公立大学、2. 大阪府立大学)

アカデミックプログラム [B講演] | 20. 材料化学—基礎と応用：口頭B講演

2024年3月20日(水) 15:55 ~ 16:55 会場 C443(4号館 [4階] 443)

**[C443-3vn] 20. 材料化学—基礎と応用**

座長：巢山 慶太郎、立石 友紀

## ◆ 日本語

15:55 ~ 16:15

[C443-3vn-01]

## MOP-酵素複合体の高機能化に向けた混合タンパク質アプローチ

○神崎 友理<sup>1</sup>、南 良友<sup>1</sup>、ルウェ バンジャマン<sup>1</sup>、大場 正昭<sup>1</sup> (1. 九州大学)

## ◆ 英語

16:15 ~ 16:35

[C443-3vn-02]

## 刺激応答性粒状ゲルを利用した4Dバイオプリンティング

○中村 圭佑<sup>1</sup>、Nikolas Di Caprio<sup>1</sup>、Jason Burdick<sup>1</sup> (1. コロラド大学ボルダー校)

## ◆ 英語

16:35 ~ 16:55

[C443-3vn-03]

短鎖エラスチン様ペプチド(FPGVG)<sub>n</sub>-アゾベンゼン複合体の光照射による自己集合能の制御○巢山 慶太郎<sup>1</sup>、前田 衣織<sup>2</sup>、野瀬 健<sup>1</sup> (1. 九州大学基幹教育院、2. 九州工業大学情報工学研究院)

アカデミックプログラム [B講演] | 21. エネルギーとその関連化学，地球・宇宙化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:10 会場 A1454(14号館 [5階] 1454)

**[A1454-3pm] 21. エネルギーとその関連化学，地球・宇宙化学**

座長：栄長 泰明、神谷 和秀

◆ 日本語

13:00 ~ 13:20

[A1454-3pm-01]

## 重アルカリ金属を用いた金属空気電池の正極反応

○多々良 涼一<sup>1</sup>、藤本 竜成<sup>1</sup>、五十嵐 大輔<sup>1</sup>、保坂 知宙<sup>1</sup>、駒場 慎一<sup>1</sup> (1. 東京理科大学)

◆ 日本語

13:20 ~ 13:40

[A1454-3pm-02]

CO<sub>2</sub>を活物質としたレドックスフロー電池の開発○兼賀 量一<sup>1</sup>、山本 旭<sup>2</sup>、吉田 寿雄<sup>2</sup>、大平 昭博<sup>1</sup> (1. 産業技術総合研究所、2. 京都大学大学院人間・環境学研究科)

◆ 日本語

13:40 ~ 14:00

[A1454-3pm-03]

## テトラシアフルバレンを基盤とする金属有機構造体の電子貯蔵性能

○若松 勝洋<sup>1</sup>、古野 壮一郎<sup>1</sup>、吉川 浩史<sup>1</sup> (1. 関西学院大学)

◆ 英語

14:10 ~ 14:30

[A1454-3pm-04]

炭酸緩衝液由来CO<sub>2</sub>の電解還元によるマルチカーボン化合物の高速・高選択合成○井上 明哲<sup>1</sup>、原田 隆史<sup>1</sup>、中西 周次<sup>1</sup>、神谷 和秀<sup>1</sup> (1. 阪大院基礎工太陽エネ研)

◆ 日本語

14:30 ~ 14:50

[A1454-3pm-05]

ダイヤモンド電極によるCO<sub>2</sub>の電解還元におけるファインバブルの影響○富崎 真衣<sup>1</sup>、櫻井 大斗<sup>2</sup>、間瀬 暢之<sup>2</sup>、栄長 泰明<sup>3</sup> (1. 九大I2CNER、2. 静大、3. 慶大理工)

◆ 日本語

14:50 ~ 15:10

[A1454-3pm-06]

## 10 mV/K級の熱起電力を発現する熱電キャパシタ

○堀家 匠平<sup>1,2</sup>、衛 慶碩<sup>2</sup>、桐原 和大<sup>2</sup>、向田 雅一<sup>2</sup>、小柴 康子<sup>1</sup>、石田 謙司<sup>1,3</sup> (1. 神戸大、2. 産総研、3. 九大)

アカデミックプログラム [B講演] | 02. 理論化学・情報化学・計算化学：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 H937(9号館 [3階] 937)

**[H937-3am] 02. 理論化学・情報化学・計算化学**

座長：杉山 佳奈美、石田 豊和

## ◆ 日本語

9:00 ~ 9:20

[H937-3am-01]

自己組織化マップと遷移状態モチーフによる有機化学反応の幾何学的分類

○松尾 勇二郎<sup>1</sup>、山口 徹<sup>1</sup>、船津 公人<sup>2</sup>、堀 憲次<sup>1,3,4</sup> (1. 株式会社TSテクノロジー、2. 奈良先端科学技術大学院大学、3. 国立開発研究法人産業総合技術研究所、4. 山口大学)

## ◆ 日本語

9:20 ~ 9:40

[H937-3am-02]

有限一次元分子集合系での一重項分裂過程と相関三重項対励起子の空間分布に関する理論研究

○宮本 孟<sup>1</sup>、岡田 健治<sup>1</sup>、岸 亮平<sup>1,2,3,4</sup>、北河 康隆<sup>1,2,3,4,5</sup> (1. 阪大院基礎工、2. 阪大QIQB、3. 阪大ICS-OTRI、4. 阪大RCSEC、5. 阪大CSRN)

## ◆ 日本語

9:40 ~ 10:00

[H937-3am-03]

ジアリールエテン誘導体への光照射による溶解度変化

○中村 優斗<sup>1</sup>、沈 君偉<sup>1</sup>、深港 豪<sup>1</sup>、原田 祐希<sup>1</sup>、中村 振一郎<sup>1</sup>、渡邊 智<sup>1</sup>、大谷 涼真<sup>1</sup> (1. 熊本大学)

## ◆ 日本語

10:00 ~ 10:20

[H937-3am-04]

次元縮約法の選択に対する低次元反応空間構築の性能検証

○堤 拓朗<sup>1</sup>、小野 ゆり子<sup>2</sup>、武次 徹也<sup>1,2</sup> (1. 北大院理、2. 北大WPI-ICReDD)

10:20 ~ 10:30

休憩

## ◆ 日本語

10:30 ~ 10:50

[H937-3am-05]

デジタルアニールを活用したヘキサベンゾコロネンのハロゲン置換による特性最適化

○橋口 和弘<sup>1</sup>、丸尾 昭人<sup>1</sup>、添田 武志<sup>1</sup>、實宝 秀幸<sup>1</sup> (1. 富士通株式会社)

## ◆ 日本語

10:50 ~ 11:10

[H937-3am-06]

高压氷における相転移の量子効果

○桑畑 和明<sup>1</sup>、立川 仁典<sup>1</sup> (1. 横浜市立大学)

## ◆ 日本語

11:10 ~ 11:30

[H937-3am-07]

## 酵素反応における基底状態不安定化仮説：バイオマス分解酵素 GH11-Xylanase の反応機構について

○石田 豊和<sup>1</sup>、Jerry Parks<sup>2</sup>、Jeremy Smith<sup>2</sup> (1. 国立研究開発法人 産業技術総合研究所、2. オークリッジ国立研究所)

---

## 自己組織化マップと遷移状態モチーフによる有機化学反応の幾何学的分類

(株式会社 TS テクノロジー<sup>1</sup>・奈良先端科学技術大学院大学<sup>2</sup>・国立開発研究法人産業総合技術研究所<sup>3</sup>・山口大学<sup>4</sup>) ○松尾 勇二郎<sup>1</sup>・山口 徹<sup>1</sup>・船津 公人<sup>2</sup>・堀 憲次<sup>1,3,4</sup>  
 Geometric Classification of Organic Chemical Reactions by Self-organizing maps and Transition State Motifs (<sup>1</sup>Transition State Technology Company Limited, <sup>2</sup>Nara Institute of Science and Technology, <sup>3</sup>National Institute of Advanced Industrial Science and Technology, <sup>4</sup>Yamaguchi University) ○Yujiro Matsuo<sup>1</sup>, Toru Yamaguchi<sup>1</sup>, Kimito Funatsu<sup>2</sup>, Kenji Hori<sup>1,3,4</sup>

We have been developing a database of transition states (TS) of chemical reactions obtained by quantum chemical calculations (TSDB). From our experience, we have found that the geometric patterns of the reaction centers of TS structures (TS motifs) of one name reaction are similar to those of different ones in many cases. This finding leads us to expect that the number of TS motifs is less than that of name reactions. If TS can be classified by these geometric features, TS motifs with different name reactions could be available as those of other name reactions. We selected 13 features for 103 TS motifs (15 reactions) and created Kohonen maps. The results suggested that TS structures classified are consistent with our chemical senses. It is particularly interesting to note that several name reactions are classified in the same cluster. We will further report the results of increasing the type, number, and features of name reactions. These results were obtained as a result of a commissioned work (JPNP19004) by the New Energy and Industrial Technology Development Organization (NEDO).

**Keywords :** *quantum chemical calculations, Transition State Database(TSDB), Transition state motifs, Kohonen's self-organizing map*

これまで我々は量子化学計算によって求められた化学反応の遷移状態(TS)を集積したデータベース(TSDB)の開発に取り組んできた。その経験から、TS構造の反応中心の幾何学的パターン(TSモチーフ)は、ある反応名のTS構造が、異なる反応名のTS構造と類似する例が多く見られた。この知見は、TSモチーフの種類は、既知の人名反応数よりも少ないことを予想させる。ここで、TSモチーフを幾何学的特徴により分類できれば、反応名が異なる反応のTSモチーフが他の人名反応のTSモチーフとして利用可能となり得る。我々は、103個(15反応)のTSモチーフについて13種の特徴量を選定し、Kohonenマップを作成した。この研究により、TSモチーフの幾何学的特徴を元に、化学的な感覚と一致する分類ができることが示唆された。特に、いくつかの人名反応が同じクラスタに分類されていることは興味深い。当日は更に人名反応の種類や数、特徴量を増やした結果について報告する。この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構(NEDO)の委託業務(JPNP19004)の結果得られた。

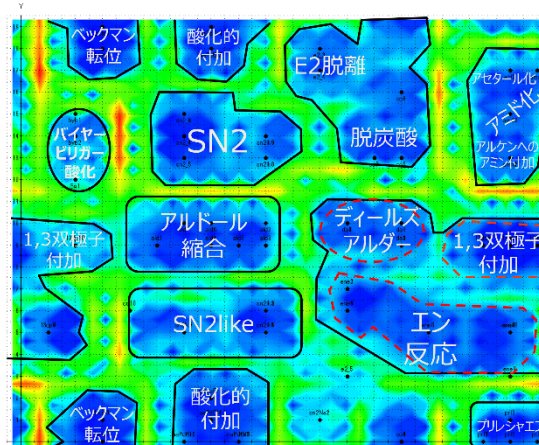


図 1. Kohonen マップによる TS の分類

## 有限一次元分子集合系での一重項分裂過程と相関三重項対励起子の空間分布に関する理論研究

(阪大院基礎工<sup>1</sup>・阪大 QIQB<sup>2</sup>・阪大 RCSEC<sup>3</sup>・阪大 ICS-OTRI<sup>4</sup>・阪大 SRN-OTRI<sup>5</sup>) ○  
宮本 孟<sup>1</sup>・岡田 健治<sup>1</sup>・岸 亮平<sup>1,2,3,4</sup>・北河 康隆<sup>1,2,3,4,5</sup>

Theoretical Study on the Singlet Fission Process and Spatial Distributions of Triplet-Pair Excitons in Finite-Sized One-dimensional Molecular Aggregates

(<sup>1</sup>Graduate School of Engineering Science, Osaka University, <sup>2</sup>QIQB, Osaka University, <sup>3</sup>RCSEC, Osaka University, <sup>4</sup>ICS-OTRI, Osaka University, <sup>5</sup>SRN-OTRI, Osaka University)

○Hajime Miyamoto,<sup>1</sup> Kenji Okada,<sup>1</sup> Ryohei Kishi,<sup>1,2,3,4</sup> Yasutaka Kitagawa,<sup>1,2,3,4,5</sup>

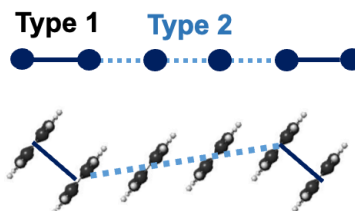
Singlet Fission (SF) is photophysical process in which one singlet exciton ( $S_1$ ) is converted to two triplet excitons ( $T_1$ ) in molecular aggregates. Recently, control of triplet exciton pair states (TT) as the intermediate states of SF has been examined from the viewpoint of the energy transfer and the control of TT spin state. In this study, we discussed correlation between structure-SF property in finite-sized one-dimensional molecular aggregate in which triplet exciton transfer integral and spatial distribution of triplet pair states are taken into account.

**Keywords :** Singlet Fission; Molecular Aggregate; Exciton Dynamics; Quantum Master Equation

一重項分裂(SF)は、光照射により生じた一重項励起子( $S_1$ )が二つの三重項励起子( $T_1$ )に変換される現象であり、有機太陽電池への応用可能性が指摘されている<sup>1)</sup>。近年、SF の中間体として生じる相関三重項対励起子(TT)状態の空間的分離過程に関する研究が、エネルギー移動やスピン状態の制御の観点から行われている<sup>2)</sup>。本研究では、三重項励起子対の空間分布に影響を与える因子の一つである分子の配列パターンに着目し、分子集合系の部分的な構造や分子間相互作用の変化が TT 分離過程も考慮した SF ダイナミクスへ与える影響について検討した。

モデル系として、Fig. 1 のような 2 種類の分子間電子カップリング(**Type 1**, **Type 2**)で特徴づけられる一次元  $N$  量体モデルを考えた。フレンケル励起子(FE)、電荷移動(CT)、TT の各透熱状態で表現したモデルハミルトニアンを、パラメータ的もしくはペンタセン 2 量体配置での量子化学計算より得られた電子カップリングから構築し、振電相互作用を考慮した量子マスター方程式法<sup>3)</sup>によって TT 分離が促進される条件を検討した。その結果、TT 間距離の増大には、**Type 1** での三重項移動積分  $t_1$  が **Type 2** での値  $t_2$  や CT-TT 間のカップリングよりも十分大きい必要があることが明らかになった。このような TT 分離を具体的な分子で実現するにはペンタセンより大きな  $S_1$ -TT エネルギー差が必要である。そこで、**Type 1** と **Type 2** での電子カップリングの組み合わせから、TT 分離に必要な単分子のエネルギーマッチング条件を逆算するモデル式を検討した。

1) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891. 2) K. Miyata et al., *Chem. Rev.* **2019**, *119*, 4261. 3) M. Nakano et al., *J. Comput. Chem.* **2019**, *40*, 89.



**Fig. 1** Model Structure of Finite-Sized one-dimensional aggregate system.



## ジアリールエテン誘導体への光照射による溶解度変化

(熊本大工<sup>1</sup>・熊本大院先端機構<sup>2</sup>) ○中村 優斗<sup>1</sup>・沈 君偉<sup>2</sup>・深港 豪<sup>1</sup>・原田 祐希<sup>2</sup>・中村 振一郎<sup>2</sup>・渡邊 智<sup>1</sup>・大谷 涼真<sup>1</sup>

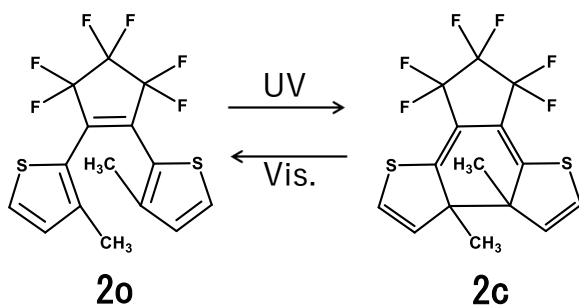
Solubility change of diarylethene derivatives by light irradiation (<sup>1</sup>*Faculty of Engineering, Kumamoto University*, <sup>2</sup>*Graduate School of Engineering, Kumamoto University*) Kensuke Kiyokawa,<sup>1</sup> ○Masato Nakamura,<sup>1</sup> Junwei Shen,<sup>2</sup> Tsuyoshi Fukaminato,<sup>1</sup> Yuki Harada,<sup>2</sup> Shinichiro Nakamura,<sup>2</sup> Satoshi Watanabe,<sup>1</sup> Ryoma Ohtani,<sup>1</sup>

Photochromic molecules are molecules that change reversibly between two structural isomers under irradiation or heat. In particular, photochromic molecules classified as P-type have high activation energy for thermal isomerization and are easily isomerized by light irradiation. Diarylethene (DAE), which is represented by P-type photochromic molecules, has various derivatives depending on the substituent and molecular structure.

In this study, a large difference of solubility of DAE derivative in octane was observed before and after light irradiation (see the figure below). We have not found any studies that report the solubility change of DAE derivatives by irradiation. Therefore, we analyzed the solubility of DAE derivatives by means of molecular orbital (MO) and molecular dynamics (MD) methods. The purpose of this study is to find appropriate computational conditions and analytical methods that can explain the experimental phenomenon of solubility change of DAE derivative. **Keywords :** *Diarylethene; solubility; Molecular orbital method; Molecular dynamics*

フォトクロミック分子は、光（熱）の作用で2つの異性体間を可逆的に変化する分子である。特に、P型に分類されるフォトクロミック分子は熱異性化の活性化エネルギーが高く、光照射によって異性化する。異性化に伴う分子構造変化により物性が変化する。P型フォトクロミック分子に代表されるジアリールエテン（DAE）は置換基や分子構造の違いにより様々な誘導体が存在する。

今回、DAE 誘導体である分子 2 の光照射前後で、オクタンに対する溶解度に大きな違いが観測された(下図)。DAE 誘導体の照射による溶解度変化について言及している報告例は見つけられていない。そのため分子軌道（molecular orbital, MO）法と分子動力学（molecular dynamics, MD）法の計算科学手法による解析を行った。本研究の目的は、溶解度変化の実験現象を再現するような適切な計算条件、解析方法を見つけることとした。



The solubility of molecule 2 in octane

温度 [°C]	溶解度 [mmol/L]	
	2o	2c
5	220	28
10	320	40
20	470	68
40	560	110
60	1200	140
80	測定無し	250

## 次元縮約法の選択に対する低次元反応空間構築の性能検証

(北大院理<sup>1</sup>・北大 WPI-ICReDD<sup>2</sup>) ○堤 拓朗<sup>1</sup>・小野ゆり子<sup>2</sup>・武次徹也<sup>1,2</sup>

Performance verification of low-dimensional reaction space construction for selecting dimensional contraction methods (<sup>1</sup>*Fac. of Sci., Hokkaido Univ.*, <sup>2</sup>*WPI-ICReDD, Hokkaido Univ.*) ○Tsutsumi Takuro,<sup>1</sup> Yuriko Ono,<sup>2</sup> Taketsugu Tetsuya<sup>1,2</sup>

Chemical reactions are described as a series of elementary reactions, which are represented by reaction paths on the potential energy surface. Automated reaction path search methods have been developed recently, enabling us to obtain a reaction path network composed of many reaction paths. So far, we have developed the reaction space projector (ReSPer) to visualize the reaction path network located in high dimension into the low-dimensional space, where humans can recognize, based on the dimensionality reduction method, the classical multidimensional scaling (CMDS). In this study, we verify the performance of a low-dimensional reaction space construction in CMDS and the principal component analysis (PCA) and discuss the advantages and limitations of both dimensionality reduction methods.

**Keywords :** Reaction Space Projector; Reaction path network; Principal component analysis; Classical multidimensional scaling; Low-dimensional reaction space

化学反応はポテンシャルエネルギー曲面 (PES) における一連の素反応過程として表現される。固有反応座標 (IRC) は素反応過程に対応する反応経路であり、反応経路自動探索法により多数の IRC で構成された反応経路ネットワークの概念が生まれた[1]。しかし、このネットワークは高次元 PES 上に存在するため、人間が視認可能な低次元空間で再現することは難しい。我々はこのような課題を解決するために、高次元データから特徴量を抽出可能な次元縮約法を利用した「反応空間投影法 (ReSPer: Reaction Space Projector)」を開発し、反応経路ネットワークの可視化に取り組んできた[2]。これまで ReSPer では、次元縮約法として古典的多次元尺度構成法 (CMDS) を利用している。一方、主成分分析 (PCA) を利用した類似ツール[3]も開発されているが、CMDS と PCA の性能について比較した試みは未だない。そこで本研究では CMDS と PCA を比較することで低次元反応空間構築の性能を検証する。

PCA と CMDS の性能は入力情報である構造間類似度に依存する。構造間類似度を適切に見積もるためには、2つの構造における座標軸を揃える必要があるが、アルゴリズムの都合上、PCA では1つの代表構造に対してすべての参照構造群を揃えることができない。一方で、CMDS は2つの構造に対して最適な座標軸を選択することができる。したがって、複雑な構造変化を含むような反応経路ネットワークの場合、ReSPer-CMDS は IRC ネットワークの連結関係や相対的な位置を再現できるが、ReSPer-PCA は IRC のネットワーク構造すら再現できない。発表当日は低次元反応空間や特徴量再構築の観点から ReSPer-CMDS と ReSPer-PCA の性能を検証する[4]。

[1] S. Maeda, Y. Harabuchi, *WIREs Comput. Mol. Sci.*, **2021**, 11, e1538S.

[2] **T. Tsutsumi**, Y. Ono, Z. Arai, T. Taketsugu, *J. Chem. Theory Comput.*, **2018**, 14, 4263.

[3] S. R. Hare, L. A. Bratholm, D. R. Glowacki, B. K. Carpenter, *Chem. Sci.*, **2019**, 10, 9954.

[4] T. Tsutsumi, Y. Ono, T. Taketsugu, *to be submitted*.

## デジタルアニーラを活用したヘキサベンゾコロネンのハロゲン置換による特性最適化

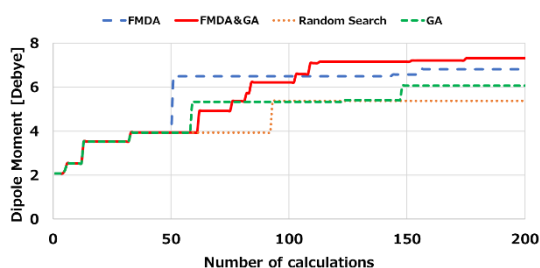
(富士通株式会社<sup>1)</sup> ○橋口 和弘<sup>1</sup>・丸尾 昭人<sup>1</sup>・添田 武志<sup>1</sup>・實宝 秀幸<sup>1</sup>

Optimization of Characteristics through Halogenation in Hexa-*peri*-hexabenzocoronene Utilizing Digital Annealer. (<sup>1</sup>*Fujitsu Ltd.*) ○Kazuhiro Hashiguchi,<sup>1</sup> Akito Maruo,<sup>1</sup> Takeshi Soeda,<sup>1</sup> Hideyuki Jippo<sup>1</sup>

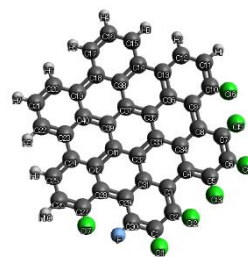
We used Fujitsu's Digital Annealer (DA) and mathematical optimization to rapidly explore Polycyclic Aromatic Hydrocarbons (PAHs) properties, focusing on hexa-*peri*-hexabenzocoronene (HBC). We converted HBC's hydrogen atom substitution into a bit representation for DA, finding the optimal solution from 36-bit combinations. By integrating machine learning, DA, and Genetic Algorithm, we efficiently performed black-box optimization. This versatile method can be applied to other molecules by altering the target compound and variables.

**Keywords :** Digital Annealer; Materials Informatics

本研究では、富士通の量子インスパイアード技術であるデジタルアニーラ (DA)<sup>1)</sup>を活用した数理最適化技術と密度汎関数理論 (DFT) 計算を組み合わせることにより、優れた特性を示す多環芳香族炭化水素 (PAHs) の高速探索を実現した。対象とした PAHs は hexa-*peri*-hexabenzocoronene (HBC) で、ハロゲン置換基の導入により諸特性が変化する。HBC の芳香環上の水素原子の置換の有無と置換種をビット表現に変換して DA 最適化を適用した。これに機械学習手法である Factorization Machine (FM) と遺伝的アルゴリズム (GA) を組み合わせて最適化した結果、化学的対称性を考慮しない場合において、36 ビットの組み合わせ、すなわち  $2^{36}$  (約 687 億) 通りの膨大な構造パターンから約 200 回の試行で最適解を見出すことができた (図 (a) および図 (b))。本手法は、近似モデル上の高速探索と大域的な探索の相乗効果が特長で、対象化合物や置換原子の種類や数など、拡張性や汎用性が高い手法と考えている。また、より厳密な特性値の解析には、構造最適化が必要であり、詳細は当日議論する。



図(a) 各アルゴリズムにおける  
ダイポールモーメント最適化の比較



図(b) FMDA&GA により見出された  
ハロゲン置換基最適化構造

1) Fujitsu. (2023, December). Quantum-Inspired Computing Digital Annealer. Retrieved from <https://www.fujitsu.com/global/services/business-services/digital-annealer/>.

## Nuclear quantum effect on the phase transition of the high-pressure ice

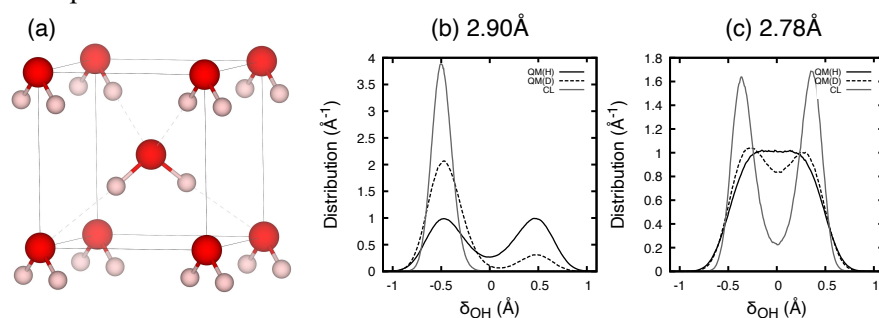
(Graduate School of Nanobioscience, Yokohama City University, Japan)

○Kazuaki Kuwahata and Masanori Tachikawa

**Keywords:** Nuclear quantum effect; Phase transition; Ice; Hydrogen atom;

Water is one of the most abundant and indispensable substances that play a pivotal role in the multitude of natural phenomena and in preserving life's existence on our planet. At room temperature and pressure ranging from 2 to 60 GPa, ice VII is a stable crystalline phase, where the oxygen atoms form a body-centered cubic structure, with the hydrogen atoms being delocalized between the two oxygen atoms (Fig. 1(a)). Infrared spectroscopy has confirmed that above 60 GPa, ice VII undergoes a phase transition to ice X, in which the hydrogen atoms lie midway between the two oxygens<sup>[1]</sup>. Although the phase transition from ice VII to ice X is a change in the symmetry of the hydrogen atom, the behavior of the hydrogen atom is still unknown due to the difficulty of conducting neutron diffraction experiments under high-pressure conditions. To address this gap in understanding, this study uses the path integral molecular dynamics method (PIMD), which can treat the nuclear quantum effect, to clarify the behavior of hydrogen atoms in the phase transition from ice VII to ice X.

We conducted three types of PIMD simulations to study the impact of the nuclear quantum effect: the simulation for hydrogen atoms (QM(H)), for deuterium atoms (QM(D)), and the classical simulation (CL). To analyze the phase transition, we used the difference in distance between the two oxygen atoms and the hydrogen atom ( $\delta_{\text{OH}}$ ) as a guide. At a lattice constant of 2.9 Å, the hydrogen atoms in the CL simulation were found to be localized on one oxygen atom, while in the QM(H) and QM(D) simulations, the hydrogen atoms were delocalized, and the distribution at  $\delta_{\text{OH}} = 0$  Å was increased. At a lattice constant of 2.9 Å, the distribution displayed two peaks, indicating the phase was ice VII. Upon reducing the lattice constant to 2.78 Å, the distribution in QM(H) displayed only one peak, suggesting that the nuclear quantum effect promotes the phase transition. Further details will be presented in a poster.



1) K. Aoki, H. Yamawaki, M. Sakashita, and H. Fujihisa, *Phys. Rev. Let.* **76**, 5, (1996)

## 酵素反応における基底状態不安定化仮説：バイオマス分解酵素 GH11-Xylanase の反応機構について

(産総研<sup>1</sup>・オークリッジ国研<sup>2</sup>) ○石田 豊和<sup>1</sup>・Jerry M. Parks<sup>2</sup>・Jeremy C. Smith<sup>2</sup>  
Ground State Destabilization hypothesis on enzymatic catalysis: Reaction mechanism of Biomass degrading enzyme GH11-xylanase  
(<sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST), <sup>2</sup>Oak Ridge National Laboratory (ORNL)) ○Toyokazu Ishida,<sup>1</sup> Jerry M. Parks,<sup>2</sup> Jeremy C. Smith<sup>2</sup>

Lignocellulose is a promising renewable energy resource because plant biomass is the most abundant natural resource on Earth. Two major chemical components of lignocellulose are cellulose and hemicellulose, and the hydrolysis of both carbohydrate polymers is a fundamental chemical step in the production of biochemical products. In nature, this essential chemical conversion is carried out by a family of enzymes known as glycoside hydrolases (GHs). To clarify the basic mechanism of biomass degradation, we have investigated the glycosylation step of GH11 xylanase, an enzyme that catalyzes the hydrolysis of lignocellulosic hemicellulose (xylan). Based on the recent neutron structure, which identified all protonation states of the enzyme, and *ab initio* QM/MM calculation, we have elucidated the detailed reaction mechanism of the glycosylation. Our focus in this presentation is on the controversial reaction mechanism, so-called the ground state destabilization hypothesis.

**Keywords :** *Enzymatic Reaction; Ground State Destabilization; Glycoside Hydrolases; Xylanase; QM/MM calculation*

木質系バイオマス資源であるリグノセルロースの主成分は多糖鎖から構成されるセルロース及びヘミセルロースであり、これら構成要素が非常に強固な繊維構造を持つため、単糖まで分解して利用するには様々な困難が知られている。この強固な構造の化学的基盤は構成糖単位間に形成されるグリコシド結合であり、グリコシド結合を加水分解する酵素は一般に Glycoside hydrolase (GH) と総称される。今回我々は、バイオマス分解酵素の一例としてヘミセルロースを分解するキシラナーゼ (Xylanase) に注目して、最新の中性子構造解析によって得られた一連の結晶構造を出発構造とし、QM/MM 計算および分子シミュレーション技術を組み合わせることで、反応機構の詳細な解析を実施した。本酵素の反応機構に関しては依然として未解明の重要問題が多数存在するが、「反応経路上において Oxocarbenium ion が反応中間体として実際に形成されるのか否か」という作業仮説に注目しつつ、反応中間体形成のメカニズムを高精度量子化学計算から検証することにより、今回は特に基底状態不安定化仮説（本系の場合、糖鎖構造の歪みに相当）に関して、QM/MM 計算による検証結果を報告する。

1) Insight into the Catalytic Mechanism of GH11 Xylanase: Computational Analysis of Substrate Distortion Based on a Neutron Structure, Toyokazu Ishida, Jerry M. Parks, and Jeremy C. Smith, *J. Am. Chem. Soc.* **2020**, 142, 17966–17980.

アカデミックプログラム [B 講演] | 03. 物理化学—構造：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 会場 A1452(14号館 [5階] 1452)

**[A1452-3am] 03. 物理化学—構造**

座長：恩田 健、米田 勇祐

## ◆ 英語

9:00 ~ 9:20

[A1452-3am-01]

強レーザー場フーリエ変換分光法によるsub-MHz精度の $\text{Kr}^+$ の超微細および微細構造の測定○安藤 俊明<sup>1</sup>、山田 佳奈<sup>1</sup>、岩崎 純史<sup>1</sup>、山内 薫<sup>1</sup> (1. 東大)

## ◆ 日本語

9:20 ~ 9:40

[A1452-3am-02]

 $\text{NO}_3 \times {}^2\text{A}_2'$  状態の  $\nu_2$  変角振動構造○福島 勝<sup>1</sup> (1. 広島市立大学)

## ◆ 日本語

9:40 ~ 10:00

[A1452-3am-03]

時間分解赤外分光法による核酸塩基水溶液の超高速電子緩和過程の研究

○鈴木 俊法<sup>1</sup>、小原 祐樹<sup>1</sup>、Srijon Ghosh<sup>1</sup>、神柱 尚太<sup>1</sup> (1. 京都大学)

## ◆ 英語

10:00 ~ 10:20

[A1452-3am-04]

内向きプロトンポンプシゾロドプシン4における反応初期中間体の発色団構造の解明

○潤井 泰斗<sup>1</sup>、水野 操<sup>1</sup>、神取 秀樹<sup>2</sup>、水谷 泰久<sup>1</sup> (1. 阪大院理、2. 名工大院工)

10:20 ~ 10:30

休憩

## ◆ 日本語

10:30 ~ 10:50

[A1452-3am-05]

フェムト秒時間分解時間領域ラマン分光による非平衡な励起状態平面化ダイナミクスの観測

○米田 勇祐<sup>1,2</sup>、小西 智暉<sup>3</sup>、齊藤 尚平<sup>3</sup>、倉持 光<sup>1,2</sup> (1. 分子研、2. 総研大、3. 京大)

## ◆ 英語

10:50 ~ 11:10

[A1452-3am-06]

可視光領域での蛍光符号化低波数コヒーレントラマン分光法

○田村 徹<sup>1</sup>、Phillip McCann<sup>1</sup>、西山 諒<sup>1</sup>、平松 光太郎<sup>1,2</sup>、合田 圭介<sup>1,3,4</sup> (1. 東大、2. 九大、3. カリフォルニア大、4. 武漢大)

## ◆ 日本語

11:10 ~ 11:30

[A1452-3am-07]

細胞内水分子構造のラマン分光解析

○安田 充<sup>1</sup>、安井 正人<sup>1</sup> (1. 慶應大)

---

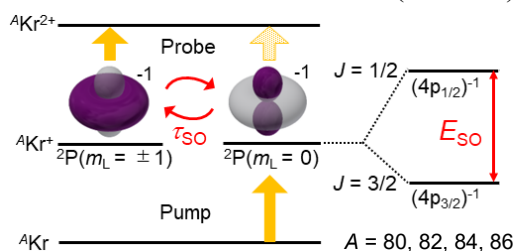
## Hyperfine and fine structures of $\text{Kr}^+$ determined by Strong-field Ultrahigh-resolution Fourier-transform Spectroscopy with sub-MHz precision

(<sup>1</sup>*School of Science, The Univ. of Tokyo*, <sup>2</sup>*Institute for Attosecond Laser Facility, The Univ. of Tokyo*) ○Toshiaki Ando,<sup>1</sup> Kana Yamada,<sup>1</sup> Atsushi Iwasaki,<sup>1</sup> Kaoru Yamanouchi<sup>1,2</sup>

**Keywords:** Intense laser science, Few-cycle laser pulses, High-resolution spectroscopy, Fourier transform spectroscopy, Hyperfine structure

By using ultrashort laser pulses, we can create electronic and/or nuclear wave packets, and observe the quantum interferences of the wave packets. The energy intervals of the states constituting the wave packets have been determined from the frequency of the quantum beats. Recently, by introducing the strong-field ionization and excitation to the quantum beat spectroscopy of atomic and molecular cations,<sup>1,2</sup> we developed a new class of spectroscopy called strong-field ultrahigh-resolution Fourier transform (SURF) spectroscopy. In the present study, by using 6-fs NIR intense laser pulses, we conduct SURF measurements of the isotopes of  $\text{Kr}^+$  ( $A = 80, 82, 83, 84, 86$ ) and observe the isotope shift of the fine-structure (FS) of  $\text{Kr}^+$  and the hyperfine structure (HFS) of  $^{83}\text{Kr}^+$ . The spectral resolution is 77 MHz, which is the inverse of the scanning pump-probe time delay (13 ns), and the resultant precision of the FS splitting energies is in the sub-MHz range. The precision of the HFS parameters obtained in the present study is 4–25 times better than that of the previous study,<sup>3,4</sup> and the isotope shift parameters of the FS are determined.

The excitation scheme for the SURF measurements is shown in Fig. 1. A strong field ionization of Kr by the pump pulse creates an electron hole in the 4p orbital. Because an electron in the  $m_L = 0$  orbital is preferentially ejected upon the ionization induced by a pump laser pulse, the  $^2\text{P}(m_L = 0)$  state of  $\text{Kr}^+$  is created. In the case of even isotopes, the electron hole evolves in time and oscillates with the period  $\tau_{\text{SO}} = h/E_{\text{SO}}$ . The oscillation of the electron hole is recorded as the oscillation of the yield of  $\text{Kr}^{2+}$  produced by the probe laser pulse, reflecting the fact that the probability of the ionization of  $\text{Kr}^+$  in the  $^2\text{P}(m_L = \pm 1)$  states to  $\text{Kr}^{2+}$  is larger than that of  $\text{Kr}^+$  in the  $^2\text{P}(m_L = 0)$  states. In the case of  $^{83}\text{Kr}^+$ , the time evolution of the electron hole is more complex because of the HFS interaction, and the oscillations are assigned to the quantum beat originating from the upper ( $J = 1/2, F'$ ) and lower ( $J = 3/2, F$ ) hyperfine sublevels.



**Fig. 1. Excitation diagram of Kr**

1) T. Ando, A. Iwasaki, K. Yamanouchi, *Phys. Rev. Lett.* **2018**, 120, 263002. 2) T. Ando, A. Liu, N. Negishi, A. Iwasaki, K. Yamanouchi, *Phys. Rev. A* **2021**, 104, 033516. 3) M. Schäfer and F. Merkt, *Phys. Rev. A* **2006**, 74, 062506. 4) T. A. Paul, J. Liu, and F. Merkt, *Phys. Rev. A* **2009**, 79, 022505.



## NO<sub>3</sub> の $\tilde{X}^2A'_2$ 状態の $\nu_2$ 変角振動構造

(広島市大情報) ○福島 勝

The  $\nu_2$  bending structure of the  $\tilde{X}^2A'_2$  state of NO<sub>3</sub> (*Graduate School of Information Science, Hiroshima City University,*) Masaru Fukushima

The <sup>14</sup>NO<sub>3</sub> and <sup>15</sup>NO<sub>3</sub> isotopomers were generated in a supersonic free jet expansion, and laser induced fluorescence (LIF) of the  $\tilde{B}^2E' - \tilde{X}^2A'_2$  electronic transition was observed. Dispersed LIF spectrum from the vibronic level at  $\sim 770\text{ cm}^{-1}$  above the vibrationless level has been measured for each of the isotopomers. (The spectra from the vibrationless level have been published [1].) One of the remarkable characteristics of the dispersed fluorescence (DF) spectrum is that the  $\nu_2(a_2'')$  fundamental is clearly observed as a member of the  $\nu_2$  progression. The  $\nu_2$  mode is an out-of-plane bending mode, and the fundamental is thus forbidden in the electronic transition. The  $\nu_2$  progression has been analyzed according to the general procedure [2], and vibrational frequency,  $\omega_2 = 720\text{ cm}^{-1}$ , and anharmonicity,  $x_{22} = +8.4\text{ cm}^{-1}$ , for <sup>14</sup>NO<sub>3</sub> have been determined. The positive anharmonicity is general trend for the out-of-plane bending mode [2]. It is thought that Jahn-Teller and Renner-Teller vibronic interactions at the  $\tilde{B}^2E'$  state are enable to interpret the observation of the forbidden  $\nu_2$  fundamental. The vibronic couplings can also reproduce the vibronic structures of all of the DF spectra observed.

**Keywords :** *Supersonic Free Jet Expansion; Laser Induced Fluorescence; Out-of-plane bending vibrational mode; Jahn-Teller vibronic interaction; Renner-Teller vibronic interaction*

NO<sub>3</sub> ラジカルは、平面  $D_{3h}$  の構造をもつ、稀なラジカルであり、分子分光学的に多くの興味をもたれている。我々は NO<sub>3</sub> の  $\tilde{B}^2E' - \tilde{X}^2A'_2$  電子遷移にレーザー誘起ケイ光 ( LIF: Laser Induced Fluorescence ) 分光法を適用し、基底  $\tilde{X}^2A'_2$  電子状態の振動構造の解明を進めている。今回、 $\tilde{B}^2E'$  電子状態のゼロ振動準位から約  $770\text{ cm}^{-1}$  ほど高い振電バンドからの分散ケイ光 ( DF: Dispersed Fluorescence ) スペクトルを測定したところ、この電子遷移では禁制の  $\nu_2(a_2'')$  基音バンドが、 $\nu_2$  プログレッションの一部として、さらに、最も強い振動バンドとして観測された (  $\nu_2$  振動モードは、面外変角モードである )。ゼロ振動準位からの DF スペクトル ( 既に報告済み [1] ) には、 $\nu_2$  基音バンドは観測されていないが、 $2\nu_2$  倍音バンドは、強く観測されている。観測された  $\nu_2$  プログレッションを通常の手法 [2] で解析し、<sup>14</sup>NO<sub>3</sub> に対し、 $\omega_2 = 720\text{ cm}^{-1}$ 、 $x_{22} = +8.4\text{ cm}^{-1}$  が得られた ( <sup>15</sup>NO<sub>3</sub> に対しては、 $\omega_2 = 716\text{ cm}^{-1}$ 、 $x_{22} = +7.7\text{ cm}^{-1}$  )。面外変角モードが正の非調和項をもつことは、一般的傾向である [2]。禁制の  $\nu_2$  基音バンドの観測は、 $\tilde{B}^2E'$  状態での Jahn-Teller および Renner-Teller 振電相互作用を考慮すると解釈可能である。この  $\tilde{B}^2E'$  状態の振電相互作用を考慮すると、全ての DF スペクトルの振動構造も解釈可能となる。

1) M. Fukushima, *J. Mol. Spectrosc.* **387**, 111646 (2022).

2) G. Herzberg, "MM II", (Van Nostrand Company, 1945).

## 時間分解赤外分光法による核酸塩基水溶液の超高速電子緩和過程の研究

(京大院理) ○鈴木俊法・小原祐樹・Srijon Ghosh・神柱尚太

Ultrafast Electronic Relaxation of Aqueous Nucleobases Studied by Time-Resolved Infrared Spectroscopy (*Graduate School of Science, Kyoto University*) ○Toshinori Suzuki, Yuki Obara, Srijon Ghosh, Shota Kamibashira

Nucleobases have fundamental importance in life science, and they are also the benchmark system of heteroaromatic molecules. Despite a plethora of studies, however, the photophysics and photochemistry of aqueous nucleobases remain elusive. Last year, we have newly introduced extreme ultraviolet time-resolved photoelectron spectroscopy and elucidated the difference in photophysics between isolated and aqueous nucleobases. The latter exhibited considerably smaller quantum yield of  $^1n\pi^*$ . In the present study, we attempted to shed new light on the photophysics of aqueous pyrimidine nucleobases (Thymine and Uracil) using time-resolved infrared spectroscopy. We excited them at 267 nm and measured time-resolved vibrational spectra with broad-band infrared pulses and a polychromator. The temporal resolution of ca. 300 fs does not enable us to probe an extremely short-lived  $^1\pi\pi^*$  state (< 300 fs), but  $^1n\pi^*$  and triplet states were clearly identified. The vibrational spectra of aqueous nucleobases at room temperature cannot be reproduced by quantum chemical calculations on a single configuration, so that we are performing molecular dynamics simulations and quantum chemical calculations to interpret the infrared spectra.

**Keywords** : Nucleobase; Infrared Spectrum; Photochemistry; Electronic Relaxation; Femtosecond

核酸塩基分子は生命科学に重要なだけでなく、最も基本的なヘテロ環化合物だが、光化学的に不明の点が多い。我々は、昨年極端紫外時間分解光電子分光を適用し[1]、気相孤立状態と水和状態の核酸塩基の光緩和過程の差を明らかにした。本研究では時間分解赤外分光を導入して水溶液中でのダイナミクスを掘り下げた。ピリミジン環化合物であるチミンとウラシルを 267 nm で励起し、C=O 伸縮振動領域の赤外スペクトルの変化をブロードバンド赤外光とポリクロメータを用いて観測した。現時点での時間分解能は 300 fs 程度であるため、極短寿命である  $^1\pi\pi^*$  状態の観測は難しいが  $^1n\pi^*$  状態や三重項状態が観測された。核酸塩基の赤外スペクトルは単純な量子化学計算では再現できないため、分子動力学計算による水和構造のサンプリングと量子化学計算による赤外スペクトルのシミュレーションを行って解釈を進めている。

1) Formation of Long-Lived Dark States during Electronic Relaxation of Pyrimidine Nucleobases Studied Using Extreme Ultraviolet Time-Resolved Photoelectron Spectroscopy, Yuta Miura, Yo-ichi Yamamoto, Shutaro Karashima, Natsumi Orimo, Ayano Hara, Kanae Fukuoka, Tatsuya Ishiyama, and Toshinori Suzuki, JACS, **145**, 3369-3381 (2023). DOI:[10.1021/jacs.2c09803](https://doi.org/10.1021/jacs.2c09803)

## Elucidation of the retinal chromophore structure for primary intermediates of an inward proton pump schizorhodopsin 4

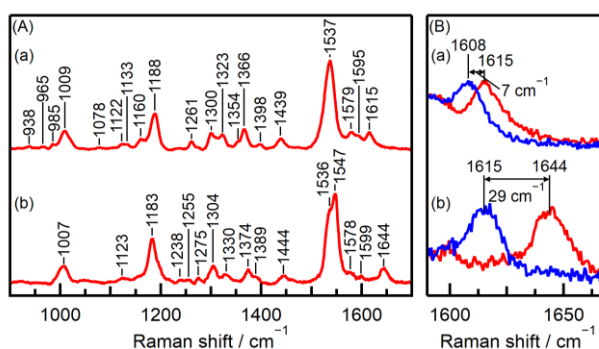
(<sup>1</sup>Graduate School of Science, Osaka University, <sup>2</sup>Graduate School of Engineering, Nagoya Institute of Technology) ○Taito Urui,<sup>1</sup> Misao Mizuno,<sup>1</sup> Hideki Kandori,<sup>2</sup> Yasuhisa Mizutani<sup>1</sup>

**Keywords:** Resonance Raman spectroscopy; Rhodopsin; Proton transport

Schizorhodopsin (SzR) is a newly discovered group of inward H<sup>+</sup>-pumping proteins.<sup>1</sup> We have previously revealed that *cis-trans* reisomerization precedes reprotonation at the Schiff base of the retinal chromophore in SzRs.<sup>2,3</sup> This order has never been observed for other H<sup>+</sup>-pumping rhodopsins and facilitates the H<sup>+</sup> uptake from the extracellular medium. However, the structural changes in the chromophore accompanying H<sup>+</sup> release into the cytoplasmic medium are poorly understood. Here, we report structural changes in the chromophore that lead to the H<sup>+</sup> release in SzR4 using time-resolved resonance Raman (RR) spectroscopy.

Samples were prepared by solubilizing and purifying SzR4 expressed in *E. coli*. Time-resolved RR spectra were obtained using 532- and 475-nm pulses for the pump and probe lights, respectively, in a time window between 100 ns and 50  $\mu$ s.

The time-resolved spectra in SzR4 contained two components attributed to the K and L intermediates (Figure 1A). Broad C–C stretching bands were observed at 1188 and 1183 cm<sup>−1</sup> for the K and L intermediates, respectively. These features show that the retinal chromophore adopts the 13-*cis* configuration in the intermediates.<sup>4</sup> The C=N stretching band exhibited deuteration shifts of 7 and 29 cm<sup>−1</sup> for the K and L intermediates, respectively (Figure 1B). It is well known that the magnitude of the deuteration shift at the C=N stretching band correlates with the hydrogen bond strength at the retinal Schiff base.<sup>5</sup> The deuteration shifts indicated that the hydrogen bond was weak in the K intermediate and was strengthened in the L intermediate. The weak hydrogen bond in the K intermediate indicates a drastic change in the hydrogen-bonding network around the Schiff base upon photoisomerization. The strong hydrogen bond in the L intermediate can be associated with lowering of the energy barrier for the H<sup>+</sup> transfer from the Schiff base. In this presentation, we discuss the transitions of the hydrogen bond strength preceding deprotonation at the Schiff base in comparison with outward proton pumps.



**Figure 1.** (A) RR spectra of the K (a) and L intermediates (b) of SzR4. (B) Enlarged views of the C=N stretching bands in H<sub>2</sub>O (red) and D<sub>2</sub>O buffers (blue) for the K (a) and L intermediates (b).

1) K. Inoue, et al., *Sci. Adv.* **2019**, 6, 12. 2) K. Hayashi, et al., *Angew. Chem. Int. Ed.* **2022**, 61, e202203149. 3) T. Urui, et al., *J. Phys. Chem. B.* in press. 4) S. O. Smith, et al., *J. Phys. Chem.* **1987**, 91, 804-819. 5) T. Baasov, et al., *Biochemistry.* **1987**, 11, 3210-3217.

## フェムト秒時間分解時間領域ラマン分光による非平衡な励起状態平面化ダイナミクスの観測

(分子研<sup>1</sup>・総研大<sup>2</sup>・京大院理<sup>3</sup>) ○米田勇祐<sup>1,2</sup>・小西智暉<sup>3</sup>・齊藤尚平<sup>3</sup>・倉持 光<sup>1,2</sup>  
 Non-equilibrium excited-state planarization dynamics observed by femtosecond time-resolved time-domain Raman spectroscopy. (<sup>1</sup>*Institute for Molecular Science*, <sup>2</sup>*Graduate Institute for Advanced Studies*, <sup>3</sup>*Graduate School of Science, Kyoto University*) ○Yusuke Yoneda,<sup>1,2</sup> Tomoaki Konishi,<sup>3</sup> Shohei Saito,<sup>3</sup> Hikaru Kuramochi<sup>1,2</sup>

Excited-state aromaticity is one of the most widely applied concepts in the field of chemistry. It has been accepted as a rational guideline for predicting conformational changes of cyclic  $\pi$ -conjugated systems induced by photoexcitation. Yet, the observation of such photoinduced structural dynamics remains challenging because it is considered to occur on the ultrafast time scale on the barrierless potential energy surface. In this work, we succeeded in tracking a non-equilibrium excited-state planarization dynamics of the cyclooctatetraene derivative, TP-FLAP, using femtosecond time-resolved time-domain Raman spectroscopy.

**Keywords :** *Femtosecond Raman Spectroscopy; Vibrational Coherence; Structural Dynamics; Excited-State Aromaticity; Photochemistry*

励起状態芳香族性は化学において広く用いられる重要な概念の一つであり、光で誘起される配座変化を推定する合理的指針として認識されてきた[1]。しかし、光励起に伴う構造変化は、バリアレスなエネルギー曲面上で進行するため、そのダイナミクスの観測は容易でない(Fig. 1a)。今回我々は、時間分解時間領域ラマン分光[2]により、励起状態で羽ばたく分子群 FLAP[3] の一つ、TP-FLAP の構造ダイナミクスを研究した。中央 cyclooctatetraene 部位の C=C 伸縮振動を含む高波数領域の時間分解ラマンスペクトルでは、2つのバンドが徐々に高波数シフトするダイナミクスが観測された(Fig. 1b)。この結果は分子が折れ曲がった構造から平面構造に変化していく過程に対応すると解釈され、非平衡な平面化ダイナミクスの観測に成功したと結論できる。

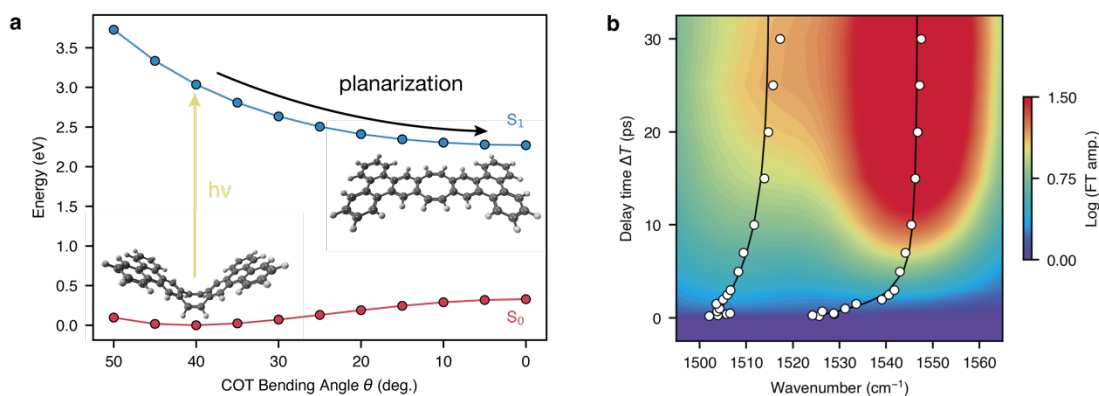


Fig. 1 (a) Potential energy surface of TP-FLAP. (b) Time-resolved Raman spectra of TP-FLAP.  
 [1] M. Rosenberg, *et al.*, *Chem. Rev.*, **2014**, *114*, 5379-5425. [2] H. Kuramochi, T. Tahara, *J. Am. Chem. Soc.*, **2021**, *143*, 9699-9717. [3] C. Yuan, *et al.*, *J. Am. Chem. Soc.*, **2013**, *135*, 8842-8845.

## Fluorescence-encoded low-frequency coherent Raman spectroscopy in the visible range

(<sup>1</sup>The University of Tokyo, <sup>2</sup>Kyushu University, <sup>3</sup>University of California, <sup>4</sup>Wuhan University)

○Tetsu Tamura<sup>1</sup>, Phillip Charles McCann<sup>1</sup>, Ryo Nishiyama<sup>1</sup>, Yasutaka Kitahama<sup>1</sup>, Kotaro Hiramatsu<sup>1,2</sup>, Keisuke Goda<sup>1,3,4</sup>

**Keywords:** fluorescence encoding; Raman spectroscopy; vibrational spectroscopy; nonlinear spectroscopy; vibronic coupling

Raman spectroscopy has the advantage of discriminating between different molecules, whereas it suffers from having a low signal intensity compared to fluorescence spectroscopy. One effective solution to this issue involves encoding the Raman signal into fluorescence. Our group recently reported fluorescence-encoded time-domain coherent Raman spectroscopy (FLETCHERS), a highly sensitive low-frequency Raman spectroscopy utilizing a femtosecond pulse pair (pump and probe pulse) sourced by a Ti:sapphire oscillator [1]. However, the fluorophores used in the previous studies were limited due to the scarcity of near-infrared fluorophores that satisfy an electronic pre-resonance condition with the Ti:sapphire laser.

In this presentation, we introduce visible FLETCHERS (vFLETCHERS), designed to operate in the visible excitation range and overcome the limited variety of detectable fluorophores present in the original FLETCHERS. It employs a non-collinear optical parametric amplifier as a femtosecond source within the 650-800 nm range. The new visible femtosecond source enables the efficient generation of Raman coherences and electronic excited states of visible fluorophores in the electronic pre-resonance condition. As a proof of concept demonstration, we acquired time-domain fluorescence interferograms using solutions of five commercial fluorophores with absorption bands in the 600-700 nm range (Fig. 1a). Fourier transform of those time-domain data yields low-frequency Raman spectra covering <1000 cm<sup>-1</sup> (Fig. 1b). These results underscore the potential of vFLETCHERS as a versatile analysis method for advancing research in materials science and biology.

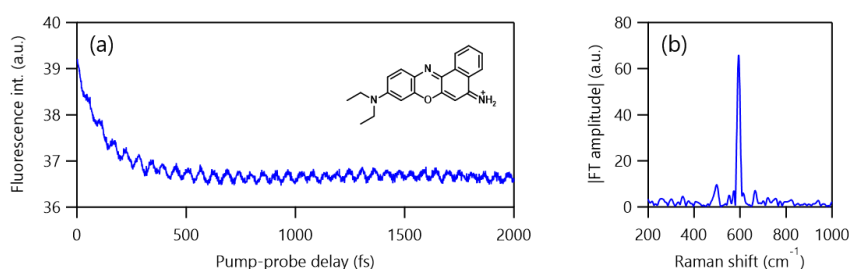


Fig. 1 (a) Fluorescence interferogram of 100-μM Nile blue solution over the time delay between the pump and probe pulses. (b) Raman spectrum obtained through Fourier transformation of the interferogram.

[1] P. C. McCann *et al*, *J. Phys. Chem. Lett.* **2021**, *12*, 7859-7865.

## 細胞内水分子構造のラマン分光解析

(慶應大) ○安田 充・安井 正人

Raman Spectroscopic Analysis of Intracellular Water Molecular Structures  
(School of Medicine, Keio University) ○Mitsuru Yasuda, Masato Yasui

Intracellular water molecules play a crucial role in regulating the three-dimensional structure of biomolecules through hydrogen bonding and hydration, profoundly influencing the expression of life functions. Unveiling the structure and dynamics of water molecules interacting with biomolecules is essential for a fundamental understanding of life phenomena. In this study, we analyzed the structural features of intracellular water molecules and visualized the distribution of various vibrational modes of both water and biomolecules within cells, utilizing Raman spectroscopy to measure the biomolecules governing biological functions and the water molecules involved in their functional expression.

The Raman spectrum of human keratinocyte (HaCaT) cells revealed various vibrational modes originating from biomolecules, including proteins and lipids. Additionally, we observed five vibration modes of water molecules: translational vibration, librational vibration, bending vibration, the combination tone of librational and bending vibrations, and stretching vibration. Further analysis through second derivative processing of the Raman spectrum allowed the identification of three distinct vibrational modes within the O-H stretching vibration band. Visualization of the distribution of water molecules in each vibrational mode disclosed a broad classification of intracellular water molecules into four distinct groups.

*Keywords : Water Molecule; Hydrogen Bonding; Raman Spectroscopy; Imaging; Cell*

細胞内の水分子は、水素結合や水和を介して生体分子の立体構造形成を制御しており、生命機能の発現に深く関与している。このときの水分子の構造やダイナミクスを明らかにすることは、生命現象を本質的に理解するうえで重要である。そこで、本研究では、ヒト表皮角化細胞 (HaCaT) を用いて、生命機能を司る生体分子と、その機能発現に関与する水分子をラマン顕微鏡 (LabRAM HR Evolution, HORIBA) により計測し、細胞内水分子の構造解析、ならびに様々な振動モードの水分子と生体分子の細胞内分布を可視化することで、水と生命現象の関係について調べた。

HaCaT 細胞のラマンスペクトルには、タンパク質や脂質をはじめとする生体分子由来の様々な振動モードが観測された。また、水分子に関しても、並進振動 ( $177\text{ cm}^{-1}$ )、束縛回転振動 ( $462\text{ cm}^{-1}$ )、変角振動 ( $1609\text{ cm}^{-1}$ )、束縛回転振動と変角振動の結合音 ( $2120\text{ cm}^{-1}$ )、伸縮振動 ( $3420\text{ cm}^{-1}$ ) の 5 つの振動モードを観測することができた。さらに、ラマンスペクトルを 2 次微分処理することで、O-H 伸縮振動バンドを 3 つの振動モードに分割し、他の水分子と水素結合を 2 つ形成している振動モード ( $3208\text{ cm}^{-1}$ )、水素結合を 1 つ形成している振動モード ( $3449\text{ cm}^{-1}$ )、水素結合を形成していない振動モード ( $3639\text{ cm}^{-1}$ ) を観測することができた。つぎに、各振動モードにおける水分子の分布を可視化したところ、細胞内の水分子分布は大まかに 4 つに分類できることが明らかとなった。詳細については当日、報告する。

アカデミックプログラム [B講演] | 04. 物理化学—物性：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 A1441(14号館 [4階] 1441)

**[A1441-3vn] 04. 物理化学—物性**

座長：網島 亮

## ◆ 英語

15:55 ~ 16:15

[A1441-3vn-01]

アルキルアミド置換ヘキサデヒドロトリベンゾ[12]アヌレン誘導体の形成する分子集合体の溶媒依存性

○笠原 遥太郎<sup>1</sup>、武田 貴志<sup>1,2</sup>、出倉 駿<sup>1</sup>、高井 淳朗<sup>3</sup>、姉帯 勇人<sup>3</sup>、久木 一朗<sup>4</sup>、竹内 正之<sup>3</sup>、芥川 智行<sup>1</sup> (1. 東北大、2. 信州大、3. 物質・材料機構、4. 阪大)

## ◆ 英語

16:15 ~ 16:35

[A1441-3vn-02]

環境刺激による有機カチオンへの固相イオン交換と物性評価

○伊藤 みづき<sup>1</sup>、眞邊 潤<sup>1</sup>、市橋 克哉<sup>1</sup>、今野 大輔<sup>1</sup>、加藤 智佐都<sup>1</sup>、藤林 将<sup>2</sup>、Goulven Cosquer<sup>3,4</sup>、井上 克也<sup>1,3,4,5</sup>、平尾 岳大<sup>1</sup>、灰野 岳晴<sup>1,3,4</sup>、芥川 智行<sup>6</sup>、高橋 仁徳<sup>7</sup>、中村 貴義<sup>7</sup>、西原 禎文<sup>1,3,5,8</sup> (1. 広島大院先進理工、2. 宇部高専、3. 広島大CResCent、4. 広島大WPI-SKCM<sup>2</sup>、5. 広島大先進セ、6. 東北大多元研、7. 北大電子研、8. JSTさきがけ)

## ◆ 英語

16:35 ~ 16:55

[A1441-3vn-03]

多価金属イオンを導入した超分子カチオンを含むNi(dmit)<sub>2</sub>塩の作製と物性評価○石川 大輔<sup>1</sup>、加藤 智佐都<sup>1</sup>、藤林 将<sup>2</sup>、Goulven Cosquer<sup>3,4</sup>、井上 克也<sup>1,3,4,5</sup>、芥川 智行<sup>6</sup>、高橋 仁徳<sup>7</sup>、中村 貴義<sup>7</sup>、西原 禎文<sup>1,3,5,8</sup> (1. 広島大院先進理工、2. 宇部高専、3. 広島大キラル国際研究拠点、4. 広島大キラルノット超物質拠点、5. 広島大先進機能物質研究センター、6. 東北大多元研、7. 北大電子研、8. JSTさきがけ)

## ◆ 日本語

16:55 ~ 17:15

[A1441-3vn-04]

4,4'-dinonyl-2,2'-bipyridineとdmit配位子をもつ非対称平面4配位型錯体を示すエレクトロクロミズムと熱的構造相転移

○久保 和也<sup>1</sup>、堀 葵<sup>1</sup>、キム ユナ<sup>2</sup>、田原 圭志朗<sup>3</sup>、梅谷 優太<sup>4</sup>、吾郷 友宏<sup>1</sup> (1. 兵庫県立大学大学院理学研究科、2. 宇都宮大学工学部、3. 香川大学創造工学部、4. 兵庫県立大学理学部)



## Solvent-dependent Molecular Assemblies of Alkylamide-substituted Hexadehydrotribenzo[12]annulene

(<sup>1</sup>Graduate School of Engineering, Tohoku University, <sup>2</sup>IMRAM, Tohoku University, <sup>3</sup>Faculty of Science, Shinshu University, <sup>4</sup>NIMS, <sup>5</sup>Graduate School of Engineering Science, Osaka University) ○Yotaro Kasahara,<sup>1</sup> Takashi Takeda,<sup>1,2,3</sup> Shun Dekura,<sup>1,2</sup> Atsuro Takai,<sup>4</sup> Hayato Anetai,<sup>4</sup> Ichiro Hisaki,<sup>5</sup> Masayuki Takeuchi,<sup>4</sup> Tomoyuki Akutagawa<sup>1,2</sup>

**Keywords:** Dehydrobenzoannulene, Molecular Assembly, Hydrogen-bond, Dielectric Property, Optical Property

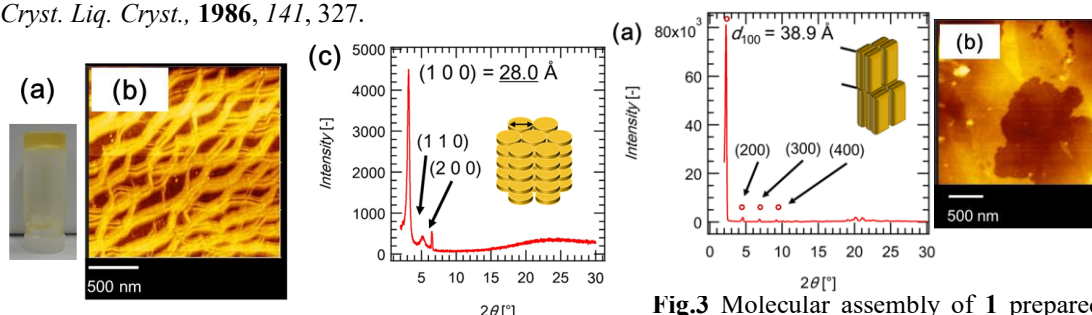
Hexadehydrotribenzo[12]annulene ([12]DBA) is a planar  $\pi$ -conjugated molecule that forms complex with transition metal in the cavity surrounded by triple bonds and exhibits emission with a large Stokes-shift.<sup>1,2</sup> Control of the molecular assembly of [12]DBA derivatives through the design of substituents could lead to the development of new functional materials.<sup>3</sup> However, it is hard to control the molecular assembly based on [12]DBA by weak interactions such as van der Waals interaction.

On the other hand, stronger interaction such as hydrogen bond could control molecular assemblies of organic materials. For example, alkylamide-substituted benzene derivatives formed 1D columnar liquid crystalline phase by intermolecular hydrogen bonds.<sup>4</sup> Herein, we prepared tetradecylamide-substituted [12]DBA (**1** in Fig. 1) and investigated its molecular assembly and physical property.

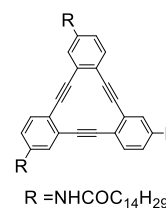
**1** formed an organogel in toluene (Fig. 2a). AFM (Fig. 2b) and PXRD (Fig. 2c) measurements of the xerogel film from toluene revealed that the molecule **1** formed fibers with hexagonal columnar structure, which reticulately tangled each other. On the other hand, **1** formed crystalline powder from CHCl<sub>3</sub>/MeCN without gelation, different from toluene. PXRD pattern of the crystalline powder (Fig. 3a) and AFM of the cast film from CHCl<sub>3</sub>/MeCN (Fig. 3b) revealed that **1** formed 2D-sheets with lamellar structure. These results revealed that molecular assemblies of **1** exhibited significant solvent-dependence.

[1] W. J. Young, *et al.*, *Chem. Rev.* **1999**, 99, 3153; [2] A. Douhal, *et al.*, *Phys. Chem. Chem. Phys.*

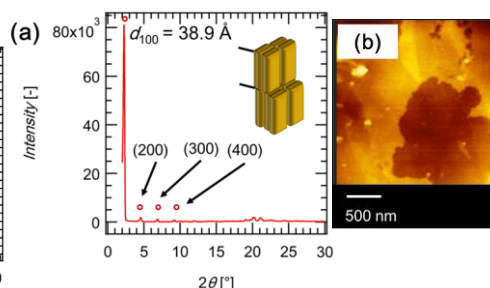
**2018**, 20, 7415; [3] Y. Kasahara, *et al.*, *Chem. Commun.* **2021**, 57, 5374; [4] Y. Matsunaga, *et al.*, *Mol. Cryst. Liq. Cryst.*, **1986**, 141, 327.



**Fig.2** Molecular assembly of **1** prepared from toluene. (a) Formation of organogel. (b) AFM image of spin-coat film on Si / SiO<sub>2</sub>. (c) PXRD pattern of cast film on glass.



**Fig. 1** Chemical structure of **1**.



**Fig.3** Molecular assembly of **1** prepared from CHCl<sub>3</sub> / MeCN. (a) PXRD pattern of crystalline powder. (b) AFM image of drop-cast film on HOPG.



## Solid-state ion exchange to organic cations by environmental stimulation and physical properties

(<sup>1</sup>Grad. Sch, Adv. Sci. Eng., Hiroshima Univ, <sup>2</sup>NIT, Ube College, <sup>3</sup>SKCM<sup>2</sup>; <sup>4</sup>CResCent; <sup>5</sup>IAMR; Hiroshima Univ., <sup>6</sup>IMRAM, Tohoku Univ., <sup>7</sup>RIES, Hokkaido Univ., <sup>8</sup>PRESTO, JST)

○Mizuki Ito,<sup>1</sup> Jun Manabe,<sup>1</sup> Katsuya Ichihashi,<sup>1</sup> Daisuke Konno,<sup>1</sup> Chisato Kato,<sup>1</sup> Masaru Fujibayashi,<sup>2</sup> Goulven Cosquer,<sup>3,4</sup> Katsuya Inoue,<sup>1,3,4,5</sup> Takehiro Hirao,<sup>1</sup> Takeharu Haino,<sup>1,3,4</sup> Tomoyuki Akutagawa,<sup>6</sup> Kiyonori Takahashi,<sup>7</sup> Takayoshi Nakamura,<sup>7</sup> Sadafumi Nishihara<sup>1,4,5,8</sup>

**Keywords:** Solid-state Ion Exchange, Organic Cation, Ion Channel, Supramolecular Cation, Ni(dmit)<sub>2</sub>

Functional materials that the uptake and removal of ions and molecules in response to the external environment can be controlled are attracting attention. However, it is difficult to capture and release ions or molecules in crystals without the use of thermal energy or pressure. In order to solve this problem, we focused on our previously developed Li<sub>2</sub>[[18]crown-6]<sub>3</sub>[Ni(dmit)<sub>2</sub>]<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> (Li salt), which has a channel structure.<sup>1</sup> By soaking single crystals of Li salt in an aqueous solution containing K<sup>+</sup> ion, complete ion exchange of Li<sup>+</sup> ion to K<sup>+</sup> ion was achieved, without loss of crystallinity.<sup>2</sup> In this work, to elucidate the ion exchange mechanism, we introduced organic cations into the crystals and evaluated their detailed structures and physical properties.

Specifically, MeNH<sub>3</sub><sup>+</sup>, EtNH<sub>3</sub><sup>+</sup>, and *n*-PrNH<sub>3</sub><sup>+</sup> ions were used for ion exchange. As results, ion exchange occurred without loss of crystallinity, and we succeeded to solve the crystal structures of the three organic salts. Crystal structure after ion exchange showed that Li<sup>+</sup> ion in Li salt were stoichiometrically exchanged with MeNH<sub>3</sub><sup>+</sup> (MeNH<sub>3</sub> salt), EtNH<sub>3</sub><sup>+</sup> (EtNH<sub>3</sub> salt), and *n*-PrNH<sub>3</sub><sup>+</sup> ion (*n*-PrNH<sub>3</sub> salt). In addition, one of the crown ether that had formed the channel structure unit was released out of the crystal during ion exchange. Furthermore, from dielectric measurements of each sample after ion exchange, we found different properties due to the difference of vibrations and motions in the crystal of each cation.

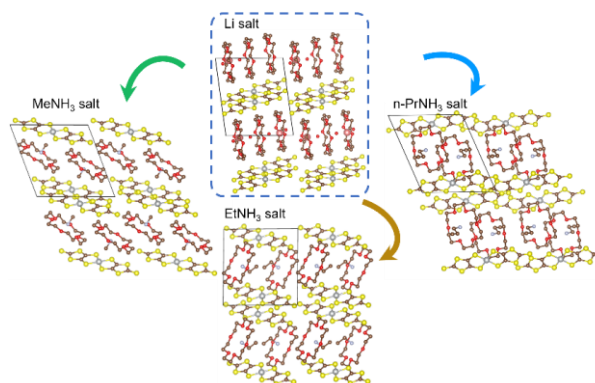


Fig. Crystal structure before and after ion exchange.

1) K. Ichihashi; S. Nishihara, *et al.*, *Chem. Mater.*, **2018**, 30, 7130–7137.

2) K. Ichihashi, S. Nishihara, *et al.*, *Angew. Chem. Int. Ed.*, **2019**, 58, 4169–4172.

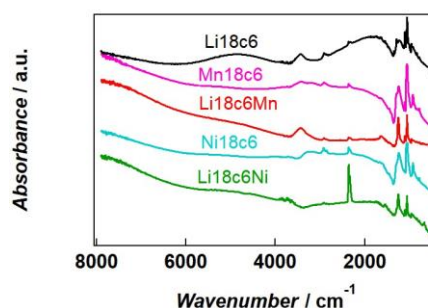
## Preparations and physical properties of Ni(dmit)<sub>2</sub> salts involving supramolecular cations with incorporated multivalent ions

(<sup>1</sup>Graduate School of Advanced Science and Engineering, Hiroshima Univ., <sup>2</sup>National Institute of Technology, Ube College, <sup>3</sup>CResCent; <sup>4</sup>IAMR; <sup>5</sup>WPI-SKCM<sup>2</sup>, Hiroshima Univ., <sup>6</sup>IMRAM, Tohoku Univ., <sup>7</sup>RIES, Hokkaido Univ., <sup>7</sup>PRESTO, JST) ○Daisuke Ishikawa,<sup>1</sup> Chisato Kato,<sup>1</sup> Masaru Fujibayashi,<sup>2</sup> Goulven Cosquer,<sup>3,5</sup> Katsuya Inoue,<sup>1,3,4,5</sup> Tomoyuki Akutagawa,<sup>6</sup> Kiyonori Takahashi,<sup>7</sup> Takayoshi Nakamura,<sup>7</sup> Sadafumi Nishihara<sup>1,3,4,8</sup>

**Keywords:** Supramolecular cation; Ni(dmit)<sub>2</sub>; Charge transfer; Solid-state ion exchange; Conductive crystal

Ni(dmit)<sub>2</sub> is well known as a building block of organic conductors, semiconductor, and magnets, depending on its oxidation state. In our research, we have established a solid-state ion exchange method using crystals that combine a supramolecular cation, which includes lithium ions, with [Ni(dmit)<sub>2</sub>]<sup>[1]</sup>. In the crystal, the one-dimensional arrangement of supramolecular cations forms an ion channel structure conducive to ion conduction. Upon immersion of the crystals in a potassium ion-containing aqueous solution, the lithium ions within the ion channel structure are exchanged with potassium ions from the solution, thereby facilitating solid-state ion exchange. Changes in the interaction between Ni(dmit)<sub>2</sub> units and significant alterations in material properties are observed before and after solid-state ion exchange.

This study aimed to elucidate the mechanism of property changes induced by previously unexplored solid-state ion exchange. In this work, we employed Ni and Mn ions as the ions encapsulated by crown ether. The successful synthesis of four novel crystals was achieved through direct synthesis using constant current electrolysis and solid-state ion exchange. Infrared spectroscopy confirmed the successful formation of the target crystals, as evidenced by the observation of peaks derived from crown ether and Ni(dmit)<sub>2</sub> in both ion-exchanged and directly synthesized crystals (Fig 1). Furthermore, it became evident that the CT band characteristic of semiconductors shifted compared to the crystal before ion exchange. This shift indicates a change in the electronic state of the Ni(dmit)<sub>2</sub>. The altered electronic state of Ni(dmit)<sub>2</sub> suggests the possibility of corresponding changes in material properties. On the day of the presentation, a detailed discussion will be provided on the relationship between ion exchange and changes in material properties based on measurements of the crystal structure, magnetic properties, and electrical properties.



**Fig 1. IR spectrum (Li18c6Mn, Li18c6Ni : Ion exchange crystal Mn18c6, Ni18c6 : Crystal fabrication)**

[1] K. Ichihashi, S. Nishihara, *et al.*, *Angew. Chem. Int. Ed.*, **2019**, 58, 4169-4172.

## 4,4'-dinonyl-2,2'-bipyridine と dmit 配位子をもつ非対称平面 4 配位型錯体が示すエレクトロクロミズムと熱的構造相転移

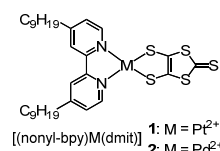
(兵庫県立大院理<sup>1</sup>・宇都宮大工<sup>2</sup>・香川大創造工<sup>3</sup>・兵庫県立大理<sup>4</sup>) ○久保 和也<sup>1</sup>・堀 葵<sup>1</sup>・キム ユナ<sup>2</sup>・田原 圭志朗<sup>3</sup>・梅谷 優太<sup>4</sup>・吾郷 友宏<sup>1</sup>

Electrochromism and Thermal Structural Phase Transitions Exhibited by Unsymmetrical Square-Planar Complexes with 4,4'-Dinonyl-2,2'-Bipyridine and Dmt Ligand. (<sup>1</sup>Graduate School of Science, University of Hyogo, <sup>2</sup>School of Engineering, Utsunomiya University, <sup>3</sup>Faculty of Engineering and Design, Kagawa University, <sup>4</sup>School of Science, University of Hyogo) ○Kazuya Kubo,<sup>1</sup> Aoi Hori,<sup>1</sup> Yuna Kim,<sup>2</sup> Keishiro Tahara,<sup>3</sup> Yuta Umetani,<sup>4</sup> Tomohiro Agou<sup>1</sup>)

Electrochromic (EC) materials are expected to be applied to components of new electronic devices such as a flexible display.<sup>1</sup> We have developed molecular EC materials based on unsymmetrical metal-dithiolene complexes.<sup>2</sup> In this work, we synthesized new unsymmetrical Pt<sup>2+</sup> and Pd<sup>2+</sup> complexes coordinated by 4,4'-dinonyl-2,2'-bipyridine (nonyl-bpy) and a dmit ligand [(nonyl-bpy)M(dmit)] (**1**: M = Pt<sup>2+</sup>, **2**: M = Pd<sup>2+</sup>). Their electrochromic behaviors and thermal structural phase transitions were investigated. Electrochemical measurements of thin films of **1** and **2** on ITO substrates showed one-reversible redox waves attribute to [M]<sup>0</sup> ↔ [M]<sup>+</sup> redox processes at +0.54 and +0.64 (V vs. Ag/Ag<sup>+</sup>), respectively. Electronic absorption spectra of the films of **1** and **2** indicated one absorption maxima at 500 nm and 502 nm in their neutral states, which were divided to two bands at 474, 656 nm and 482, 686 nm in their one-electron oxidation states, respectively. Measurements of differential scanning calorimetry of **1** and **2** indicated endothermic peaks at 111 °C and 102 °C for the heating processes below their melting points at 185 °C and 218 °C, respectively.

**Keywords** : Unsymmetrical complex; Squar-planar complex; Dithiolene complex; Thermal structural phase transition; Electrochromism

エレクトロクロミック(EC)材料は、フレキシブルディスプレイなどの新たな電子デバイスへの応用が期待されている。<sup>1</sup> 我々は、非対称型金属ジチオレン錯体分子を用いた EC 材料開発を行っている。<sup>2</sup> 本研究では新たに、4,4'-dinonyl-2,2'-bipyridine (nonyl-bpy) と dmit 配位子が Pt<sup>2+</sup> および Pd<sup>2+</sup> イオンに結合した非対称型錯体[(nonyl-bpy)M(dmit)] (**1**: M = Pt<sup>2+</sup>, **2**: M = Pd<sup>2+</sup>) を合成し、これらの EC 挙動と熱的構造相転移について検討した。



ITO 基板上に作製した錯体 **1** と **2** の薄膜の電気化学測定を行ったところ、それぞれ +0.54 と +0.64 (V vs. Ag/Ag<sup>+</sup>) に 0 価 ↔ +1 価に起因する可逆な酸化還元波を示した。中性状態の錯体薄膜 **1** と **2** の電子吸収スペクトルは、それぞれ 500 nm と 502 nm に一つの吸収極大をもつ。一電子酸化状態ではそれらの吸収帯が、474, 656 nm および 482, 686 nm と二つの吸収極大に変化した。錯体 **1** と **2** の示差走査熱量分析測定は、融点 (**1**: 185 °C, **2**: 218 °C) 以下の加熱過程で 111 °C と 102 °C に吸熱ピークを示した。

1) R. J. Mortimer, *Annu. Rev. Mater. Res.* **2011**, *41*, 241. 2) 久保和也ら、特願 2022-51935.

アカデミックプログラム [B講演] | 05. 物理化学—反応：口頭B講演

2024年3月20日(水) 9:30 ~ 11:40 A1455(14号館 [5階] 1455)

**[A1455-3am] 05. 物理化学—反応**

座長：古部 昭広、村越 敬

## ◆ 英語

9:30 ~ 9:50

[A1455-3am-01]

ペロブスカイトナノ結晶とペリレンビスイミド誘導体からなるヘテロ構造の制御

○久保 直輝<sup>1</sup>、山内 光陽<sup>2</sup>、増尾 貞弘<sup>1</sup> (1. 関西学院大学、2. 京大化研)

## ◆ 日本語

9:50 ~ 10:10

[A1455-3am-02]

フェムト秒過渡吸収顕微鏡を用いたフィコシアニンたんぱく質結晶内におけるエネルギー移動反応観測

○片山 哲郎<sup>1</sup>、上田 柊斗<sup>1</sup>、梅名 泰史<sup>2</sup>、古部 昭広<sup>1</sup> (1. 徳島大学、2. 名古屋大学)

## ◆ 日本語

10:10 ~ 10:30

[A1455-3am-03]

マイクロ構造電極における酸素発生触媒能の動画観測評価

○芦澤 大輝<sup>1</sup>、福島 知宏<sup>2</sup>、村越 敬<sup>2</sup> (1. 北大院総化、2. 北大院理)

10:30 ~ 10:40

休憩

## ◆ 日本語

10:40 ~ 11:00

[A1455-3am-04]

真空中のポリオール添加水液滴の凍結過程：凍結時間の観測と分子動力学シミュレーションによる解析

○吉岡 拓哉<sup>1</sup>、荒川 雅<sup>1</sup>、秋山 良<sup>1</sup>、寺寄 亨<sup>1</sup> (1. 九大)

## ◆ 英語

11:00 ~ 11:20

[A1455-3am-05]

拮抗する二種類の酵素反応のカップリングに基づく自律的かつ再帰的なpH変化を示す系の設計と応用

○板谷 昌輝<sup>1</sup>、Paola Albanese<sup>2</sup>、Nadia Valletti<sup>2</sup>、Gábor Holló<sup>3</sup>、Sándor Kurunczi<sup>4</sup>、Robert Horvath<sup>4</sup>、Federico Rossi<sup>2</sup>、István Lagzi<sup>1</sup> (1. ブダペスト工科経済大学、2. シエナ大学、3. ローザンヌ大学、4. ハンガリーエネルギー研究所)

## ◆ 日本語

11:20 ~ 11:40

[A1455-3am-06]

酸化剤濃度に依存した運動・変形が発現する化学振動反応を内包した自己駆動液滴

○久世 雅和<sup>1</sup>、松尾 宗征<sup>2,3</sup>、白石 允梓<sup>1</sup>、中田 聡<sup>3</sup>、西森 拓<sup>1</sup> (1. 明治大学 先端数理科学インスティテュート、2. 東京大学大学院 総合文化研究科、3. 広島大学大学院 統合生命科学研究科)

## Controlling Heterostructures Composed of a Perylene Bisimide Derivative and a Perovskite Nanocrystal

(<sup>1</sup>Kwansei Gakuin University, <sup>2</sup>ICR, Kyoto University)

○Naoki Kubo<sup>1</sup>, Mitsuaki Yamauchi<sup>2</sup>, Sadahiro Masuo<sup>1</sup>

**Keywords:** Perylene Bisimide; Perovskite Nanocrystal; Molecular Assembly; Energy Transfer; Quantum Dot

High-order aggregates (superlattices) of perovskite nanocrystals (NCs) can show distinctive photophysical properties, *e.g.*, superfluorescence, attributed to collective interactions in aggregated structures, not obtain from single NCs. Furthermore, it is expected that constructing heterogeneous superlattice composed of the NCs and functional organic dyes can induce new photophysical properties based on the interaction between NCs and dyes. Generally, the mixture of the NCs and dyes undergoes a random coaggregation and/or a narcissistic self-sorting to individual aggregates, so constructing the heterogeneous superlattice is challenging task. Recently, we have proposed a new methodology to form novel NC aggregated structures by coaggregation with supramolecular aggregates of organic dyes with adhesion moieties to NCs as a template.<sup>1,2</sup> However, whether the final coaggregates of NCs and dyes can afford a superlattice is unpredictable. Herein, we report controlling heterostructures composed of a CsPbBr<sub>3</sub> perovskite NC (NC) and a perylene bisimide derivative (**PBI**) depending on condition of the self-assembled **PBI**s before mixing with the NCs.

Upon mixing the NC and various aggregation conditions of **PBI** (monomers, small aggregates, or large aggregates), the NC and **PBI** underwent coaggregation into disorder, high-order (heterogeneous superlattice), and low-order heterostructures. The high-order coaggregates showed a Roman-pavement-like structure, in which the arranged NCs and assembled **PBI**s are alternately connected (Fig.1), as visualized using transmission electron microscopy. Furthermore, spectroscopic measurement revealed that the high-order heterostructure was formed via an alteration in the  $\pi$ - $\pi$  stacking mode between **PBI**s on the flat surface of the NC. In addition, we revealed that the high-order heterostructure exhibited more efficient energy transfer from the NC to the **PBI**s compared to the low-order heterostructure.

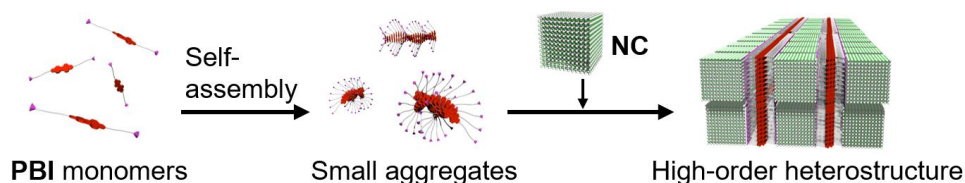


Fig.1 Schematic of self-assembly of **PBI** and coaggregation into high-order heterostructure.

1) M. Yamauchi, S. Yamamoto, S. Masuo, *Angew. Chem. Int. Ed.* **2021**, 60, 6473-6479.

2) N. Kubo, M. Yamauchi, S. Yamamoto, S. Masuo, *Bull. Chem. Soc. Jpn.*, **2021**, 94, 1799-1803.

## フェムト秒過渡吸収顕微鏡を用いたフィコシアニンたんぱく質結晶内におけるエネルギー移動反応観測

(徳大 pLED 研<sup>1</sup>、徳大院理工<sup>2</sup>、JST 創発<sup>3</sup>、名大 SR セ<sup>4</sup>)

○片山 哲郎<sup>1,2,3</sup>、上田 柊斗<sup>2</sup>、梅名泰史<sup>4</sup>、古部 昭広<sup>1,2</sup>

Observation of energy transfer reactions in a phycocyanin protein crystal as revealed by femtosecond transient absorption microscopy

○Tetsuro Katayama<sup>1,2,3,4</sup>, Shuto Ueda<sup>1</sup>, Yasumi Umena<sup>5</sup>, Akihiro Furube<sup>1,2,3</sup> (Faculty of Science and Technology, Tokushima University<sup>1</sup>, Graduated school of Science and Technology, Tokushima University<sup>2</sup>, Institute of post-LED Photonics, Tokushima University<sup>3</sup>, JST FOREST<sup>4</sup>, Aichi SR Center, Nagoya University<sup>5</sup>)

Energy transfer reactions are important reaction processes in photosynthetic systems as natural systems and in solar cells as artificial systems. Especially in natural systems, the energy transfer reaction from the phycobilisome to the photoreaction system is of great importance. In recent years, with the improvement of crystallization technology for these protein systems, photoexcited states and subsequent electron transfer reaction systems at the atomic level have been discussed by free electron X-ray laser experiments. However, because of difficulty of measuring reactions in microcrystals, the difference in the chemical reaction between the crystalline phase and the solution phase is still unknown. In this study, femtosecond transient absorption dichroism on the microscope was measured to clarify the energy transfer reaction between phycocyanin dyes in phycobilisomes in the crystalline phase.

**Keywords :** *Transient absorption microscopy; Time-resolved spectroscopy, Protein crystal;*

近年、時間分解 X 線自由電子レーザー分光によりたんぱく質結晶において原子レベルでの構造変化ダイナミクスが観測可能となってきた。さらに、たんぱく質結晶系の分子間エネルギー移動反応の速度定数、反応因子を可視光域の電子スペクトル変化から理解することは、電子的な分子間相互作用が原子レベルの距離、分子配向変化を誘起する機構の詳細を解明する基礎的観点からだけでなく高効率光電変換系の設計指針を得る応用的観点からも重要である。本研究では顕微鏡下で発光の偏光解消計測およびフェムト秒過渡吸収二色性計測を行い、単一フィコシアニンタンパク質結晶中のエネルギー移動反応を観測した。観測波長 640 nm においてフィコシアニンたんぱく質中色素のフィコシアノビリリンにおける異方性値が 1 ps, 17 ps で減衰する挙動が観測された。これらはピコ秒程度の短い時間領域でエネルギー移動反応が生じていることを示唆している。発表ではこれらの偏光依存性の観点から三量体間のエネルギー移動反応の詳細について議論する。

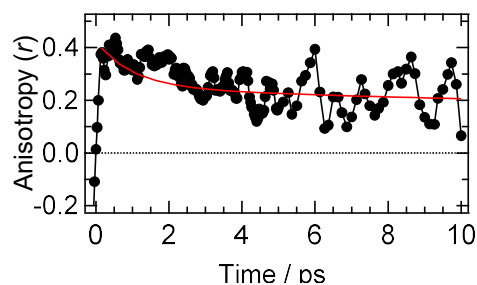


Fig.1 Time profiles of transient absorption anisotropy of phycocyanin crystal excited with 550 nm.



## マイクロ構造電極における酸素発生触媒能の動画観測評価

(北大院総化<sup>1</sup>・北大院理<sup>2</sup>) ○荻澤 大輝<sup>1</sup>・福島 知宏<sup>2</sup>・村越 敬<sup>2</sup>

Evaluation of oxygen evolution reaction in micro-structured electrode by video observation  
(Department of Chemistry, Faculty of Science, Hokkaido University)

○Daiki Ashizawa, Tomohiro Fukushima, Kei Murakoshi

Efficient oxygen evolution reaction (OER) catalysts are demanded for the water electrolysis. Here, micro-structured electrodes were fabricated for the utilization of strong coupling state for OER. Micro-structured substrate was fabricated by photolithography method and vapor deposition of Ni. The catalytic activity of micro-structured electrode was evaluated by the video observation of the bubble evolution from each micro-structured electrodes.

**Keywords :** oxygen evolution reaction; micro-structured electrode; bubble analysis

【序論】近年水の電気分解が注目されているが、水素発生反応と同時に進行する酸素発生反応(OER)のエネルギー損失が大きいことが問題となっている。従来では様々な触媒開発に加えて、電極-電解質界面近傍の水和構造変調による酸素発生触媒活性の向上が行われてきた。近年では水分子が共振器モードと強結合状態を形成した際には水和構造が変化する<sup>1)</sup>と同時に水の解離速度が向上することが提案されており<sup>2)</sup>、強結合状態を酸素発生反応へと導入することによって触媒活性を変調可能であると期待される。本研究では、共振器配列構造などのマイクロ構造電極を作製し、構造からの酸素発生気泡を観測することによって構造に依存した触媒活性変調を評価した。

【実験】合成石英ガラス基板にフォトリソグラフィ手法を用いてマイクロ構造を作製した後に、Ti 4 nm, Ni 200 nm を蒸着することによってマイクロ構造電極を作製した。電位掃引に依存した気泡発生を 1 秒間に 60 フレームの速度で動画観測し撮像視野内の構造を評価した。また、画像解析ソフトを用いて電位に依存した気泡成長を追跡した。溶液としては 1 M NaClO<sub>4</sub> aq. + 3 mM NaOH aq. (pH 11 unbuffered)を用いた。

【結果・考察】マイクロ構造電極作製においては、深さ 1 μm 程度の矩形な共振器配列構造を溝幅 1.0 μm から 5.3 μm までサブマイクロメートルオーダーで制御し作製した。Figure には溝幅 5.2 μm の構造電極における OER 発生気泡の観測例を示す。気泡体積の成長速度より構造電極の OER 電流値は 50 μA 程度と見積もられた。同様にして各構造電極の OER 触媒活性を評価した。

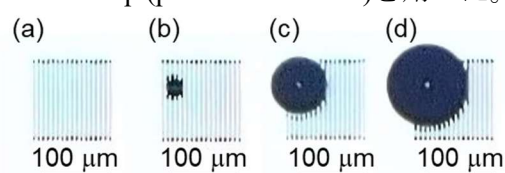


Figure. Analysis of bubble formation on micro-structured electrode by software. Potential;  $E = 2.58$  V vs. RHE ( $t = 0$ ) (a)  $t = 0$  s, (b)  $t = 17$  ms, (c)  $t = 183$  ms, (d)  $t = 350$  ms. Solution; 1 M NaClO<sub>4</sub> aq. + 3 mM NaOH aq. (pH 11 unbuffered). Cavity length is 5.2 μm.

1) T. Fukushima, S. Yoshimitsu, K. Murakoshi, *J. Am. Chem. Soc.* **2022**, 144 (27), 12177.

2) J. M. Bowman, Q. Yu, *Nat. Commun.* **2023**, 14, 3572.

## 真空中のポリオール添加水液滴の凍結過程： 凍結時間の観測と分子動力学シミュレーションによる解析

(九大院理<sup>1</sup>) ○吉岡 拓哉<sup>1</sup>・荒川 雅<sup>1</sup>・秋山 良<sup>1</sup>・寺崎 亨<sup>1</sup>

Freezing processes of droplets of polyol aqueous solutions in a vacuum: Freezing-time measurement and MD simulation (<sup>1</sup>*Department of Chemistry, Kyushu University, Japan*)

○Takuya Yoshioka,<sup>1</sup> Masashi Arakawa,<sup>1</sup> Ryo Akiyama,<sup>1</sup> Akira Terasaki<sup>1</sup>

Micro droplets of pure water freeze rapidly in a vacuum by evaporative cooling via a supercooled state.<sup>1)</sup> On the other hand, droplets of ethylene glycol (EG) were found to survive as a liquid for tens of seconds due to radiative heating that competes with rather slow evaporative cooling of EG.<sup>2)</sup> In the present study, we measured freezing time (time required for freezing) of droplets of polyol aqueous solutions to investigate the effects of addition of polyol. As shown in Fig. 1, the freezing of droplets made an increasing delay as the EG concentration was raised. For numerical analysis of the experimentally obtained freezing curve (the fraction of frozen droplets as a function of time), we need to know ice nucleation rates as a function of temperature. To this end, we carry out molecular dynamics simulations to analyze this temperature dependence.

**Keywords :** water droplet; freezing dynamics; evaporative cooling; polyol aqueous solution; molecular dynamics simulation

直径数十マイクロメートルの水液滴を真空中に導入すると、急速な蒸発冷却により、過冷却状態を経て数ミリ秒で凍結する<sup>1)</sup>。一方で、エチレングリコール (EG) の液滴は、室温の輻射加熱効果が蒸発冷却と拮抗し、真空中でも凍結しないことが報告されている<sup>2)</sup>。そこで、微量のポリオール化合物 (EG、グリセリン (GL) など) を水液滴に添加し、凍結に与える影響を調べた。図 1 に示す通り、凍結時間はポリオール濃度の増加に従って遅延したが、同じ濃度の水溶液では、ポリオールの種類が違っていても、液滴径のばらつきによる誤差の範囲内で一致した。凍結核生成温度 ( $T_H$ ) の低下 ( $\Delta T_H = T_{H, \text{water}} - T_{H, \text{solution}}$ ) を考えて凍結曲線を数値シミュレーションしたところ、凍結時間は再現された一方で、その立ち上がりが実験結果よりも緩やかになる傾向が、濃度の増加とともに顕著となった。凍結曲線の精確な再現には、凍結核生成速度の温度依存性を考える必要がある。純水の凍結核生成速度の温度依存性には報告があるが<sup>3)</sup>、水溶液についてはない。そこで MD 計算を用いて凍結核生成速度を算出し、純水と溶液との違いを比較した。

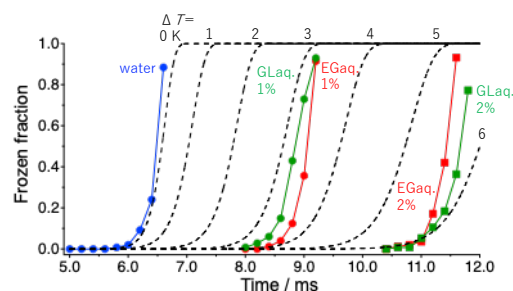


Fig.1 Freezing curves of 40- $\mu\text{m}$  droplets of pure water and aqueous solutions of EG and GL along with curves simulated assuming ice-nucleation-temperature depression  $\Delta T_H = 0, 1, 2, 3, 4, 5$ , and  $6$  K.

1) K. Ando, M. Arakawa, and A. Terasaki, *Phys. Chem. Chem. Phys.* **2018**, *20*, 28435. 2) K. Ando, M. Arakawa, and A. Terasaki, *Chem. Lett.* **2016**, *45*, 961. 3) P. Stöckel, I. M. Weidinger, H. Baumgärtel, and T. Leisner, *J. Phys. Chem. A* **2005**, *109*, 2540.

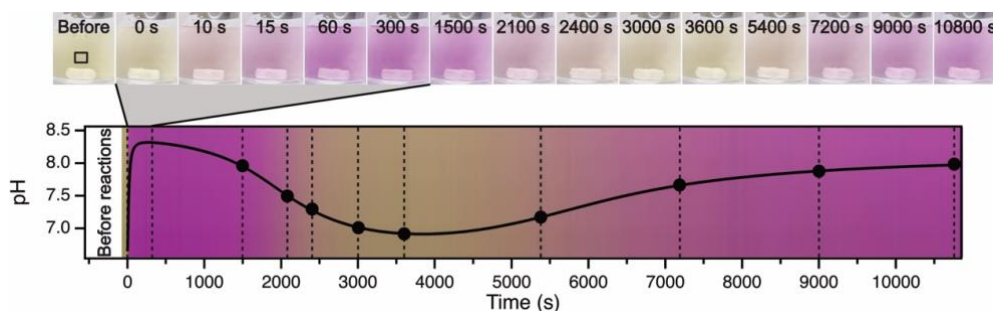


## Design and Applications of Autonomously Recursive pH Changes Through the Coupling of Two Antagonistic Enzymatic Reactions

(<sup>1</sup>Department of Physics, Institute of Physics, Budapest University of Technology and Economics, <sup>2</sup>Department of Earth, Environmental and Physical Sciences, University of Siena, <sup>3</sup>Department of Fundamental Microbiology, University of Lausanne, <sup>4</sup>Institute of Technical Physics and Materials Science, HUN-REN Centre for Energy Research, <sup>5</sup>ELKH-BME Condensed Matter Research Group, Budapest University of Technology and Economics) **○Masaki Itatani**,<sup>1</sup> Paola Albanese,<sup>2</sup> Nadia Valletti,<sup>2</sup> Gábor Holló,<sup>3</sup> Sándor Kurunczi,<sup>4</sup> Robert Horvath,<sup>4</sup> Federico Rossi,<sup>2</sup> István Lagzi<sup>1,5</sup>

**Keywords:** Nonlinear Chemistry, Self-organization, Enzymatic Reactions, Artificial Cell, Non-equilibrium

The design of reaction networks exhibiting autonomous and recursive pH changes, which is ubiquitous in living systems, is a crucial strategy for developing smart materials because they can combine with many bio-related molecular self-assembly. However, such autonomous reaction systems have been limited to a couple of classical chemical oscillators, such as the Belousov-Zhabotinsky reaction in open systems. In this study, we constructed a chemical reaction network having autonomously recursive pH changes with a mild pH range by coupling two antagonistic enzymatic reactions consisting of  $H^+$  and  $OH^-$ -producing steps, namely urea-urease and ester-esterase reactions. The basic properties of the designed system have been investigated in a batch reactor, and it exhibited recursive pH changes over a time range between the neutral and weak base (Figure 1), which was controllable depending on the concentration and types of enzymes and substrates. It is noted that this behavior was processed autonomously without any extra-physicochemical operations, even though it was a closed system completely. Furthermore, we constructed a numerical skeleton model to understand the mechanism of the obtained pH dynamics. Also, the developed pH-regulating system was applied as a dominator to control some pH-responsive molecular self-assembling processes, such as micelle-vesicle and sol-gel transitions, to demonstrate some potential applications.



**Figure 1.** Obtained autonomously recursive pH dynamics in a batch reactor, where pH is indicated by phenol red (snapshots of the reactor at upper part), and the measured pH is plotted with the color change (lower part). Experiments were carried out with [ethyl acetate] = 30 mM, [urea] = 10 mM, [esterase] = 0.4 U/mL, [urease] = 1.0 U/mL, [KCl] = 100 mM, and  $T = 25 \pm 0.5^\circ\text{C}$ .

## 酸化剤濃度に依存した運動パターンの分岐が発現する化学振動反応を内包した自己駆動液滴

(明治大 MIMS<sup>1</sup>・東京大院総合文化<sup>2</sup>・広島大院統合生命<sup>3</sup>) ○久世 雅和<sup>1</sup>・松尾 宗征<sup>2,3</sup>・白石 允梓<sup>1</sup>・中田 聡<sup>3</sup>・西森 拓<sup>1</sup>

Self-propelled motion and deformation of the Belousov-Zhabotinsky droplet depending on the concentration of the oxidizing agent (<sup>1</sup>*Meiji Institute for Advanced Study of Mathematical Sciences (MIMS), Meiji University*, <sup>2</sup>*Graduate School of Graduate School of Arts and Sciences, The University of Tokyo*, <sup>3</sup>*Graduate School of Integrated Sciences for Life, Hiroshima University*) ○Masakazu Kuze,<sup>1</sup> Muneyuki Matsuo,<sup>2</sup> Masashi Shiraishi,<sup>1</sup> Satoshi Nakata,<sup>3</sup> Hiraku Nishimori<sup>1</sup>

In order to elucidate the mechanism of biological self-propelled behavior, a novel self-propelled system was constructed by introducing the Belousov-Zhabotinsky (BZ) reaction, which is well known as an oscillating chemical reaction. In this study, the self-propelled motion and deformation of the BZ droplets in an oil phase were observed as a function of the concentration of oxidant of the BZ reaction, sodium bromate ( $[\text{NaBrO}_3]$ ).

In the BZ droplets in the oil phase, the spatio-temporal patterns were formed, and these patterns enabled to observe the deformation and self-propulsion. The driving force in this system is considered to be the flow, which is generated by the difference in the interfacial tension of the BZ solution since the interfacial tension of the BZ solution in the oxidized state is higher than that in the reduced state.

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

生物の運動を模倣・再現する無生物モデル実験系として、Belousov-Zhabotinsky (BZ) 反応を用いて、自発的に運動・変形する新規自己駆動体の構築を目的とした。BZ 反応は、金属触媒が酸化・還元を自発的に繰り返す化学振動反応として知られる。本研究では、オレイン酸とスクアランを混合した油相に、界面活性剤を含む BZ 反応溶液を滴下し、BZ 液滴を調製した。本実験では、BZ 反応の酸化剤として知られる臭素酸ナトリウムの濃度 ( $[\text{NaBrO}_3]$ ) をパラメータとして、液滴の自発的な運動・変形様相を観測した。

$[\text{NaBrO}_3] < 0.10 \text{ M}$  および  $[\text{NaBrO}_3] > 0.50 \text{ M}$  の場合、液滴の運動や変形は観測されなかった。一方で、その中間の濃度領域では、化学波の伝播方向と同期した液滴の往復運動、アメーバ様の変形を伴う運動、分裂、融合など、多様な運動・変形パターンが発現した。このメカニズムについて、BZ 反応溶液は、BZ 反応の金属触媒であるフェロインが酸化状態と還元状態にあるときでそれぞれ異なる界面張力を示すことから、化学波（局所的な酸化状態）が油水界面に到達することによって界面張力が変化し、張力差に起因する流れが生じ、この流れを駆動力として液滴が駆動したと考察した。

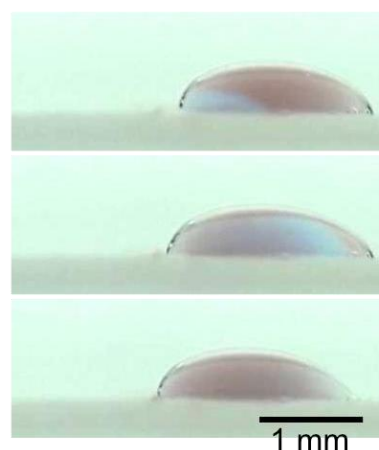


図 1. 液滴の自己駆動.  
(Side view, Interval: 5 s.)

アカデミックプログラム [B講演] | 06. 分析化学：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 A1453(14号館 [5階] 1453)

**[A1453-3am] 06. 分析化学**

座長：火原 彰秀、南 豪

## ◆ 日本語

9:00 ~ 9:20

[A1453-3am-01]

UV吸収による環境中の鉛イオンの簡便な測定を目指したペプチド固定化マイクロビーズの開発

○吉田 秀平<sup>1</sup>、吉田 光輝<sup>1</sup>、鶴岡 孝章<sup>1</sup>、臼井 健二<sup>1</sup> (1. 甲南大学FIRST)

## ◆ 英語

9:20 ~ 9:40

[A1453-3am-02]

Development of quantitative barcode readout on microfluidic paper-based analytical devices (μPADs)

○Yanawut Manmana<sup>1</sup>, Yuki Hiruta<sup>1</sup>, Daniel Citterio<sup>1</sup> (1. Keio University)

## ◆ 英語

9:40 ~ 10:00

[A1453-3am-03]

Electrochemical detection of dopamine based on metal oxide/carbonaceous catalyst

○Alagan Jeevika<sup>1</sup>, Arinori Inagawa<sup>1</sup>, Yuna Kim<sup>1</sup>, Ken-ichi Iimura<sup>1</sup> (1. Utsunomiya University)

10:00 ~ 10:10

休憩

## ◆ 日本語

10:10 ~ 10:30

[A1453-3am-04]

吸収分光法に基づくマイクロ光ファイバーpHセンサーを用いた炭素作用電極および酸化チタン光触媒表面の局所pH変化のその場観測

○NGUYEN DUC QUANG<sup>1</sup>、宇佐美 久尚<sup>1</sup> (1. 信州大学)

## ◆ 英語

10:30 ~ 10:50

[A1453-3am-05]

塗布型導電性MOF薄膜デバイスによる多種アミンガス検出

○大代 晃平<sup>1</sup>、佐々木 由比<sup>1</sup>、本間 信孝<sup>2</sup>、中島 毅彦<sup>2</sup>、南 豪<sup>1</sup> (1. 東大生研、2. トヨタ自動車)

## ◆ 英語

10:50 ~ 11:10

[A1453-3am-06]

酸化アルミニウム生成in-situ観察による結晶多形現象の起源探究

○榊原 雅也<sup>1</sup>、中室 貴幸<sup>1</sup>、中村 栄一<sup>1</sup> (1. 東京大学)

## ◆ 日本語

11:10 ~ 11:30

[A1453-3am-07]

## ガンマ線誘起陽電子消滅寿命測定による酸化セリウムの格子欠陥評価

○道志 智<sup>1</sup>、前田 和紀<sup>1</sup>、平 義隆<sup>2</sup>、渡邊 真太<sup>3</sup>、平出 哲也<sup>4</sup> (1. 大阪技術研、2. 分子研、3. AGC 先端基盤研究所、4. 原子力機構)

---

## UV 吸収による環境中の鉛イオンの簡便な測定を目指したペプチド固定化マイクロビーズの開発

(甲南大学 FIRST) ○吉田秀平・吉田光輝・鶴岡孝章・臼井健二

An Easy-Handling Measurement System for Lead Ions in the Environment using UV Absorption Measurement with Peptide-Immobilized Microbeads (*Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University*)

○Shuhei Yoshida, Koki Yoshida, Takaaki Tsuruoka, Kenji Usui

Pb<sup>2+</sup> pollution and poisoning are globally serious problems. ICP-AES and ICP-MS measurements are well-used to investigate these environmental pollutions. However, organic compounds in samples interfere with ICP measurements. Hence, novel methods that easily detect Pb<sup>2+</sup> from mixture solutions such as sea water, blood, and so on are necessary. Recently, we tried a simple separation of Pb<sup>2+</sup> using peptide-immobilized beads and UV absorption measurement to easily detect Pb<sup>2+</sup> from these mixture solutions. Now, we can detect and quantify Pb<sup>2+</sup> under sub-nM conditions in sea water, river water, and so on. This approach with changing peptide sequences would contribute to the easy detection of a variety of metal ions for environmental measurements.

**Keywords :** Peptide immobilization, Microbeads, Lead pollution, Environmental measurement, UV absorption measurement

現在、重金属による環境汚染が世界的に深刻な問題となっている<sup>1)</sup>。特に、鉛イオン (Pb<sup>2+</sup>) による汚染が深刻な問題となっている<sup>2)</sup>。Pb<sup>2+</sup>をはじめとする重金属による汚染の調査には ICP 測定が用いられているが、試料の前処理が煩雑、測定装置の普及率が低いといった課題がある。そのため、簡便に環境中の Pb<sup>2+</sup>を選択的に分離し、汎用性の高い装置で検出する手法が求められている。そこで本研究ではマイクロビーズに固定化したペプチドを用いた Pb<sup>2+</sup>の選択的な分離と UV 吸収による Pb<sup>2+</sup>の検出を試みた。ペプチドは様々な金属イオンと選択的に結合できることが明らかとなっている<sup>3)</sup>。さらに、ペプチドは様々な化学修飾が可能である。その一つとして、マイクロサイズのビーズに固定化できることも知られており、標的イオンと結合したペプチドを溶液から分離することが可能である<sup>4)</sup>。本実験では、環境水中での分解耐性を付与したペプチド配列を設計、マイクロビーズに固定化し、溶液中から Pb<sup>2+</sup>をペプチド固定化ビーズに分離した。その後、EDTA を用いてペプチドビーズに結合した Pb<sup>2+</sup>を遊離させ、EDTA-Pb(II)由来の UV 吸収を測定することで Pb<sup>2+</sup>を検出、定量した。その結果、本手法を用いて数百 nM の Pb<sup>2+</sup>を定量することに成功した。さらに、海、川、池の水において数百 nM の Pb<sup>2+</sup>の定量に成功している。今後、ペプチド配列の変更を行うことで Pb<sup>2+</sup>以外の金属種の検出も期待できる。

1) S. Bolisetty, M. Peydayesh and R. Mezzenga, *Chem. Soc. Rev.*, **2019**, 48, 463. 2) The Toxic Truth: Children's Exposure to Lead Pollution Undermines a Generation of Future Potential. N. Rees and R. Fuller, *United Nations International Children's Emergency Fund*, **2020**. 3) R. Nian, D. S. Kim, T. Nguyen, L. Tan, C. W. Kim, I. K. Yoo and W. S. Choe, *J. Chromatogr. A*, **2010**, 1217, 5940. 4) H. Miyazaki, Y. Hamada, H. Takaishi, Y. Minamino, H. Ikeda, H. Mekata, M. Takaishi, K. Yamashita and K. Usui, *Analyst*, **2020**, 145, 3211.

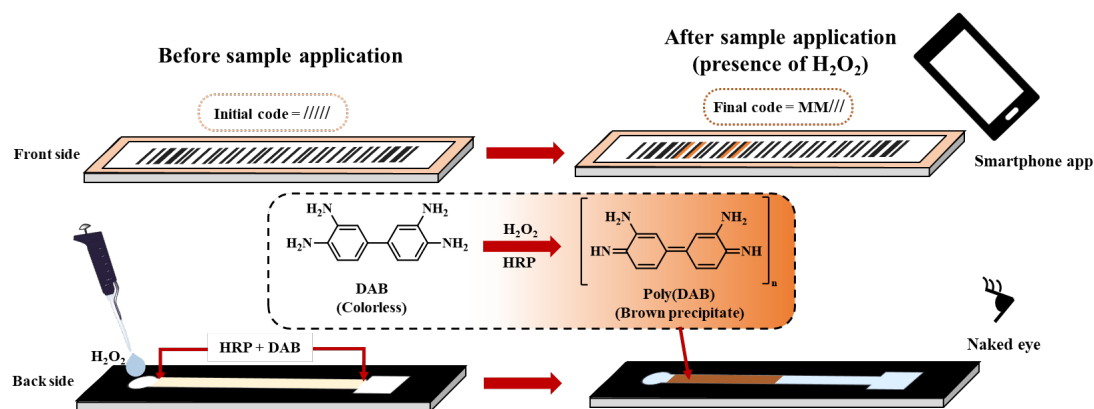
## Development of Quantitative Barcode Readout on Microfluidic Paper-based Analytical Devices ( $\mu$ PADs)

(<sup>1</sup>*Department of Applied Chemistry, Keio University*) ○Yanawut Manmana<sup>1</sup>, Yuki Hiruta<sup>1</sup>, Daniel Citterio<sup>1</sup>

**Keywords:** Paper-based analytical device, Barcode, Distance-based, Smartphone

The development of Point-of-care (POC) testing devices is one of the hot research topics to replace traditional laboratory equipment. In order to make these devices more affordable and accessible to the general public, one of the most recent advances in POC is the development of reading strategies that can be simply interpreted without the use of any sophisticated instrument.<sup>1,2</sup> Barcode technology is a modern method used for data storage and information encoding. With the widespread access to smartphones in recent years, barcodes can be readily read without the need for any dedicated equipment. In addition, the output data from the smartphone can be interpreted, stored, and sent to a professional for additional data analysis. Many  $\mu$ PADs with barcode output have been developed.<sup>3,4</sup> Despite the fact that many barcode detection schemes have been developed for  $\mu$ PADs, the previously reported barcode approaches can provide only a “yes/no” answer for analyte detection. To the best of our knowledge, the application of a barcode for quantitative analyte detection on  $\mu$ PADs has not been reported yet.

Herein, quantitative barcode readout was studied for the first time. A  $\mu$ PAD fabrication strategy with a barcode was investigated using the enzymatic reaction of horseradish peroxidase (HRP), 3,3'-diaminobenzidine (DAB), and  $\text{H}_2\text{O}_2$  as a model system. The polymerization of DAB to polyDAB results in a color change, and a relationship between length of the color changed section and  $\text{H}_2\text{O}_2$  concentration can be observed by the naked eye. Moreover, the barcode pattern changes can be read using a smartphone application. Parameters affecting the detection performance were studied. The developed  $\mu$ PAD offers end-users more simplicity and can be used as a standalone device or in connection with other digital devices.



- 1) K. Yamada, D. Citterio, in *Applications of Microfluidic Systems in Biology and Medicine*, ed. M. Tokeshi, Springer, Singapore, 2019; pp 353–382.
- 2) Z. Li, M. You, Y. Bai, Y. Gong, F. Xu, *Small Methods* 2020, 4 (4).
- 3) A. Katoh, K. Maejima, Y. Hiruta, D. Citterio, *Analyst* 2020, 145 (18), 6071–6078.
- 4) M. Yang, W. Zhang, W. Zheng, F. Cao, X. Jiang, *Lab Chip* 2017, 17 (22), 3874–3882.

## Electrochemical Detection of Dopamine Based on Metal Oxide/Carbonaceous Catalyst

(<sup>1</sup>Center for Innovation Support, Institute for Social Innovation and Cooperation, Utsunomiya University, <sup>2</sup>Faculty of Engineering, Utsunomiya University) ○Alagan Jeevika,<sup>1</sup> Inagawa Arinori,<sup>2</sup> Yuna Kim,<sup>2</sup> Ken-ichi Iimura<sup>2</sup>

**Keywords:** Metal oxide; Hydrothermal synthesis; Neurotransmitter; Electrochemical sensor; Carbonaceous nanocomposite

Dopamine (3,4-dihydroxy-phenyl-ethyl amine) (DA), is an important neurotransmitter among the catecholamine family. It plays a vital role as a hormone and as well as a neurotransmitter in the brain and body. Inadequate or surplus levels of DA cause serious illness, mainly Schizophrenia and Parkinson's disease [1]. Hence, monitoring DA concentration in the human body is highly desirable. The current research focuses on the development of electrocatalysts based on metal oxide and carbon nanomaterials for the detection of DA. Herein, GdMnO<sub>3</sub> and GdMnO<sub>3</sub>/F-GN nanocomposites were synthesized by hydrothermal and followed by ultrasonication techniques. The as-synthesized nanocomposites were confirmed by several analytical methods, such as X-ray diffractometry (XRD), field emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS). The obtained results revealed that the produced nanocomposite was highly crystalline in nature with a desired particle morphology. The electrocatalytic activity of as-synthesized nanocomposite was investigated towards the determination of dopamine level in buffer solutions using electrochemical techniques [2]. The GdMnO<sub>3</sub>/F-GN/GCE showed the reversible oxidation peak potential with uppermost current intensity, as compared to their free electrodes. Also, the GdMnO<sub>3</sub>/F-GN nanocomposite-modified electrode displays good repeatability, reproducibility, considerable stability, and high selectivity under optimal conditions. These results confirm that the proposed electrochemical sensor could be used for monitoring the level of DA in the biological samples.

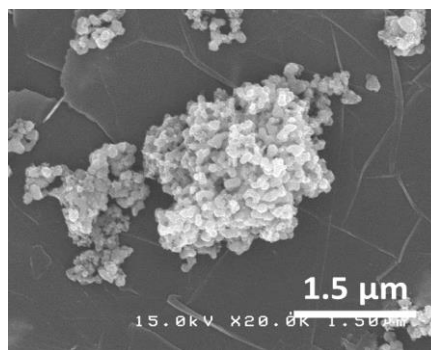


Fig.1 SEM micrograph of GdMnO<sub>3</sub>/F-GN.

**Acknowledgment:** This work is supported by 3C fund of Utsunomiya University.

- [1] P. K. Gopi, B. Muthukutty, S-M. Chen, T-W. Chen, X. Liu, A. A. Alothman, M. A. Ali, and S. M. Wabaidur, *New J. Chem.*, **2020**,44, 18431-18441.  
[2] N. F. Atta, A. Galal, D. M. El-Said, *ACS Omega* **2019**, 4, 17947–17955.

## 吸収分光法に基づくマイクロ光ファイバーpH センサーを用いた炭素作用電極および酸化チタン光触媒表面の局所 pH 変化のその場観測

(信大院総医理工) ○Nguyen Duc Quang ・宇佐美 久尚

In-situ measurement of local pH changes on carbon working electrode and titanium dioxide photocatalyst surfaces using novel microfiber pH sensor based on absorption spectroscopy (Graduate School of Medicine, Science and Technology, Shinshu University) ○Quang Duc Nguyen, Hisanao Usami

Photocatalytic water splitting is composed of oxidation of water to oxygen plus protons and reduction of protons to hydrogen. In-situ measurement of pH close to the surface of the photocatalyst will give crucial information to discuss reaction mechanism. In this study a novel micro-pH sensor was developed by depositing a pH sensitive dye, bromo phenol blue (BPB), on a borosilicate glass fiber. The fiber was Ag-plated with a slit of about 200  $\mu\text{m}$  wide and BPB dye incorporated in the silica-titania gel was deposited on it. Spatial resolution of the sensor was approximately 200  $\mu\text{m}$  along the fiber axis and ca. 20  $\mu\text{m}$  in radial direction of the fiber. The pH in aqueous electrolyte at ca. 50  $\mu\text{m}$  apart from a carbon electrode decreased under anodic condition and increased under cathodic condition. The micro-pH sensor was also applied to measure pH at ca. 50  $\mu\text{m}$  apart from  $\text{TiO}_2$  film under irradiation of uv light.

**Keywords :** Micro pH Sensor; Absorption Spectroscopy; Optical Fiber; Spatial Resolution; Photocatalyst Reaction

水を完全分解する光触媒の酸化側では水からプロトンが生成され、還元側ではプロトンが基質として消費される。このため、光触媒近傍の pH を局所的に測定できれば反応機構の解明に寄与することが期待される。本研究では、ホウケイ酸ガラスファイバーに pH 指示薬（ブロモフェノールブルー, BPB）を担持したマイクロ pH センサーを開発し、光触媒近傍の局所 pH を測定することを検討した。ガラスファイバーの表面を銀コートして巾 300  $\mu\text{m}$  のマイクロスリットを形成し、ここにシリカーチタニアゲルを用いて BPB 色素を担持した。このセンサーの空間分解能は、ファイバー軸方向に約 300  $\mu\text{m}$ 、半径方向に約 30  $\mu\text{m}$  である。この pH センサーをカーボン作用極から 50  $\mu\text{m}$  離して設置して電解に伴う pH 変化を 0.1 M の硫酸ナトリウム水溶液中で測定すると、酸化的条件下で pH は減少し、還元的条件では増加した。また、このマイクロ pH センサーをガラス表面に担持した酸化チタン膜から 50  $\mu\text{m}$  離して設置すると、371 nm の紫外光励起条件下の水分解反応に伴って、pH は 6.85 からわずかに低下した。

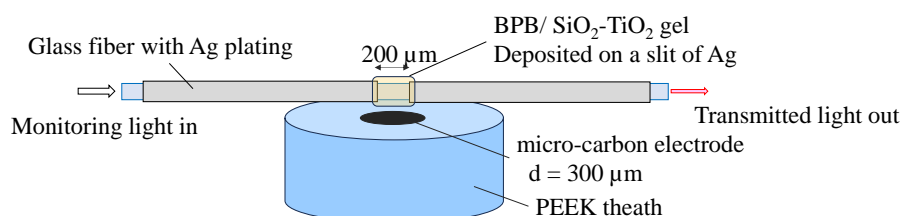


Fig. 1 Schematic model of micro pH sensor located ca. 50  $\mu\text{m}$  over a micro-carbon electrode



## Multi-Amine Gas Detection Using a Solution-Processed Conductive Metal-Organic Framework Thin-Film Device

(<sup>1</sup>*Institute of Industrial Science, The University of Tokyo*, <sup>2</sup>*TOYOTA MOTOR CORPORATION*) ○Kohei Ohshiro,<sup>1</sup> Yui Sasaki,<sup>1</sup> Nobutaka Honma,<sup>2</sup> Katsuhiko Nakajima,<sup>2</sup> Tsuyoshi Minami<sup>1</sup>

**Keywords:** Metal-Organic Framework; Pattern Recognition; Solution Process; Gas Analysis; Conductive Device

Metal-organic frameworks (MOFs) are self-assembled porous materials comprising metal ions and organic ligands, which possess favorable recognition abilities to gas molecules. In addition, their conductivity can be endowed with MOFs by employing the appropriate building blocks, indicating that conductive gas sensing can be performed.<sup>1</sup> In this study, we herein propose a solution-processed layer-by-layer method<sup>2</sup> to fabricate a uniform and reproducible thin film MOF layer for a conductive gas sensor device. In this approach, a MOF layer was obtained by slit-coating cycles with a metal ion (i.e., a copper(II) ion) and an organic ligand (i.e., 2,3,6,7,10,11-hexahydroxytriphenylene) using a robotic dispenser (Fig. 1(a)). The fabricated conductive MOF sensor device quantitatively responded to ammonia gas, and the limit of detection was estimated to be 47 ppb. Figure 1(b) shows conductive responses with a gas structural dependency against six amine gas species (i.e., ammonia, propylamine, isopropylamine, *n*-butylamine, *t*-butylamine, and cyclohexylamine), suggesting the applicability of the MOF sensor to pattern recognition for the discrimination of gas species. Indeed, the target amine gases were discriminated by data processing with linear discriminant analysis (LDA) with 100% correct classification (Fig. 1(c)), which revealed the feasibility of the simultaneous detection of various gas species. Overall, this demonstration clarified the usability of the slit-coating method in the fabrication of the MOF layer and the amine detection ability of the conductive MOF device. The details of the device fabrication, characterization of the conductive MOF thin film, and its sensing results will be shown in the presentation.

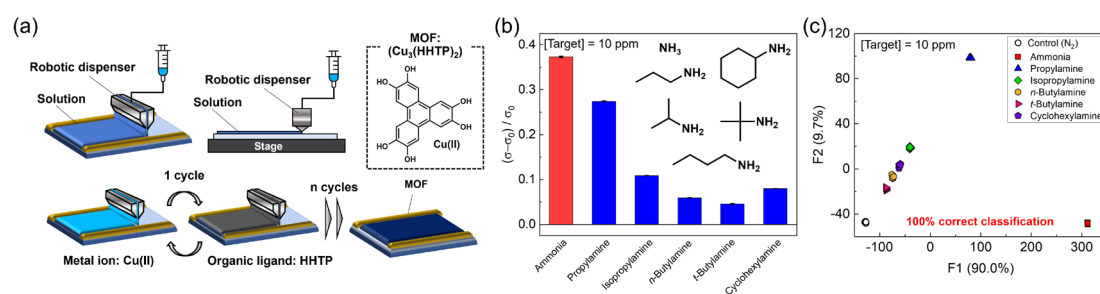


Fig. 1(a) Schematic illustration of the slit-coating method for MOF fabrication. (b) Selectivity test results against six amine gases. (c) LDA canonical score plot for the qualitative assay.

- 1) D. Zhao, et al., *Adv. Sci.* **2021**, 9, 2104374.
- 2) G. Xu et al., *Angew. Chem. Int. Ed.* **2017**, 256, 16510.
- 3) K. Ohshiro, T. Minami et al., *Analyst*, **2022**, 147,1055 (Cover, HOT Article).

## Exploring the Origin of Polymorphism through In-situ Observation of Aluminum Oxide Formation

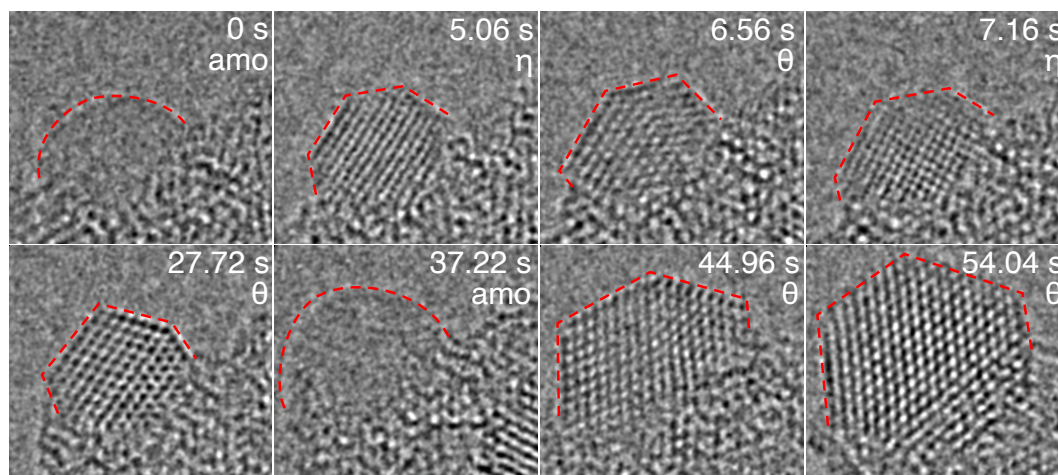
(<sup>1</sup>*Department of Chemistry, The University of Tokyo*)

○Masaya Sakakibara,<sup>1</sup> Takayuki Nakamuro,<sup>1</sup> Eiichi Nakamura<sup>1</sup>

**Keywords:** Crystallization; Crystal Polymorphism; Transmission Electron Microscopy; Atomic Resolution; Cluster

A wide range of compounds is known to crystallize into several crystal structures (polymorphs), and the phenomenon is called polymorphism.<sup>1</sup> Since polymorphs generally exhibit different chemical and physical properties, precise control of polymorphism is essential, especially in the field of materials engineering. Besides its importance, however, rational control of polymorphism has not been realized due to the lack of detailed understanding of the mechanism of polymorph selection during crystallization. Here we report the direct observation of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) crystallization which revealed the role of structural dynamics on the nucleating clusters in polymorph selection by single-molecule atomic-resolution time-resolved electron microscopy (SMART-EM).<sup>2</sup>

Through SMART-EM observation, the in-situ formation of  $\text{Al}_2\text{O}_3$  clusters on the surface of  $\text{Al}(\text{OH})_3$  and the structural fluctuation of these clusters were recorded (Figure). Although all the clusters at 298 K eventually crystallized into  $\theta$ - $\text{Al}_2\text{O}_3$  (44.96-54.04 s),  $\eta$ - $\text{Al}_2\text{O}_3$ , another type of crystal structure, was also transiently detected during the fluctuation (e.g., 5.06 and 7.16 s). This result suggests that polymorph selection in crystal nucleation is a stochastic rather than a deterministic process.<sup>3</sup> Furthermore, variable temperature experiments revealed that the polymorph selectivity can be tuned by modulating the structural fluctuation of nucleating clusters.



1) A. J. C-. Cabeza *et al.*, *Chem. Soc. Rev.* **2015**, 44, 8619. 2) E. Nakamura, *Acc. Chem. Res.* **2017**, 50, 1281. 3) Y. Chen *et al.*, *Nat. Phys.* **2021**, 17, 121.

## ガンマ線誘起陽電子消滅寿命測定による酸化セリウムの格子欠陥評価

(大阪技術研<sup>1</sup>・分子研<sup>2</sup>・AGC 先端基盤研究所<sup>3</sup>・原子力機構<sup>4</sup>) ○道志 智<sup>1</sup>・前田 和紀<sup>1</sup>・平 義隆<sup>2</sup>・渡邊 真太<sup>3</sup>・平出 哲也<sup>4</sup>

Evaluation of the lattice defects for CeO<sub>2</sub> by using gamma-ray induced positron annihilation lifetime measurement (<sup>1</sup>*Osaka Research Institute of Industrial Science and Technology*, <sup>2</sup>*Institute of Molecular Science*, <sup>3</sup>*AGC Inc. Innovative Technology Laboratories*, <sup>4</sup>*Japan Atomic Energy Agency*) ○Satoru Dohshi,<sup>1</sup> Kazuki Maeda,<sup>1</sup> Yoshitaka Taira,<sup>2</sup> Shinta Watanabe,<sup>3</sup> Tetsuya Hirade,<sup>4</sup>

Gamma-ray induced positron annihilation lifetime (GiPALS) measurement is a highly sensitive method which can detect the lattice defects such as oxygen vacancies. The main advantage of GiPALS measurement is 1) the influence of source components can be neglected and 2) the measurement can be performed under various conditions. In this study, we report on a GiPALS measurement at UVSOR-III and theoretical investigation using first-principles calculations of lattice defects in cerium oxide, a common catalytic material.

**Keywords :** *Gamma-ray; Positron annihilation lifetime measurement; Oxygen vacancy; Cerium Oxide*

陽電子消滅寿命測定 (PALS) は格子欠陥などの単原子空孔を高感度に検出できる分析方法である。一般的な陽電子源としては、<sup>22</sup>Na などβ<sup>+</sup>崩壊する放射性同位元素が利用されるが、エネルギーが 1.022 MeV 以上のガンマ線からも対生成と呼ばれる現象によって試料内部で陽電子を発生させることが可能である。この手法を利用した PALS 測定をガンマ線誘起陽電子消滅寿命測定法 (GiPALS) と呼んでいる。GiPALS は、従来の測定法と比較してバックグラウンドを 2 桁近く小さくでき、また陽電子源を試料内部に入れないため、高温高压などの過酷な環境での測定が可能であるという利点がある。一方、酸化セリウム (CeO<sub>2</sub>) の酸素欠陥は触媒活性に影響を及ぼすことが報告されており<sup>1)</sup>、触媒反応中の酸素欠陥の状態や濃度について高感度にその場測定することが求められている。CeO<sub>2</sub> については、陽電子消滅寿命スペクトルは 2 成分 (200 ps 以下の短寿命成分と 350~400 ps 程度の長寿命成分) で fitting できることが報告されている。しかし、実際にはバルクで自由消滅する成分 (バルク成分)、格子欠陥にトラップされて消滅する成分 (欠陥成分)、および表面にトラップされて消滅する成分 (表面成分) の 3 成分は少なくとも存在すると考えられる。そこで、本研究では、粒子径の異なる、つまり、バルク中での陽電子消滅割合が異なる CeO<sub>2</sub> のガンマ線誘起陽電子消滅寿命測定を行い、3 成分で fitting することで、各成分を帰属した。また、第一原理計算により、CeO<sub>2</sub> の陽電子消滅寿命におけるバルク成分、欠陥成分、表面成分を理論的に検討した。

実験方法および結果については、当日報告する。

1) X Liu, et al, *J. Am. Chem. Soc.* **2009**, *131*, 3140.

アカデミックプログラム [B講演] | 06. 分析化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 A1453(14号館 [5階] 1453)

**[A1453-3vn] 06. 分析化学**

座長：稲川 有徳、高貝 慶隆

## ◆ 日本語

15:55 ~ 16:15

[A1453-3vn-01]

凍結水溶液中に形成されたマイクロ構造を利用する粒子のサイズ分級法

○稲川 有徳<sup>1</sup>、君島 惇哉<sup>1</sup>、上原 伸夫<sup>1</sup> (1. 宇都宮大学)

## ◆ 日本語

16:15 ~ 16:35

[A1453-3vn-02]

相分離混相流を溶離液として使用するHPLCシステムの開発—緩衝液を使った三成分系溶離液のシリカカラム分離への影響—

○西村 亮哉<sup>1</sup>、居原田 健志<sup>1</sup>、塚越 一彦<sup>1</sup> (1. 同志社大学)

## ◆ 英語

16:35 ~ 16:55

[A1453-3vn-03]

リテンションインデックスプロット(RI-plot)を用いたWAX材料の構造評価

○海野 祐馬<sup>1,2</sup>、北浦 健大<sup>1</sup>、山田 宏明<sup>1</sup>、北川 慎也<sup>2</sup>、中村 清香<sup>3</sup>、渡邊 亮太<sup>3</sup>、佐藤 浩昭<sup>3</sup> (1. 住友ゴム工業、2. 名工大院工、3. 産総研機能化学)

## ◆ 英語

16:55 ~ 17:15

[A1453-3vn-04]

金ナノ粒子を用いた脂質混合物からの膜タンパク質特異的脂質のスクリーニング

○ワングアムヌイポン スパコーン<sup>1</sup>、川井 隆之<sup>1</sup>、木下 祥尚<sup>1</sup>、松森 信明<sup>1</sup> (1. 九州大学)

## 凍結水溶液中に形成されたマイクロ構造を利用する粒子のサイズ分級法

(宇都宮大工) ○稲川 有徳・君島 惇哉・上原 伸夫

Size-selective separation of microparticles within microstructure formed in a frozen aqueous solution (Faculty of Engineering, Utsunomiya University) ○Arinori Inagawa, Junya Kimijima, Nobuo Uehara

A frozen aqueous solution was integrated into a microfluidic device as a size-tunable separation field for the size-selective separation of micro/nanospheres. The width of the ice grain boundaries formed in the frozen aqueous solution could be varied by controlling the operating temperature. An aqueous sucrose solution sample-dispersing was introduced into the chamber and frozen and ice grain boundaries were generated to reach their ends to the microfluidic channel. Electric field was applied to the ice sample for particle migration by altering the operating temperature since the operating temperature can control the physical interaction between the ice wall and the micro/nanospheres. This enables size-selective migration of the target micro/nanospheres. The eluted spheres in the microchannel were passed through the eluting solution collected at the outlet. We achieved size-selective separation and collection of microspheres and nanospheres.

**Keywords :** Freeze concentrated solution; size-tunable separation; nanospheres; electrophoresis

マイクロ流体デバイス中で水溶液を凍結し、その内部に形成されたナノ・マイクロ構造をサイズチューナブルな分離場として利用するサイズ分級法を確立した<sup>1)</sup>。凍結水溶液中で形成される氷グレインバウンダリーの幅は、作用温度により制御できる。試料であるマイクロ・ナノ粒子を分散させたスクロース水溶液をマイクロ流路の壁面で凍結し、氷グレインバウンダリーがマイクロ流路に対して垂直に形成するようにした。作用温度を制御しながら電気泳動によりマイクロ粒子をマイクロ流路中に溶出させた (Figure 1)。作用温度により、氷壁と粒子間の物理的相互作用を制御できるため、これを利用してサイズ選択的な粒子の分離を実現した (Figure 2)。本手法の適用可能性を探索するためエクソソームと細胞の分離を試みた。

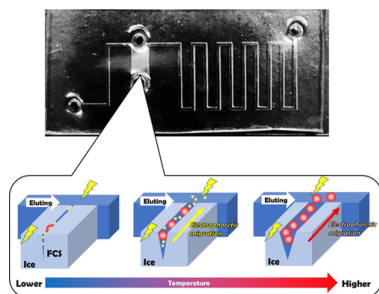


Figure 1. Schematic illustration of the separation mechanism

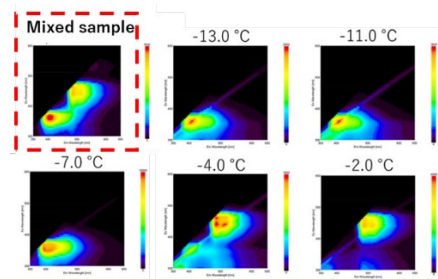


Figure 2. Separation behavior of micro/nanoparticles by this method

1) J. Kimijima, A. Inagawa, N. Uehara, *Anal. Chem.*, **2023**, 95, 14963.

## 相分離混相流を溶離液として使用する HPLC システムの開発—緩衝液を使った三成分系溶離液のシリカカラム分離への影響—

(同志社大理工<sup>1)</sup>) ○西村 亮哉<sup>1</sup>・居原田 健志<sup>1</sup>・塚越 一彦<sup>1</sup>

Development of HPLC System Using Phase-separation Multiphase Flow as an Eluent - Effects of the Ternary Mixed Solution Including Buffer on Silica Column Separation - (<sup>1</sup>*Faculty of Science and Engineering, Doshisha University*) ○Ryoya Nishimura,<sup>1</sup> Takeshi Iharada,<sup>1</sup> Kazuhiko Tsukagoshi<sup>1</sup>

We have developed an HPLC system that uses a phase-separation multiphase flow as an eluent. When chromatography was performed on a silica column using a two-phase separation mixed solution of water / acetonitrile / ethyl acetate as the eluent, a reversed-phase mode was observed regardless of the polarity of the eluent (20 °C). This is thought to be due to the dissociation of the silanol groups on the surface of the silica particles, which causes electrostatic interaction with the hydrophilic substance and causes repulsion, which causes it to elute first. In order to suppress the dissociation of silanol groups, a formic acid buffer / acetonitrile / ethyl acetate mixed solution with a lower pH was used as the eluent, and better separation performance was observed. Based on the study of the influence of pH of the eluent, measurements were performed in phase-separation mode (0 °C). In phase-separation mode, partitioning occurred not only between the mobile phase and the packing material but also between the mobile phases, achieving chromatographic separation.

**Keywords :** HPLC; Chromatography; Phase-separation multiphase flow; Two-phase separation mixed solution; Formic acid buffer / acetonitrile / ethyl acetate

我々は相分離混相流を溶離液として使用する HPLC システムを開発した<sup>1)</sup>。溶離液として、水/アセトニトリル/酢酸エチル系の二相分離混合液を用いた。三成分系混合液を溶離液として ODS カラムまたはシリカカラムを用いてクロマトグラフィーを行ったところ、シリカカラムでの測定において、溶離液の極性の大きさに関係なく親水性物質 2,6-Naphthalenedisulfonic acid (NDS)が疎水性物質 1-Naphthol (NA)よりも先に溶出する逆相モードの挙動を示した(20 °C)。シリカ粒子表面のシラノール基の解離によって、NDS との間に静電的相互作用が引き起こされ、それによる反発により NDS が先に溶出したと考えられる。したがって、まずは相分離モード(0 °C)を使う前の通常の分離モード(20 °C)において以下の基礎的検討を行った。シラノール基の解離を抑制するために、pH を下げたギ酸緩衝液/アセトニトリル/酢酸エチル系混合液を溶離液として用いて、シリカカラムでの測定を行った。一定条件下において、水を使用した三成分系よりギ酸緩衝液を使用した三成分系混合液の方が、モデル試料(NA+NDS)に対してより良い分離性能が見られた。しかし、酢酸エチルはギ酸緩衝液中の水素イオンを触媒として加水分解反応を引き起こす。加水分解によって酢酸が生成されるにつれ、溶離液の水素イオン濃度が上昇することから、溶離液の pH がクロマトグラムへ与える影響についても調べた。これらの検討を踏まえ、相分離モード(0 °C)におけるモデル試料の分離を行った。相分離モードでは移動相と充填剤間の分配だけでなく、移動相間での分配も起こり、クロマト分離が達成された。

1) K. Tsukagoshi, Analytical Sciences, 2023, DOI: <https://doi.org/10.1007/s44211-023-00442-1>

## Characterization of structural isomers in wax using retention index plots

(<sup>1</sup>Sumitomo Rubber Industries, <sup>2</sup>Nagoya Institute of Technology, <sup>3</sup>National Institute of Advanced Industrial Science and Technology (AIST)) ○Unno Yuma<sup>1,2</sup>, Kitaura Takehiro<sup>1</sup>, Yamada Hiroaki<sup>1</sup>, Kitagawa Shinya<sup>2</sup>, Nakamura Sayaka<sup>3</sup>, Watanabe Ryota<sup>3</sup>, Sato Hiroaki<sup>3</sup>

**Keywords:** Gas chromatography, Retention index, Paraffin wax, Structural characterization

Waxes, polyolefin materials, are often used to improve the ozone resistance of rubber products. The chain length (carbon number) distribution and their structural isomers of the wax in the products affect its ozone resistance. Gas chromatography (GC) is a typical method used for analyzing waxes. However, when the composition of waxes is complex, the interpretation of the chromatograms is time-consuming and difficult. To resolve this problem, we employed the retention index plot (RI-plot)<sup>1)</sup>. The retention time of a normal alkane is converted to RI value using corresponding carbon number as an integer. Therefore, RI values for structural isomers, eluted between the normal alkanes, have fractional parts. In RI-plot, the relationship between the rounded integer part of RI (NRI) and the difference between RI and NRI (dRI) are plotted on two-dimensional map, as shown in Fig.1, to easy understanding of the complex chromatogram containing various isomers.

In this study, paraffin waxes were analyzed using GC-time-of-flight mass spectrometry (GC-TofMS) and RI-plot. The groups of normal alkanes, two saturated hydrocarbon components with branched structures, and one hydrocarbon component with a cyclic structure at the end of the chain were clearly visualized in the RI-plot. Furthermore, the RI-plot from the extracted ion chromatogram (EIC) using specific fragment was effective for the detection of specific hydrocarbon isomers with high sensitivity.

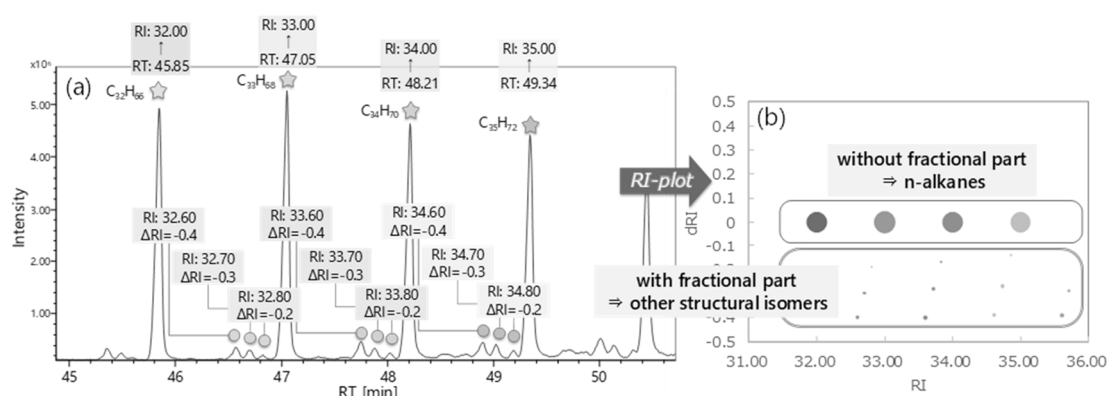


Fig.1 Structural characterization of paraffin wax by GC-TofMS:  
(a) chromatogram and (b) corresponding RI-plot

1) S. Nakamura, et al., The 22nd International Symposium on Anal. and App. Pyrolysis, 2018/6/4, Kyoto.



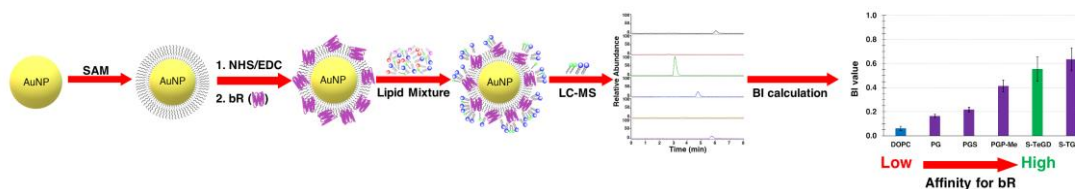
## Gold nanoparticle-based screening of membrane protein-specific lipid from lipid mixture

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

**Keywords:** protein-lipid interaction; Gold nanoparticle; bacteriorhodopsin; liquid chromatography-mass spectrometry

Membrane proteins (MPs) are influenced by the binding of specific lipids. Our previous work introduced a methodology to systematically analyze MP-lipid interactions, utilizing surface plasmon resonance (SPR).<sup>1</sup> In this approach, the SPR gold sensor chip underwent modification with a self-assembled monolayer (SAM) to amplify the MP immobilization comparing with the commercial sensor chip.<sup>1</sup> The SPR-based method showed that S-TGD-1 is a lipid with the highest affinity for archaeal bacteriorhodopsin (bR). A subsequent study revealed that the lipid markedly promotes bR trimer formation, photocycle, and proton pumping.<sup>2</sup> However, the time-consuming lipid purification process was still the main challenge. In this study, to solve this problem, a new approach has been devised by using gold nanoparticles (AuNPs) instead of the gold sensor chips.

AuNPs surface was modified with SAM, on which MP was covalently conjugated. Subsequently, the MP-immobilized AuNPs were combined with a lipid mixture and pulldown experiment was conducted to screen MP-specific lipids.<sup>3</sup> To demonstrate this concept, bR was adopted as a model MP. The fabrication of the bR-immobilized AuNPs was confirmed by dynamic light scattering and electron micrograph. Then, pulldown experiments was performed by mixing bR-immobilized AuNPs with lipid mixture extracted from bR-producing archaea, and the recovered lipids were quantified by liquid chromatography-mass spectrometry (LC-MS). To remove non-specific lipids efficiently, washing conditions was optimized. A new binding index (BI) was developed in order to reproduce the reported lipid affinity for bR.<sup>1</sup> Consequently, the previously underexplored and low-abundant glycolipid S-TeGD was identified as a new candidate for bR-specific lipids.<sup>3</sup> This method circumvents the tedious lipid purification process, thus accelerating the lipid screening from complex lipid mixtures.



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. 3) S. Wangamnuayporn, M. Kinoshita, T. Kawai, N. Matsumori, *Anal. Biochem.* **2024**, 687, 115447.



アカデミックプログラム [B講演] | 07. 無機化学：口頭B講演

📅 2024年3月20日(水) 13:00 ~ 15:10 🏢 A1444(14号館 [4階] 1444)

**[A1444-3pm] 07. 無機化学**

座長：猿山 雅亮、後藤 真人

## ◆ 英語

13:00 ~ 13:20

[A1444-3pm-01]

Trinuclear molecular complexes showing redox-switchable magnetic properties

○Aristide Maximilien Sacha Colin<sup>1,2</sup>, Yiting Wang, Nathalie Bridonneau<sup>2</sup>, François Lambert<sup>2</sup>, Zakaria Halime<sup>2</sup>, Nicolas Suaud<sup>3</sup>, Shin-ichi Ohkoshi<sup>1</sup>, Mohammed Bouammali<sup>3</sup>, Nathalie Guihéry<sup>3</sup>, Talal Mallah<sup>2</sup> (1. University of Tokyo - Graduate School of Science, 2. Université Paris-Saclay, ICMO, 3. Université de Toulouse Paul Sabatier, LCPQ)

## ◆ 英語

13:20 ~ 13:40

[A1444-3pm-02]

イオン性ナノ結晶超格子のカチオン交換反応

○エン シャ<sup>1</sup>、雅亮 猿山<sup>2</sup>、利治 寺西<sup>2</sup> (1. 京都大学理学研究科、2. 京都大学化学研究所)

## ◆ 英語

13:40 ~ 14:00

[A1444-3pm-03]

エトキシオリゴシロキサンから誘導されるポリシロキサンの性質およびそのシリカゲルへの変換

○佐藤 陽平<sup>1</sup>、速水 良平<sup>1</sup>、山本 一樹<sup>1</sup>、郡司 天博<sup>1</sup> (1. 東京理科大学)

14:00 ~ 14:10

休憩

## ◆ 英語

14:10 ~ 14:30

[A1444-3pm-04]

異常高原子価イオンを含むBaFeO<sub>3</sub>の酸素脱離・吸収

○渡邊 滯<sup>1</sup>、後藤 真人<sup>1</sup>、島川 祐一<sup>1</sup> (1. 京都大学)

## ◆ 日本語

14:30 ~ 14:50

[A1444-3pm-05]

ダブルペロブスカイトLn<sub>2</sub>LiFeO<sub>6</sub>のサイト置換効果

○後藤 真人<sup>1</sup>、島川 祐一<sup>1</sup> (1. 京都大学)

## ◆ 英語

14:50 ~ 15:10

[A1444-3pm-06]

ダブルペロブスカイト酸化物R<sub>2</sub>BaFe<sub>2</sub>O<sub>6</sub>における逐次相転移の希土類金属依存性

○飯星 眞<sup>1</sup>、後藤 真人<sup>1</sup>、島川 祐一<sup>1</sup> (1. 京都大学)

## Trinuclear molecular complexes showing redox-switchable magnetic properties

(<sup>1</sup>Graduate School of Science, The University of Tokyo, <sup>2</sup>ICMMO, Université Paris-Saclay, <sup>3</sup>LCPQ, Université de Toulouse) ○Aristide Maximilien Sacha Colin<sup>1,2</sup>, Yiting Wang, Nathalie Bridonneau<sup>2</sup>, François Lambert<sup>2</sup>, Zakaria Halime<sup>2</sup>, Nicolas Suaud<sup>3</sup>, Shin-ichi Ohkoshi<sup>1</sup>, Mohammed Bouammali<sup>3</sup>, Nathalie Guihéry<sup>3</sup>, Talal Mallah<sup>2</sup>

**Keywords:** Molecular Magnetism, Redox switch, Exchange coupling, Spin Interaction

This work deals with the rational design of transition metal-based polynuclear complexes with the purpose of controlling the interaction between the magnetic centers by using a redox active central ligand as some examples have been reported [1]. These molecules could find an application as multi-qbit/SMM systems whose properties are tuned through a redox stimulus. One trinuclear complex based on the central hexahydroxytriphenylene (HHTP) redox active ligand is studied [2]. Its redox states are characterized by spectroelectrochemical measurements and isolation of the first oxidized and first reduced states are reported.

In doing so and with the addition of magnetic measurements, a switch in the magnetic behavior is observed. It occurs from a state where the central ligand is paramagnetic and possess a single electron (that magnetically couples the three metallic centers) to a state for which the diamagnetic central ligand isolates the magnetic centers.

Ab initio calculations show interesting insights in the electronic structure of the studied species. More precisely, the properties of the HHTP ligand are investigated and allow to explain the experimentally observed properties of the complexes [3].

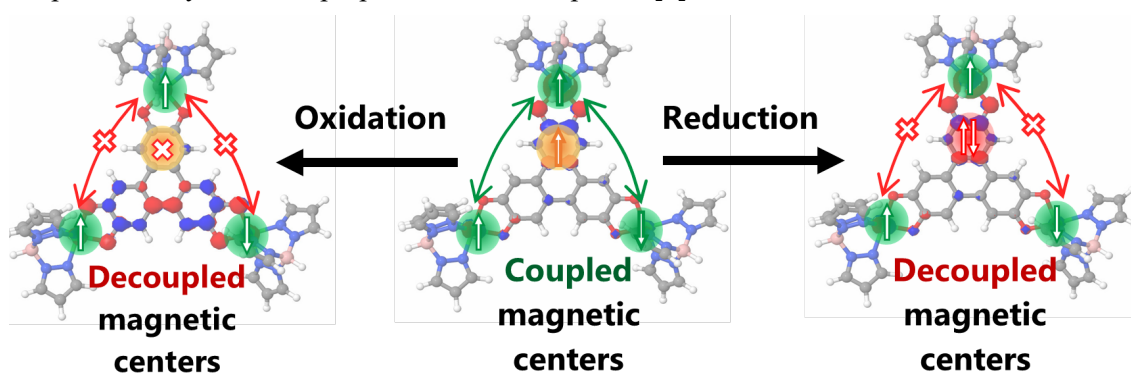


Figure-1: Concept scheme of the Coupling/Decoupling redox switch in  $[\text{Ni}_3(\text{HHTP})(\text{HBTp}^{(\text{Ph},\text{hPh})}_3)_3]$

[1] Ma, X., *et al.* 2019. *J. Am. Chem. Soc.* 141, 7721–7725. <https://doi.org/10.1021/jacs.9b03044>

[2] Wang, Y., *et al.* 2019. *Chem. Commun.* 55, 12336–12339. <https://doi.org/10.1039/C9CC05183J>

[3] Suaud, N. *et al.*, 2023, *Chem. Eur. J.*, e202302256. <https://doi.org/10.1002/chem.202302256>

## Cation Exchange Reactions of Ionic Nanocrystal Superlattices

(<sup>1</sup>Graduate School of Science, Kyoto University, <sup>2</sup>Institute for Chemical Research, Kyoto University) ○Yan Xia,<sup>1</sup> Masaki Saruyama,<sup>2</sup> Toshiharu Teranishi<sup>2</sup>

**Keywords:** Nanocrystal; Superlattice; Cation exchange

Semiconductor ionic nanocrystals (NCs) with well-controlled size and morphology have been extensively studied as luminescent materials, photocatalysts, and so on. In recent studies, NC superlattices (SLs) formed by assembling NC building blocks have attracted much attention because of their collective properties through the coupling of electrons, spins, or dipoles between neighboring NCs, which cannot be realized by individual NCs or corresponding bulk counterparts.<sup>1</sup> Nevertheless, the exploration of unique properties of SLs is still in its infancy, mainly due to the difficulty in producing high-quality SLs in sufficient quantities through the conventional methods involving multiple careful preparation steps and limited scalability.

In this study, we show the rapid and scalable synthesis of various ionic NC SLs through the facile cation exchange (CE) reaction. Parent three-dimensional  $\text{Cu}_{2-x}\text{S}$  SLs can be synthesized using a one-step chemical liquid phase reaction with controlled alkylamine concentration (**Fig. 1a**). The CE reaction was successfully applied to replacing almost all the parent  $\text{Cu}^+$  cations with foreign metal cations, resulting in various new NC SLs with the same morphology and arrangement system as the parent SLs (**Fig. 1b**). In addition, we also found that the addition of polyvinylpyrrolidone (PVP) during the CE reaction can prevent the structural damage of the parent NC SLs (**Fig. 1c**). This work is expected to facilitate the expansion of NC SLs library and the exploration of collective optical functions. This work was supported by JST-CREST (JPMJCR21B4) and JST-FOREST (JPMJFR213I).

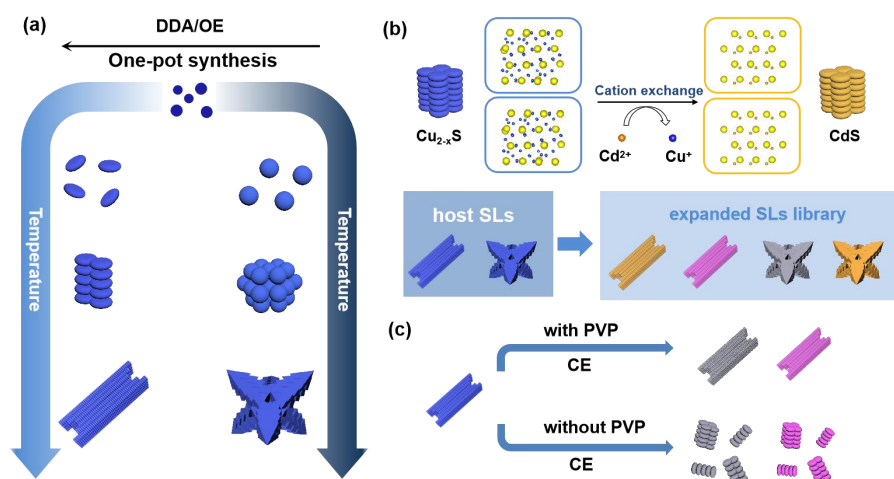


Fig.1 Schematic of self-assembly of NCs and CE reactions of parent SLs.

1) G. Rainò, M. A. Becker, M. I. Bodnarchuk *et al. Nature*, **2018**, 563, 671-675.

## Preparation and properties of polysiloxane using ethoxyoligosiloxanes and their transformation to silica gels

(Graduate School of Science and Technology, Tokyo University of Science) ○ Yohei Sato,<sup>1</sup> Ryohei Hayami,<sup>1</sup> Kazuki Yamamoto,<sup>1</sup> Takahiro Gunji<sup>1</sup>

**Keywords:** Siloxane, Sol-gel reaction, Silica, Silane, Hydrolysis

Hydrolysis and condensation of alkoxyasilane is one of the most representative methods of the synthesis of silica materials. Linear alkoxyoligosiloxanes have been estimated to be formed by the hydrolysis and condensation of alkoxyasilane in the initial stage of sol-gel method based on gas chromatography/mass spectrum and nuclear magnetic resonance spectrum. Recently, we found that the hydrolysis behavior is depended on the structure of ethoxyoligosiloxane. In this work, we will report the preparation and properties of polysiloxane in detail using ethoxyoligosiloxanes and their transformation to silica gels (Fig. 1).

Polysiloxanes were prepared as a condensate (Cs) of tetraethoxysilane (TEOS), hexaethoxydisiloxane (HEDS), and octaethoxytrisiloxane (OETS). Cs was isolated by trimethyl silylation.  $M_w$ ,  $M_w/M_n$ , and QEt/ Si-Me<sub>3</sub> ratio of Cs were approximately 3500, 1.3, and 1.2, respectively. Moreover, Cs were separated to the low and high molecular weight components (LS and HS) as a distillate and residue by vacuum distillation, respectively. Because QEt/ Si-Me<sub>3</sub> ratios of Cs-LS and Cs-HS were similar, Cs was estimated to be separated well. Cs was mainly composed of Q<sup>3</sup> for Si(OEt)(O<sub>0.5</sub>)<sub>3</sub> and Q<sup>4</sup> for Si(O<sub>0.5</sub>)<sub>4</sub> structures on <sup>29</sup>Si NMR regardless of molecular weight such as LS and HS. The yields of Cs-LS and Cs-HS were difference depend on the starting materials. Cs-LS is estimated that mainly composed of 6-membered ladder structures which contains some isomers based on MS and <sup>29</sup>Si NMR.

Silica gels as noted XGs were obtained by aging of Cs followed by heating at 100, 300, 500, 700, or 900 °C. XGs showed micropore by heating at 100–700 °C and nonporous structure by heating at 900 °C. Micropore structures were found to be the difference of Cs as shown in Fig. 2 ( $d_{\text{micro}}$ ; TEOS: 1.1nm, HEDS, OETS: 1.4 nm).

These results were considered to reflect the chemical properties of raw materials.

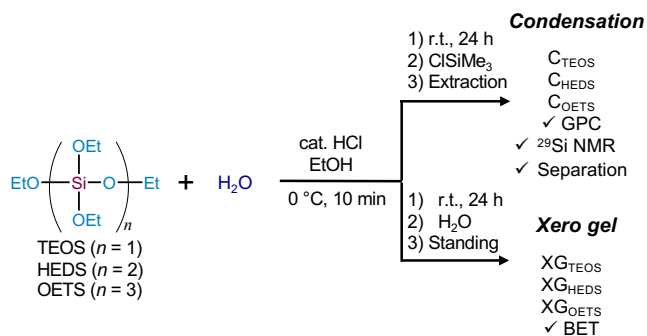


Fig. 1 Preparation of Cs and XGs

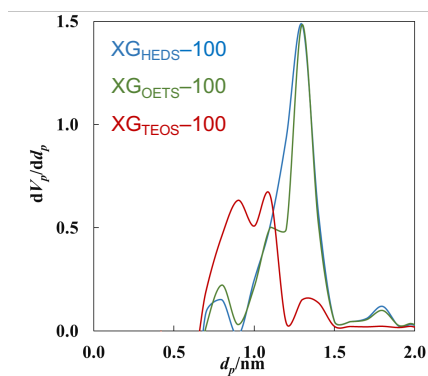


Fig. 2 Micropore-size distribution of XGs

## Oxygen release and incorporation of BaFeO<sub>3</sub> with unusually high valence Fe<sup>4+</sup>

(<sup>1</sup>*Institute for Chemical Research, Kyoto University*) ○Rei Watanabe,<sup>1</sup> Masato Goto,<sup>1</sup> Yuichi Shimakawa<sup>1</sup>

**Keywords:** Unusually High Valence Ion; Oxygen Release/Incorporation; Perovskite-type Oxide

Transition-metal oxides containing unusually high valence cations can readily release their oxygen ions to relieve the electronic instability of the unusual valence states. In this work, we focus on 3C-, 6H-, and 12R-type polymorphs of BaFeO<sub>3</sub> containing Fe<sup>4+</sup>. The 3C-type simple perovskite structure BaFeO<sub>3</sub> consists of corner-sharing FeO<sub>6</sub> octahedra, while the 6H- and 12R-type BaFeO<sub>3</sub> contain both corner-sharing and face-sharing octahedra in the hexagonal perovskite structures (Figure 1). The 3C-type BaFeO<sub>3</sub> was obtained by annealing the oxygen-deficient perovskite BaFeO<sub>2.5</sub> in ozone at 200 °C. The 6H- and 12R-type hexagonal perovskite were prepared by synthesis under high-pressure and high-temperature conditions.

From the thermogravimetric analysis experiments shown in Figure 2, when the samples were heated in ambient air, we found that the sample weight decreased due to oxygen release at relatively low temperatures such as 130 °C for the 3C, 320 °C for the 6H, and 460 °C for the 12R structures. Interestingly, upon cooling after heating in air, the 12R-type BaFeO<sub>3</sub> reversibly incorporated oxygen, while the 3C-type compound did not. Thus, the oxygen release/incorporation behavior is strongly dependent on the crystal structure with corner-sharing and/or face-sharing octahedra. Detailed results on the oxygen release/incorporation behaviors and the corresponding structural changes will be discussed.

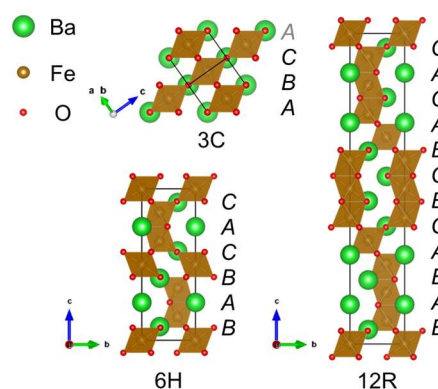


Fig. 1. Crystal structures of BaFeO<sub>3</sub>

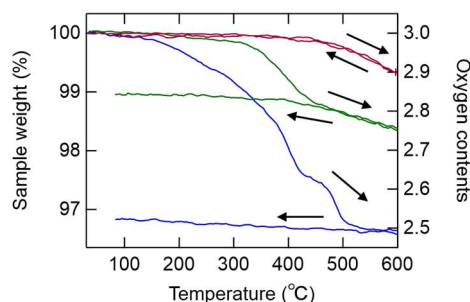


Fig. 2. Results of thermogravimetry measurements for 3C- (blue), 6H- (green), and 12R- (red) type BaFeO<sub>3</sub> in air.

## ・ダブルペロブスカイト $Ln_2LiFeO_6$ のサイト置換効果

(京大化研<sup>1</sup>) ○後藤 真人<sup>1</sup>・島川 祐一<sup>1</sup>

Site substitution effects in double perovskites  $Ln_2LiFeO_6$  (<sup>1</sup> ICR, Kyoto university) ○Masato Goto,<sup>1</sup> Yuichi Shimakawa,<sup>1</sup>

We focus on *B*-site-ordered double perovskites  $Ln_2LiFeO_6$  ( $Ln = La, Nd, Sm, \text{ and } Eu$ ), where unusually high valence  $Fe^{5+}$  ions adopt face-centered-cubic lattices, from the viewpoint of geometrical spin frustration. In this study, we succeeded in partially substituting  $Ca^{2+}$  at the  $Ln^{3+}$  site and  $Mn^{5+}$  at the  $Fe^{5+}$  site. We will report the substitution effects on their structural and physical properties.

**Keywords :** *B-Site-Ordered Double Perovskite; Geometrically Frustrated Magnet; Unusually High Valence Ion; High Pressure Synthesis*

幾何学的フラストレート格子をもつ磁性体は反強磁性秩序の抑制に起因した新奇磁性の発現の舞台として注目を集めている。磁性イオンが面心立方格子を形成する *B* サイト岩塩秩序型ダブルペロブスカイト  $A_2BB'O_6$  は、その代表的な物質系の一つであり、bond valence glass などの興味深い磁性が多く報告されている<sup>[1]</sup>。最近我々は、高温高压合成法を用いて、異常高原子価の  $Fe^{5+}$  が面心立方格子を形成する  $Ln_2LiFeO_6$  ( $Ln = La, Nd, Sm, Eu$ ) の合成に成功し、得られた物質の構造物性相関を解明した<sup>[2,3]</sup>。本研究では、 $La_2LiFeO_6$  の  $La^{3+}$  サイトに  $Ca$  イオンを一部置換した物質  $La_{2-x}Ca_xLiFeO_6$ 、及び  $Fe^{5+}$  サイトに  $Mn^{5+}$  イオンを一部置換した物質  $La_2LiFe_{1-x}Mn_xO_6$  の合成を試み、得られた化合物の結晶構造や  $Fe$  の価数、及び置換に伴う磁性の変化を調査した。

$Ca$  イオン置換体、及び  $Mn$  イオン置換体について、それぞれ仕込み比が  $x = 0.5$  までの試料の合成に成功した。母体である  $La_2LiFeO_6$  と同様に、置換体はいずれも菱面体晶の結晶構造をもつことが分かった (図 1)。また、磁性に着目すると、母体では大きな反強磁性的相互作用が支配的 (ワイス温度  $\theta_{CW} \sim -90$  K) である一方で、 $Ca$  置換体では固溶量  $x$  の増大に伴い  $\theta_{CW}$  が増加することが判明した (図 2)。講演では、 $Mn$  置換体も含めて結果の詳細を示すとともに、それらのサイト置換効果について議論する予定である。

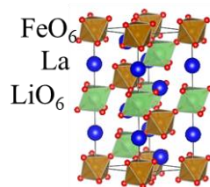


図 1.  $La_2LiFeO_6$  の結晶構造。

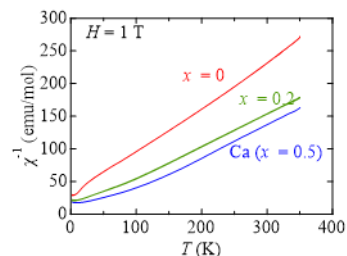


図 2.  $La_{2-x}Ca_xLiFeO_6$  の逆帯磁率の温度依存性。

- [1] M.A. de Vries *et al.*, Phys. Rev. Lett. **104**, 177202 (2010). [2] P. Xiong *et al.*, Inorg. Chem. **55**, 6218, (2016). [3] M. Goto *et al.*, J. Am. Chem. Soc., **143**, 19207 (2021).

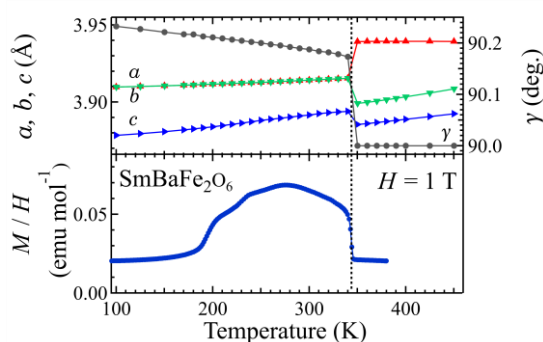
## The Structural and Magnetic Dependence of the Successive Phase Transition Behaviours of Rare-earth Layered Perovskites $RBaFe_2O_6$

(<sup>1</sup>*Institute for Chemical Research, Kyoto University*) ○Makoto Iihoshi,<sup>1</sup> Masato Goto,<sup>1</sup> Yuichi Shimakawa,<sup>1</sup>

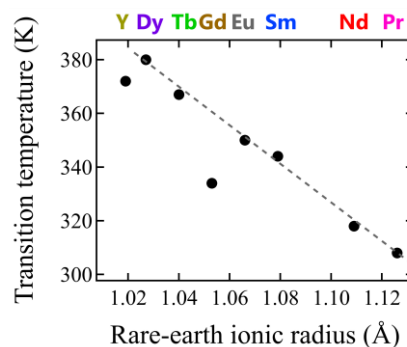
**Keywords:** Phase Transition; Perovskite; Rare-earth Metal; Crystal Structure; Magnetic Property

Phase transitions caused by relieving charge instability have been investigated as one of the most important and interesting phenomena in solid-state chemistry. The successive phase transitions that were recently found in  $SmBaFe_2O_6$  show changes in structural and magnetic properties (Fig.1) to relieve the instability of mixed and unusually high valence  $Fe^{3.5+}$ .<sup>[1]</sup> In this study we synthesised series of isostructural compounds  $RBaFe_2O_6$  with various rare-earth ions ( $R = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y$ ) and investigated their phase transition behaviours.

Rare-earth layered perovskites  $RBaFe_2O_6$  were synthesised by topotactic ozone-oxidation from oxygen-deficient precursors  $RBaFe_2O_5$ . Layered ordering of the rare-earth and Ba ions at the *A*-site was confirmed by structure analysis with Synchrotron X-ray powder diffraction (SXPD) data, and the oxygen contents of the obtained sample were determined to be 6 from thermogravimetric analysis. Temperature-variable SXPD and magnetisation measurements revealed that each compound showed a structural transition with a sudden increase in magnetic susceptibility above room temperature, followed by additional anomalies at lower temperatures. In the presentation, structural, magnetic and charge transition behaviours of the compounds with the mixed and unusually high valence Fe ions and the effects of the magnetic moment and ionic size of *A*-site rare-earth metals will be discussed (Fig.2).



**Fig.1** Temperature dependences of reduced lattice constants and magnetic susceptibility of  $SmBaFe_2O_6$ .



**Fig.2** Structural transition temperature against rare-earth ionic radius.

1) M. Iihoshi, *et. al.*, *J. Amer. Chem. Soc.* **2023**, *145*, 10756-10762



アカデミックプログラム [B講演] | 08. 触媒：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 A1457(14号館 [5階] 1457)

**[A1457-3am] 08. 触媒**

座長：大洞 康嗣、邨次 智

## ◆ 英語

9:00 ~ 9:20

[A1457-3am-01]

白金-ガドリニウム合金ナノ粒子電極触媒の調製と高耐久酸素還元活性

○森山 拓海<sup>1</sup>、邨次 智<sup>1</sup>、唯 美津木<sup>1,2</sup> (1. 名大院理、2. 名大物国セ)

## ◆ 日本語

9:20 ~ 9:40

[A1457-3am-02]

酸素発生反応電極触媒としてのハイエントロピースピネル酸化物ナノ粒子の開発とその反応メカニズムの解析

○岩瀬 和至<sup>1</sup>、加藤 涼雅<sup>1</sup>、筈居 高明<sup>1</sup>、本間 格<sup>1</sup> (1. 東北大学)

## ◆ 英語

9:40 ~ 10:00

[A1457-3am-03]

紫外可視拡散反射分光システムによる触媒水素化反応のその場観察

○Risheng Li<sup>1,2</sup>、川波 肇<sup>1,2</sup>、小平 哲也<sup>2</sup> (1. 筑波大学、2. 国立研究開発法人産業技術総合研究所)

## ◆ 英語

10:00 ~ 10:20

[A1457-3am-04]

1,3-ジエンの酸化的アミノ化反応におけるパラジウムナノクラスターの触媒ダイナミクス

○田原 一輝<sup>1</sup>、藤原 哲晶<sup>2</sup>、鳥居 一幸<sup>1</sup>、鈴木 健之<sup>3</sup>、長谷川 淳也<sup>4</sup>、大洞 康嗣<sup>1</sup> (1. 関西大化学生命工、2. 京大院工、3. 阪大産研、4. 北大触媒研)

10:20 ~ 10:30

休憩

## ◆ 英語

10:30 ~ 10:50

[A1457-3am-05]

POM-担持Agナノ粒子複合化触媒を用いたアルコールとアニリンの酸化的カップリングによるイミンの高選択的な合成

○福田 正次<sup>1</sup>、吉川 聡一<sup>1</sup>、山添 誠司<sup>1</sup> (1. 東京都立大学)

## ◆ 日本語

10:50 ~ 11:10

[A1457-3am-06]

層状複水酸化物-金属酸化物クラスター複合体の合成とその触媒応用

○高橋 浩耀<sup>1</sup>、吉川 聡一<sup>1</sup>、山添 誠司<sup>1</sup> (1. 東京都立大学)

## ◆ 英語

11:10 ~ 11:30

[A1457-3am-07]



Catalytic carboxylation and decarboxylation approach for the construction of bicyclic intermediates as core structural motifs in Natural products

○Sangita Karanjit<sup>1</sup>, Emiko Tanaka<sup>1</sup>, Rei Majima<sup>1</sup>, Ryota Sato<sup>1</sup>, Kosuke Namba<sup>1</sup> (1. Tokushima University)

---

## Creation of Platinum-Gadolinium Alloy Nanoparticle Electrocatalysts for Durable Oxygen Reduction Reaction

(<sup>1</sup>Dept. Chem. Grad. Sch. Sci., Nagoya Univ., <sup>2</sup>RCMS, Nagoya Univ.)

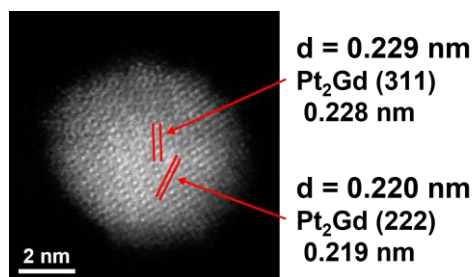
○Takumi Moriyama,<sup>1</sup> Satoshi Muratsugu,<sup>1</sup> Mizuki Tada<sup>1,2</sup>

**Keywords:** Platinum; Gadolinium; Alloy Nanoparticle; Electrocatalyst; Oxygen Reduction Reaction

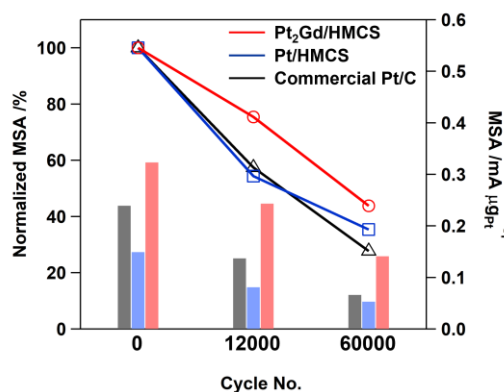
Platinum (Pt) - gadolinium (Gd) alloy nanoparticles are expected to be applied as highly durable oxygen reduction reaction (ORR) electrocatalysts;<sup>1</sup> however, the preparation of Pt-Gd alloy nanoparticles is not easy due to the oxophilic property of Gd. There were several reports on Pt-Gd electrocatalysts but broad size distribution and phase separation of alloy nanoparticles were observed.<sup>2</sup> In this study, we investigated the preparation of Pt-Gd alloy nanoparticle electrocatalysts with narrow size distribution on a porous carbon support and the prepared catalysts exhibited high ORR activity and durability compared with Pt catalysts without alloy formation.

Pt and Gd complexes, (1,5-cyclooctadiene)dimethylplatinum(II) ( $\text{Pt}(\text{C}_8\text{H}_{12})(\text{CH}_3)_2$ ) and *tris*(tetramethylcyclopentadienyl)gadolinium(III) ( $\text{Gd}(\text{C}_9\text{H}_{13})_3$ ) were grafted on a mesoporous carbon sphere (HMCS<sup>3</sup>, 1148 m<sup>2</sup>/g), and the solid sample was reduced under water- and oxygen-prohibited conditions. In the HAADF-STEM image of the prepared sample (**Pt<sub>2</sub>Gd/HMCS**), lattice patterns attributed to Pt<sub>2</sub>Gd (311) and (222) planes were clearly observed (**Figure 1**). The formation of Pt<sub>2</sub>Gd alloy nanoparticles was also confirmed by XRD, Pt *L*<sub>III</sub>-edge XAFS, and Gd 4d XPS. The size distribution of the Pt<sub>2</sub>Gd alloy nanoparticles on **Pt<sub>2</sub>Gd/HMCS** was found to be narrow ( $5.9 \pm 1.7$  nm) compared to reported Pt<sub>2</sub>Gd alloy particles.<sup>2</sup>

**Pt<sub>2</sub>Gd/HMCS** showed higher ORR initial activity than **Pt/HMCS** (Pt nanoparticles prepared without Gd species), and the improvement of the durability of ORR activity was observed on **Pt<sub>2</sub>Gd/HMCS** (**Figure 2**). The active structure of **Pt<sub>2</sub>Gd/HMCS** for the ORR reaction will be also discussed.



**Figure 1.** HAADF-STEM image of **Pt<sub>2</sub>Gd/HMCS**.



**Figure 2.** Changes in MSAs for 60,000 ADT cycles on **Pt<sub>2</sub>Gd/HMCS**, **Pt/HMCS** and commercial Pt/C.

- 1) Escudero-Escribano, M. et al. *Science*. **2016**, 352, 73.
- 2) Hu, Y. et al. *J. Am. Chem. Soc.* **2020**, 142, 953.
- 3) Wan, X.-K. et al. *Dalton Trans.* **2021**, 50, 6811.

## 酸素発生反応電極触媒としてのハイエントロピースピネル酸化物ナノ粒子の開発とその反応メカニズムの解析

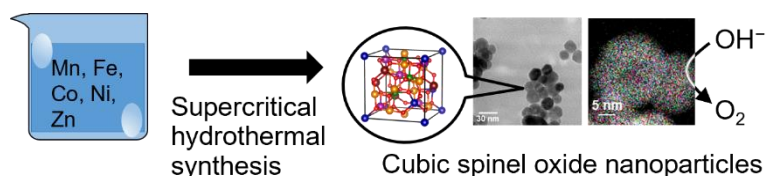
(東北大多元研<sup>1)</sup>) ○岩瀬 和至<sup>1</sup>・加藤 涼雅<sup>1</sup>・笈居 高明<sup>1</sup>・本間 格<sup>1</sup>

Development of high-entropy spinel oxide nanoparticles as oxygen evolution electrocatalysts and their reaction mechanism analysis (<sup>1</sup>*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○Kazuyuki Iwase,<sup>1</sup> Ryoga Kato,<sup>1</sup> Takaaki Tomai,<sup>1</sup> Itaru Honma<sup>1</sup>

The electrochemical oxygen evolution reaction (OER) is an important anodic reaction of electrochemical water splitting for hydrogen production. Recently, high-entropy oxides composed of more than five metal elements have begun attracting attention as OER catalysts. In the present study, we synthesized high-entropy spinel oxide (HE-SO) nanoparticles composed of first five transition metal elements using supercritical fluids processing. HE-SO nanoparticles with an average particle size of about 19 nm, in which the five elements were homogeneously distributed, were obtained. The obtained HE-SO functioned as OER catalysts (overpotential was 330 mV). [1] Synchrotron X-ray absorption spectroscopy (XAS) measurements of the obtained HE-SO under potential-applied conditions (in-situ XAS measurements) showed a clear difference in the potential-dependent changes in XAS spectra compared to results for oxides consisting of only a single metal. [2]

**Keywords :** Oxygen evolution reaction, Nanomaterials, High-entropy oxides, Electrocatalysts

電気化学的酸素発生反応(OER)は、水分解による水素製造のアノード反応として注目されている。種々の遷移金属からなる酸化物触媒は、非貴金属のみからなるものでも塩基性条件で比較的高い OER 活性を有することから注目されている。近年、主に 5 種以上の金属元素からなるハイエントロピー酸化物が OER 触媒材料として注目され始めている。発表者らは、無機ナノ粒子の合成に好適な超臨界流体を用いて、第一遷移金属元素の 5 元素からなるハイエントロピースピネル酸化物(HE-SO)ナノ粒子の合成を試みた。その結果、5 元素が均一に固溶した平均粒子径 19 nm 程度の HE-SO ナノ粒子が得られた。また、得られた HE-SO は OER 触媒として機能することを見出した(過電圧 330 mV)。[1] また、得られた HE-SO の電位印加条件下での放射光測定(in-situ XAS 測定)を行ったところ、HE-SO と単一の金属のみからなる酸化物材料の XAS スペクトルには電位依存的な変化に明確な違いが見られた。[2] 当日は触媒活性評価および構造解析、in-situ XAS 測定の結果の詳細も議論する。



1) **K. Iwase** et al., *ACS Appl. Energy Mater.*, 5, 8, 9292–9296 (2022). 2) **K. Iwase** et al., in preparation.

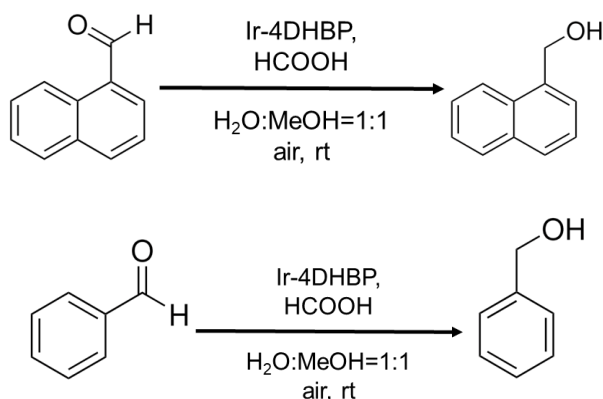
## The in situ UV-vis-diffuse-reflectance spectroscopy observation of the transfer hydrogenation of aromatic aldehyde catalyzed by a highly active Iridium-based catalyst

(<sup>1</sup>Graduate School of Science and Technology, University of Tsukuba, <sup>2</sup>National Institute of Advanced Industrial Science and Technology) ○Risheng Li,<sup>1,2</sup> Tetsuya Kodaira,<sup>2</sup> Hajime Kawanami<sup>1,2</sup>

**Keywords:** Aromatic aldehyde; Iridium-based catalyst; transfer hydrogenation; In situ UV-vis-diffuse-reflectance spectroscopy

Reduction reactions stand as fundamental processes in organic chemistry, representing some of the most straightforward transformations. When aryl aldehydes undergo reduction, the outcome is the formation of alcohols. These alcohols serve as crucial intermediates in the synthesis of both bulk chemicals and pharmaceutical compounds.<sup>1</sup> Nielsen group reported the application of precisely defined pincer Ru and Ir catalysts for the transfer hydrogenation of furanic aldehydes derived from bioresources, conducted without the presence of a base.<sup>2</sup> However, due to the lack of efficient in situ analytical method besides NMR spectroscopy, there is no explicitly proposed mechanism theory of the reduction.

In this research, we applied our in situ UV-vis-diffuse-reflectance spectroscopy to monitor the process of transfer hydrogenation reactions of benzaldehyde and 1-naphthaldehyde catalyzed by Ir-4DHBP complex at room temperature. Formic acid was used as the hydrogen donor in this reaction. By the application of this in situ technique, we observe the change of intermediates and calculate the reaction rate from the consumption of the reactants. Moreover, in order to confirm the results obtained by our in situ method, we also conducted the analysis by GC-MS, LC-MS, and NMR spectroscopy.



1) E. A. Verochkina, N. V. Vchislo, I. B. Rozentsveig, *Molecules*, **2021**, 26, 4297. 2) R. Padilla, Z. Ni, D. Mihrin, R. Wugt Larsen, M. Nielsen, *ChemCatChem*, **2023**, 15(2).

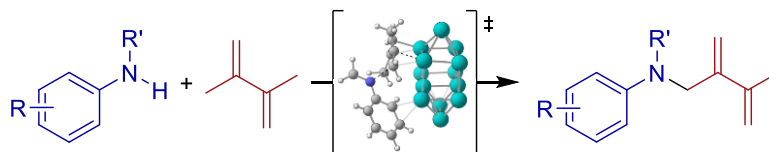
## Catalytic dynamics of palladium nanoclusters in oxidative amination of 1,3-dienes

(<sup>1</sup> Faculty of Chemistry, Materials & Bioengineering, Kansai University, <sup>2</sup> Graduate School of Engineering, Kyoto University, <sup>3</sup> SANKEN, Osaka University, <sup>4</sup> Institute for Catalysis, Hokkaido University) ○ Kazuki Tabaru,<sup>1</sup> Tetsuaki Fujihara,<sup>2</sup> Kazuyuki Torii,<sup>1</sup> Takeyuki Suzuki,<sup>3</sup> Jun-ya Hasegawa,<sup>4</sup> Yasushi Obora<sup>1</sup>

**Keywords:** Palladium nanoclusters; Palladium nanoparticles; Oxidative amination; 1,3-Dienes; DFT calculation

Pd-catalyzed oxidative coupling has served as powerful tool in terms of an atom- and step economical system.<sup>1</sup> The reaction proceeds under a Pd(0)/Pd(II) system, and inherently involved re-oxidation of the catalyst, requiring the presence of oxidants such as metal salts, quinones, and molecular oxygen. In the catalytic reaction, the resulting Pd(0) species would be re-oxidized to Pd(II) species or formed into Pd aggregates having a range of diameters through a deactivated process of catalysts. Therefore, the catalytic solution involved a various forms of palladium catalysts such as monomeric complexes and palladium nanoclusters (Pd NCs).<sup>2</sup> However, the precise role of the Pd NCs in the oxidative coupling has been unclear and the monomeric palladium complex contributes exclusively to their catalysis.<sup>3</sup>

Here, we found that the role of Pd NCs in oxidative coupling, leading to the development of an unprecedented amination with 1,3-dienes. The Pd NCs, synthesized by reduction of palladium acetate with hexamethyldisilane allowed to react with 1,3-dienes and aromatic amines to form oxidative coupling products, in which the remaining conjugated 1,3-diene can act as a synthetic linchpin. By combining several wet-experiments, synchrotron X-ray radiation experiments (X-ray absorption fine structure and small angle X-ray scattering), and computational studies based on the density functional theory, we confirmed that multiple interactions between the Pd NCs and substrates including 1,3-dienes and aromatic amines contribute to the formation of the oxidative coupling product. This unique mechanism depends on the characteristic feature of adjacent palladium atoms in the Pd NCs rather than the monomeric metal complexes.



- Pd NCs-catalyzed unprecedented oxidative coupling with 1,3-diene
- Multiple metal interactions between Pd NCs and substrates
- XAFS, SAXS, DFT investigations for mechanistic studies

1) a) K. Tabaru, Y. Obora, *Eur. J. Org. Chem.* **2022**, e202200618. b) K. Tabaru, Y. Obora, *Synlett* doi: 10.1055/a-2227-1020. 2) M. V. Polynski, V. P. Ananikov, *ACS Catal.*, **2019**, 9, 3991. 3) D. Wang, A. B. Weinstein, P. B. White, S. S. Stahl, *Chem. Rev.* **2018**, 118, 2636.

## Highly selective synthesis of imines through oxidative coupling of alcohols and anilines using POM-supported Ag NPs composite catalysts

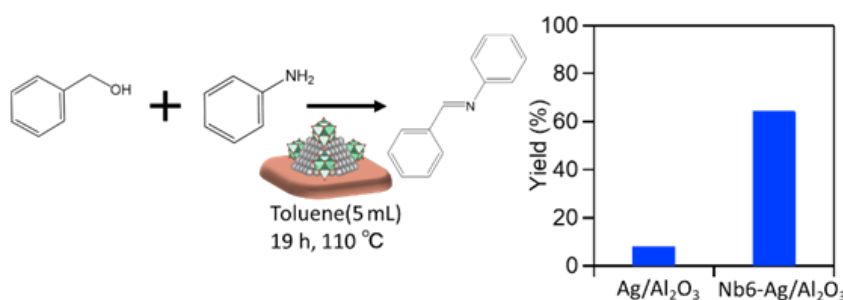
(Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University)

○Shoji Fukuda, Soichi Kikkawa, Seiji Yamazoe

**Keywords:** Polyoxometalate; Supported Ag nanoparticles; Base catalysis

The synthesis and catalytic application of metal nanoparticles (NPs) using metal oxide clusters (polyoxometalates, POMs) as protective ligands has attracted much attention in recent years. It is expected NPs and POMs to play the cooperative roles at the metal NPs-POM interface. The basic POMs could be modified the surface of supported Au NPs, and the activity for reduction of aromatic nitro compounds using  $H_2$  was enhanced by POM modification due to the bifunctional roles of the reduction ability of Au NPs and the base catalytic ability of POMs<sup>1)</sup>. In this study, basic POM was modified to supported Ag NPs on  $Al_2O_3$  support and the obtained catalyst was applied to oxidative coupling of alcohols and amines that Au or Pd NPs catalyst were typically used in the presence of external base.

$[Nb_6O_{19}]^{8-}$  was adsorbed on the surface of Ag nanoparticles by stirring supported Ag nanoparticles in aqueous solution of  $[Nb_6O_{19}]^{8-}$ . The prepared sample was named as Nb6-Ag/ $Al_2O_3$ . The selective adsorption of  $[Nb_6O_{19}]^{8-}$  on supported Ag nanoparticles was confirmed by elemental mapping by STEM and XAFS. Nb6-Ag/ $Al_2O_3$  showed higher imine yield in oxidative coupling reaction of benzyl alcohol and aniline than Ag/ $Al_2O_3$  (Fig. 1). The catalytic activity of Ag/ $Al_2O_3$  was enhanced by the addition of base because the formation rate of benzaldehyde, which is intermediate species, increased in base condition. Thus,  $[Nb_6O_{19}]^{8-}$  on the surface of Ag nanoparticles plays as base and improves this oxidative coupling reaction without the addition of any external base.



**Fig. 1** Synthesis and yield of imines by oxidative coupling reaction of alcohols and anilines.

1) S. Kikkawa, S. Fukuda, J. Hirayama, N. Shirai, R. Takahata, K. Suzuki, K. Yamaguchi, T. Teranishi, S. Yamazoe, *Chem. Commun.*, **2022**, 58, 9018.

## 層状複水酸化物-金属酸化物クラスター複合体の合成とその触媒応用

(都立大院理) ○高橋 浩耀・吉川 聡一・山添 誠司

Synthesis of layered double hydroxide - metal oxide cluster composites and their catalytic applications (<sup>1</sup>Tokyo Metropolitan University) ○Koyo Takahashi,<sup>1</sup> Soichi Kikkawa,<sup>1</sup> Seiji Yamazoe<sup>1</sup>

Anionic metal oxide clusters (polyoxometalate, POM) consisting of dozens of metal oxide units exhibit unique acid and base properties that are unpredicted from the corresponding bulk metal oxides<sup>1)</sup>. We have reported that  $[\text{M}_6\text{O}_{19}]^{8-}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) and  $[\text{Nb}_{10}\text{O}_{28}]^{6-}$  showed the strong base property and catalytic activity for Knoevenagel condensation and  $\text{CO}_2$  fixation reaction as Bronsted and Lewis base catalysts, respectively<sup>2,3)</sup>. In this study, we synthesized the composites of POM and layered double hydroxide (LDH) that hydroxide sheet cation incorporated POM anions in the interlayers to develop heterogeneous base catalysts using  $[\text{Nb}_6\text{O}_{19}]^{8-}$  and  $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ . POM-LDH composites were synthesized by reconstruction of calcined LDH in POM aqueous solution<sup>4)</sup>. X-ray powder diffraction showed that the peaks derived from (00 $l$ ) ( $l = 3, 6, 9$ ) facets newly appeared at lower degrees in addition to the original peaks, suggesting the synthesis of POM-LDH composites. We will report on the base catalytic activity of POM-LDH composites evaluated by Knoevenagel condensation reaction.

**Keywords :** Metal oxide cluster, Layered double hydroxide, Base catalyst

数個から数十個の金属酸化物ユニットで構成されるアニオン性金属酸化物クラスター (polyoxometalate, POM) はバルクの金属酸化物からは予想できない特異な酸・塩基性を示す<sup>1)</sup>. 我々は $[\text{M}_6\text{O}_{19}]^{8-}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) や $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ が強塩基性を示し, Bronsted および Lewis 塩基触媒として Knoevenagel 縮合反応や  $\text{CO}_2$  固定化反応に活性を示すことを見出している<sup>2,3)</sup>. 本研究では,  $[\text{Nb}_6\text{O}_{19}]^{8-}$  及び  $[\text{Nb}_{10}\text{O}_{28}]^{6-}$  の不均一系塩基触媒への応用を目的とし, 層状複水酸化物 (layered double hydroxide, LDH) の水酸化物カチオンシートの層間に POM を内包した POM-LDH 複合体を合成した. LDH の焼成により得た酸化物を POM 水溶液中で再構築する方法<sup>4)</sup>を用いて POM-LDH 複合体を合成した. 図 1 に示す X 線粉末回折 (XRD) パターンからは, 再構築により LDH の (00 $l$ ) ( $l = 3, 6, 9$ ) 面由来の回折に加えて, より低角度側にシフトした回折線を確認した. 層間に POM がインターカレートされ層間距離が広がった LDH が得られたと考えている. 発表では, 得られた POM-LDH 複合体の塩基触媒特性について, Knoevenagel 縮合反応により議論する.

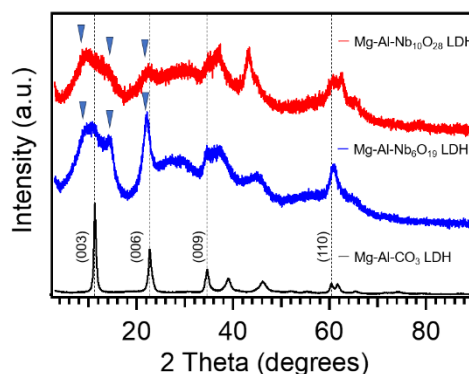


図 1 LDH の XRD パターン

- 1) K. Kamata *et al.*, *Catalysts*, **2017**, 7, 345., 2) S. Hayashi *et al.*, *J. Phys. Chem. C*, **2018**, 122, 29398., 3) S. Hayashi *et al.*, *Chem. Asian J.* **2017**, 12, 1635., 4) R. Choumane *et al.*, *RSC Adv.*, **2021**, 11, 36951.



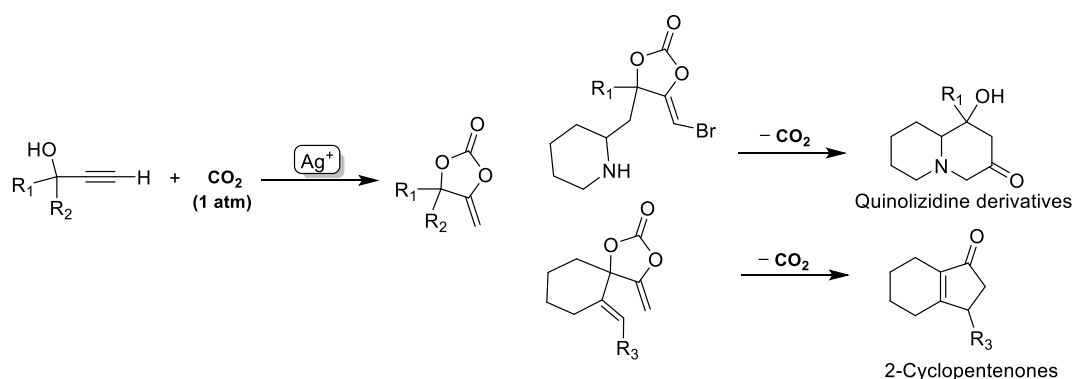
## Catalytic carboxylation and decarboxylation approach for the construction of bicyclic intermediates as core structural motifs in natural products

(<sup>1</sup>Graduate School of Pharmaceutical Science, Tokushima University)

○Sangita Karanjit<sup>1</sup>, Emiko Tanaka<sup>1</sup>, Rei Majima<sup>1</sup>, Ryota Sato<sup>1</sup>, Kosuke Namba<sup>1</sup>

**Keywords:** Silver catalyst, fused-bicyclic core, carboxylation, decarboxylation

Carboxylation is a process of chemical fixation of CO<sub>2</sub>, particularly attractive in the field of organic and green synthesis because it utilizes CO<sub>2</sub> as an abundant C1 source which has indirect role as an environmental pollutant. There have been numerous advances on the metal-catalyzed synthesis of various organic compounds utilizing CO<sub>2</sub> as a C1 source. Among them, the reactions of CO<sub>2</sub> with unsaturated alcohols to afford cyclic carbonates through carboxylative cyclization process is one of the promising green routes. These compounds not only have potential biological activities but also show a wide range of application in organic synthesis for being important building blocks in the synthesis of many biologically active natural products, and pharmaceuticals. We recently developed a mild and efficient, reusable heterogeneous silver catalyst immobilized on silica support<sup>1</sup> via alkoxysilane linkage (Im<sup>+</sup>Cl<sup>-</sup>@SiO<sub>2</sub>) for the synthesis of cyclic carbonates from propargyl alcohols and CO<sub>2</sub>. In this work, decarboxylation of these cyclic carbonates gave fused-bicyclic structures having cyclopentenones and azabicyclic systems which form the core skeleton in many natural products. This decarboxylation strategy which is simple, mild, efficient, and green route involves the elimination of CO<sub>2</sub> as the driving force for the construction of fused-bicyclic key intermediates containing cyclopentenone and azabicyclic unit.



1) S. Karanjit, E. Tanaka, L. K. Shrestha, A. Nakayama, K. Ariga, and K. Namba, *Catal. Sci. Technol.* **2022**, *12*, 3778.



アカデミックプログラム [B講演] | 08. 触媒：口頭B講演

📅 2024年3月20日(水) 13:00 ~ 15:30 📍 A1458(14号館 [5階] 1458)

**[A1458-3pm] 08. 触媒**

座長：影島 洋介、小寺 正徳

## ◆ 英語

13:00 ~ 13:20

[A1458-3pm-01]

窒素含有炭素材料の光触媒作用を利用した抗菌特性評価

○川口 雅之<sup>1</sup>、三宅 一樹<sup>1</sup>、村上 飛龍<sup>1</sup>、齊藤 安貴子<sup>1</sup>、森田 成昭<sup>1</sup> (1. 大阪電気通信大学)

## ◆ 英語

13:20 ~ 13:40

[A1458-3pm-02]

大面積化に向けた反応器による過酸化水素の人工光合成

○潘 振華<sup>1</sup>、片山 建二<sup>1</sup>、Shu Hu<sup>2</sup>、Chiheng Chu<sup>3</sup> (1. 中央大学、2. イェール大学、3. 浙江大学)

## ◆ 日本語

13:40 ~ 14:00

[A1458-3pm-03]

メタン存在下における光触媒水分解反応の特異的な促進

○斎藤 晃<sup>1</sup>、佐藤 宏祐<sup>1</sup>、東 泰佑<sup>1</sup>、杉本 敏樹<sup>1,2</sup> (1. 分子科学研究所、2. 総合研究大学院大学)

## ◆ 英語

14:00 ~ 14:20

[A1458-3pm-04]

アルカン酸化と水素生成を同時駆動する光レドックスカスケード触媒系の構築

○小林 厚志<sup>1</sup> (1. 北海道大学)

14:20 ~ 14:30

休憩

## ◆ 英語

14:30 ~ 14:50

[A1458-3pm-05]

非混和性二相溶液間を自発的に移動する電子伝達体により水の酸化と統合された新規光触媒反応系の開発

○板垣 廉<sup>1,2</sup>、中田 明伸<sup>1,3</sup>、鈴木 肇<sup>1</sup>、富田 修<sup>1</sup>、張 浩徹<sup>4</sup>、阿部 竜<sup>1</sup> (1. 京大院工、2. 学振DC1、3. JSTさきがけ、4. 中大理工)

## ◆ 英語

14:50 ~ 15:10

[A1458-3pm-06]

Scalable and efficient water-splitting photocatalyst sheets based on carbon-based conductors

○Chen Gu<sup>1</sup>、Yi-Wen Ma<sup>1</sup>、Tsuyoshi Takata<sup>1</sup>、Takashi Hisatomi<sup>1</sup>、Yuta Nishina<sup>3</sup>、Nobuyuki Zettsu<sup>1</sup>、Kazunari Domen<sup>1,2</sup> (1. Shinshu University, 2. The University of Tokyo, 3. Okayama University)

## ◆ 英語

15:10 ~ 15:30

[A1458-3pm-07]

Development of charge carrier-selective heterodyne transient grating spectroscopic technique and its application in the distinction of surface trap states in hematite

○Woon Yong Sohn<sup>1</sup> (1. Chungbuk National University)

---

## Antimicrobial property evaluation using photocatalytic action of carbonaceous materials containing nitrogen

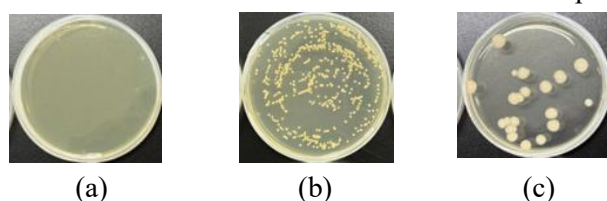
(<sup>1</sup>*Faculty of Engineering, Osaka Electro-Communication University*) ○ Masayuki Kawaguchi,<sup>1</sup> Kazuki Miyake,<sup>1</sup> Hiryu Murakami,<sup>1</sup> Akiko Saito,<sup>1</sup> Shigeaki Morita<sup>1</sup>

**Keywords:** Carbonaceous Materials Containing Nitrogen; Photocatalytic Properties; Antimicrobial Properties; Visible Light Irradiation; Reaction Mechanism

Photocatalysts such as titanium dioxide (TiO<sub>2</sub>) and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) have been studied to purify polluted water and air and to electrolyze water at low voltage.<sup>1</sup> Among the photocatalysts, materials with antimicrobial properties under visible light irradiation have attracted attention in recent years in order to protect people's living environment from various viruses. We previously prepared carbonaceous materials containing nitrogen (called "C/N materials" in this presentation) and investigated their application to capacitors<sup>2,3</sup> and photocatalysts.<sup>4</sup> In this presentation, we report antimicrobial property evaluation using photocatalytic action of the C/N materials with the irradiation of visible light.

C/N materials having compositions C<sub>2</sub>N,<sup>2</sup> C<sub>3</sub>N<sup>3</sup> and C<sub>6</sub>N<sub>9</sub>H<sub>3</sub><sup>5</sup> were prepared by thermal decomposition of organic compounds. Yeast was applied onto the C/N material and the antimicrobial properties were evaluated by the colony forming unit (CFU) counting after irradiation with visible light. Comparisons were also made with cases where titanium oxide, which has photocatalytic properties, was used and cases where no light irradiation was used. Figure 1 shows an example of the CFU results of C<sub>2</sub>N compared with the case of TiO<sub>2</sub>. Almost no colonies were observed on the agar medium treated with the C/N materials (Fig. 1-a), indicating antimicrobial activity due to photocatalytic action caused by visible light irradiation.

We have measured UV-visible spectra of the C/N materials to investigate the mechanism of photocatalytic action of the materials and will discuss it at the presentation.



**Figure 1.** The CFU results of (a) C<sub>2</sub>N with irradiation of visible light, (b) C<sub>2</sub>N without irradiation of light, (c) TiO<sub>2</sub> with irradiation of visible light.

The authors would like to thank Nippon Soda Co., Ltd for providing the precursors of C/N materials and supporting this research.

1) W. Iqbal, *et. al*, *Catal. Sci. Technol.* **2018**, 8, 4576. 2) M. Kawaguchi, T. Yamanaka, Y. Hayashi, H. Oda, *J. Electrochem. Soc.* **2010**, 157, A35. 3) M. Kawaguchi, A. Itoh, S. Yagi, H. Oda, *J. Power Sources* **2007**, 172, 481. 4) M. Kawaguchi, Y. Ishida, *CARBON2013*, Rio de Janeiro, Brazil, **2013** Abstract No. 113. 5) M. Kawaguchi, K. Nozaki, *Chem. Mater.* **1995**, 7, 257.

## Photosynthesis of hydrogen peroxide by a scaled-up reactor

(<sup>1</sup>Department of Applied Chemistry, Chuo University, <sup>2</sup>Department of Chemical and Environmental Engineering, Yale University, <sup>3</sup>Faculty of Agriculture, Life, and Environmental Sciences, Zhejiang University) ○Zhenhua Pan,<sup>1</sup> Kenji Katayama,<sup>1</sup> Shu Hu,<sup>2</sup> Chiheng Chu<sup>3</sup>

**Keywords:** Photocatalyst, Hydrogen peroxide, Panel reactor

Particulate photocatalysis (PC) has been widely investigated for environmentally friendly production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).<sup>1</sup> Yet, most existing PC systems for H<sub>2</sub>O<sub>2</sub> generation are based on powder suspensions, which are not applicable to large-scale H<sub>2</sub>O<sub>2</sub> synthesis.<sup>2, 3</sup> Consequently, the development of a scalable PC system has remained a formidable obstacle, impeding the practical implementation of H<sub>2</sub>O<sub>2</sub> photosynthesis.

In this study, we report a flexible photocatalyst sheet based on visible-light-responsive BiVO<sub>4</sub> ( $\lambda < 520$  nm) for the scalable production of H<sub>2</sub>O<sub>2</sub> from water and oxygen. We successfully upscaled the production by deploying BiVO<sub>4</sub> photocatalyst sheets in a 1-m<sup>2</sup>-flow-by reactor in a 4×4-panels array (Figure 1). The H<sub>2</sub>O<sub>2</sub> synthesis on this panel reactor exhibited durability, with no loss of activity over one -month field test.

To illustrate the practical utility of the photosynthesized H<sub>2</sub>O<sub>2</sub>, we applied it to disinfection, achieving over 99.9% inactivation of a coronavirus surrogate within 60 minutes. Furthermore, a techno-economic analysis demonstrates the economic viability of H<sub>2</sub>O<sub>2</sub> photosynthesis using the panel reactor. Our findings underscore the scalability and economic feasibility of photocatalytic H<sub>2</sub>O<sub>2</sub> generation, enhancing its readiness for practical applications.

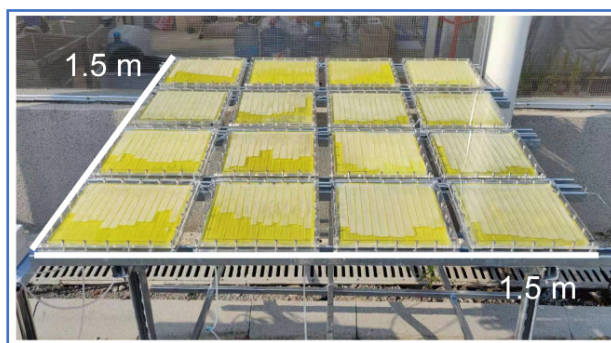


Figure 1 Digital photo of the 1-m<sup>2</sup> arrayed panel flow reactor.

1. Y. Xue, Y. Wang, Z. Pan and K. Sayama, *Angew. Chem. Int. Ed.*, **2020**, 60, 1433-7851.
2. T. Liu, Z. Pan, K. Kato, J. J. M. Vequizo, R. Yanagi, X. Zheng, W. Yu, A. Yamakata, B. Chen, S. Hu, K. Katayama and C. Chu, *Nat. Commun.*, **2022**, 13, 7783.
3. T. Liu, Z. Pan, J. J. M. Vequizo, K. Kato, B. Wu, A. Yamakata, K. Katayama, B. Chen, C. Chu and K. Domen, *Nat. Commun.*, **2022**, 13, 1034.

## メタン存在下における光触媒水分解反応の特異的な促進

(分子研<sup>1</sup>・総研大<sup>2</sup>) ○斎藤 晃<sup>1</sup>・佐藤 宏祐<sup>1</sup>・東 泰佑<sup>1</sup>・杉本 敏樹<sup>1,2</sup>

Accelerating Photocatalytic Water Splitting by Methane Molecules (<sup>1</sup>*Department of Materials Molecular Science, Institute for Molecular Science*, <sup>2</sup>*Graduate Institute for Advanced Studies, SOKENDAI*) ○Hikaru Saito,<sup>1</sup> Hiromasa Sato,<sup>1</sup> Taisuke Higashi,<sup>1</sup> Toshiki Sugimoto<sup>1,2</sup>

Interfacial water systems on solid surfaces are a crucial energy conversion platform in the field of catalysis<sup>1)</sup>. However, it remains a challenge to control reactivity of interfacial water species for enhancing catalytic performance. Here, we report that incorporation of methane in the interfacial water systems on the Pt/Ga<sub>2</sub>O<sub>3</sub> surfaces<sup>2)</sup> dramatically accelerate the photocatalytic water splitting (2H<sub>2</sub>O→2H<sub>2</sub>+O<sub>2</sub>). By infrared absorption spectroscopy, we revealed that the structure of the hydrogen bond network of the interfacial water was reconstructed by methane. Because hydrogen bonding has significant impact on the hole transfer process at catalyst–water interfaces<sup>3)</sup>, this reconstruction of the hydrogen bond network indicates the increase in the reactive interfacial water species that easily accept photogenerated holes. Thus, our study demonstrates the critical impacts of the interfacial hydrogen bond network on the water splitting activity. Notably, the enhancement mechanism induced by methane is stark contrast to the conventional promoter molecules such as methanol as a hole scavenger<sup>4)</sup>. Therefore, our study also provides a novel method for enhancing photocatalytic performance.

**Keywords :** *Water Splitting; Methane; Photocatalysis; Interfacial Hydrogen Bond; Infrared Absorption Spectroscopy*

固体と水分子の界面は光触媒や電極触媒をはじめとした重要な反応場である<sup>1)</sup>。そのため、触媒性能の向上のためには界面水分子の反応性制御が鍵となる。本研究では、水とメタンが共存する Pt/Ga<sub>2</sub>O<sub>3</sub> 光触媒系<sup>2)</sup>において水分解反応(2H<sub>2</sub>O→2H<sub>2</sub>+O<sub>2</sub>)の活性が劇的に向上することを見出した。赤外吸収分光法によってメタンによる光触媒表面の吸着水への影響を調べた結果、メタンが存在すると吸着水の O–H 伸縮振動ピークが特異的に波数シフトしており、水素結合環境が変調されていることが明らかとなった。吸着水の水素結合状態は光触媒表面からの電荷移動と密接に関わっている<sup>3)</sup>ことから、メタン導入によって光誘起正孔を受け取りやすい吸着水の増加が活性向上に寄与していると考えられる。このように、本研究では吸着水の水素結合環境がマクロな触媒性能と密接に関わっていることを実証した。また、吸着水の水素結合環境を変調によって水分子を活性化させるというメタンの役割はメタノールに代表される正孔犠牲剤による水素生成の促進<sup>4)</sup>とは全く異なり、新たな活性向上のコンセプトを提供するものである。

本研究は JST さきがけ[JPMJPR16S7]、JST-CREST[JPMCR22L2]、JSPS 科研費[JP22J1039; JP22H00296]、自然科学研究機構分野融合型共同研究事業[01112104]、環境省「地域資源循環を通じた脱炭素化に向けた革新的触媒技術の開発・実証事業」の支援の下で実施された。

- 1) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori, S. Saito, *Coord. Chem. Rev.* **2022**, 472, 214773.
- 2) H. Sato, A. Ishikawa, H. Saito, T. Higashi, K. Takeyasu, T. Sugimoto, *Commun. Chem.* **2023**, 6, 8; H. Saito, H. Sato, T. Higashi, T. Sugimoto, *Angew. Chem. Int. Ed.* **2023**, 62, e202306058; F. Amano, A. Ishikawa, H. Sato, C. Akamoto, S. P. Singh, S. Yamazoe, T. Sugimoto, *Catal. Today* **2024**, 426, 114375.
- 3) K. Shirai, G. Fazio, T. Sugimoto, D. Selli, L. Ferraro, K. Watanabe, M. Haruta, B. Ohtani, H. Kurata, C. D. Valentin, Y. Matsumoto, *J. Am. Chem. Soc.* **2018**, 140, 1415–1422.
- 4) V. Kumaravel, S. Mathew, J. Bartlett, S. C. Pillai, *Appl. Catal. B* **2019**, 244, 1021–1064.

## Development of photoredox cascade catalyst for alkane-oxidation and solar hydrogen production

(Faculty of Science, Hokkaido University) ○Atsushi Kobayashi

**Keywords:** Photocatalyst; Hydrogen production; Alkane oxidation; Photosensitization; Electron mediation

Solar water splitting reaction has been attracted considerable attention as a means of building a sustainable *hydrogen* society. However, water splitting producing hydrogen and oxygen cannot provide valuable organic chemicals. To overcome this issue, we have constructed a photo-redox cascade catalyst (PRCC) consisting of Ru(II) dual-dye sensitized Pt-TiO<sub>2</sub> photocatalyst that generates hydrogen photocatalytically not only from redox-reversible electron donors<sup>1)</sup> but also hydroxyl group-containing biomass.<sup>2)</sup> In this work, to extend this strategy to oxidative transformation of various organic substrates, a new PRCC system was designed by using *N*-hydroxyphthalimide (NHPI) as an hydrogen-atom transfer (HAT) catalyst which generates carbon radicals while extracting hydrogen atoms from less reactive alkanes (Figure 1). H<sub>2</sub> successfully evolved in the 5 mM NHPI solution and the estimated turn over number per Ru(II) dye (PS TON) over 97 indicates the photocatalytic H<sub>2</sub> production as a result of NHPI oxidation. The activity was remarkably enhanced by increasing the NHPI concentration to 30 mM and addition of 0.1 M ethylbenzene (EB) or toluene (Tol), suggesting the HAT reaction from EB/Tol by phthalimido-*N*-oxyl (PINO) radical generated by the proton-coupled one-electron oxidation of NHPI. Further, a large isotope effect was observed by replacing from Tol to the deuterated one (Tol-d<sub>8</sub>), suggesting that the HAT reaction by PINO is the rate-limiting step in this PRCC system. Details will be discussed.

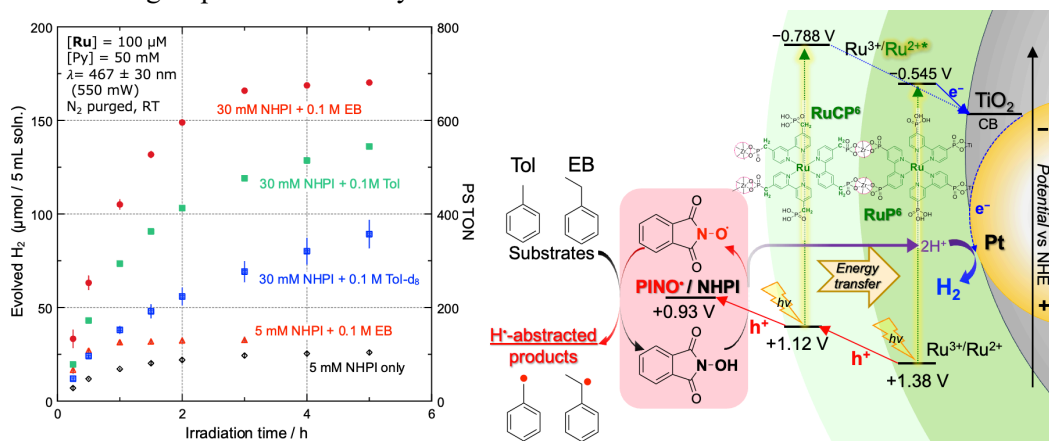


Figure 1. (left) Photocatalytic H<sub>2</sub> production and (right) schematic energy diagram of PRCC coupled with HAT reaction from EB/Tol.

1) N. Yoshimura, M. Yoshida, A. Kobayashi, *J. Am. Chem. Soc.* **2023**, 145, 6035.

2) A. Kobayashi, *Angew. Chem. Int. Ed.* **2023**, 62, e202313014.

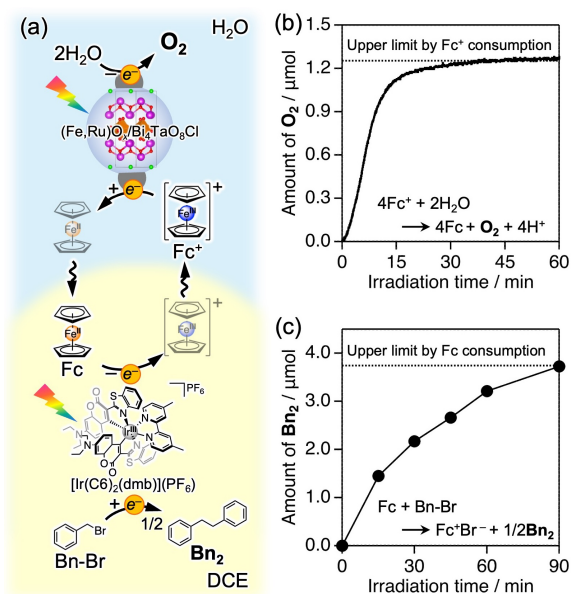
## Photocatalytic System Integrated with Water Oxidation by a Liquid-Liquid Phase-Migrating Electron Mediator

(<sup>1</sup>Grad. Sch. of Eng., Kyoto Univ., <sup>2</sup>JSPS Research Fellow DC1, <sup>3</sup>PRESTO/JST, <sup>4</sup>Fac. of Sci. Eng., Chuo Univ.) ○Ren Itagaki,<sup>1,2</sup> Akinobu Nakada,<sup>1,3</sup> Hajime Suzuki,<sup>1</sup> Osamu Tomita,<sup>1</sup> Ho-Chol Chang,<sup>4</sup> Ryu Abe<sup>1</sup>

**Keywords:** Photocatalyst; Separation of Reaction Fields; Electron Mediator; Photoinduced Electron Transfer; Phase Migration

Photocatalytic molecular conversions giving value added product are of great interest. Ideally, it is desirable to utilize water as an electron source for these molecular conversion reactions. Artificial Z-scheme reaction system composed of two-different photocatalysts is a potential strategy to connect various reductive molecular conversions with water oxidation, as demonstrated in overall water splitting.<sup>1</sup> However, it is basically difficult to perform organic molecular conversions integrated with water oxidation due to low solubility of organic reactants in water. In this study, we develop a stepwise Z-scheme photocatalytic system utilizing a water/1,2-dichloroethane (DCE) biphasic solution with a ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) phase-migrating electron mediator to connect reductive coupling of benzyl bromide in DCE phase and water oxidation (Figure 1a).

In an aqueous solution,  $(\text{Fe,Ru})\text{O}_x$ -modified  $\text{Bi}_4\text{TaO}_8\text{Cl}$  photocatalyzed water oxidation with a  $\text{Fc}^+$  electron acceptor, generating  $\text{O}_2$  and  $\text{Fc}$  (Figure 1b). On the other side,  $\text{Fc}$  can be utilized as an electron donor for photocatalytic reduction of benzyl bromide ( $\text{Bn-Br}$ ) with an  $[\text{Ir}(\text{C6})_2(\text{dmb})](\text{PF}_6)$  photoredox catalyst in a DCE phase (Figure 1c). Importantly, the latter reaction regenerated  $\text{Fc}^+$  which is spontaneously going back to aqueous phase.<sup>2</sup> Eventually, the  $\text{Fc}^+/\text{Fc}$  redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of  $\text{Bn-Br}$  coupled with water oxidation.



**Figure 1.** (a) Conceptual scheme of a biphasic photocatalysis. Time course of half reactions of (b)  $\text{O}_2$  evolution using  $(\text{Fe,Ru})\text{O}_x/\text{Bi}_4\text{TaO}_8\text{Cl}$  and  $\text{Fc}^+$  electron acceptor and (c) dibenzyl ( $\text{Bn}_2$ ) formation using  $[\text{Ir}(\text{C6})_2(\text{dmb})](\text{PF}_6)$  and  $\text{Fc}$  electron donor.

1) Abe, R.; Tang, J. *et al. Chem. Rev.* **2018**, *118*, 5201.

2) Itagaki, R.; Takizawa, S.; Chang, H.-C.; Nakada, A. *Dalton Trans.* **2022**, *51*, 9467.



## Scalable and efficient water-splitting photocatalyst sheets based on carbon conductors

(<sup>1</sup>Research Initiative for Supra-Materials, Shinshu University, <sup>2</sup>National Institute of Advanced Industrial Science and Technology, <sup>3</sup>Institute for Engineering Innovation, The University of Tokyo, <sup>4</sup>Department of Materials Chemistry, Shinshu University, <sup>5</sup>Graduate School of Natural Science and Technology, Okayama University, <sup>6</sup>Office of University Professors, The University of Tokyo) ○Chen Gu<sup>1</sup>, Tsuyoshi Takata<sup>1</sup>, Yi-Wen Ma<sup>1</sup>, Miseki Yugo<sup>2</sup>, Li-Hua Lin<sup>1</sup>, Hiroshi Nishiyama<sup>3</sup>, Mamiko Nakabayashi<sup>3</sup>, Nobuyuki Zettsu<sup>4</sup>, Yuta Nishina<sup>5</sup>, Takashi Hisatomi<sup>1</sup> and Kazunari Domen<sup>1,6</sup>

**Keywords:** Oxsulfide, electron transfer, Photocatalyst sheet, Visible light

Particulate photocatalyst sheet is a structure that can potentially realize scalable and economical solar-to-hydrogen energy conversion via overall water splitting (OWS). In our previous study, a 100 m<sup>2</sup>-scale photocatalyst sheet/panel system based on Al-doped SrTiO<sub>3</sub> (STO:Al) was developed.<sup>1</sup> However, the STH is still below the level (5% or higher) targeted for practical and scaled industrial applications. This gap is difficult to overcome with STO:Al because it cannot utilize visible light which accounts for the majority of solar energy.<sup>2</sup>

A two-step excitation system, also known as a Z-scheme system, is an approach to utilize long-wavelength visible light efficiently in OWS.<sup>3</sup> However, the size of most efficient Z-scheme photocatalyst sheets is typically 10 cm<sup>2</sup> or less, which is far below practical and industrial requirements. The size is limited by the need for an elaborate and complicated particle transfer process that involves the evaporation of conductive materials and the peeling and transfer of the composite using an adhesive film during sheet formation.

In this work, we demonstrate efficient Z-scheme OWS using scalable particulate photocatalyst sheets composed of cocatalyst-loaded Sm<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>S<sub>2</sub> and BiVO<sub>4</sub> combined with carbon material, where the use of vacuum processes or organic media during the sheet fabrication and Z-scheme OWS was ruled out. The carbon material-based photocatalyst sheets exhibited higher activity in OWS than the conventional sheet using Au as the electron conductor, and the problems of back reaction, stability, and pressure dependence were largely solved by refining the surface modification procedure.

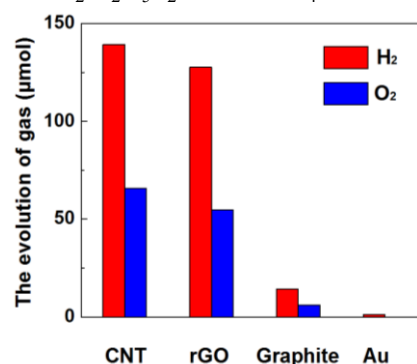


Figure 1. The ZOWS activity of sheets with different electron mediators

- 1) Nishiyama *et al.*, *Nature* **2021**, 598, 304.
- 2) Takata *et al.*, *Nature* **2020**, 581, 411.
- 3) Nandy *et al.*, *Joule* **2023**, 7, 1641–1651.

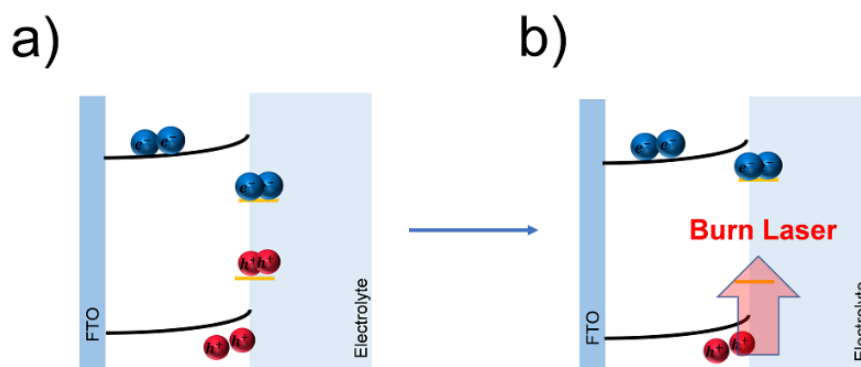


## Development of Charge Carrier-Selective Heterodyne Transient Grating Spectroscopic Technique and Its Application in the Distinction of Surface Trap States in Hematite

(Department of Chemistry, Chungbuk National University) Young Hyun Kim Yu Gyeong Bae  
and ○Woon Yong Sohn

**Keywords:** Hematite; Photo-electrochemical water splitting; Trap state; Time-resolved spectroscopy

We newly developed a spectroscopic technique which is named charge carrier-selective heterodyne transient grating (CS-HD-TG) method for the distinction of the surface trap states existing in the photocatalysts and photovoltaic materials. For the measurement of the CS-HD-TG response, a burn laser was employed which could induce the depletion of the photo-excited charge carriers trapped in the surface states. In this study, the population of the photo-excited holes in hematite could be depleted by the excitation of the electrons originating from the valence band when the wavelength of the burn laser was resonant as shown in the Scheme. In addition, as a case study, we measured the CS-HD-TG responses of hematite under bias condition with and without the burn laser and revealed that two distinct trap states co-exist at the surface in the hematite film and only one of them could act as the reaction intermediate for oxygen evolution reaction (OER), which is consistent with former studies.<sup>1-3</sup>



Schematic illustrations of photo-generated charge carriers in a photoanode a) without burn laser and b) with burn laser.

1) Zandi, O.; Hamann, T. W., *J. Phys. Chem. Lett.* **2014**, 5, 1522. 2) Palmolahti, L.; Ali-Löytty, H.; Khan, R.; Saari, J.; Tkachenko, N. V.; Valden, M., *J. Phys. Chem. C* **2020**, 124, 13094. 3) Pan, Z.; Chen, S.; Katayama, K., *J. Phys. Chem. C* **2023**, 127, 3904.

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 F1231(12号館 [3階] 1231)

**[F1231-3vn] 09. 錯体化学・有機金属化学**

座長：近藤 美欧、畑中 翼

## ◆ 英語

15:55 ~ 16:15

[F1231-3vn-01]

配位高分子融液のCO<sub>2</sub>に対する反応性○西口 大智<sup>1</sup>、門田 健太郎<sup>1</sup>、堀毛 悟史<sup>1</sup> (1. 京都大学)

## ◆ 日本語

16:15 ~ 16:35

[F1231-3vn-02]

TADF有機分子を光増感剤 Mn(II)錯体を触媒として用いたCO<sub>2</sub>還元光触媒反応○井上 麗<sup>1</sup>、Elena Bassan<sup>2</sup>、Francesco Calogero<sup>2</sup>、Simone Potenti<sup>2</sup>、Andrea Gualandi<sup>2</sup>、Pier Cozzi<sup>2</sup>、Paola Ceroni<sup>2</sup>、玉置 悠祐<sup>3</sup>、石谷 治<sup>1,4</sup> (1. 東京工業大学、2. ボローニャ大学、3. 産業技術総合研究所、4. 広島大学)

## ◆ 英語

16:35 ~ 16:55

[F1231-3vn-03]

水溶性ロジウム触媒によるCO<sub>2</sub>光還元における選択的ギ酸生成のメカニズム○イドンソブ<sup>1</sup>、山内 幸正<sup>1</sup>、酒井 健<sup>1</sup> (1. 九大院理)

## ◆ 英語

16:55 ~ 17:15

[F1231-3vn-04]

分子内電子移動を活用した光還元種生成量子収率の向上とその原理

○細川 直輝<sup>1</sup>、石谷 治<sup>1,2</sup> (1. 東京工業大学、2. 広島大学)

## Reactivity of coordination polymer melt toward CO<sub>2</sub>

(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>Graduate School of Science, Kyoto University) ○Taichi Nishiguchi,<sup>1</sup> Kentaro Kadota,<sup>2</sup> Satoshi Horike<sup>2</sup>

**Keywords:** Coordination polymer; Melting; CO<sub>2</sub>

The interactions and reactions of gas molecules in liquid materials are of fundamental interest and, in particular, the reactivity of CO<sub>2</sub> was extensively investigated in organic and inorganic liquids. The reversible reactivity between ionic liquids and CO<sub>2</sub> has been studied for CO<sub>2</sub> capture.<sup>1</sup> The reduction reaction of CO<sub>2</sub> into carbon materials by liquid gallium metal was also reported in recent years.<sup>2</sup> On the other hand, the reaction of CO<sub>2</sub> in organic–inorganic hybrid liquids remains unexplored due to their structural complexity and limited examples. Melting coordination polymers (CPs) have emerged as a novel class of liquids with high compositional and structural tunability.<sup>3</sup>

We report a reaction between CO<sub>2</sub> and Cu(2-isopropylimidazolate) (**1**) melt. Whereas crystalline **1** was inert to CO<sub>2</sub> at room temperature, **1** melted at 143 °C to give a liquid rapidly reacting with CO<sub>2</sub>. Thermogravimetric analysis (TGA) of **1** under a CO<sub>2</sub> flow observed a weight increase equivalent to the 9.8 mol% CO<sub>2</sub> uptake to Cu (Fig. a). A systematic series of isostructural CPs with different alkyl groups indicated the dependence of the reactivity on the structure of component molecules. Fourier-transformed infrared (FT-IR) and Raman spectra confirmed the formation of carbonyl groups in the amorphous product after the reaction with CO<sub>2</sub>. (Fig. b) X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS) and solid-state nuclear magnetic resonance (SS-NMR) revealed the state of Cu and chemical environment of the ingested CO<sub>2</sub> in the product, suggesting the reduction of CO<sub>2</sub> in **1** melt.

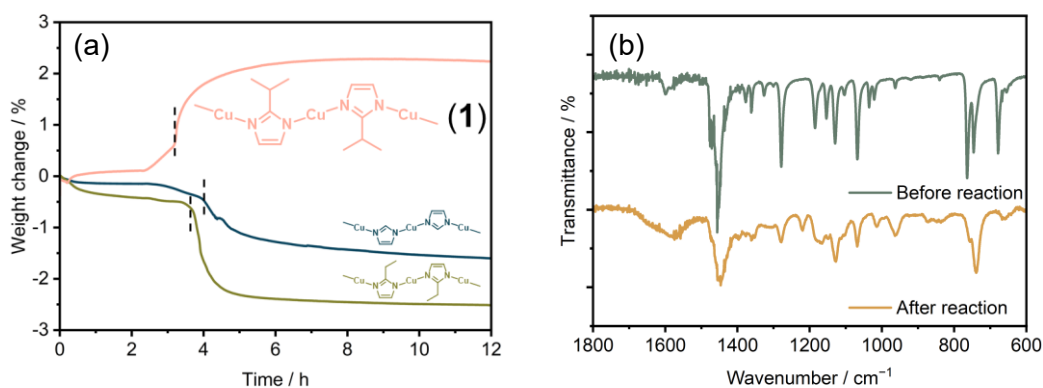


Fig. (a) TGA profiles of **1**, Cu(2-ethylimidazolate), and Cu(imidazolate) under a CO<sub>2</sub> flow. **1** showed a weight increase up to 2.3 w/w%, indicating the reaction between **1** melt and CO<sub>2</sub>. Melting points are indicated with hashed lines. (b) FT-IR spectra of **1** before and after the reaction with CO<sub>2</sub>.

- 1) S. Zhang *et al.*, *Chem. Rev.* **2017**, *117*, 9625.; 2) K. Kalantar-Zadeh *et al.*, **2022**, *34*, 2105789.;
- 3) S. Horike *et al.*, *Chem. Rev.* **2022**, *122*, 4163.

## TADF 有機分子を光増感剤 Mn(I)錯体を触媒として用いた CO<sub>2</sub> 還元光触媒反応

(東工大<sup>1</sup>・Univ. Bologna<sup>2</sup>・産総研<sup>3</sup>・広島大<sup>4</sup>) ○井上 麗<sup>1</sup>・Elena Bassan<sup>2</sup>・Francesco Calogero<sup>2</sup>・Simone Potenti<sup>2</sup>・Andrea Gualandi<sup>2</sup>・Pier Giorgio Cozzi<sup>2</sup>・鴨川 径<sup>1</sup>・Paola Ceroni<sup>2</sup>・玉置 悠祐<sup>3</sup>・石谷 治<sup>1,4</sup>

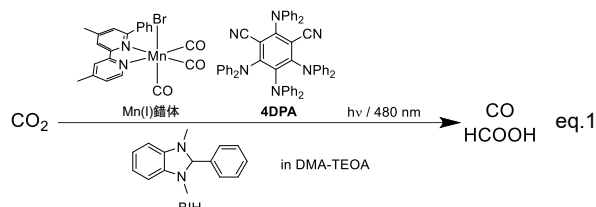
Photocatalytic CO<sub>2</sub> reduction using TADF organic molecules as photosensitizers and a Mn(I) complex as a catalyst. (<sup>1</sup>*School of Science, Tokyo Institute of Technology*, <sup>2</sup>*Dipartimento di Chimica Ciamician, Universita' di Bologna*, <sup>3</sup>*National Institute of Advanced Industrial Science and Technology*, <sup>4</sup>*Graduate school of Advanced Science and Engineering, Hiroshima University*) ○Rei Inoue,<sup>1</sup> Elena Bassan,<sup>2</sup> Francesco Calogero,<sup>2</sup> Simone Potenti,<sup>2</sup> Andrea Gualandi,<sup>2</sup> Pier Giorgio Cozzi,<sup>2</sup> Kei Kamogawa,<sup>1</sup> Paola Ceroni,<sup>2</sup> Yusuke Tamaki,<sup>3</sup> Osamu Ishitani<sup>1,4</sup>

Our group previously reported that the thermally activated delayed fluorescence (TADF) organic molecules with long excitation lifetimes, can be used as photosensitizers in photocatalytic CO<sub>2</sub> reduction.<sup>1)</sup> In this study, we investigate mechanistic details of the photocatalytic CO<sub>2</sub> reduction using one of the TADF organic molecules, **4DPA**, BIH as a reductant, and a Mn(I)-complex catalyst (eq.1). In the photocatalytic reaction using a higher concentration of BIH (0.1 M), the quantum yield of CO<sub>2</sub> reduction ( $\Phi_{\text{CO}+\text{HCOOH}} = 22.8\%$ ) was lower than that using a lower concentration of BIH (0.01M,  $\Phi_{\text{CO}+\text{HCOOH}} = 42.2\%$ )

**Keywords** : photocatalytic CO<sub>2</sub> reduction; TADF; Organic photosensitizer; Mn(I) complex; Singlet excited state and Triplet excited state

当研究室では、可視光を吸収し、長い励起寿命を有する熱活性遅延蛍光 (TADF) 分子を光増感剤に用いた CO<sub>2</sub> 還元光触媒反応について研究している<sup>1)</sup>。本発表では、比較的高い光触媒能を示した **4DPA** を光増感剤、Mn(I)錯体を光触媒として用いた CO<sub>2</sub> 還元光触媒反応 (eq.1) について詳細に検討した。

加えた還元剤 BIH が 0.1 M の場合、CO<sub>2</sub> 還元の量子収率( $\Phi_{\text{CO}+\text{HCOOH}}$ )は 22.8%であったが、0.01 M まで薄くすると、 $\Phi_{\text{CO}+\text{HCOOH}}$  は逆に 42.2%まで上昇した。この現象は、**4DPA** の励起一重項状態( $S_1$ )と励起三重項状態( $T_1$ )が BIH によって消光される割合が変化することで起こることが分かった。即ち、BIH が濃く、寿命の短い  $S_1$  が BIH により優先的に還元的消光を受けると、生成した 1 重項イオン対間の逆電子移動が効率よく進行し  $\Phi_{\text{CO}+\text{HCOOH}}$  は低下する。一方、BIH 濃度が低く、寿命の長い  $T_1$  の還元的消光が主に進行すると、生成された 3 重項イオン対における逆電子移動は起こりにくいいため、**4DPA**<sup>•</sup> 生成収率が向上し、その結果  $\Phi_{\text{CO}+\text{HCOOH}}$  が上昇したことが分かった。



1) E. Bassan, R. Inoue, D. Fabry, F. Calogero, S. Potenti, A. Gualandi, P. G. Cozzi, K. Kamogawa, P. Ceroni, Y. Tamaki, O. Ishitani, *Sustainable Energy Fuels*, **2023**, 7, 3454-3463.

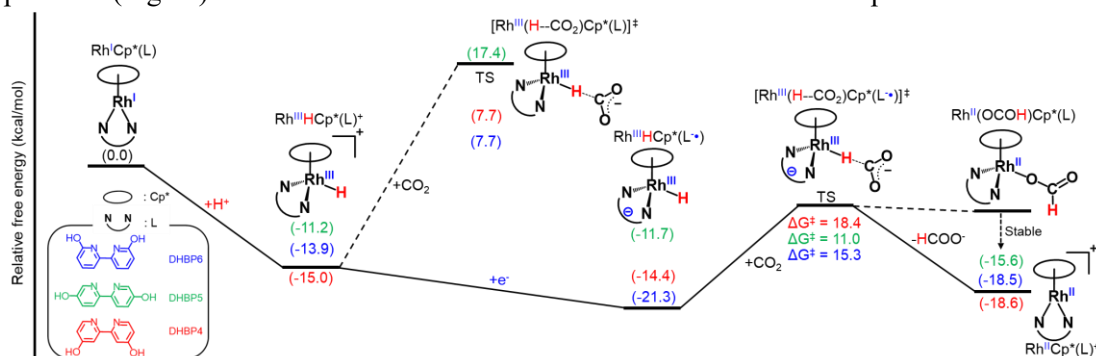
## Mechanism of Selective Formate Formation in the Photoreduction of CO<sub>2</sub> by Water-Soluble Rhodium Catalysts

(<sup>1</sup>Dept. Chem. Kyushu University) ○Dongseob LEE<sup>1</sup>, Kosei YAMAUCHI<sup>1</sup>, Ken SAKAI<sup>1</sup>

**Keywords:** Photocatalysis, CO<sub>2</sub> reduction, Rhodium catalyst, formate selectivity, DFT studies

Due to the urgent need to address global warming and climate change, significant efforts have been dedicated to reduce the atmospheric CO<sub>2</sub> concentration. Photocatalytic CO<sub>2</sub> reduction has emerged as a promising approach to convert CO<sub>2</sub> into valuable chemical fuels like carbon monoxide and formic acid. Notably, it has been reported that rhodium complexes with a pentamethylcyclopentadienyl ligand (Cp\*) show high selectivity in CO<sub>2</sub> reduction to formate.<sup>[1]</sup> In spite of the reports showing such selective formate formation, the studies attempting to clarify the detailed operational principles that govern the formate selectivity is still limited.<sup>[2]</sup> Therefore, there is a recognized need to clarify the role of functional groups on the ligands.

In the above context, we have designed and prepared three water-soluble Rh(Cp\*) complexes with a general formula of [Rh(Cp\*)(DHBP<sub>n</sub>)Cl]Cl (DHBP<sub>n</sub>=*n,n'*-dihydroxy-2,2'-bipyridine, *n*=4,5,6). [Rh(Cp\*)(DHBP4)]Cl, [Rh(Cp\*)(DHBP5)]Cl, and [Rh(Cp\*)(DHBP6)]Cl. These catalysts were employed for photocatalytic CO<sub>2</sub> reduction reactions in a mixed-solvent (MeCN/H<sub>2</sub>O/TEOA, 4:1:1 v/v) in the presence of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as a photosensitizer and BIH as a sacrificial electron donor. The primary products evolved were H<sub>2</sub> and formate. Overall activity decreases as the proportion of water is increased, except for [Rh(Cp\*)(DHBP5&6)]Cl which exhibits a remarkable increase in formate production as the water content increases. To provide further insights into the selectivity of formate production reactions, we conducted DFT calculations to develop energy diagrams, leading to validate some important factors that govern the reaction products (Figure). The detailed results and discussion will be made in the presentation.



1. A. K. Mengele, S. Rau, *Inorganics*, **2017**, 5, 35.
2. T. K. Todorova, T. N. Huan, X. Wang, H. Agarwala, M. Fontecave, *Inorg. Chem.*, **2019**, 58, 6893.

## Intramolecular electron transfer inducing increase of the photochemical formation quantum yield of reduced species and its fundamentals

(<sup>1</sup>Tokyo institute of technology, <sup>2</sup>Hiroshima University) ○Naoki Hosokawa,<sup>1</sup> Osamu Ishitani<sup>1,2</sup>

**Keywords:** Quantum yield, Redox photosensitizer, Photo-induced electron transfer, Intramolecular electron transfer, Multinuclear metal complex

Photochemical formation of one-electron reduced species (OERS) of the photosensitizer (PS) is an important initiation process of the redox photocatalytic reactions, and the quantum yield of this process ( $\Phi_{\text{OERS}}$ ) crucially affects the overall quantum yields of the redox photocatalytic reactions. We studied the photochemical formation processes of OERS of Os(II), Re(I) and Ru(II) complexes,<sup>1,2</sup> and reported that  $\Phi_{\text{OERS}}$  in these complexes are suppressed by back electron transfer from the generated OERS to the oxidized reductant in the solvate cage. This back electron transfer process more rapidly proceeds in the case that the distance between the OERS of PS and the oxidized reductant in the solvent cage is shorter just after the forward electron transfer proceeds. Therefore, increase of the distance between the OERS and the oxidized reductant should be a key to increase  $\Phi_{\text{OERS}}$ .

In this presentation, we report a new method to make this distance longer, i.e., introduction of an electron accepting unit into PS. For this purpose, we synthesized novel Os(II) and Ru(II) binuclear complexes of which two complex units are connected with a linear alkyl chain with  $n=2$  (**OsC2Ru**) and 6 (**OsC6Ru**) (Figure). We already reported that intramolecular electron transfer from the OERS of the PS unit to the electron accepting unit is strongly dependent on the distance between them.<sup>3</sup> Their photophysical and electrochemical properties of **OsC2Ru** and **OsC6Ru** were similar to those of the corresponding Os(II) and Ru(II) mononuclear complexes. On the other hand,

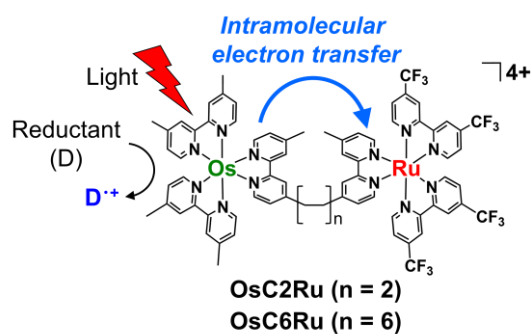


Figure. Structure of novel binuclear complexes  
case of **OsC2Ru** ( $\Phi_{\text{OERS}} = 0.2$ ) was 10 times higher than that of the Os(II) mononuclear complex ( $\Phi_{\text{OERS}} = 0.02$ ). However, the quantum yield of **OsC6Ru** was lower than that of **OsC2Ru**. Since intramolecular electron transfer from the OERS of the Os unit to the Ru unit in **OsC2Ru** is much faster than that in **OsC6Ru**, this rapid spatial separation of the reduced unit and the oxidized reductant via intramolecular electron transfer should increase  $\Phi_{\text{OERS}}$ .

1) K. Ozawa and O. Ishitani et al., *J. Chem. Phys.* **2020**, 153, 154302. 2) N. Hosokawa and O. Ishitani et al., *Annual Meeting on Photochemistry*, **2022**, 3C07. 3) Y. Yamazaki and O. Ishitani et al., *Inorg. Chem.* **2019**, 58, 11480.

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 F1232(12号館 [3階] 1232)

**[F1232-3vn] 09. 錯体化学・有機金属化学**

座長：大木 靖弘、劔 隼人

## ◆ 日本語

15:55 ~ 16:15

[F1232-3vn-01]

パックマン型ポルフィリン配位子を有する二核Cu, Zn錯体の酸化還元挙動とCO<sub>2</sub>還元反応メカニズム○竹山 知志<sup>1</sup>、檜垣 達也<sup>2</sup>、大木 靖弘<sup>2</sup>、太田 雄大<sup>1</sup> (1. 山陽小野田市立山口東京理科大学、2. 京都大学)

## ◆ 英語

16:15 ~ 16:35

[F1232-3vn-02]

固液界面でのCu(phen)錯体の2核化およびアルコール空気酸化促進

○久米 晶子<sup>1</sup>、安倍 大貴<sup>1</sup> (1. 広島大学大学院先進理工系科学研究科)

## ◆ 英語

16:35 ~ 16:55

[F1232-3vn-03]

多核銅錯体を触媒とするH<sub>2</sub>O<sub>2</sub>によるメタン酸化の合理化：μ-O・活性種とH<sub>2</sub>O<sub>2</sub>効率○藤川 恭祐<sup>1</sup>、亀谷 陽平<sup>2</sup>、田中 皐晴<sup>1</sup>、四宮 聖菜<sup>1</sup>、塩田 淑仁<sup>2</sup>、吉澤 一成<sup>2</sup>、小寺 政人<sup>1</sup> (1. 同志社大学大学院、2. 九州大学)

## ◆ 英語

16:55 ~ 17:15

[F1232-3vn-04]

シクロペンタジエニルフェノキシ配位子を有する新規サマリウム錯体の合成と窒素固定に対する反応性

○光本 泰知<sup>1</sup>、西林 仁昭<sup>1</sup> (1. 東大院工)

## パッカマン型ポルフィリン配位子を有する二核 Cu, Zn 錯体の酸化還元挙動と CO<sub>2</sub> 還元反応メカニズム

(山理大工<sup>1</sup>・京大化研<sup>2</sup>) ○竹山 知志<sup>1</sup>・檜垣 達也<sup>2</sup>・大木 靖弘<sup>2</sup>・太田 雄大<sup>1</sup>

Redox behavior of dinuclear Cu and Zn porphyrin dimers and their CO<sub>2</sub> reduction mechanisms (<sup>1</sup>Department of Applied Chemistry, Sanyo-Onoda City University, <sup>2</sup>Institute for Chemical Research, Kyoto University) ○ Tomoyuki Takeyama,<sup>1</sup> Tatsuya Higaki,<sup>2</sup> Yasuhiro Ohki,<sup>2</sup> Takehiro Ohta<sup>1</sup>

The M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) (M = Cu, Zn), as shown in Figure 1(a), have been synthesized to elucidate their catalytic CO<sub>2</sub> reduction mechanisms. The electrochemical and spectroelectrochemical UV-vis-NIR and EPR measurements revealed four quasi-reversible reduction events (Figure 1(c-d), black lines). The reduction process occurs only on the ligand side under Ar. Under CO<sub>2</sub> saturated conditions, M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) (M = Cu, Zn) exhibited a significant irreversible current, indicating the electrocatalytic activity of reduced complexes, [M<sub>2</sub>(Por<sub>2</sub>)]<sup>3-</sup>, for CO<sub>2</sub> reduction (Figure 1(c-d), red lines). In this presentation, the mechanism of CO<sub>2</sub> reduction by M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) (M = Cu, Zn) will be discussed in detail.

**Keywords :** Metal-porphyrin complexes, Redox reaction, CO<sub>2</sub> reduction

生体内金属酵素に着想を得て設計されたパッカマン型二核 Fe ポルフィリン錯体は、CO<sub>2</sub> を CO へ変換する電気化学的還元反応を高効率に触媒することが知られている<sup>[1]</sup>。本研究では、中心金属を Cu<sup>II</sup> または Zn<sup>II</sup> に置換した錯体 (M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>); M = Cu, Zn) を合成し、その CO<sub>2</sub> 還元触媒能と還元メカニズムの解明に取り組んだ。M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) の Ar 下 DMF 中におけるサイクリックボルタモグラム(CV)を測定したところ、4 つの準可逆な酸化還元対が観測された (図 1(c-d), 黒線)。分光電気化学測定と電解 EPR 測定により得られたスペクトル変化から、M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) の還元過程は配位子上でのみ起こることが示唆された。次いで、CO<sub>2</sub> 飽和条件下における CV を測定したところ、[M<sub>2</sub>(Por<sub>2</sub>)]<sup>3-</sup> の生成電位において触媒電流が流れることが分かった (図 1(c-d), 赤線)。このことは [M<sub>2</sub>(Por<sub>2</sub>)]<sup>3-</sup> が CO<sub>2</sub> 還元反応の反応活性種であることを示している。

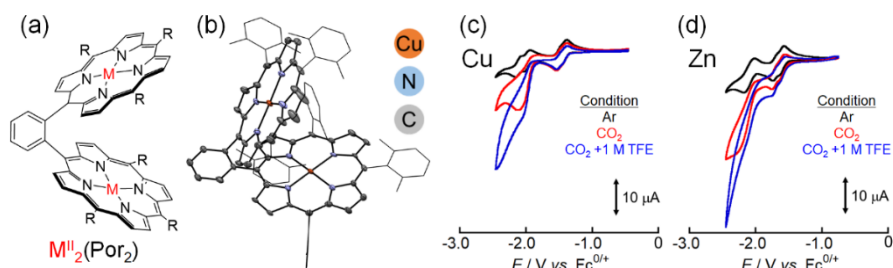


図 1. M<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) の分子構造(a)と Cu<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) の結晶構造 (b). Cu<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) (c)と Zn<sup>II</sup><sub>2</sub>(Por<sub>2</sub>) (d) の DMF 溶液のサイクリックボルタモグラム. 黒線は Ar 条件下, 赤線は CO<sub>2</sub> 飽和条件下, 青線は CO<sub>2</sub> 飽和および 1 M トリフルオロ酢酸共存下での測定結果.

1) Z. N. Zahran *et al.*, *Sci. Rep.*, **2016**, 6, 24533.



## Binucleation of Cu(phen) at Solid/Liquid Interface toward Enhanced Aerobic Alcohol Oxidation

(<sup>1</sup>Graduate School of Advanced Science and Engineering, Hiroshima University) ○Shoko Kume,<sup>1</sup> Taiki Abe<sup>1</sup>

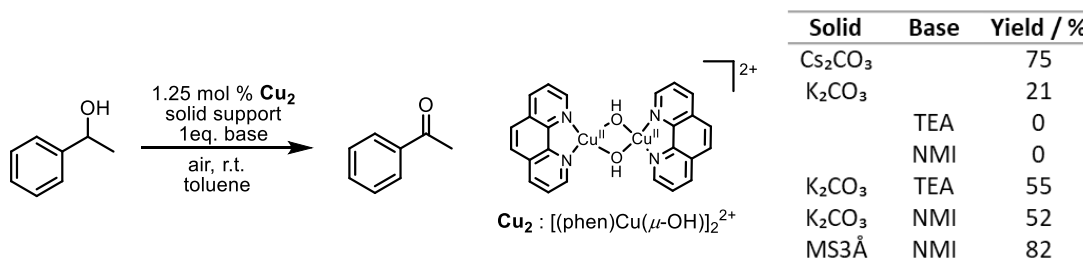
**Keywords:** Oxygen Activation, Alcohol Oxidation, Copper Binuclear Complex, Phenanthroline

Copper catalysts efficiently activate oxygen molecule and operate multielectron transfer with redox-active ligand or Cu<sub>n</sub> multinuclear structure.<sup>1</sup> Aerobic alcohol oxidation with Cu(bpy)/N-oxyl cocatalyst system<sup>2</sup> has been extensively studied, while cocatalyst-free reaction path also works in some systems. We have found that Cu(phen) species without cocatalyst can effectively catalyze alcohol oxidation when it is dispersed on solid substrate.

Several solid supports were found to be effective in alcohol oxidation, while some of them needed additional base. The reaction immediately initiates with [(phen)Cu(μ-OH)]<sub>2</sub><sup>2+</sup> (**Cu<sub>2</sub>**) while induction periods were observed with mononuclear Cu(I)(phen) or Cu(II)(phen). These results suggests formation of Cu(II) dimer fixed on solid surface is essential to enter the catalytic cycle.

The stoichiometry of O<sub>2</sub> and alcohol was 1:2, indicating the water is sole byproduct during the aerobic oxidation. The rate determining step is reaction of O<sub>2</sub> with Cu(I) specie, and **Cu<sub>2</sub>**, which has been considered inactive, seems to oxidizes alcohol rapidly via 2e<sup>-</sup> transfer on solid support.

The catalysis proceeded very efficiently at the initial stage of the reaction, but abruptly deactivated when moderate amount of product was produced (~50%). We found that the produced water from oxygen competes against alcohol in binding to the copper center, and causes significant suppression of alcohol oxidation at the later stage of the catalysis. Solid support also promotes the aerobic oxidation through removal of produced water, and almost quantitative conversion was achieved by condition of solid support.



1) Arndtsen, Stahl et al., *ACS Cent. Sci.*, **2017**, 4, 314–321.

2) Stahl et al., *J. Am. Chem. Soc.*, **2011**, 133, 16901.

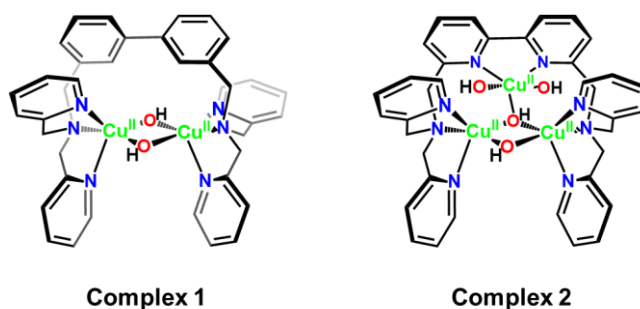
## Streamlining of methane oxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by multicopper complexes: $\mu$ -O• active species and H<sub>2</sub>O<sub>2</sub> efficiency

(<sup>1</sup>Department of Molecular Chemistry and Biochemistry, Doshisha University, <sup>2</sup>Institute for Material Chemistry and Engineering, Kyushu University) ○ Kyosuke Fujikawa<sup>1</sup>, Yohei Kametani<sup>2</sup>, Kosei Tanaka<sup>1</sup>, Seina Shinomiya<sup>1</sup>, Yoshihito Shiota<sup>2</sup>, Kazunari Yoshizawa<sup>2</sup>, Masahito Kodera<sup>1</sup>

**Keywords:** copper-oxygen reactive species, dicopper complex, tricopper complex, methane oxidation, H<sub>2</sub>O<sub>2</sub> activation

The direct oxidation of inert alkane to alcohol or aldehyde is the key process for the efficient synthesis of various chemical products. However, the process often requires cleavage process of the C-H bond with high BDE of the alkane. Thus, the development of the catalysts which can form the highly reactive active species capable of cleaving strong C-H bond is required.

The streamlining of alkane oxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by iron complexes was attained by the formation of Fe(V)=O active species. Meanwhile, Cu-catalyzed alkane oxidation with H<sub>2</sub>O<sub>2</sub> is almost Fenton type reaction with generating HO•, a non-selective oxidant which often causes the suicide reaction. Recently, we found that a copper complex with the tridentate *N*-methyl-*N,N*-di(pyridylmethyl)amine ligand forms the Cu<sup>II</sup><sub>2</sub>- $\mu$ -O• dicopper active species upon reaction with H<sub>2</sub>O<sub>2</sub> and can suppress the Fenton type reaction. This is improved by a dicopper complex **1** of dinucleating ligand having two *N,N*-di(pyridylmethyl)amine tethered by a biphenyl group (Fig 1). A tricopper complex **2** of similar ligand modified with bipyridyl tether group (Fig 1) highly enhanced the H<sub>2</sub>O<sub>2</sub> efficiency. In this study, we report that **1** and **2** form the  $\mu$ -O• active species able to selectively cleave the strong C-H bond of alkane, and the third copper site of **2** plays a key role in more efficient formation of the active species.



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

## シクロペンタジエニルフェノキシ配位子を有する新規サマリウム錯体の合成と窒素固定に対する反応性

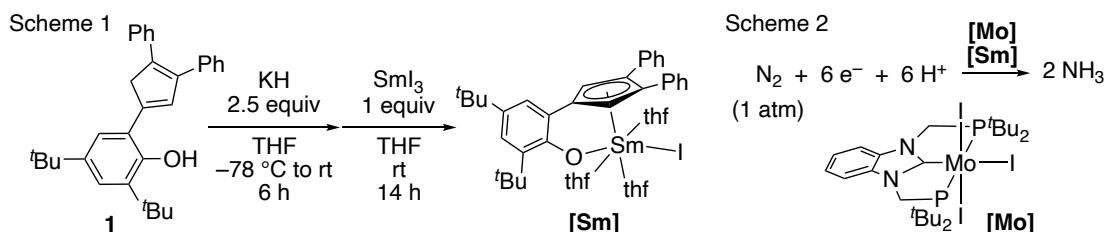
(東大院工) ○光本 泰知・西林 仁昭

Synthesis and Reactivity of Novel Samarium Complexes Bearing Cyclopentadienyl-Phenoxy Ligands toward Nitrogen Fixation (*School of Engineering, The University of Tokyo*) ○Taichi Mitsumoto, Yoshiaki Nishibayashi

Recently, we developed molybdenum-catalyzed ammonia formation using samarium diiodide as a reductant and alcohols or water as a proton source under ambient reaction conditions. This reaction requires a stoichiometric amount of samarium diiodide as a reductant. To develop samarium-catalyzed ammonia formation, we have designed and prepared novel samarium complexes bearing cyclopentadienyl-phenoxy ligands and investigated their reactivities toward ammonia formation. The reaction of ligand **1** with 2.5 equivalents of potassium hydride and further 1 equivalent of samarium triiodide afforded a samarium complex bearing a cyclopentadienyl-phenoxy ligand (Scheme 1). In this presentation, we will also report results of ammonia formation catalyzed by molybdenum and samarium complexes (Scheme 2). **Keywords** : Ammonia Formation; Samarium Complex; Cyclopentadienyl-Phenoxy Ligand; Molybdenum Catalyst; Proton-Coupled Electron Transfer

当研究室では最近、二ヨウ化サマリウム(II)を還元剤、水およびアルコールをプロトン源として用いることで、ピンサー型配位子を有するモリブデン錯体が温和な条件下での触媒的なアンモニア合成反応において極めて高い触媒活性を示すことを報告した<sup>1)</sup>。この反応では、化学量論量のサマリウム(II)還元剤が必要であった。実用化を実現するためには、触媒量のサマリウム錯体を用いたアンモニア合成反応系の開発が求められている。サマリウム錯体の触媒化には、反応後のサマリウム(III)錯体を元のサマリウム(II)錯体へと1電子還元して、還元剤として再利用する必要がある。

本研究ではサマリウム錯体の触媒化を目指し、シクロペンタジエニルフェノキシ配位子<sup>2)</sup>を有する新規サマリウム錯体を設計合成し、その反応性について検討した。配位子**1**に対して2.5当量の水素化カリウムを反応させることでシクロペンタジエニルフェノキシニカリウム塩( $K_2[1]$ )を調製し、さらに1当量の三ヨウ化サマリウムを反応させることでシクロペンタジエニルフェノキシ配位子を有するサマリウム錯体([Sm])を合成した(Scheme 1)。本発表では、モリブデン([Mo])およびサマリウム錯体[Sm]を触媒として用いるアンモニア合成反応の結果と合わせて報告する(Scheme 2)。



1) Y. Ashida, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Nature* **2019**, 568, 536. 2) Zhang, Y.; Wang, J.; Mu, Y.; Shi, Z.; Lü, C.; Zhang, Y.; Qiao, L.; Feng, S. *Organometallics* **2003**, 22, 3877.

この成果は、NEDO の委託業務(JPNP21020)の結果得られたものです。

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 F1233(12号館 [3階] 1233)

**[F1233-3vn] 09. 錯体化学・有機金属化学**

座長：伊藤 亮孝、小林 厚志

## ◆ 英語

15:55 ~ 16:15

[F1233-3vn-01]

抗酸化物質検出を指向したニトロキシドラジカル結合型室温発光性Irポルフィリンの開発

○楊川 博久<sup>1</sup>、村田 慧<sup>1</sup>、石井 和之<sup>1</sup> (1. 東大生研)

## ◆ 英語

16:15 ~ 16:35

[F1233-3vn-02]

Vaulted-structure induced efficient solid-state phosphorescence in *trans*-bis(iminomethylpyrrolato)platinum(II) complexes○Shufang HUANG<sup>1</sup>, Soichiro Kawamorita<sup>1</sup>, Takeshi Naota<sup>1</sup> (1. Osaka University)

## ◆ 日本語

16:35 ~ 16:55

[F1233-3vn-03]

マンガン(II)錯体が示すマグネトルミネッセンス

○壬生 託人<sup>1</sup>、松岡 亮太<sup>1</sup>、草本 哲郎<sup>1,2</sup> (1. 大阪大学、2. JSTさきがけ)

## ◆ 日本語

16:55 ~ 17:15

[F1233-3vn-04]

室温で長寿命な可視光発光を示す亜鉛錯体の合成および光物性評価

○岩本 秀光<sup>1</sup>、和田 啓幹<sup>1,2</sup>、砂田 祐輔<sup>1,2,3</sup> (1. 東大院工、2. 東大生研、3. JST さきがけ)

## Development of room-temperature phosphorescent iridium porphyrins linked to a nitroxide radical for detecting antioxidants

(<sup>1</sup>IIS, The Univ. of Tokyo) ○Hirohisa Yanagikawa,<sup>1</sup> Kei Murata,<sup>1</sup> Kazuyuki Ishii<sup>1</sup>

**Keywords:** Excited multiplet state; Porphyrin; Nitroxide radical; Phosphorescence probe; Antioxidant

Recently, the spin manipulations in the excited states, i.e., room temperature phosphorescence due to spin-orbit coupling and triplet-triplet annihilation energy upconversion based on the spin-spin interactions, have attracted considerable attention for developing new photofunctional materials.<sup>1,2</sup> By the use of the spin-spin interactions between the excited triplet chromophore and doublet radicals,<sup>3</sup> our laboratory has developed a fluorescence probe, silicon phthalocyanine linked to two TEMPO radicals (R2c), for detecting ascorbic acid (Figure 1).<sup>4</sup> Although the fluorescence of R2c is quenched by TEMPO radicals, the fluorescence due to the phthalocyanine moiety increases after the reaction of the TEMPO radicals with ascorbic acid.

In this study, in order to develop phosphorescence probes for detecting antioxidants, we synthesized novel iridium porphyrins linked to an iminonitroxide (IN) radical and investigated their photophysical properties and the reactivity with antioxidants (Figure 2). Although the iridium porphyrins are phosphorescent at room temperature due to the large spin orbit coupling on the iridium ion, the phosphorescence of **1** was quenched by the spin-spin interaction with the IN radical. Furthermore, in contrast to R2c, the phosphorescence of **1** increased after the reaction of the IN radical with catechol. Thus, we developed new phosphorescence probes using both the spin-orbit coupling and spin-spin interactions.

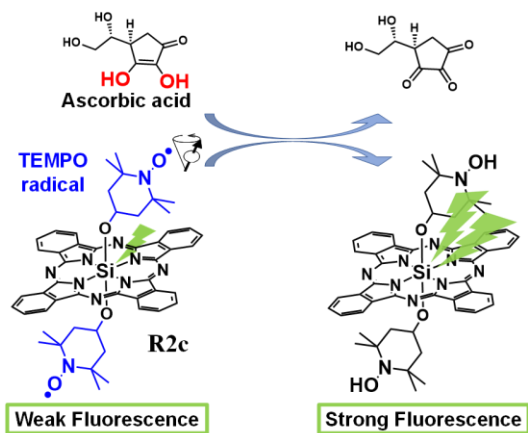


Figure 1. A fluorescence probe for detecting ascorbic acid (R2c).

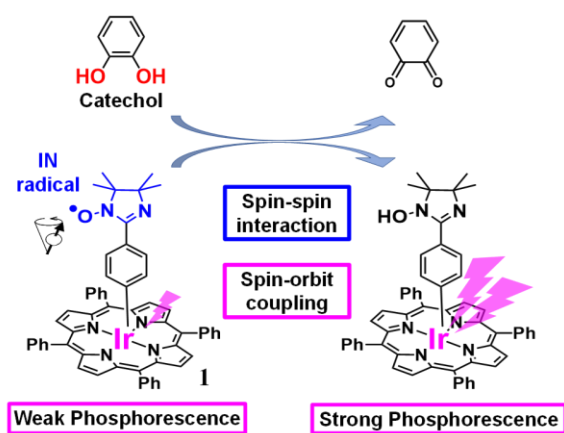


Figure 2. A phosphorescence probe for detecting catechol (**1**).

1) M. A. Baldo, et al, *Nature*. **2000**, 403, 750. 2) T. N. Singh-Rachford, et al, *Coord. Chem. Rev.* **2010**, 254, 2560. 3) K. Ishii, et al, *J. Am. Chem. Soc.* **1996**, 118, 13079. 4) K. Ishii, et al, *Chem. Com.* **2011**, 47, 4932.

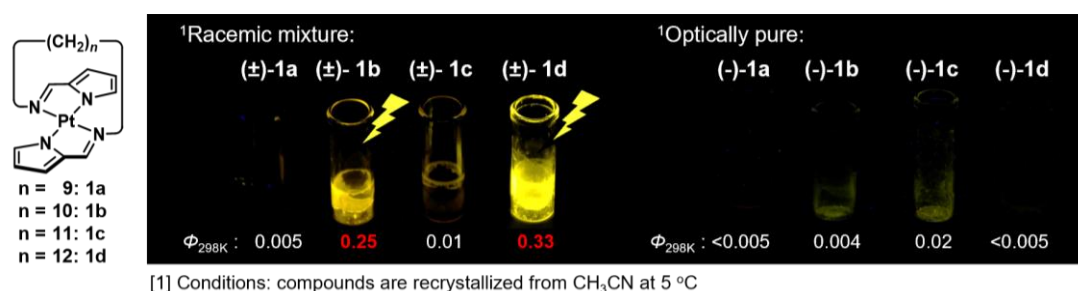
## Vaulted-structure Induced Efficient Solid-state Phosphorescence in *trans*-Bis(iminomethylpyrrolato)platinum(II) Complexes

(<sup>1</sup>Graduate School of Engineering Science, Osaka University) ○Shufang Huang,<sup>1</sup> Soichiro Kawamorita,<sup>1</sup> Takeshi Naota<sup>1</sup>

**Keywords:** Solid-State Phosphorescence; Vaulted Structure, Minimum Energy Crossing Point; Platinum

Phosphorescent metal complexes having aggregation-induced emission (AIE) represent a significant advancement in the field of luminescent materials, such as OLEDs and bioimaging sensors. Based on our program has been aimed at the development of phosphorescent materials which show strong emission in solid state induced by molecular design,<sup>1</sup> the present study achieved efficient AIE by design of vaulted-structured platinum(II) complexes. Specifically, a series of *trans*-bis(iminomethylpyrrolato)platinum(II) complexes bearing polymethylene chain ( $n = 9$ –12) over the platinum atom (complexes **1a**–**d**) do not display luminescent properties in the solution state, however, the racemic mixture of complexes **1b** and **1d** ( $n = 10$  and 12) were found to exhibit strong emission in the crystalline state. The same emission enhancement cannot be observed in complexes **1a** ( $n = 9$ ) and **1c** ( $n = 11$ ).

Vaulted complexes **1a**–**d** displayed non-emission in solution state while **1b** and **1d** exhibit strong emission in the crystalline state at 298 K ( $\Phi_{298K} = 0.25$  and 0.33, respectively), obtained from CH<sub>3</sub>CN, 5 °C (Figure 1). However, when the alkyl chain has an odd-numbered length ( $n=9$ , **1a** and  $n=11$ , **1c**), their crystals do not emit light, and only complexes with an even-numbered chain ( $n=10$ , **1b** and  $n=12$ , **1d**) demonstrate specific AIE. In addition, non-vaulted complexes exhibit non-emission in both solution and crystalline states. Furthermore, this vaulted-structure induced AIE is dependent on various factors. Under the same conditions, crystals that are optically pure don't show emission. These findings suggest that the unique vaulted molecular structure, with specific chain lengths, can lead to particular packing arrangements that effectively suppresses the deactivation of excited states.



**Figure 1.** Molecular structure of vaulted complexes and photographs of their crystals (obtained from CH<sub>3</sub>CN, 5 °C; left: racemic mixture, right: optically pure) under UV irradiation ( $\lambda_{ex} = 365$  nm)

1) T. Naota, *et al. J. Am. Chem. Soc.* **2011**, *133*, 6493–6496.

## マンガン(II)錯体が示すマグネトルミネッセンス

(大阪大学<sup>1</sup>・JST さきがけ<sup>2</sup>) ○壬生 託人<sup>1</sup>・松岡 亮太<sup>1</sup>・草本 哲郎<sup>1,2</sup>

Magnetoluminescence of a manganese(II) complex (<sup>1</sup>Osaka University, <sup>2</sup>JST-PRESTO)

○Takuto Mibu,<sup>1</sup> Ryota Matsuoka,<sup>1</sup> Tetsuro Kusamoto<sup>1,2</sup>

Magneto-optical effects, in which magnetism contributes to photophysical properties of materials, have been extensively studied for their application to optical devices. Among magneto-optical effects, magnet field effects on luminescence (Magnetoluminescence, MagLum) have been attracting attention as the unique properties of the materials exhibiting both luminescence and magnetic properties. MagLum in molecular materials has been mainly studied in the system of luminescent radicals and the mechanism has been proposed to be based on the  $S = 1/2$  spin-spin interaction between radicals. In this study, we investigated MagLum in high-spin ( $S = 5/2$ ) manganese (II) complexes showing phosphorescence originating from d-d transitions and discussed the mechanism. We doped  $[\text{Mn}^{\text{II}}(\text{dppmO}_2)_3](\text{BF}_4)_2$  (Fig. a) into  $[\text{Zn}^{\text{II}}(\text{dppmO}_2)_3](\text{BF}_4)_2$  crystal at various weight percent (wt%), and investigated the magnetic field dependence of their luminescence properties. As a result, we observed distinct MagLum in the doped samples with any wt% (Fig. b), where the spectral changes upon increasing magnetic field were different from those observed in radical-doped crystals reported previously<sup>1)</sup>.

**Keywords :** *manganese(II) ion, luminescence, magnetic metal complexes*

磁気光学効果の研究の中でも、発光特性が磁場に応答し変化するマグネトルミネッセンス (MagLum) が近年注目され始めている。分子性物質の MagLum は、磁性と発光特性を併せ持つラジカル分子 ( $S = 1/2$ ) を中心に研究されており、複数のラジカル分子間に働く磁気相互作用に基づく物性の発現機構が提案されてきた<sup>1)</sup>。本研究では、報告例の限られた d-d 遷移に由来するりん光を示す高スピンマンガン(II)錯体 ( $S = 5/2$ ) における MagLum を調査し、その発現機構について考察した。

実際に、 $[\text{Mn}^{\text{II}}(\text{dppmO}_2)_3](\text{BF}_4)_2$  (Fig. a) を非磁性等価体である  $\text{Zn}^{\text{II}}$  錯体に様々な重量分率で分散することで、MagLum 挙動の dope 率依存性を調査した。その結果、いずれの dope 率においても明瞭な MagLum が観測され (Fig. b)、そのスペクトル変化はこれまでのラジカルドーブ結晶で見られたものとは異なっていた<sup>1)</sup>。発表当日は、本系における MagLum の推定機構や dope 率依存性について報告予定である。

1) T. Kusamoto, Y. Teki, H. Nishihara, *et al.*, *Chem. Sci.*, **2021**, 12, 2025–2029.

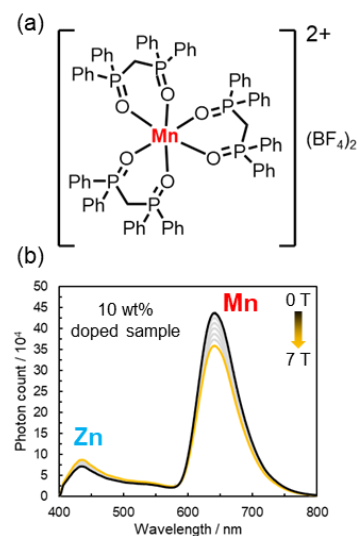


Fig. (a) Chemical structure of  $[\text{Mn}^{\text{II}}(\text{dppmO}_2)_3](\text{BF}_4)_2$ . (b) Magnetic field effect in emission spectra of 10 wt%  $\text{Mn}^{\text{II}}$  complex doped sample at 4.2 K ( $\lambda_{\text{ex}} = 285 \text{ nm}$ ).

## 室温で長寿命な可視光発光を示す亜鉛錯体の合成および光物性評価

(東大院工<sup>1</sup>・東大生研<sup>2</sup>・JST さきがけ<sup>3</sup>) ○岩本 秀光<sup>1</sup>・和田 啓幹<sup>1,2</sup>・砂田 祐輔<sup>1,2,3</sup>

Synthesis and photophysical properties of a Zn complex showing long-lived visible light emission at ambient temperature (<sup>1</sup> *Graduate School of Engineering, The University of Tokyo*, <sup>2</sup> *Institute of Industrial Science, The University of Tokyo*, <sup>3</sup> *JST PRESTO*) ○Hidemitsu Iwamoto,<sup>1</sup> Yoshimasa Wada,<sup>1,2</sup> Yusuke Sunada<sup>1,2,3</sup>

So far, zinc(Zn) complexes that emit in the visible light spectrum primarily feature emissions originating from the ligands, with the Zn center rarely contributing to the formation of such excited states. This study aimed to create a Zn complex that utilizes the atomic orbitals of Zn center for visible light emission, through the design and synthesis of novel Zn complexes. We have newly developed a mononuclear Zn complex **1** that exhibits bright green photoluminescence with quantum yields of approximately 30%, which lasts on the ms-order in the solid state at ambient temperature. This long lifetime is considered to be occurred through the formation of long-lived triplet states. We report our findings on **1** based on comprehensive analyses, including single-crystal X-ray structural analysis, various photophysical measurements, and quantum chemical calculations, specifically focusing on the contribution of the Zn center to the emission. We also applied **1** to photocatalytic isomerization reactions making use of its long-lived triplet states. We demonstrated that in the presence of a catalytic amount of **1**, *E* → *Z* isomerization of alkenes proceeds under blue LED light irradiation, showing that **1** works as the photocatalyst.

**Keywords** : zinc; visible light emission; heavy atom effect

従来、可視光域に発光を示す亜鉛錯体において、そのほとんどは配位子に由来する発光であり、亜鉛中心は低エネルギーな励起状態の形成に関与しないことが知られている<sup>1)</sup>。本研究では、亜鉛の軌道を利用した可視光発光を示す錯体の実現を目的に、新規亜鉛錯体の設計・合成を行った。合成した錯体 **1** は、固体状態において、鮮やかな緑色発光を示すことがわかり、その発光量子収率は室温においても 30% 程度の値を示した。加えて、発光寿命測定の結果、数 ms の長い発光成分からなることがわかり、スピン禁制な三重項励起状態を経由した発光であることが示唆された。錯体 **1** に対し、単結晶 X 線構造解析および種々の光物性測定、量子化学計算による多角的な解析により、亜鉛中心の発光への寄与に関する考察を行った。また、その長寿命な三重項励起状態を活かし、錯体 **1** を用いた光触媒反応も検討した。アルケンの光異性化反応を検討したところ、触媒量の錯体 **1** 添加条件において、青色 LED 光照射下、*E* → *Z* 異性化反応が速やかに進行することが確認され、錯体 **1** が光触媒として機能することもわかった。

1) O. Mrózek, M. Mitra, B. Hupp, A. Belyaev, N. Lüdtke, D. Wagner, C. Wang, O. S. Wenger, C. M. Marian, A. Steffen, *Chem. Eur. J.*, **2023**, 29, e202203980.



アカデミックプログラム [B 講演] | 09. 錯体化学・有機金属化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 F1234(12号館 [3階] 1234)

**[F1234-3vn] 09. 錯体化学・有機金属化学**

座長：大竹 研一、芳野 遼

## ◆ 英語

15:55 ~ 16:15

[F1234-3vn-01]

波打ち構造を持つ二次元MOFsの機械的性質

○大谷 亮<sup>1</sup>、大場 正昭<sup>1</sup> (1. 九州大学)

## ◆ 英語

16:15 ~ 16:35

[F1234-3vn-02]

Glassy nonporous Zn coordination polymer for gas separation

○Xin Zheng<sup>1</sup>, Shin-ichiro Noro<sup>1</sup> (1. Fac. of Env. Earth Sci., Hokkaido Univ.)

## ◆ 英語

16:35 ~ 16:55

[F1234-3vn-03]

配位高分子二元系の共融現象

○田部 博康<sup>1</sup>、Karnjana Atthawilai<sup>2</sup>、堀毛 悟史<sup>1,2</sup> (1. 京大、2. タイ王国ウィタヤシリメティー科学技術大学院大学)

## ◆ 日本語

16:55 ~ 17:15

[F1234-3vn-04]

有機金属構造体の合成後修飾による二次配位部位に基づく不均一系触媒の設計

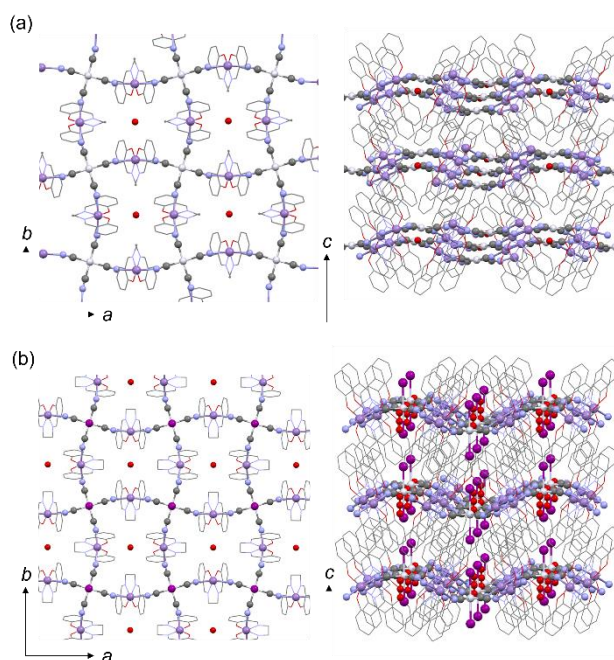
○相本 美咲<sup>1</sup>、Pavel Usov<sup>1</sup>、和田 雄貴<sup>1</sup>、松本 隆也<sup>1,2</sup>、河野 正規<sup>1</sup> (1. 国立大学法人東京工業大学、2. ENEOS株式会社)

## Mechanical properties of 2D-MOFs composed of undulating layers

(<sup>1</sup>*Department of Chemistry, Faculty of Science, Kyushu University*) ○ Ryo Ohtani,<sup>1</sup> Masaaki Ohba,<sup>1</sup>

**Keywords:** Compression; Metal-organic framework; Coordination polymer

Two-dimensional (2D) metal-organic frameworks (MOFs) are a class of materials that exhibit various functionalities based on anisotropic layered structures constructed by strong in-plane connectivity and weak van der Waals interlayer interaction. However, anisotropic mechanical properties and their modulation of 2D-MOF crystals have not been rarely investigated. Herein, we report compression and elastic properties of 2D-MOFs,  $[\text{Mn}(\text{salen})]_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{Mn}(\text{salen})]_2[\text{PtI}_2(\text{CN})_4] \cdot \text{H}_2\text{O}$  (**2**) composed of undulating-hollow-layers.<sup>[1]</sup> These two MOFs incorporate structural differences involving the zigzag angles of undulating layers, giving rise to opposite trends in anisotropic compressibility caused by compression-induced structural transformation between flattening and rippling of the layers. In addition, pseudo negative-linear-compression along the layer-stacking direction occurred by **1** via a hyperfilling phenomenon of alcohol molecules, which are pressure-transmitting media in the high-pressure experiments, into the interlayer spaces. These compression behaviors were also impacted by the crystal morphology such as single crystals and powder forms. Moreover, **1** and **2** exhibited higher Young's modulus along in-plane direction than that of out-of-plane direction. This characteristic elastic property is inverted and counterintuitive comparing with other 2D-materials, which reflects the hollow-layer structure.



[1] R. Ohtani, R. Yamamoto, T. Aoyama, A. Grosjean, M. Nakamura, J. K. Clegg, S. Hayami, *Inorg. Chem.* **2018**, 57, 11588-11596.

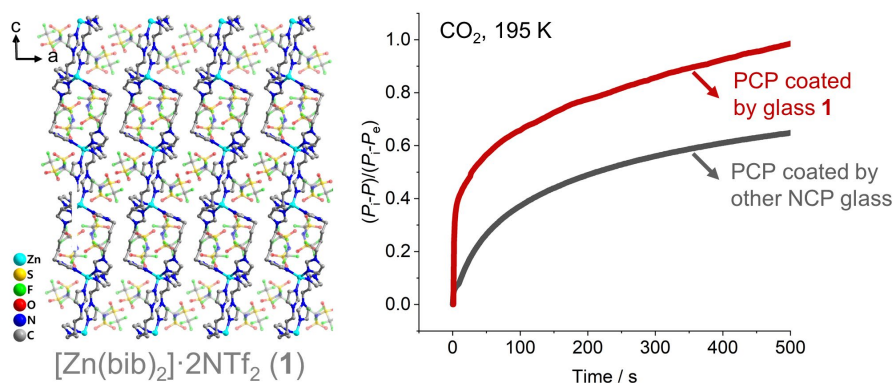
## Glassy nonporous Zn coordination polymer for gas separation

(Faculty of Environmental Earth Science, Hokkaido Univ.) ○Xin Zheng, Shin-ichiro Noro

**Keywords:** Nonporous Coordination Polymers, Phase Transitions, Selective Gas Permeation

Unlike porous coordination polymers (PCPs), which have shown considerable promise in gas sorption and separation, nonporous coordination polymers (NCPs) have received limited attention due to their lack of porous structures. Drawing inspiration from the solution-diffusion mechanism observed in nonporous organic polymer membranes,<sup>1</sup> we are synthesizing glassy NCPs comprising flexible building units.<sup>2</sup> The glassy NCPs enable the formation of defect-free membranes essential for efficient gas separation.

In this study, we report a new Zn(II) NCP,  $[\text{Zn}(\text{bib})_2] \cdot 2\text{NTf}_2$  (**1**, bib = 1,4-bisimidazole butane,  $\text{NTf}_2^-$  = bis(trifluoromethylsulfonyl)amide), where one Zn(II) ion coordinates with four bib ligands to form the one-dimensional chain and  $\text{NTf}_2^-$  anions are uncoordinated. The  $d^{10}$  Zn(II) ion provides a flexible coordination geometry ranging from tetrahedral to square planar, while the bib ligand with long alkyl chains and  $\text{NTf}_2^-$  anions with highly delocalized negative charges can further enhance the flexibility of **1**. As a result, **1** showed the low melting point (110 °C) and wide liquid phase range (110~445 °C). The high processability and  $\text{NTf}_2^-$ -derived  $\text{CO}_2$ -philicity<sup>3</sup> of **1** prompted us to explore its potential for serving as a defect-free  $\text{CO}_2$  separation layer. Glassy **1** was coated on the surface of PCP crystals, resulting in the composite that exhibited enhanced  $\text{CO}_2/\text{N}_2$  selectivity. Compared with the composite coated by other NCP glass,<sup>2</sup> the glassy **1**-coated composite showed a more facile  $\text{CO}_2$  permeation. The comprehensive findings of the glassy **1** for  $\text{CO}_2$  separation will be presented.



- 1) J. G. Wijmans, R. W. Baker, *J. Membr. Sci.* **1995**, 107, 1. 2) X. Zheng, M. Kato, Y. Uemura, D. Matsumura, I. Yagi, K. Takahashi, S. Noro, T. Nakamura, *Inorg. Chem.* **2023**, 62, 1257. 3) X. Zheng, K. Fukuhara, Y. Hijikata, J. Pirillo, H. Sato, K. Takahashi, S. Noro, T. Nakamura, *Commun. Chem.* **2020**, 3, 143.

## Solder-like Eutectic Behaviors of Binary Coordination Polymers

(<sup>1</sup>Institute for Advanced Study, Kyoto University, <sup>2</sup>VISTEC, <sup>3</sup>Graduate School of Science, Kyoto University) ○Hiroyasu Tabe<sup>1</sup>, Karnjana Atthawilai<sup>2</sup>, Satoshi Horike<sup>1,2,3</sup>

**Keywords:** Binary compound; Phase diagram; Metal-organic framework; Melting point depression

Binary compounds are defined as mixtures of two immiscible crystals without complete solid solubility. The binary compounds consist of metals, inorganic salts, or organic polymers, and their states and composition at various temperatures are described in phase diagrams. The eutectic melting is defined as crystal melting at temperatures lower than melting points ( $T_m$ ) of the constituents. Binary compounds showing eutectic behavior have been used as functional materials such as Pb-Sn solders.

Coordination polymers (CPs) or metal-organic frameworks (MOFs) are solid crystalline materials. Their binary phase diagram is not explored because binary compounds of CPs with both miscibility in the liquid state and recrystallization ability have not been reported. In this study, binary phase diagrams are explored using a series of CPs consisting of  $\text{Ag}^+$  ions, dinitrile with various lengths of alkyl chain, and counter anions.<sup>1</sup>

$T_m$  of mixtures of  $\text{Ag}(\text{adiponitrile})_2(\text{BF}_4)$  (**1**, Fig. 1A) and  $\text{Ag}(\text{adiponitrile})(\text{CH}_3\text{SO}_3^-)$  (**2**, Fig. 1B) (**1**<sub>x</sub>**2**<sub>y</sub>,  $x$  and  $y$  are the molar ratios of **1** and **2**, respectively) were lower than  $T_m$  of **1** and **2** (132°C and 148°C, respectively), as revealed by differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD) patterns (Fig. 1C). The phase diagram of **1**<sub>x</sub>**2**<sub>y</sub> indicated that **1**<sub>0.6</sub>**2**<sub>0.4</sub> and single  $T_m$  at 108 °C are the eutectic ratio and the eutectic temperature ( $T_e$ ), respectively (Fig. 1D). Infrared (IR) spectra and powder X-ray diffraction (PXRD) patterns of the mixtures at various temperatures indicate that the ligand-exchange reactions of the crystal surfaces are the reason for eutectic melting.

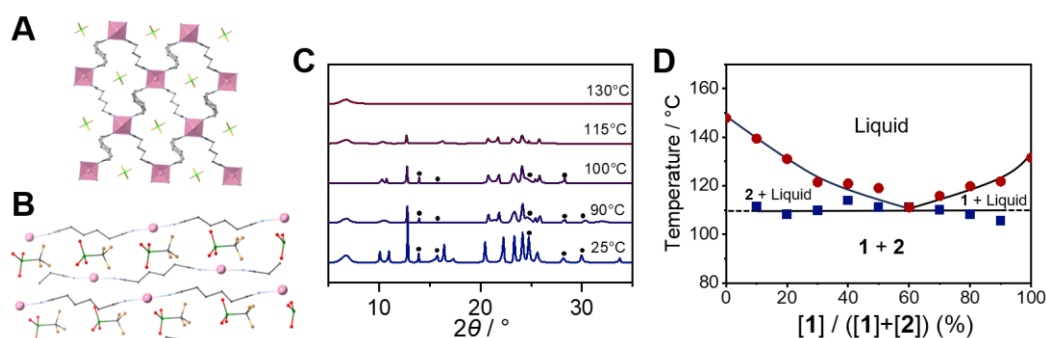


Figure 1. Crystal structure of (A) **1** and (B) **2**. C, N, Ag, B, F, O, and S atoms are colored gray, light blue, pink, light green, orange, red and green, respectively. (B) PXRD patterns of **1**<sub>0.8</sub>**2**<sub>0.2</sub>. ● represent peaks derived from **2**. (C) Binary phase diagram of **1**<sub>x</sub>**2**<sub>y</sub>.

1) L. Carlucci, G. Ciani, D. M. Proserpiob, S. Rizzato, *CrystEngComm*, **2002**, 4, 413.

## 有機金属構造体の合成後修飾による二次配位部位に基づく不均一系触媒の設計

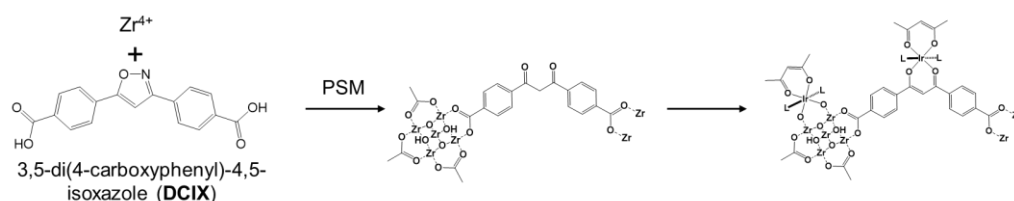
(東工院理<sup>1</sup>・ENEOS<sup>2</sup>) ○相本 美咲<sup>1</sup>・Pavel M. Usov<sup>1</sup>・和田 雄貴<sup>1</sup>・松本 隆也<sup>1,2</sup>・河野 正規<sup>1</sup>

Heterogeneous catalyst design based on secondary coordination sites inside post-synthetically modified metal-organic frameworks (<sup>1</sup>*Graduate School of Science, Tokyo Institute of Technology*, <sup>2</sup>*Central Technical Research Laboratory, ENEOS Corporation*)○Misaki Aimoto<sup>1</sup>, Pavel M. Usov<sup>1</sup>, Yuki Wada<sup>1</sup>, Takaya Matsumoto<sup>1,2</sup>, Masaki Kawano<sup>1</sup>

Metal-organic frameworks (MOFs) are porous polymeric materials composed of metal ions and organic multidentate ligands. Due to their chemical tunability and highly ordered structures, MOFs have advantages over other solid supports. In this study, a novel ligand was developed and combined with Zr ions to create frameworks. The catalytic centers were incorporated directly into the ligand allowing for a very high density of active sites while maintaining pore access. The ligand, 3,5-di(4-carboxyphenyl)-4,5-isoxazole (DCIX), has carboxylate groups at both ends that can bridge Zr cluster units, and isoxazole ring in the middle that can be converted into a diketone moiety by post-synthetic modification. The newly revealed coordination sites could accommodate Ir centers to create catalytically active complexes immobilized within frameworks. The structural properties of the resultant MOFs were investigated using a variety of diffraction and spectroscopic techniques and their heterogeneous catalytic activity was tested.

**Keywords :** *Metal-organic frameworks, Post-synthetic modification, Catalyst*

有機金属構造体 (MOF) は金属イオンと有機多座配位子からなる細孔性高分子である。MOF はその化学的可変性と高度に秩序化された構造により、他の固体担体にはない利点を備えている。本研究では新規配位子を開発し、Zr イオンと結合させることでフレームワークを作成した。触媒中心を配位子に直接組み込むことで、細孔へのアクセスを維持したまま、非常に高密度の活性サイトを実現した。新規配位子の 3,5-di(4-carboxyphenyl)-4,5-isoxazole (DCIX) は両端に Zr クラスターに橋渡しできるカルボキシレート基が存在し、中央には合成後の修飾によってジケトン部分に変換できるイソオキサゾール環を持つ。新たに明らかになった配位部位は、Ir 中心を収容し、フレームワーク内に固定化された触媒活性錯体を作り出すことができる。得られた MOF の構造特性は、さまざまな回折および分光学的手法を用いて調べられ、不均一系での触媒活性が試験された。



アカデミックプログラム [B 講演] | 11. 有機化学—構造有機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 E1113(11号館 [1階] 1113)

**[E1113-3pm] 11. 有機化学—構造有機化学**

座長：若宮 淳志、川畑 公輔

## ◆ 英語

13:00 ~ 13:20

[E1113-3pm-01]

 $\pi$ 共役系骨格内における様々な酸化状態の超原子価アンチモン化合物の合成と光学特性○谷村 和哉<sup>1</sup>、権 正行<sup>1</sup>、田中 一生<sup>1</sup> (1. 京大院工)

## ◆ 日本語

13:20 ~ 13:40

[E1113-3pm-02]

ポルフィリン修飾ポリチオフェンによるキラル増幅を利用したセンシング

○本告 潤之介<sup>1</sup>、福原 学<sup>1</sup> (1. 東京工業大学)

## ◆ 英語

13:40 ~ 14:00

[E1113-3pm-03]

超原子価スズ化合物の7配位化による光学特性と刺激応答性の評価

○権 正行<sup>1</sup>、森崎 祐介<sup>1</sup>、田中 一生<sup>1</sup> (1. 京大院工)

## ◆ 日本語

14:00 ~ 14:20

[E1113-3pm-04]

スピロフルオレンを導入したシクロペンタチオフェンを $\pi$ 共役リンカーとする非縮環型電子受容性分子の開発と波長選択型有機太陽電池への応用○陣内 青萌<sup>1</sup>、家 裕隆<sup>1</sup> (1. 大阪大学)

14:20 ~ 14:30

休憩

## ◆ 英語

14:30 ~ 14:50

[E1113-3pm-05]

キノイド構造を有する超電子供与性分子の合成と応用

○松尾 崇也<sup>1,2</sup>、川畑 公輔<sup>1,2</sup>、瀧宮 和男<sup>1,2,3</sup> (1. 東北大院理、2. 理研CEMS、3. 東北大WPI-AIMR)

## ◆ 英語

14:50 ~ 15:10

[E1113-3pm-06]

カルコゲン相互作用に基づく超分子的有機半導体の分子集積と電荷輸送

○田中 優成<sup>1</sup>、森 達哉<sup>1</sup>、小路口 由佳<sup>1</sup>、ヤン ユソク<sup>1</sup>、安田 琢磨<sup>1,2</sup> (1. 九大院工、2. 九大高等研)

## ◆ 英語

15:10 ~ 15:30

[E1113-3pm-07]

# 含窒素芳香族化合物の部分的に分離したフロンティア軌道を利用した光機能性ホウ素錯体の創出

○伊藤 峻一郎<sup>1</sup>、高橋 宏昌<sup>1</sup>、田中 一生<sup>1</sup> (1. 京大院工)

---

## Synthesis and Optical Properties of $\pi$ -Conjugated Molecules Containing Hypervalent Antimony in Various Oxidation States

(Graduate School of Engineering, Kyoto University)

○ Kazuya Tanimura, Masayuki Gon, Kazuo Tanaka

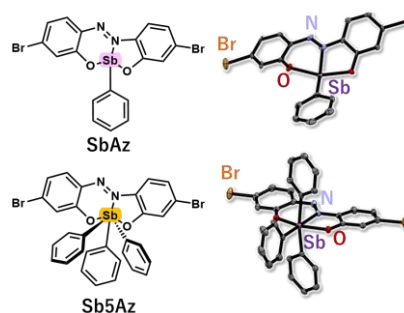
**Keywords:**  $\pi$ -Conjugated Molecules; Hypervalent Compounds; Antimony; Different Oxidation number; Optical Properties

Recently, main group elements have been introduced into  $\pi$ -conjugated scaffolds for functionalization. However, heavy main group elements have not been studied much because of difficulty handling and high toxicity. Our group previously reported hypervalent compounds combined with heavy elements and  $\pi$ -conjugated scaffolds to explore the usage of heavy main group elements.<sup>[1-3]</sup> In the hypervalent state, heavy elements have electronic contributions to  $\pi$ -conjugated scaffolds and stimuli-responsiveness to Lewis bases.

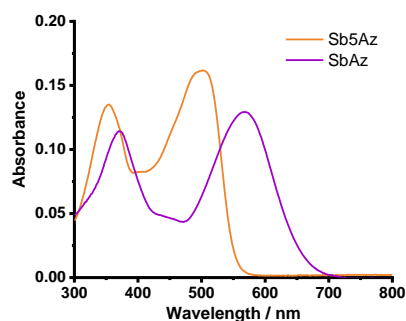
This research focuses on “Antimony (Sb)” in group 15, fifth period. Antimony has different oxidation numbers (+3 and +5), so various hypervalent antimony compounds were reported.<sup>[4, 5]</sup> We newly synthesized hypervalent antimony compounds **SbAz** and **Sb5Az** (Figure 1) with different oxidation numbers.

From their crystal structure in Figure 1, **SbAz** showed pseudo-trigonal bipyramidal geometry, while **Sb5Az** showed octahedral geometry. The absorption spectra of **SbAz** and **Sb5Az** implied significant differences in electronic states (Figure 2). According to density functional theory (DFT) calculation, these differences were caused by the electronic contribution of the hypervalent state. In this presentation, we will describe the electronic effects of hypervalent antimony in more detail and the changes of **SbAz** by chemical oxidation.

[1] Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, 27, 7561–7571. [2] Gon, M.; Ito, S.; Tanaka, K.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **2021**, 94, 2290–2301. [3] Tanimura, K.; Gon, M.; Tanaka, K. *Inorg. Chem.* **2023**, 62, 4590–4597. [4] Yamamoto, Y.; Fujikawa, H.; Fujishima, H.; Akiba, K. *J. Am. Chem. Soc.* **1989**, 111, 2276–2283. [5] Akiba, K.; Nakata, H.; Yamamoto, Y.; Kojima, S. *Chem. Lett.* **1992**, 8, 1559–1562.



**Figure 1.** Chemical structure and crystal structure of hypervalent antimony compounds, **SbAz** and **Sb5Az**.



**Figure 2.** Absorption spectra of **SbAz** (purple line) and **Sb5Az** (orange line) ( $1.0 \times 10^{-5}$  M in toluene).



## ポルフィリン修飾ポリチオフェンによるキラル増幅を利用したセンシング

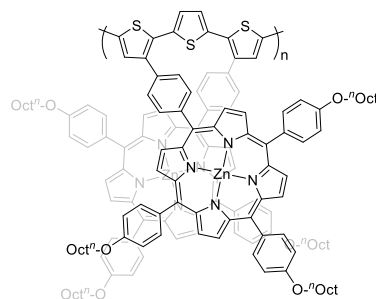
(東工大理<sup>1</sup>) ○本告 潤之介<sup>1</sup>・福原 学<sup>1</sup>

Chiral-Amplification Sensing by Porphyrin-Polythiophene Conjugates (<sup>1</sup>*Department of Chemistry, Tokyo Institute of Technology*) ○Junnosuke Motoori,<sup>1</sup> Gaku Fukuhara<sup>1</sup>

In this study, we demonstrated a signal-amplification sensing via the chiral amplification behavior. Therefore, we synthesized polymer chemosensors composed of polythiophene as a dynamic polymer backbone and porphyrin as a molecular binder. The obtained polythiophene-porphyrin conjugates showed distinctive exciton couplings upon the addition of chiral amines. In this presentation, the chiroptical properties and molecular recognition behavior of the chemosensors will be discussed.

**Keywords:** Polythiophene; Chiral Sensing; Porphyrin

我々は化学センサーから得られるシグナルを増幅することで高感度に検体を検出する手法 (Supramolecular allosteric signal-amplification sensing, SASS) の開発に取り組んでいる<sup>1</sup>。そこでシグナル増幅をさせる手法の一つとしてキラル増幅に着目した。キラル増幅とは高分子主鎖にキラル側鎖を低割合や低いエナンチオマー過剰率で導入した動的高分子が、100%のキラルな側鎖や片方のエナンチオマーから構成されるホモポリマーと同等の円二色性(CD)強度を示す現象である<sup>2</sup>。キラル増幅によるシグナル増幅が見込める **Por-PT** を新たな化学センサーとして設計した。この化学センサーは、分子を認識する際にキラルにねじる (エキシトンキラリティー) 構造を形成するポルフィリンを分子認識部位として、主鎖骨格が柔軟で従来から SASS を実現しているポリチオフェンを高分子主鎖として用いている。このポリマー化学センサーはより大きなキラル増幅を起こすために側鎖のねじれが主鎖に伝播しやすい設計とした。本発表では **Por-PT** の分子認識能並びにキラル増幅について発表する。



**Figure 1.** Structure of **Por-PT**.

1) (a) Fukuhara, G. *J. Incl. Phenom. Macrocycl. Chem.* **2019**, 93, 127. (b) Fukuhara, G. *Polym. J.* **2021**, 53, 1325. (c) Fukuhara, G. *J. Photochem. Photobiol. C: Photochem. Rev.* **2020**, 42, 100340. (d) Mizuno, H. Fukuhara, G. *Acc. Chem. Res.* **2022**, 55, 1748.

2) (a) Palmans, A. R. A.; Vekemans, J. A. J. M.; Havinga, E. E. H.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2648. (b) Green, M. M.; Cheon, K.-S.; Yang, S.-Y.; Park, J.-W.; Swansburg, S.; Liu, W. *Acc. Chem. Res.* **2001**, 34, 672. (c) Yashima, E.; Ousaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. *Chem. Rev.* **2016**, 116, 13752.

## Evaluation of Optical and Stimuli-Responsive Properties Based on Seven-Coordinated Hypervalent Tin(IV) Compounds

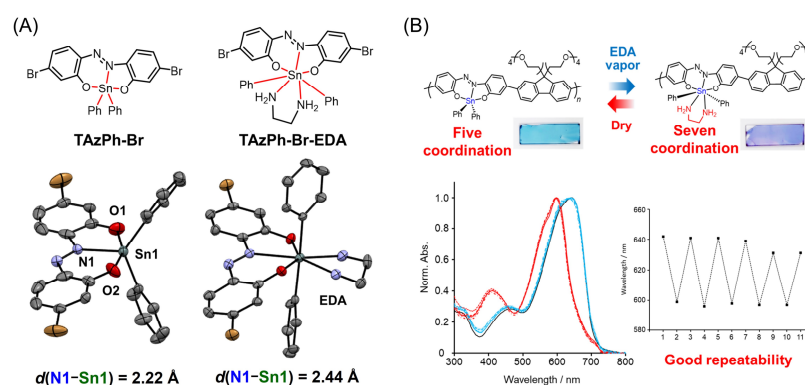
(Graduate School of Engineering, Kyoto University)

○Masayuki Gon, Yusuke Morisaki, Kazuo Tanaka

**Keywords:** hypervalent bond;  $\pi$ -conjugated polymer; luminescence; tin; near-infrared

A hypervalent compound is a class of molecules where a main-group element has more than 8 electrons in its valence shell beyond the limits of the Lewis octet rule. We recently proved unique electronic contribution of hypervalent bonds originating from polarized three-center four-electron (3c-4e) bonds to  $\pi$ -conjugated systems through hypervalent tin-fused azobenzene (TAz) compounds.<sup>1,2)</sup> In addition, luminescent chromisms both in solution and solid states were observed based on reversible coordination-number change of the TAz compounds from five to six.<sup>1)</sup> Furthermore, vapochromism was monitored from the  $\pi$ -conjugated polymer film composed of the TAz units upon exposure of coordinating solvent vapor such as dimethyl sulfoxide (DMSO).<sup>3)</sup> Herein, We newly found seven-coordinated state with a bidentate ligand and will explain the optical properties.

Figure 1A shows chemical structures and ORTEP drawings of synthesized TAz compound (**TAzPh-Br**) and its ethylene diamine (EDA) adduct (**TAzPh-Br-EDA**). **TAzPh-Br** had trigonal bipyramidal geometry in the five-coordinated structure. On the other hand, treatment of EDA changed the coordination number from five to seven and the resulted **TAzPh-Br-EDA** showed pentagonal bipyramidal geometry accompanied by the elongation of nitrogen–tin (N–Sn) bond. Additionally, the  $\pi$ -conjugated polymer film including the TAz units exhibited vapochromism upon exposure of EDA vapor with good repeatable optical properties (Figure 1B).



**Figure 1.** (A) Chemical structures and ORTEP drawings of TAz compounds. (B) Vapochromism of the  $\pi$ -conjugated polymer film including TAz units.

1) Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, 27, 7561. 2) Gon, M.; Tanimura, K.; Yaegashi, M.; Tanaka, K.; Chujo, Y. *Polym. J.* **2021**, 53, 1241. 3) Gon, M.; Morisaki, Y.; Tanimura, K.; Tanaka, K.; Chujo Y. *Mater. Chem. Front.* **2023**, 7, 1345.

## スピロフルオレンを導入したシクロペンタチオフェンを $\pi$ 共役リンカーとする非縮環型電子受容性分子の開発と波長選択型有機太陽電池への応用

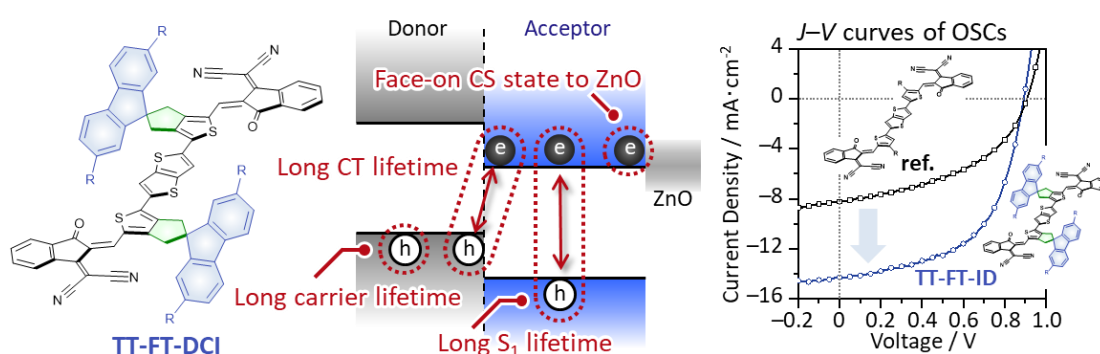
(阪大産研<sup>1</sup>・阪大 ICS-OTRI<sup>2</sup>) ○陣内 青萌<sup>1,2</sup>・家 裕隆<sup>1,2</sup>

Development of thiophene-based non-fused electron acceptors bearing orthogonally fused fluorene units and application to wavelength-selective organic photovoltaics (<sup>1</sup>SANKEN, Osaka University, <sup>2</sup>ICS-OTRI, Osaka University) ○Seihou Jinnai,<sup>1,2</sup> Yutaka Ie,<sup>1,2</sup>

We designed and synthesized novel non-fused electron-acceptors (TT-FT-DCI) using spirofluorene-flanked cyclopentathiophene unit (FT) as a  $\pi$ -conjugated linker that provides both planar  $\pi$ -conjugated backbone and molecular arrangement control. The OSC properties of the TT-FT-DCI were evaluated and showed a power conversion efficiency of 7.1%. The structures, properties, OSC characteristics, and exciton dynamics, as well as application to green light wavelength-selective OSCs will be presented.

**Keywords :** Organic Photovoltaics; Organic Semiconductors; Exciton; Structure-property Relationships;  $\pi$ -Conjugated Compounds

本研究では、スピロフルオレン構造を導入したシクロペンタチオフェンユニット (FT)<sup>1,2)</sup> を  $\pi$  共役リンカーとする非縮環型電子受容性分子 TT-FT-DCI と、FT の代わりに 3-(2-octyldodecyl)thiophene (T) を導入した TT-T-DCI を合成した。両化合物の OSC 特性を評価したところ TT-FT-DCI は 7.1% の良好なエネルギー変換特性 (PCE) を示し、TT-T-DCI では 3.4% の PCE であった。詳細な分光分析の結果、FT を導入することで主鎖の剛直性が向上することが示唆された。さらに、時間分解分光分析を通じて、TT-FT-DCI は光励起状態、電荷移動状態、電荷キャリア等の高エネルギー種がそれぞれ長寿命である事が明らかとなった。さらに、TT-FT-DCI を用いた発電層では分離した電荷が電極界面で face-on 配向となっている事が示唆された<sup>3)</sup>。本発表では FT ユニットの特徴を利用した緑色波長選択型 OSC の検討についても述べる<sup>4)</sup>。



1) Y. Ie, M. Endou, S. K. Lee, R. Yamada, H. Tada, Y. Aso, *Angew. Chem. Int. Ed.* **2011**, *50*, 11980. 2) Y. Ie, Y. Okamoto, T. Inoue, T. Seo, T. Ohto, R. Yamada, H. Tada, Y. Aso, *J. Am. Chem. Soc.* **2021**, *143*, 599. 3) S. Jinnai, K. Murayama, K. Nagai, M. Mineshita, K. Kato, A. Muraoka, A. Yamakata, A. Saeki, Y. Kobori, Y. Ie, *J. Mater. Chem. A* **2022**, *10*, 20035. 4) S. Jinnai, N. Shimohara, K. Ishikawa, K. Hama, Y. Iimuro, T. Washio, Y. Watanabe, Y. Ie, *Faraday Discuss.* **2024**, *in press* (DOI: 10.1039/D3FD00141E).

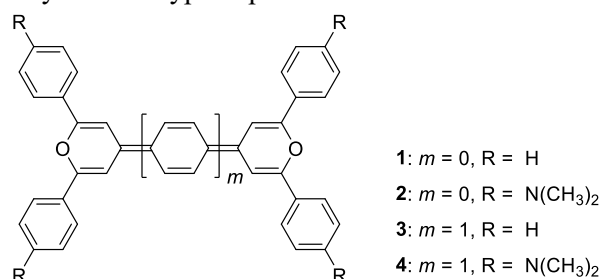
## Synthesis and Application of Super-Electron-Donating Molecules with Quinoid Structure

(<sup>1</sup>Graduate school of Science, Tohoku University, <sup>2</sup>RIKEN Center for Emergent Matter Science (CEMS), <sup>3</sup>Advanced Institute for Materials Research (WPI-AIMR), Tohoku University)  
 ○Takaya Matsuo<sup>1,2</sup>, Kohsuke Kawabata<sup>1,2</sup>, Kazuo Takimiya<sup>1,2,3</sup>

**Keywords:** n-Type dopant; n-Type organic thermoelectrics; HOMO energy level; Molecular design; Pyranylidene

$\pi$ -Conjugated molecules with high-lying HOMO energy levels ( $E_{\text{HOMOS}}$ ) have been extensively studied as electron-donor molecules for charge-transfer complex formation. However, the  $E_{\text{HOMOS}}$  of such electron-donor molecules are not sufficiently high to donate electrons (n-dope) to LUMOs of typical n-type organic semiconductors, which are around  $-4.0$  eV or higher. Recently, based on a previously reported electron-donor molecule (**1**) we have developed dipyranylidene-based molecules with high-lying  $E_{\text{HOMOS}}$ .<sup>1,2</sup> Among these, **2** has an extremely high-lying  $E_{\text{HOMO}}$  approaching  $-4.0$  eV, which acted as an n-type dopant.<sup>3</sup> In this study, to further enhance electron-donating ability, we introduced a *p*-quinodimethane structure in the center of **1** and **2**, and thus developed **3** and **4**, respectively, and investigated their electronic structures and functions as n-type dopants.

The quinoidal structures of **3** and **4** were confirmed by single-crystal X-ray analysis. Absorption maximums of **3** and **4** were red-shifted around 600 nm relative to those of **1** and **2** around 500 nm, indicating the quinoidal structures of **3** and **4** contributed to narrowing the gaps of  $E_{\text{HOMOS}}$  and  $E_{\text{LUMOS}}$ . The  $E_{\text{HOMOS}}$  estimated from cyclic voltammetry of **3** ( $-4.22$  eV) and **4** ( $-3.88$  eV) are higher than those of **1** ( $-4.50$  eV) and **2** ( $-4.08$  eV), respectively, whose trend agrees with those of theoretically estimated  $E_{\text{HOMOS}}$ . **3** and **4** acted as n-type dopants to poly(benzimidazobenzophenanthroline) (BBL), an n-type semiconducting polymer, and the electrical conductivities of BBL doped with **3** and **4** were higher by more than  $10^3$  and  $10^6$  times than that of BBL doped with **1**, respectively. These results indicated that quinoidal  $\pi$ -extension is an effective molecular design for super-electron-donating molecules with  $E_{\text{HOMOS}}$  higher than  $-4.0$  eV, which potentially act as n-type dopants.



- 1) T. Matsuo, K. Kawabata, and K. Takimiya, *Adv. Energy Sustainability Res.* **2021**, 2, 2100084.
- 2) T. Matsuo, K. Kawabata, and K. Takimiya, *Bull. Chem. Soc. Jpn.* **2022**, 95, 1047.
- 3) T. Matsuo, K. Kawabata, and K. Takimiya, *under revision*.

## Supramolecular Organization and Charge Carrier Transport of Organic Semiconductors Based on Chalcogen Interactions

(<sup>1</sup>Graduate School of Engineering, Kyushu University, <sup>2</sup>Institute for Advanced Study, Kyushu University) ○Yusei Tanaka,<sup>1</sup> Tatsuya Mori,<sup>1</sup> Yuka Kojiguchi,<sup>1</sup> Yu Seok Yang,<sup>1</sup> Takuma Yasuda<sup>1,2</sup>

**Keywords:** organic semiconductors; field-effect transistors; single crystals; chalcogen interactions; heteroacenes

Heteroatom-incorporated  $\pi$ -conjugated molecules, referred to as heteroacenes, have been actively elaborated for the application of organic field-effect transistors (OFETs). Chalcogens, 16 group elements, are the most important elements in the design of heteroacenes. In particular, sulfur-containing heteroacenes have been actively explored as high-performance OFET materials. Previously, we developed a sulfur containing organic semiconductor DTT-8.<sup>1</sup> This compound self-organized via supramolecular S $\cdots$ S interactions and exhibited excellent charge transport properties over  $10\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ .

In this study, we successfully developed a series of chalcogen-incorporated heteroacenes (Fig. 1a). We carried out systematic studies on the heavy chalcogen substitution from sulfur to selenium and tellurium. In particular, the substitution of heavier chalcogen atoms caused the interesting dual emission behavior consisting of fluorescence and phosphorescence. In addition, these molecules self-organized via supramolecular chalcogen interactions, providing effective intermolecular electronic coupling (Fig. 1b). Consequently, a high hole mobilities over 20 and  $1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  were obtained in the single-crystal OFETs of the sulfur- and tellurium-containing compounds, respectively (Fig. 1c). This study emphasizes the importance of our molecular design featuring supramolecular chalcogen interactions.

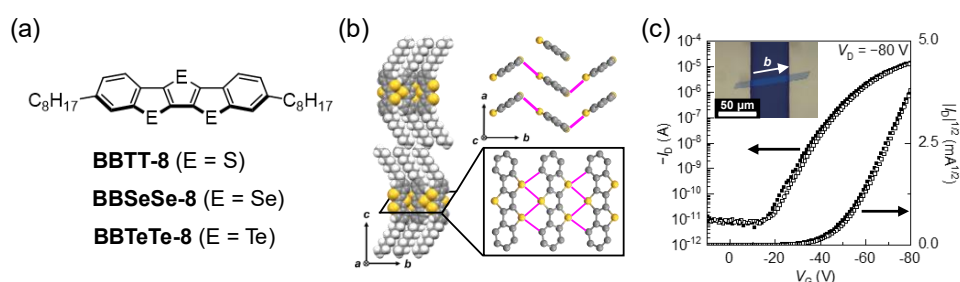


Fig.1 (a) Molecular structures of heteroacenes series developed in this study. (b) Crystal structures of BBTT-8. (c) Transfer characteristics of single crystal OFETs based on BBTT-8.

- 1) Y. S. Yang, T. Yasuda, H. Kakizoe, H. Mieno, H. Kino, Y. Tateyama, C. Adachi, *Chem. Commun.* **2013**, 49, 6483.

## Development of Photofunctional Boron Complexes Based on Partly Separated Frontier Orbitals of Nitrogen-Containing Aromatic Compounds

(Graduate School of Engineering, Kyoto University) ○ Shunichiro ITO, Hiromasa TAKAHASHI, Kazuo TANAKA

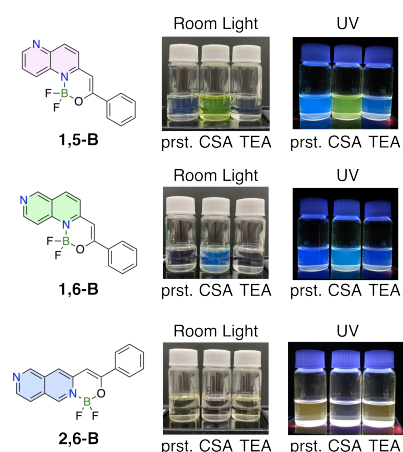
**Keywords:** Boron Complex; Near-Infrared Emission; Stimuli-Responsive Emission; Nitrogen-Containing Aromatics

Luminescent boron complexes have been studied because their fruitful photophysical properties, for instance, high photoluminescence quantum yields and high biocompatibility. Nitrogen-containing aromatic compounds, such as pyridine and quinoline, have enabled us to access their boron complexes with functional properties. However, there are limited examples of complexes with multiple nitrogen atoms in a single aromatic ring, *e.g.*, pyrazine, and naphthyridine. We have recently reported a series of pyrazine-based binuclear boron complexes exhibit near-infrared emission, which is useful for biological imaging. Their low-energy emission was achieved by the characteristic frontier orbital distribution of pyrazine, called partly separated frontier orbitals (PSFO), where the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are not overlapped at specific atoms. In the case of pyrazine, the nitrogen atoms contribute highly to its LUMO but hardly to its HOMO. Therefore, the boron complexation more efficiently lowers its LUMO, resulting in the small HOMO–LUMO gap.<sup>1</sup> Taking this finding into account, we envisioned that further functional luminophores could be developed by using PSFO of other heterocyclic aromatics.

Herein, we have synthesized naphthyridine-based boron complexes with various isomers of naphthyridines and evaluated their photophysical properties (Figure 1). As a result, it was revealed that only **2,6-B** exhibits the apparent intramolecular charge transfer property and that **1,5-B** and **2,6-B** show the drastically responsive emission toward acid addition. These properties would be derived from their PSFO, which is absent in **1,6-B**.

### Reference

1) Takahashi, H.; Watanabe, H.; Ito, S.; Tanaka, K.; Chujo, Y. *Chem. Asian J.* **2023**, *18*, e202300489.



**Figure 1.** Structures of synthesized complexes and photos of their solutions. (prst., pristine solution; CSA, after addition of (+)-10-comphorsulfonic acid; TEA, after neutralization by triethyl amine.)

アカデミックプログラム [B講演] | 11. 有機化学—構造有機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 E1121(11号館 [2階] 1121)

**[E1121-3pm] 11. 有機化学—構造有機化学**

座長：庄子 良晃、石垣 侑祐

## ◆ 英語

13:00 ~ 13:20

[E1121-3pm-01]

アミド埋込型 $\pi$ 共役系分子の機能開拓○森下 大輝<sup>1</sup>、伊藤 喜光<sup>1,2</sup> (1. 東大院工、2. JSTさきがけ)

## ◆ 英語

13:20 ~ 13:40

[E1121-3pm-02]

アセン類のL-regionをジフェニレン縮環によって $\pi$ 拡張した含七員環PAHの合成と物性○久田 雅人<sup>1</sup>、清水 大貴<sup>1</sup>、松田 建児<sup>1,2</sup> (1. 京大院工、2. 京大福井セ)

## ◆ 英語

13:40 ~ 14:00

[E1121-3pm-03]

チオフェン縮環ナノベルトの合成と性質

○周戸 大季<sup>1</sup>、Philipp Wiesener<sup>2</sup>、Elena Kolodzeiski<sup>2</sup>、水上 輝市<sup>3</sup>、Harry Mönig<sup>2</sup>、Saeed Amirjalayer<sup>2</sup>、Henning Klaasen<sup>2</sup>、Bart Jan Ravoo<sup>2</sup>、君塚 信夫<sup>3</sup>、八木 亜樹子<sup>1</sup>、伊丹 健一郎<sup>1</sup> (1. 名古屋大学、2. ミュンスター大学、3. 九州大学)

## ◆ 英語

14:00 ~ 14:20

[E1121-3pm-04]

ジチンビスキノジメタンの配座変化を鍵とするドミノ酸化還元反応の実証

○張本 尚<sup>1</sup>、田所 朋樹<sup>1</sup>、杉山 聡一郎<sup>1</sup>、鈴木 孝紀<sup>1</sup>、石垣 侑祐<sup>1</sup> (1. 北大院理)

14:20 ~ 14:30

休憩

## ◆ 英語

14:30 ~ 14:50

[E1121-3pm-05]

亜鉛を用いたカルボアニオン型環化反応による新規スピロ共役分子のダイバージェント合成

○福間 翔太<sup>1</sup>、Rui Shang<sup>1</sup>、中村 栄一<sup>1</sup> (1. 東京大学)

## ◆ 日本語

14:50 ~ 15:10

[E1121-3pm-06]

弓形構造を構成単位とするオリゴチオフェン2次元シートの光・電子物性と階層構造制御

○名倉 和彦<sup>1</sup>、町田 崇<sup>1</sup>、中西 尚志<sup>1</sup> (1. 物質・材料研究機構)

## ◆ 日本語

15:10 ~ 15:30

[E1121-3pm-07]

実在反芳香族分子の近接積層 $\pi$ 二量体に対する量子化学計算に基づくエネルギー分割解析

○杉森 亮太<sup>1</sup>、岸 亮平<sup>1,2,3,4</sup>、北河 康隆<sup>1,2,3,4,5</sup> (1. 阪大院基礎工、2. 阪大RCSEC、3. 阪大QIQB、4. 阪大ICS-OTRI、5. 阪大CSRN)

---

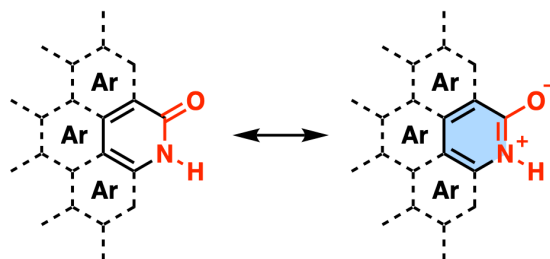


## Functional Exploration of Amide-Embedded $\pi$ -Conjugated Molecules

(<sup>1</sup>*Graduate School of Engineering The University of Tokyo*, <sup>2</sup>*PRESTO, JST*) ○Daiki Morishita,<sup>1</sup> Yoshimitsu Itoh<sup>1,2</sup>

**Keywords:**  $\pi$ -Conjugated System, Polycyclic Aromatic Hydrocarbons, Aromaticity, Amide

Amide ( $-\text{CO}-\text{NH}-$ ) has a double bonding character on the C–N bond due to its resonance structure.<sup>1,2</sup> However, no attempt has been made to utilize the electron delocalization through this C–N bond in functional  $\pi$ -systems. Here, we propose "amide-embedded  $\pi$ -conjugated molecules" in which some of the C=C bonds of a polycyclic aromatic hydrocarbon are replaced by amide C–N bonds.<sup>3</sup> Spectroscopic measurements and DFT calculations on these molecules have revealed that the C–N bond of the amide functions as part of the  $\pi$ -conjugated system. We further propose a new crystal engineering strategy that utilizes the hydrogen bonding of the amides embedded in the  $\pi$ -conjugated system.



- 1) L. Pauling *et al.*, *Proc. Natl. Acad. Sci. USA* **1951**, 37, 205–211.
- 2) R. B. Corey, L. Pauling, *Proc. R. Soc. Lond. B* **1953**, 141, 10–20.
- 3) D. Morishita, Y. Itoh, *submitted for publication*.

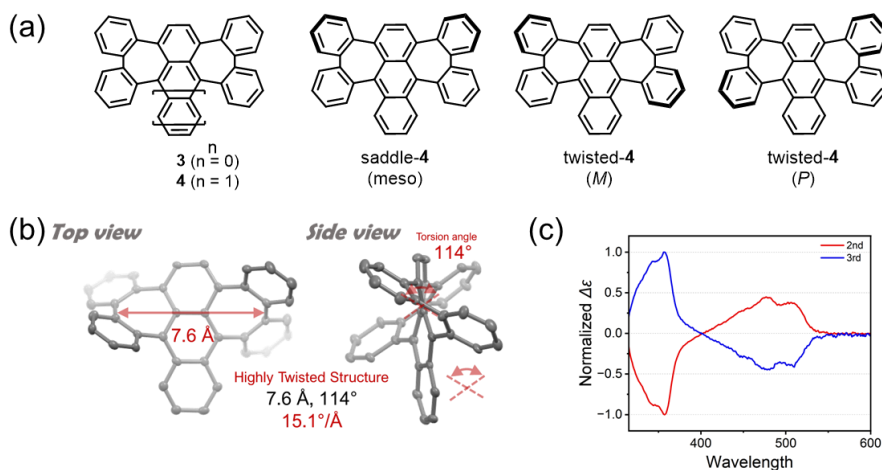
## Synthesis and Properties of Doubly *peri*-Diphenylene-fused Acene Derivatives

(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>Fukui Institute for Fundamental Chemistry, Kyoto University) Masato Hisada,<sup>1</sup> Daiki Shimizu,<sup>1</sup> Kenji Matsuda<sup>1, 2</sup>

**Keywords:** non-planar structure; seven-membered ring; twisted conformation; saddle conformation; chirality

One of the molecular design strategies for curved  $\pi$ -systems is to embed non-hexagonal rings into the structure.  $\pi$ -Extension at L-regions of  $\pi$ -systems with diphenylene introduces seven-membered rings and non-planarity to the  $\pi$ -systems. In this line, we have reported doubly diphenylene-fused pyrrolopyridazine **1** and tetraazaphthalene **2** with [7-6-7] successive ring-fused structures.<sup>1</sup> X-ray analysis revealed that **1** showed a saddle-like structure in the crystal, and **2** showed a twisted structure with a degree of twist of  $13.0^\circ/\text{\AA}$ . Despite the non-planar structure, compounds **1** and **2** showed effective  $\pi$ -conjugation over the molecule.

Herein, we synthesized doubly diphenylene-fused naphthalene **3** and anthracene **4** (Fig. 1a). X-ray analysis revealed a twisted structure of **4** with a degree of twist of  $15.1^\circ/\text{\AA}$  (Fig. 1b), which is one of the largest values for  $\pi$ -systems. In solution, however, **4** exists as an 18/41/41 mixture of one achiral conformer with a saddle-like structure (*meso*), and two twisted enantiomers (*P* and *M*), which were separated by chiral HPLC. The saddle-like conformer of **4** gradually underwent isomerization into the twisted conformer with a half-life of *ca.* 200 min. The CD spectra of the two enantiomers showed mirror images (Fig. 1c). The saddle and twisted conformers of **4** showed the lowest energy absorption bands at 500 nm and 520 nm in  $\text{CHCl}_3$ , respectively. Both conformers of **4** exhibited a fluorescence band at 550 nm in  $\text{CHCl}_3$ . The fluorescence quantum yield of the twisted conformer of **4** (0.62) was larger than that of the saddle conformer (0.49) due to the slower non-radiative decay in the twisted conformation.



**Fig. 1.** (a) Structures of **3** and **4**, (b) crystal structure of **4**, and (c) CD spectra of the enantiomers of **4**.

1. M. Hisada, D. Shimizu, K. Matsuda, *J. Org. Chem.* **2022**, *87*, 9034; *Org. Lett.* **2022**, *24*, 3707.

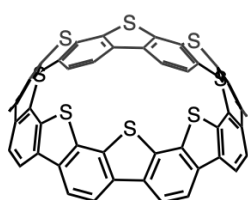
## Thiophene-fused aromatic belts

(<sup>1</sup>Graduate School of Science, Nagoya University, <sup>2</sup>Institute of Physics, University of Münster, <sup>3</sup>Institute of Solid State Theory, <sup>4</sup>Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, <sup>5</sup>Institute of Organic Chemistry, University of Münster, University of Münster, <sup>6</sup>Institute of Transformative Bio-Molecules (WPI-ITbM))

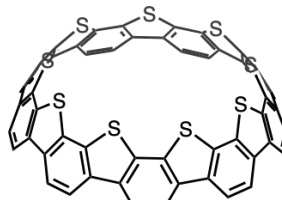
○Hiroki Shudo,<sup>1</sup> Philipp Wiesener,<sup>2</sup> Elena Kolodzeiski,<sup>3</sup> Kiichi Mizukami,<sup>4</sup> Harry Mönig,<sup>2</sup> Saeed Amirjalayer,<sup>3</sup> Henning Klaasen,<sup>5</sup> Bart Jan Ravoo,<sup>5</sup> Nobuo Kimizuka,<sup>4</sup> Akiko Yagi,<sup>1,6</sup> Kenichiro Itami<sup>1,6</sup>

**Keywords:** Nanobelts; Cycloparaphenylenes; Fused thiophene; S<sub>N</sub>Ar reaction

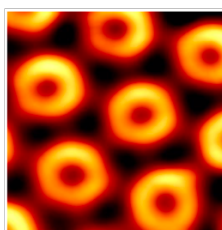
Thiophene-containing compounds play a central role in chemistry as the basic backbone of p-type organic semiconductors, molecular conductors, and light-emitting materials. Aromatic belts, on the other hand, have been actively synthesized as structurally attractive compounds. However, there are still many kinds of nanobelts that have not been synthesized such as cyclophenacenes. Herein we report the one-step synthesis of thiophene-fused aromatic belts (thiophene belts) from partially fluorinated CPPs.<sup>1</sup> The thiophene belts have structural features representing a fusion of cyclothiophene and cycloparaphenylene. By looking from another angle, thiophene belt is isoelectronic with cyclophenacene. Their unique structures and properties were uncovered by X-ray crystallography and photophysical measurement. Furthermore, STM measurements of the thiophene belts showed 2D-layer assembly of the molecules on metal surfaces.



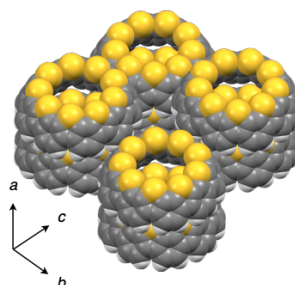
[8]thiophene belt



[9]thiophene belt



STM image



packing structure

1) Shudo, H.; Kuwayama, M.; Segawa, Y.; Yagi, A.; Itami, K. *Chem. Commun.* **2023**, 59, 13494–13497.

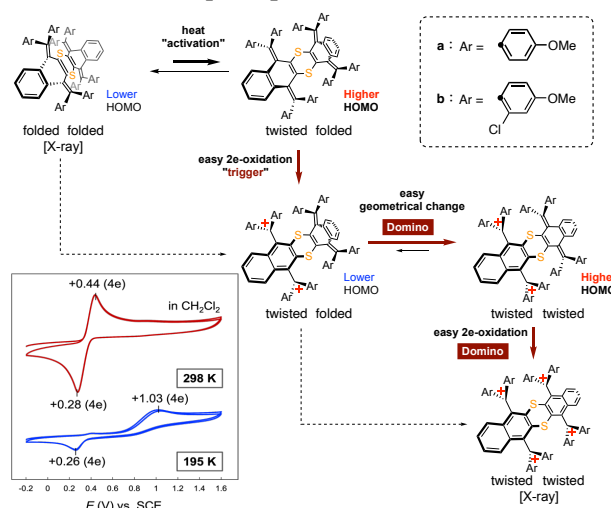
## Domino-Redox Reaction Induced by a Conformational Change of Dithiin-Bisquinodimethane

(<sup>1</sup>*Faculty of Science, Hokkaido University*) ○Takashi Harimoto,<sup>1</sup> Tomoki Tadokoro,<sup>1</sup> Soichiro Sugiyama,<sup>1</sup> Takanori Suzuki,<sup>1</sup> Yusuke Ishigaki<sup>1</sup>

**Keywords:** Domino-Redox Reaction, Quinodimethane, Cyclic Voltammetry, Cation

Domino reactions are intramolecular reactions in which a single event triggers the conversion of a starting material to a product, which then provides a substrate for the next reaction until a stable final product is obtained. They have contributed greatly to green chemistry such as by improving the reaction efficiency and simplifying the workup process, thanks to the generation of multiple bonds in a single step. However, it is difficult to apply the concept of domino reactions to redox reactions due to electrostatic reasons, since in general, an electron transfer reaction produces a positively or negatively charged species. As a result, the oxidation/reduction reaction proceeds in a stepwise manner with an anodic/cathodic shift of the electric potential for the subsequent process.

Herein, we newly designed and synthesized dithiin-bisquinodimethane (SS-BQD) derivatives **1**, in which the redox-active QD units are connected by a nonplanar dithiin skeleton, which allows steric repulsion and/or electronic interaction between electrophores for specific conformers, such as folded (**F**) and twisted (**T**) forms with different electronic structures. We envisaged that the flexibility of the dithiin backbone and the change in electronic structures could be utilized to precisely control the redox behavior. Indeed, variable temperature (VT)-electrochemical and VT-<sup>1</sup>H NMR measurements showed



**Figure** SS-BQD **1a** induces domino-redox reaction, unlike *ortho*-substituted SS-BQD **1b**.

that SS-BQD **1a** undergoes a smooth change in conformation, and thus the metastable **T-F** conformer can be partially generated with an increase in temperature (activation), which undergoes facile apparent 2e-transfer (trigger). In the resulting dication **1a**<sup>2+</sup>, the steric repulsion and interelectrophore interaction cause a facile change in structure from the as-generated **T**<sup>2+</sup>-**F** conformer to the **T**<sup>2+</sup>-**T** conformer (domino), which facilitates the subsequent oxidation (domino) to **1a**<sup>4+</sup> of the **T**<sup>2+</sup>-**T**<sup>2+</sup> conformer (Fig.). This is the first successful demonstration of the domino-redox reaction of multi-redox systems consisting of the same kind of electrophores based on a change in the HOMO level due to a drastic change in the molecular conformation.<sup>1</sup>

1) T. Harimoto, T. Tadokoro, S. Sugiyama, T. Suzuki, Y. Ishigaki, *Angew. Chem. Int. Ed.* **2024**, 63, e202316753.

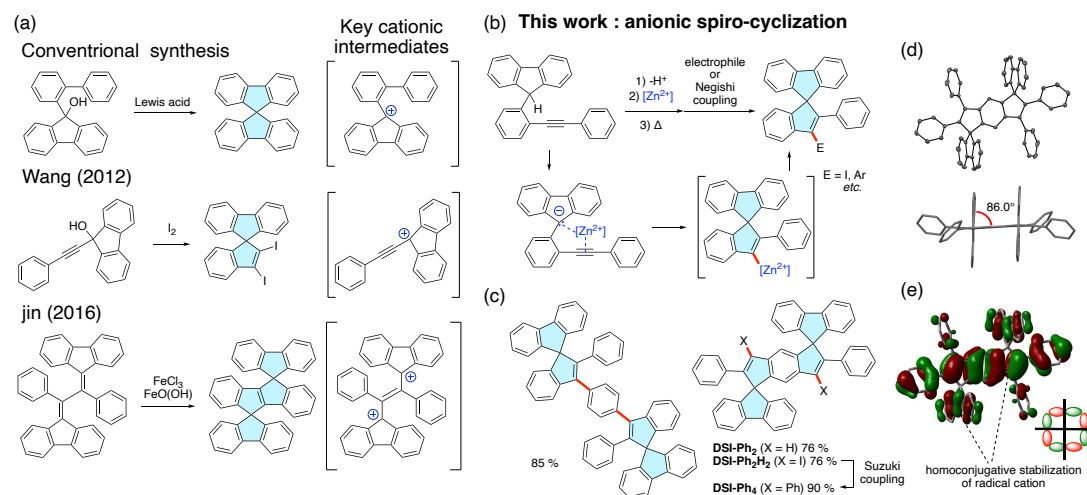
## Zn-Mediated Anionic Cyclization for Divergent Synthesis of Spiro-Conjugated Molecules

(<sup>1</sup>Graduate School of Science, Department of Chemistry, The University of Tokyo)

○Shota Fukuma<sup>1</sup>, Rui Shang<sup>1</sup>, Eiichi Nakamura<sup>1</sup>

**Keywords:** Spiro Conjugation; Organic Electronics; Cyclization Reaction

Spiro conjugated organic semiconductors have been attracting considerable attention in the field of organic optoelectronics due to their high solution processability and radical stabilization effect, which facilitates the printable formation of high-performance charge transporting layers in electronic devices.<sup>1</sup> However, current synthesis of spiro conjugated molecules heavily relies on carbocation cyclization<sup>2,3</sup>, thereby limiting the molecular design and derivatization pathways. We herein report a Zn-mediated anionic 5-*endo-dig* spiro-cyclization method, applicable to the formation and one-pot derivatization of various spiro  $\pi$  molecules. This reaction allows for the divergent synthesis of new organic semiconductors with either p-type or n-type character based on a spiro-indene or dispiro-s-dihydroindacene (DSI) backbone. The newly developed multiply spiro-conjugated molecules have high solubility and large radical stabilization effect, attributed to the orthogonal alignment of  $\pi$  planes, as confirmed by experimental and computational studies. These findings suggest that the newly developed compounds hold great promise as materials for printable electronics.



**Figures.** (a) Previously reported spiro-cyclization reactions. (b) Anionic 5-*endo-dig* spiro cyclization. (c) Example of compounds synthesized in this work. (d) Crystal structure of DSI-Ph<sub>4</sub>. (e) Calculated SOMO orbital of DSI-Ph<sub>4</sub> radical cation.

1) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011–1055. 2) Zhou, C.; Chen, X.; Lu, P.; Wang, Y. *Tetrahedron* **2012**, *68*, 2844–2850. 3) Zhao, J.; Xu, Z.; Oniwa, K.; Asao, N.; Yamamoto, Y.; Jin, T. *Angew. Chem., Int. Ed.* **2016**, *55*, 259–263.

## 弓形構造を構成単位とするオリゴチオフエン 2 次元シートの光・電子物性と階層構造制御

(物質・材料研究機構<sup>1</sup>) ○名倉 和彦<sup>1</sup>・町田 崇<sup>1</sup>・中西 尚志<sup>1</sup>

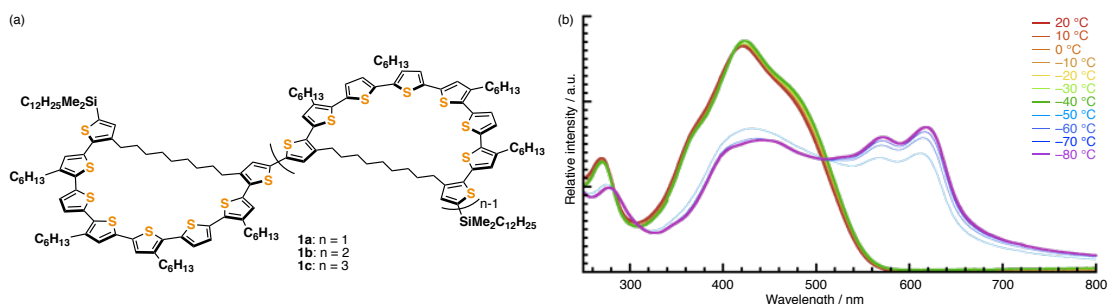
Optoelectronic Properties and Hierarchical Structure Control of 2D Oligothiophene Sheets based on Bow-shaped Building Unit (<sup>1</sup>*National Institute for Materials Science*) ○Kazuhiko Nagura,<sup>1</sup> Takashi Machida,<sup>1</sup> Takashi Nakanishi<sup>1</sup>

Hierarchical structure control of 1D  $\pi$ -conjugated oligomers and polymers is essential to achieve unique optoelectronic properties and high conductivity. Therefore, the development of molecular design that enables extended  $\pi$ -conjugation and stacked structures with extensive overlap is one of the challenging issues in the field of  $\pi$ -conjugated materials. Herein, we designed and synthesized a series of 2D sheet-like folded oligothiophenes based on a bow-shaped building unit. We revealed that the formation of a 2D sheet structure led to extended effective conjugation length and aggregation formation with significant spectral changes.

**Keywords :** Oligothiophene, 2D Sheet, Hierarchical Structure, Effective Conjugation Length

1次元 $\pi$ 共役オリゴマーやポリマーの階層構造の精密制御は、特異な光・電子物性や導電性の発現において必要不可欠である<sup>1)</sup>。そのため、 $\pi$ 共役を効果的に拡張し、積層させる分子設計の確立は重要な課題である。

今回、 $\pi$ 共役鎖がフォールドした2次元シート状オリゴチオフエン**1**を設計、合成した(Figure 1a)。弓形二次構造をもつオクチチオフエン誘導体の酸化的ホモカップリングおよびC-Hアリール化により単分散なオリゴマー**1b-c**を得た。得られたオリゴマー**1**は、2次元シート状構造の長軸および短軸に対応する遷移双極子モーメントをもつ電子遷移や高い酸化電位を示した。これらはチオフエン23量体に相当する有効共役長をもち、高度に拡張した $\pi$ 共役をもつことを明らかにした。また、オリゴマー**1b-c**が、低温の希薄溶液や薄膜状態において顕著な吸収スペクトルの長波長シフトを伴う会合体を形成することを見出した(Figure 1b)。



**Figure 1.** (a) Molecular structure of sheet-shaped oligothiophenes **1a-c**, and (b) temperature-dependent absorption spectra of **1b** in  $CH_2Cl_2$ .

1) L. Zhang, N. S. Colella, F. Liu, S. Trahan, J. K. Baral, H. H. Winter, S. C. B. Mannsfeld, A. L. Briseno, *J. Am. Chem. Soc.* **2013**, *135*, 844.



## 実在反芳香族分子の近接積層 $\pi$ 二量体に対する量子化学計算に基づくエネルギー分割解析

(阪大院基礎工<sup>1</sup>・阪大 RCSEC<sup>2</sup>・阪大 QIQB<sup>3</sup>・阪大 ICS-OTRI<sup>4</sup>・阪大 SRN-OTRI<sup>5</sup>)  
 ○杉森亮太<sup>1</sup>・岸亮平<sup>1,2,3,4</sup>・北河康隆<sup>1,2,3,4,5</sup>

Theoretical study on relationship between open-shell character and intermolecular interaction energy in closely- $\pi$ -stacked aggregates composed of antiaromatic molecules

(<sup>1</sup>Graduate School of Engineering Science, Osaka University, <sup>2</sup>RCSEC, Osaka University, <sup>3</sup>QIQB, Osaka University, <sup>4</sup>ICS-OTRI, Osaka University, <sup>5</sup>SRN-OTRI, Osaka University)  
 ○Ryota Sugimori<sup>1</sup>, Ryohei Kishi<sup>1,2,3,4</sup>, Yasutaka Kitagawa<sup>1,2,3,4,5</sup>

Several antiaromatic systems have been reported to exhibit closely  $\pi$ -stacked structures. These molecular systems are expected to be candidates for novel functional materials from the viewpoints of the possibility of utilizing intermolecular conjugation and excellent external-field-induced response properties. This study focused on realistic, closely  $\pi$ -stacked antiaromatic molecular aggregates systems and investigated their intermolecular interaction energies and energy partitioning analysis by high-precision quantum chemical calculations. Based on the results, we discuss the mechanism of energy stabilization in the  $\pi$ -stacked antiaromatic molecular aggregates.

**Keyword:**  $\pi$ -stacked aromaticity, antiaromatic molecules, intermolecular interaction, quantum chemical calculation.

$4n$  個の  $\pi$  電子をもつ環状  $\pi$  共役分子である反芳香族分子は、小さな HOMO-LUMO gap ( $\Delta_{hl}$ ) を有する比較的不安定な系として知られている。摂動論に基づけば、この小さな  $\Delta_{hl}$  は、優れた応答物性や特異な分子集合構造の形成の起源としても期待される。後者に関しては、小さな  $\Delta_{hl}$  により分子間に大きな軌道相互作用が生じることで、近接した対面  $\pi$  積層構造の実現可能性が指摘されており[1]、集合系の安定化機構や分子間の非局在化による電子、光学物性の向上など、分子材料の新規機能発現・制御機構として期待されている。実験的には、反芳香族ポルフィリン分子である  $\text{Ni}^{\text{II}}$ -ノルコロール分子が近接した分子配置に伴う構造や物性変化が報告されたが[2]、その実現例は多くない。反芳香族分子の近接  $\pi$  積層による安定化機構が十分に明らかになっていないことも一つの要因と考えられる。

本研究では、忍久保らにより最近合成が報告されたアルキル鎖で繋がれた  $\text{Ni}^{\text{II}}$ -ノルコロール二量体に着目した(Fig. 1)。近接した対面積層型の二量体構造を示すこの系における分子間相互作用エネルギーの分割解析を高精度量子化学計算により検討し、(1)系全体の安定化に対する  $\text{Ni}^{\text{II}}$ -ノルコロール主骨格部分の分子間軌道相互作用による寄与の定量化、(2)置換基部分由来の相互作用による安定化の定量化とその役割の解明、の2点を議論した。得られた結果をもとに、実在反芳香族分子の近接安定化の機構を議論し、一般的な設計指針の構築に役立つ因子の抽出を試みた。

[1] C. Corminboeuf et al., *Org. Lett.*, **9**, 3263 (2007). [2] R. Nozawa et al., *Nat. Commun.*, **7**, 13620 (2016); *Nat. Commun.*, **10**, 3576 (2019); H. Kawashima et al., *J. Am. Chem. Soc.*, **143**, 10676 (2021).

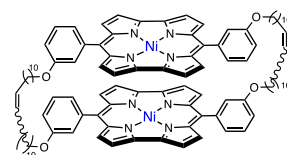


Fig. 1 Structures of Norcorrole dimer tethered with two flexible alkyl chains

アカデミックプログラム [B 講演] | 11. 有機化学—構造有機化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:00 会場 E1122(11号館 [2階] 1122)

**[E1122-3pm] 11. 有機化学—構造有機化学**

座長：長谷川 真士、八木 亜樹子

## ◆ 英語

13:00 ~ 13:20

[E1122-3pm-01]

ヘテロ原子を導入した混み合った $\pi$ 共役アルケンのメカノクロミズム特性○山田 航平<sup>1</sup>、安達 洋平<sup>1</sup>、大下 浄治<sup>1</sup> (1. 広島大)

## ◆ 日本語

13:20 ~ 13:40

[E1122-3pm-02]

赤色・近赤外領域で強発光特性を示すアルミニウム二核三重螺旋錯体の合成

○小西 悠斗<sup>1</sup>、星野 友<sup>1,2</sup>、小野 利和<sup>1,2</sup> (1. 九大院工、2. 九大CMS)

## ◆ 日本語

13:40 ~ 14:00

[E1122-3pm-03]

ヒドリンダセン骨格を含む水溶性シクロパラフェニレン：水中でのアクリジニウム塩の包接と可視光フォトレドックス触媒への展開

○土戸 良高<sup>1</sup>、森戸 良<sup>1</sup>、小坂田 耕太郎<sup>2</sup>、井手 智仁<sup>3</sup>、河合 英敏<sup>1</sup> (1. 東理大理、2. 東工大化生研、3. 東京高専物質工)

## ◆ 英語

14:00 ~ 14:20

[E1122-3pm-04]

末端 $\pi$ 拡張型[7]ヘリセン誘導体の非線形分子ばね特性○胡 維哲<sup>1</sup>、村田 靖次郎<sup>1</sup>、廣瀬 崇至<sup>1</sup> (1. 京都大学化学研究所)

## ◆ 日本語

14:20 ~ 14:40

[E1122-3pm-05]

1,1'-ビアズレン骨格で構成される不斉ヘリセン化合物とそのカチオンラジカルの構造と性質

青山 大樹<sup>1</sup>、成田 昌弘<sup>1</sup>、五島 健太<sup>1</sup>、村藤 俊宏<sup>2</sup>、井川 和宣<sup>3</sup>、河崎 悠也<sup>1</sup>、友岡 克彦<sup>1</sup>、○谷 文都<sup>1</sup> (1. 九州大学、2. 山口大学大学院、3. 熊本大学大学院)

## ◆ 英語

14:40 ~ 15:00

[E1122-3pm-06]

末端2,1,3-チアジアゾール基を持つヘテロ[n]ヘリセンのホモキラル結晶におけるらせん状カラム配列

○張 政<sup>1</sup>、村田 靖次郎<sup>1</sup>、廣瀬 崇至<sup>1</sup> (1. 京都大学化学研究所)



## Mechanochromism of overcrowded bistricyclic aromatic ene with various heteroatoms

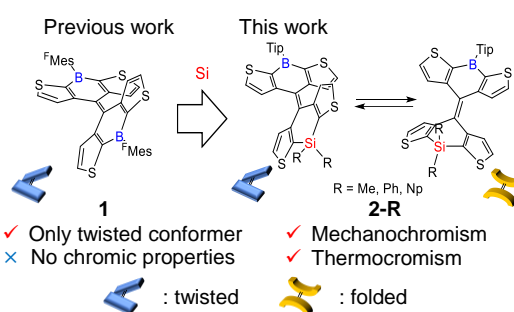
(<sup>1</sup> Smart Innovation Program, Graduate School of Advanced Science and Engineering, Hiroshima University) ○Kohei Yamada,<sup>1</sup> Yohei Adachi,<sup>1</sup> Joji Ohshita<sup>1</sup>

**Keywords:** boron; overcrowded alkene; conformational isomer; chromic properties

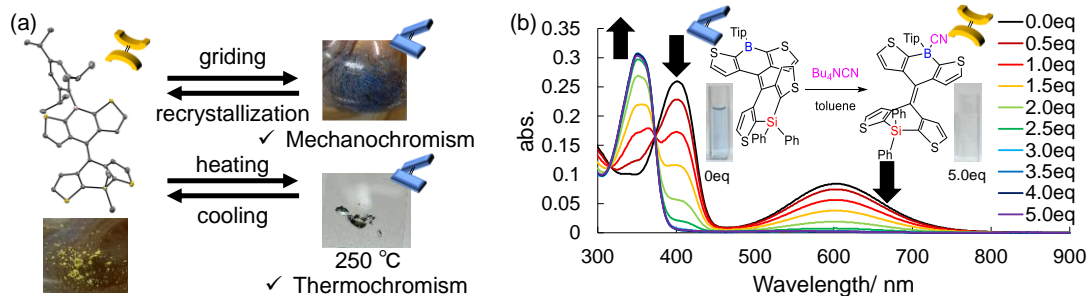
Overcrowded bistricyclic aromatic enes (BAEs) are compounds consisting of two tricyclic structures linked by a C=C double bond, and have a variety of conformers such as twisted and folded conformers due to the steric hindrance in the *fold* regions. Since these isomers have different absorption bands in the visible region, BAEs have been studied for use in stimuli-responsive materials.

We previously reported a boron-containing BAE (**1**), which existed dominantly in a twisted conformer because the tricyclic structures were very rigid due to the presence of sp<sup>2</sup> boron atoms, resulting in the no chromic properties.<sup>1</sup> In this work, assuming that the energy difference between the isomers can be reduced by making the tricyclic structure flexible, we synthesized **2-Me**, **2-Ph**, and **2-Np** with a silicon atom in **1** (Figure 1). The

solution of **2-Me** was blueish in solution, however, the recrystallized solids of **2-Me** were yellowish (Figure 2a). The crystal structure showed a folded conformer, and when the crystals were ground or heated, they changed from yellowish to blueish and were found to have chromic properties. This result may be due to the small energy difference between isomers as expected. Titration experiments were then performed (Figure 2b). With the addition of Bu<sub>4</sub>NCN into the solution, the long wavelength absorption band gradually decreased, and a new absorption band appeared at the short wavelengths, suggesting that the folded conformer became dominant in the presence of cyanide. This is the first example of chemochromism of BAEs toward Lewis bases, indicating the potential application of heteroatom containing BAEs for sensor materials.



**Figure 1** Structure of boron-containing BAEs.



**Figure 2** (a) Single-crystal X-ray structure and chromic properties of **2-Me**. (b) Absorption data for titrations of **2-Ph** with Bu<sub>4</sub>NCN aliquots in toluene.

1) Y. Adachi, T. Nomura, S. Tazuhara, H. Naito and J. Ohshita, *Chem. Commun.* **2021**, 57, 1316.

## 赤色・近赤外領域で強発光特性を示すアルミニウム二核三重螺旋錯体の合成

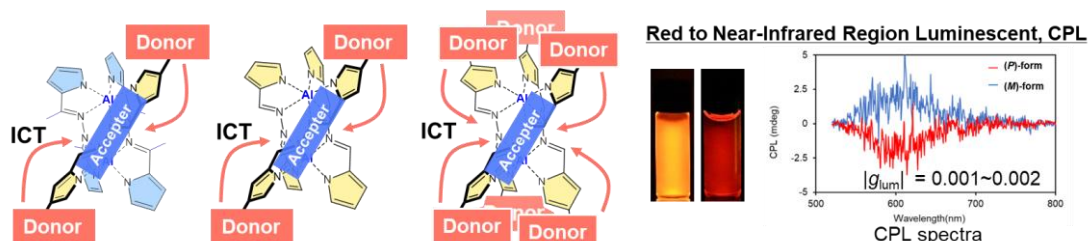
(九大院工<sup>1</sup>・九大CMS<sup>2</sup>) ○小西 悠斗<sup>1</sup>・星野 友<sup>1,2</sup>・小野 利和<sup>1,2</sup>

Synthesis of Aluminum-based Dinuclear Triple-Stranded Helicates Exhibiting Strong Luminescence in the Red to Near-Infrared Regions (<sup>1</sup> Graduate school of Engineering, Kyushu University, <sup>2</sup> Center for Molecular Systems (CMS), Kyushu University) ○Yuto Konishi,<sup>1</sup> Yu Hoshino,<sup>1</sup> Toshikazu Ono,<sup>1,2</sup>

Functional dyes that exhibit absorption and emission in the red to near-infrared (NIR) regions are expected to be used as bioimaging and security inks. Moreover, circularly polarized luminescence (CPL) materials have potential to apply advanced optical materials and chiral environmental imaging. We recently reported aluminum-based dinuclear triple-stranded helicates (ALPHY) and found that these showed blue, yellow and orange CPL with large Stokes shifts.<sup>1)</sup> In this study, by modification of the ALPHY complexes with various substituents, a series of helicates that exhibit red-to-NIR emission with large Stokes shift by intramolecular charge transfer and excited-state dynamic structural change, CPL properties in the red to NIR regions were also observed. In this presentation, we will present the details of the emission mechanism based on the results of computational chemistry.

**Keywords :** Red to Near-Infrared Region Luminescent, Multinuclear metal complex, Aluminum complexes, Helicate, Circularly polarized luminescence

赤色・近赤外領域において光吸収、発光特性を示す機能性色素は、バイオイメージングやセキュリティインクへの応用が期待されている。また、円偏光発光 (CPL) を示す機能性色素はキラル環境イメージングへの応用も期待される。近年、我々はシッフ塩基配位子とアルミニウムとの錯形成による二核三重螺旋錯体 (ALPHY) を報告し、らせん不斉による青・黄・橙の CPL 材料として機能することを見出した<sup>1)</sup>。本研究では ALPHY に着目し、置換基修飾に伴う分子内電荷移動と励起状態構造緩和と由来する大きなストークスシフトと赤色・近赤外発光、らせん不斉に由来する CPL 特性を示す材料創製を行った。本発表では計算化学の結果を踏まえた発光メカニズムと、量子収率向上に関するアプローチについても詳細に議論する。



### Acknowledgement

This study is supported by MEXT Program: Data Creation and Utilization-Type Material Research and Development Project Grant Number JPMXP1122714694.

1) T. Ono et. al., *Angew. Chem. Int. Ed.* **2021**, 60, 2614–2618.

## ヒドリンダセン骨格を含む水溶性シクロパラフェニレン:水中でのアクリジニウム塩の包接と可視光フォトレドックス触媒への展開

(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>, 森戸良<sup>1</sup>, 小坂田耕太郎<sup>2</sup>, 井手智仁<sup>3</sup>, 河合 英敏<sup>1</sup>

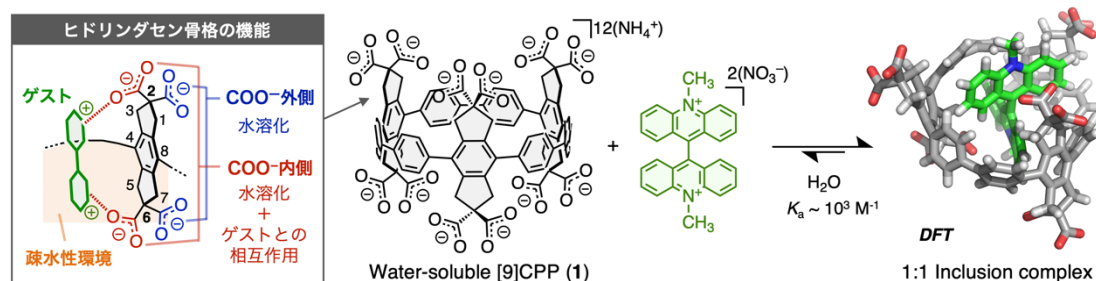
A Water-Soluble Cycloparaphenylene Containing Hydrindacene Units: Encapsulation of Acridinium Salts in Water and Its Application to Visible-Light Photoredox Catalyst (<sup>1</sup>Tokyo Univ. of Sci., <sup>2</sup>Tokyo Inst. of Tech., <sup>3</sup>Natl. Inst. of Tech., Tokyo Col.) ○Yoshitaka Tsuchido<sup>1</sup>, Ryo Morito<sup>1</sup>, Kohtaro Osakada<sup>2</sup>, Tomohito Ide<sup>3</sup>, Hidetoshi Kawai<sup>1</sup>

We have synthesized a [9]cycloparaphenylene (CPP) derivative (**1**) containing three hydrindacene (1,2,3,5,6,7-hexahydro-*s*-indacene) units with four carboxylates at the 2,6-positions *via* a macrocyclic gold complex. This macrocyclic compound (**1**) exhibits remarkable water solubility and encapsulates a bisacridinium salt in water. Theoretical calculations of the host-guest complex revealed HOMO localized on the CPP and LUMO localized on the guest molecule. A mixture of **1** and bisacridinium salt promoted oxidative dimerization of 4-methoxybenzylamine to the corresponding imines upon blue LED irradiation in water under aerobic condition.

**Keywords** : Cycloparaphenylene, Water soluble, Host-guest chemistry, photocatalyst.

本研究では、大環状金錯体を経由する CPP 合成法<sup>[1]</sup>を利用し、4つのカルボキシレートを含むヒドリンダセン (1,2,3,5,6,7-ヘキサヒドロ-*s*-インダセン) 骨格が3ユニット組み込まれた[9]CPP誘導体 (**1**)を合成した。化合物**1**は9枚のベンゼン環を主骨格とした剛直な有機分子であるにもかかわらず、高密度に導入された極性基によって著しく高い水溶性 (約 25 g L<sup>-1</sup>) を示し、さらに水中で強い青色蛍光を呈した。

化合物**1**と種々のゲスト分子との水中での会合を評価したところ、ビスアクリジニウム塩などの電子アクセプター性のゲスト分子を内包し、CPP側にHOMO、ゲスト側にLUMOが局在化したホストゲスト会合体を形成することが明らかとなった<sup>[2]</sup>。触媒量の化合物**1**とビスアクリジニウム塩の存在下、水中、青色LED照射下において4-メトキシベンジルアミンの酸化的二量化が進行し、イミンが生成した。



1) Y. Tsuchido, R. Abe, T. Ide, K. Osakada *Angew. Chem. Int. Ed.* **2020**, 59, 22928. 2) R. Morito, T. Kataoka, K. Saito, K. Osakada, T. Ide, Y. Tsuchido, H. Kawai, *Submitted*.

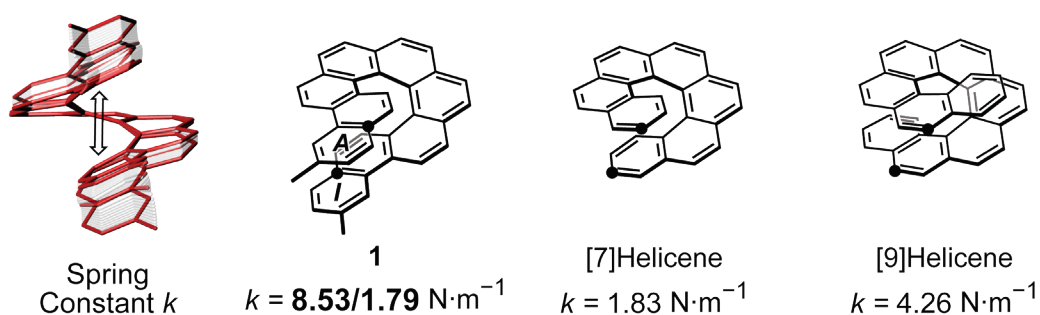
## Non-linear Molecular Spring Properties of a Laterally $\pi$ -Extended [7]Helicene Derivative

(<sup>1</sup>Institute for Chemical Research, Kyoto University, <sup>2</sup>PRESTO, Japan Science and Technology Agency) ○Weizhe Hu,<sup>1</sup> Yasujiro Murata,<sup>1</sup> Takashi Hirose<sup>1,2</sup>

**Keywords:** Helicenes; Molecular Springs; Non-Covalent Interactions; Polymorphism

Helically twisted  $\pi$ -conjugated molecules, i.e., carbohelicenes, have potential applications as molecular springs in terms of their helical ladder geometries.<sup>1–3</sup> In this work, a laterally  $\pi$ -extended [7]helicene derivative **1** was synthesized to investigate the effect of  $\pi$ -extension on molecular spring properties (Figure 1).

After synthesis and separation of enantiomers, i.e., (*P*)-**1** and (*M*)-**1**, two polymorphs were obtained as homochiral single crystals. In one polymorph (Polymorph A), an elongated molecular geometry was observed, while in the other polymorph (Polymorph B), a contracted geometries was observed. The dihedral angle between the terminal rings A and I was determined as  $\theta_{AI} = 37.2^\circ$  for Polymorph A and  $\theta_{AI} = 0.2^\circ$  for Polymorph B, respectively, suggesting a flexible spring-like mechanical properties. Non-covalent Interaction (NCI) calculations of crystal geometries suggested a significant inter- and intra-molecular  $\pi$ – $\pi$  interaction between terminal rings A and I in the Polymorph A and B, respectively. The energy changes during spring-like structural deformations were investigated by theoretical calculations at the B3LYP-GD3BJ/6-311G(2d,p) level, showing a non-linear stress-strain curve with a two-step spring constant ( $k = 8.53/1.79 \text{ N}\cdot\text{m}^{-1}$ ) for **1**, which is in sharp contrast to that of [7]helicene and [9]helicene with single molecular spring constant ( $k = 1.83 \text{ N}\cdot\text{m}^{-1}$  and  $4.86 \text{ N}\cdot\text{m}^{-1}$ , respectively). The emergence of the non-linear stress-strain curve for **1** is likely attributed to the intramolecular  $\pi$ – $\pi$  interactions at the laterally  $\pi$ -extended aromatic rings.



**Figure 1.** Molecular spring properties of **1**, [7]helicene, and [9]helicene. The helical structures were stretched by increasing the distance between the two carbon atoms highlighted by black circle.

1) P. Karak, J. Choudhury, *Chem. Sci.* **2022**, *13*, 11163. 2) Y. Nakakuki, T. Hirose, K. Matsuda, *J. Am. Chem. Soc.* **2018**, *140*, 15461. 3) Y. Nakahara, M. Higashi, R. Funayama, Y. Horii, H. Osuga, H. Sakamoto, M. Oda, S. Kado, K. Kimura, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 544.

## 1,1'-ビアズレン骨格で構成される不斉ヘリセン化合物とそのカチオンラジカルの構造と性質

(九州大<sup>1</sup>・山口大<sup>2</sup>・熊本大<sup>2</sup>) 青山 大樹<sup>1</sup>・成田 昌弘<sup>1</sup>・五島 健太<sup>1</sup>・村藤 俊宏<sup>2</sup>・井川 和宣<sup>3</sup>・河崎 悠也<sup>1</sup>・友岡 克彦<sup>1</sup>・○谷 文都<sup>1</sup>

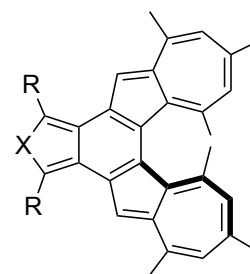
Structures and properties of 1,1'-biazulene-based chiral helicene compounds and their cation radicals (<sup>1</sup>Kyushu University, <sup>2</sup>Yamaguchi University, <sup>3</sup>Kumamoto University) Hiroki Aoyama,<sup>1</sup> Masahiro Narita,<sup>1</sup> Kenta Goto,<sup>1</sup> Toshihiro Murafuji,<sup>2</sup> Kazunobu Igawa,<sup>3</sup> Yuuya Kawasaki,<sup>1</sup> Katsuhiko Tomooka,<sup>1</sup> ○Fumito Tani<sup>1</sup>

Chiral helicene radicals are of interest as chemical species that possess both chirality and unpaired electron spin(s).<sup>1</sup> However, there have been very few examples of stable helicene radicals. On the other hand, 1,1'-biazulene is known to produce a relatively stable cation radical. Therefore, we have designed and synthesized a helicene compound, **AIBTh** (bisazuleno-isobenzothiophene, Figure 1) that contains a 1,1'-biazulene skeleton. Its stable cation radical was isolated and analyzed by X-ray crystallography.<sup>2</sup> We have further prepared a new pyrrole-based helicene having sterically protecting mesityl groups on its alpha positions. The new compound, called **AIBPyr** (bisazulenoisobenzopyrrole, Figure 1), gave also stable cation radical.

**Keywords** : helicene; azulene; chiral; cation radical; oxidation

光学活性ヘリセンは芳香環が縮環してらせん構造を形成している化合物であり、その不斉を活かした機能性材料としての応用が期待されている。特に、ヘリセンラジカルは、キラリティーと不対電子スピンの両方を持つ化学種として注目されているが<sup>1</sup>、安定なヘリセンラジカルの例は極めて限られている。一方、ナフタレンの構造異性体であるアズレンは分極したπ電子系に由来した特徴的な性質を有し、アズレン2分子からなる1,1'-ビアズレンは比較的安定なカチオンラジカルを生成することが知られている。そこで我々は、1,1'-ビアズレン骨格から構成されるヘリセン化合物

**AIBTh** (bisazuleno-isobenzothiophene, Figure 1) を設計・合成した。その安定なカチオンラジカルを単離し、X線結晶構造解析をおこなった<sup>2</sup>。さらに、ピロールのα位に立体保護のためにメシチル基を導入した新しいヘリセンを合成し、**AIBPyr** (bisazulenoisobenzopyrrole, Figure 1) と名付けた。この新しいヘリセン化合物も安定なカチオンラジカルを与えた。



**AIBTh** : X = S, R = Bu

**AIBPyr** : X = NH, R = mesityl

Figure 1. Azulene-based helicenes

1) F. Tani, M. Narita, T. Murafuji, *ChemPlusChem*, **2020**, 85, 2093-2104.

2) M. Narita, T. Teraoka, T. Murafuji, Y. Shiota, K. Yoshizawa, S. Mori, H. Uno, S. Kanegawa, O. Sato, K. Goto, F. Tani, *Bull. Chem. Soc. Jpn.*, **2019**, 92, 1867-1873.

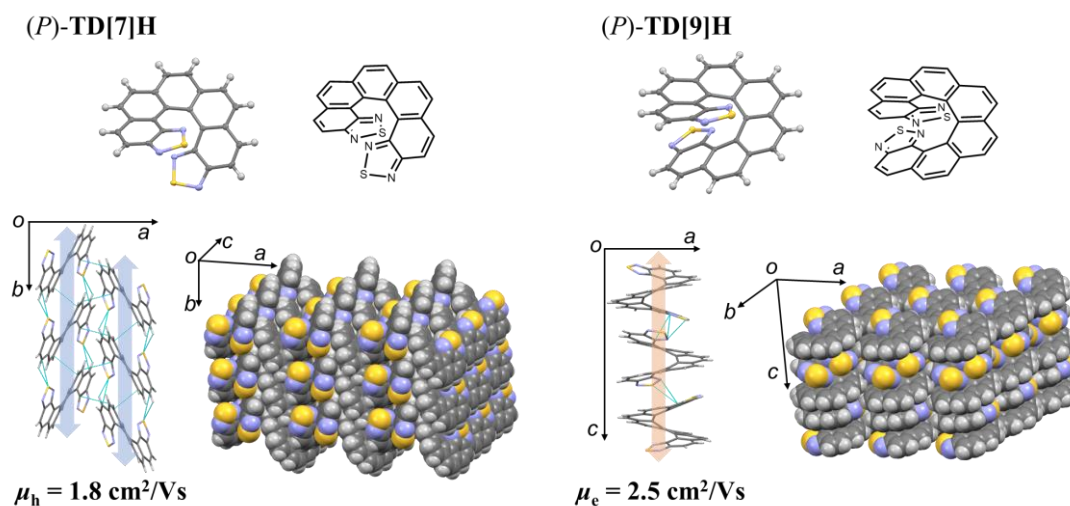
## Homochiral Helical Columnar Arrangements of Hetero[*n*]helicenes with Terminal 2,1,3-Thiadiazole Groups in the Crystalline State

(<sup>1</sup>*Institute for Chemical Research, Kyoto University*, <sup>2</sup>*PRESTO, Japan Science and Technology Agency (JST)*.) ○Zheng Zhang,<sup>1</sup> Yasujiro Murata,<sup>1</sup> Takashi Hirose<sup>1,2</sup>

**Keywords:** Crystal Structures; Carrier Mobility; Intermolecular Interactions; Helicenes

Introducing chirality into organic semiconductors enables the fabrication of functional chiral materials such as circularly polarized light (CPL) selective detectors, chiroptical switches, and chirality-induced spintronic devices<sup>1</sup>. High carrier mobility in the solid state is necessary to achieve high-performance organic electronic devices. However, the relationship between the molecular arrangement of chiral  $\pi$ -conjugated molecules and carrier mobility is currently unclear.

In this work, hetero[*n*]helicene derivatives with 2,1,3-thiadiazole rings, i.e., **TD[7]H** and **TD[9]H**, were synthesized<sup>2</sup> and their chiral single crystal structures were investigated. For hetero[7]helicene derivative (*P*)-**TD[7]H**, a head-to-tail packing structure was observed with C–H $\cdots$ S interactions. On the other hand, hetero[9]helicene derivative (*P*)-**TD[9]H** exhibited a helical columnar structure with N $\cdots$ S interactions and the helical axis of molecule was parallel to the helical axis of the columnar packing. According to theoretical calculations<sup>3</sup>, (*P*)-**TD[7]H** has a high hole mobility ( $\mu_h = 1.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) along the *b*-axis, while (*P*)-**TD[9]H** has a high electron mobility ( $\mu_e = 2.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) along the columnar axis. Details of the crystal structures and theoretical calculations of charge mobility will be discussed in the presentation.



1) C. Zhang, X. Wang, L. Qiu, *Front. Chem.* **2021**, 9, 711488. 2) Z. Zhang, Y. Murata, T. Hirose, *Tetrahedron* **2023**, 142, 133514. 3) L.-F. Ji, J.-X. Fan, G.-Y. Qin, N.-X. Zhang, P.-P. Lin, A.-M. Ren, *J. Phys. Chem. C* **2018**, 122, 21228.



アカデミックプログラム [B講演] | 12. 有機化学—有機結晶・超分子化学：口頭B講演

📅 2024年3月20日(水) 15:55 ~ 17:15 🏢 E1123(11号館 [2階] 1123)

**[E1123-3vn] 12. 有機化学—有機結晶・超分子化学**

座長：越智 里香、大城 宗一郎

## 🎤 日本語

15:55 ~ 16:15

[E1123-3vn-01]

ペプチド型超分子ファイバーと界面活性剤ミセルの複合化による動的不安定性の創発

○窪田 亮<sup>1</sup>、鳥越 祥吾<sup>1</sup>、濱中 佑也<sup>1</sup>、長尾 和俊<sup>1</sup>、浜地 格<sup>1,2</sup> (1. 京大院工、2. JST ERATO)

## 🎤 英語

16:15 ~ 16:35

[E1123-3vn-02]

リングからファイバーへの構造転移を示す自己集合性アゾベンゼン二量体

○須田 奈月<sup>1</sup>、花山 博紀<sup>2</sup>、矢貝 史樹<sup>3</sup> (1. 千葉大院融合理工、2. 千葉大院工、3. 千葉大IAAR)

## 🎤 英語

16:35 ~ 16:55

[E1123-3vn-03]

高速AFMを利用した光誘起超分子構造変換のリアルタイム観察

○玉木 健太<sup>1</sup>、花山 博紀<sup>2</sup>、矢貝 史樹<sup>3</sup> (1. 千葉大院融合理工、2. 千葉大工学研究院、3. 千葉大IAAR)

## 🎤 日本語

16:55 ~ 17:15

[E1123-3vn-04]

短いアルコキシ修飾でフィルムを与えるフルオランテン縮環プロペラン

○加藤 研一<sup>1</sup>、内田 雄太<sup>1</sup>、金田 知也<sup>1</sup>、橘 智紀<sup>1</sup>、大谷 俊介<sup>1</sup>、生越 友樹<sup>1,2</sup> (1. 京大、2. 金沢大)

## ペプチド型超分子ファイバーと界面活性剤ミセルの複合化による動的不安定性の創発

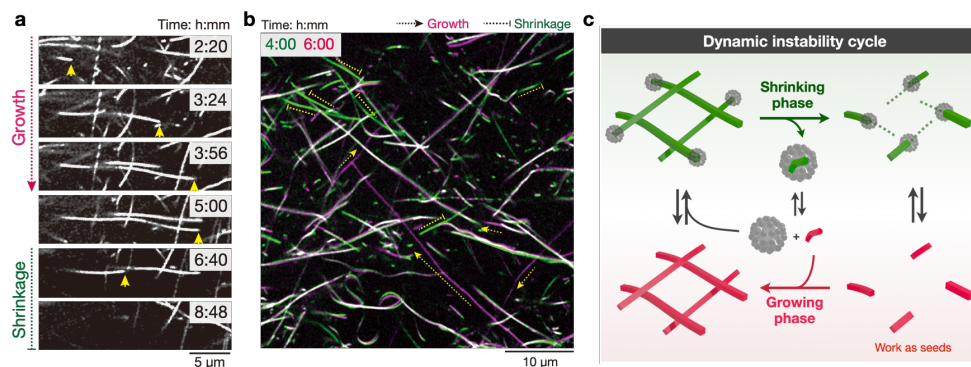
(京大院工<sup>1</sup>・JST ERATO<sup>2</sup>) ○窪田 亮<sup>1</sup>・鳥越祥吾<sup>1</sup>・濱中佑也<sup>1</sup>・長尾和俊<sup>1</sup>・浜地格<sup>1,2</sup>

Emergence of dynamic instability by hybridization of peptide-type supramolecular fibers and surfactant micelles (<sup>1</sup>*Graduate School of Engineering, Kyoto University*, <sup>2</sup>*JST ERATO*) ○Ryou Kubota,<sup>1</sup> Shogo Torigoe,<sup>1</sup> Yuya Hamanaka,<sup>1</sup> Kazutoshi Nagao,<sup>1</sup> Itaru Hamachi<sup>1,2</sup>

Supramolecular chemistry currently faces the challenge of controlling nonequilibrium dynamics, like the dynamic instability of microtubules. This study presents the emergence of the dynamic instability by hybridization of peptide-type supramolecular nanofibers with surfactant micelles. As visualized by real-time confocal imaging, the addition of micelles to nanofibers induces simultaneous growth and shrinkage of nanofibers in a non-synchronized manner during a monotonic decrease in the total fiber number. This dynamic events unexpectedly persists for 6 days and are driven not by chemical reactions but by noncovalent supramolecular interactions between peptide-type nanofibers and surfactant micelles.

**Keywords :** *Supramolecular fibers; confocal microscopy; Nonequilibrium; Micelle; Dynamics*

微小管は、高エネルギー化合物である GTP 存在下、自発的に伸長・収縮を繰り返す動的不安定性を示し、運動・物質輸送・細胞分裂等の生理機能を果たす。人工系において、生体内で観測される非平衡ダイナミクスを模倣できれば、自律運動・階層的な異方性を示すソフトマテリアルを構築できると期待される。しかしながら、動的不安定性のような非平衡系を人工超分子で再現する化学技術は未だ乏しい。本研究で、我々はジペプチド型ゲル化剤からなる超分子ファイバー<sup>1</sup> に対して、界面活性剤ミセルを添加すると、超分子ファイバーの伸長・収縮が 6 日間に渡って持続する動的不安定性を発現することを見出した(Figure)<sup>2</sup>。



**Figure.** (a) Time-lapse confocal images of growth and shrinkage of supramolecular nanofibers. (b) Overlay of confocal images at different time points (green: 4 h, magenta: 6 h after addition of micelles). (c) Plausible mechanism of the dynamic instability.

1) R. Kubota, K. Nagao, W. Tanaka, R. Matsumura, T. Aoyama, K. Urayama, I. Hamachi. *Nature Commun.* 11, 4100 (2020). 2) S. Torigoe, K. Nagao, R. Kubota, I. Hamachi. *Submitted*.



## Ring-Fiber Transition of Self-assembled Azobenzene Dyad

(<sup>1</sup>Graduate School of Science and Engineering, Chiba University, <sup>2</sup>Graduate School of Engineering, Chiba University, <sup>3</sup>Institute for Advanced Academic Research, Chiba University) ○Natsuki Suda,<sup>1</sup> Hiroki Hanayama,<sup>2</sup> Shiki Yagai<sup>3</sup>

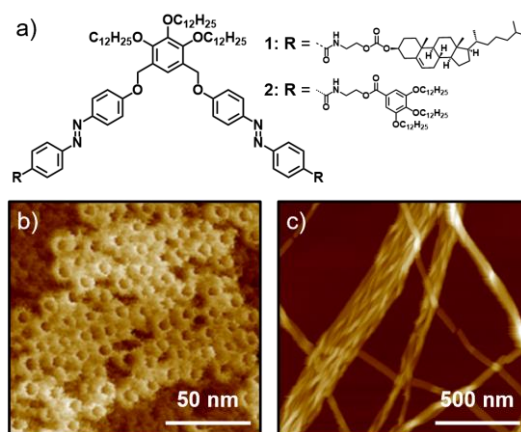
**Keywords:** Self-assembly; Structural transition; Pathway complexity; Seeded polymerization; Azobenzene

Seeded supramolecular polymerization is one of the key strategies that allow control over the kinetics of the supramolecular polymerization process, while most of the previously reported metastable species were stable only at low concentrations due to low activation barrier in spontaneous nucleation.<sup>1)</sup> However, for the application of supramolecular polymers, control over supramolecular polymerization at much higher concentrations would be required. To overcome this limitation, a method using the intermolecularly interacted aggregates which is stable at high concentration as metastable species is proposed.<sup>2)</sup> As another strategy, we herein report topological stabilization of metastable aggregated species<sup>3)</sup> for the use of seeded supramolecular polymerization.

Recently we reported that a scissors-shaped azobenzene dyad **1** possessing strongly aggregative cholesterol units affords two distinct supramolecular polymorphs: nanorings as kinetically trapped products and 1D fibers as thermodynamic products.<sup>4)</sup> Since the discrete nanorings were highly stable and could be dissolved at millimolar concentrations, we expected that the use of such nanorings as metastable species would realize a seeded supramolecular polymerization at high concentration. However, nanorings of **1** was highly stable even under millimolar concentration upon addition of fibers. In this study therefore we newly synthesized dyad **2**, of which nanorings are stable only kinetically and can be converted to thermodynamically stable fibers (Fig. 1a).

Cooling a hot solution of **2** ( $c = 300 \mu\text{M}$ ) in nonpolar solvent to 20 °C afforded only nanorings (Fig. 1b). Aging of this homogeneous nanoring solution for 1-day resulted in the formation of fibrous aggregates (Fig. 1c). The amount of nanorings decreased over the course of a day, indicating that nanorings were spontaneously converted to the fibers. The addition of separately prepared short fibers to the nanoring solution initiated polymerization to convert nanorings to fibers within 1 hour. Because the nanoring of **2** was highly soluble, we could conduct seeded polymerization at 10 mM and observed gel formation after several hours.

1) S. Ogi, F. Würthner et al., *J. Am. Chem. Soc.* **2015**, *137*, 3300. 2) H. Choi, S. Ogi, S. Yamaguchi et al., *J. Am. Chem. Soc.* **2021**, *143*, 2953. 3) A. Suzuki, S. Yagai et al., *J. Am. Chem. Soc.* **2019**, *141*, 13196. 4) N. Suda, S. Yagai et al., *Chem. Sci.* **2022**, *13*, 3249.



**Figure 1.** a) Molecular structure of **1** and **2**. b,c) AFM images of b) nanorings and c) fibers of **2**.

(<sup>1</sup>Graduate School of Science and Engineering, Chiba University, <sup>2</sup>Graduate School of Engineering, Chiba University, <sup>3</sup>Institute for Advanced Academic Research, Chiba University) ○Kenta Tamaki,<sup>1</sup> Hiroki Hanayama,<sup>2</sup> Shiki Yagai<sup>3</sup>

Biomolecular machines modulate their functions by changing aggregated structures of protein subunits, either spontaneously or in response to external stimuli. In artificial molecular systems, similar structural transformations between different aggregated states have been reported, which attracts attention for application to adaptable materials. These responsive systems are typically analyzed by static microscopic observation as well as spectroscopic measurements of transition processes between kinetically and thermodynamically stable states. In contrast, *in-situ* observation of the dynamic transformation process remains challenging.

Here we attempted high-speed AFM imaging of a photo-induced dynamic transformation of self-assembled structures from crystalline nanosheets to polymeric nanofibers. The molecular building block utilized in this study is a barbituric acid-functionalized azobenzene **1** (Fig. 1a). The *trans*-isomer of **1** afforded crystalline nanosheets composed of infinite hydrogen-bonded species (tapes) (Fig. 1b).<sup>1</sup> Upon UV-irradiation to induce *trans*–*cis* isomerization, these nanosheets transformed into nanofibers composed of discrete hydrogen-bonded cyclic hexamers (rosettes) (Fig. 1c).<sup>2</sup> This photo-induced sheet–fiber transformation could be visualized by high-speed AFM imaging at liquid–solid interface (Fig. 1d). It was found that the nanofiber formation takes place from a specific side of nanosheet, which reflects the anisotropic nature of nanosheet.

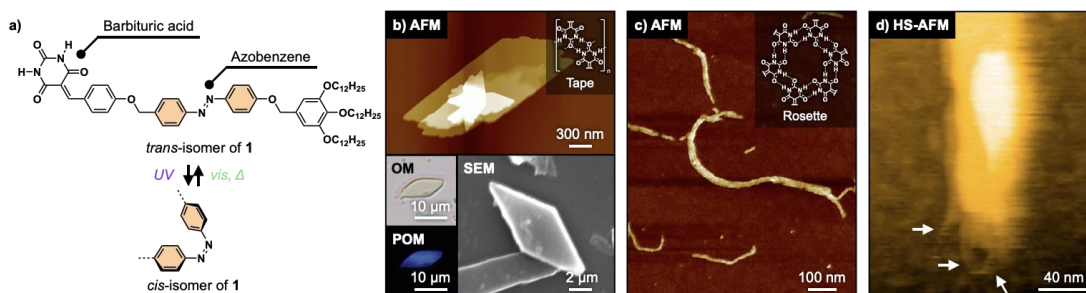


Figure 1. a) Chemical structure of molecule **1**. b) AFM, OM, POM, and SEM images of 2D crystalline nanosheets composed of tapes. c) AFM image of 1D soluble nanofibers composed of rosettes. d) Representative HS-AFM image of the structural transformation.

- 1) S. Yagai et al., *Chem. Sci.* **2022**, *13*, 1281; 2) S. Yagai et al., *Acc. Mater. Res.* **2022**, *3*, 259.

## 短いアルコキシ修飾でフィルムを与えるフルオランテン縮環プロペラン

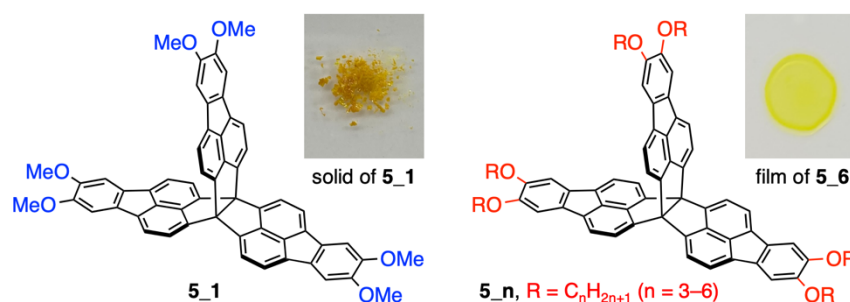
(京大院工<sup>1</sup>・京大工<sup>2</sup>・金沢大 WPI-NanoLSI<sup>3</sup>) ○加藤 研一<sup>1</sup>・内田 雄太<sup>2</sup>・金田 知也<sup>1</sup>・橘 智紀<sup>2</sup>・大谷 俊介<sup>1</sup>・生越 友樹<sup>1,3</sup>

Alkoxyated Fluoranthene-Fused [3.3.3]Propellanes: Film Formation against High  $\pi$ -Core Content (<sup>1</sup>*Graduate School of Engineering, Kyoto University*, <sup>2</sup>*Faculty of Engineering, Kyoto University*, <sup>3</sup>*WPI Nano-LSI, Kanazawa University*) ○Kenichi Kato,<sup>1</sup> Yuta Uchida,<sup>2</sup> Tomoya Kaneda,<sup>1</sup> Tomoki Tachibana,<sup>2</sup> Shunsuke Ohtani,<sup>1</sup> Tomoki Ogoshi<sup>1,3</sup>

Amorphous solids are crucial for practical applications including formation of uniform films. To obtain such molecular glass materials, organic compounds have been designed by using nonplanar and unsymmetric structures and flexible substituents to increase the number of stable conformations and intermolecular contact patterns.<sup>1-3</sup> In this work, we prepared an alkoxyated fluoranthene-fused [3.3.3]propellane,<sup>4,5</sup> a rigid three-dimensional (3D) skeleton, which was found to afford a film despite the high molecular symmetry ( $D_{3h}$ ) and relatively short alkoxy chains. A series with varying lengths of alkoxy groups (**5**<sub>n</sub>, n = 3–6) were further investigated by differential scanning calorimetry (DSC) and a set of optical measurements.

**Keywords** : Amorphous; Glass; Film; Fluoranthene; Propellane

非晶質固体は均一なフィルム形成をはじめとして実用面で重要な材料である。分子性ガラスの設計指針としては、非平面で非対称な構造を用いること、柔軟な置換基を組み込むことで安定な配座および相対分子配置の数を増やすことが挙げられる。<sup>1-3</sup> 本研究では、立体骨格であるフルオランテン縮環プロペラン<sup>4,5</sup>の周辺部にアルコキシ基を導入した分子 (**5**<sub>n</sub>, n = 3–6) を合成したところ、高い分子対称性 ( $D_{3h}$ ) や比較的短いアルコキシ鎖にもかかわらず容易にフィルムを与えることが明らかになった。アルコキシ鎖長を変更した一連の分子群について、示差走査熱量測定 (DSC) や各種光学測定の結果を報告する。



1) Y. Kasahara, I. Hisaki, T. Akutagawa, T. Takeda, *Chem. Commun.* **2021**, 57, 5374. 2) H.-H. Chou, H.-H. Shiha, C.-H. Cheng, *J. Mater. Chem.* **2010**, 20, 798. 3) J. Jayakumar, W.-L. Wu, C.-L. Chang, T.-Y. Han, L.-Y. Ting, C.-M. Yeh, H.-W. Hung, H.-H. Chou, *Org. Electron.* **2021**, 88, 106013. 4) T. Kubo, S. Miyazaki, T. Kodama, M. Aoba, Y. Hirao, H. Kurata, *Chem Commun.* **2015**, 51, 3801. 5) T. Kodama, Y. Hirao, T. Nishiuchi, T. Kubo, *ChemPlusChem* **2017**, 82, 1006.

アカデミックプログラム [B講演] | 12. 有機化学—有機結晶・超分子化学：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 E1131(11号館 [3階] 1131)

**[E1131-3vn] 12. 有機化学—有機結晶・超分子化学**

座長：伊藤 傑、北川 大地

## ◆ 日本語

15:55 ~ 16:15

[E1131-3vn-01]

アルキル置換シクロヘキシル基を持つn型有機半導体のレンガ型結晶構造と電荷輸送特性

○熊谷 翔平<sup>1</sup>、荒井 勇太郎<sup>1</sup>、渡辺 豪<sup>2,3</sup>、石井 宏幸<sup>4</sup>、佐藤 寛泰<sup>5</sup>、竹谷 純一<sup>6,7</sup>、岡本 敏宏<sup>1,7</sup> (1. 東工大、2. 北里大、3. 神奈川県産総研、4. 筑波大、5. (株) リガク、6. 東大、7. CREST (JST))

## ◆ 日本語

16:15 ~ 16:35

[E1131-3vn-02]

強アクセプター性ナフタレンを基盤とした棒状分子の合成と固体構造

○田中 彩樹<sup>1</sup>、松尾 匠、林 正太郎 (1. 高知工科大学)

## ◆ 日本語

16:35 ~ 16:55

[E1131-3vn-03]

*tert*-Butyl修飾による発光性分子の結晶構造制御：光物性からレーザー発振まで○東 蒼一郎<sup>1</sup>、松尾 匠<sup>1</sup>、林 正太郎<sup>1</sup> (1. 高知工大)

## ◆ 日本語

16:55 ~ 17:15

[E1131-3vn-04]

フッ素化 $\pi$ 共役系分子からなる発光性柔軟性分子結晶の創成と光機能○中林 真宏<sup>1</sup>、松尾 匠<sup>1</sup>、林 正太郎<sup>1</sup> (1. 高知工科大学)

## アルキル置換シクロヘキシル基を持つ n 型有機半導体のレンガ塀様結晶構造と電荷輸送特性

(東工大物質理工<sup>1</sup>・北里大未来工<sup>2</sup>・神奈川県産総研<sup>3</sup>・筑波大数物<sup>4</sup>・リガク<sup>5</sup>・東大院新領域<sup>6</sup>・JST CREST<sup>7</sup>) ○熊谷翔平<sup>1</sup>・荒井勇太郎<sup>1</sup>・渡辺 豪<sup>2,3</sup>・石井宏幸<sup>4</sup>・佐藤寛泰<sup>5</sup>・竹谷純一<sup>6,7</sup>・岡本敏宏<sup>1,7</sup>

Brickwork packing structures and electron-transport properties of n-type organic semiconductors bearing alkyl-substituted cyclohexyl groups (<sup>1</sup>*School of Materials and Chemical Technology, Tokyo Institute of Technology*, <sup>2</sup>*School of Frontier Engineering, Kitasato University*, <sup>3</sup>*KISTEC*, <sup>4</sup>*Department of Pure and Applied Sciences, University of Tsukuba*, <sup>5</sup>*Rigaku Corporation*, <sup>6</sup>*Graduate School of Frontier Sciences, The University of Tokyo*, <sup>7</sup>*CREST, JST*)○Shohei Kumagai,<sup>1</sup> Yutaro Arai,<sup>1</sup> Go Watanabe<sup>2,3</sup>, Hiroyuki Ishii<sup>4</sup>, Hiroyasu Sato<sup>5</sup>, Jun Takeya<sup>6,7</sup>, Toshihiro Okamoto<sup>1,7</sup>

Crystalline organic semiconductors have been developed for high-performance thin-film transistor applications. Recent developments of benzo[*de*]isoquinolino[1,8-*gh*]quinolinetetracarboxylic diimide (BQQDI)-based organic semiconductors provide robust and high-mobility n-channel transistors relying on the brickwork-like packing structures.<sup>1</sup> In particular, a cyclohexyl-substituted BQQDI demonstrates an isotropic brickwork motif which is promising for high electron mobilities,<sup>2</sup> whereas it simultaneously shows too low processability to investigate the properties thoroughly. In this work, the cyclohexyl group is functionalized by short alkyl groups to investigate the effects on processability, crystal structure and electron-transport properties (Fig. 1). The isotropic brickwork was consistent when methyl, ethyl and n-propyl substitutions were applied. Details of crystal structures and electron-transport properties will be discussed in the presentation.

**Keywords:** Organic Semiconductor; Substituent Effect; Single Crystal; Field-Effect Transistor; Electron-transport Property

結晶性有機半導体は高性能薄膜トランジスタに有用であり、盛んに研究がなされている。中でも、近年開発されたベンゾ[*de*]イソキノリノ[1,8-*gh*]キノリンジイミド (BQQDI) 誘導体はレ

ンガ塀様結晶構造に基づく二次元的な電子伝導経路を有し、ロバストで高移動度の n 型トランジスタ特性を示す (Fig. 1)<sup>1</sup>。特にシクロヘキシル基を導入することで等方的なレンガ塀構造を形成し、高電子移動度が期待されたが、デバイスプロセス性が十分でないため、詳細な基礎・応用物性研究にはより発展的な分子設計が必要であった<sup>2</sup>。本研究では、シクロヘキシル環上に短鎖アルキル基を置換することで、プロセス性や結晶構造、電子輸送特性への影響を調べた。メチル・エチル・n-プロピル基で置換しても等方的なレンガ塀構造は維持されることがわかった。当日はその他の置換基効果や、計算や薄膜トランジスタ評価による電子輸送特性についても議論する。

1) S. Kumagai *et al.*, *Acc. Chem. Res.* **2022**, 55, 660. 2) C. P. Yu *et al.*, *Commun. Chem.*, **2021**, 4, 155.

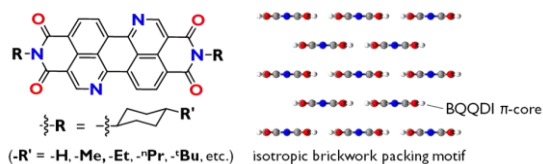


Fig. 1 BQQDI 誘導体の分子構造とレンガ塀様結晶構造様式.

## 強アクセプター性ナフタレンを基盤とした棒状分子の合成と固体構造

(高知工大院工<sup>1)</sup>) ○田中 彩樹<sup>1</sup>・松尾 匠<sup>1</sup>・林 正太郎<sup>1</sup>

Synthesis and Solid Structure of Strong Acceptor Naphthalene-based Rod-shaped Molecules  
(<sup>1</sup>*Graduate School of Engineering, Kochi University of Technology*)○Saki Tanaka,<sup>1</sup> Takumi Matsuo,<sup>1</sup> Shotaro Hayashi<sup>1</sup>

Polycyclic aromatic hydrocarbons (PAHs) have attracted much attention due to their unique semiconducting properties. Therefore, their crystal structure is important in optical and semiconductor devices. The solubility of the naphthalene, a  $\pi$ -conjugated system in PAHs, is well, but their effective-conjugated system is the smallest. In addition, diazole-based naphthalenes containing chalcogen elements are known to have strong acceptor, but these are less studied. Here, we synthesized extended electron-acceptors, naphtho[1,2-c:5,6-c']bis[1,2,5]oxadiazole (NOz) and naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz), -based molecules **1** and **2**. Single crystal X-ray structure analysis of the crystals indicates that molecule **1** and molecule **2** form bricklayer and pitched- $\pi$ -stack crystal structure, respectively. These results indicate that different chalcogen elements in the diazoles are strongly affect the molecular assembled morphology.

**Keywords** : Naphthalenes; Strong Acceptors; Rod-shaped Molecules; Crystals; Donor-Acceptor Structure

多環芳香族化合物 (PAH) は環構造の違いにより固有の光物性と半導性を示す。そのため、その分子集合形態・結晶構造は光・半導体デバイスにおいて重要である。PAHの中で $\pi$ 共役系が最小であるナフタレンの溶解性は非常に優れている。だが、他のPAHと比べ、ナフタレン誘導体の研究はあまり行われていない。また、カルコゲン元素を含むジアゾール系化合物は強アクセプター性を持ち、特徴的な分子間相互作用を誘発することが知られている<sup>2)</sup>。カルコゲンジアゾールを有するナフタレン誘導体は、その分子集合形態の考察において新たな知見を与えると考えられる。そこで、本研究は naphtho[1,2-c:5,6-c']bis[1,2,5]oxadiazole (NOz), naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz)を基盤とした分子**1**, **2**を合成した (Figure 1a)。それぞれの得た結晶 (Figure 1b) に対して単結晶 X 線構造解析を行ったところ、分子**1**は brick layer、**2**では pitched- $\pi$ -stack で結晶構造を形成していた。このことからジアゾールに含まれるカルコゲン元素が異なることで分子集合形態において大きな影響を及ぼすことが明らかとなった。

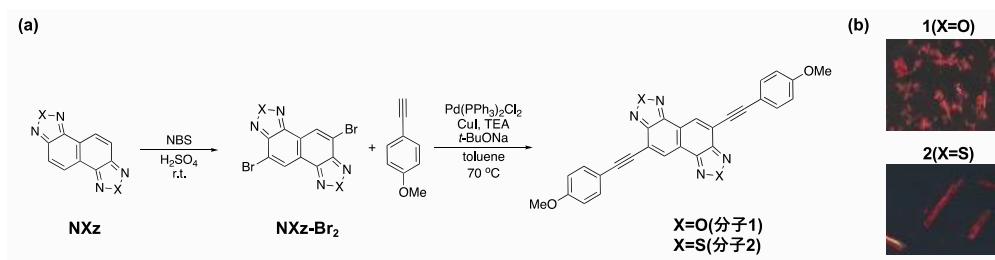


Figure 1. (a) Synthesis of **1** and **2**. (b) Microscope images of the obtained crystals **1** and **2**.

1) K. Kawasima, et. al. *Chem. Mater.* **2015**, 27, 6558–6570.

2) N. Nagao, et. al. *J. Am. Chem. Soc.* **1998**, 120, 3104–3110.



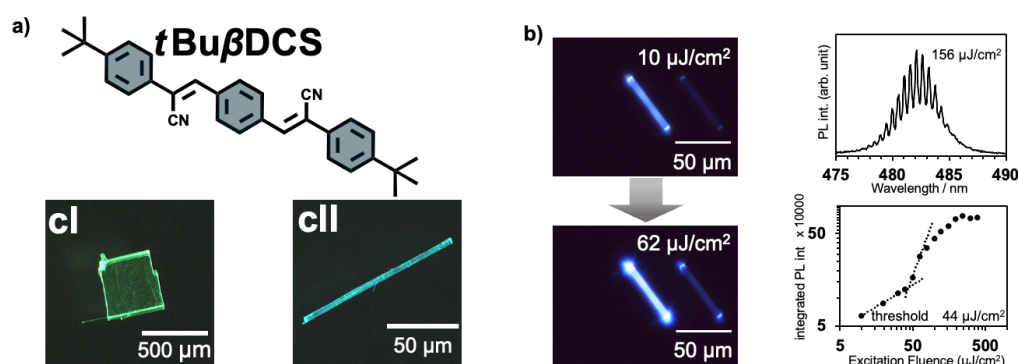
## *tert*-Butyl 修飾による発光性分子の結晶構造制御：光物性からレーザー発振まで

(高知工大環境理工<sup>1)</sup>) ○東 蒼一朗<sup>1</sup>・松尾 匠<sup>1</sup>・林 正太郎<sup>1</sup>

Controlling Crystal Structure of Luminescent Molecules by *tert*-Butyl Engineering: From Their Optical Properties to Laser Oscillation (<sup>1</sup>*School of Environmental Science and Engineering, Kochi University of Technology*) ○Soichiro Azuma,<sup>1</sup> Takumi Matsuo,<sup>1</sup> Shotaro Hayashi<sup>1</sup>

It is known that creating lasing organic crystals from the level of molecular design is difficult. We focused on dicyanostyrylbenzene (DCS) which exhibits aggregation-induced emission (AIE) and high luminescence quantum yield in crystalline states, but there is no report on laser oscillation. Thus, to improve the crystal structure and crystal processability, we designed *tert*-butyl-appended DCS. Here, we have successfully obtained polymorphs **cI** and **cII** from newly synthesized *tert*-butyl-appended DCS, resulting in high quantum yields. Interestingly, **cII** crystals exhibited laser oscillation due to excitation density-dependent emission amplification and Fabry–Pérot resonance.

レーザー発振する有機結晶を分子構造の段階から設計することは困難な課題である。我々は凝集誘起発光 (AIE) や結晶状態で高い発光量子収率( $\Phi_{PL}$ )を示すジシアノスチリルベンゼン (DCS) に着目したが、DCS 結晶は高い  $\Phi_{PL}$  を示しながらもレーザー発振の報告例は無い<sup>1)</sup>。本研究では、結晶構造制御を期待し *tert*-Butyl を修飾した DCS 分子を合成・結晶化し 2 種類の結晶多形 **cI**, **cII** を得ることに成功した(Figure 1 a)。単結晶構造解析の結果、分子の捻れに起因して多形化しており、極大蛍光波長と  $\Phi_{PL}$  は **cI** で 500 nm と 530 nm,  $\Phi_{PL}$ =0.721、**cII** では 481 nm と 520 nm,  $\Phi_{PL}$ =0.906 であった。興味深いことに、**cII** 結晶のみがパルス光励起下で狭線化増幅発光挙動を示し、増幅閾値は 44  $\mu\text{J}/\text{cm}^2$  と見積もられた。高分解能発光スペクトル測定では結晶端での Fabry–Pérot 共振に基づいて等間隔に鋭いマルチモードスペクトルが得られた (Figure 1 b)。したがって、**cII** 結晶は高い固体発光性によりレーザー機能を有することがわかった。



**Figure 1.** a) Chemical structure of *t*Bu $\beta$ DCS and fluorescence microscope image of each crystal. b) Lasing behavior in **cII**.

1) Johannes Gierschner *et. al.*, *J. Phys. Chem. C* **2017**, 121, 23166-23183.

## フッ素化 $\pi$ 共役系分子からなる発光性柔軟性分子結晶の創成と光機能

(高知工大) ○中林 真宏・松尾 匠・林 正太郎

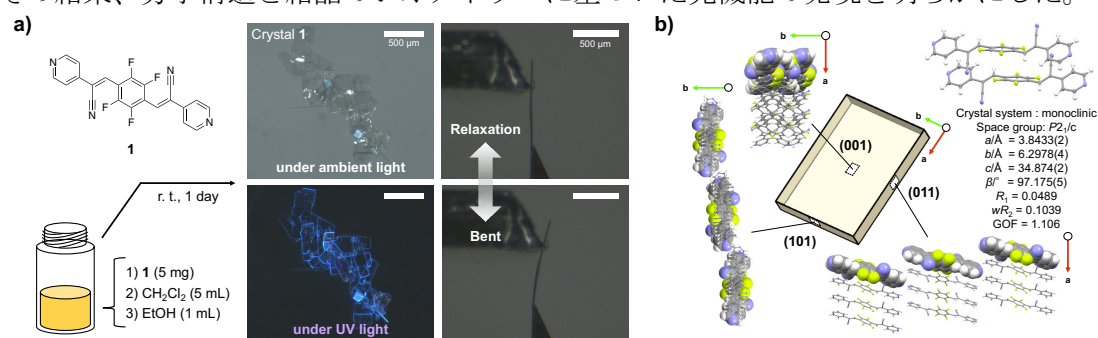
Synthetic Design of Nitrogen-containing Lewis Basic  $\pi$ -Conjugated Molecules toward Fluorescent Molecular Cocrystals (*Kochi University of technology*) ○Mahiro Nakabayashi, Takumi Matsuo, Shotaro Hayashi

Organic crystals are based on various intermolecular interactions between organic molecules. Organic crystals having flexible functionalities (elasticity) and unique optical properties have been developed in recent years<sup>[1]</sup>. However, molecular design for elasticity is not progressed so far. Therefore, to apply applications in flexible devices, we have developed crystal designs that give flexibility. In this study, we designed and synthesized the fluorinated  $\pi$ -conjugated molecule **1** (Figure 1a). Single-crystal X-ray structure analysis of crystal **1** showed appropriate intermolecular interactions for flexibility (Figure 1b). Moreover, spectroscopic properties were investigated for the crystal, resulting in fluorescent properties based on molecule structure and crystal geometry.

**Keywords** : Fluorine;  $\pi$ -Conjugated Molecules; Crystals; Flexibility; Optical Properties

有機結晶は、有機分子が分子間相互作用を介して秩序的かつ密に詰まった構造体である。近年、 $\pi$  共役分子系において柔軟性を有する分子結晶が創出されており、フレキシブルな光・電子デバイスへの展開が期待されている<sup>[1]</sup>。しかしながら、有機結晶に柔軟性を付与するためには分子間相互作用を精密に制御する必要があり、適切な分子設計を必要とする。本研究では、フッ素の静電相互作用を駆使することによって発光性柔軟性分子結晶の創出を達成した。

柔軟性分子結晶を誘起するフッ素化発光性  $\pi$  共役系分子 **1** を設計、合成、結晶化をした (Figure 1a)。単結晶 X 線構造解析の結果、分子結晶の柔軟性が分子間相互作用に基づいていることを明らかにした (Figure 1b)。次に結晶について分光特性を調査した。その結果、分子構造と結晶のジオメトリーに基づいた光機能の発現を明らかにした。



**Figure 1.** a) Structure of the fluorinated  $\pi$ -conjugated molecule **1** and photographs crystal **1**. b) Crystal structure of crystal **1**.

[1] Owczarek M.; Hujsak K. A.; Ferris D. P.; Prokofjevs A.; Majerz I.; Szklarz P.; Zhang H.; Sarjeant A. A.; Stern C. L.; Jakubas R.; Hong S.; Dravid V. P. and Stoddart J. F. *Nat. Commun.* **2016**, 7, 13108.



アカデミックプログラム [B講演] | 13. 有機化学—反応機構・光化学・電気化学：口頭B講演

2024年3月20日(水) 15:55 ~ 16:55 E1132(11号館 [3階] 1132)

**[E1132-3vn] 13. 有機化学—反応機構・光化学・電気化学**

座長：佐藤 英祐、松本 浩一

## ◆ 日本語

15:55 ~ 16:15

[E1132-3vn-01]

レドックス活性イオン液体を触媒、電解質および反応メディアとする電解水素発生系の開発

○佐藤 綾<sup>1</sup>、星野 友<sup>1</sup>、鳶越 恒<sup>1</sup> (1. 九大院工)

## ◆ 英語

16:15 ~ 16:35

[E1132-3vn-02]

流動電位を用いる電解重合法の開発

○岩井 優<sup>1</sup>、佐藤 宏亮<sup>1</sup>、長谷川 丈二<sup>2</sup>、石塚 紀生<sup>3</sup>、松川 公洋<sup>4</sup>、富田 育義<sup>1</sup>、稲木 信介<sup>1</sup> (1. 東京工業大学、2. 名古屋大学、3. エマオス京都、4. 京都工芸繊維大学)

## ◆ 日本語

16:35 ~ 16:55

[E1132-3vn-03]

電気化学的炭素挿入に基づく多置換芳香環の構築

○信田 尚毅<sup>1</sup>、森本 達也<sup>1</sup>、今野 祐希<sup>1</sup>、跡部 真人<sup>1</sup> (1. 横浜国立大学)

## レドックス活性イオン液体を触媒、電解質および反応メディアとする電解水素発生系の開発

(九大院工<sup>1</sup>) ○佐藤 綾<sup>1</sup>・星野 友<sup>1</sup>・寫越 恒<sup>1</sup>

Development of Hydrogen Generation System Using Redox-active Ionic Liquid as Catalyst, Electrolyte and Reaction Media (<sup>1</sup>*Graduate School of Engineering, Kyushu University*) ○Aya Sato,<sup>1</sup> Yu Hoshino,<sup>1</sup> Hisashi Shimakoshi<sup>1</sup>

Hydrogen is energy source that can replace fossil fuels, and many studies have been conducted on hydrogen generation by electrolysis. In this study, we focused on Redox-active Ionic Liquid (RIL) and aimed to develop hydrogen generation system in which RIL has the functions of reaction media, supporting electrolyte and mediator.

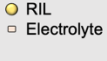
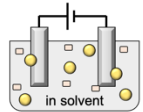
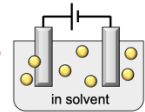
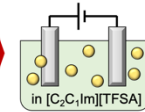
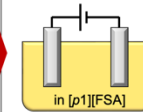
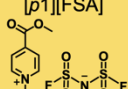
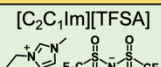
A new RIL, **[p1][FSA]**, was successfully synthesized in a two-step process, and we confirmed that it has redox activity and ability to reduce proton. In experiments of electrolysis (Table 1.), hydrogen was generated under condition A (**[p1][FSA]** was added to the supporting electrolyte solvent). When **[p1][FSA]** was added to DMF (condition B) or **[C<sub>2</sub>C<sub>1</sub>Im][TFSA]** solvent (condition B'), hydrogen generation was also observed.

**Keywords** : Ionic Liquid, Hydrogen generation, Electrolysis, Redox-activity

水素は化石燃料に代わるエネルギー源として注目されており、電気分解による水素発生研究がこれまで多く行われてきた。我々はそのメディアとしてレドックス活性イオン液体 (Redox-active Ionic Liquid, RIL)に着目した。イオン液体は電気化学において溶媒や支持電解質として用いられ、さらに酸化還元応答を示す RIL はその電子授受能から、触媒反応系開発への利用が期待される<sup>1)</sup>。本研究では RIL を溶媒・支持電解質・触媒的に用いた電解水素発生系の開発を行うため、4つの条件 (A~C)に分けて研究達成を目指した (Table 1)。

新規 RIL である **[p1][FSA]**を2ステップで合成に成功し、電気化学特性評価によりレドックス活性およびプロトン還元能を持つことが分かった。電解実験では、支持電解質溶液にプロトン源 (酢酸)と**[p1][FSA]**を加えた条件 A や、支持電解質非存在下の溶媒中に酢酸と**[p1][FSA]**を加えた条件 B、**[C<sub>2</sub>C<sub>1</sub>Im][TFSA]**イオン液体中に酢酸と**[p1][FSA]**を加えた条件 B'において、定電位電解法にてそれぞれ水素生成を観測した。

Table 1. Conditions of hydrogen generation systems.

	Condition A	Condition B	Condition B'	Condition C
 ● RIL □ Electrolyte	 in solvent	 in solvent	 in <b>[C<sub>2</sub>C<sub>1</sub>Im][TFSA]</b>	 in <b>[p1][FSA]</b>
Mediator	<b>[p1][FSA]</b>	<b>[p1][FSA]</b>	<b>[p1][FSA]</b>	<b>[p1][FSA]</b>
Electrolyte	<i>n</i> -Bu <sub>4</sub> N <sup>+</sup> PF <sub>6</sub> <sup>-</sup>		<b>[C<sub>2</sub>C<sub>1</sub>Im][TFSA]</b>	
Solvent	CH <sub>3</sub> CN	DMF		

1) H. Shimakoshi, N. Houfuku, L. Chen, Y. Hisaeda, *Green Energy&Environment*, **2019**, 4, 116.

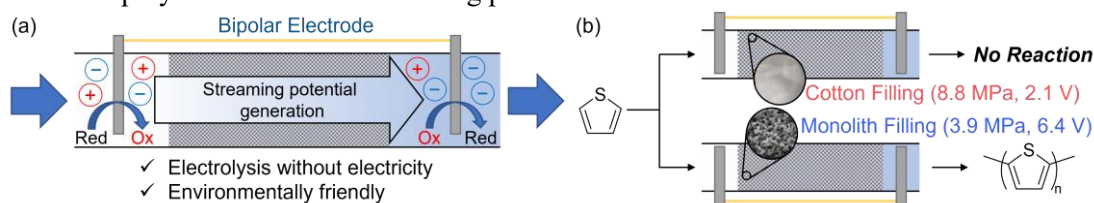
## Development of the Electropolymerization Method Using a Streaming Potential

(<sup>1</sup>*School of Materials and Chemical Technology, Tokyo Institute of Technology*, <sup>2</sup>*Institute of Material and Systems for Sustainability, Nagoya University*, <sup>3</sup>*Emaus Kyoto*, <sup>4</sup>*Materials Innovation Lab, Kyoto Institute of Technology*) ○Suguru Iwai,<sup>1</sup> Kosuke Sato,<sup>1</sup> George Hasegawa,<sup>2</sup> Norio Ishizuka,<sup>3</sup> Kimihiro Matsukawa,<sup>4</sup> Ikuyoshi Tomita,<sup>1</sup> Shinsuke Inagi<sup>1</sup>

**Keywords:** Bipolar Electrochemistry; Electropolymerization; Streaming Potential; Conducting Polymer; Flow Electrochemistry

Bipolar electrodes (BPEs) driven in external electric fields have unique features such as wireless nature, gradient potential and so on. Due to these characteristics, BPEs have been attracting more and more attention.<sup>1</sup> However, undesired reactions may occur on the driving electrodes, which are necessary to generate the external electric field. To solve this problem, we focus on the streaming potential ( $E_{\text{str}}$ ), generated by the flow of the low-concentration electrolyte.  $E_{\text{str}}$  is a potential difference between the inlet and the outlet of the narrow channel.<sup>2</sup> The use of  $E_{\text{str}}$  eliminates the need for driving electrodes and undesired reactions can be suppressed. In the previous work,  $E_{\text{str}}$  was generated in the cotton wool-filled channel and electropolymerizations of pyrrole and 3,4-ethylenedioxythiophene proceeded.<sup>3</sup> However, the value of  $E_{\text{str}}$  was insufficient to conduct electropolymerizations of other monomers. Furthermore, a large pressure drop of ca. 10 MPa had to be applied to generate  $E_{\text{str}}$ , which should be reduced for practical use.

In this study, we investigated the condition with the low-pressure drop and high  $E_{\text{str}}$ . As a result of the screening of filling materials, a polymer monolith, a porous material with continuous pores, could generate a larger  $E_{\text{str}}$  with less pressure drop compared to the cotton wool filling. For the electropolymerization of thiophene, the desired polythiophene was deposited on the anode with using the monolith material, while no polymer was obtained in the case using the cotton wool. The improved method could expand the scope of monomers for electropolymerization with streaming potentials.



**Figure 1.** (a) Concept of electrolysis with  $E_{\text{str}}$ . (b) Performance of electropolymerization of thiophene with different filling materials.

1) N. Shida, Y. Zhou, S. Inagi, *Acc Chem. Res.*, **2019**, 52, 2598–2608.

2) A. V. Delgado, F. González-Caballero, R. J. Hunter, L. K. Koopal, J. Lyklema, *J. Colloid Interface. Sci.*, **2007**, 309, 194–224.

3) S. Iwai, T. Suzuki, H. Sakagami, K. Miyamoto, Z. Chen, M. Konishi, E. Villani, N. Shida, I. Tomita, S. Inagi, *Commun. Chem.*, **2022**, 5, 66.

## 電気化学的炭素挿入に基づく多置換芳香環の構築

(横国大院工<sup>1</sup>・JST さきがけ<sup>2</sup>) ○信田 尚毅<sup>1,2</sup>・森本 達也<sup>1</sup>・今野 祐希<sup>1</sup>・跡部 真人<sup>1</sup>

Construction of Polysubstituted Aromatic Rings based on Electrochemical Carbon Insertion  
(<sup>1</sup>Graduate School of Engineering, Yokohama National University, <sup>2</sup>JST PRESTO) ○Naoki Shida,<sup>1,2</sup> Tatsuya Morimoto,<sup>1</sup> Yuki Konno,<sup>1</sup> Mahito Atobe<sup>1</sup>

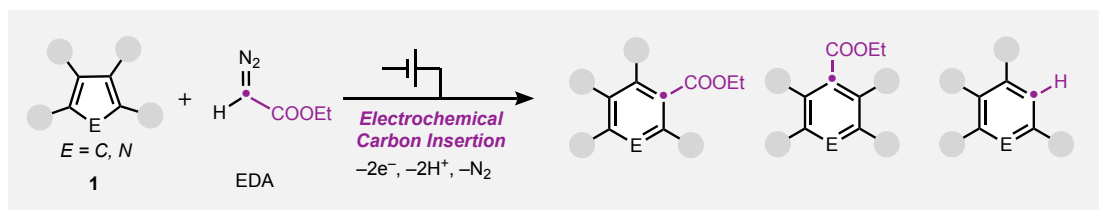
For the synthesis of polysubstituted aromatic compounds, which are building blocks for pharmaceuticals and functional materials, many reactions have been developed to introduce functional groups to the periphery of aromatic rings.<sup>1</sup> On the other hand, ring expansion reactions based on atomic insertion have been intensively studied in recent years from the viewpoint of skeletal editing.<sup>2</sup> In carbon insertion reactions, ring expansion using carbene equivalents with increased oxidation degree has been reported, but there are few examples of ring expansion reactions combined with electron transfer reactions.

In this study, we report the synthesis of polysubstituted aromatic compounds by ring expansion by the electrochemical oxidation of a five-membered ring precursor in the presence of ethyl diazoacetate (EDA) via radical cation intermediate. We succeeded in synthesizing six-membered heteroaromatic compounds from nitrogen-containing five-membered rings such as pyrrole and indole, as well as arenes from indene and cyclopentadiene.

**Keywords :** Electrosynthesis; Insertion reaction; Skeletal editing; Radical cation; Anodic oxidation

医薬品や機能材料のビルディングブロックとして有用な多置換芳香族化合物を合成するために、芳香環の周縁部分への機能団導入反応や環化反応が数多く開発されてきた<sup>1</sup>。一方、原子挿入に基づく環拡大反応は、骨格編集反応の観点から近年精力的に研究が行われている<sup>2</sup>。炭素挿入反応においては、酸化度の上がったカルベン等価体を用いた環拡大が報告されているが、電子移動反応を組み合わせた環拡大反応の報告例は少ない。

本研究では、5員環化合物のラジカルカチオンを鍵中間体とし、ジアゾ酢酸エチル (EDA) との反応により環拡大による多置換芳香族化合物の合成を報告する。本手法により、ピロール・インドールといった含窒素5員環を原料とした6員環ヘテロ芳香族化合物の合成、および、インデン・シクロペンタジエンを原料とするアレーン類の合成に成功した。



1) Q. Zhao, C. Peng, G. Zhan, B. Han, *RSC Adv.* **2020**, *10*, 40983.

2) J. Jurczyk, J. Woo, S. F. Kim, B. D. Dherange, R. Sarpong, M. D. Levin, *Nat. Synth.* **2022**, *1*, 352.

アカデミックプログラム [B講演] | 14. 有機化学—芳香族・複素環・ヘテロ原子化合物：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 E1133(11号館 [3階] 1133)

**[E1133-3vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物**

座長：井本 裕顕、北村 充

## ◆ 英語

15:55 ~ 16:15

[E1133-3vn-01]

機械学習を活用したMayr反応性パラメータの予測と含窒素複素芳香族分子のマンニッヒ型反応における新規求核剤の探索

○大石 峻也<sup>1,2</sup>、大塚 尚哉<sup>1,2</sup>、丸山 莉央<sup>1</sup>、鈴木 敏泰<sup>1</sup>、楳山 儀恵<sup>1,2</sup> (1. 分子研、2. 総研大)

## ◆ 英語

16:15 ~ 16:35

[E1133-3vn-02]

新規キノリン系大環状化合物の開発

○シュ ウエイ<sup>1</sup>、木原 和輝<sup>1</sup>、野仲 はる<sup>1</sup>、八神 諒汰<sup>1</sup>、武田 彩海<sup>1</sup>、田代 奨吾<sup>1</sup>、熊谷 直哉<sup>1,2</sup> (1. 慶大院薬、2. 微化研)

## ◆ 英語

16:35 ~ 16:55

[E1133-3vn-03]

キノリン/インドール環状4量体 (Q<sub>2</sub>ln<sub>2</sub>) の誘導体合成および機能探索○木原 和輝<sup>1</sup>、小林 透威<sup>1</sup>、木村 美玲<sup>1</sup>、Wei Xu<sup>1</sup>、熊谷 直哉<sup>1,2</sup> (1. 慶大院薬、2. 微化研)

## ◆ 日本語

16:55 ~ 17:15

[E1133-3vn-04]

環状ジケトン類の結合切断戦略によるメタルフリー型ヘテロ環合成

○要藤 友佑<sup>1</sup>、知名 秀泰<sup>2</sup>、宮尾 優希<sup>1</sup>、佐々 裕隆<sup>1</sup>、菊嶋 孝太郎<sup>1</sup>、土肥 寿文<sup>1</sup> (1. 立命館大薬、2. 長浜バイオ大バイオ)

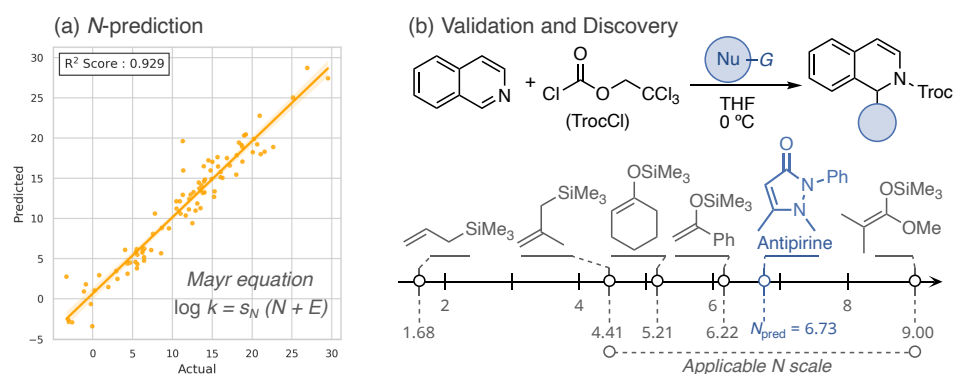
## Prediction of Mayr reactivity parameters by machine learning and its utilization in the discovery of potential nucleophile in Mannich-type reaction of *N*-hetero aromatics

(<sup>1</sup>*Institute for Molecular Science*, <sup>2</sup>*SOKENDAI*) ○Shunya Oishi,<sup>1, 2</sup> Naoya Ohtsuka,<sup>1, 2</sup> Rio Maruyama,<sup>1</sup> Toshiyasu Suzuki,<sup>1</sup> Norie Momiyama<sup>1, 2</sup>

**Keywords:** Machine learning, Reactivity parameter, Mannich-type reaction

Understanding chemical reactivity remains an essential and ongoing challenge in organic chemistry. Mayr's reactivity parameter<sup>1</sup> was developed as an indicator towards the generalization of chemical reactivity, allowing for semi-quantitative prediction of the reaction rate constant. Their relative reactivity can be directly assessed by comparing the *N*-value of different nucleophiles or the *E*-value of different electrophiles. Recently, 1254 of *N*-values and 352 of *E*-values were reported based on their experiments of kinetic analysis. Although Mayr's reactivity parameters have excellent potentials as indicators in the development of chemical reactions, their application has been reported in only two examples exploring the scope of nucleophiles. This is probably attributed to the versatility of organic molecules that were not encompassed by Mayr's reported values.

To address this issue, we successfully created a highly accurate prediction model of reactivity parameters (*N*, *E* value) using machine learning, which enables the representation of chemical reactivity for various organic molecules in specific values. Validity of reactivity scales was evaluated on Mannich-type reaction of isoquinoline with silyl nucleophiles in Mayr's database.<sup>2</sup> From the perspectives of *N* and *E* values, it was quantitatively elucidated that nucleophiles with *N* values ranging from 4.41 to 9.00 were found to be applicable in the reactions of isoquinoline. Furthermore, by applying the developed model to commercially available chemicals, Antipyrine (*N*<sub>pred</sub> = 6.73) and its analogs were quantitatively discovered as novel nucleophiles. The Mannich-type reaction with Antipyrine produced the analog of the small drug "Famprofazone", demonstrating the utility of Mayr's reactivity parameters in the discovery of a new entry of nucleophile.



1) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed.* **1994**, *33*, 938–957.

2) <https://www.cup.lmu.de/oc/mayr/reaktionsdatenbank2>

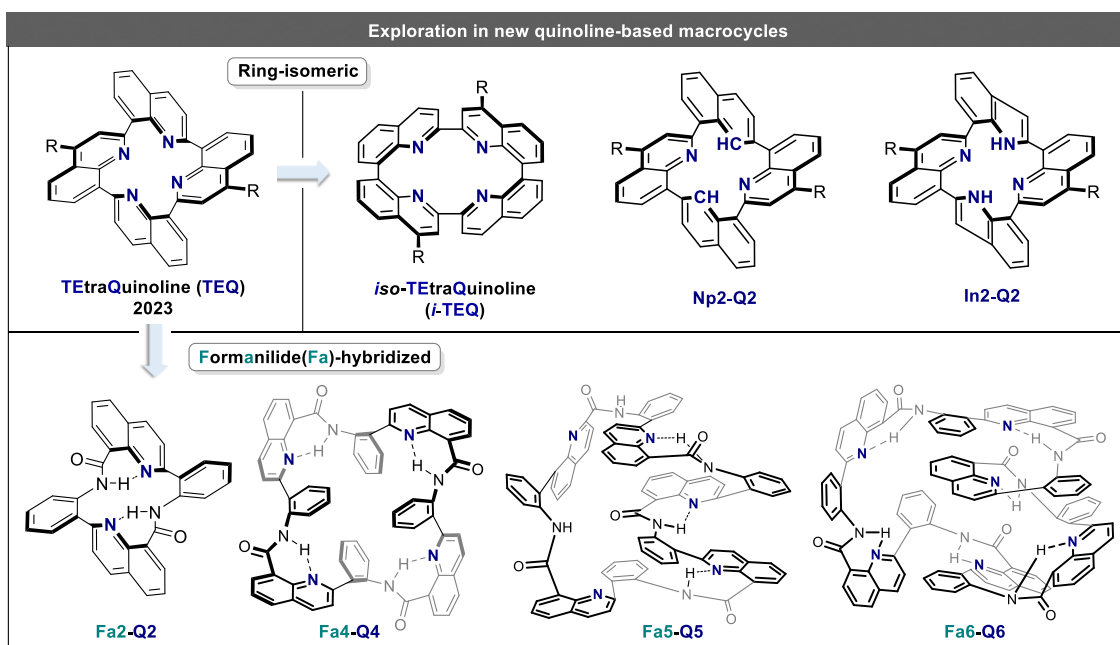
## Design of Novel Quinoline-based Macrocylic Compounds

(<sup>1</sup>Graduate School of Pharmaceutical Sciences, Keio University, <sup>2</sup>Institute of Microbial Chemistry) OWei Xu,<sup>1</sup> Kazuki Kihara,<sup>1</sup> Haru Nonaka,<sup>1</sup> Ryota Yagami,<sup>1</sup> Ayami Takeda,<sup>1</sup> Shogo Tashiro,<sup>1</sup> Naoya Kumagai<sup>1,2</sup>

**Keywords:** quinoline, macrocyclic compounds, heterocyclic compounds

Macrocyclic compounds have unique properties and are of great interest in various fields, including supramolecular chemistry, medicinal chemistry, and materials science. In recent years, our group has been devoted to the study of quinoline-based macrocyclic architectures,<sup>1</sup> and disclosed the synthesis of TEtraQuinoline (TEQ)<sup>2</sup> as a non-planar porphyrinoid tetradentate nitrogen ligand. Based on the unique structure and properties of TEQ, we are interested in the design of ring-isomeric architectures such as head-to-head type *iso*-TEtraQuinoline (*i*-TEQ), hybridized tetrameric macrocycles Np2Q2 and In2Q2, comprising of naphthalene (Np) x2/quinoline (Q) x2 and indole (In) x2/quinoline (Q) x2, respectively. Despite the similar saddle-shaped structure, they showed distinct chemical behaviors from TEQ.

We also designed and synthesized a series of hybridized macrocycles comprising of formanilide (Fa) and quinoline (Q). They had flexible but diverse structures depending on the number of Fa and Q subunits. As confirmed by NMR experiments and X-ray crystallography, Fa2Q2 and Fa4Q4 showed  $C_2$  and  $S_4$ -symmetric structures, respectively. In contrast, Fa5Q5 and Fa6Q6 displayed entire structures with lower symmetry, and part of their structures featured helical architecture due to intramolecular hydrogen bonds. Properties of these macrocycles will be discussed, including the complexation ability of Fa2Q2 with  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$ .



1) S. Adachi, M. Shibasaki, N. Kumagai, *Nature Commun.* **2019**, 10, 3820.

T. Kobayashi, N. Kumagai, *Angew. Chem. Int. Ed.* **2023**, 62, e202307896.

2) W. Xu, Y. Nagata, N. Kumagai, *J. Am. Chem. Soc.* **2023**, 145, 2609.



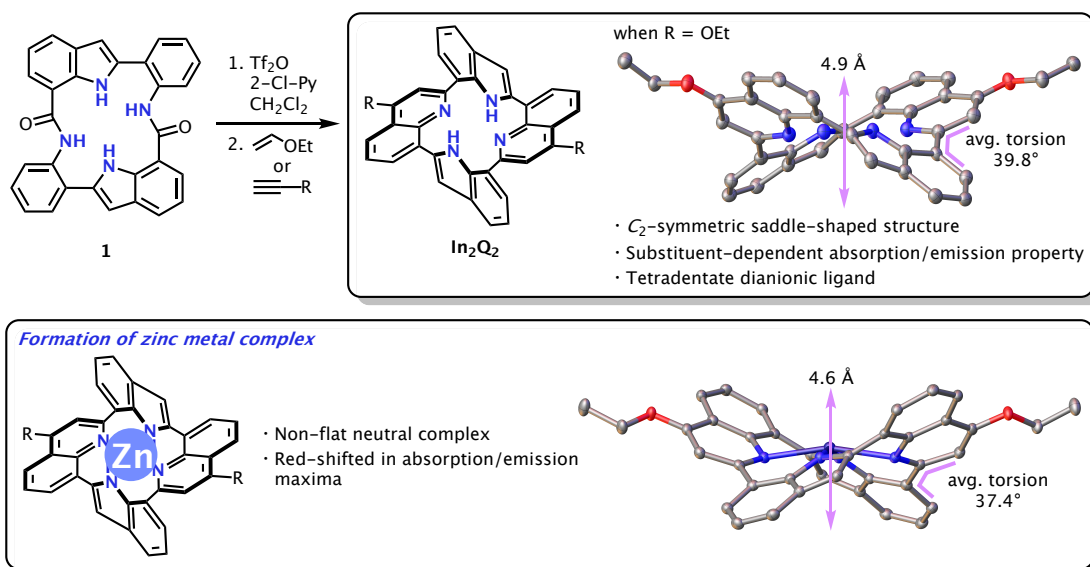
## Synthesis and Functional Exploration of Quinoline-Indole Hybridized Cyclic Tetramer ( $\text{In}_2\text{Q}_2$ ) Derivatives

(<sup>1</sup>Graduate School of Pharmaceutical Sciences, Keio University, <sup>2</sup>Institute of Microbial Chemistry) ○Kazuki Kihara,<sup>1</sup> Toi Kobayashi,<sup>1</sup> Mirei Kimura,<sup>1</sup> Wei Xu,<sup>1</sup> Naoya Kumagai<sup>1,2</sup>

**Keywords:** Macrocyclic Molecule, Indole, Quinoline, Metal Complex

Based on our recent study on a quinoline tetramer, TEtraQuinoline (TEQ),<sup>1</sup> we have designed a new non-flat porphyrin-like 4-nitrogen macrocycle  $\text{In}_2\text{Q}_2$ , in which two indole (In) and quinoline (Q) units are diagonally located and concatenated. We synthesized a series of  $\text{In}_2\text{Q}_2$  derivatives bearing various substituents on the periphery of the macrocycle from macrocyclic diamide **1** and vinyl ether/alkyne in the presence of  $\text{TiF}_4$ /2-chloropyridine.  $\text{In}_2\text{Q}_2$  has a  $C_2$ -symmetric saddle-shaped structure similar to TEQ, but it is conformationally flexible for ring-flipping even with substituents at the 4-position of the quinoline rings.

$\text{In}_2\text{Q}_2$  derivatives were emissive in both solution phase and solid state with absorption maxima ranging from 307–340 nm, and emission maxima ranged from 456–527 nm. In addition,  $\text{In}_2\text{Q}_2$  accommodated metal cations such as  $\text{Zn}^{2+}$  to give a non-flat neutral metal complex without significant conformational change. Smaller vertical sizes (from 4.9 to 4.6 Å) were observed, along with smaller dihedral angles at the indole-quinoline linkages (average torsion angle from 39.4 to 37.4°). Complexation with  $\text{Zn}^{2+}$  also induced a red-shift in both absorption and emission maxima. The synthesis of polysubstituted  $\text{In}_2\text{Q}_2$  with higher flipping energy and a general study on the formation of complexes with other metal cations are also discussed.



1) W. Xu, Y. Nagata, N. Kumagai, *J. Am. Chem. Soc.* **2023**, *145*, 2609.



## 環状ジケトン類の結合切断戦略によるメタルフリー型ヘテロ環合成

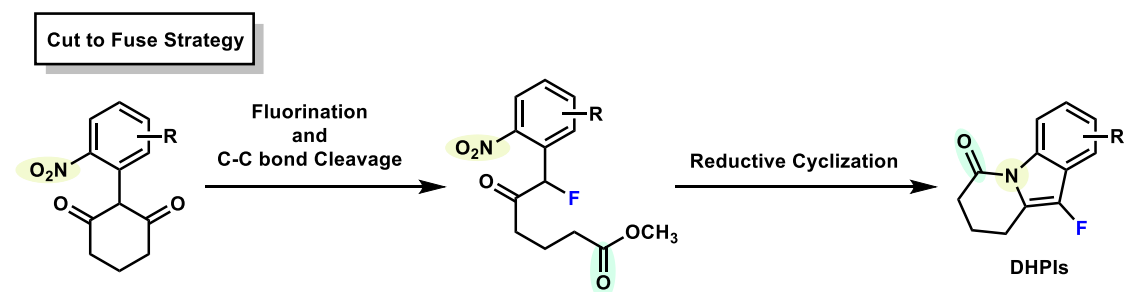
(立命館大薬<sup>1</sup>・長浜バイオ大バイオ<sup>2</sup>) ○要藤 友佑<sup>1</sup>・知名 秀泰<sup>2</sup>・宮尾 優希<sup>1</sup>・佐々裕隆<sup>1</sup>・菊畠 孝太郎<sup>1</sup>・土肥 寿文<sup>1</sup>

Metal-free Heterocyclic Synthesis by Bond Cleavage Strategy of Cyclic Diketones (<sup>1</sup>*College of Pharmaceutical Science, Ritsumeikan University*, <sup>2</sup>*Faculty of Bioscience, Nagahama Institute of Bio-Science and Technology*) ○Yusuke Yoto,<sup>1</sup> Hideyasu China,<sup>1</sup> Yuki Miyao,<sup>1</sup> Hirotaka Sasa,<sup>1</sup> Kotaro Kikushima,<sup>1</sup> Toshifumi Dohi<sup>1</sup>

The synthesis of fluorinated indoles, which involves the introduction of a fluorine atom, can sometimes result in undesired side reactions. In this study, we present a new method for the conversion of cyclic diketones to fluoroketoesters, followed by C-C bond cleavage and derivatization. This C-C bond cleavage-type fluorinating ring-opening reaction proceeds smoothly in the presence of methanol and a carbonate base, and can convert various 2-arylcyclohexadiones to the corresponding linear arylfluoroketoesters. The *o*-nitroaryl product can be derivatized by metal-free reductive cyclization to dihydropyrido[1,2a]indolone (DHPI), an intermediate in the synthesis of monoterpene indole alkaloids.

**Keywords :** Fluorinative ring opening reaction; C-C bond cleavage; Metal-free heterocyclic synthesis; DHPIs

含フッ素インドール類の合成法として、インドール類のフッ素化反応が報告されているが、酸化やジフルオロ化反応といった副反応が同時に進行する<sup>1)</sup>。当研究室では環状ジケトン類への温和な条件下でのジクロロ化およびジブロモ化に続く C-C 結合切断反応により、鎖状ハロケトエステルへと変換する手法を見出している<sup>2)</sup>。今回我々は、本法によるメタルフリー型含フッ素ヘテロ環合成法を志向し、その鍵反応となる C-C 結合切断型フッ素化開環反応を見出した。本反応はメタノールと無機塩基の共存下で円滑に進行し、種々の 2-アリアルシクロヘキサジオン類を鎖状エステル類へと変換できる。特に *o*-ニトロアリアル生成物は還元的環化反応へと供することで、モノテルペンインドールアルカロイド合成中間体のジヒドロピリド[1,2a]インドラロン類 (DHPIs) へと導けた。



1) S. Handa *et al.* *ChemSusChem*. **2019**, 12, 3037.

2) H. China, T. Dohi *et al.* *Asian J. Org. Chem.* **2015**, 4, 1065; *Russ. Chem. Bull.* **2020**, 69, 1804.

アカデミックプログラム [B講演] | 15. 有機化学—脂肪族・脂環式化合物, 新反応技術: 口頭B講演

2024年3月20日(水) 13:00 ~ 15:40 会 E1142(11号館 [4階] 1142)

**[E1142-3pm] 15. 有機化学—脂肪族・脂環式化合物, 新反応技術**

座長: 吉野 達彦、矢島 知子

## ◆ 英語

13:00 ~ 13:20

[E1142-3pm-01]

外輪型キラル二核ルテニウム触媒による分子間不斉ナイトレン移動型反応の開発

○牧野 思子<sup>1</sup>、桐生 昇一<sup>1</sup>、森 康平<sup>1</sup>、宮澤 拓<sup>1</sup>、熊谷 悠平<sup>1</sup>、東田 皓介<sup>2</sup>、小島 正寛<sup>1</sup>、吉野 達彦<sup>1</sup>、松永 茂樹<sup>1,2</sup> (1. 北大院薬、2. 京大院理)

## ◆ 英語

13:20 ~ 13:40

[E1142-3pm-02]

キラルπ-銅(II)錯体触媒によるイソキノリニウムイリドとα,β-エナミド及びα,β,γ,δ-ジエナミドの位置、配向、化学、エキソ及びエナンチオ選択的脱芳香族[3+2]環化付加反応

○郭 威威<sup>1</sup>、石原 一彰<sup>1</sup> (1. 名古屋大学)

## ◆ 英語

13:40 ~ 14:00

[E1142-3pm-03]

キラルスルフィド触媒によるプロモラクトン化を介したα位にアリル基とプロパルギル基を有するカルボン酸の速度論的光学分割

○奥野 研<sup>1</sup>、Bun Chan<sup>1</sup>、白川 誠司<sup>1</sup> (1. 長崎大学)

14:00 ~ 14:10

休憩

## ◆ 英語

14:10 ~ 14:30

[E1142-3pm-04]

10-Phenylphenothiazine-Catalyzed Bromo-Perfluoroalkylation of Unactivated Olefins

○Koto Tagami<sup>1,2</sup>, Dominique Cahard<sup>2</sup>, Tomoko Yajima<sup>1</sup> (1. Ochanomizu University, Japan, 2. CNRS, University of Rouen Normandy, France)

## ◆ 英語

14:30 ~ 14:50

[E1142-3pm-05]

N-ヘテロ環カルベン触媒によるラジカル-ラジカルカップリングを介したβ-アミドケトンのジアステレオ選択的合成

○佐藤 由季也<sup>1</sup>、隅田 有人<sup>2</sup>、大宮 寛久<sup>1</sup> (1. 京大化研、2. 医科歯科大生材研)

14:50 ~ 15:00

休憩

## ◆ 英語

15:00 ~ 15:20

[E1142-3pm-06]

## 亜硝酸エステルを用いる芳香族ニトロソ化反応とジアゾ化合物への誘導

○橋床 亜伊瑠<sup>1</sup>、中尾 優希<sup>1</sup>、北之園 拓<sup>1</sup>、山下 恭弘<sup>1</sup>、小林 修<sup>1</sup> (1. 東京大学)

---

◆ 英語

15:20 ~ 15:40

[E1142-3pm-07]

Development of biocompatible chiral scandium catalyst

○Watchara Srimontree<sup>1</sup>, Taku Kitanosono<sup>1</sup>, Yasuhiro Yamashita<sup>1</sup>, Shū Kobayashi<sup>1</sup> (1. Graduate School of Science, The University of Tokyo)

---

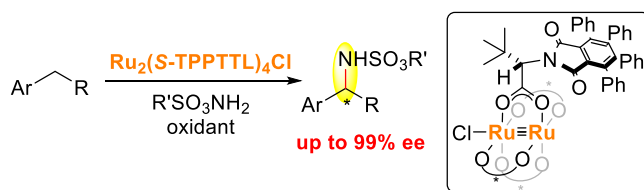
## Chiral Paddle-wheel Diruthenium Complexes for Catalytic Enantioselective Intermolecular Nitrene Transfer Reactions

(<sup>1</sup>Graduate School of Pharmaceutical Sciences, Hokkaido University, <sup>2</sup>Graduate School of Science, Kyoto University) ○ Kotoko Makino,<sup>1</sup> Shoichi Kiryu,<sup>1</sup> Kohei Mori,<sup>1</sup> Taku Miyazawa,<sup>1</sup> Yuhei Kumagai,<sup>1</sup> Kosuke Higashida,<sup>2</sup> Masahiro Kojima,<sup>1</sup> Tatsuhiko Yoshino,<sup>1</sup> Shigeki Matsunaga<sup>1,2</sup>

**Keywords:** Ruthenium catalysis, Asymmetric catalysis, Nitrene, C–H amination

Inspired by the chemistry of chiral paddle-wheel dirhodium complexes, we recently developed chiral paddle-wheel Ru(II)-Ru(III) catalysts.<sup>1</sup> We found that diruthenium complexes serve as more effective catalysts in nitrene transfer reactions, including intramolecular C–H amination reactions and aziridination. In pursuit of addressing more challenging nitrene transfer reactions, we directed our efforts to demonstrate the application of the diruthenium complex in intermolecular benzylic C–H amination reactions. The nitrene transfer reaction catalyzed by Rh(II) catalysts exhibited insufficient enantioselectivity, reaching up to 93% ee in previous reports.<sup>2</sup> We attributed the insufficient results to the limitation of enantiocontrol solely through ligand modification. As a novel approach, we explored the exchange of the central metal, presuming it to be an effective strategy to increase enantioselectivity.

To demonstrate the efficacy of diruthenium catalysts, we examined the enantioselective intermolecular benzylic C–H amination reactions. Through catalyst screening, we identified that the Ru(II)-Ru(III) catalyst bearing the new chiral ligand, (*S*)-TPPTTL,<sup>3</sup> provided remarkable enantioselectivity, reaching up to 99% ee. The improved enantioselectivity would be due to the narrower chiral environment and stronger interaction with a substrate compared with those of existing catalysts. Moreover, we found that the Ru catalyst achieved superior enantiocontrol compared to Rh catalysts under the same reaction conditions. Consequently, we indicated that the design of catalysts with a modified central metal has the potential to serve as an efficient strategy for improving the enantioselectivity.



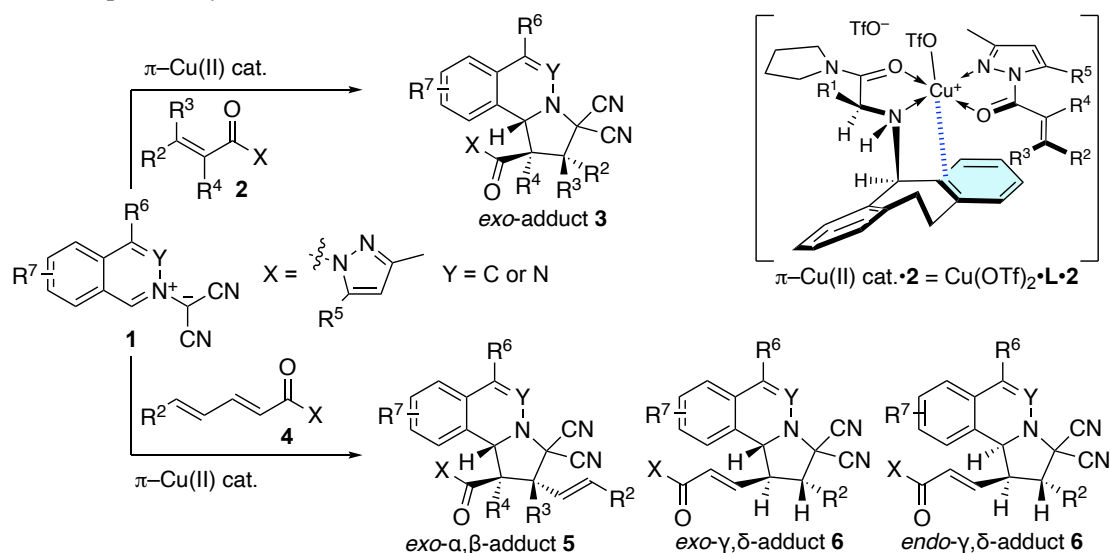
- 1) Miyazawa, T.; Suzuki, T.; Kumagai, Y.; Takizawa, K.; Kikuchi, T.; Kato, S.; Onoda, A.; Hayashi, T.; Kamei, Y.; Kamiyama, F.; Anada, M.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Nat. Catal.* **2020**, *3*, 851.
- 2) a) Fanourakis, A.; Williams, B. D.; Paterson, K. J.; Phipps, R. J. *J. Am. Chem. Soc.* **2021**, *143*, 10070.  
b) van den Heuvel, N.; Mason, S. M.; Mercado, B. Q.; Miller, S. J. *J. Am. Chem. Soc.* **2023**, *145*, 12377.
- 3) Fu, J.; Ren, Z.; Bacsá, J.; Musaev, D. G.; Davies, H. M. L. *Nature* **2018**, *564*, 395.

# Chiral $\pi$ -Cu(II) Complex-catalyzed Site-, Regio-, Chemo- and Enantioselective Dearomative [3+2] Cycloaddition of Isoquinolinium ylides with $\alpha,\beta$ -Enamides and $\alpha,\beta,\gamma,\delta$ -Dienamides

(Graduate School of Engineering, Nagoya University) ○Weiwei Guo, Kazuaki Ishihara

**Keywords:** Asymmetric Catalysis; [3+2] Cycloaddition; Enantioselective; Site-selective; Remote Control

In our group, we have studied to develop enantioselective reactions catalyzed by  $\pi$ -Cu(II) complexes, which are prepared from  $\text{CuX}_2$  and L-amino acid-derived amides (mono-peptides) *in situ*.<sup>1)</sup> Here, we report a highly effective chiral  $\pi$ -Cu(II) complex-catalyzed dearomative [3+2] cycloaddition reaction of isoquinolinium ylides with  $\alpha,\beta$ -enamides and  $\alpha,\beta,\gamma,\delta$ -dienamides in site-, regio-, chemo-, exo- and enantioselective manners. Remote asymmetric control was realized in the [3+2] cycloaddition reactions of isoquinolinium ylides with  $\alpha,\beta,\gamma,\delta$ -dienamides. Besides, perfect  $\alpha,\beta$ -site-selectivity was observed in the enantioselective [3+2] cycloadditions with  $\delta$ -phenyl- $\alpha,\beta,\gamma,\delta$ -dienamides. Our method is applicable to various substrates including  $\alpha$ -substituted or  $\alpha,\beta$ -enamides which exhibit intrinsically low reactivity, and allows the synthesis of pyrroloisoquinoline derivatives with up to three chiral carbon centers, including those featuring fluorine and trifluoromethyl groups, as well as quaternary carbon centers.



## References

For recent examples of  $\pi$ -Cu(II) catalysis, see: (a) W. Guo, M. Hori, Y. Ogura, K. Nishimura, K. Oki, T. Ikai, E. Yashima, K. Ishihara, *J. Am. Chem. Soc.* **2023**, *145*, 27080; (b) L. Yao, K. Takeda, K. Ando, K. Ishihara, *Chem. Sci.* **2023**, *14*, 2441; (b) K. Nishimura, Y. Ogura, K. Takeda, W. Guo, and K. Ishihara, *Org. Lett.* **2022**, *24*, 7685. (c) K. Nishimura, Y. Wang, Y. Ogura, J. Kumagai, K. Ishihara, *ACS Catal.* **2022**, *12*, 1012.

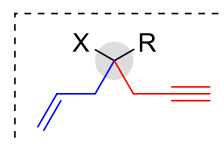
## Kinetic Resolution of $\alpha$ -Allyl- $\alpha$ -Propargyl Carboxylic Acids via Chiral Sulfide-Catalyzed Bromolactonization

(<sup>1</sup>Graduate School of Fisheries and Environmental Sciences, Nagasaki University, <sup>2</sup>Graduate School of Engineering, Nagasaki University) ○Ken Okuno,<sup>1</sup> Bun Chan,<sup>2</sup> Seiji Shirakawa<sup>1</sup>

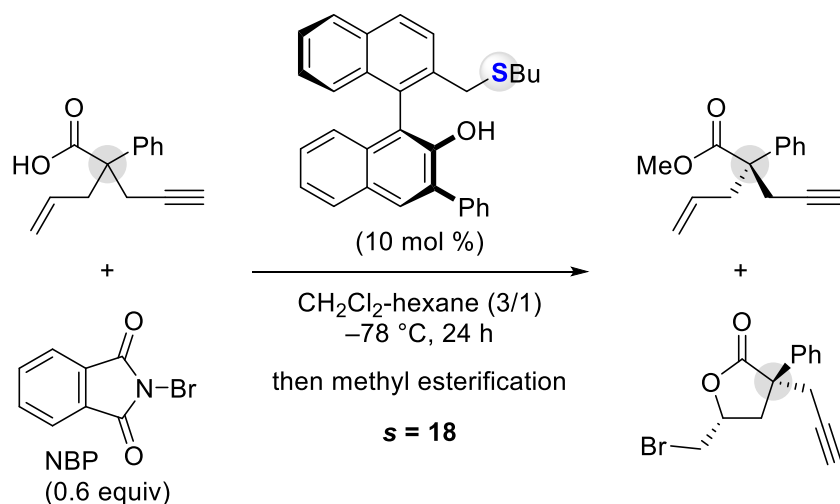
**Keywords:** Asymmetric Catalysis; Carboxylic Acids; Kinetic Resolution; Lactones; Organocatalysis

Kinetic resolution of racemic compounds is one of the most important methods to prepare optically active molecules. For efficient kinetic resolution, however, significant different substituents are generally required at a chiral center in substrates. Due to the difficulty in discriminating one of enantiomers, kinetic resolution of racemic molecules bearing similar substituents has remained a formidable challenge.

**Challenging substrate**  
for kinetic resolution



In this context, we became interested in the catalytic kinetic resolution of racemic compounds bearing both allyl and propargyl groups, which are similar but useful substituents, at a chiral center. Herein, we report our approach to achieving a kinetic resolution of  $\alpha$ -allyl- $\alpha$ -propargyl carboxylic acids bearing an all-carbon quaternary stereocenter via chiral bifunctional sulfide-catalyzed bromolactonization.<sup>1</sup>



1) K. Okuno, B. Chan, S. Shirakawa, *Adv. Synth. Catal.* **2023**, 365, 1496–1504.

## 10-Phenylphenothiazine-Catalyzed Bromo-Perfluoroalkylation of Unactivated Olefins

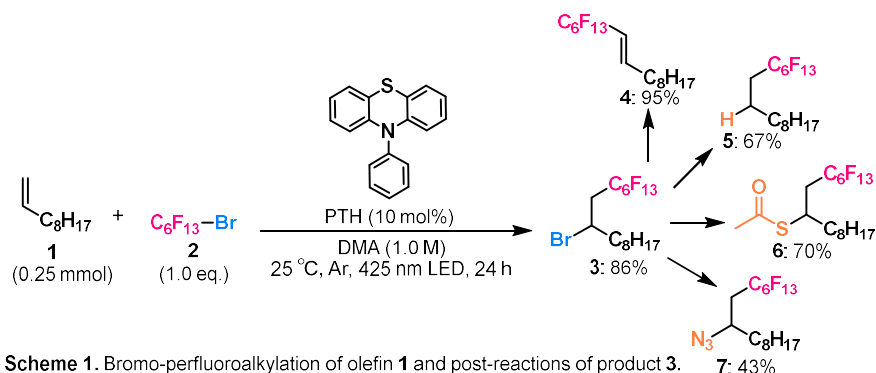
(<sup>1</sup> Graduate School of Humanities and Sciences, Ochanomizu University, Japan <sup>2</sup> UMR 6014 CNRS COBRA, University of Rouen Normandy, France)

○Koto Tagami,<sup>1,2</sup> Dominique Cahard,<sup>2</sup> Tomoko Yajima<sup>1</sup>

**Keywords:** Perfluoroalkylation; Bromination; Photocatalysis; Visible-light; Green Chemistry

Fluoroalkyl groups are one of the most important and common motifs for pharmaceuticals, agrochemicals, and functional materials; hence, the development of new synthetic methods for fluoroalkylation are highly desired. Specifically, radical perfluoroalkylations of simple olefins using commercially available perfluoroalkyl halides are useful methods for directly introducing long-chain perfluoroalkyl groups.<sup>1</sup> In recent years, sustainable transition metal-free photocatalysts have attracted great attention,<sup>2</sup> leading to the widespread development of visible-light induced radical perfluoroalkylations. During our own investigation, we have found that metal-free, visible-light induced bromo-perfluoroalkylation of unactivated olefins proceeds smoothly in the presence of 10-phenylphenothiazine (PTH) as an organic photocatalyst.

To illustrate our work, the reaction of 1-decene (**1**) and perfluorohexyl bromide (**2**) yielded the bromoperfluoroalkylated product **3** in 86% yield. Furthermore, compound **3** can be post-functionalized to yield compounds **4–7** (Scheme 1).



**Scheme 1.** Bromo-perfluoroalkylation of olefin **1** and post-reactions of product **3**.

The presentation will include a detailed discussion of the reaction conditions, the scope of olefins and perfluoroalkyl bromides, and the reaction mechanism.

1) T. Liu, J. Liu, J. He, Y. Hong, H. Zhou, Y-L, Liu, S. Tang, *Synthesis*, **2022**, 54, 1919. 2) N. A. Romero, D. A. Nicewicz, *Chem. Rev.*, **2016**, 116, 10075. 3) N. J. Treat, H. Sprafke, J. W. Kramer, P. G. Clark, B. E. Barton, J. Read de Alaniz, B. P. Fors, C. J. Hawker, *J. Am. Chem. Soc.*, **2014**, 136, 16096.

## N-ヘテロ環カルベン触媒によるラジカル-ラジカルカップリングを介したβ-アミドケトンのジアステレオ選択的合成

(京大化研<sup>1</sup>・医科歯科大生材研<sup>2</sup>) ○佐藤 由季也<sup>1</sup>・隅田 有人<sup>2</sup>・大宮 寛久<sup>1</sup>

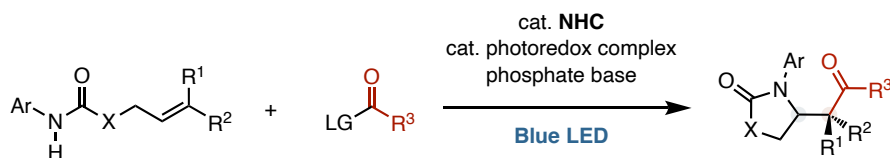
Diastereoselective Congested β-Amido Ketone Synthesis via NHC-Catalyzed Radical-Radical Coupling (<sup>1</sup> *Institute of Chemical Research, Kyoto University*, <sup>2</sup> *Institute of Biomaterials Bioengineering, Tokyo Medical and Dental University*) ○Yukiya Sato,<sup>1</sup> Yuto Sumida,<sup>2</sup> Hirohisa Ohmiya<sup>1</sup>

N-Heterocyclic carbene catalysis merging with photoredox PCET enabled amidoacylation of alkenes to construct sterically congested cyclic β-amido ketone skeleton bearing α-tertiary or quaternary carbon centers with high diastereoselectivity. The reaction involves generating amidyl radicals via oxidative PCET under photoredox catalysis, followed by rapid intramolecular cyclization to form the carbon-centered radical. The precise control of electron transfer in the two radical generation mechanisms is required to achieve this diastereoselective radical-radical coupling.

**Keywords :** *N-Heterocyclic Carbene; PCET; Radical Radical Coupling; Photoredox Catalyst*

含窒素環状・鎖状化合物は、天然物や医薬品にみられる重要な骨格である。近年、光駆動型プロトン共役電子移動 (PCET) を利用した窒素中心ラジカルの発生、続く環化反応に基づく含窒素化合物の合成法が報告されている。これらの手法は、温和な条件下、窒素中心ラジカルにアクセスできることから、直截的かつ官能基許容性に優れた手法である。しかし、用いる塩基や基質の結合解離エネルギー、触媒の酸化還元電位などのさまざまな要因に支配されるため反応制御が困難である。

このような背景のもと、我々は、可視光駆動型 PCET に基づく N-ヘテロ環カルベン (NHC) 触媒系を用いた、アルケンのアミドアシル化反応を開発した<sup>1)</sup>。可視光照射下、光酸化還元触媒と塩基を用いることで、分子内にアルケンをもつアミド化合物の窒素中心にラジカルが発生する (酸化的 PCET 過程)。生じた窒素中心ラジカルは、分子内環化を速やかに引き起こし、アルキルラジカルを与える。一方で、アシルイミダゾールと NHC 触媒から生じるアシルアゾリウム中間体の光酸化還元触媒による一電子還元により、ケチルラジカルが生じる。これら各々の触媒サイクルから生じた 2 種類の異なるラジカル (アルキルラジカルとケチルラジカル) が交差ラジカルカップリングを起こすことで、かさ高い β-アミドケトン体がジアステレオ選択的に得られる。



1) Sato, Y.; Miyamoto, Y.; Matsui, T.; Sumida, Y.; Ohmiya, H. *Chem. Catal.* **2023**, 3, 100736.



## Acid-free Aromatic Nitrosation Using Organic Nitrite toward Diazotization

(School of Science, The Univ. of Tokyo) ○ Airu HASHIDOKO, Yuki NAKAO, Taku KITANOSONO, Yasuhiro YAMASHITA, Shū KOBAYASHI

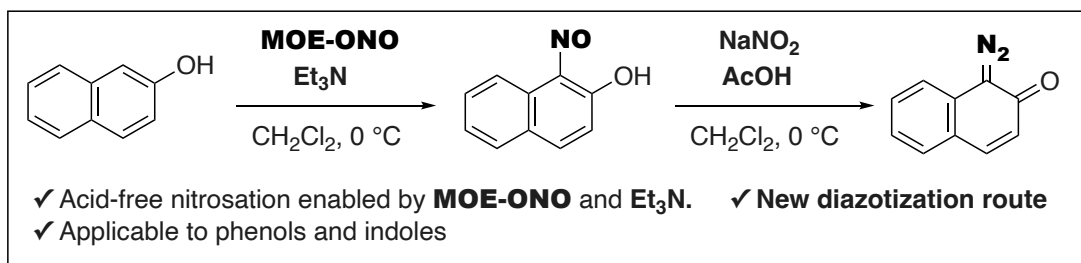
**Keywords:** Organic Nitrite; NO Cation; Nitrosation; Triethylamine; Diazotization

Aromatic compounds with nitrogen-containing functional groups comprise one of the most important classes of compounds. Among them, we focused on nitroso compounds due to their limited exploration and synthetic challenges. There is room for improvements in aromatic nitrosation through electrophilic substitution reaction, as it requires a large amount of acid for the formation of NO cation, the active species.

In this study, we present an acid-free aromatic nitrosation reaction utilizing 2-methoxyethyl nitrite (MOE-ONO) that was developed in our laboratory. It efficiently generates NO<sub>x</sub> radicals under mild conditions for several C–N bond forming reactions.<sup>1</sup> Here, we leverage its ability to serve as an NO cation source.

To achieve this, competing side reactions caused by NO<sub>x</sub> radicals should be suppressed. Through careful investigation, we found that the addition of triethylamine effectively suppressed unwanted nitration caused by NO<sub>x</sub> radicals, to afford the desired nitroso compounds in good yields. Notably, replacing MOE-ONO with *tert*-butyl nitrite, a common organic nitrite, gave no desired product at all. To elucidate these intriguing reactivities, we conducted several control experiments and spectrometric analyses.

Furthermore, the obtained nitroso compounds were successfully converted into the corresponding diazo compounds in good yields. This series of transformations were applicable to various phenols, enabling a novel diazotization process through readily accessible nitrosophenols as intermediates. In this presentation, we will delve into the details of this study.



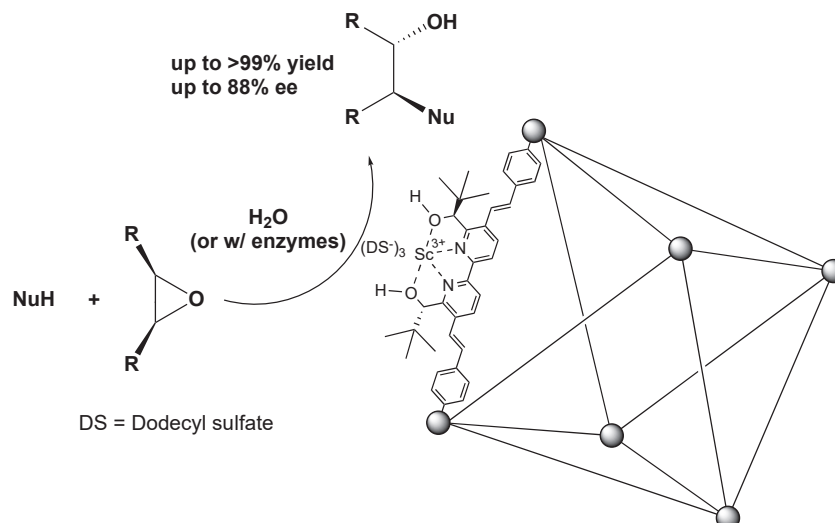
- 1) Kitanoosono, T.; Hashidoko, A.; Yamashita, Y.; Kobayashi, S. *Chem. Asian J.* **2022**, *17*, e202200457.

## Development of Biocompatible Chiral Scandium Catalyst

(School of Science, The Univ. of Tokyo) ○Watchara SRIMONTREE, Taku KITANOSONO, Yasuhiro YAMASHITA, Shū KOBAYASHI

**Keywords:** Lewis Acid Catalyst; Metal-Organic Framework; Asymmetric Synthesis; Reaction in Water; Biocompatible Reaction

Biocompatible reactions using Lewis acid catalysts are highly challenging, as controlling non-toxicity, selectivity, and side reactions in biological environments is difficult.<sup>1</sup> To address this, we propose a new biocompatible catalyst based on a chiral 4,4'-[2,2'-bipyridine]-5,5'-diylbis(ethene-2,1-diyl)dibenzoic acid (H<sub>2</sub>BPVB) immobilized on a UiO-67 (BPY)-type MOF. This water-stable Sc-MOF was synthesized through post-synthetic modification with scandium dodecyl sulfate.<sup>2</sup> Even with low catalyst loading, it effectively catalyzed asymmetric ring-opening reactions of epoxides in water, demonstrating a broad substrate scope, excellent yields, and high enantioselectivities. Furthermore, the new catalyst exhibits excellent reusability and tolerates well in the presence of glutathione and proteins, with minimal leaching of Lewis acid species. Finally, our strategy for designing and synthesizing water-stable chiral MOFs opens the door to a diverse range of MOFs are suitable for various asymmetric organic reactions in water, including those with potential biomedical applications.



1) Inaba, H.; Kanamaru, S.; Arisaka, F.; Kitagawa, S.; Ueno, T. *Dalton Trans.* **2012**, 41, 11424–11427.

2) Kitanosono, T.; Lu, F.; Masuda, K.; Yamashita, Y.; Kobayashi, S. *Angew. Chem. Int. Ed.* **2022**, 61, e202202335.

アカデミックプログラム [B 講演] | 15. 有機化学—脂肪族・脂環式化合物，新反応技術：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 E1143(11号館 [4階] 1143)

**[E1143-3vn] 15. 有機化学—脂肪族・脂環式化合物，新反応技術**

座長：山下 恭弘、野上 敏材

## ◆ 英語

15:55 ~ 16:15

[E1143-3vn-01]

マイクロフロー装置によるビニルモノマーのシークエンスオリゴマー合成

○ユ ドウン<sup>1</sup>、岡本 和紘<sup>1</sup>、吉岡 里佳子<sup>1</sup>、中里 遼平<sup>1</sup>、芦刈 洋祐<sup>1</sup>、永木 愛一郎<sup>1</sup> (1. 北海道大学)

## ◆ 英語

16:15 ~ 16:35

[E1143-3vn-02]

三成分連結反応を基盤とするペプチド鎖高速伸長法の開発

○杉澤 直斗<sup>1</sup>、安東 章<sup>1</sup>、布施 新一郎<sup>1</sup> (1. 名大院創薬)

## ◆ 英語

16:35 ~ 16:55

[E1143-3vn-03]

不均一系酸触媒を用いる連続フローエポキシド・アジリジン開環反応

○西澤 健<sup>1</sup>、齋藤 由樹<sup>1</sup>、小林 修<sup>1</sup> (1. 東京大学)

## ◆ 英語

16:55 ~ 17:15

[E1143-3vn-04]

マイクロフローリアクター中でのアシルアンモニウム/ピリジニウムイオンによるH-ホスホネートの化学選択的アシル化反応の開発

○北村 宙士<sup>1</sup>、布施 新一郎<sup>1</sup> (1. 名大院創薬)

## マイクロフロー装置によるビニルモノマーのシーケンスオリゴマー合成

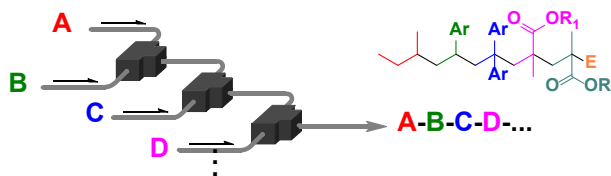
(北大院理) ○YOO Dong-eun・岡本 和紘・吉岡 里佳子・中里 遼平・芦刈 洋祐・永木 愛一郎

Sequenced oligomerization of vinyl monomers using microflow system (*Faculty of Science, Hokkaido University*) ○ Dong-eun Yoo, Kazuhiro Okamoto, Rikako Yoshioka, Ryohei Nakasato, Yosuke Ashikari, and Aiiciro Nagaki

Completely sequenced polymerization of diverse series of monomers has been recognized as an ultimate way for the synthesis of artificially sequenced molecules having functions comparable to biological molecules such as proteins, nucleic acids, and sugars. However, efficient synthesis of such macromolecules by polymerization reactions has not been reported yet since it is difficult to control simultaneous initiation and one-by-one propagation using multiple monomers. Utilizing features of our flow microreactor system for fast addition of one monomer to the anionic initiator followed by the fast quenching, we have achieved selective anionic mono-addition of vinyl monomers with an organolithium initiator. The controlled initiation also enabled further sequenced molecular control with one-to-one correspondence. Thus, we have achieved mono-addition of the initiator and the vinyl monomer followed by controlled oligomerization with another monomer into the sequenced molecule. Further introduction of functional groups into the living termini of the sequenced molecules has also been achieved by quenching with various electrophiles. The present method provides an innovative approach to the synthesis of artificial sequenced units attached to the oligomer units with precise microflow control.

**Keywords:** *flow microreactor; anionic polymerization; flash reaction; sequenced oligomer*

多様なモノマーを用いる完全配列制御されたポリマーの合成はタンパク質、核酸、糖鎖などの生体分子に匹敵する機能を獲得可能な人工シーケンス分子の合成を可能にする究極の方法である。しかし一斉に開始反応を起こし、続いて異なるモノマーを一分子ずつ生長反応へと組み込むことができないため、重合反応によってそのような高分子を効率的に合成することは未だ報告されていない。我々はフローマイクロリアクターの特徴を活用したアニオン性開始剤に対するモノマーの速い付加反応と続く速い反応停止により、有機リチウム開始剤を用いたビニルモノマーのアニオン性選択的モノ付加反応を達成した。開始反応の制御はさらなる1対1対応の分子配列制御を可能にし、開始剤とビニルモノマーのモノ付加の後、別のモノマーをオリゴマーとして導入することも可能である。重合末端に対して様々な求電子試薬を用いた反応停止により、さらなる官能基の導入も達成した。本手法はオリゴマーユニットと人工的な配列制御分子ユニットとを併せ持つ画期的な分子を合成する方法を提供する。



## Development of rapid peptide chain elongation *via* a three-component coupling approach

(Graduate School of Pharmaceutical Sciences, Nagoya University) ○Naoto Sugisawa, Akira Ando, Shinichiro Fuse

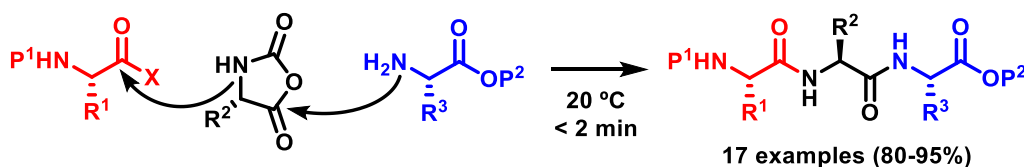
**Keywords:** Micro-flow;  $\alpha$ -Amino Acid *N*-Carboxy Anhydride; Peptide; Acylation; Leuchs Method

Peptides have attracted attention as drugs and drug candidates. The most conventional peptide chain elongation repeats 1) coupling of an activated N-terminus-protected amino acid with N-terminus-free amino acid (or peptide). 2) removal of the N-terminus protecting group. This leads to increase in number of reaction steps and a large amount of waste derived from coupling agents (DCC: 206, HATU: 380, COMU: 428) and protecting groups (Fmoc: 223, Cbz: 135, Boc: 105).

$\alpha$ -Amino acid *N*-carboxy anhydride ( $\alpha$ -NCA) is a cyclic compound that has both nucleophilicity and electrophilicity. Three-component coupling (3CC) using  $\alpha$ -NCA, activated N-terminus-protected amino acid, and C-terminus-protected amino acid is an ideal approach for peptide chain elongation because it can skip the purification of intermediates and deprotection steps. Although the step-wise peptide chain elongation approaches using  $\alpha$ -NCA have been reported, they are rarely used due to difficulty in suppressing undesired oligomerization/polymerization of labile  $\alpha$ -NCA.

Micro-flow technologies allow precise control of both the reaction time and temperature. Our group reported rapid and mild synthetic approaches of NCA and its derivatives using micro-flow technologies.<sup>1-3</sup> We successfully suppressed the undesired reactions by rapid mixing of micro-flow technology and realized the one-flow, rapid and mild 3CC approach.<sup>4</sup> The key to success was the rapid generation of amino acid chloride and its coupling with  $\alpha$ -NCA in the presence of *i*-Pr<sub>2</sub>NEt and *N*-methylimidazole. The developed approach afforded structurally diverse 17 tripeptides in high to excellent yields (80-95%). The total synthesis of beefy meaty peptide (octapeptide) was achieved by repeating the 3CC approach.

developed approach    ☒ one-flow    ☒ no column chromatography



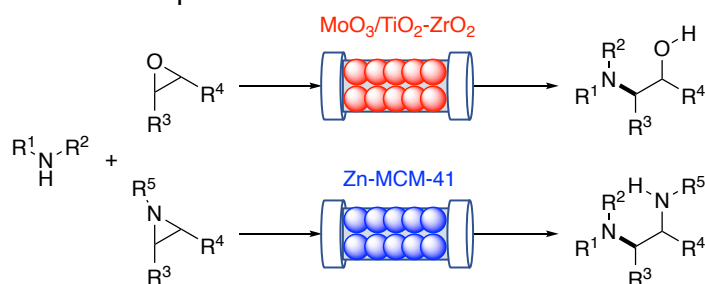
1) Y. Otake, H. Nakamura, S. Fuse, *Angew. Chem. Int. Ed.* **2018**, 57, 11389. 2) N. Sugisawa, Y. Otake, H. Nakamura, S. Fuse, *Chem. Asian J.* **2020**, 15, 79. 3) N. Sugisawa, H. Nakamura, S. Fuse, *Chem. Commun.* **2020**, 56, 4527. 4) N. Sugisawa, A. Ando, S. Fuse, *Chem. Sci.* **2023**, 14, 6986.

## Continuous-flow Aminolysis of Epoxides and Aziridines Utilizing Heterogeneous Catalysts

(School of Science, The Univ. of Tokyo) ○ Ken NISHIZAWA, Yuki SAITO, Shū KOBAYASHI

**Keywords:** Heterogeneous catalyst; Solid-acid catalyst; API synthesis; Continuous-flow reaction; Sequential-flow synthesis

Carbon–nitrogen (C–N) bonds are abundant in biologically active molecules, with over 80% of currently used APIs containing at least one.<sup>1</sup> Despite their prevalence, constructing C–N bonds often relies on substitution reactions such as reactions of haloalkanes and amines, resulting in problems such as overalkylation and generation of byproducts. These byproducts, often inorganic salts, are particularly problematic for continuous-flow reactions due to potential clogging.<sup>2</sup> In this work, we address these challenges by developing an aminolysis of epoxides and aziridines using heterogeneous acid catalysts. A different approach to C–N bond formation involves ring-opening of epoxides and their nitrogen analogues, aziridines, with amines. These reactions offer a compelling approach to synthesizing  $\beta$ -amino alcohols or 1,2-diamines with 100% atom economy, making them well-suited for continuous-flow systems. Given that previously reported methods often require aqueous or neat conditions,<sup>3</sup> efficient heterogeneous catalyst which can work even in organic solvent are crucial for optimal flow reactions. Although the traditional titania-zirconia ( $\text{TiO}_2$ - $\text{ZrO}_2$ ) showed low activity in the initial study, we discovered that highly acidic  $\text{MoO}_3$  supported on  $\text{TiO}_2$ - $\text{ZrO}_2$  displayed remarkable activity. This catalyst demonstrated broad substrate tolerance towards various amines and epoxides and was successfully applied in a sequential-flow synthesis of the precursor of rivaroxaban, an API for anticoagulant medication. Interestingly,  $\text{MoO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  showed no activity in the aminolysis of aziridines. This prompted further investigation into solid acid catalysts, culminating in the development of Zn(II) immobilized on mesoporous silica MCM-41 ( $\text{Zn-MCM-41}$ ). This catalyst exhibited exceptional activity and durability for aziridine activation. We will delve deeper into these recent advancements in this presentation.



1) Taylor, R.D. *et al. J. Med. Chem.* **2014**, 57, 5845.

2) Kobayashi, S. *et al. J. Org. Chem.* **2020**, 85, 5132.

3) Thirumalaikumar, M. *et al. Org. Prep. Proced. Int.* **2022**, 54, 1.

## Chemo-selective acylation of *H*-phosphonate with acyl ammonium / pyridinium ion in a micro-flow reactor

(<sup>1</sup>Graduate School of Pharmaceutical Sciences, Nagoya University)

○Hiroshi Kitamura,<sup>1</sup> Shinichiro Fuse<sup>1</sup>

**Keywords:** continuous-flow; *H*-phosphonate; acyl ammonium; phosphonoformate ester; phosphotriester

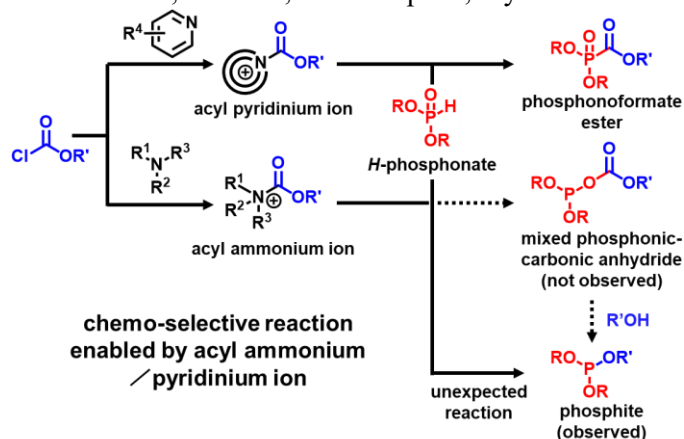
Organophosphorus compounds are useful as pharmaceuticals and agricultural chemicals. Phosphonoformate esters have been studied as prodrugs for HIV. Phosphotriesters have garnered much attention as oligonucleotide therapeutics, pesticides, flame retardants, and so on. *H*-Phosphonate is one of the most important building blocks for organophosphorus compounds. Therefore, a synthetic approach for phosphonoformate esters and phosphotriesters directly from *H*-phosphonates as common intermediates is attractive, however, there is no method that demonstrates chemo-selective synthesis of phosphonoformate esters and phosphotriesters directly from *H*-phosphonates.

Our group reported that acyl ammonium / pyridinium ion derived from chloroformate can preferably react with C-terminal and N-terminal of peptide, respectively<sup>1)</sup> presumably because of the difference of charge distribution. Then, we speculated that *in situ* generated acyl ammonium / pyridinium ion enabled chemo-selective acylation for syntheses of phosphonoformate esters and phosphotriesters from *H*-phosphonates. We utilized micro-flow technology which enables precise control of reaction conditions to avoid undesired reactions of unstable acyl ammonium / pyridinium ion.

We examined nucleophilic amines in the reaction of *H*-phosphonate with chloroformate. In the presence of base, chloroformate was activated with nucleophilic amines to afford acyl ammonium / pyridinium ion and they were reacted with *H*-phosphonate. Expectedly, acyl pyridinium ion afforded phosphonoformate ester, however, to our surprise, acyl ammonium ion did not afford mixed phosphonic-carbonic anhydride but afforded phosphite. As phosphite can be easily oxidized to the corresponding phosphotriester, we achieved chemo-selective syntheses for phosphonoformate ester and phosphotriester from *H*-phosphonate. Reaction mechanism was also studied.

1) Shamoto, O.; Komuro, K.;

Sugisawa, N.; Chen, T.-H.; Nakamura, H.; Fuse, S. *Angew. Chem. Int. Ed.* **2023**, 62, e202300647.



アカデミックプログラム [B講演] | 16. 天然物化学・ケミカルバイオロジー：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 H933(9号館 [3階] 933)

**[H933-3vn] 16. 天然物化学・ケミカルバイオロジー**

座長：深谷 圭介、西川 慶祐

## ◆ 英語

15:55 ~ 16:15

[H933-3vn-01]

生合成模倣渡環反応によるマンザミンアルカロイド型骨格の合成

○和山 稔明<sup>1</sup>、大栗 博毅<sup>1</sup> (1. 東京大学)

## ◆ 英語

16:15 ~ 16:35

[H933-3vn-02]

Keramaphidin BとIngenamineの全合成

○栗原 悠熙<sup>1</sup>、八木 みのり<sup>1</sup>、野口 嵩史<sup>1</sup>、安福 悠<sup>1</sup>、沖田 采音<sup>1</sup>、深谷 圭介<sup>2</sup>、占部 大介<sup>2</sup>、大石 毅<sup>3</sup>、千田 憲孝<sup>1</sup>、岡村 俊孝<sup>1</sup>、佐藤 隆章<sup>1</sup> (1. 慶大理工、2. 富山県大工、生医工研セ、3. 慶大医)

## ◆ 英語

16:35 ~ 16:55

[H933-3vn-03]

セコドラスタン型ジテルペン Isolinearol の合成研究

○鶴田 智暉<sup>1</sup>、吉野 優季花<sup>1</sup>、西川 慶祐<sup>1</sup>、森本 善樹<sup>1</sup> (1. 大阪公立大学)

## ◆ 日本語

16:55 ~ 17:15

[H933-3vn-04]

炭素連結型シアロ糖鎖の統一的合成を志向したC-グリコシル化反応の検討

○竹田 大樹<sup>1</sup>、寄立 麻琴<sup>1</sup>、的場 博亮<sup>1</sup>、平井 剛<sup>1</sup> (1. 九州大学大学院)



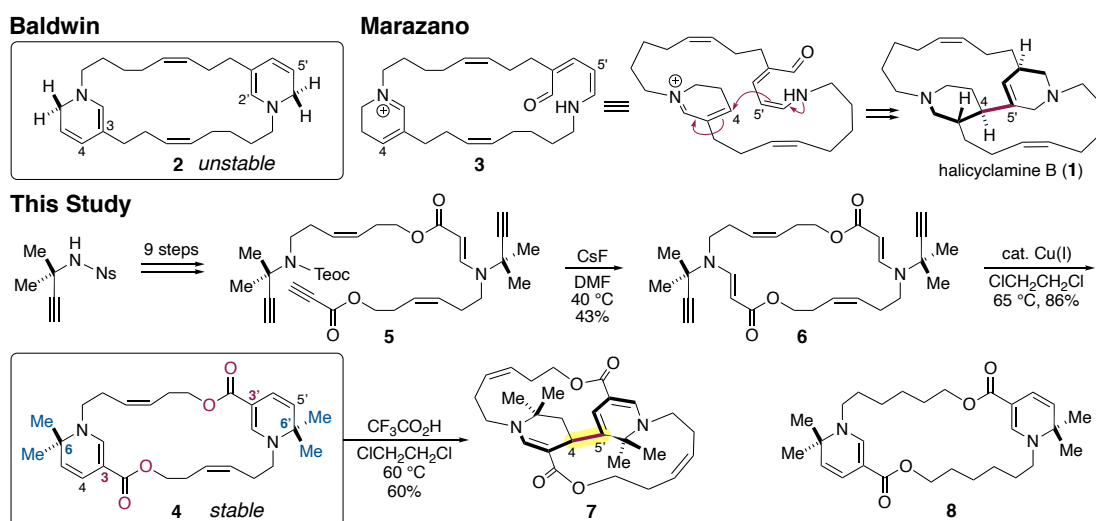
## Synthesis of a Manzamine Alkaloid-type Macrocyclic Scaffold via Biomimetic Transannular Cyclization of Dihydropyridines

(Graduate School of Science, The University of Tokyo) ○Toshiaki Wayama, Hiroki Oguri

**Keywords:** Manzamine Alkaloids; Dihydropyridine; Halicyclamine; Transannular Cyclization Reaction; Biomimetic Synthesis

Marine-derived manzamine alkaloids exemplified by manzamine A, halicyclamine B (**1**), and keramaphidin B exert anti-malarial and anti-tuberculosis activities.<sup>1</sup> The hypothetical biosynthetic pathway proposed by Baldwin and Whitehead involves a  $C_2$ -symmetric achiral macrocyclic intermediate **2** bearing 1,6-dihydropyridines (1,6-DHPs). Marazano postulated an alternative biosynthetic hypothesis, suggesting that intramolecular conjugate addition of intermediate **3** would yield the bicyclic scaffolds of halicyclamines such as **1**. Previous attempts for biomimetic transannular cyclizations of macrocyclic precursors relevant to manzamine alkaloids have been unsuccessful, primarily due to the instability of the biosynthetic intermediate **2**, which involves the disproportionation reaction of 1,6-DHPs.

The substantially stabilized  $C_2$ -symmetric precursor **4**, featuring both *gem*-disubstitution at C6 and electron-withdrawing group at C3 of 1,6-DHPs, was designed and synthesized through macrocyclization (**5**→**6**) via hetero-conjugate addition, followed by Cu(I)-catalyzed DHP formation. Biomimetic transannular cyclization of **4** proceeded with an exquisite control of regio-selectivity to form the halicyclamine-type macrocyclic scaffold **7** in 60% yield.<sup>2</sup> The *cis*-double bonds incorporated into the alkyl loops played a crucial role in achieving the biomimetic transannular cyclization, while such cyclization was unsuccessful with **8**, which has fully saturated alkyl chains. Further biomimetic synthetic efforts will be presented.



1) Arai, M.; Sobou, M.; Vilchéze, C.; Baughn, A.; Hashizume, H.; Pruksakorn, P.; Ishida, S.; Matsumoto, M.; Jacobs, W. R.; Kobayashi, M. *Bioorg. Med. Chem.* **2008**, *16*, 6732.

2) Wayama, T.; Arai, Y.; Oguri, H. *J. Org. Chem.* **2022**, *87*, 5938; Wayama, T.; Oguri, H. *Org. Lett.* **2023**, *25*, 3596.

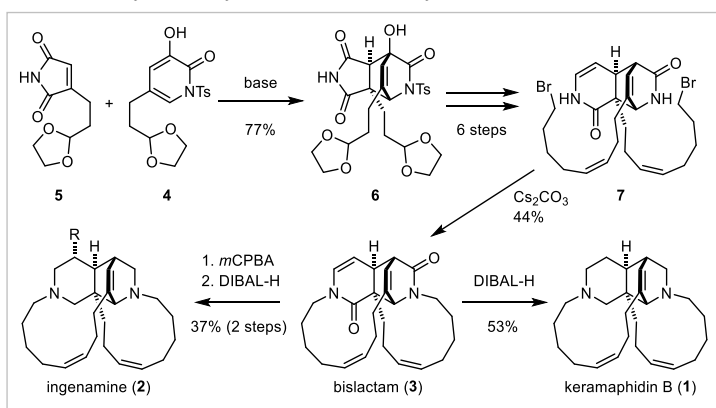
## Total Synthesis of Keramaphidin B and Ingenamine

(<sup>1</sup>Faculty of Science and Technology, Keio University, <sup>2</sup>School of Medicine, Keio University, <sup>3</sup>Biotechnology Research Center and Department of Biotechnology, Toyama Prefectural University) ○Yuki Kurihara,<sup>1</sup> Minoru Yagi,<sup>1</sup> Takashi Noguchi,<sup>1</sup> Haruka Yasufuku,<sup>1</sup> Ayane Okita,<sup>1</sup> Keisuke Fukaya,<sup>3</sup> Daisuke Urabe,<sup>3</sup> Takeshi Oishi,<sup>2</sup> Noritaka Chida,<sup>1</sup> Toshitaka Okamura,<sup>1</sup> Takaaki Sato<sup>1</sup>

**Keywords:** Total synthesis; Alkaloids; Keramaphidin; Diels-Alder reaction; Macrocyclization

Keramaphidin B (**1**) and ingenamine (**2**) are a member of the manzamine alkaloids, which share the two distinct macrocyclic amines.<sup>1</sup> They exhibit a wide range of biological activities including antimalarial and antituberculosis activities. In spite of their intriguing biological activities, their medicinal studies have been overlooked due to the structural complexity.<sup>2</sup> The synthesis of keramaphidin B (**1**) and ingenamine (**2**) requires solutions of two synthetic challenges: 1) the synthesis of a tricyclic skeleton, and 2) the construction of two macrocyclic amines. We envisioned bislactam **3** as a common intermediate for these two natural products. Two amide carbonyl groups were installed to the common intermediate to stabilize amine groups seen in natural products. In addition, the enamide group could become a handle to install the hydroxy group in the synthesis of ingenamine (**2**).

The first key reaction was the Diels-Alder reaction between 2-hydroxypyridone **4** and maleimide **5**. Base-catalyzed activation of the hydroxy group in **4** promoted the intermolecular Diels-Alder reaction, giving diazatricyclic framework **6** including a quaternary carbon center in 77% yield. Dibromide **7** was efficiently prepared through the two-directional synthesis by taking advantage of the pseudo structural symmetry. The second key reaction was the double macrocyclic alkylation. A solution of **7** was treated with Cs<sub>2</sub>CO<sub>3</sub> at room temperature, and then heated to 60 °C, providing bislactam intermediate **3** in 44% yield. Finally, epoxidation and DIBAL-H reduction of **3** achieved the total synthesis of keramaphidin B (**1**) and ingenamine (**2**).



- (1) (a) Kobayashi, J.; Tsuda, M.; Kawasaki, N. Matsumo, K.; Adachi, T. *Tetrahedron Lett.* **1994**, 35, 4383. (b) Kong, F.; Andersen, R. J. *Tetrahedron Lett.* **1994**, 35, 1643.  
 (2) (a) Baldwin, J. E.; Claridge, T. D. W.; Culshaw, A. J.; Heupel, F. A.; Lee, V.; Spring, D. R.; Whitehead, R. C.; Boughtflower, R. J.; Mutton, I. M.; Upton, R. J. *Angew. Chem. Int. Ed.* **1998**, 37, 2661. (b) Meng, Z.; Fürstner, A. *J. Am. Chem. Soc.* **2020**, 142, 11703. (c) Meng, Z.; Spohr, S. M.; Tobegen, S.; Farès, C.; Fürstner, A. *J. Am. Chem. Soc.* **2021**, 143, 14402.

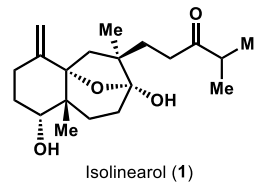
## Synthetic Studies on the Seco-Dolastane-Type Diterpene Isolinearol

( Graduate School of Science, Osaka Metropolitan University )

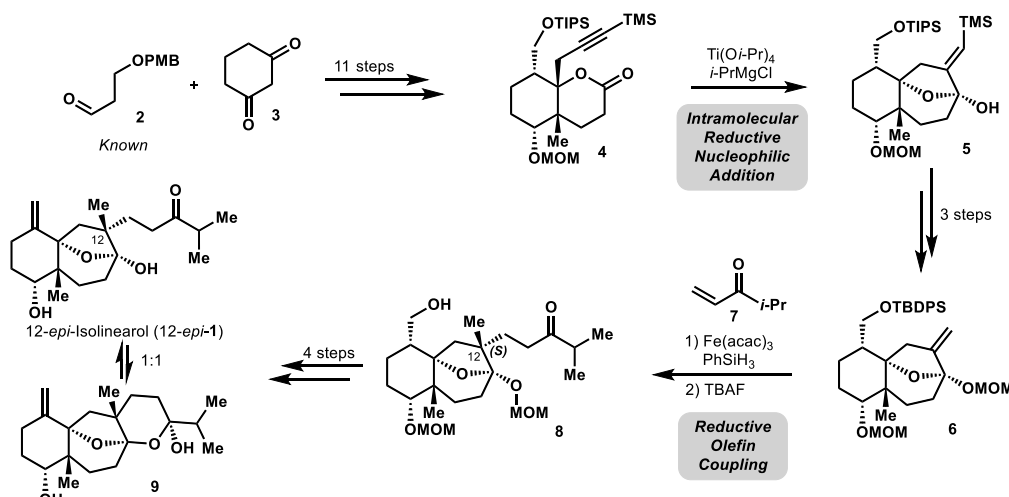
○Tomoki Tsuruta, Yukika Yoshino, Keisuke Nishikawa, and Yoshiki Morimoto

**Keywords:** Asymmetric Synthesis; Diterpenoid; Antifouling Activity; Intramolecular Reductive Nucleophilic Addition; Reductive Olefin-Coupling

Isolinearol (**1**) is the *seco*-dolastane-type diterpenoid isolated from the brown alga *Canistrocarpus cervicornis* in 1986 by Kelecom et al.<sup>1)</sup> The *trans*-bicyclo[5.4.0]undecane skeleton of **1** has a hemiketal bridge and five chiral centers. Isolinearol exhibits the potent antifouling activity against the mussel *Perna perna* without damaging the mussel.<sup>2)</sup> Its bioactivity could be expected to be applied to the development of environmentally friendly alternative antifoulings. We have been interested in the bioactivity evaluation and structure-activity relationships and embarked on the synthesis of **1**.



First, we synthesized the lactone **4** from the known aldehyde **2**<sup>3)</sup> and 1,3-cyclohexanedione (**3**). Treatment of **4** with a titanium tetraisopropoxide (  $\text{Ti}(\text{O}i\text{-Pr})_4$  ) and an isopropylmagnesium chloride (  $i\text{-PrMgCl}$  ) gave the hemiketal **5**, through an intramolecular reductive nucleophilic addition of a TMS-protected terminal alkyne to a lactone moiety.<sup>4)</sup> The hemiketal **5** was converted to the olefin **6** in three steps. Reductive olefin coupling of **6** and enone **7** using a ferric acetylacetonate (  $\text{Fe}(\text{acac})_3$  ) and a phenylsilane (  $\text{PhSiH}_3$  ),<sup>5)</sup> and the following desilylation provided the adduct **8** with (*S*)-configuration at C12. Finally, the three-step construction of the *exo*-olefin moiety and the following deprotection of MOM groups afforded a 1:1 equilibrium mixture of 12-*epi*-isolinearol (12-*epi*-**1**) and the tetracyclic hemiketal **9**. We are currently investigating the installation of a ketone side chain with the correct stereochemistry for **1**.



1) A. Kelecom et al. *J. Nat. Prod.* **1986**, 49, 570. 2) R. C. Pereira et al. *J. Appl. Phycol.* **2009**, 21, 341. 3) D. A. Evans et al. *J. Am. Chem. Soc.* **1990**, 112, 7001. 4) F. Sato et al. *J. Am. Chem. Soc.* **1996**, 118, 2208. 5) P. S. Baran et al. *J. Am. Chem. Soc.* **2017**, 139, 2484.

## 炭素連結型シアロ糖鎖の統一的合成を志向した C-グリコシル化反応の検討

(九大院薬) ○竹田 大樹、寄立 麻琴、的場 博亮、平井 剛

Investigation of C-glycosylation reactions oriented toward the unified synthesis of C-linked sialoglycans (Graduate School of Pharmaceutical Sciences, Kyushu University) ○ Daiki Takeda, Makoto Yoritate, Hiroaki Matoba, Go Hirai

Sialoglycans, which are glycans containing sialic acid at non reducing terminal, involve in a lot of biological phenomena. Previously, we reported synthetic methods for sialidase-resistant pseudo-ganglioside GM3 with a C-glycoside linkage through intramolecular Ireland-Claisen rearrangement reaction<sup>1</sup>. Despite its high efficiency for stereoselective C-glycoside formation, it required mutiple synthetic steps and applications to a different-type of pseudo-sialoglycans was difficult. This time, we planned and investigated intermolecular cross-coupling reaction with bicyclic sialic acid derivatives.

**Keywords :** Sialic acid; Sialoglycan; Intermolecular cross-coupling

シアロ糖鎖は、糖鎖の非還元末端にシアル酸を1分子以上もつ糖鎖の総称であり、多様な生命現象に関与している。当研究室ではシアロ糖鎖の1種であるガングリオシド GM3 の炭素連結型アナログの合成を報告した<sup>1</sup>。本分子の特長である炭素連結部の構築は、合成序盤の分子内転位反応(1→2)を基盤としており、後の変換に多工程を要する上、多様な擬シアロ糖鎖への適用は困難であった。そこで、分子間クロスカップリングを鍵反応とした炭素連結型擬シアロ糖鎖の合成法を立案、検討した。

大員環含有シアル酸<sup>2</sup>から得た Br 糖 3 や Cl 糖 4 をドナーとして、可視光還元クロスカップリング反応<sup>3</sup>の適用を試みたが、基質の還元や二量化が進行した。一方、低原子価金属を用いる還元的クロスカップリング<sup>4</sup>では、これらの副反応が抑制され、カップリング生成物を得ることに成功した。本発表ではこれらの詳細を報告する。

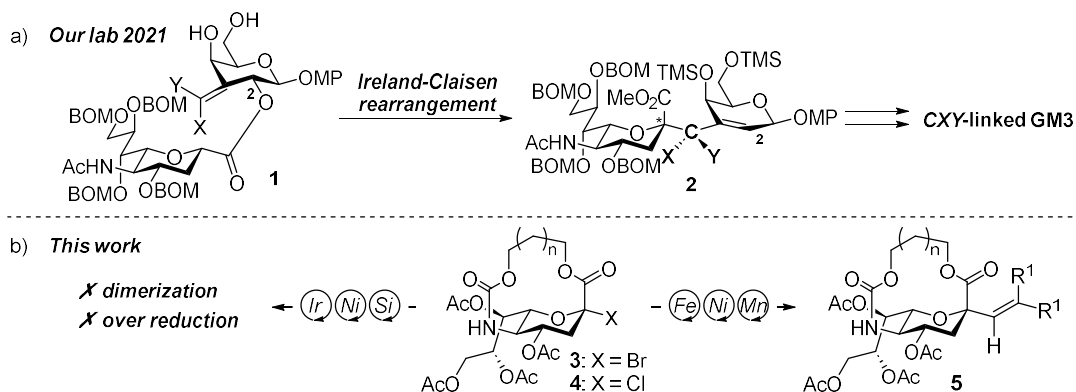


Fig 1. a) Previous synthetic method of C-sialoside via Ireland-Claisen rearrangement.

b) Intermolecular cross-coupling of sialic acid derivatives for direct C-glycosylation.

1) Hirai, G.; Sodeoka, M. *et al. JACS Au* **2021**, 1, 137.; 2) Ando, H. *et al. Science* **2019**, 364, 677.

3) Hirai, G. *et al. J. Am. Chem. Soc. in press.*; 4) Chen, G.; Koh, M. J. *et al. Nat. Synth.* **2022**, 1, 235.

アカデミックプログラム [B講演] | 16. 天然物化学・ケミカルバイオロジー：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 H935(9号館 [3階] 935)

## [H935-3vn] 16. 天然物化学・ケミカルバイオロジー

座長：小椋 章弘、松丸 尊紀

## ◆ 日本語

15:55 ~ 16:15

[H935-3vn-01]

システインホルミル化による標的タンパク質選択的切断法の開発と機能制御応用

○善明 直輝<sup>1</sup>、松本 侑也<sup>1</sup>、安田 斉弘<sup>1</sup>、内之宮 祥平<sup>1</sup>、進藤 直哉<sup>1</sup>、田畑 香織<sup>1</sup>、王子田 彰夫<sup>1</sup> (1. 九大院・薬)

## ◆ 英語

16:15 ~ 16:35

[H935-3vn-02]

多機能ナノ材料合成のためのクリッカブルな二反応性小型金ナノクラスター

○渡邊 賢司<sup>1</sup>、Mao Qiyue<sup>2</sup>、Zhang Zhouen<sup>1</sup>、畑 真知<sup>2</sup>、小寺 政人<sup>2</sup>、北岸 宏亮<sup>2</sup>、丹羽 節<sup>1,3,4</sup>、細谷 孝充<sup>1,4</sup> (1. 理化学研究所、2. 同志社大学、3. 九州大学、4. 東京医科歯科大学)

## ◆ 日本語

16:35 ~ 16:55

[H935-3vn-03]

ホスフィン酸リガンドに基づく低親和性  $\text{Ca}^{2+}$  蛍光プローブの開発と細胞内  $\text{Ca}^{2+}$  イメージングへの応用○坂間 亮浩<sup>1</sup>、熊田 怜<sup>1</sup>、新藤 豊<sup>2,3</sup>、黒沼 柚花<sup>1</sup>、岩澤 尚子<sup>1</sup>、チッテリオ ダニエル<sup>1</sup>、岡 浩太郎<sup>2,3,4,5</sup>、蛭田 勇樹<sup>1</sup> (1. 慶大理工・応化、2. 慶大理工・生命情報、3. 北里大未来工、4. 早大理工総研、5. 高雄医大・医)

## ◆ 英語

16:55 ~ 17:15

[H935-3vn-04]

Th2型バイアス型の糖脂質抗原の合成とCD1d-糖脂質複合体の機能解析

○末吉 耕大<sup>1</sup>、岸 惇一郎<sup>1</sup>、井貫 晋輔<sup>1,2</sup>、松丸 尊紀<sup>1</sup>、藤本 ゆかり<sup>1</sup> (1. 慶應義塾大学理工学部、2. 京都大学大学院薬学研究科)

## システインホルミル化による標的タンパク質選択的切断法の開発と機能制御応用

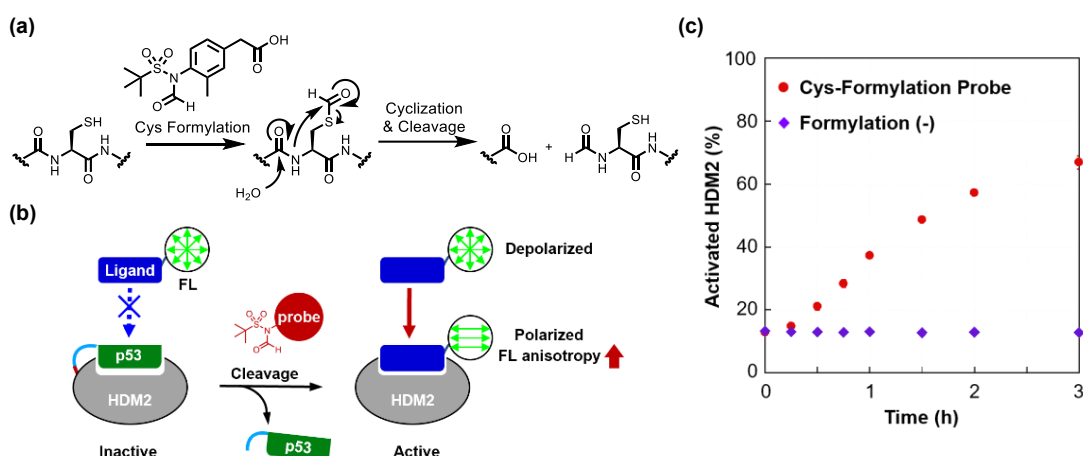
(九大院薬) ○善明 直輝、松本 侑也、安田 斉弘、内之宮 祥平、進藤 直哉、田畑 香織、王子田 彰夫

Protein Chemical Cleavage by Cysteine Formylation for Functional Regulation (*Graduate School of Pharmaceutical Science, Kyushu University*) ○Naoki Zenmyo, Yuya Matsumoto, Akihiro Yasuda, Shohei Uchinomiya, Naoya Shindo, Kaori Tabata, Akio Ojida

In functional analysis of proteins, chemical modification with small molecule is useful for function analysis and regulation of protein of interest (POI). Although a number of selective protein labeling method have been reported, chemical protein cleavage method has been poorly developed. Recently, We found that formylation of Cysteine residue induces cleavage of amide bond of peptide backbone. In this method, we evaluated the sequence selectivity and found that Asp-Cys and Asn-Cys sequence were cleaved in high efficiency. We also achieved site-selective cleavage and functional regulation of proteins by using formylation affinity probe.

**Keywords :** Protein Cleavage, Chemical Modification, Warhead, Cysteine Formylation, Functional Regulation

タンパク質を低分子により化学的に修飾する手法は、標的タンパク質の機能化・機能制御が可能であり、タンパク質研究において広く利用されている。一方、タンパク質配列を化学的に切断して、その機能を制御する報告は限られている。最近当研究室では、システイン側鎖を *S*-ホルミル化することでタンパク質配列主鎖のペプチド結合切断が誘起される手法を見出した。本手法についてモデルペプチドを用いた配列選択性の検討を行い、Asp-Cys 配列および Asn-Cys 配列を有する基質で切断反応が効率的に進行することを明らかにした。さらに、*S*-ホルミル化反応分子の反応性調節により標的タンパク質選択的な切断法に適用し、In Vitro での活性化を含む機能制御および細胞表層上でのアフィニティー化学切断への応用を行った。



(a) Plausible Mechanism of Protein Cleavage by Cys Formylation. (b, c) Functional regulation of p53 domain fused HDM2 using chemical cleavage with cysteine formylation probe.

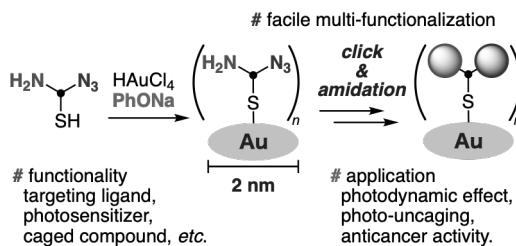
## 多機能ナノ材料合成のためのクリッカブルな 二反応性小型金ナノクラスター

(理研 BDR<sup>1</sup>・同志社大理工<sup>2</sup>・九大院薬<sup>3</sup>・医科歯科大生材研<sup>4</sup>) ○渡邊 賢司<sup>1</sup>, Qiyue Mao<sup>2</sup>, Zhouen Zhang<sup>1</sup>, 畑 真知<sup>2</sup>, 小寺 政人<sup>2</sup>, 北岸 宏亮<sup>2</sup>, 丹羽 節<sup>1,3,4</sup>, 細谷 孝充<sup>1,4</sup>  
Clickable bisreactive small gold nanoclusters for preparing multifunctionalized nanomaterials (<sup>1</sup>RIKEN BDR, <sup>2</sup>Fac. Sci. Eng., Doshisha Univ., <sup>3</sup>Grad. Sch. Phar. Sci., Kyusyu Univ., <sup>4</sup>IBB, Tokyo Med. & Dent. Univ.) ○Kenji Watanabe<sup>1</sup>, Qiyue Mao<sup>2</sup>, Zhouen Zhang<sup>1</sup>, Machi Hata<sup>2</sup>, Masahito Kodera<sup>2</sup>, Hiroaki Kitagishi<sup>2</sup>, Takashi Niwa<sup>1,3,4</sup>, Takamitsu Hosoya<sup>1,4</sup>

Metal nanoparticles bearing two different connecting groups are important intermediates in the synthesis of multifunctional nanomaterials. We have succeeded in synthesizing small gold nanoclusters (2 nm) bearing azido and amino groups through the reduction of tetrachloroauric(III) acid with sodium phenoxide in the presence of tripeptide thiol. The resulting bisreactive gold nanoclusters were conjugated with an anticancer compound connected to an indolizine moiety for photoinduced uncaging, a photodynamic therapy agent acting as a photosensitizer for uncaging. The significant phototoxicity exhibited by the gold nanoclusters underscores the potential utility of this method in advanced synthesis of anticancer nanomaterials.

**Keywords:** Gold nanoclusters; Azide; Amine; Click reaction; Uncaging

従来のアジド基を持つ金ナノクラスターの合成では、アジド基を持つチオールが存在下、塩化金(III)酸を水素化ホウ素ナトリウムで還元する方法が用いられる。しかし、本法では塩化金(III)酸の強いルイス酸性のため、アジド基の大部分がアミノ基に還元される。このため、アジド基とアミノ基を均等に金ナノクラスター上に配列することが困難であった。我々は、アジド基、アミノ基およびチオール基を持つトリペプチドの存在下、ナトリウムフェノキシドを用いて塩化金(III)酸を還元すると、アジド基を損なうことなく金ナノクラスターが得られることが見出した<sup>1)</sup>。この二反応性ナノクラスターを用いることで、赤色光照射で抗がん剤を放出するインドリジン化合物<sup>2)</sup>や光増感剤、ターゲティングリガンなど様々な機能性分子を金ナノクラスターに簡便に導入することができた。最後に、これらの金ナノクラスターの抗がん活性をヒト肺がん由来A549細胞を用いて検証し、赤色光照射により顕著な細胞毒性を示すことを明らかにした。



1) K. Watanabe, Q. Mao, Z. Zhang, M. Hata, M. Kodera, H. Kitagishi, T. Niwa, T. Hosoya, *Chem. Sci.* **2024**, advance article, doi.org/10.1039/D3SC04365G.

2) K. Watanabe, N. Terao, I. Kii, R. Nakagawa, T. Niwa, T. Hosoya, *Org. Lett.* **2020**, 22, 5434; K. Watanabe, N. Terao, T. Niwa, T. Hosoya, *J. Org. Chem.* **2021**, 86, 11822; K. Watanabe, A. Kuratsu, D. Hashizume, T. Niwa, T. Hosoya, *Commun. Chem.* **2022**, 5, 91.

## ホスフィン酸リガンドに基づく低親和性 $\text{Ca}^{2+}$ 蛍光プローブの開発と細胞内 $\text{Ca}^{2+}$ イメージングへの応用

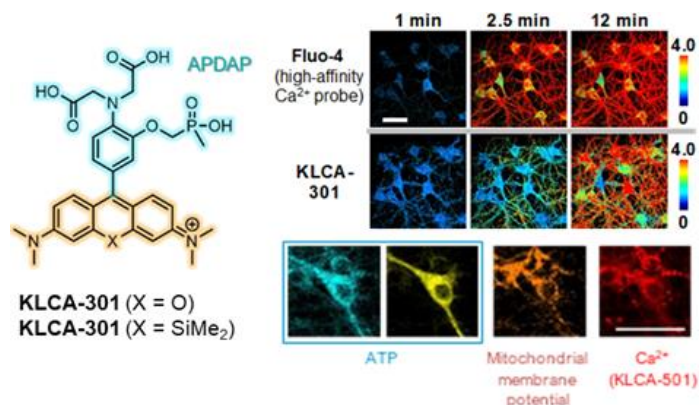
(慶大理工・応化<sup>1</sup>、慶大理工・生命情報<sup>2</sup>、北里大未来工<sup>3</sup>、早大理工総研<sup>4</sup>、高雄医大・医<sup>5</sup>) ○坂間 亮浩<sup>1</sup>・熊田 怜<sup>1</sup>・黒沼 柚花<sup>1</sup>・新藤 豊<sup>2,3</sup>・岩澤 尚子<sup>1</sup>・チッテリオ ダニエル<sup>1</sup>・岡 浩太郎<sup>2,3,4,5</sup>・蛭田 勇樹<sup>1</sup>

Development of Phosphinate Ligand-Based Low-Affinity  $\text{Ca}^{2+}$  Fluorescent Probes and Application to Intracellular  $\text{Ca}^{2+}$  Imaging (<sup>1</sup>Dept. of Applied Chemistry, Keio Univ., <sup>2</sup>Dept. of Biosciences & Informatics, Keio Univ., <sup>3</sup>Sch. of Frontier Engineering, Kitasato Univ., <sup>4</sup>Waseda Research Institute for Science and Engineering, Waseda Univ., <sup>5</sup>Coll. of Medicine, Kaohsiung Medical Univ.) ○Akihiro Sakama,<sup>1</sup> Rei Kumada,<sup>1</sup> Yutaka Shindo,<sup>2,3</sup> Yuzuka Kuronuma,<sup>1</sup> Naoko Iwasawa,<sup>1</sup> Daniel Citterio,<sup>1</sup> Kotaro Oka,<sup>2,3,4,5</sup> Yuki Hiruta<sup>1</sup>

Divalent metal ions such as calcium ion ( $\text{Ca}^{2+}$ ) and magnesium ion ( $\text{Mg}^{2+}$ ) are essential for regulation of various cellular activities. In this research, we developed the rhodamine-type fluorescent probes KLCA-301 and KLCA-501 employing a phosphinate ligand APDAP<sup>1)</sup> as a target binding site. The applicability of KLCA series as low-affinity  $\text{Ca}^{2+}$  probes was indicated through the evaluation of fluorescence response to  $\text{Ca}^{2+}$  and intracellular  $\text{Ca}^{2+}$  imaging including the simultaneous visualization of the change in  $\text{Ca}^{2+}$  and ATP concentrations, and in mitochondrial inner membrane potential in neurons.<sup>2)</sup>

**Keywords :** Functional Fluorescent Probe; Cell Imaging; Calcium Ion

カルシウムイオン ( $\text{Ca}^{2+}$ ) やマグネシウムイオン ( $\text{Mg}^{2+}$ ) をはじめとする 2 価金属イオンは様々な細胞活動の調節に不可欠である。その濃度変化は多くの細胞機能に関係しており、即時的なモニタリングのための多様な蛍光プローブの開発が求められている。本研究では、標的結合部位としてホスフィン酸リガンド APDAP<sup>1)</sup> を用いたローダミン系蛍光プローブ KLCA-301 および KLCA-501 を開発した。 $\text{Ca}^{2+}$  に対する蛍光応答より、KLCA シリーズが低親和性  $\text{Ca}^{2+}$  プローブとして利用できることが示唆された。共染色した神経細胞のグルタミン酸刺激に対する蛍光応答を比較したところ、KLCA-301 は高親和性  $\text{Ca}^{2+}$  プローブ Fluo-4 では検出されなかった細胞内  $\text{Ca}^{2+}$  の二段階目の大きな上昇を可視化することができた。また、KLCA-501 を用い、神経細胞内の  $\text{Ca}^{2+}$  と ATP 濃度、ミトコンドリア内膜電位の変化のマルチカラーイメージングに成功した<sup>2)</sup>。



1) Walter, E. R. H.; Fox, M. A.; Parker, D.; Williams, J. A. G. *Dalton Trans.* **2018**, 47, 1879–1887.

2) Kumada, R.; Sakama, A.; Shindo, Y.; Kuronuma, Y.; Iwasawa, N.; Citterio, D.; Oka, K.; Hiruta, Y. *Anal. Chem.* **2023**, 95, 16683–166913.

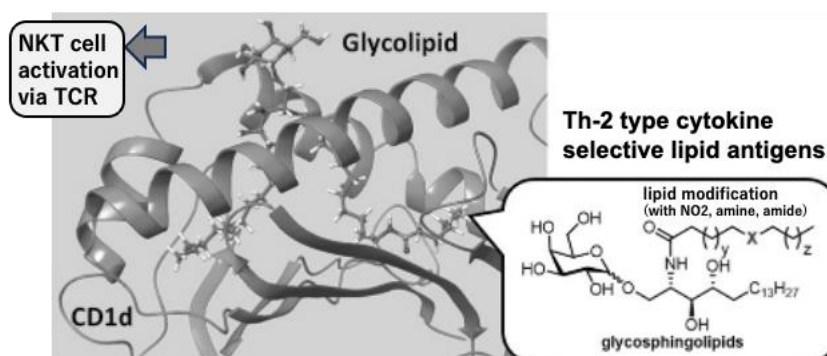


## Synthesis of Th2-biased glycolipid antigens and biofunctional analysis of the CD1d-glycolipid complexes

(<sup>1</sup>Faculty of Science and Technology, Keio University, <sup>2</sup>Graduate School of Pharmaceutical Sciences, Kyoto University) ○Kodai Sueyoshi,<sup>1</sup> Junichiro Kishi,<sup>1</sup> Shinsuke Inuki,<sup>1,2</sup> Takanori Matsumaru,<sup>1</sup> Yukari Fujimoto<sup>1</sup>

**Keywords:** Glycolipid; CD1d; Immunomodulation; Cytokines

On antigen presenting cells, CD1d recognizes lipid antigens to form complexes, leading to the activation of NKT cells and secretion of various cytokines to modulate the immune system. Through exploration of various CD1d ligands, we have previously revealed that binding affinity and cytokine secretion selectivity can be manipulated through modification of the lipid moiety of glycolipids.<sup>1</sup> In the present study, for further exploration of the functions of CD1d ligand antigens, we focused especially on Th2-biased glycolipids, and synthesized novel  $\alpha$ -GalCer derivatives and analyzed its functions. Namely, for modulation of the cytokine selectivity, acyl groups of the sphingolipids were modified with the nitro group. Nitrated unsaturated fatty acids were synthesized with highly *E*-selective method. These were then condensed with a glycolipid intermediate, prepared from D-galactose and phytosphingosine as previously reported,<sup>1</sup> to give the target  $\alpha$ -GalCer derivatives. Along with the previously reported amine and amide modified  $\alpha$ -GalCer structures,<sup>1a</sup> the biological activities of the synthesized nitrated  $\alpha$ -GalCer derivatives were evaluated through competitive binding affinity assays with the CD1d protein, antigen presenting cell (APC)-free assay and cytokine secretion assay using mouse splenocytes. The results showed that  $\alpha$ -GalCer derivatives with nitrated lipids exhibits increased binding to CD1d, and significant Th2-selective cytokine induction ability. MD simulations were also performed to analyze the motion of the ligand within the CD1d-ligand complex, and the results would be further discussed in the presentation.



- 1) a) Inuki, S.; Kashiwabara, E.; Hirata, N.; Kishi, J.; Nabika, E.; Fujimoto, Y. *Angew. Chem. Int. Ed.* **2018**, *57*, 9655. b) Kishi, J., Inuki, S., Kashiwabara, E., Suzuki, T., Dohmae, N., Fujimoto, Y. *ACS Chem. Biol.* **2020**, *15*, 353.

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 H932(9号館 [3階] 932)

**[H932-3am] 17. 生体機能関連化学・バイオテクノロジー**

座長：平山 祐、野中 洋

## ◆ 英語

9:00 ~ 9:20

[H932-3am-01]

近赤外蛍光性金属ナノプローブの開発と生体イメージングへの応用

○田中 慎一<sup>1</sup>、和達 大樹<sup>2</sup>、新岡 宏彦<sup>3</sup> (1. 呉工業高等専門学校、2. 兵庫県立大学、3. 大阪大学)

## ◆ 英語

9:20 ~ 9:40

[H932-3am-02]

腫瘍セラノスティクスを指向した抗がん剤複合化ガドリニウム酸化物ナノ粒子の合成

○王 星辰<sup>1</sup>、木村 祐<sup>1</sup>、今井 悠太<sup>1</sup>、三浦 理紗子<sup>1</sup>、今井 宏彦<sup>2</sup>、近藤 輝幸<sup>1</sup> (1. 京大院工、2. 京大院情報)

## ◆ 日本語

9:40 ~ 10:00

[H932-3am-03]

脳内リガンド指向性化学とクリックケミストリーの組み合わせによるグルタミン酸受容体の高速ラベル化戦略

○坂本 清志<sup>1,2</sup>、白岩 和樹<sup>1</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup> (1. 京大院工、2. JST ERATO)

## ◆ 日本語

10:00 ~ 10:20

[H932-3am-04]

生きたマウス脳内でのミクログリア選択的化学標識と機能解析への展開

○王 萌初<sup>1</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup> (1. 京都大学大学院工学研究科、2. JST ERATO)

10:20 ~ 10:30

休憩

## ◆ 英語

10:30 ~ 10:50

[H932-3am-05]

特定の酵素活性を持つ細胞選択的にclick to release 反応を起こす新規ケミカルツールの開発

○伊藤 廉<sup>1</sup>、神谷 真子<sup>2,3</sup>、浦野 泰照<sup>1,4</sup> (1. 東大院薬、2. 東工大院生命理工、3. 東京工業大学国際先駆研究機構、4. 東大院医)

## ◆ 英語

10:50 ~ 11:10

[H932-3am-06]

精密に設計された超偏極分子プローブ群を用いる複数のアミノペプチダーゼ活性の生体内同時検出

○谷田部 浩行<sup>1</sup>、斎藤 雄太郎<sup>1</sup>、高草木 洋一<sup>2,3</sup>、斎藤 圭太<sup>2</sup>、山本 和俊<sup>4</sup>、Murali Krishna<sup>4</sup>、山東 信介<sup>1</sup> (1. 東大院工、2. 量子科学技術研究開発機構、3. 千葉大院融合理工、4. 米国国立衛生研究所)

## ◆ 英語

11:10 ~ 11:30

[H932-3am-07]

ラマン分光法を用いた nectriatide の細胞内動態解析

○三宅 良介<sup>1</sup>、安藤 正浩<sup>2</sup>、小林 啓介<sup>3</sup>、供田 洋<sup>3</sup>、大城 太一<sup>3</sup>、竹山 春子<sup>1,2,4,5</sup> (1. 早大院・先進理工、2. 早大・ナノライフ創新研、3. 北里大院・薬、4. 産総研・早大CBBD-OIL、5. 早大・生命動態研)

---

## 近赤外蛍光性金属ナノプローブの開発と生体イメージングへの応用

(呉高専<sup>1</sup>・兵庫県大理<sup>2</sup>・阪大院情<sup>3</sup>) ○田中 慎一<sup>1</sup>・和達 大樹<sup>2</sup>・新岡 宏彦<sup>3</sup>

Near-Infrared Luminescent Platinum Nanoclusters for *in vivo* Imaging and Biomedical Application (<sup>1</sup>National Institute of Technology, Kure College, <sup>2</sup>Graduate School of Material Science, University of Hyogo, <sup>3</sup>Graduate School of Information Science and Technology, Osaka University) ○Shin-ichi Tanaka,<sup>1</sup> Hiroki Wadati,<sup>2</sup> Hirohiko Niioka<sup>3</sup>

Biomedical imaging has become an indispensable tool in the fields of cancer diagnosis and therapy. Our near-infrared (NIR) emitting (Em = 630 to 820 nm)<sup>1-3)</sup> (Fig. (a)) platinum (Pt) nanoclusters possessed low cytotoxicity and excellent photostability, and could be utilized as a fluorescent probe for highly sensitive optical imaging of cancer on both the cellular and the animal level. After conjugating with an antibody, Pt nanoclusters preferentially bounded on the surface of breast cancer cells (MDA-MB-231) (Fig. (b)) and can effectively be accumulated tumor tissues. Our NIR luminescent Pt nanoclusters promise to be a useful fluorescent probe for *in vivo* imaging and biomedical application.

**Keywords :** *platinum nanocluster; near-infrared light; in vivo imaging; cancer specificity; biomedical application*

癌診断・治療の研究を進めるためには、生体内で機能する生体分子の挙動について分子レベルで観察可能な生体計測技術が有効な手段となりうる。そこで、本研究では化学的に安定で毒性の少ない白金を用いて近赤外蛍光性(630～820 nm)<sup>1-3)</sup> (Fig. (a))白金ナノプローブを開発し、乳癌の転移活性化因子(PAR1) (Fig. (b))及び乳癌モデルマウスの癌組織の特異的標識に成功することで、本プローブの生体イメージングへの応用可能性を実証した。本計測技術を開発することによって、癌診断・治療や再生医療などの研究を飛躍的に発展できるだけでなく、未だに正確な理解が得られていない多くの生命システムの統合的理解についても期待される。

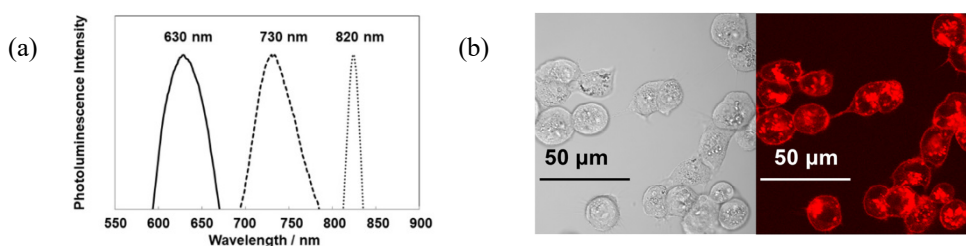


Figure (a) The luminescence spectra of the synthesized red to NIR emitting Pt nanoclusters, (b) brightfield (left) and confocal luminescence (right) images of living MDA-MB-231 cells incubated with anti-PAR1-red-emitting Pt nanoclusters.

- 1) S. Tanaka et al., *ACS Omega* **2020**, 5, 23718.
- 2) S. Tanaka et al. *Opt Mat Express*, **2013**, 3, 157.
- 3) S. Tanaka et al. *Angew Chem Int Ed*, **2011**, 50, 431.

## Synthesis of Anti-cancer Drug-conjugated Gadolinium Oxide Nanoparticles Directed toward Cancer Theranostics

(<sup>1</sup>Graduate School of Engineering and <sup>2</sup> Graduate School of Informatics, Kyoto University)

○Xingchen Wang,<sup>1</sup> Yu Kimura,<sup>1</sup> Yuta Imai,<sup>1</sup> Risako Miura,<sup>1</sup> Hirohiko Imai,<sup>2</sup> Teruyuki Kondo<sup>1</sup>

**Keywords:** Theranostics; Gadolinium Oxide; Photoacoustic Imaging; Magnetic Resonance Imaging; Anti-cancer Agent

Theranostics is emerged as a novel paradigm in clinical medicine that combines diagnostics and therapeutics into a single approach.<sup>1</sup> We have already developed gelatin-modified Gd<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) which are a dual photoacoustic (PA) / magnetic resonance (MR) imaging probe effective for diagnosis of cancer.<sup>2</sup> Based on these results, this study focused on widening potential of these nanoparticles by conjugation of two distinct anti-cancer drugs, respectively, as a theranostics probe for advanced cancers.

In this study, two kinds of typical anti-cancer drugs were conjugated to gelatin-modified Gd<sub>2</sub>O<sub>3</sub> NPs, respectively. First, doxorubicin hydrochloride (DOX), an intercalator at DNA strands, was conjugated with gelatin-coated Gd<sub>2</sub>O<sub>3</sub> NPs through electrostatic and hydrophobic interactions of DOX with gelatin. In addition, the conjugation of cisplatin (CDDP), a crosslinker of DNA bases, with gelatin-coated Gd<sub>2</sub>O<sub>3</sub> NPs through the coordination of functional groups in gelatin to platinum was also successful. These two kinds of novel anti-cancer drug-conjugated gelatin-coated Gd<sub>2</sub>O<sub>3</sub> NPs demonstrated that both NPs could construct the drug delivery systems (DDS) targeting the advanced cancers due to the high drug loading. The loading amount of DOX was saturated at the DOX / COO<sup>-</sup> ratio of 0.98, while the loading ratio of Pt / COO<sup>-</sup> was 0.53. These novel NPs exhibited high stability under physiological conditions, and the functional evaluation indicated that the release of anti-cancer drugs (DOX or CDDP) was highly depending on the concentration of matrix metalloproteinase-2 (MMP-2). The cytotoxicity of these NPs towards human cervical adenocarcinoma (HeLa) cells was investigated in the presence or absence of MMP-2 and MMP-9. In addition, the contrast of both MR and PA images was enhanced with these NPs *in vitro*. The results clarified that the release of DOX and CDDP from anti-cancer drug-conjugated gelatin-coated Gd<sub>2</sub>O<sub>3</sub> NPs was highly affected by the degradation of gelatin by MMP-2 secreted from HeLa cells, and these NPs could contribute to DDS of anti-cancer drugs.

This comprehensive study not only emphasizes the successful synthesis of anti-cancer drug-conjugated gelatin-coated Gd<sub>2</sub>O<sub>3</sub> NPs but also underscores their potential enabling both the controlled release of anti-cancer drugs and DDS of drugs to around a cancer. In summary, novel anti-cancer drug-conjugated gelatin-coated Gd<sub>2</sub>O<sub>3</sub> NPs were shown to be a highly effective theranostics probe.

- 1) Kelkar, S. S.; Reineke, T. M. *Bioconjugate Chem.* **2011**, 22 (10), 1879–1903.
- 2) Kimura, Y.; Kondo, T. *et al. Adv. Healthcare Mater.* **2012**, 1, 657–660.
- 3) Pawan K. Singal, D.Sc. *et al. N. Engl. J. Med.* **1998**, 339, 900–905.
- 4) Nishiyama, N. Okazaki, S. *et al. Cancer Res.* **2003**, 63 (24), 8977–8983.

## 脳内リガンド指向性化学とクリックケミストリーの組み合わせによるグルタミン酸受容体の高速ラベル化戦略

(京大院工<sup>1</sup>・JST ERATO<sup>2</sup>) ○坂本 清志<sup>1,2</sup>・白岩 和樹<sup>1</sup>・野中 洋<sup>1,2</sup>・浜地 格<sup>1,2</sup>  
Rapid labeling strategy for endogenous glutamate receptors by a combination of in-brain LDAI chemistry and click reaction (<sup>1</sup>*Graduate School of Engineering, Kyoto University*, <sup>2</sup>*JST ERATO*) ○Seiji Sakamoto,<sup>1,2</sup> Kazuki Shiraiwa,<sup>1</sup> Hiroshi Nonaka,<sup>1,2</sup> Itaru Hamachi<sup>1,2</sup>

We reported that ligand-directed alkoxyacylimidazole (LDAI) chemistry can be applied for the selective chemical labelling of endogenous neurotransmitter receptors in living mouse brains.<sup>1)</sup> In this study, for extending the in-brain LDAI chemistry, we explored the new strategy allowing the rapid and selective chemical modification of neurotransmitter receptors in living mouse brain by a combination of LDAI chemistry and inverse electron demand Diels–Alder (IEDDA) click reaction. In the strategy, we initially introduced trans-cyclooctene (TCO) functionality on endogenous glutamate receptors in living mouse brain using the LDAI chemistry. In the second step, fluorophore-conjugated methytetrazine (MeTz) reagents were directly administrated into the mouse brain, which allowed the rapid chemical labeling of target receptors *via* IEDDA click reaction. By employing a variety of labeling reagents and MeTz-modified fluorophores, we found the cLogP value is a useful indicator for efficient labeling of proteins in living mouse brain. Moreover, we attempted to modify the target receptors with MeTz conjugated peptides for mapping the protease activity in the proximity of neurotransmitter receptors in living mouse brain.

**Keywords :** *In-brain Ligand-directed Chemistry; Click Chemistry; Glutamate Receptor; Chemical Labeling of Protein*

これまで我々は、アシルイミダゾール基を反応基とするリガンド指向性化学 (LDAI 化学) を用いて、生きたマウス脳内に存在する神経伝達物質受容体の選択的的化学標識が可能であることを報告してきた<sup>1)</sup>。本講演では、LDAI 化学と逆電子要請型 Diels-Alder 反応 (IEDDA 反応) を組み合わせることで、生きたマウス脳内の標的受容体に対し、高速かつ選択的に機能性分子を修飾する手法の開発を試みた。具体的には、LDAI 化学を用いて、グルタミン酸受容体に、trans-cyclooctene (TCO) 基を特異的に導入した。次に、蛍光色素を標識した methytetrazine (MeTz) 試薬をマウス脳内に投与することで、IEDDA クリック反応を介した標的受容体の高速ラベル化を実現した。また、様々な LDAI ラベル化剤や MeTz 修飾色素を用いることで、生きたマウス脳内での効率的タンパク質ラベル化に cLogP 値が有用な指標となることを見出した。さらに、MeTz 基で修飾したペプチド基質を受容体上に修飾することによって、生きたマウス脳内における神経伝達物質受容体近傍でのプロテアーゼ活性の mapping を試みたのでその詳細について報告する。

1) Bioorthogonal chemical labeling of endogenous neurotransmitter receptors in living mouse brains, H. Nonaka *et al.*, *Proc. Natl. Acad. Sci. USA*. **2024**, in press.

## 生きたマウス脳内でのミクログリア選択的化学標識と機能解析への展開

(京大院工<sup>1</sup>、JST ERATO<sup>2</sup>) ○王 萌初<sup>1</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup>

Selective Chemical Labeling and Functional Analysis of Microglia in the Live Mouse Brain (<sup>1</sup>*Graduate School of Engineering, Kyoto University*, <sup>2</sup>*ERATO, JST*)

○Mengchu Wang<sup>1</sup>, Hiroshi Nonaka<sup>1,2</sup>, Itaru Hamachi<sup>1,2</sup>

Microglia are a class of glial cell found in the brain, which function as immune cells in the central nervous system. Recently, it has become clear that microglia also play an important role in the formation, maintenance, and functional expression of neural circuits. Against this background, there is an increasing need to analyze the function and dynamics of microglia in detail. On the other hand, studies using microglia isolated from the brain or acute brain sections, often include the alteration of the properties of microglia during the sample preparation process, and thus it is difficult to accurately capture their functions. It is ideal to analyze the function and dynamics of microglia in the live brain.

We have successfully developed ligand-directed chemistry, a method for selective chemical modification of proteins.<sup>1</sup> By using the ligand-directed chemistry that has an acyl imidazole group as a reactive group (LDAI chemistry), selective labeling of neurotransmitter receptors such as AMPA-type glutamate receptors (AMPA receptors) is carried out in the live mouse brain and thereby, elucidation of the unknown dynamics of AMPARs are revealed.<sup>2</sup> In this study, we attempted to label a receptor specifically expressed in microglia using LDAI chemistry for the analysis of microglia function. Fluorescence imaging and Western blot analysis showed that the functional probes were selectively tethered to the target receptor of microglia.

**Keywords :** *Ligand directed chemistry; Microglia; In vivo*

脳内に存在するグリア細胞の一種であるミクログリアは中枢神経系における免疫細胞として知られているが、近年その他の機能も併せ持つことが明らかになりつつある。そのような背景から、ミクログリアの機能や動態を詳細に解析することの重要性が高まってきている。一方で、脳から単離したミクログリアや急性脳切片を用いた実験系では、サンプル調整過程でミクログリアの性質が変化してしまうため、機能を正確に捉えることが難しいことが多い。そのため、ミクログリアの機能や動態を生きた脳内で解析することが求められている。

我々はこれまでにタンパク質の選択的化学修飾法であるリガンド指向性化学の開発を行ってきた<sup>1</sup>。アシルイミダゾール基を反応基とするリガンド指向性化学 (LDAI 化学) を用いることで、AMPA 型グルタミン酸受容体 (AMPA 受容体) など神経伝達物質受容体の生きたマウス脳内でのラベル化や、それを用いた AMPAR の未知動態の解明に成功している<sup>2</sup>。今回、我々はミクログリアに特異的に発現する受容体を標的とした LDAI 化学を用いて、生きたマウス脳内のミクログリアに機能解析のためのプローブを導入する手法の開発を試みた。蛍光イメージングやウエスタンブロット等の結果より、マウスの脳で標的受容体を選択的に化学標識できていることが明らかになり、今後、ミクログリアの詳細な機能解析に活用できることが示唆された。

1) S. Wakayama *et al.*, *Nat. Commun.*, **8**, 14850 (2017).

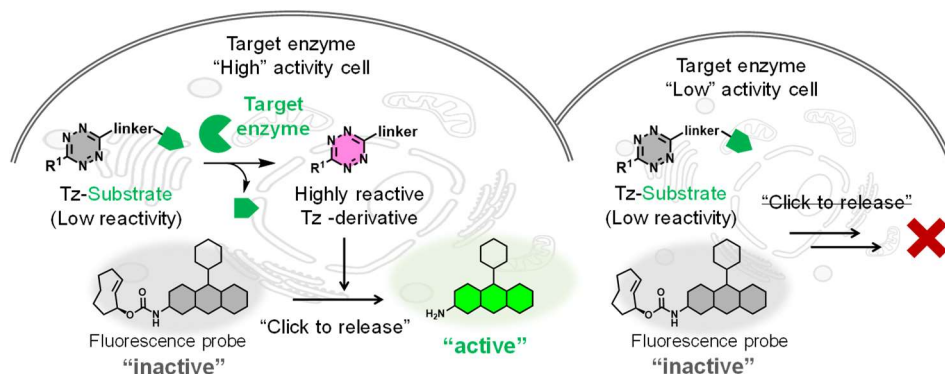
2) H. Nonaka *et al.*, *Proc. Natl. Acad. Sci. USA*, in press (2024).

## Development of novel chemical tools to induce click-to-release reactions selectively in cells with specific enzyme activities

(<sup>1</sup>Graduate School of Pharmaceutical Science, The University of Tokyo, <sup>2</sup>Department of Life Science and Technology, Tokyo Institute of Technology, <sup>3</sup>LiSM/IRFI, <sup>4</sup>Graduate School of Medicine, The University of Tokyo) ○Ren Ito<sup>1</sup>, Mako Kamiya<sup>2,3</sup>, Yasuteru Urano<sup>1,4</sup>

**Keywords:** Click chemistry; Chemical biology; Click to release; bioorthogonal chemistry

“Click-to-release” is a chemical reaction wherein the click reaction between 2-trans-cyclooctene (2TCO) derivatives bearing carbamate moiety and tetrazine (Tz) induces the liberation of the amine from 2TCO derivatives. This reaction realizes the highly bio-orthogonal design of prodrugs<sup>1</sup> and caged-protein<sup>2</sup>. Although there is a report on a photo-caged dihydrotetrazine that is converted to tetrazine upon light irradiation to activate click-to-release reaction<sup>3</sup>, activation of click-to-release reaction in a cell-specific manner remains challenging. In this study, we aimed to develop a method for selectively restoring click-to-release reactivity in an enzyme-dependent manner to release caged small molecules selectively in target cells. For this purpose, we first developed a green-light-emitting TCO-caged fluorophore (2TCO-HMRG) that restores its fluorescence through a click-to-release reaction with Tz. Then, we evaluated the click-to-release reactivity of various Tz derivatives by using 2TCO-HMRG, and we serendipitously discovered Tz derivative with distinct reactivity despite their similar structures. Based on this discovery, we aimed to develop Tz-probes whose click to release reactivity can be restored through target enzyme reactions by introducing enzyme substrate moiety into the discovered Tz derivatives. As a result, we developed Tz-probes whose click-to-release reactivity can be activatable upon reaction with carboxypeptidase, esterase, and aminopeptidase. Particularly, the click-to-release reactivity of Tz-probe targeting aminopeptidase could be restored in live cells with high target aminopeptidase activity, demonstrating the possibility of cell-selective release of the molecules of interest.



1) *Nat. Commun.* **9**, 1484 (2018) 2) *ACS Cent Sci* **2**, 325–331 (2016) 3) *Nat. Chem.* **14**, 1078–1085 (2022).



## 精密に設計された超偏極分子プローブ群を用いる複数のアミノペプチダーゼ活性の生体内同時検出

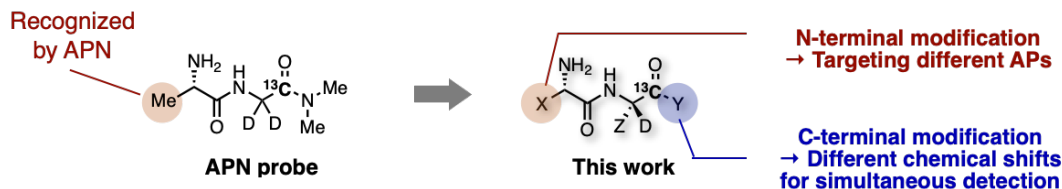
(東大院工<sup>1</sup>・量子科学技術研究開発機構<sup>2</sup>・千葉大院融合理工<sup>3</sup>・米国国立衛生研究所<sup>4</sup>) ○谷田部 浩行<sup>1</sup>・齋藤 雄太朗<sup>1</sup>・高草木 洋一<sup>2,3</sup>・齋藤 圭太<sup>2</sup>・山本 和俊<sup>4</sup>・Murali C. Krishna<sup>4</sup>・山東 信介<sup>1</sup>

Simultaneous detection of multiple aminopeptidase activities *in vivo* using precisely designed hyperpolarized molecular probes (<sup>1</sup>*Graduate School of Engineering, The University of Tokyo*, <sup>2</sup>*National Institutes for Quantum Science and Technology*, <sup>3</sup>*Graduate School of Science, Chiba University*, <sup>4</sup>*National Institutes of Health, USA*) ○ Hiroyuki Yatabe<sup>1</sup>, Yutaro Saito<sup>1</sup>, Yoichi Takakusagi<sup>2,3</sup>, Keita Saito<sup>2</sup>, Kazutoshi Yamamoto<sup>4</sup>, Murali C. Krishna<sup>4</sup>, Shinsuke Sando<sup>1</sup>

Aminopeptidases (APs), which specifically cleave N-terminal amino acid residues of peptides, are known to be important biomarkers, so simultaneous detection of multiple AP activities is useful for the diagnosis of various diseases<sup>1)</sup>. Nuclear magnetic resonance (NMR) is a technique that can simultaneously detect and visualize multiple target molecules through differences in chemical shifts. However, due to its low sensitivity, it is generally difficult to detect target molecules other than water *in vivo*. In this study, we focused on dynamic nuclear polarization (DNP)<sup>2)</sup>, which improves the sensitivity of NMR, and designed and developed DNP-NMR molecular probes for simultaneous detection of multiple AP activities *in vivo*. By utilizing our recently developed molecular probe that can detect APN activity *in vivo* as a basic scaffold<sup>3)</sup>, we have developed a series of DNP-NMR molecular probes with precisely controlled enzymatic selectivity and chemical shifts.

**Keywords :** Hyperpolarization, Nuclear magnetic resonance, Aminopeptidase, Molecular probe, Simultaneous detection

アミノペプチダーゼ (AP) は、ペプチドの N 末端アミノ酸残基を特異的に切断する重要なバイオマーカーとして知られる。複数の AP 活性の同時検出は様々な疾患の診断に有用である<sup>1)</sup>。核磁気共鳴法 (NMR) は、化学シフトの違いによって複数の標的分子を同時に検出できる手法である。しかし、NMR は感度が低いため、水以外の生体内標的分子を検出することは一般に難しい。本研究では、NMR の感度を向上させる動的核偏極法 (DNP) に着目し<sup>2)</sup>、複数の生体内 AP 活性の同時検出に向けた DNP-NMR 分子プローブ群の設計および開発を行った。近年我々が開発した生体内 APN 活性を検出可能な分子プローブを基本骨格とすることで<sup>3)</sup>、酵素選択性と化学シフトを緻密に制御した DNP-NMR 分子プローブ群を開発した。



Y. Saito, H. Yatabe, *et al. Sci. Adv.* **2022**, 8, eabj2667.

1) F. Vargas, *et al. Int. J. Mol. Sci.* **2020**, 21, 5615. 2) J. H. Ardenkjær-Larsen *et al. Proc. Natl. Acad. Sci. U.S.A.* **2003**, 100, 10158. 3) Y. Saito, *et al. Sci. Adv.* **2022**, 8, eabj2667.

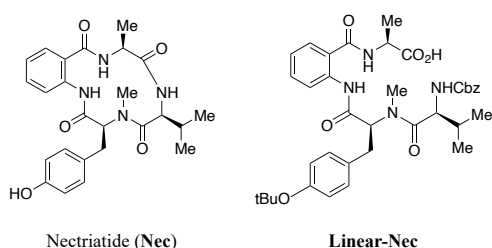
## Analysis of the intracellular dynamics of nectriatide, a potentiator of amphotericin B, using Raman microspectroscopy

(<sup>1</sup>Grad. Sch. Adv. Sci. Eng., Waseda Univ., <sup>2</sup>Res. Org. Nano Life Innov., Waseda Univ., <sup>3</sup>Grad. Sch. Pharm. Sci., Kitasato Univ., <sup>4</sup>CBBD-OIL, AIST-Waseda Univ., <sup>5</sup>Inst. Adv. Res. Biosyst. Dyn., Waseda Univ.) ○ Ryosuke Miyake,<sup>1</sup> Masahiro Ando,<sup>2</sup> Keisuke Kobayashi,<sup>3</sup> Hiroshi Tomoda,<sup>3</sup> Taichi Ohshiro,<sup>3</sup> Haruko Takeyama<sup>1,2,4,5</sup>

**Keywords:** antifungal medicine, amphotericin B, potentiator of amphotericin B, natural product, Raman spectroscopy

Nectriatide (**Nec**) is a cyclic tetrapeptide isolated from *Nectriaceae* sp. BF-0114<sup>1)</sup>. **Nec** does not exhibit antifungal activity at 64 µg/mL. However, when combined with amphotericin B (AmB) at 32 µg/mL, it enhances the antifungal activity of AmB by 16 times. In the process of the total synthesis of **Nec**, we identified a linear intermediate (**linear-Nec**) that showed stronger activity than **Nec**<sup>2)</sup>. Similarly, **linear-Nec** does not demonstrate antifungal activity at 64 µg/mL, but when used in combination with AmB at 8 µg/mL, it increases the antifungal activity of AmB by 16-fold. To elucidate the mechanism of action of **Nec**, we synthesized various chemical probes to identify its target molecule. As a result, we have previously revealed that it shows affinity with ergosterol. In this study, we used Raman microspectroscopy to investigate the interaction between ergosterol and **linear-Nec** in living cells in a non-labeled, minimally invasive manner.

We treated *Saccharomyces cerevisiae* with 64 µg/mL of **linear-Nec** at 30°C for one hour. Using Raman microspectroscopy, we detected ergosterol and **linear-Nec** within the cells. By applying multivariate curve resolution-alternating least squares (MCR-ALS) analysis<sup>2)</sup>, we visualized both ergosterol and **linear-Nec**. This was achieved by extracting spectral components and their intensity distribution, originating from these compounds. Our results indicate that **linear-Nec** interacts with ergosterol co-localized within living cells, suggesting a direct interaction between ergosterol and **linear-Nec** in the cellular environment.



compound		MIC <sup>1</sup> (µg/mL)	Ratio <sup>2</sup>
AmB alone		1.0	1
AmB + nectriatide ( <b>Nec</b> )	2 µg/mL	1.0	1
	8 µg/mL	0.50	2
	32 µg/mL	0.063	16
AmB + <b>linear-Nec</b>	2 µg/mL	0.25	4
	8 µg/mL	0.063	16
	32 µg/mL	0.031	32

1: MIC = Minimum Inhibitory Concentration of fungal growth by over 90%

2: Ratio (MIC<sub>AmB</sub>/MIC<sub>AmB+compound</sub>)

- 1) Fukuda T. *et al. J. Nat. Prod.* **82**, 2673-2681 (2019)
- 2) Nagai K. *et al. J. Antibiot.* (in press)
- 3) Ando M. *et al. J Biomed Opt.* **19**, 011016 (2013)

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 H936(9号館 [3階] 936)

**[H936-3am] 17. 生体機能関連化学・バイオテクノロジー**

座長：稲葉 央、金原 数

## ◆ 英語

9:00 ~ 9:20

[H936-3am-01]

Development of Artificial Metalloproteins from Hemophore of *Acinetobacter baumannii* for Antibacterial Applications○Viet Quoc Nguyen<sup>1</sup>, Shinya Ariyasu<sup>1</sup>, Yuichiro Aiba<sup>1</sup>, Hiroshi Sugimoto<sup>2</sup>, Osami Shoji<sup>1</sup> (1. Grad. Sch. of Sci., Nagoya Univ., 2. RIKEN SPring-8)

## ◆ 英語

9:20 ~ 9:40

[H936-3am-02]

Artificial Vesicular and Fibrous Assembly of Amphiphilic Peptide WR9 in Living Cells

○Qinxuan Yang<sup>1</sup>, Takuzo Aida<sup>1</sup>, Takayuki Miki<sup>1</sup> (1. The Univ. of Tokyo)

## ◆ 英語

9:40 ~ 10:00

[H936-3am-03]

Analytical chromatography for insulin fibrillation monitoring

○ティラサラ ピトワラカンカナマゲ<sup>1</sup>, Wijak Yospanya<sup>1</sup>, Kazushi Kinbara<sup>1</sup> (1. 東京工業大学)

## ◆ 英語

10:00 ~ 10:20

[H936-3am-04]

ATP responsive 2-dimensional scaffold from biomolecular machines exhibiting enhanced catalytic activity

○Tonmoy Ray<sup>1</sup>, Takuzo Aida<sup>1,2</sup>, Hideki Taguchi<sup>3</sup>, Tatsuya Niwa<sup>3</sup> (1. The University of Tokyo, 2. Center for Emergent Matter Science, RIKEN, 3. Tokyo Institute of Technology (TITECH))

10:20 ~ 10:30

休憩

## ◆ 日本語

10:30 ~ 10:50

[H936-3am-05]

スピロピラン修飾Tau由来ペプチドによる微小管構造の可逆的光操作

○稲葉 央<sup>1</sup>、阪口 みなも<sup>1</sup>、渡 宗英<sup>1</sup>、角五 彰<sup>2</sup>、松浦 和則<sup>1</sup> (1. 鳥取大院工、2. 京大院理)

## ◆ 英語

10:50 ~ 11:10

[H936-3am-06]

人工触媒反応による転写活性化を介した新規抗がん戦略の開発

○山梨 祐輝<sup>1</sup>、高丸 慎平<sup>1</sup>、東屋 勇都<sup>1</sup>、上村 祐悟<sup>1</sup>、岡部 篤史<sup>2</sup>、海渡 智史<sup>3</sup>、鯨井 智也<sup>4</sup>、胡桃坂 仁志<sup>4</sup>、岩間 厚志<sup>3</sup>、金田 篤志<sup>2</sup>、山次 健三<sup>1</sup>、川島 茂裕<sup>1</sup>、金井 求<sup>1</sup> (1. 東大院薬、2. 千葉大院医、3. 東大医科研、4. 東大定量研)

🇯🇵 日本語

11:10 ~ 11:30

[H936-3am-07]

抗原タンパク質修飾ペプチドファイバーの細胞内取り込み制御

○若林 里衣<sup>1</sup>、樋口 亜也斗<sup>1</sup>、難波江 友紀<sup>1</sup>、神谷 典穂<sup>1</sup>、後藤 雅宏<sup>1</sup> (1. 九州大学)

---

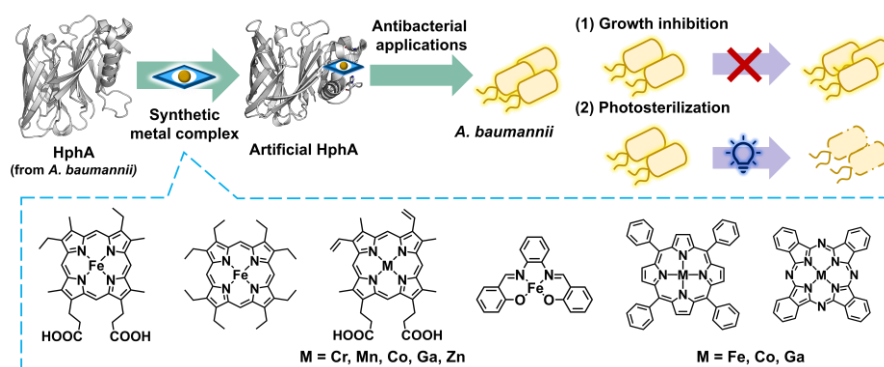
## Development of Artificial Metalloproteins from Hemophore of *Acinetobacter baumannii* for Antibacterial Applications

(<sup>1</sup>Graduate School of Science, Nagoya University, <sup>2</sup>RIKEN SPring-8) ○ Viet Quoc Nguyen,<sup>1</sup> Shinya Ariyasu,<sup>1</sup> Yuichiro Aiba,<sup>1</sup> Hiroshi Sugimoto,<sup>2</sup> Osami Shoji<sup>1</sup>

**Keywords:** Bioinorganic Chemistry; Hemoproteins; Artificial Metalloproteins; Antibacterial Therapy

*Acinetobacter baumannii* is a gram-negative and opportunistic bacterial pathogen which is associated with hospital and community-acquired infections worldwide. Especially, multidrug-resistant strains of *A. baumannii* have been posing a great threat to public health. A recent study has reported that under iron restrictive conditions, *A. baumannii* can secrete a hemophore called HphA to obtain heme from hosts for use as an iron source.<sup>1</sup> Meanwhile, our group has been researching about another hemophore, HasA, which is secreted by some other gram-negative bacteria such as *Pseudomonas aeruginosa* for the same purpose. We have succeeded in the reconstitution of HasA with various synthetic metal complexes through heme substitution, and applied the artificial HasA proteins to the treatment of *P. aeruginosa* by exploiting the bacterial heme uptake system.<sup>2</sup> Although HphA and HasA differ greatly in their structures and heme coordinating ligands, they share some properties, such as the high exposure of heme binding pocket. Therefore, we proposed that it is possible to also incorporate non-native metal complexes into HphA.

In this work, we first confirmed that HphA can capture synthetic metal complexes of various structures and metal centers (**Figure**). Secondly, some of the artificial HphA proteins were investigated for their antibacterial activity against *A. baumannii* strain AB5075-UW, including growth inhibitory effect under iron-limiting conditions, and application in photosterilization. As a result, we discovered some potential candidates of HphA for the treatment of the pathogen. Furthermore, we performed X-ray crystallography to study the protein structure and binding of the synthetic cofactor by HphA.



1) T. J. Bateman et al., *Nat. Commun.* **2021**, 12, 6270. 2) Y. Shisaka and O. Shoji, *Coord. Chem. Rev.* **2022**, 472, 214793.

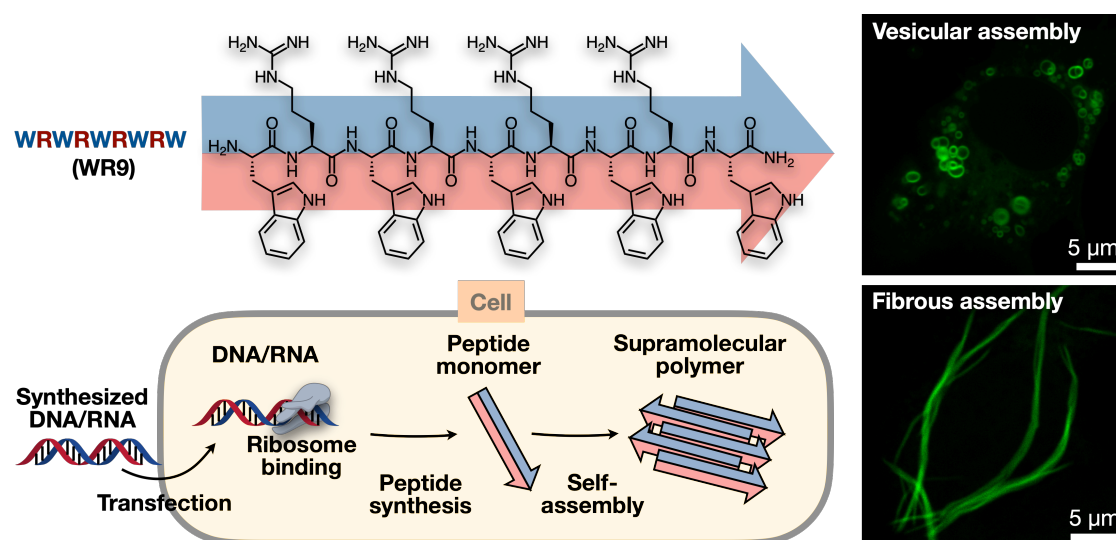
## Artificial Vesicular and Fibrous Assembly of Amphiphilic Peptide WR9 in Living Cells

(<sup>1</sup>Graduate School of Engineering, The University of Tokyo) ○Qinxuan Yang<sup>1</sup>, Takuzo Aida<sup>1</sup>, Takayuki Miki<sup>1</sup>

**Keywords:** Amphiphilic peptides, Intracellular assembly, Genetically encodable peptides, Supramolecular chemistry, Self-assembly structures

In living cells, compartmentation is essential for different life processes. In organelles compartmentalized by lipid bilayers, specific subsets of biomolecules are enriched to carry out their unique function. From the viewpoint of synthetic biology, various efforts to develop synthetic organelles, so-called “protocells,” have been devoted to generating artificial functions by encapsulating biomolecules into liposomes in test tubes. However, there is no report of constructing such liposomes in living cells to build organelles in a bottom-up fashion due to the complicated and crowded cytoplasmic environment. At the same time, we reported an approach for intracellular supramolecular polymerization using genetically programmable peptides.<sup>1</sup> Herein, using this technique, we demonstrate different assembly structures we achieved in living cells which act as a scaffold for constructing *de novo* organelles.

Based on the general rule for beta-sheet self-assembling peptide design, that is, alternating repeats of hydrophobic- and hydrophilic-amino-acid sequences, we tested various peptide sequences. In detail, we prepared plasmid DNA coding for peptide-fused sfGFP (super folder green fluorescent protein) and delivered them into COS-7 cells by lipofection. A peptide sequence consisting of 9 alternating arginine and tryptophan (WR9) formed intriguing morphologies including vesicles and fibers in COS-7 cells. This finding holds potential for constructing artificial membrane-bound organelles and cytoskeleton networks in living cells.



1) T. Miki, *Nat. Commun.* **2021**, *12*, 3412.

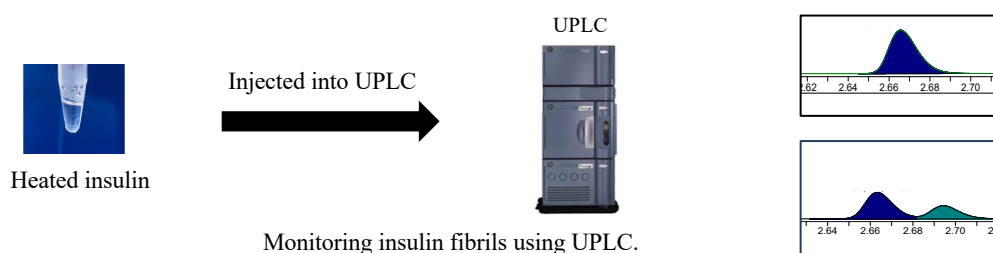
## Analytical chromatography for monitoring insulin fibrillation

(<sup>1</sup>*School of Life Science and Technology, Tokyo Institute of Technology*, <sup>2</sup>*Cell Biology Center, Institute of Innovative Research, Tokyo Institute of Technology*, <sup>3</sup>*Living Systems Materialogy Research Group, International Research Frontiers Initiative, Tokyo Institute of Technology*)  
 ○ Pituwala Kankanamge Thirasara Sammani,<sup>1</sup> Wijk Yospanya,<sup>1</sup> Tatsuya Niwa,<sup>2</sup> Hideki Taguchi,<sup>2</sup> Kazushi Kinbara<sup>1,3</sup>

**Keywords:** Insulin fibrillation, Ultra performance liquid chromatography (UPLC), LCMS

Protein fibrillation is a key factor in the progression of various diseases including Alzheimer's, Parkinson's, and type-2 diabetes. Insulin, amyloid proteins for diabetes treatment, serves as a common model for studying fibril kinetics due to its easy accessibility and handling. Under certain conditions such as low pH and high temperature, insulin can form a cross-beta structure which eventually leads to fibrillation. Fibrillation causes problems in the storage and manufacture of insulin and reduces the effectiveness of diabetes treatment.<sup>2</sup>

The thioflavin T assay, a technique that uses thioflavin T as a fluorescent probe that increases its emission when bound to the cross-beta structure, is widely used to detect protein fibrils.<sup>3</sup> However, several issues can affect the accuracy and precision of the quantitative measurements, including the nonlinear relationship between fibril concentration and fluorescence intensity, competitive binding between Thioflavin T and other additives, and large fibril aggregation.<sup>4</sup> To address this issue, we introduced a new method to study insulin fibrillation. Instead of quantifying insulin fibrils, we analyzed the soluble insulin content using ultra performance liquid chromatography (UPLC). This approach not only allows for the quantification of the insulin content but also enables the identification of the deamidated insulin, which was confirmed by mass spectrometry. Deamidation is a post-translational modification which can induce the fibrillation.<sup>5</sup> This methodology would have the potential to be applied in understanding the early stages of other amyloid fibrils in the future.



- 1) F. Librizzi, C. Rischel, *Protein Sci.* **2005**, 14, 3129–3134.
- 2) R.J. Woods, J. Alarcón, E. McVey, R.J. Pettis, *J. Diabetes Sci. Technol.* **2012**, 6, 265–276.
- 3) R. Sabaté, S.J. Saupe, *Biochem. Biophys. Res. Commun.* **2007**, 360, 135–138.
- 4) S.A. Hudson, H. Ecroyd, T.W. Kee, J.A. Carver, *FEBS J.* **2009**, 276, 5960–5972.
- 5) Y.P. Y. Lam, C.K. C. Chiu, C. A. Wootton, I. Hands-Portman, M. Li, M. P. Barrow, P. B. O'Connor, *Chem. Commun.* **2020**, 56, 9787–9790.



## 2-Dimensional ATP Responsive Biomaterial from Biomolecular Machine GroEL Exhibiting Independent and Enhanced Catalytic Activity

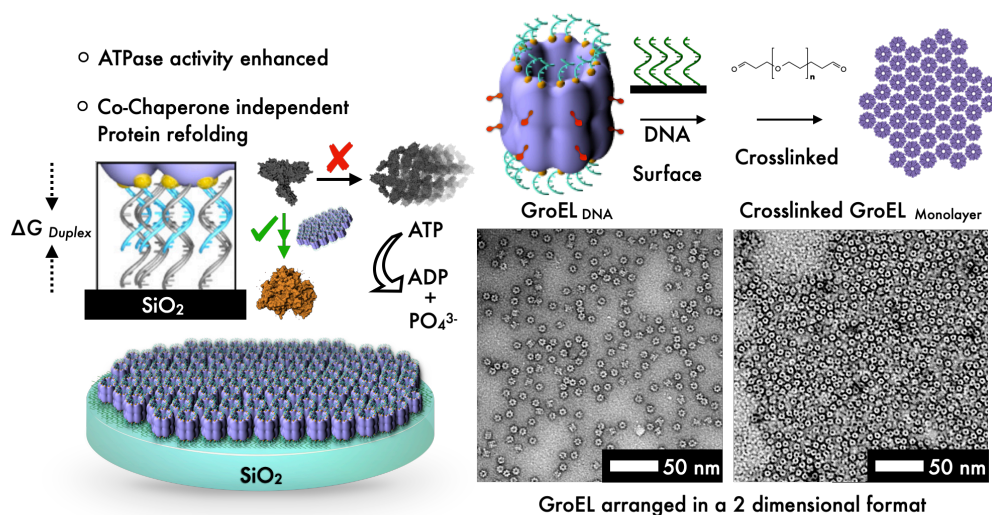
(<sup>1</sup>Graduate School of Engineering, The University of Tokyo, <sup>2</sup>RIKEN Center for Emergent Matter Science, <sup>3</sup>Institute of Innovation Research, Tokyo Institute of Technology)

○Tonmoy Ray<sup>1</sup>, Hideki Taguchi<sup>3</sup>, and Tatsuya Niwa<sup>3</sup>, Takuzo Aida<sup>1,2\*</sup>

**Keywords:** Biomolecular machine; Surface immobilization; Enzyme catalysis; Porous Materials; Stimuli Responsive

Naturally occurring membranous structures are formed by the precision lateral assembly of monomeric building blocks such as lipids or proteins<sup>1</sup>. However, achieving functional two-dimensional (2D) structures from proteins as building blocks is still a big synthetic challenge. We utilize DNA appended GroEL mutants as shape-persistent building blocks for the construction of an endogenous-stimuli-responsive, porous 2D sheet. Our lab has pioneered the use of GroEL for nanotubular supramolecular polymerization.<sup>2-4</sup>

The current design demonstrates the structural advantage of mutated variant of GroEL<sub>DNA</sub>, which has densely functionalized DNA motifs on its apical domain site-specifically. To support this precision 2-D lateral assembly structure a DNA coated surface was engineered. Upon annealing conditions, an excess of monomeric units preferentially hybridize and align themselves on to the substrate surface. Further the design has been optimized to crosslink the assembly and exfoliate from the surface using DNA toehold mediated mechanism. To our surprise an enhanced ATPase activity was observed and further a verified proof of concept was illustrated using a large size guest refolding during immobilization.



### [References]

- [1] *Microbiol. Rev.* **2014**, *38*, 823. [2] *JACS* **2013**, *135*, 11509. [3] *JACS* **2015**, *137*, 4658. [4] *JACS* **2016**, *138*, 11152. [5] *JACS* **2018**, *140*, 26. [6] *JACS* **2020** *142*, *31*, 13310.



## スピロピラン修飾 Tau 由来ペプチドによる微小管構造の可逆的光操作

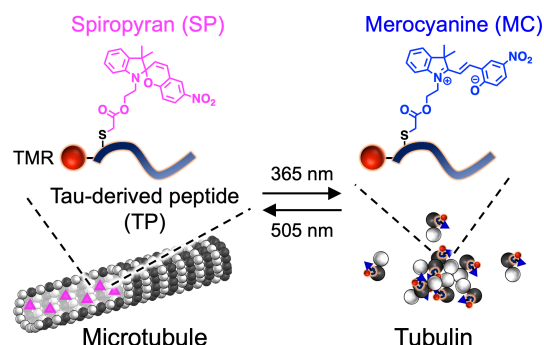
(鳥取大院工<sup>1</sup>・京大院理<sup>2</sup>) ○稲葉 央<sup>1</sup>・阪口 みなも<sup>1</sup>・渡 宗英<sup>1</sup>・角五 彰<sup>2</sup>・松浦 和則<sup>1</sup>

Reversible photocontrol of microtubule structures by spiropyran-modified Tau-derived peptides (<sup>1</sup>*Graduate School of Engineering, Tottori University*, <sup>2</sup>*Graduate School of Science, Kyoto University*) ○Hiroshi Inaba,<sup>1</sup> Minamo Sakaguchi,<sup>1</sup> Soei Watari,<sup>1</sup> Akira Kakugo,<sup>2</sup> Kazunori Matsuura<sup>1</sup>

Microtubules are one of the cytoskeletons that are hollow nanotubes with 15 nm inner diameter. We have developed a Tau-derived peptide (TP) that binds to the inner surface of microtubules and have achieved the encapsulation of various nanomaterials into microtubules by using TP.<sup>1</sup> Herein, we conjugated spiropyran, which is reversibly converted to merocyanine by light, to TP toward a reversible photocontrol of microtubule structures.<sup>2</sup> The peptide with spiropyran at the N-terminus stabilized microtubules, whereas the same peptide with the merocyanine form did not exert the effect. Reversible formation and dissociation of microtubules were achieved using this peptide and irradiation with UV and visible light.

**Keywords :** Peptide; Microtubules; Spiropyran; Photoisomerization; Photocontrol

細胞骨格の一種である微小管はチューブリンタンパク質からなる内径 15 nm のチューブ状集合体である。微小管構造を光で制御することで、モータータンパク質と組み合わせた運動材料開発や細胞応用への展開が期待できる。我々は微小管内部に結合する Tau 由来ペプチド (TP) を開発し、TP を用いた微小管内部への分子導入を達成している<sup>1</sup>。本研究では、フォトクロミック分子であるスピロピラン (SP) / メロシヤニン (MC) 修飾 TP の光異性化を利用した微小管構造の光制御を目指した (Fig. 1)<sup>2</sup>。TP の異なる位置に Cys を有し、N 末端に赤色蛍光色素 tetramethylrhodamine (TMR) を導入した 4 種類のペプチドを合成した。Cys に SP を修飾した全てのペプチドの微小管への結合が共焦点レーザー走査型顕微鏡により確認された。中でも、N 末端の Cys に SP を導入したペプチドでは微小管の安定化が見られ、MC 体では安定化効果はなかった。このペプチドを用い、UV 光 (365 nm) と可視光 (505 nm) の照射による異性化を利用して微小管の形成・解離の可逆的な光スイッチングに成功した。



**Fig. 1.** スピロピラン修飾 Tau 由来ペプチドによる微小管構造の光制御

1) H. Inaba, K. Matsuura, *Bull. Chem. Soc. Jpn.*, **2021**, 94, 2100 (Account).

2) H. Inaba, M. Sakaguchi, S. Watari, S. Ogawa, A. M. R. Kabir, A. Kakugo, K. Sada, K. Matsuura, *ChemBioChem*, **2023**, 24, e202200782.

## 人工触媒反応による転写活性化を介した新規抗がん戦略の開発

(東大院薬<sup>1</sup>・千葉大院医<sup>2</sup>・東大医科研<sup>3</sup>・東大定量研<sup>4</sup>) ○山梨 祐輝<sup>1</sup>、高丸 慎平<sup>1</sup>、東屋 勇都<sup>1</sup>、上村 祐悟<sup>1</sup>、岡部 篤史<sup>2</sup>、海渡 智史<sup>3</sup>、鯨井 智也<sup>4</sup>、胡桃坂 仁志<sup>4</sup>、岩間 厚志<sup>3</sup>、金田 篤志<sup>2</sup>、山次 健三<sup>1</sup>、川島 茂裕<sup>1</sup>、金井 求<sup>1</sup>

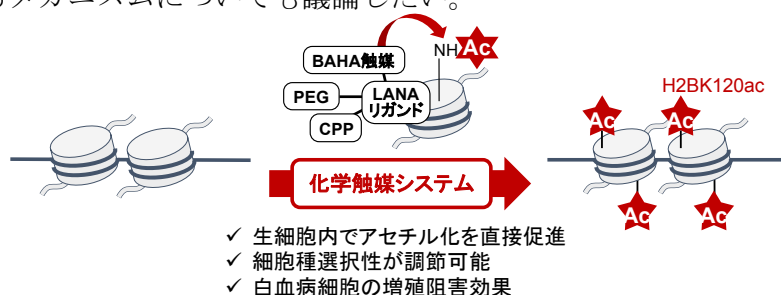
In-cell Catalysis for Histone Modification and Anti-cancer Transcriptional Activation (<sup>1</sup>Graduate School of Pharmaceutical Sciences, The University of Tokyo, <sup>2</sup>Graduate School of Medicine, Chiba University, <sup>3</sup>The Institute of Medical Science, The University of Tokyo, <sup>4</sup>Institute for Quantitative Biosciences, The University of Tokyo) ○Yuki Yamanashi,<sup>1</sup> Shinpei Takamaru,<sup>1</sup> Yuto Azumaya,<sup>1</sup> Yugo Kamimura,<sup>1</sup> Atsushi Okabe,<sup>2</sup> Satoshi Kaito,<sup>3</sup> Tomoya Kujirai,<sup>4</sup> Hitoshi Kurumizaka,<sup>4</sup> Atsushi Iwama,<sup>3</sup> Atsushi Kaneda,<sup>2</sup> Kenzo Yamatsugu,<sup>1</sup> Shigehiro Kawashima,<sup>1</sup> Motomu Kanai<sup>1</sup>

Chemical modification of histones dynamically regulates gene transcription and is closely related to disease pathogenesis including human cancer. Targeting epigenome is thus a promising strategy for cancer chemotherapy. Here we show that chemical intervention into epigenome by a histone acetylation catalyst system reprogramed transcription profile of cancer cells. The novel catalyst BAHA-LANA-PEG-CPP44 selectively entered leukemia cells, bound to chromatin, and acetylated endogenous histones, especially at H2BK120, in HAT-independent manner. We further demonstrate that the in-cell chemical catalysis retarded proliferation of leukemia cells via transcriptional changes of tumor-related genes and reduced their tumorigenic potential in mice. Our catalyst enabling direct intervention into the cancer epigenome network is orthogonal to drugs targeting histone-modifying enzymes and may lead to a novel anti-cancer strategy.

**Keywords :** Histone acetylation; In-cell catalysis; Epigenome manipulation;

DNA と共に核内でクロマチンを構成するヒストンタンパク質は、様々な翻訳後修飾を受けることでエピゲノムを構成し、遺伝子発現を制御する。ヒストンテールのアセチル化レベルの低下は、多くのがんにおいてみられるエピゲノムの異常であり、その人工的な制御は疾患の治療戦略になりうる。本研究では、独自に開発したリジンアセチル化触媒コア<sup>1</sup>を用いて、白血病細胞選択的にヒストン H2B の 120 番目のリジン (H2BK120) をアセチル化する触媒システムを開発した。

この触媒システムを白血病細胞に適用した結果、触媒によるヒストンアセチル化が、がん関連遺伝子の転写活性化を介して細胞増殖を抑制し、マウスでの腫瘍形成能を低下させることが示唆された。これは、化学触媒によってがんエピゲノムを直接操作するという、従来のエピゲノム創薬とは全く異なるメカニズムによる治療概念を提示し、新規抗がん戦略への展開が期待される。本発表では、がん関連遺伝子が選択的に転写活性化されるメカニズムについても議論したい。



1) *J. Am. Chem. Soc.* **2021**, *143*, 14976.

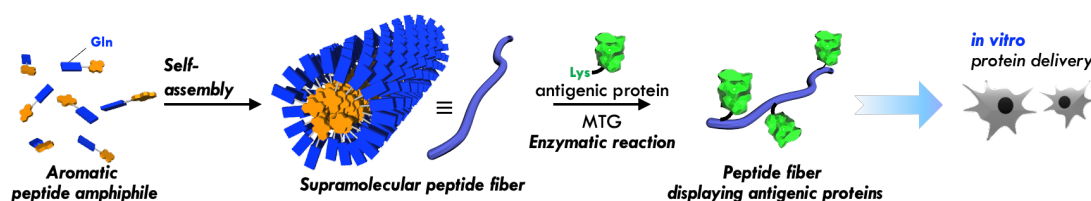
## 抗原タンパク質修飾ペプチドファイバーの細胞内取り込み制御

(九大院工) ○若林 里衣・樋口 亜也斗・難波江 友紀・神谷 典穂・後藤 雅宏  
Control of intracellular delivery of antigenic protein-modified peptide fibers (<sup>1</sup>*Graduate School of Engineering, Kyushu University*) ○Rie Wakabayashi, Ayato Higuchi, Yuki Nabae, Noriho Kamiya, Masahiro Goto

We have reported self-assembled peptide fibers that can be post-modified with proteins by an enzymatic reaction. These self-assembled peptides are composed of aromatic group and hydrophobic amino acid sequence as a self-assembly part and microbial transglutaminase (MTG)-reactive glutamine residue as an enzyme-reactive part and can display proteins with MTG-reactive lysine residue on the fibrous assembly. The proteins displayed on the peptide fibers can be efficiently delivered into immune cells. In this presentation, we will report on the influence of the properties of peptide fibers on the intracellular delivery of antigenic proteins displayed on the fibers with various peptide sequences for the potential vaccine application.

**Keywords :** *Peptide; Self-assembly; Vaccine; Intracellular delivery*

我々はこれまでに酵素反応によりタンパク質を事後修飾可能な自己組織化ペプチドファイバーを報告している<sup>1)</sup>。この自己組織化ペプチドは自己組織化部位に芳香族置換基と疎水性アミノ酸を、酵素反応部位に微生物由来トランスグルタミナーゼ (MTG) 反応性の Gln 残基を持ち、MTG 反応性の Lys 残基を持つタンパク質をファイバー表層に提示可能である。また、ペプチドファイバーに提示されたタンパク質は、免疫細胞への送達効率が向上することも確認している。今回、このタンパク質提示ペプチドファイバーのワクチン応用を志向し、ペプチド配列を改変した様々なペプチドファイバーに抗原タンパク質を修飾し、細胞内取り込みに与える影響について評価したので報告する。



1) R. Wakabayashi *et al.*, *Chem. Commun.*, **2019**, 55, 640; *Int. J. Mol. Sci.*, **2021**, 22, 3459.

アカデミックプログラム [B 講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 H931(9号館 [3階] 931)

**[H931-3pm] 17. 生体機能関連化学・バイオテクノロジー**

座長：真鍋 良幸、田村 朋則

## ◆ 英語

13:00 ~ 13:20

[H931-3pm-01]

過酸化亜硝酸塩 (ONOO<sup>-</sup>) 応答性タンパク質ラベリングの開発○朱 浩<sup>1</sup>、宇野 寛彬<sup>1</sup>、松葉 恭一<sup>1</sup>、浜地 格<sup>1,2</sup> (1. 京都大学、2. JST ERATO)

## ◆ 英語

13:20 ~ 13:40

[H931-3pm-02]

チロシナーゼを用いた生細胞と*in vivo*での近傍ラベル化法○松田 侑奈<sup>1</sup>、朱 浩<sup>1</sup>、Jae Hoon Oh<sup>2</sup>、美野 丈晴<sup>1</sup>、石川 守<sup>2</sup>、中村 秀樹<sup>1,3</sup>、辻川 宗男<sup>2</sup>、野中 洋<sup>1,2</sup>、浜地 格<sup>1,2</sup> (1. 京大院工、2. JST ERATO、3. 京大白血球センター)

## ◆ 英語

13:40 ~ 14:00

[H931-3pm-03]

疾患バイオマーカーを検出して光るシンセティックセルのボトムアップ構築

○筒井 啓太<sup>1</sup>、吉川 優<sup>1</sup>、松浦 友亮<sup>2</sup>、築地 真也<sup>1</sup> (1. 名工大院工、2. 東工大地球生命研)

## ◆ 日本語

14:00 ~ 14:20

[H931-3pm-04]

メンプレンコンタクト動態を可視化する分割型蛍光プローブの開発

阿喰 萌香<sup>1</sup>、○吉川 優<sup>1</sup>、筒井 啓太<sup>1</sup>、中津 史<sup>2</sup>、築地 真也<sup>1</sup> (1. 名工大院工、2. 新潟大院医歯)

14:20 ~ 14:30

休憩

## ◆ 日本語

14:30 ~ 14:50

[H931-3pm-05]

SLIPTによるマウス内シグナル操作

○田原 海<sup>1</sup>、吉川 優<sup>1</sup>、高倉 加奈子<sup>2</sup>、寺井 健太<sup>3</sup>、松田 道行<sup>2,3</sup>、築地 真也<sup>1</sup> (1. 名工大院工、2. 京大院生命、3. 京大院医)

## ◆ 英語

14:50 ~ 15:10

[H931-3pm-06]

環状ペプチドヘテロダイマーリガンド探索系の構築

○大野 湧仁<sup>1</sup>、Alexander Vinogradov<sup>1</sup>、菅 裕明<sup>1</sup> (1. 東京大学)

## ◆ 英語

15:10 ~ 15:30

[H931-3pm-07]

## 人工ヘムタンパク質モデル錯体による水中での硫化水素の捕捉および硫化水素中毒解毒剤としての応用

○中上 敦貴<sup>1</sup>、堀谷 正樹<sup>2</sup>、北岸 宏亮<sup>1</sup> (1. 同志社大学、2. 佐賀大学)

---

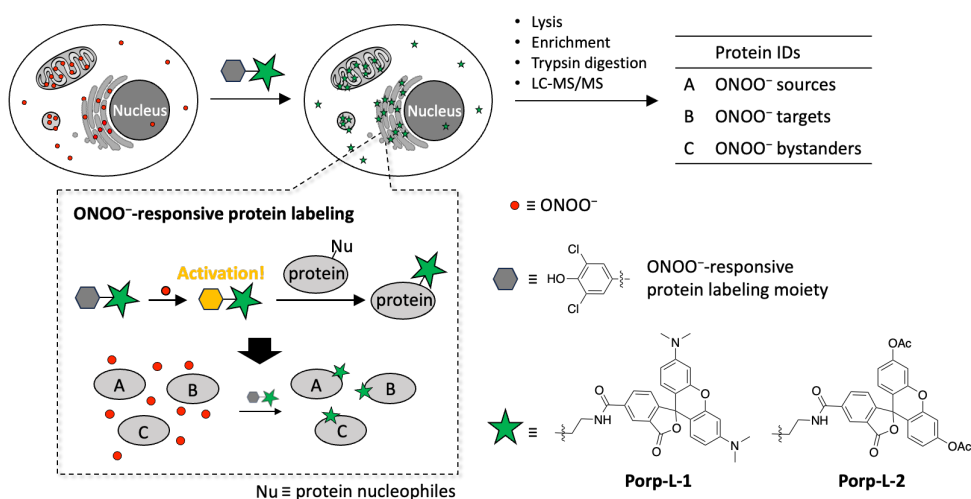
## Development of ONOO<sup>-</sup>-responsive protein labeling for ROS/RNS conditional proteomics

(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>ERATO, JST) ○Hao Zhu,<sup>1</sup> Hiroaki Uno,<sup>1</sup> Kyoichi Matsuba,<sup>1</sup> Itaru Hamachi<sup>1,2</sup>

**Keywords:** peroxynitrite; reactive oxygen species; reactive nitrogen species; proteomics

Peroxynitrite (ONOO<sup>-</sup>) is a member of the main reactive oxygen/nitrogen species (ROS/RNS). When produced in cells, ONOO<sup>-</sup> can undergo protein oxidation and nitration, which triggers cellular response ranging from subtle modulations of cell signaling to overwhelming oxidative and nitrative stress.<sup>1</sup> While biological ONOO<sup>-</sup> can be measured by antibodies against protein 3-nitrotyrosine and fluorescent sensors, most of them are not yet satisfactory in specificity and sensitivity for ONOO<sup>-</sup>. Moreover, the current methods are insufficient for the efficient and comprehensive analysis of ONOO<sup>-</sup>-associated proteins.

We are developing a new method for the study of biological ONOO<sup>-</sup>, which utilizes chemical proteomics for the comprehensive identification of the protein neighbors of ONOO<sup>-</sup>, namely conditional proteomics.<sup>2-4</sup> This method relies on ONOO<sup>-</sup>-responsive protein labeling reagents (Porp-L) that can be selectively and sensitively activated by ONOO<sup>-</sup> and transformed to highly reactive intermediates for immediate protein labeling. The ONOO<sup>-</sup>-surrounding protein labeled by Porp-L can be identified by LC-MS/MS, which reveals a group of proteins related to ONOO<sup>-</sup> generation, modification, and localization. In this presentation, I will introduce our efforts on the development of Porp-L and demonstrate its application in ROS/RNS conditional proteomics in living cells.



- 1) P. Pacher *et al.* *Physiol. Rev.* **2007**, 87, 315-424.
- 2) T. Miki *et al.* *Nat. Methods* **2016**, 13, 931-937.
- 3) Y. Nishikawa *et al.* *ACS Chem. Biol.* **2019**, 14, 397-404.
- 4) H. Zhu *et al.* *J. Am. Chem. Soc.* **2020**, 142, 15711-15721.

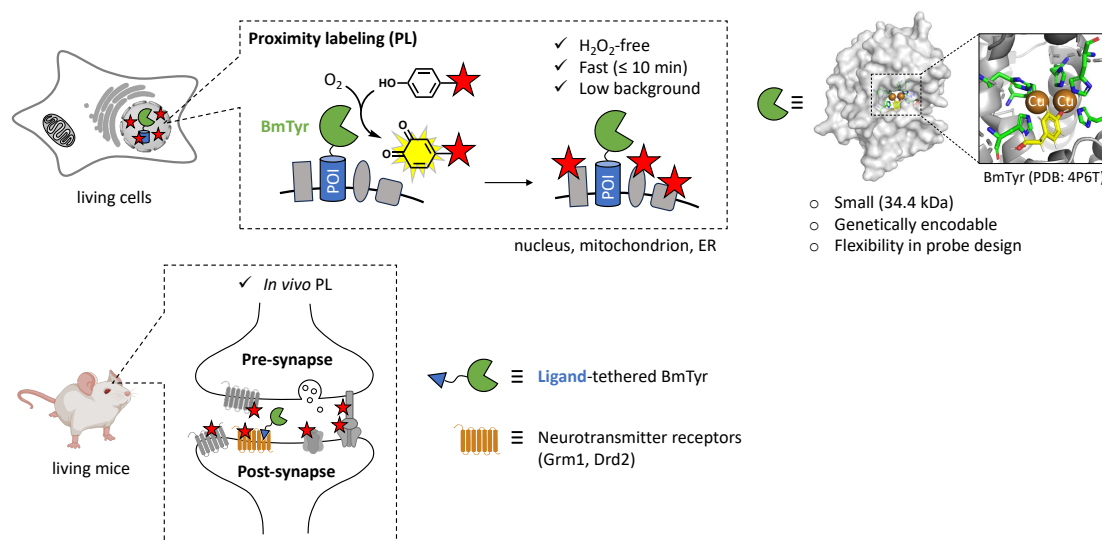
## Tyrosinase-based proximity labeling in living cells and *in vivo*

(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>JST ERATO, <sup>3</sup>Kyoto University Hakubi Center for advanced research) ○Yuna Matsuda<sup>1</sup>, Hao Zhu<sup>1</sup>, Jae Hoon Oh<sup>2</sup>, Takeharu Mino<sup>1</sup>, Mamoru Ishikawa<sup>2</sup>, Hideki Nakamura<sup>1,3</sup>, Muneo Tsujikawa<sup>2</sup>, Hiroshi Nonaka<sup>1,2</sup>, Itaru Hamachi<sup>1,2</sup>

**Keywords:** Proximity labeling, Proteomics, Tyrosinase, Quinone

Characterizing the protein constituents of a specific organelle and protein neighbors of a protein-of-interest (POI) is essential for understanding the function and state of the organelle and protein networks associated with the POI. Enzyme-based proximity labeling (PL) has emerged as a promising technology for specific and efficient spatial proteomics. Nevertheless, enzymes adopted for PL still have a few of limitations. H<sub>2</sub>O<sub>2</sub> (1 mM) used in peroxidase-based PL, such as APEX and HRP, raises the concern of cellular toxicity, which makes it unsuited to *in vivo* application. BioID is kinetically slow, and it takes hours to obtain sufficient biotinylated proteins in cells. TurboID exhibits uncontrolled and continuous biotinylation once expressed due to its high affinity to the endogenous biotin. Therefore, new enzymes are keenly desirable for the more flexible and broader application of PL.

In this work, we demonstrate a bacterial tyrosinase (BmTyr) as a new PL enzyme suitable for H<sub>2</sub>O<sub>2</sub>-free, fast (≤ 10 min in living cells), and low-background protein tagging. BmTyr is genetically encodable and enables subcellular-resolved PL and proteomics in living cells. We further designed ligand-tethered BmTyr for *in vivo* PL that enable to unveil the surrounding proteome of a targeted neurotransmitter receptor in its resident synapse in a live mouse brain. Overall, BmTyr is a promising enzyme that can improve and expand the PL-based applications and discoveries.



1) Hyun-Woo, R. *et al. Science* **339**, 1328–1331 (2013). 2) Roux, K. J., Kim, D. I., Raida, M. & Burke, B. J. *Cell Biol.* **196**, 801–810 (2012). 3) Branon, T. C. *et al. Nat. Biotechnol.* **36**, 880–887 (2018).



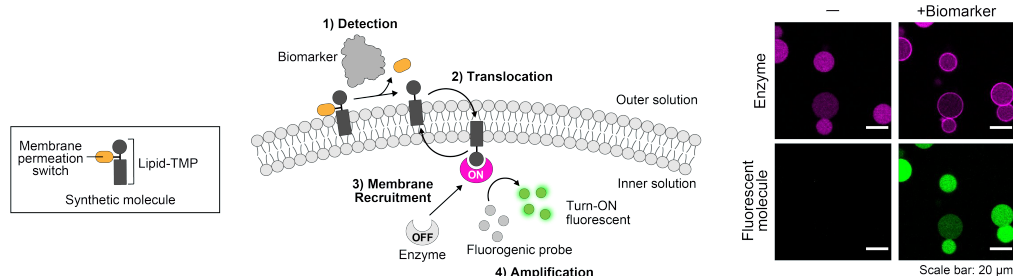
## Bottom-up construction of synthetic cell sensors for biomarker detection

(<sup>1</sup>Graduate School of Engineering, Nagoya Institute of Technology, <sup>2</sup>Earth-Life Science Institute, Tokyo Institute of Technology) ○ Keita Tsutsui,<sup>1</sup> Masaru Yoshikawa,<sup>1</sup> Tomoaki Matsuura,<sup>2</sup> Shinya Tsukiji<sup>1</sup>

**Keywords:** Synthetic cell, Liposome, Biosensor, Signal transduction, Fluorescence

Cells detect a tiny amount of extracellular molecules and transmit the signal across the plasma membrane into the intracellular milieu. The transmitted signal is then amplified by sequential biochemical processes, allowing cells to induce cellular responses. The construction of synthetic “cell-like” molecular systems that can achieve such integrated signal transduction not only contributes to the understanding of cellular systems but also leads to the creation of novel molecular technologies for biosensing and bioengineering applications. Recently, Hunter et al. reported a membrane-embedded synthetic transducer capable of generating fluorescent signals in liposomes in response to metal ions.<sup>1</sup> Zelikin et al. also developed synthetic receptors that can activate a zymogen in liposomes in response to biological stimuli such as alkaline phosphatase (biomarker).<sup>2</sup> However, these systems still suffer from low signal amplification efficiency. Therefore, the bottom-up construction of synthetic cells with the capacity to achieve (i) detection, (ii) transmembrane signal transduction, and (iii) signal amplification with high efficiency remains a fundamental challenge in chemistry and synthetic biology.

To this end, we focused on protein-membrane recruitment. In natural cellular systems, many proteins are recruited from the cytoplasm to the plasma membrane upon cell stimulation. Such membrane recruitment elevates local protein concentration, serving as a fundamental mechanism for cells to enhance various biochemical processes efficiently on the membrane. However, the design of synthetic cell systems that can control protein membrane recruitment inside liposomes has yet to be established. Therefore, we first developed a novel synthetic signal transduction system that induces protein membrane recruitment in the presence of specific biomarker enzymes. In this system, we use a lipid-tethered small-molecule ligand containing an “enzyme-responsive membrane permeability switch” as a synthetic transducer (**Fig. 1**). The synthetic transducer is membrane-impermeable, but it binds to the liposome outer membrane in the absence of its target enzyme. However, the membrane permeability switch is cleaved in the presence of the target enzyme, allowing the molecule to permeate into the liposome and recruit its binding protein to the inner membrane. Furthermore, by coupling the synthetic transducer-mediated protein recruitment strategy with reporter proteins such as TEV protease and split BS2 esterase, we developed a synthetic cell sensor platform capable of detecting biomarker enzymes with amplified fluorescent signals.



**Fig. 1** The schematic illustration of the synthetic cell sensor system developed in this work.

1) M. J. Langton et al., *J. Am. Chem. Soc.* **2017**, *139*, 6461. 2) A. B. Sogaard, et al., *Nat Commun.* **2023**, *14*, 1646.



## メンブレンコンタクト動態を可視化する分割型蛍光プローブの開発

(名工大院工<sup>1</sup>・新潟大院医歯<sup>2</sup>) 阿喰 萌香<sup>1</sup>・○吉川 優<sup>1</sup>・筒井 啓太<sup>1</sup>・中津 史<sup>2</sup>・築地 真也<sup>1</sup>

Development of split fluorescent probes for visualizing membrane contact site dynamics (<sup>1</sup>Graduate School of Engineering, Nagoya Institute of Technology, <sup>2</sup>Graduate School of Medical and Dental Sciences, Niigata University) Moeka Ajiki<sup>1</sup>, ○Masaru Yoshikawa<sup>1</sup>, Keita Tsutsui<sup>1</sup>, Fubito Nakatsu<sup>2</sup>, Shinya Tsukiji<sup>1</sup>

In recent years, it has become evident that the endoplasmic reticulum (ER) forms membrane contact sites (MCSs) with various organelles and the plasma membrane (PM) to control cellular processes. Despite their crucial role in cell physiology, the spatiotemporal dynamics of MCSs remain largely unknown due to the lack of methods suitable for visualizing MCS in live cells. In this study, we focused on splitFAST, a reversible fluorescence complementation system that allows the detection of association and dissociation of N-FAST/C-FAST fragments in the presence of a fluorogenic dye, HBR. Here we demonstrate that ORP5-mediated ER-PM contact sites can be visualized with HBR fluorescence by using PM-targeted N-FAST and ER-targeted ORP5-fused C-FAST constructs. We also report the engineering of novel splitFAST variants that show improved reversibility.

**Keywords:** Membrane contact, Split protein, Chemogenetic fluorescent probe, Plasma membrane, Endoplasmic reticulum

真核細胞の内部には、ゴルジ体やミトコンドリア、小胞体 (ER) などに代表される膜に包まれた構造体 (オルガネラ) が多数存在する。従来、異なるオルガネラは物理的・空間的に隔絶されているものと考えられてきた。しかし近年、オルガネラ同士、または細胞膜 (PM) とオルガネラの近接によりメンブレンコンタクト (以下、コンタクト) と呼ばれる膜-膜接触部位が形成され、そこで物質や情報の直接的な交換や、多様な細胞生理機能の制御が行われていることが明らかとなってきた<sup>1)</sup>。コンタクトの機能や制御機構の解明は生物学上重要であり、その形成や解消といった動態をライブセルで時空間的に解析する可視化技術が求められている。その先駆的なツールとして splitGFP 法が報告されているが、splitGFP は自己再構成しやすく、可逆性に乏しいため、生理条件下では見られないコンタクト形成を人為的に誘導してしまうといった問題点がある<sup>2)</sup>。

そこで本研究では、分割型タンパク質を利用した発蛍光システムである「splitFAST」<sup>3)</sup>に着目し、可逆的かつ時空間的なコンタクト検出が可能な新規蛍光プローブの開発に着手した。splitFAST は、FAST と呼ばれるタンパク質を 2 つのフラグメント (N-FAST および C-FAST) に分割したもので、それぞれのフラグメント同士が近接すると FAST が再構成され、小分子化合物 HBR と結合して蛍光を発する。今回我々は、コンタクト形成による近接を splitFAST の再構成に利用できれば、コンタクトを蛍光検出できると考えた。概念実証として、ORP5 タンパク質が形成する ER-PM コンタクトに着目し、N-FAST を PM 上に、C-FAST を ORP5 に連結して ER 上に発現させたところ、ORP5 を介した ER-PM コンタクト形成部位が HBR 蛍光で可視化された。また、薬剤処理によるコンタクト解消後には蛍光が減弱する様子が見られ、コンタクト動態を可逆的に検出可能であることも確認された。本発表では、本ツールによる生細胞内コンタクト動態の時空間的な解析および、可逆性の向上した splitFAST 変異体のエンジニアリングについて報告する。

1) W. A. Prontz et al., *Nat. Rev. Mol. Cell Biol.* **2020**, 21, 7–24. 2) F. Nakatsu et al., *Curr. Opin. Chem. Biol.* **2023**, 73, 102262. 3) A. G. Tebo et al., *Nat. Commun.* **2019**, 10, 2822.

## SLIPT によるマウス内シグナル操作

(名工大院工<sup>1</sup>・京大院生命<sup>2</sup>・京大院医<sup>3</sup>) ○田原 海<sup>1</sup>・吉川 優<sup>1</sup>・高倉 加奈子<sup>2</sup>・寺井 健太<sup>3</sup>・松田 道行<sup>2,3</sup>・築地 真也<sup>1</sup>

Cell Signal Manipulation in Living Mice by SLIPT (<sup>1</sup>*Graduate School of Engineering, Nagoya Institute of Technology*, <sup>2</sup>*Graduate School of Biostudies, Kyoto University*, <sup>3</sup>*Graduate School of Medicine, Kyoto University*) ○Kai Tahara,<sup>1</sup> Masaru Yoshikawa,<sup>1</sup> Kanako Takakura,<sup>2</sup> Kenta Terai,<sup>3</sup> Michiyuki Matsuda,<sup>2,3</sup> Shinya Tsukiji<sup>1</sup>

Developing tools to manipulate specific signaling molecules and pathways in living animals, i.e., in vivo, is one of the challenges in chemical biology. We have previously developed SLIPT, a technology for controlling intracellular protein localization with self-localizing ligands. SLIPT can manipulate various signaling pathways by inducing the plasma membrane localization of tag-fused signaling proteins expressed in culture cells. To extend the SLIPT tool to in vivo, in this study, we developed a new self-localizing ligand and tag protein pair that works in the blood of mice. The new SLIPT system allowed us to control the intracellular localization and activation of tag-fused signaling proteins, such as Raf and PI3K, in living mice. **Keywords :** Mouse, Signal transduction, Protein localization, Self-localizing ligand

生きた動物個体内 (in vivo) の特定のシグナル分子の活性を特異的に操作する技術は、細胞内や細胞間の情報伝達が in vivo 環境下でどのように制御されているのかを分子レベルで解析する強力な基盤ツールとなる。しかし、in vivo で使用可能なシグナル分子操作ツールの開発はいまだ萌芽期にあり、一部の GPCR やイオンチャネル型受容体の制御ツールが報告されているにすぎない。したがって、生命システムを司るさまざまな細胞内シグナル分子や情報伝達経路を動物個体内で汎用的に操作することのできる in vivo 分子操作ツールを開発することは、ケミカルバイオロジーにおける大きな課題の1つである。

我々はこれまで、局在性リガンドによるタンパク質の細胞内局在制御技術「SLIPT (self-localizing ligand-induced protein translocation) 法」の開発に取り組んできた<sup>1-3)</sup>。SLIPT 法は、任意のタグ融合シグナルタンパク質の細胞内局在移行を誘導することで、さまざまなシグナル分子・経路の活性を幅広く操作することができる。そのため、SLIPT 法を in vivo に展開することができれば、任意のシグナル分子や情報伝達経路を動物個体内で自在に操作可能な革新的な化学遺伝学ツールになるものと期待される。そこで本研究では、SLIPT 法の in vivo 利用を目指し、マウス血液中で機能する局在性リガンドとタグタンパク質を新規に開発した。このペアを用いると、生きたマウスの体内で標的タンパク質の細胞膜移行を誘導することができ、受容体直下のさまざまなシグナル伝達のマウス内操作が可能であった。本発表では、我々が開発した in vivo SLIPT ツールの基本設計からマウスへの応用までの詳細を報告する。

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) S. Suzuki et al. *Cell Chem. Biol.*, **2022**, 29, 1446–1464.

## Construction of a Platform for the Discovery of Macrocyclic Peptide Heterodimer Ligands

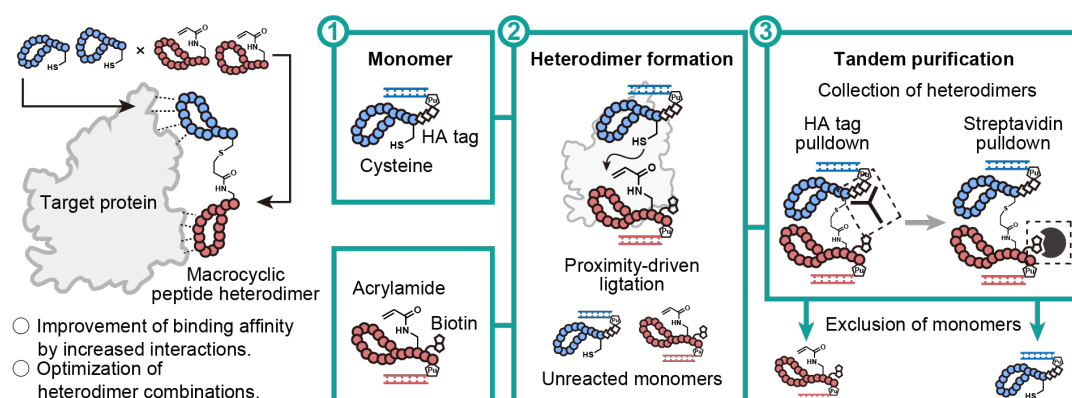
(<sup>1</sup>Graduate School of Science, The University of Tokyo) ○ Yuto Ohno,<sup>1</sup> Vinogradov Alexander,<sup>1</sup> Hiroaki Suga<sup>1</sup>

**Keywords:** mRNA display, macrocyclic peptides, bioconjugation, binding surface, library size

In the search for novel drug candidates, powerful *de novo* discovery methods such as phage<sup>1</sup> and mRNA display<sup>2</sup> are routinely used to obtain peptide ligands to therapeutic proteins of choice. Peptide macrocyclization improves the binding ability and *in vivo* stability of the resulting ligands, and is a common technique to improve the screening outcomes<sup>3</sup>. However, it may still be difficult to identify potent and selective ligands to proteins without well-defined binding pockets. We hypothesized that cyclic peptide heterodimers could be used to increase the surface area of the interaction, thereby enabling their binding to shallow protein surfaces.

In this study, building upon the macrocyclic peptide ligand discovery platform, the RaPID system<sup>4</sup>, we constructed a platform to discover peptide heterodimers that bind to target proteins. First, a peptide library containing a cysteine residue and HA tag, as well as the second library bearing acrylamide and biotin moieties are produced by *in vitro* translation. These libraries are then mixed in the presence of a target protein. When the peptides bind to the protein, the cysteine thiol in one peptide can react with the acrylamide from the neighboring ligand, thus forming a heterodimer. Such heterodimers interact with the protein over a large surface area, and therefore are expected to have high affinities and specificities for the target. During selection, the heterodimers can be selectively recovered by a tandem purification process consisting of anti-HA antibody and streptavidin pulldowns.

In this presentation, we will discuss the construction and evaluation of a simple model system, and the results of the ligand discovery against a therapeutic target protein.



1) *Chem. Rev.* **1997**, 97, 391-410. 2) *Chem. Rev.* **2019**, 119, 10360-10391. 3) *J. Am. Chem. Soc.* **2019**, 141, 4167-4181. 4) *Chem. Biol.* **2011**, 18, 1562-1570.

## 人工ヘムタンパク質モデル錯体による水中での硫化水素の捕捉および硫化水素中毒解毒剤としての応用

(同志社大理工<sup>1</sup>・佐賀大農<sup>2</sup>) ○中上 敦貴<sup>1</sup>・堀谷 正樹<sup>2</sup>・北岸 宏亮<sup>1</sup>

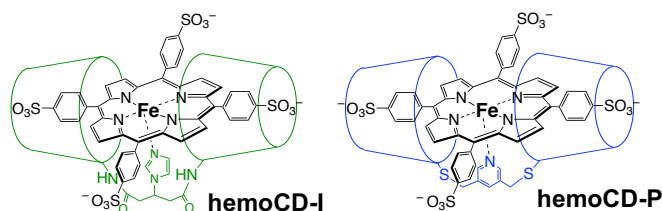
Interaction of artificial heme protein model compounds with hydrogen sulfide in water and its application as an antidote against hydrogen sulfide poisoning

(<sup>1</sup>Faculty of Science and Engineering, Doshisha University, <sup>2</sup>Faculty of Agriculture, Saga University) ○Atsuki Nakagami,<sup>1</sup> Masaki Horitani,<sup>2</sup> Hiroaki Kitagishi<sup>1</sup>

Hydrogen sulfide (H<sub>2</sub>S) plays the physiological role as a gaseous signaling molecule in biological system, while it can cause lethal intoxication at higher concentration. In previous studies, we have successfully developed the artificial synthetic heme protein model, hemoCDs<sup>1)</sup> (Fig. 1). In this work, we found that hemoCD-I, having an imidazole linker, shows stronger interaction with H<sub>2</sub>S than hemoCD-P and methemoglobin (methHb) in water at physiological pH (Table. 1). Spectroscopic studies also revealed that bound H<sub>2</sub>S is catalytically metabolized by hemoCD-I via its oxygen-bound complex (Fig. 2). Besides, the interaction of hemoCD-I with H<sub>2</sub>S *in vivo* also confirmed through poisoning mouse model experiments. Therefore, we proved the effectiveness of hemoCD-I as an antidote for hydrogen sulfide.

**Keywords :** Porphyrin; Cyclodextrin; Hemeprotein model; Hydrogen sulfide; Antidote

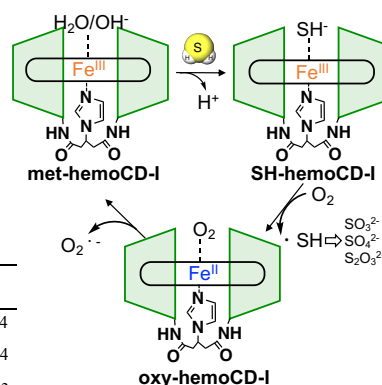
硫化水素(H<sub>2</sub>S)はシグナル分子として生理機能を有する一方、高濃度への曝露は硫化水素中毒を引き起こし、死に至る危険性がある。我々はこれまでにシクロデキストリンダイマーと水溶性鉄ポルフィリン(FeTPPS)からなる包接錯体「hemoCD」を人工ヘムタンパク質モデルとして報告している<sup>1)</sup>(Fig. 1)。今回、我々は特にイミダゾールを架橋部位に用いた hemoCD-I が水中において高い H<sub>2</sub>S 捕捉能を示すことを見出した (Table 1)。hemoCD-I に捕捉された H<sub>2</sub>S はさらなる反応を示し、酸素錯体を経由して、H<sub>2</sub>S を触媒的に消費することを各種分光測定により明らかとした (Fig. 2)。さらに hemoCD-I による生体内 H<sub>2</sub>S の捕捉能を動物実験により確認した。硫化水素中毒モデルマウスに対する hemoCD-I の投与により、有意な生存率の向上が得られ、hemoCD-I が生体内でも H<sub>2</sub>S を捕捉し、硫化水素中毒解毒剤としても有効であることを示した。



**Fig. 1.** The structures of hemoCDs.

**Table. 1.** Thermodynamic and kinetic parameters of various sulfide receptors in water at pH 7.4.

	$K_{app}$ (M <sup>-1</sup> )	$k_{on}$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_{off}$ (s <sup>-1</sup> )
<b>hemoCD-I</b>	$2.5 \times 10^6$	$1.5 \times 10^3$	$5.9 \times 10^{-4}$
<b>hemoCD-P</b>	$1.2 \times 10^5$	$1.0 \times 10^2$	$8.4 \times 10^{-4}$
<b>metHb</b>	$2.8 \times 10^5$	$9.9 \times 10^2$	$3.5 \times 10^{-3}$



**Fig. 2.** Catalytic metabolism of H<sub>2</sub>S by hemoCD-I.

1) Kitagishi, H.; Kano, K., *Chem. Commun.*, **2021**, 57, 148.

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 H934(9号館 [3階] 934)

**[H934-3pm] 17. 生体機能関連化学・バイオテクノロジー**

座長：梶原 康宏、珠玖 仁

## ◆ 英語

13:00 ~ 13:20

[H934-3pm-01]

抗体修飾による小児髄髄芽腫を対象とした薬物輸送システムの開発

○渡邊 隆義<sup>1</sup>、水野 隼斗<sup>2</sup>、乗松 純平<sup>1</sup>、Cabral Horacio<sup>1</sup>、川内 大輔<sup>2</sup>、安楽 泰孝<sup>3</sup> (1. 東京大学、2. 国立精神・神経医療研究センター、3. 東京工業大学)

## ◆ 英語

13:20 ~ 13:40

[H934-3pm-02]

Synthesis of Shortwave-Infrared (SWIR) Organic Fluorescent Probes for Deep Tissue Molecular Imaging of Breast Cancer.

○Mahadeva Swamy Makanahalli Madegowda<sup>1</sup>, Yuta Murai<sup>1</sup>, Setsuko Tsuboi<sup>2</sup>, Aravind Kanda Swamy<sup>1</sup>, Takashi Jin<sup>2</sup>, Kenji Monde<sup>1</sup> (1. Faculty of Advanced Life Science, Hokkaido University, 2. Center for Biosystems Dynamics Research, RIKEN)

## ◆ 日本語

13:40 ~ 14:00

[H934-3pm-03]

表皮再生促進効果を期待した薬剤ラッピング高接着性ナノシートの創製と機能評価

○芝 耀汰<sup>1</sup>、谷神 絃太<sup>1</sup>、布山 忠裕<sup>1</sup>、住吉 秀明<sup>2</sup>、稲垣 豊<sup>2</sup>、岡村 陽介<sup>1,3</sup> (1. 東海大院工、2. 東海大医、3. 東海大マイクロ・ナノ研)

## ◆ 英語

14:00 ~ 14:20

[H934-3pm-04]

アレルギーの根本治療を目指した鼻粘膜へのリポソームDDSの開発

○佳月 李<sup>1</sup>、森田 直樹<sup>2</sup>、三浦 理紗子<sup>1</sup>、木村 祐<sup>1</sup>、新藏 礼子<sup>2</sup>、近藤 輝幸<sup>1</sup> (1. 京大院工、2. 東大定量生命科学研究所)

14:20 ~ 14:30

休憩

## ◆ 英語

14:30 ~ 14:50

[H934-3pm-05]

新規サンプリング法を用いた核磁気共鳴法による糖と水の相互作用解析

○森口 達也<sup>1</sup>、真木 勇太<sup>1,2</sup>、岡本 亮<sup>1,2</sup>、梶原 康宏<sup>1,2</sup> (1. 阪大院理、2. 阪大院理フォアフロント研究センター)

## ◆ 日本語

14:50 ~ 15:10

[H934-3pm-06]

生体模倣システムのための多孔膜電極デバイス

○伊野 浩介<sup>1</sup>、宇田川 喜信<sup>1</sup>、阿部 博弥<sup>1</sup>、珠玖 仁<sup>1</sup> (1. 東北大学)

---

◆ 英語

15:10 ~ 15:30

[H934-3pm-07]

出芽酵母の画像活性分取におけるAI画像解析法の有効性評価

林 実加<sup>1</sup>、大貫 慎輔<sup>1</sup>、Yating Tsai<sup>1</sup>、○丁 天本<sup>1</sup>、磯崎 瑛宏<sup>2,1</sup>、大矢 禎一<sup>1</sup>、合田 圭介<sup>1,3,4,5</sup> (1. 東京大学、2. 立命館大学、3. カリフォルニア大学ロサンゼルス校、4. 武漢大学、5. CYBO)

---

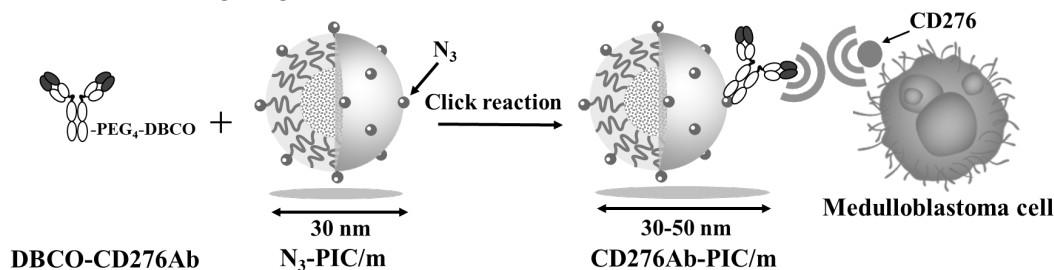
## Ligand Installation to Polymeric Micelles for the Targeting of Pediatric Medulloblastoma

(<sup>1</sup>Graduate School of Engineering, The University of Tokyo, <sup>2</sup>National Center of Neurology and Psychiatry, <sup>3</sup>Tokyo Institute of Technology) ○ Takayoshi Watanabe,<sup>1</sup> Hayato Laurence Mizuno,<sup>2,3</sup> Jumpei Norimatsu,<sup>1</sup> Takumi Obara,<sup>1</sup> Horacio Cabral,<sup>1</sup> Daisuke Kawauchi,<sup>2</sup> Yasutaka Anraku<sup>3</sup>

**Keywords:** CD276; medulloblastoma; micelles; ligand installation; anti-CD276 antibody

Medulloblastoma is one of the most malignant brain tumors in the pediatric population. It comprises 20% of all childhood brain tumors, and the 5-year survival rate is 40–60% [1]. While various strategies have been implemented to optimize the treatment efficiency, including chemotherapy, the low drug accumulation in brain tumor tissues and the limited cellular uptake of drugs has limited the efficacy [2]. Recently, the conjugation of drugs to ligand molecules with high affinity to tumor cells has attracted much attention for enhancing drug internalization into target cells [3]. Moreover, combining tumor-targeting ligands with nano-scaled drug carriers can potentially improve a drug loading capacity and accumulation to the target lesion [4]. Herein, we focused on targeting CD276/B7-H3, which is highly expressed on the cell membrane of medulloblastoma [5], as a strategy for enhancing the cellular uptake of ligand-installed nanocarriers.

Anti-CD276 antibody-conjugated nanocarriers were constructed by click chemistry using azide-bearing polyion complex micelles (N<sub>3</sub>-PIC/m) and DBCO-modified antibodies. The anti-CD276 antibody-conjugated micelle (CD276Ab-PIC/m) showed a size around 40 nm. Moreover, they significantly enhanced the internalization into medulloblastoma cells when compared to the micelles without ligand. The uptake of CD276Ab-PIC/m was also reduced when co-incubated with free anti-CD276 antibodies, suggesting that the targeting was mediated by the CD276 on the surface of tumor cells [6]. Furthermore, increasing the number of antibodies on the surface of the micelles boosted the cell internalization efficiency. These findings underscore the potential of CD276Ab-PIC/m as a promising strategy to enhance medulloblastoma targeting.



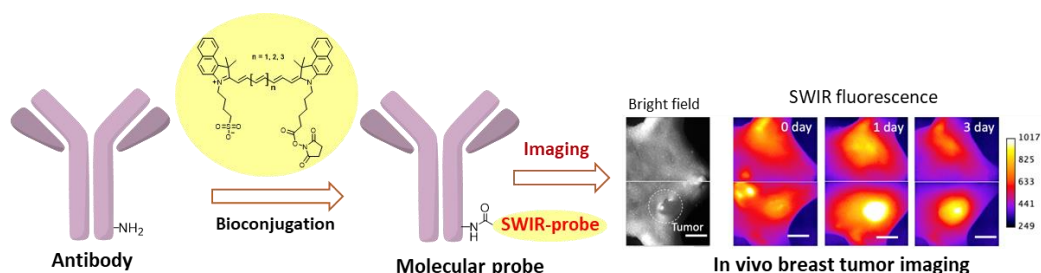
- [1] Ostrom, Q.T. *Neuro-Oncol.* **2018**, *20*, 1–86. [2] Kim, J. *PNAS* **2020**, *117*, 24205–24212  
 [3] Bao, R. *J. Mol. Pharm.* **2019**, *16*, 339–348. [4] Miura, Y. *ACS nano* **2013**, *10*, 8583–8592  
 [5] Li, S. *Clin. Transl. Oncol.* **2022**, *24*, 1204–1208. [6] Watanabe, T. *Polymers* **2023**, *15*, 1808

## Synthesis of Shortwave-Infrared (SWIR) Organic Fluorescent Probes for Deep Tissue Molecular Imaging of Breast Tumor.

(<sup>1</sup>Faculty of Advanced Life Science, Hokkaido University, <sup>2</sup>Center for Biosystems Dynamics Research, RIKEN) ○Mahadeva Swamy Makanahalli Madegowda<sup>1</sup>, Yuta Murai<sup>1</sup>, Setsuko Tsuboi<sup>2</sup>, Aravind Kanda Swamy<sup>1</sup>, Takashi Jin<sup>2</sup>, Kenji Monde<sup>1</sup>

**Keywords:** Fluorescence imaging; Organic dye; Molecular probe; Shortwave-infrared; Deep tissue imaging

Fluorescence-guided intraoperative cancer detection is an effective method for surgical removal of solid tumors. Looking at the food & drug administration (FDA) approved and clinical trial near-infrared (NIR) probes, only indocyanine green (ICG) and its analogues are approved for biomedical applications. Extending molecular imaging into the shortwave-infrared (SWIR, 900 – 1400 nm) region provides deep tissue visualization of biomolecules of living system resulting from the negligible tissue autofluorescence and scattering. Recent advances in deep tissue penetration by SWIR light could significantly enhance the clinical applications of fluorescence-guided intraoperative cancer detection and surgery.<sup>1</sup> Although several SWIR emitting organic probes have been reported,<sup>2</sup> development of clinically applicable fluorophores is still challenging. Herein, we present the synthesis of  $\pi$ -conjugation extended ICG analogues and their antibody labeling agents as SWIR-emitting probes. The covalent conjugation reaction was performed between developed organic dyes and monoclonal antibodies to synthesize molecular probes for specific biomolecular imaging of breast tumor. Using molecular probes, we demonstrate high-contrast in vivo optical imaging of breast tumors in living mice (Fig.1).<sup>3</sup> Furthermore, we show long-term (38 days) SWIR fluorescence imaging of breast tumor shrinkage induced by Kadcyla (antibody-drug conjugate). This study provides a general strategy for SWIR fluorescence molecular imaging with biocompatible, water-soluble, and clinically applicable SWIR emitting cyanine probes.



**Figure 1.** Schematic representation for the conjugation of an *N*-succinimidyl ester derivative of SWIR probe to the antibody followed by in-vivo SWIR fluorescence imaging of breast tumor.

- 1) C. Li, G. Chen, Y. Zhang, F. Wu, Q. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 14789.
- 2) S. Zhu, R. Tian, A. L. Antaris, X. Chen, H. Dai, *Adv. Mater.* **2019**, *31*, e1900321.
- 3) M. M. M. Swamy, Y. Murai, K. Monde, S. Tsuboi, T. Jin, *Bioconjugate Chem.* **2021**, *32*, 1541.



## 表皮再生促進効果を期待した薬剤ラッピング高接着性ナノシートの創製と機能評価

(東海大院工<sup>1</sup>・東海大医<sup>2</sup>・東海大マイクロ・ナノ研<sup>3</sup>) ○芝 燿汰<sup>1</sup>・谷神 絃太<sup>1</sup>・布山 忠裕<sup>1</sup>・住吉 秀明<sup>2</sup>・稲垣 豊<sup>2</sup>・岡村 陽介<sup>1,3</sup>

Fabrication and Evaluation of Drug-Wrapped Adhesive Nanosheets with Epidermal Regeneration Ability (<sup>1</sup>Graduate School of Engineering, Tokai University, <sup>2</sup>Tokai University School of Medicine, <sup>3</sup>Micro/Nano Technology Center, Tokai University) ○Yota Shiba<sup>1</sup>, Genta Yagami<sup>1</sup>, Tadahiro Fuyama<sup>1</sup>, Hideaki Sumiyoshi<sup>2</sup>, Yutaka Inagaki<sup>2</sup>, Yosuke Okamura<sup>1,3</sup>

Treatment of skin defects using artificial dermis requires epidermal transplantation from other sites in the body<sup>1), 2)</sup>. We have reported that moon jellyfish collagen possesses excellent epidermal regeneration ability<sup>3)</sup>. However, there is a limit to the amount of collagen injected into artificial dermis due to its low solubility in water. On the other hand, nanosheets with the thickness of nanometer scale exhibit high adhesive properties that allow to be attached to various interfaces by only physical adsorption<sup>4)</sup>. In this study, we propose a fabrication method of a collagen-wrapped nanosheets composed of biodegradable poly(lactic acid) (PLA) nanosheet for promoting the epidermal regeneration ability. An aqueous solution of sodium polystyrene sulfonate (PSS) as a sacrificial layer was spin-coated on SiO<sub>2</sub> substrate. A toluene solution of PLA was then spin-coated on the PSS-coated substrate. When the substrate was immersed in water, the freestanding PLA nanosheet (38 × 38 mm<sup>2</sup>) was peeled off while maintaining the shape of the substrate. The PLA nanosheet was recovered on a Teflon mesh. Another PLA nanosheet (13 × 13 mm<sup>2</sup>) was pressed onto the recovered PLA nanosheet. An aqueous solution of Moon jellyfish collagen was dropped and dried on the PLA nanosheets. Finally, the PLA nanosheet adhered on Teflon mesh was folded and wrapped the jellyfish collagen. The detailed results on epidermal regeneration ability in diabetic mice will be released on the 104th CSJ annual meeting.

**Keywords :** *polymer nanosheet, drug wrapping, moon jellyfish collagen, wound healing*

現在、皮膚欠損創の治療には人工真皮が使用されている<sup>1)</sup>。しかし、その最表面は多孔質のため、表皮が進展しにくく、表皮移植を要する<sup>2)</sup>。他方、ミズクラゲのコラーゲンは優れた表皮再生能を有することが見出されているが、その担持量の少なさに課題がある<sup>3)</sup>。また、膜厚がナノ厚のナノシートは、物理吸着のみで様々な界面に貼付可能となる高接着性が発現することが見出されている<sup>4)</sup>。本研究では、生分解性高分子であるポリ乳酸 (PLA) からなるナノシートでミズクラゲコラーゲンをラッピングした新規薬剤ラッピング材の創製法を提案し、さらなる表皮再生能の向上を狙う。

SiO<sub>2</sub> 基板上にポリスチレンスルホン酸ナトリウム水溶液にてスピンコート (4000 rpm, 60 s) して犠牲層とした。続いて、PLA のトルエン溶液にて同条件にてスピンコートした。次に、水中にて基板ごと浸漬させたところ、基板の形状を維持した状態で PLA ナノシート (38 × 38 mm<sup>2</sup>) を剥離できた。テフロンメッシュ上に回収した PLA ナノシートの上に別途調製した PLA ナノシート (13 × 13 mm<sup>2</sup>) を押し当て、転写した。また、転写した PLA ナノシート上にミズクラゲコラーゲン水溶液を滴下後、乾燥させた。最後に、PLA ナノシート (38 × 38 mm<sup>2</sup>) をテフロンメッシュごと折りたたみ、ミズクラゲコラーゲンをラッピングする手法を確立した。現在、糖尿病モデルマウスを使用した表皮再生能評価を進めており、当日併せて報告する。

1) Koide M. *et al. J. Bio. Mater. Res.* **27**, 79-87 (1993), 2) Burke Jf. *et al. Ann. Surg.* **194**, 413-427 (1981),

3) Sumiyoshi H. *et al. Regen. Ther.* **18**, 223-230 (2021), 4) Okamura Y. *et al. Adv. Mater.* **21**, 4388-4392 (2009).

## Development of Liposome-based Drug Delivery System to Nasal Mucosa for Radical Allergy Treatment

(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>Institute for Quantitative Biosciences., The Univ. of Tokyo) ○Jiayue Li, <sup>1</sup> Naoki Morita, <sup>2</sup> Risako Miura, <sup>1</sup> Yu Kimura, <sup>1</sup> Reiko Shinkura, <sup>2</sup> Teruyuki Kondo<sup>1</sup>

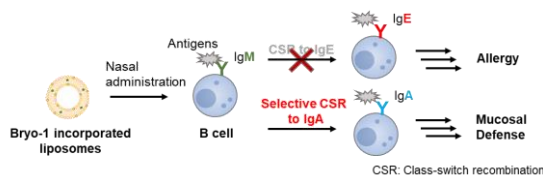
**Keywords:** Drug delivery system; Liposome; Class-switching

Allergic symptoms occur by the overproduction of IgE antibody. It was reported that dysregulated immune response can be corrected through liposome-based drug delivery systems (DDS) targeting antigen-presenting cells (APCs) in immunotherapy by modulation of antigen-specific T- and B-cell responses as well as inhibition of the recruitment of mast cells, which enables to reduce the release of histamine.<sup>1,2</sup> In contrast, the radical treatment of allergies requires both the development of novel ideal medicines to enhance the production of IgA antibody and the construction of DDS system to APCs in the nasal mucosa, efficiently. By random screening of over 6,000 compounds, Shinkura and coworkers found that Bryostatin-1 (Bryo-1) showed extremely high activity for inhibition of IgE-related allergic reactions with enhancing the defense of nasal mucosa against antigens through the selective production of IgA antibody by nasal administration of Bryo-1.<sup>3</sup>

In this study, we found the small molecular compounds as well as Bryo-1 which are effective for IgA class-switching. We will report that they were incorporated smoothly in liposomes with different surface charges and the cellular uptake of

them on APCs was investigated. As a result, both cationic and anionic liposomes enhanced the interaction with nasal mucosa and APCs through electrostatic and receptor-mediated interactions as well as resisting mucociliary clearance, which prompted us to develop a basic liposome carrier for the APCs-targeting nasal DDS.

The Bryo-1 incorporated neutral (DOPC), cationic (DOTAP/DOPC), and anionic (DOPS/DOPC) liposomes were prepared successfully by the thin film method. Three kinds of Bryo-1 incorporated liposomes and the Rh-PE labeled liposome were analyzed by DLS, which showed clearly the formation of nanoparticles with *ca.* 120 nm. In addition, the ELS analysis of  $\zeta$ -potential showed that the surface charge varied depending on the added ionic lipids. Investigation of cellular uptake indicated the stronger interaction between cells and charged liposomes incorporating Bryo-1, and their IgA class-switching activity was almost the same as free Bryo-1. Consequently, the present study highlighted that the charged liposomes were highly efficient DDS carrier of Bryo-1 for the radical treatment of allergies.



**Scheme 1.** Selective class-switching to IgA to enhance the mucosal defense.

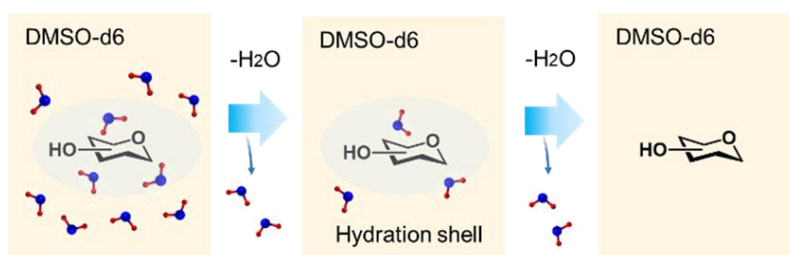
1) Akdi, C. A. *et al. J Allergy Clin Immunol.* **2011**, *127*, 18-27. 2) Frew, A. J. *J. Allergy Clin Immunol.* **2010**, *125*, S306-313. 3) Shinkura, R.; Yamamoto, K. *PCT Int. Appl.*, WO 2018/034318 A1 (2017).

## Unique NMR analysis of water behavior around glycans

(<sup>1</sup>Graduate School of Science, and <sup>2</sup>Forefront Research Center, Graduate School of Science, Osaka University) ○Tatsuya Moriguchi<sup>1</sup>, Yuta Maki<sup>1,2</sup>, Ryo Okamoto<sup>1,2</sup>, Yasuhiro Kajihara<sup>1,2</sup>

**Keywords:** NMR, hydration, glycan, glycoprotein

The glycans of glycoproteins regulate protein functions. However, the clear processes are still unknown. We hypothesize that glycans regulate water behavior around glycoproteins.<sup>1,2</sup> In order to verify this hypothesis, we have investigated interaction between sugar and water by a newly established unique system enabling control of amounts of water in an NMR tube (Figure). This new system can regulate water amount ranging from over 100 equivalents to one equivalent of water against sugar molecules even under low concentration of sugars. Therefore, this system enabled us to analyze both the interaction between sugars and bulk-like water molecules, and the behavior of hydration water molecules.



In order to measure the interaction of sugars with water, we made a sugar sample in DMSO changing of both amounts of water and sugar of interest. Then, we measured <sup>1</sup>H NMR, T1, and T2 relaxation in the presence of water ranging from 100 equivalents to 1 equivalent even for dilute sugar samples.

As a result, we successfully observed a signal that seems to be sugar hydrated water. We have performed these NMR measurements for methyl- $\alpha$ -glucoside, methyl- $\alpha$ -galactoside, methyl- $\alpha$ -mannoside, trehalose, and complex type *N*-glycans.

From the measurement of <sup>1</sup>H NMR, we found which hydroxyl groups in a sugar accessed water by analyzing <sup>1</sup>H peak shifts of hydroxy group dependent on water amounts.

Among these sugars, the T2 relaxation of *N*-glycan remarkably decreased compared to other monosaccharides, indicating a large glycan could interact with water very much. In this presentation, we also discuss how glycans of glycoproteins control water behavior in detail.

1) Maki. Y, Okamoto. R, Izumi. M, Kajihara. Y, *J. Am. Chem. Soc.* **2020**, *142*, 49, 20671-20679.

2.) Okamoto. R, Orii. R, Shibata. H, Maki. Y, Tsuda. S, Kajihara. Y., *Chem. Eur. J.* **2023**, e202203553.

## Porous Electrode Device for Microphysiological Systems

(Graduate School of Engineering, Tohoku University) ○Kosuke Ino, Yoshinobu Utagawa, Hiroya Abe, Hitoshi Shiku

**Keywords:** Electrochemical Device; Microphysiological System; Porous Membrane; Cell Analysis

Microphysiological systems (MPSs) are gathering considerable attention for drug screening instead of animal tests. Within the systems, cells are three-dimensionally (3D) cultured to prepare cellular spheroids exhibiting in-vivo functions. Additionally, cells are cultured on porous membranes to mimic in-vivo-like interfaces, such as those found in the lung, gut, and vascular organs. For evaluating them, gene analysis techniques like qPCR and histological analysis are commonly used to evaluate these systems. However, cells are damaged during these analyses, prompting the need for alternative approaches that do not harm the cells. In this study, we focused on electrochemical approaches, as they enable the measurement of cellular functions without causing cell damage.<sup>1</sup> In our previous studies, cellular spheroids were placed on a CMOS-based electrode array device to visualize the respiratory activities and cell differentiation levels of 3D cultured stem cells. In this study, an electrochemical sensor is integrated into a porous membrane. Fig. 1 illustrates the fabrication process to prepare the porous electrode device for cell culture and analysis. As a demonstration, human umbilical vein endothelial cells (HUVECs) were used to create a cellular monolayer, and released nitric oxide (NO) was successfully measured. In the future, this approach will be widely adopted in microphysiological systems.

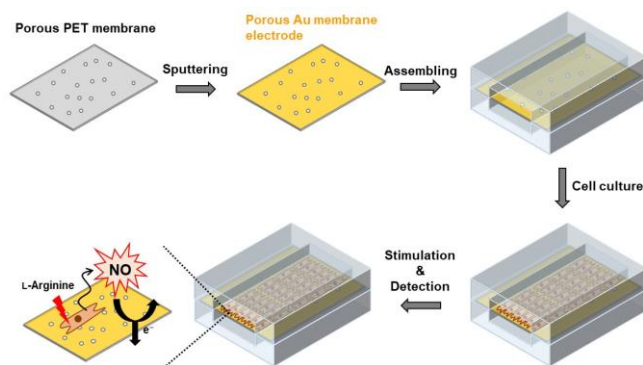


Fig. 1. Device fabrication, cell culture, and cell analysis. Reprinted with permission from the reference.<sup>3</sup> Copyright 2023 American Chemical Society.

1) A. Konno et al., *Curr. Opin. Electrochem.*, 39, 101270, 2023

2) K. Ino et al., *Angew. Chem. Int. Edit.*, 56, 6818, 2017; Y. Kanno et al., *Anal. Chem.*, 89, 12778, 2017

3) Y. Utagawa et al., *Anal. Chem.* in press, DOI: 10.1021/acs.analchem.3c03684.

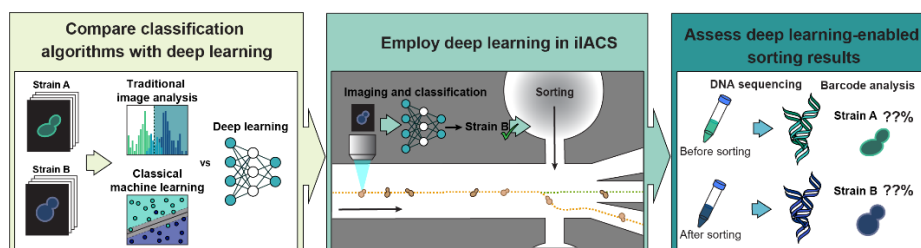
## 出芽酵母の画像活性分取における AI 画像解析法の有効性評価

(東大院理<sup>1</sup>・東大院新領域<sup>2</sup>・立命館大理工<sup>3</sup>・UCLA<sup>4</sup>・武漢大<sup>5</sup>・CYBO<sup>6</sup>) Mika Hayashi<sup>1</sup>・大貫 慎輔<sup>2</sup>・Yating Tsai<sup>2</sup>・○丁 天本<sup>1</sup>・磯崎 瑛宏<sup>1,3</sup>・大矢 禎一<sup>2</sup>・合田 圭介<sup>1,4,5,6</sup>  
Investigating the effectiveness of employing artificial intelligence in image-activated sorting of budding yeast (<sup>1</sup>*School of Science, University of Tokyo*, <sup>2</sup>*Graduate School of Frontier Sciences, University of Tokyo*, <sup>3</sup>*College of Science and Engineering, Ritsumeikan University*, <sup>4</sup>*UCLA*, <sup>5</sup>*Wuhan University*, <sup>6</sup>*CYBO*) Mika Hayashi,<sup>1</sup> Shinsuke Ohnuki,<sup>2</sup> Yating Tsai,<sup>2</sup> ○Tianben Ding,<sup>1</sup> Akihiro Isozaki,<sup>1,3</sup> Yoshikazu Ohya,<sup>2</sup> Keisuke Goda<sup>1,4,5,6</sup>

Recent advancements in artificial intelligence (AI) have led to the widespread use of deep learning (DL) techniques in cell image data analysis. However, their superiority over traditional image analysis methods was not obvious in image-activated cell sorting (IACS) due to time constraint in high-throughput sorting. This study contrasts DL with traditional feature gating and machine learning (ML) methods in sorting budding yeast mutants, assessing the effectiveness of AI in IACS<sup>1)</sup>. We show that while both classical ML and DL enhance enrichment beyond feature gating, ML shows a lesser improvement with greater time consumption compared to DL. Additionally, IACS experiments with a DL classifier on mixed mutant populations, followed by downstream DNA sequencing, demonstrated a notable 15.1-fold target enrichment from a cell mixture containing a 5% target mutant, thereby confirming the effectiveness of DL for this application.

**Keywords :** Cell Sorting; Machine Learning; Image Analysis; Microscopy; High-Throughput Imaging

近年の人工知能 (AI) の進歩に伴い、細胞画像データの解析と分類に深層学習 (DL) が広く採用されるようになった。しかし、画像活性細胞分取 (IACS) においては、分取までの時間的制約から、AI 解析法の従来手法に対する優位性は明白ではなかった。本研究では、出芽酵母の変異体分取における DL と従来のゲーティングや機械学習 (ML) 手法を比較し、IACS での AI 解析法の効果を定量的に評価した<sup>1)</sup>。ML と DL は双方ともゲーティングを超える細胞濃縮を可能とするが、ML は DL に比べて計算時間が長く、改善は限定的であった。また、混合変異体集団に対する IACS と後続の DNA シーケンシング実験により、DL による解析手法で 5% の標的変異体を含む細胞混合物から 15.1 倍の標的濃縮が可能であることを示した。本講演では、これらの結果から IACS における AI 画像解析技術の有効性について述べる。



1) M. Hayashi et al. "Is AI essential? Examining the need for deep learning in image-activated sorting of *Saccharomyces cerevisiae*," *Lab Chip*, 2023, **23**, 4232.

アカデミックプログラム [B講演] | 17. 生体機能関連化学・バイオテクノロジー：口頭B講演

2024年3月20日(水) 15:55 ~ 17:15 会場 H936(9号館 [3階] 936)

**[H936-3vn] 17. 生体機能関連化学・バイオテクノロジー**

座長：小野田 晃、神谷 典穂

## ◆ 英語

15:55 ~ 16:15

[H936-3vn-01]

Immobilization of Proteins on Triazolecarbaldehyde-linked Polymer Resin

○Shiyu Wang<sup>1</sup>, Akira Onoda<sup>1,2</sup> (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

## ◆ 英語

16:15 ~ 16:35

[H936-3vn-02]

Enhancing Enzymatic Breakdown of Polyethylene Terephthalate by Cutinase Tethering Hydrophobic Moiety at N-terminus

○Md Sadikur Rahman Shuvo<sup>1</sup>, Joel Muyomba<sup>1</sup>, Akira Onoda<sup>1,2</sup> (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

## ◆ 英語

16:35 ~ 16:55

[H936-3vn-03]

Expanding the Substrate Specificity of Alcohol Dehydrogenase from *Geotrichum candidum* NBRC 4597 toward Diaryl Ketones by Site-directed Mutagenesis○Zhongyao Tang<sup>1</sup>, Yuuki Takagi<sup>1</sup>, Afifa Ayu Koesoema<sup>1</sup>, Tomoko Matsuda<sup>1</sup> (1. Tokyo Institute of Technology)

## ◆ 英語

16:55 ~ 17:15

[H936-3vn-04]

キチン粉末を利用したアフィニティ精製手法の開発：立体選択的シクロプロパン化反応の触媒として働くヘムタンパク質探索への応用

○竹内 康基<sup>1</sup>、岩木 元直<sup>1</sup>、加藤 俊介<sup>1</sup>、林 高史<sup>1</sup> (1. 大阪大学)

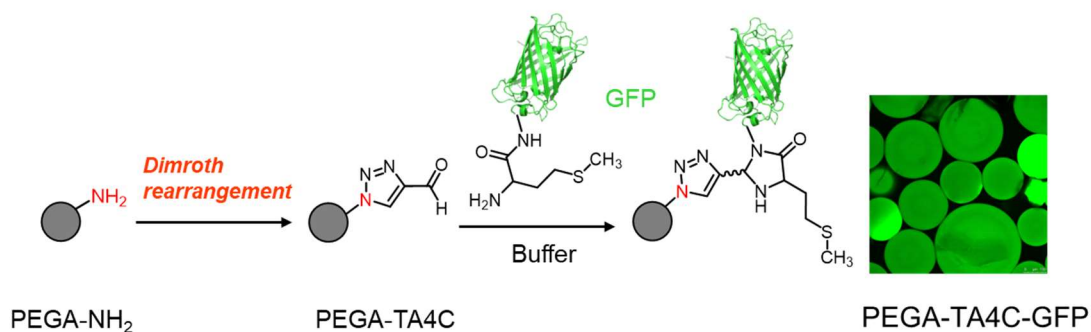
## Immobilization of Proteins on Triazolecarbaldehyde-linked Polymer Resin

### Resin

(<sup>1</sup>Graduate School of Environmental Science, Hokkaido University, <sup>2</sup>Graduate School of Environmental Earth Science, Hokkaido University) ○Shiyu Wang<sup>1</sup>, Akira Onoda<sup>1,2</sup>

**Keywords:** N-terminus modification, protein immobilization, polymer resin

The immobilization of proteins on the surface of solid materials has significantly broadened the applications of proteins in biotechnology and materials science. Since N-terminal modification of proteins is generally considered to preserve the activity of proteins, the facile method for protein immobilization via N-terminus is needed.<sup>1</sup> Here we have established a convenient method for the direct functionalization of surfaces of polymer resin to immobilize proteins at their N-terminus. We utilized 1*H*-1,2,3-triazole-4-carbaldehyde (TA4C) to selectively attach to the N-terminus of native proteins. The surface of a polymer resin containing (2-aminoprop-1-yl)polyethylene glycol (PEGA-NH<sub>2</sub>) was functionalized with TA4C, enabling specific N-terminal modifications of native proteins.<sup>2</sup> Green fluorescent protein (GFP) was efficiently linked to the surface of the resin in one-step. The differences in immobilization efficiency between N-terminal immobilization and physical adsorption were observed via fluorescence microscopy. This indicates successful immobilization of proteins on the resin material. We also tested the immobilization of lipase AK via N-terminus and investigated the catalytic activity of the enzymes. The result shows that the activity of enzymes immobilized via N-terminus retains more than that of the enzymes immobilized with the non-specific covalent modification.



**Figure1.** Immobilization of proteins via N-terminus onto the surface of polymer resin modified with 1*H*-1,2,3-triazole-4-carbaldehyde

### References

- 1) B. Koo, N. S. Dolan, K. Wucherer, H.K. Munch and M. B. Francis, *Biomacromolecules*, 2019, 20, 3933–3939
- 2) A. Onoda, N. Inoue, E. Sumiyoshi, T. Hayashi, *ChemBioChem*, 2020, 21, 1274.

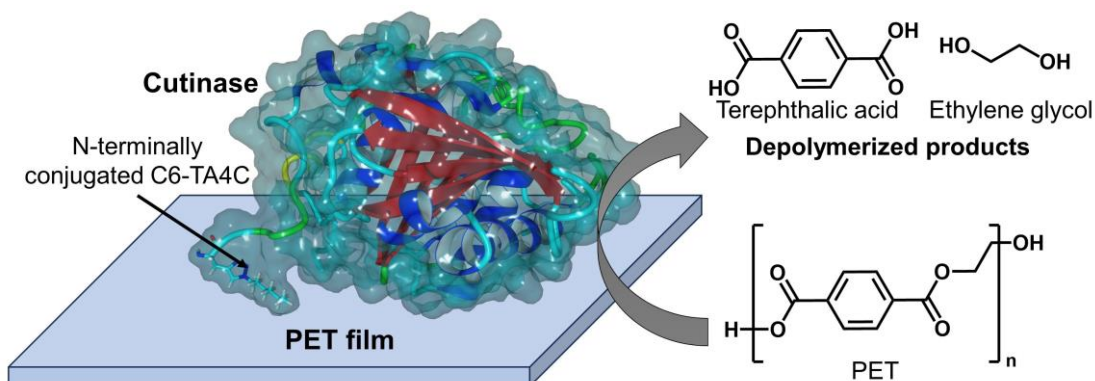


## Enhancing Enzymatic Breakdown of Polyethylene Terephthalate by Cutinase Tethering Hydrophobic Moiety at N-terminus

(<sup>1</sup>Graduate School of Environmental Science, Hokkaido University, <sup>2</sup>Faculty of Environmental Earth Science, Hokkaido University) ○Md Sadikur Rahman Shuvo,<sup>1</sup> Joel Muyomba,<sup>1</sup> Akira Onoda<sup>1,2</sup>

**Keywords:** Polyethylene terephthalate, Biodegradation, Cutinase, N-terminal modification, Hydrophobic interaction

The extensive use of synthetic polymer polyethylene terephthalate (PET) has raised environmental concerns due to its persistence in ecosystems causing harm to terrestrial and marine habitats. The cutinase enzyme derived from *Thermobifida cellulosilytica* exhibits the capability to decompose PET into terephthalic acid. This work aims at modifying cutinase with hydrophobic moiety at the N-terminus for better adsorption to the PET film. The conjugation of 1-hexyl-1*H*-1,2,3-triazole-4-carbaldehyde (C6-TA4C) at the N-terminus of cutinase incorporates a hydrophobic tether<sup>1</sup>. However, this modification does not alter the enzymatic activity and kinetics of cutinase for the substrate *p*-nitrophenyl butyrate. Treatment of 0.25 cm<sup>2</sup> PET film for 7 days by C6-TA4C conjugated cutinase (C6-Cut) shows 1.8 times higher release of terephthalic acid than unconjugated cutinase (Cut). A noticeable decrease in the water contact angle (WCA) was observed in PET films subjected to a 7-days treatment with C6-Cut (70.1°) and Cut (75.8°) in comparison to the untreated PET film (79.5°). This observation suggests an elevated level of surface exposure of hydroxyl and carboxyl groups in PET films treated with C6-Cut, as indicated by the lower WCA values. X-ray photoelectron spectroscopy (XPS) analysis revealed a higher quantity of adsorbed nitrogen in the PET film treated with C6-Cut compared to Cut during a 12-hour incubation period. Scanning electron microscopy (SEM) illustrated that C6-Cut induced a rougher surface with pits in the PET film, in contrast to the smoother surface observed with Cut. The incorporation of C6-TA4C at the N-terminus facilitated a robust attachment of cutinase to PET, thereby enhancing the degradation process.



1) Onoda, A. *et al.*, *ChemBioChem*, 21, 1274-1278 (2020)



## Expanding the Substrate Specificity of Alcohol Dehydrogenase from *Geotrichum candidum* NBRC 4597 toward Diaryl Ketones by Site-directed Mutagenesis

(<sup>1</sup>Tokyo Institute of Technology) ○Zhongyao Tang<sup>1</sup>, Yuuki Takagi<sup>1</sup>, Afifa Ayu Koesoema<sup>1</sup>, Tomoko Matsuda<sup>1</sup>

**Keywords:** Alcohol Dehydrogenase; Site-directed Mutagenesis; Diaryl Ketone; Asymmetric Reduction

An alcohol dehydrogenase from *Geotrichum candidum* NBRC 4597 (*GcAPRD*) is a novel enzyme that has been demonstrated to catalyze various prochiral ketones to the corresponding (*S*)-alcohols by following Prelog's rule.<sup>1</sup> Moreover, the amino acid residue in the small substrate binding pocket, Trp288, showed control of activity and (*R*)-selectivity towards halogenated acetophenones.<sup>2</sup> However, catalyzing the reduction of diaryl ketones to its corresponding diaryl alcohols, important pharmaceutical intermediates, remains challenging for *GcAPRD*.

In this research, we determined that the single mutant, Trp288Ala, has activity towards 2-(4-chlorobenzoyl)pyridine and its analogs, but the activity requires further improvement for producing the corresponding alcohols in the preparative scale (Fig). With docking simulation, we predicted that the double-mutant constructed by simultaneous site-directed mutagenesis in Phe56 (in the large substrate binding pocket) and Trp288 has the potential to improve the activity.

At first, a single mutation in Phe56 was constructed to enlarge the entrance of the large pocket to increase the enzymatic activity toward acetophenone and its halogenated analogs. Then, based on the results of Trp288 mutants and Phe56 mutants, a new double-mutant, *GcAPRD* Phe56Ile/Trp288Ala, was constructed. In the analytical scale reductions of 2-(4-chlorobenzoyl)pyridine and its analogs, Phe56Ile/Trp288Ala showed higher activity than single mutants, which indicated this new mutant has the potential to produce important pharmaceutical intermediates of H1 antagonists, such as pheniramine.

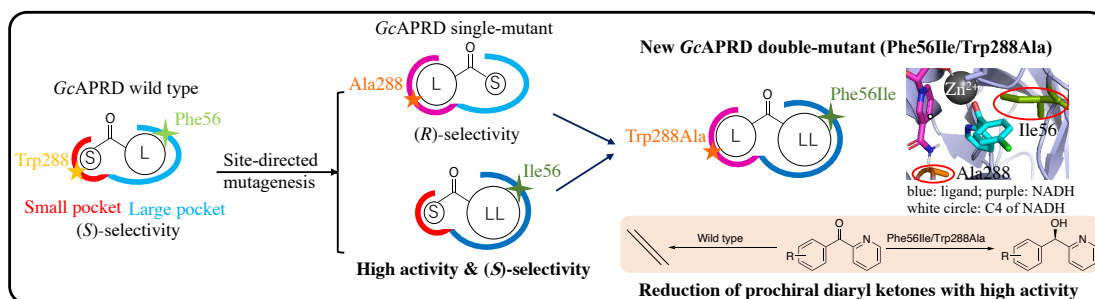


Fig. Site-directed mutagenesis of Trp288 and Phe56 for the reduction of diaryl ketones

1) Nakata Y, Fukae T, Kanamori R, *et al. Appl. Microbiol. Biotechnol.*, **2010**, 86, 625.

2) Koesoema A A, Standley D M, Ohshima S, *et al. Tetrahedron Letters*, **2020**, 61, 151820.

## Development of a Chitin-based Affinity Purification System: Applications for Enzyme Screening for Hemoprotein-catalyzed Stereodivergent Synthesis of Cyclopropane

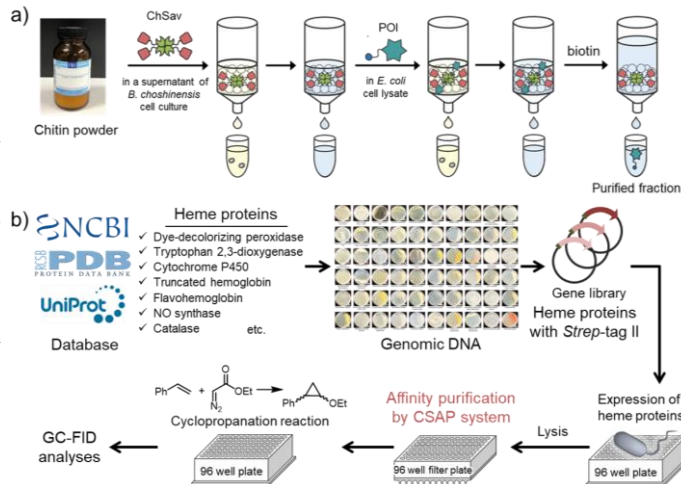
(Graduate School of Engineering, Osaka University) ○Koki Takeuchi, Shunsuke Kato, Takashi Hayashi

**Keywords:** Enzyme Screening; Heme Proteins; Cyclopropanation; Affinity Purification; Chitin

With the rapid advancement of biotechnology, biocatalysis has recently attracted much attention as a sustainable technology for producing valuable chemicals. An important aspect of enhancing the versatility of biocatalysis is the discovery of new enzymes with new catalytic activities and high selectivities. Typically, a strategy for finding new enzymes involves a high-throughput screening (HTS) of diverse protein libraries. *In vitro* screening using purified protein libraries offers significant advantages in terms of data accuracy without the influence of cellular contaminants. However, current affinity purification methods are highly cost-intensive due to the use of expensive chromatography matrices.

To overcome this problem, our group has recently developed a new low-cost affinity purification system, which we call CSAP (chitin- and streptavidin-mediated affinity purification) system.<sup>1</sup> The CSAP system is based on ChSav, an engineered streptavidin variant fused to a chitin-binding protein. Since ChSav has sufficient binding ability for both chitin and *Strep*-tag II, POIs with *Strep*-tag II sequence can be efficiently purified by a low-cost chitin powder as a chromatography matrix (Figure 1a). Furthermore, we next performed high-throughput screening of hemoprotein libraries to discover new enzymes which catalyze stereodivergent synthesis of cyclopropanes as demonstration of the CSAP system (Figure 1b). As first, gene libraries of diverse heme proteins were prepared according to enzyme databases. After the expression and purification of these

a) libraries by the CSAP system, styrene cyclopropanation with ethyl diazoacetate was conducted. As a result, bacterial hemoglobin from *S. novella* was found to afford (*S,S*)-product with high stereoselectivity (>96% de, >98% ee). In contrast, truncated hemoglobin from *S. roseum* provided a (*S,R*)-product with high stereoselectivity (>96% de, >98% ee). Herein, we will present the details of the CSAP system and the results of enzyme screening.



**Figure 1.** a) Purification method by CSAP system.

b) Enzyme screening using CSAP system.

1) S. Kato, K. Takeuchi, M. Iwaki, T. Hayashi *et al.*, *Angew. Chem. Int. Ed.*, **2023**, 62, e202303764.

アカデミックプログラム [B講演] | 18. 高分子：口頭B講演

📅 2024年3月20日(水) 9:00 ~ 11:10 📍 D342(3号館 [4階] 342)

**[D342-3am] 18. 高分子**

座長：小林 裕一郎、廣瀬 大祐

## ◆ 日本語

9:00 ~ 9:20

[D342-3am-01]

スルホニルホスホロアミド酸構造を側鎖に有する脂溶性らせん状ポリ(フェニルアセチレン)のらせん誘起と静的記憶

○西川 裕基<sup>1</sup>、惣名 翔大<sup>1</sup>、廣瀬 大祐<sup>2</sup>、前田 勝浩<sup>2,3</sup> (1. 金沢大院新学術、2. 金沢大院自然、3. 金沢大 WPI-NanoLSI)

## ◆ 日本語

9:20 ~ 9:40

[D342-3am-02]

超分子硫黄含有ポリマーの合成とその特性

○小林 裕一郎<sup>1,2,3</sup>、山岸 佑輝<sup>1</sup>、北野 大輝<sup>1</sup>、堀口 顕義<sup>1</sup>、西村 龍人<sup>1</sup>、橋本 駿<sup>1</sup>、神岡 龍之介<sup>1</sup>、山口 浩靖<sup>1</sup> (1. 阪大院理、2. ICS-OTRI、3. 阪大FRC)

## ◆ 英語

9:40 ~ 10:00

[D342-3am-03]

高効率環状ポリマー合成ーシクロデキストリン誘導体との擬ポリロタキサン形成に基づくによる高濃度ポリエチレングリコールの環化反応ー

○シャオ チュンリン<sup>1</sup>、辻 佳弘<sup>1</sup>、小林 裕一郎<sup>1</sup>、原田 明<sup>1</sup>、山口 浩靖<sup>1</sup> (1. 阪大)

10:00 ~ 10:10

休憩

## ◆ 日本語

10:10 ~ 10:30

[D342-3am-04]

金属酵素の活性制御を利用した環境適応性人工細胞の創製

○東 小百合<sup>1</sup>、Taniya Chakraborty<sup>2</sup>、Yanjun Zheng<sup>3</sup>、Azadeh Alavizargar<sup>3</sup>、Andreas Heuer<sup>3</sup>、Seraphine Wegner<sup>3</sup> (1. 岐阜大学、2. マックスプランク医学研究所、3. ミュンスター大学)

## ◆ 英語

10:30 ~ 10:50

[D342-3am-05]

Fabrication of chitosan nanofiber-based sponge materials using freeze-thaw method

○H.P.M. PANCHABASHINI<sup>1</sup>、Akihide Sugawara<sup>1</sup>、Hiroshi Uyama<sup>1</sup> (1. Osaka University)

## ◆ 英語

10:50 ~ 11:10

[D342-3am-06]

Application of Hierarchically Porous Chitosan Monolith on Enzyme Immobilization

○HAJILI EMIL<sup>1</sup> (1. Osaka University)

## スルホニルホスホロアミド酸構造を側鎖に有する脂溶性らせん状ポリ(フェニルアセチレン)のらせん誘起と静的記憶

(金沢大院新学術<sup>1</sup>・金沢大院自然<sup>2</sup>・金沢大 WPI-NanoLSI<sup>3</sup>) ○西川 裕基<sup>1</sup>・惣名 翔大<sup>1</sup>・廣瀬 大祐<sup>2</sup>・前田 勝浩<sup>2,3</sup>

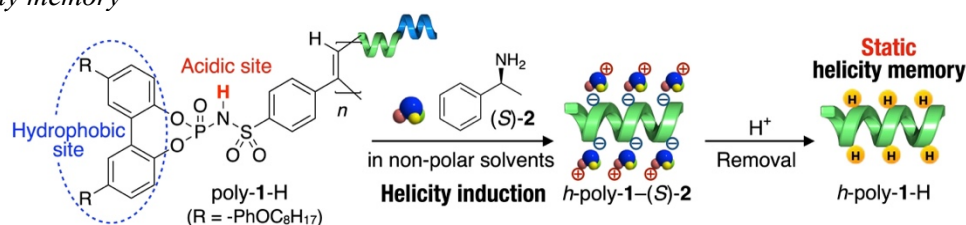
Helicity Induction and Static Memory of a Lipophilic Helical Poly(phenylacetylene) Bearing a Sulfonylphosphoramidic Acid Structure (<sup>1</sup>*Graduate School of Frontier Science of Initiative, Kanazawa University*, <sup>2</sup>*Graduate School of Natural Science and Technology, Kanazawa University*, <sup>3</sup>*Nano Life Science Institute (WPI-NanoLSI), Kanazawa University*) ○ Yuki Nishikawa,<sup>1</sup> Shota Sona,<sup>1</sup> Daisuke Hirose,<sup>2</sup> Katsuhiko Maeda<sup>2,3</sup>

Stereoregular poly(phenylacetylene)s (PPAs) bearing Brønsted acid pendants can form a one-handed helical structure via ion-pair formation with optically active amines. However, the induced helical structure immediately racemize after removal of the amines, which has been a serious problem for its application as a chiral Brønsted acid in non-polar solvents.

Herein, we synthesized a novel lipophilic PPA (poly-1-H) bearing a sulfonylphosphoramidic acid structure covered with a hydrophobic biphenyl group with long alkyl chains and investigated its helicity induction and memory properties (Figure 1).

Poly-1-H was soluble in various non-polar solvents. In the presence of an optically active amine (*S*)-2, poly-1-H formed a one-handed helical structure in non-polar solvents. Unlike conventional Brønsted acid-type PPAs, the helical structure induced in poly-1-H was maintained after acidification with a stronger acid to remove (*S*)-2 (static helicity memory).

**Keywords :** Helical polymer; Poly(phenylacetylene); Brønsted acid; Helicity induction; Helicity memory



**Figure 1.** Schematic illustration of helicity induction in poly-1-H with chiral (*S*)-2 and subsequent helicity memory by acidification with a stronger acid (static helicity memory) in non-polar solvents.

ブレンステッド酸構造を側鎖に有する立体規則性ポリ(フェニルアセチレン)誘導体(PPA)は、光学活性アミンとのイオン対形成を介して一方向巻きのらせん構造を形成する。しかし、アミンを除去すると誘起されたらせん構造は瞬時にラセミ化するため、疎水性溶媒中でキラルなブレンステッド酸として利用することは困難であった。

本研究では、スルホニルホスホロアミド酸構造を介して長鎖アルキル基を有するビフェニル構造を側鎖に導入した脂溶性ブレンステッド酸型 PPA (poly-1-H) を合成し、そのらせん誘起および記憶特性について調査した (Figure 1)。

Poly-1-H は、広範な疎水性溶媒に良好な溶解性を示し、光学活性アミン(*S*)-2 存在下、疎水性溶媒中において一方向巻きのらせん構造を形成した。従来のブレンステッド酸型 PPA の場合とは異なり、poly-1-H に誘起されたらせん構造は、強酸により(*S*)-2 を除去した後も、記憶として安定に保持された(静的らせん記憶)。

## 超分子硫黄含有ポリマーの合成とその特性

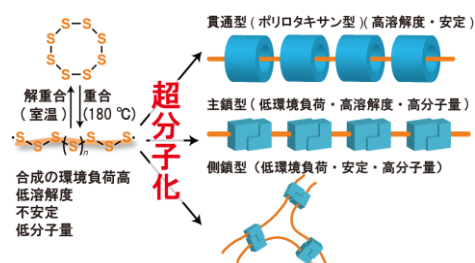
(阪大院理<sup>1</sup>・ICS-OTRI<sup>2</sup>・阪大FRC<sup>3</sup>) ○小林 裕一郎<sup>1,2,3</sup>・山岸 佑輝<sup>1</sup>・北野 大輝<sup>1</sup>・堀口 顕義<sup>1</sup>・西村 龍人<sup>1</sup>・橋本 駿<sup>1</sup>・神岡 龍之介<sup>1</sup>・山口 浩靖<sup>1,2,3</sup>

Preparation of sulfur-containing polymer and their properties (<sup>1</sup>Graduate School of Science, Osaka University, <sup>2</sup>ICS-OTRI, Osaka University, <sup>3</sup>FRC, Osaka University) ○ Yuichiro Kobayashi,<sup>1,2,3</sup> Yuki Yamagishi,<sup>1</sup> Daiki Kitano,<sup>1</sup> Akiyoshi Horiguchi,<sup>1</sup> Ryuto Nishimura,<sup>1</sup> Shun Hashimoto,<sup>1</sup> Ryunosuke Kamioka,<sup>1</sup> Hiroyasu Yamaguchi<sup>1,2,3</sup>

Sulfur is produced as a byproduct of oil refining, of which 7 million tons are dumped above ground each year. Since sulfur-containing polymers can be synthesized from sulfur, a surplus resource, they are attracting attention from the perspective of Sustainable Development Goals (SDGs). Furthermore, since sulfur exhibits unique properties such as high capacitance, high refractive index, and reversible bond formation and dissociation, it is expected to be applied to battery materials, lenses, and self-healing materials. Sulfur-containing polymers can be easily obtained by simply heating sulfur to high temperatures. However, the high-temperature conditions are environmentally hazardous, and the resulting sulfur-containing polymers have low solubility, instability, and low molecular weight, making it difficult to implement them in society despite their potential to create highly functional materials. In this presentation, we describe supramolecular sulfur-containing polymers developed by the authors to solve these problems by introducing the supramolecular concept of self-assembly of molecules through weak interactions into sulfur-containing polymers.

**Keywords :** Sulfur; Sulfur-containing polymer; Supramolecule; Rotaxane; Supramolecular polymer

硫黄は年間 700 万トン地上投棄されており、持続可能な開発目標の観点から有効利用が求められている。その方法の一つとして、硫黄ポリマーを用いた材料作製が注目されている。硫黄ポリマーは硫黄を加熱するという簡便な方法で得られるが、室温で解重合が起こる不安定さ、汎用有機溶媒へ溶解しないという加工性の悪さなどの問題がある。この問題解決のために、硫黄とビニルモノマーとの共重合法や、多官能性ビニルモノマーを用いた逆加硫法など様々な手法が開発されている。逆加硫法は硫黄ポリマー間を有機化合物で架橋した構造の硫黄含有ポリマーを与えることから、高静電容量や高屈折率などの優れた性質を持った硫黄含有ポリマー材料を創製できる手法として近年特に注目を集めている。本発表ではこれまでの共重合や架橋（逆加硫法）などの従来法とは異なる、超分子科学的手法により硫黄含有ポリマーを合成した（超分子硫黄含有ポリマー）ので報告する。超分子科学的な連結ユニットを硫黄含有ポリマーへ導入することで、硫黄からなるポリマーの不安定や低加工性等の課題を克服するとともに、ケミカルリサイクル性を付与することに成功した。

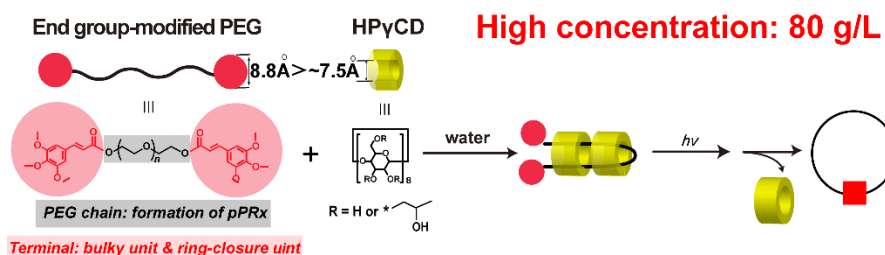


## Highly efficient cyclic polymer synthesis - Cyclization of highly concentrated polyethylene glycol based on pseudo-polyrotaxane formation with cyclodextrin derivatives

(<sup>1</sup>Graduate School of Science, Osaka University, <sup>2</sup>Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, <sup>3</sup>The Institute of Scientific and Industrial Research Osaka University) ○XIAO CHUNLIN<sup>1</sup>, Yoshihiro Tsuji<sup>1</sup>, Yuichirou Kobayashi<sup>1,2</sup>, Akira Harada<sup>3</sup>, Hiroyasu Yamaguchi<sup>1,2</sup>

**Keywords:** Cyclic polymer, Cyclodextrin, pseudo-Polyrotaxane, Photocycloaddition

Cyclic polymers (CPs) display unique properties due to their ring-like structure and lack of end groups.<sup>1</sup> However, conventional preparation via ring-closing reactions requires low concentrations (0.1 g/L). This inefficient preparation has prevented in-depth research and applications of CPs. Previously, we reported cyclization assisted by *pseudo*-polyrotaxane (pPRx) constituted of poly(ethylene glycol) ( $M_n = 400$  g/mol) (PEG400) and  $\gamma$ -cyclodextrin ( $\gamma$ CD).<sup>2</sup> In high concentration (60 g/L), a propenyl group-modified PEG chain formed double-stranded pPRx with  $\gamma$ CD, rendering two propenyl end groups approaching each other. Successive ring-closure was achieved through a thiol-ene click reaction using a dithiol reagent. This method gave a 14% yield of cyclic PEG400, however, high molecular weight (MW) products were produced. In this presentation, we report to apply (*E*)-3,4,5-trimethoxycinnamic acid (TCA) terminal-modified PEG to form water-soluble double-stranded pPRx with 2-hydroxypropyl- $\gamma$ -cyclodextrin (HP $\gamma$ CD). TCA serves as both the functional groups for the ring-closure and the bulky end groups for regulating the inclusion motif of pPRx. Given the larger molecular size of TCA compared to the cavity size of HP $\gamma$ CD, the pPRx formed in solution is likely derived from the inclusion of a single PEG chain folding to a U-like shape by HP $\gamma$ CD. This favors the intramolecular cyclization of TCA-modified PEG by the [2+2] photocycloaddition of cinnamoyl terminals to yield the cyclic polymer at high concentration (80 g/L). This cyclization strategy was approved to be applicable for not only the cyclization of PEG ( $M_n = 2,000$  g/mol) with a yield of 66% at 80 g/L, but also for PEG with relatively higher MW ( $M_n = 4,000$  g/mol) in a 45% yield at 80 g/L.<sup>3</sup>



1) a) Haque, F.; Grayson, S. *Nat. Chem.* **2020**, 12, 433-444. b) Geiser, D.; Hocker, H. *Macromolecules* **1980**, 13, 653-656. 2) Tsuji, Y.; Kobayashi, Y.; Xiao, C.; Harada, A.; Yamaguchi, H. *Chem. Lett.* **2023**, 52, 1-4. 3) Xiao, C.; Kobayashi, Y.; Tsuji, Y.; Harada, A.; Yamaguchi, H. *ACS Macro Lett.* **2023**, 12, 1498-1502.



## 金属酵素の活性制御を利用した環境適応性人工細胞の創製

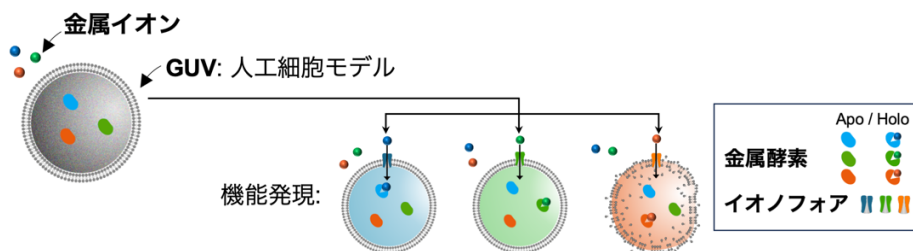
(岐阜大高等研究院<sup>1</sup>・マックスプランク医学研究所<sup>2</sup>・ミュンスター大<sup>3</sup>) ○東 小百合<sup>1</sup>・Taniya Chakraborty<sup>2</sup>・Yanjun Zheng<sup>3</sup>・Azadeh Alavizargar<sup>3</sup>・Andreas Heuer<sup>3</sup>・Seraphine V. Wegner<sup>3</sup>

Metalloregulation leads to the different cell behaviors in artificial cells (<sup>1</sup> *Institute for Advanced Study, Gifu University*, <sup>2</sup> *Max Planck Institute For Medical Research*, <sup>3</sup> *University of Münster*)  
○Sayur Higashi,<sup>1</sup> Taniya Chakraborty<sup>2</sup>・Yanjun Zheng<sup>3</sup>・Azadeh Alavizargar<sup>3</sup>・Andreas Heuer<sup>3</sup>・Seraphine V. Wegner<sup>3</sup>

Living cells are skilled at adapting to ever-changing environments. Mimicking the cellular adaptivity in artificial cells could provide a step to life-like systems capable of differentiation. Here, we create a lipid-based artificial cell harboring plural apo-metalloenzymes. Selective activation of an apo-metalloenzyme inside the compartment are regulated by extracellular metal ions and their ionophores. Three different behaviors were exhibited in response to the external stimuli. Utilizing ionophores as decision factors for cell functions would be suitable for designing novel adaptive artificial cells.

**Keywords :** artificial cell, metalloenzyme, ionophore, differentiation

近年、様々な細胞現象の理解およびバイオ材料への応用を目指し、細胞の構成因子から構造や機能を模倣・再現した人工細胞の開発が進められてきた。機能面に着目すると、細胞が有する遺伝子の発現系、ATPの自己生成、複数の酵素反応からなる代謝系、細胞分裂や融合という重要かつ基礎的な機能を有する人工細胞が報告されてきた<sup>1,2)</sup>。上記の反応の多くは、外部からの1つのinputに対して1つのoutputとして発現されるよう設計されている。一方で、潜在的に複数のoutputを持ち、inputの種類に応じて「ある1つの」outputを示す『環境適応性』を有する人工細胞は世界的にも例がほとんどない。しかし、実際に我々の細胞は周囲の変化に対して優れた環境適応性を有している。そこで我々は、イオノフォアをトランスポーターとして用いることで、人工細胞に環境適応性を実現させた。巨大リポソーム (GUV) に異なる金属イオンで活性化される3種類の金属(依存性)酵素を同時に内包した。GUV外に3種類の異なる金属イオンが共存する時、特定のイオノフォアを系中に加えることでGUV内の1種類の酵素が選択的に活性化し、GUVの性質が変わる。すなわち、イオノフォアを選択が人工細胞の機能発現を制御する。



1) B. C. Buddingh and J. C. M. van Hest, *Acc. Chem. Res.*, **2017**, 50, 769–777.

2) C. Guindani et al., *Angew. Chem. Int. Ed.*, **2022**, 61, e202110855.

## Fabrication of chitosan nanofiber-based sponge materials using freeze-thaw method

(<sup>1</sup>Graduate School of Engineering, Osaka University)

○H.P.M. Panchabashini<sup>1</sup>, Akihide Sugawara<sup>1</sup>, Hiroshi Uyama<sup>1</sup>

**Keywords:** Freeze–Thaw Method, Sponge Material, Chitosan Nanofibers, Fire Retardancy, Thermal Insulation

**Introduction:** Sponges, with their fibrous porous materials and 3D network, demonstrate reversible compressibility, mechanical integrity, and low specific gravity. The typical properties of sponges can be combined with many advantageous properties to make them applicable in different fields such as water purification, biomedical applications, electrical applications, etc. In this work, we employed the freeze-thaw method to compose chitosan nanofibers (CSNFs) and dialdehyde carboxymethyl cellulose (DACMC), which are based on natural polymers to synthesize a sponge material (**Fig. 1a** and **b**).

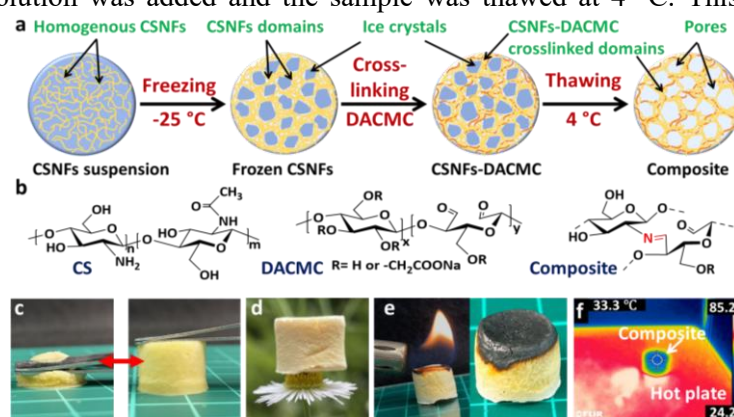
**Experimental:** First, an aqueous suspension of 2.5 wt% CSNFs was frozen at -25 °C. Then 5.0 wt% DACMC aqueous solution was added and the sample was thawed at 4 °C. This thermal treatment was continued for five cycles.

### Results and discussion:

The porous composite was successfully synthesized, a sponge in the wet state and a light material in the dry state (**Fig. 1c** and **d**). Also, it showed high pH stability even in acidic conditions such as pH 2, compared to pure CSNFs samples. The great shape recoverability and pH stability were attributed to the formation of imine bond crosslinks between the amine groups of CSNFs and aldehyde groups of DACMC during

the freeze-thaw cycles (**Fig. 1a**). Upon the gradual thawing step, DACMC was incorporated into concentrated CSNFs domains which were formed along the ice crystals at the freezing steps. The imine bond crosslinking and ionic interactions between cationic CSNFs and anionic DACMC were effectively formed at such polymer-rich domains, contributing to the production of the stable 3D porous structure of the sponge materials. Also, this process effectively overcame the challenges associated with the sudden precipitation of poly-ionic materials upon mixing by utilizing ice crystals as a rigid template. Moreover, compared to the commonly used commercially available foams, the material showed excellent fire retardancy and thermal insulation in the dry state (**Fig. 1e** and **f**). Remarkably, when exposed to an open flame, the composite did not ignite but formed a protective char layer that effectively prevented the spread of flames. In the wet state, it showed good adsorption properties of Cu<sup>2+</sup> ions, and the adsorbed ions could be desorbed using ethylenediaminetetraacetic acid. This simply processed bio-material-based composite is a multifunctional promising material in different industries.

1. Lozinsky VI, *Trends Biotechnol.* **2003**, 21, 445.



**Fig. 1:** (a) Schematic illustration of the synthesis process of the CSNFs-based sponge material by freeze-thaw method. (b) Chemical structures of CS and DACMC and imine bond between CS and DACMC. Images of (c) wet sample with sponge behavior, (d) light dry material, and (e) dry composite after exposure to an open flame. (f) IR image of a composite on a hot plate.



## Application of Hierarchically Porous Chitosan Monolith on Enzyme Immobilization

(<sup>1</sup>Graduate School of Engineering, Osaka University) ○Emil Hajili,<sup>1</sup> Akihide Sugawara,<sup>1</sup> Yu-I Hsu,<sup>1</sup> and Hiroshi Uyama<sup>1</sup>

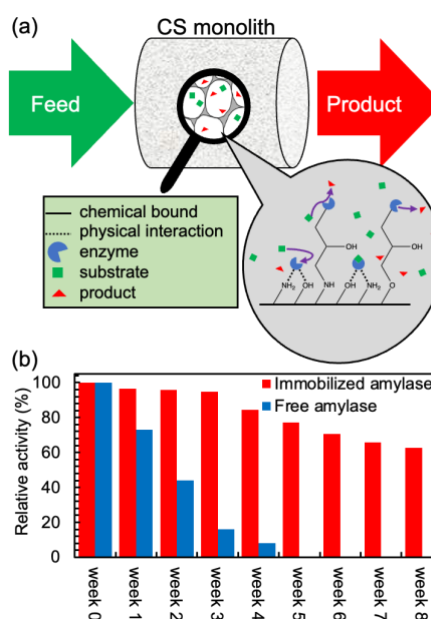
**Keywords:** chitosan; monolith; porous materials; enzyme immobilization;  $\alpha$ -amylase

Enzymes are widely used catalysts in various industries due to their efficiency and environmentally friendly nature. Immobilizing enzymes offers benefits such as improved stability, reusability, and easy separation from reaction media.<sup>1</sup> This study proposes a method that combines physical adsorption and covalent bonding to immobilize  $\alpha$ -amylase on a hierarchically porous chitosan (CS) monolith.

The monolith was fabricated using a thermally induced phase separation technique (TIPS) applied to chemically modified chitin, which is then converted into CS through hydrolysis and deacetylation processes. Herein, dibutyl chitin (DBC) was used as a starting material and dissolved in DMSO, followed by the addition of deionized water at 85 °C. The solution was cooled at 25 °C to perform the phase separation. Hydrolysis with NaOH solution produced the chitin (CT) monolith,<sup>2</sup> which was cross-linked using epichlorohydrin. Subsequently, high-concentration alkali treatment was applied to deacetylate the CT monolith into the CS monolith.<sup>3</sup> The monolith with immobilized enzyme was prepared by circulating an  $\alpha$ -amylase phosphate buffer solution into the CS monolith using a peristaltic pump. The CS monolith utilizes amino and glycidyl groups for physical adsorption and covalent bonding, respectively, resulting in strong enzyme binding and improved stability (**Fig. 1a**).

The immobilized  $\alpha$ -amylase on the CS monolith proved to be a reliable support material for enhancing the stability of  $\alpha$ -amylase across various pH levels and temperatures. The hierarchically porous structure of the monolith enables efficient enzyme utilization in a flow system. Compared to the free enzyme, the immobilized enzyme retains over 60% of its activity after 8 weeks, while the free enzyme loses all activity within a month (**Fig. 1b**). Additionally, unlike the free enzyme, the immobilized enzyme on the CS monolith demonstrated the ability to be reused multiple times. Moreover, the CS monolith exhibited versatility by successfully immobilizing other enzymes like lipase and catalase, offering higher loading capacities and improved activity compared to their soluble forms. These findings emphasize the wide range of applications for the CS monolith as a support material in diverse enzymatic processes.

1) S. Jemli, *Crit. Rev. Biotechnol.* **2016**, 36, 246. 2) E. Hajili, *Carbohydr. Polym.* **2022**, 275, 118680. 3) E. Hajili, *ACS Sustainable Chem. Eng.* **2023**, 11, 5473.



**Fig. 1** (a) Catalytic reaction via immobilized enzyme in CS monolith. (b) The storage stability of free and immobilized  $\alpha$ -amylase on the CS monolith.

アカデミックプログラム [B講演] | 18. 高分子：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 D342(3号館 [4階] 342)

**[D342-3pm] 18. 高分子**

座長：Li Feng、西川 剛

## ◆ 英語

13:00 ~ 13:20

[D342-3pm-01]

イソプロペニルボロン酸エステルの制御ラジカル重合と解重合

○金澤 共晃<sup>1</sup>、西川 剛<sup>1</sup>、大内 誠<sup>1</sup> (1. 京都大学大学院)

## ◆ 英語

13:20 ~ 13:40

[D342-3pm-02]

活性化エステルを側鎖に有するアクリレートとジエンのラジカル交互共重合と後反応による光分解性高分子の精密合成

○黒田 啓太<sup>1</sup>、大内 誠<sup>1</sup> (1. 京都大学)

## ◆ 日本語

13:40 ~ 14:00

[D342-3pm-03]

ラジカル共重合反応の電子スピン共鳴分光(ESR)法による詳細な観測

○梶原 篤<sup>1</sup> (1. 奈良教育大学)

## ◆ 日本語

14:00 ~ 14:20

[D342-3pm-04]

MOFの一次元ナノ細孔での非対称二重鎖高分子の合成

○亀谷 優樹<sup>1</sup>、山口 麟太郎<sup>1</sup>、植村 卓史<sup>1</sup> (1. 東京大学)

14:20 ~ 14:30

休憩

## ◆ 日本語

14:30 ~ 14:50

[D342-3pm-05]

重合度が規定された精密アクリルオリゴマーの合成と側鎖変換反応

○辻 爽太郎<sup>1</sup>、永井 薫子<sup>1</sup>、小野 利和<sup>1,2</sup>、鳶越 恒<sup>1</sup>、星野 友<sup>1,2</sup> (1. 九大院工、2. 九大分子システムセ)

## ◆ 英語

14:50 ~ 15:10

[D342-3pm-06]

種々の置換基を導入した3-メチレンフタリド誘導体の重合と分解，モノマー再生

○千葉 耀太<sup>1</sup>、高坂 泰弘<sup>1,2,3</sup> (1. 信州大学繊維学部、2. 信州大学先鋭材料研究所、3. JSTさきがけ)

## ◆ 日本語

15:10 ~ 15:30

[D342-3pm-07]

植物原料由来のケミカルリサイクル可能な非天然型高分子多糖類の合成

○リ ホウ<sup>1</sup>、水上 湧太<sup>2</sup>、笥 祐人<sup>2</sup>、田島 健次<sup>1</sup>、山本 拓矢<sup>1</sup>、磯野 拓也<sup>1</sup>、佐藤 敏文<sup>1,3</sup> (1. 北海道大学・工学研究院、2. 北海道大学・総合化学院、3. 北海道大学・ICReDD List-PF)

---

## Controlled Radical Polymerization of Isopropenyl Boronate and Depolymerization

(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>JST-PRESTO) ○Tomoaki Kanazawa<sup>1</sup>, Tsuyoshi Nishikawa<sup>1,2</sup>, Makoto Ouchi<sup>1</sup>

**Keywords:** Boron; Reversible Deactivation Radical Polymerization (RDRP); Depolymerization; Atom-transfer Radical Polymerization (ATRP); Copper catalyst

A concept of chemical recycling to monomer (CRM) from polymer has drawn attention toward development of sustainable polymer materials. Polymers that are produced via ring-opening polymerization are more accessible for the CRM concept because polymers can be restored to the cyclic monomer via depolymerization. On the other hand, it is more challenging to realize CRM with polymers via addition polymerization. Isopropenyl- or vinylidene-type compounds are the possible monomers for CRM, such as methyl methacrylate (MMA),  $\alpha$ -methyl styrene, and isobutylene, because they exhibited relatively low ceiling temperatures due to the existence of methyl group at  $\alpha$ -position. It is well recognized that MMA is generated via bulk depolymerizations in pyrolysis of PMMA, and in particular, some recent studies have revealed controlled depolymerization of PMMA via the activation of controlled terminal group.<sup>1-3</sup>

In this research, we studied depolymerization of the poly(isopropenylboronic acid pinacol ester) [poly(IPBpin)]<sup>4</sup> (Figure 1). We then synthesized poly(IPBpin) carrying bromide at terminal with high fidelity via reversible deactivation radical polymerization (RDRP) of IPBpin using copper catalyst [Cu(0)] system at room temperature. Interestingly, the resultant polymer underwent depolymerization via activation of the bromide terminal with the same catalyst at higher temperature (100°C), and 70% of the repeating units were converted into monomer. We also synthesized some types of copolymers of MMA and IPBpin to see effects of sequence on depolymerization.

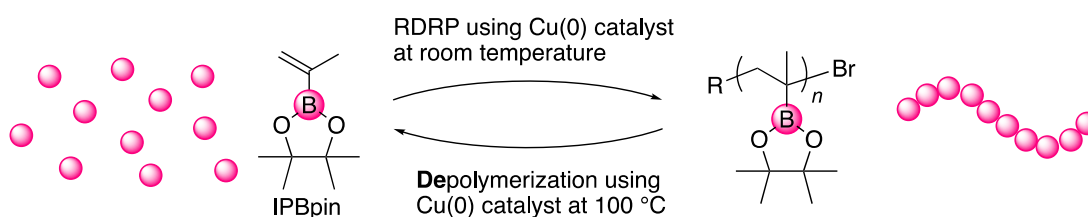


Figure 1. Copper-catalyzed RDRP of IPBpin and Depolymerization.

1) Sawamoto, M.; Ouchi, M.; et al. *Eur. Polym. J.*, **2019**, *120*, 109181. 2) Matyjaszewski, K.; et al. *Macromolecules*, **2021**, *54*, 5526. 3) Matyjaszewski, K.; Anastasaki, A.; et al. *J. Am. Chem. Soc.*, **2023**, *145*, 21146. 4) Nishikawa, T.; Ouchi, M. *Angew. Chem. Int. Ed.*, **2019**, *58*, 12345.

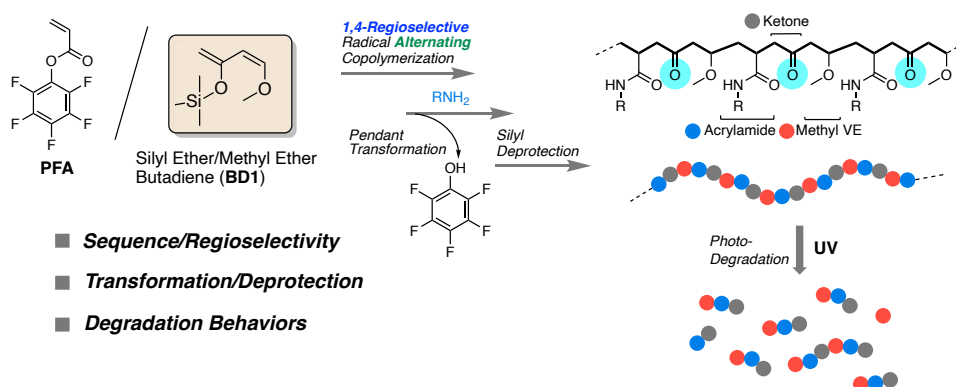
## Radical Alternating Copolymerization of Activated Ester Pendant Acrylate with Diene and Post-Polymerization Modification for Precision Syntheses of Photo-Degradable Polymers

(<sup>1</sup>Graduate School of Engineering, Kyoto University) ○Keita Kuroda,<sup>1</sup> Makoto Ouchi<sup>1</sup>

**Keywords:** Radical Polymerization; Copolymerization; Diene; Polymer Degradation; Post-Polymerization Modification

The current polymer-waste pollution has encouraged chemists to develop on-demand degradable polymers that are stable as materials but turn into degradable after use. The addition polymerization of vinyl monomers, which is most widely used for polymer synthesis, affords stable and robust polymers made of the repetitive carbon-carbon backbone, but hence they are not degradable. One possible approach making such vinyl polymers degradable is an incorporation of a special bond to trigger the backbone degradation through migration of radical species.

In this work, we focused on an introduction of a ketone group as the trigger bond in polymer chain via radical copolymerization. Some previous researches showed that ketone units can be introduced via radical copolymerization with cyclic monomers<sup>2</sup> or diene monomers<sup>3</sup>, but they were randomly incorporated resulted in less efficient degradation. Our effort is directed to the periodic introduction toward efficient degradation into well-defined low molecular weight compounds. The key monomer is 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (BD1). The radical copolymerization with acrylate carrying an activated ester pendant (PFA) progressed in alternating and 1,4-regio-selective manner. The resulting copolymers underwent post-polymerization modification and deprotection of the silyl group leading to sequence-controlled copolymers made of acrylamide, ketone, and methyl vinyl ether. The resultant copolymers were degradable under light irradiation through the activation of ketone.



1) M. Ouchi, et al, *Angew. Chem. Int. Ed.* **2023**, 62, e202305252. 2) T. Endo, et al, *J. Polym. Sci. C. Polym. Lett.* **1989**, 27, 1-4. 2) K. Nagai, et al, *J. Polym. Sci. A. Polym. Chem.* **1990**, 28, 2845-2856.

## ラジカル共重合反応の電子スピン共鳴分光 (ESR) 法による詳細な観測

(奈良教育大) ○梶原 篤

Detailed Observation of Radical Co-polymerizations by Electron Spin Resonance (ESR) Spectroscopy (Nara University of Education) ○Atsushi Kajiwara

Styrene and maleic anhydride are typical examples of systems that undergo alternating radical copolymerization. Styrene polymerizes on its own, but maleic anhydride has low polymerizability on its own. When polymerized in a mixed system, alternating copolymerization occurs. The reaction mechanism has been studied in various ways.

Professor Li Fu-Mian of Peking University proposed the possibility that styrene and maleic anhydride form charge-transfer complexes and that the charge-transfer complexes are integrated and continuously add to each other. In collaboration with Prof. Li, the reaction mechanism was investigated by ESR.

The ESR observation of the alternating copolymerization system of styrene/maleic anhydride gave only complex spectra that were difficult to analyze; by using the RAFT reagent, information on the structure of the propagating chain end was obtained, and it was found that the growing end of the alternating copolymerization system was predominantly the maleic anhydride end. The reaction mechanism was then further investigated by observing the addition of initiator-generated radicals to the first monomer by time-resolved ESR.

**Keywords :** Alternating Copolymerization; ESR/EPR; Time-resolved ESR; Styrene; Maleic Anhydride

スチレンと無水マレイン酸は交互ラジカル共重合をする系の代表的な例である(図)。スチレンは単独でも重合するが、無水マレイン酸は単独では重合性は低い。混合系で重合すると交互共重合が起こる。その反応機構についてはこれまでもさまざまに研究されてきた。北京大学の李福綿教授はスチレンと無水マレイン酸が電荷移動錯体を形成することから、電荷移動錯体が一体となって連続的に付加する可能性を提案していた。李教授と共同で ESR を用いて反応機構について検討した。

スチレン/無水マレイン酸の交互共重合の系を ESR で観測しても解析困難な複雑なスペクトルが得られるのみである。RAFT 試薬を利用することにより、交互共重合系の成長末端は無水マレイン酸末端が優勢であることが分かった<sup>1)</sup>。次いで、時間分解 ESR で開始剤から発生したラジカルが一つ目のモノマーに付加する反応を観測して、反応機構についてさらに検討した。

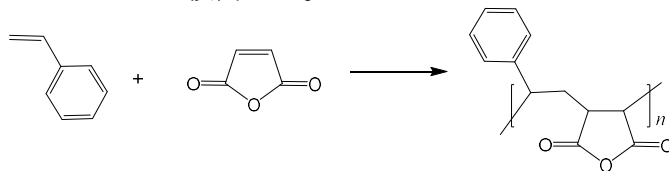


図 スチレンと無水マレイン酸の交互共重合

- 1) F-S. Du, M-Q. Zhu, H-Q. Guo, Z-C. Li, F-M. Li, M. Kamachi, A. Kajiwara, *Macromolecules*, **2002**, 35, 6739-6741.

## MOF の一次元ナノ細孔での非対称二重鎖高分子の合成

(東大院工) ○亀谷 優樹・山口 麟太郎・植村 卓史

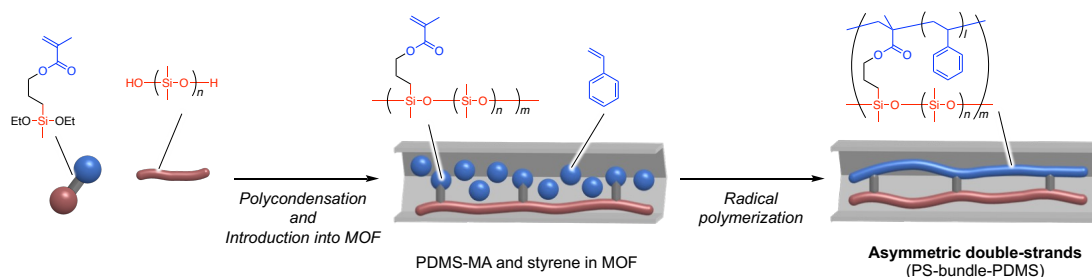
Synthesis of asymmetric double-stranded polymer in the one-dimensional nanopore of MOF  
(Graduate School of Engineering, The University of Tokyo)

○Yuki Kametani, Rintaro Yamaguchi, Takashi Uemura

Asymmetric double-stranded polymers are expected to exhibit unique properties reciprocally influenced by the individual properties of each chain, such as chain stiffness, entanglement, and solubility. The parallel arrangement of immiscible heteropolymers would also contribute to intriguing properties. While synthesizing asymmetric double-stranded polymers has been difficult, we herein demonstrated their synthesis through polymerization along a polymer chain within the one-dimensional pores of a metal-organic framework (MOF).

As shown in the figure, polydimethylsiloxane (PDMS) with methacrylate groups on the side chain (PDMS-MA) was synthesized and introduced into one-dimensional pores of a MOF. Radical polymerization of styrene in the presence of PDMS-MA within the nanochannels gave an asymmetric double-stranded polymer consisting of PDMS and polystyrene (PS-bundle-PDMS). After the polymerization, PS-bundle-PDMS was isolated by removing MOF and homopolymers of styrene.

**Keywords :** radical polymerization, metal-organic frameworks, polystyrene, polydimethylsiloxane, crosslink



異種高分子鎖を平行に架橋した非対称二重鎖高分子は、鎖の硬さや絡み合い、溶解性などにおいて、それぞれの鎖が影響し合った特殊な性質が期待される。また、混ざりにくい異種高分子が強制的に近接させられた構造に基づく特性にも興味をもたれる。これまで非対称二重鎖高分子は合成困難だったが、本研究では金属有機構造体 (MOF) の一次元細孔を用いて高分子鎖に沿った重合を制御し、その合成を可能にした。

図に示すように、側鎖にメタクリレートをもつポリジメチルシロキサン (PDMS-MA) を合成し、MOF の一次元細孔にスチレンと共に導入した。この状態でラジカル重合を行うと、細孔に沿ってスチレンと PDMS-MA のメタクリレートの共重合が進行し、ポリスチレン (PS) と PDMS からなる非対称二重鎖高分子 (PS-bundle-PDMS) が生成する。重合後、酸やキレート剤を用いて MOF を除去し、副生するスチレンのホモポリマーも除去して PDMS-bundle-PS を得た。

## 重合度が規定された精密アクリルオリゴマーの合成と側鎖変換反応

(1. 九大院工、2. 九大分子システムセ) ○辻 爽太郎<sup>1</sup>・永井 薫子<sup>1</sup>・小野 利和<sup>1,2</sup>・  
 嵩越 恒<sup>1</sup>・星野 友<sup>1,2</sup>

Synthesis of precision oligomer by radical polymerization and their side chain conversion  
 (<sup>1</sup>Graduate School of Engineering, Kyushu University, <sup>2</sup>Center for Molecule system (CMS))  
 ○Sotaro Tsuji<sup>1</sup>, Yukiko Nagai<sup>1</sup>, Toshikazu Ono<sup>1,2</sup>, Hisashi Shimakoshi<sup>1</sup>, Yu Hoshino<sup>1,2</sup>

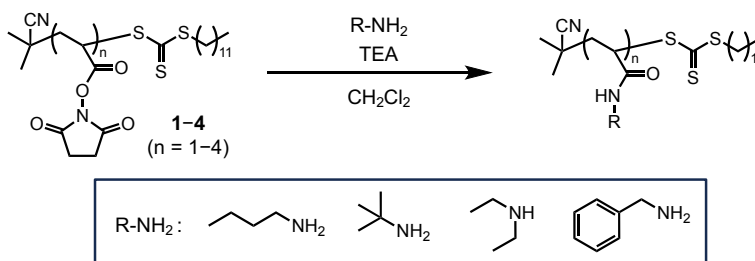
Synthetic polymers have random monomer arrangement and chain length distribution. Recently, precision oligomers with defined monomer sequences and molecular weights have been synthesized and shown to high functionality, such as sequence-specific molecular recognition to biomolecules<sup>1)</sup>. However, the synthesis of precision oligomers is complicated, and their structural diversification is limited. In this study, precision oligomers with various side-chain structures were synthesized by the side-chain conversion reaction between precision oligomers bearing activated ester and amino compounds. Precision oligomers **1-4** bearing activated ester groups with degrees of polymerization of 1, 2, 3, and 4 were synthesized by RAFT polymerization. Subsequently, precision oligomers with various side chain structures were synthesized by coupling reactions of activated esters with amino compounds.

**Keywords :** Precision oligomers, RAFT polymerization, Activated ester, Post-polymerization modification, High-performance liquid chromatography

ラジカル重合によって得られる合成高分子はランダムなモノマー配列や鎖長分布をもつ。最近、リビングラジカル重合技術とフラッシュカラムクロマトグラフィー技術を組み合わせることで、規定されたモノマーの配列と分子量を有する精密オリゴマーが合成された。精密オリゴマーは生体分子に配列特異的に分子認識できるなど、高い機能性を示すことが明らかになっている<sup>1)</sup>。しかし、精密オリゴマーの合成には多段階の重合と分離といった煩雑なプロセスを必要とするため、その構造の多様化には限界がある。本研究では精密オリゴマーの側鎖構造の多様化を目指し、活性エステルを担持した精密オリゴマーを用いたアミノ化合物による側鎖変換反応に成功した。

RAFT 重合と順相フラッシュカラムクロマトグラフィーによる分離精製によって、重合度が 1, 2, 3, 4 の活性エステル基を有する精密オリゴマー**1-4**を合成した。続いて活性エステルとアミノ化合物のカップリング反応により、様々な側鎖構造を有する精密オリゴマーを合成した。

1) Y. Hoshino et al. *Angew. Chemie-Int. Ed.*, **2020**, 59, 679–683.



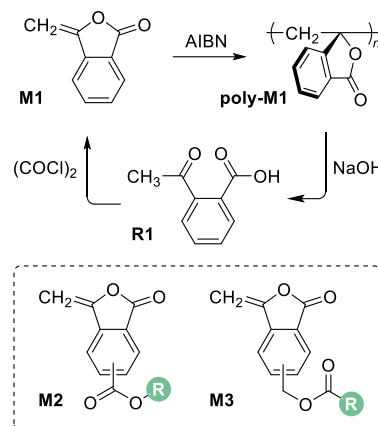


## Polymerization, Degradation, and Monomer Recycling of 3-Methylene Phthalide Carrying Various Substituents

(1. Fac. of Textile Sci. and Tech., Shinshu University, 2. Research Initiative for Supra-Materials, Shinshu University, 3. JST PRESTO) ○Yota Chiba<sup>1</sup>, Yasuhiro Kohsaka<sup>1,2,3</sup>

**Keywords:** Cyclic Styrene-derivatives, Chemical Recycling, Sustainable Polymer, Resource Circulation, Depolymerization

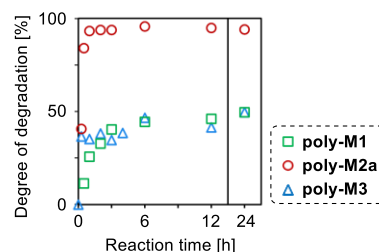
**[Introduction]** Chemical recycling of vinyl polymers to their monomers or precursors is a challenging issue because of the difficulty of quantitative and selective scission of the carbon main-chain. Depolymerization, yielding monomers stepwisely from the polymer chain-end, is a promising approach for chemical recycling. However, depolymerization by radical mechanism usually accompanies some side reactions, and quantitative recovery of monomers is possible only for limited examples of polymers, such as poly(methyl methacrylate).<sup>1</sup> We recently reported the chemical recycling of poly(3-methylene phthalide) (**poly-M1**) obtained via free radical polymerization.<sup>2</sup> **Poly-M1** depolymerized to **R1**, the monomer precursor, through the hydrolysis of the ester group in the cyclic pendant at 70 °C. Despite its good recyclability, the poor solubility of **poly-M1** remains an issue that hinders further research in material engineering. Herein, a series of **M1** derivatives with a substituted aromatic ring, **M2** and **M3**, were prepared to improve the solubility. The effects of the pendant groups on polymer degradability and monomer recyclability were also investigated.



**[Result and Discussion]** **M1**, **M2a** (R = C<sub>3</sub>H<sub>7</sub>), **M2b** (R = C<sub>7</sub>H<sub>15</sub>), and **M3** (R = CH<sub>3</sub>) were polymerized using AIBN (Table). **Poly-M2** and **poly-M3** exhibited improved solubility compared to **poly-M1**, which was soluble only in heated aprotic polar solvents. **P1**, **P2a**, and **P3** were reacted with 10 M NaOH aq. (3 equiv. for the repeating units) in DMSO at 25 °C (Fig). **P2a** was quantitatively degraded into the corresponding monomer precursor within 1 h, whereas the degradation of **P1** and **P3** was saturated at 50%. Our previous report suggested that the depolymerization of **poly-M1** occurs via a combination of an anionic mechanism and a retro-aldol reaction. As both elemental reactions were expected to be promoted by the electron-withdrawing group on the aromatic ring, the high degradability of **P2a** was attributed to the electron-withdrawing effect of the alkoxy-carbonyl group. The efficiency of recycling **M2** and **M3** from the degradation products is also discussed in terms of the reaction steps and yields.

**Table.** Polymerization using AIBN (2 mol%) at 65 °C in DMF and solubilities of the yielded polymers

Monomer	R	<i>M<sub>n</sub></i>	<i>Đ</i>	Solubility		
				DMSO	CHCl <sub>3</sub>	acetone
		[–]	[–]			
<b>M1</b>	–	15000	2.28	–/+ (80 °)	–	–
<b>M2a</b>	C <sub>3</sub> H <sub>7</sub>	80200	2.40	+	+	–
<b>M2b</b>	C <sub>7</sub> H <sub>15</sub>	31600	3.48	+	+	+
<b>M3</b>	CH <sub>3</sub>	72000	2.75	+	+	–



**Fig.** The time growth of degree of degradation calculated from SEC curves.

(1) Lohmann, V. *et al. Chem. Sci.* **2024**, DOI: 10.1039/D3SC05143A. (2) Chiba, Y. *et al. ACS Macro Lett.* **2023**, 12, 1672.

## 植物原料由来のケミカルリサイクル可能な非天然型高分子多糖類の合成

(北大院工<sup>1</sup>・北大院総化<sup>2</sup>・北大 ICR/DD List-PF<sup>3</sup>) ○リ ホウ<sup>1</sup>・水上 湧太<sup>2</sup>・寛 祐人<sup>2</sup>・田島健次<sup>1</sup>・山本拓矢<sup>1</sup>・磯野拓也<sup>1</sup>・佐藤敏文<sup>1,3</sup>

Chemically Recyclable Unnatural Polysaccharides Synthesized from Biomass Resources (<sup>1</sup>Faculty of Engineering, Hokkaido University, <sup>2</sup>Graduate School of Chemical Sciences and Engineering, Hokkaido University, <sup>3</sup>ICReDD List-PF, Hokkaido University) ○Feng Li<sup>1</sup>, Yuta Mizukami<sup>2</sup>, Yuto Kakehi<sup>2</sup>, Kenji Tajima<sup>1</sup>, Takuya Yamamoto<sup>1</sup>, Takuya Isono<sup>1</sup>, Toshifumi Satoh<sup>1,3</sup>

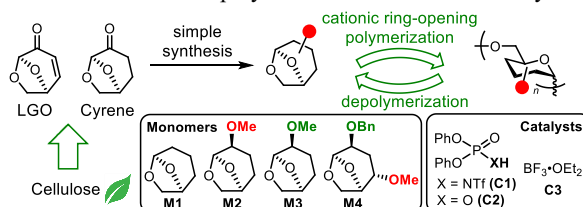
Accessing unnatural polysaccharide analogs and investigating their biological activities and material properties have been enduring research interests. However, these efforts have often faced challenges, especially the issues related to synthetic complexity and scalability. Here, we reported a chemical synthesis of unnatural (1→6)-polysaccharides using levoglucosenone (LGO) and dihydrolevoglucosenone (Cyrene<sup>TM</sup>), which are derived from cellulose. Through versatile monomer synthesis from LGO and Cyrene, followed by cationic ring-opening polymerization, (1→6)-polysaccharides with various tailored substituent patterns were achieved. The synthesized (1→6)-polysaccharides exhibit high thermal stability and high transparency. Additionally, these polymers exhibit excellent closed-loop chemical recyclability. **Keywords** : Biomass Resource; Polysaccharide; Acetal; Polymerization; Recycle

多糖類は地球上で最も豊富なバイオマス資源であり、主鎖や側鎖の形態により多様な性質を示す。また、主鎖骨格にはアセタールを有しており、分解やケミカルリサイクルが容易である<sup>1)</sup>。したがって、多糖類の構造-物性関係を探求し、持続可能な高分子材料開発に活用することが期待される。しかし、非天然型多糖類の合成は困難であり構造-物性関係の十分な探索はなされていない。そこで本研究では、セルロースの分解物を原料とする多様な非天然型多糖類の合成法を確立し、それらの物性およびケミカルリサイクル性を調査した。

具体的には、セルロースの熱分解により得られるレボグルコセノン (LGO) やジヒドロレボグルコセノン (Cyrene<sup>TM</sup>) から簡単な有機反応によりアセタールモノマー (M1-M4) を合成し、そのカチオン開環重合を行った (Scheme 1)。C1 や C3 を酸触媒として用いることで重合を達成し多様な非天然型多糖類の化学合成に成功した。合成したポリアセタールはいずれも 5% 重量減少温度が 260 °C 以上と十分な熱安定性を有し、ガラス転移温度は置換基のかさ高さが増加するにつれて高くなった。また、いずれのポリアセタールもほぼ定量的なケミカルリサイクル性を示した。

1) Niu, J. *et al.*, *Nat. Chem.* **2023**, *15*, 1276.

**Scheme 1.** Unnatural polysaccharide from LGO and Cyrene



アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2024年3月20日(水) 9:00 ~ 11:30 A1442(14号館 [4階] 1442)

**[A1442-3am] 19. コロイド・界面化学**

座長：三友 秀之、石田 拓也

## ◆ 日本語

9:00 ~ 9:20

[A1442-3am-01]

金属間化合物ナノ粒子の局在表面プラズモン共鳴

○竹熊 晴香<sup>1</sup>、佐藤 良太<sup>1</sup>、飯田 健二<sup>2</sup>、川脇 徳久<sup>3</sup>、治田 充貴<sup>1</sup>、寺西 利治<sup>1</sup> (1. 京大、2. 北大、3. 東理大)

## ◆ 日本語

9:20 ~ 9:40

[A1442-3am-02]

プラズモニック規則合金ナノ粒子群の創製

○佐藤 良太<sup>1</sup>、竹熊 晴香<sup>1</sup>、飯田 健二<sup>2</sup>、川脇 徳久<sup>3</sup>、治田 充貴<sup>1</sup>、寺西 利治<sup>1</sup> (1. 京大化研、2. 北大触媒研、3. 東理大理)

## ◆ 日本語

9:40 ~ 10:00

[A1442-3am-03]

反応性粗視化分子動力学法およびトポロジカルデータ解析を用いたシリカ凝集過程の検討

○笹原 茂生<sup>1</sup>、上條 由人<sup>1</sup>、尾関 寿美男<sup>2</sup> (1. 富士化学株式会社、2. 信州大学)

## ◆ 日本語

10:00 ~ 10:20

[A1442-3am-04]

ケイ酸ソーダ水溶液のゲル化にともなうシリカ骨格構造の形成過程

○上條 由人<sup>1</sup>、尾関 寿美男<sup>2</sup>、笹原 茂生<sup>1</sup> (1. 富士化学(株)、2. 信州大)

10:20 ~ 10:30

休憩

## ◆ 日本語

10:30 ~ 10:50

[A1442-3am-05]

インジウムアンチモン量子ドットの湿式合成と短波長赤外フォトダイオードへの応用

○白幡 直人<sup>1,2,3</sup>、Subhashri Chatterjee<sup>1,2</sup> (1. 物質・材料研究機構、2. 北大、3. 中大)

## ◆ 日本語

10:50 ~ 11:10

[A1442-3am-06]

サイズに依存したCdTeナノ粒子の発光性能への欠陥の影響

○高畑 遼<sup>1,2</sup>、猿山 雅亮<sup>1</sup>、山添 誠司<sup>3</sup>、寺西 利治<sup>1,2</sup> (1. 京大化研、2. 京大院理、3. 都立大院理)

## ◆ 英語

11:10 ~ 11:30

[A1442-3am-07]

## Au ナノ粒子および量子ドットをコアとした有機無機ハイブリッドデンドリマーによる交互積層超格子

○佐藤 梨奈<sup>1</sup>、谷地 昶拓<sup>1</sup>、松原 正樹<sup>2,3</sup>、陶山 めぐみ<sup>1</sup>、三友 秀之<sup>4</sup>、玉田 薫<sup>5</sup>、村松 淳司<sup>1,2</sup>、蟹江 澄志<sup>1,2</sup> (1. 東北大多元研、2. 東北大SRIS、3. 仙台高専、4. 北大電子研、5. 九大先導研)

---

## 金属間化合物ナノ粒子の局在表面プラズモン共鳴

(京大化研<sup>1</sup>・北大触媒研<sup>2</sup>・東理大理<sup>3</sup>) ○竹熊 晴香<sup>1</sup>・佐藤 良太<sup>1</sup>・飯田 健二<sup>2</sup>・川脇 徳久<sup>3</sup>・治田 充貴<sup>1</sup>・寺西 利治<sup>1</sup>

Localized Surface Plasmon Resonance Properties of Intermetallic Compound Nanoparticles (<sup>1</sup>*Institute for Chemical Research, Kyoto University*, <sup>2</sup>*Institute for Catalysis, Hokkaido University*, <sup>3</sup>*Faculty of Science, Tokyo University of Science*) ○Haruka Takekuma,<sup>1</sup> Ryota Sato,<sup>1</sup> Kenji Iida,<sup>2</sup> Tokuhisa Kawawaki,<sup>3</sup> Mitsutaka Haruta,<sup>1</sup> Toshiharu Teranishi<sup>1</sup>

Research of localized surface plasmon resonance (LSPR) has predominantly centered around group 11 metals such as Au, Ag, Cu and their alloy nanoparticles (NPs) with *fcc* structure. Here, we synthesized the C1 (CaF<sub>2</sub>-type) structured PtIn<sub>2</sub> NPs by liquid-phase method. The C1-PtIn<sub>2</sub> NPs exhibited LSPR in visible region (552 nm) without containing group 11 metals. In addition, we succeeded to synthesize the spherical B2 (CsCl-type) structured AuCd NPs and verified their LSPR in the UV region (337 nm), despite the 50% Au content. We believe that the intermetallic compound NPs will significantly contribute to advancing plasmonics as novel plasmonic materials.

**Keywords :** Localized Surface Plasmon Resonance, Nanoparticles, Intermetallic Compound, Ordered Alloy

M. Faraday による Au コロイドの着色原理解明以降 160 余年、可視域の局在表面プラズモン共鳴 (LSPR) は、11 族元素 (Cu, Ag, Au) を含む *fcc* 構造ナノ粒子を中心に展開されてきた。我々は最近、C1 (CaF<sub>2</sub> 型) 構造の PtIn<sub>2</sub> ナノ粒子が可視域に LSPR 吸収 (552 nm) を示すことを発見した (図)<sup>1)</sup>。*fcc*-Au クラスタについての光励起電子ダイナミクス<sup>2)</sup>の理論研究<sup>2)</sup>に倣い、約 600 個の原子からなるナノ粒子モデルに対し第一原理計算を行った結果、C1-PtIn<sub>2</sub> NPs の可視 LSPR の主な起源が (1) 貴金属の割合が減少したことによる、可視光でのバンド間遷移の減少、(2) Pt 原子の束縛 d 電子による強いスクリーニング効果であることが強く示唆された。

この知見から、11 族元素を含んでいても、本質的に可視域以外に LSPR を示す球状金属間化合物ナノ粒子が設計できる。我々が合成した B2 (CsCl 型) 構造の AuCd ナノ粒子は、Au ナノ粒子の LSPR (522 nm) とは大きく異なり、紫外域 (337 nm) に明瞭な吸収ピークを示した (図)。このような金属間化合物ナノ粒子による LSPR の探索は、プラズモニクスの発展に寄与すると考える。

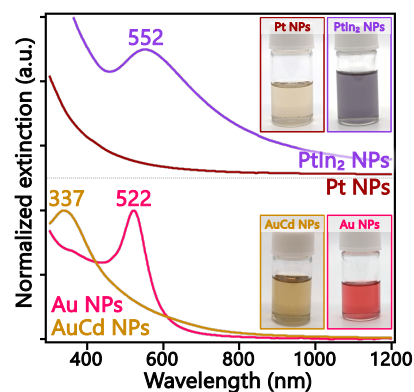


図 *fcc*-Pt、C1-PtIn<sub>2</sub>、*fcc*-Au、B2-AuCd ナノ粒子の消衰スペクトル

1) H. Takekuma, R. Sato, T. Teranishi *et al.*, *Adv. Sci.*, in press.

2) K. Iida, M. Noda, K. Nobusada *et al.*, *J. Phys. Chem. A* **2014**, *118*, 11317–11322.

## プラズモニック規則合金ナノ粒子群の創製

(京大化研<sup>1</sup>・北大触媒研<sup>2</sup>・東理大理<sup>3</sup>) ○佐藤 良太<sup>1</sup>・竹熊 晴香<sup>1</sup>・飯田 健二<sup>2</sup>・川脇 徳久<sup>3</sup>・治田 充貴<sup>1</sup>・寺西 利治<sup>1</sup>

Development of Plasmonic Ordered Nanoalloys (<sup>1</sup>*Institute for Chemical Research, Kyoto University*, <sup>2</sup>*Institute for Catalysis, Hokkaido University*, <sup>3</sup>*Faculty of Science Division I, Tokyo University of Science*) ○Ryota Sato,<sup>1</sup> Haruka Takekuma,<sup>1</sup> Kenji Iida,<sup>2</sup> Tokuhisa Kawawaki,<sup>3</sup> Mitsutaka Haruta,<sup>1</sup> Toshiharu Teranishi<sup>1</sup>

We have found that spherical ordered nanoalloys with electronic structures like those of coinage metals, namely, Au, Ag and Cu exhibit distinct LSPR absorption peaks in and near the visible region. In this presentation, in addition to introducing specific examples of plasmonic ordered alloy nanoparticles, we discuss the importance of electronic structure and crystal structure in the design of highly plasmonic ordered alloy nanoparticles in terms of photo-induced electron dynamics.

**Keywords:** *Localized Surface Plasmon Resonance (LSPR), Inorganic Nanoparticle, Ordered Alloy (Intermetallic Compound), Photo-Induced Electron Dynamics, Plasmonics*

ナノサイズの貨幣金属 (Au、Ag、Cu) は、合成の容易さと高い安定性から、可視域に局在表面プラズモン共鳴 (LSPR) を示すプラズモン材料として、プラズモニクスの発展を牽引してきた。一方で、貨幣金属と類似のプラズモン特性を有するコロイド状規則合金ナノ粒子に関する研究は、意外にも皆無に等しい。その一因として、プラズモン特性が明瞭に発現する十分な大きさ ( $d < 10$  nm) を有し、かつ還元が困難な卑金属を含む単分散規則合金ナノ粒子を合成する手法に乏しい点が挙げられる。我々は、粒径制御が容易な貴金属ナノ粒子を種粒子とするシード媒介成長法に着目し、様々な規則合金ナノ粒子の合成と粒径制御を可能とする新たな手法を確立することで、この問題を克服し、*B2-PdIn* ナノ粒子や *C1-PtIn<sub>2</sub>* ナノ粒子<sup>1</sup>などの規則合金ナノ粒子が可視域に明瞭な LSPR 吸収ピークを示すことを実証した (図 1)。これらの規則合金ナノ粒子は、貨幣金属を除く後期遷移金属と前期典型元素で構成され、元素の組み合わせと組成によって価電子数が制御されることで、貨幣金属に類似の電子構造を有している。一方、第一原理計算に基づく光誘起電子ダイナミクスのシミュレーションでは、貨幣金属と比較した際の自由電子ダイナミクスの類似性とは対照的に、束縛電子ダイナミクスの相違性が示された。この規則合金に特有の光学応答は結晶構造に依るところが大きく、結晶構造がプラズモン特性の制御因子になり得ることが明らかになった。このように、モデル材料となる貨幣金属と規則合金の類似性や相違性を明らかにし、制御因子を特定することで、新規プラズモニック規則合金ナノ粒子群の材料設計指針を提唱する。

1) H. Takekuma, R. Sato, T. Teranishi *et al.*, *Adv. Sci.*, in press



図 1. 各金属ナノ粒子分散液の色調  
(左から Ag、Au、C1-PtIn<sub>2</sub>、B2-PdIn)



## 反応性粗視化分子動力学法およびトポロジカルデータ解析を用いたシリカ凝集過程の検討

(富士化学<sup>1</sup>・信大理<sup>2</sup>) ○笹原 茂生<sup>1</sup>・上條 由人<sup>1</sup>・尾関 寿美男<sup>2</sup>

Investigation of silica aggregation processes using reactive coarse-grained molecular dynamics and topological data analysis (<sup>1</sup>Fuji Chemical Co., Ltd., <sup>2</sup>Faculty of Science, Shinshu University) ○Shigeo Sasahara,<sup>1</sup> Yuito Kamijo,<sup>1</sup> Sumio Ozeki<sup>2</sup>

The reactions of silicic acid are used in the production of silica gel or colloidal silica, and in civil engineering. This reaction is known to affect the physical properties of products depending on conditions of reaction such as pH or temperature. In this study, MD simulation of the aggregation process of silicate were performed using Sticky-Martini force field<sup>1)</sup>. MD simulation was started with a random configuration having 2100 SiO<sub>4</sub> molecules and 31100 coarse-grained water particles. The number of clusters decreased after 10<sup>3</sup> ps, when Q<sub>2</sub> structure was achieved maximum. The change of SiO<sub>4</sub> coordinates with time elapsed was analyzed by persistent homology and machine learning. PCA with vectorized persistent diagrams (PDs) were performed. 4 classes of reaction stages were classified from PCA scores.

**Keywords :** *Reactive Coarse-Grained Molecular Dynamics; Sodium Silicate; Persistent homology; Gelation*

ケイ酸の反応はシリカゲル、コロイダルシリカ、土木材料等に利用されている。この反応は pH, 温度などの条件によって製品の物性に影響を及ぼすことが知られている。本研究では、Sticky-Martini 力場<sup>1)</sup>を用いてシリカの凝集していく過程の MD 計算を行った。SiO<sub>4</sub> 2100 個, 粗視化した水粒子 31100 個をランダムに配置して初期構造とした。時間経過とともに縮合度  $c$  が増加していく様子がみられた。Q<sub>2</sub> が最大になる 10<sup>3</sup> ps を過ぎるとクラスターの数は急激に減少した。SiO<sub>4</sub> の座標データについてパーシステントホモロジーおよび機械学習による解析を行い、構造形成していく過程についての検討を行った。ベクトル化したパーシステント図 (PD) について PCA 解析を行い、そのスコア値をもとに 4 つのクラスの反応ステージに分類した。PD および PCA の結果を学習データとして分類モデルを構築し、構造形成していく過程について検討する。

1) Sticky-MARTINI as a reactive coarse-grained model for molecular dynamics simulations of silica polymerization. A. P. Carvalho, S. M. Santos, G. Pérez-Sánchez, *et al. npj Comput. Mater.* **2022**, 8, 49.

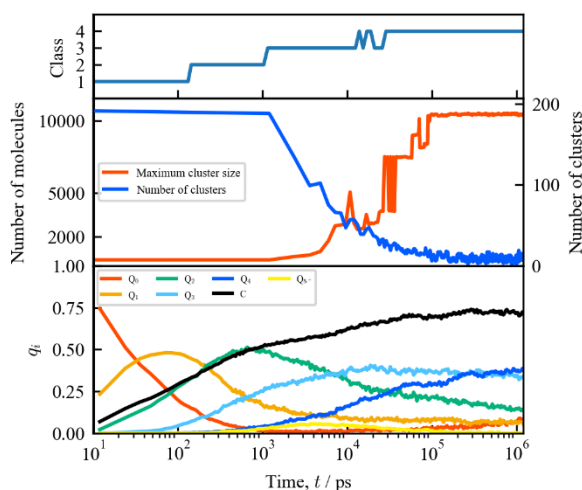


Figure Time dependence of the class obtained from PCA results, the number of clusters, the maximum cluster size and the molar fraction of each  $Q_n$  species.

## ケイ酸ソーダ水溶液のゲル化にともなうシリカ骨格構造の形成過程

(富士化学(株)<sup>1</sup>・信大理<sup>2</sup>) ○上條 由人<sup>1</sup>・尾関 寿美男<sup>2</sup>・笹原 茂生<sup>1</sup>

Formation process of silica skeleton structure during gelation of sodium silicate solution (<sup>1</sup>Fuji Chemical Co., Ltd., <sup>2</sup>Faculty of Science, Shinshu University) ○Yuito Kamijo<sup>1</sup>, Sumio Ozeki<sup>2</sup>, Shigeo Sasahara<sup>1</sup>

Sodium silicate has the property to polymerize and gel when acids or salts are added. It is important to understand the structural changes of the silica skeletons during gelation process since the physical properties after gelation depend on the aggregation structure. In this study, we report the formation process of silica skeletons under acidic conditions using sodium silicate with a  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio of 3.8.

The sodium silicate solution diluted with pure water was mixed with dilute sulfuric acid to prepare a pH = 4. Fig. 1 shows the storage,  $G'$ , and loss,  $G''$ , modulus of acidic silicate solution as a function of reaction time. The gelation time,  $t_{\text{sg}}$ , was set as the time when  $G' = G''$ , and the measurement time,  $t$ , was normalized as  $(t - t_{\text{sg}})/t_{\text{sg}}$ . The siloxane bonds increase due to the dehydration condensation reaction up to  $(t - t_{\text{sg}})/t_{\text{sg}} = 0$ , but remain almost unchanged after  $(t - t_{\text{sg}})/t_{\text{sg}} = 0$  from FT-IR spectroscopy. In addition, we will discuss with results obtained from small-angle X-ray scattering (SAXS) measurements.

**Keywords :** Sodium Silicate; Gelation; Small angle X-ray scattering(SAXS)

ケイ酸ソーダは酸や塩を加えることで、ケイ酸イオンが重合しゲル化する性質があることから、土木・建築分野で利用されている。ゲル化後の物理的特性は凝集構造に依存するため、ゲル化過程におけるシリカ骨格の構造変化を理解することは重要である。本研究では、 $\text{SiO}_2/\text{Na}_2\text{O}$  のモル比 3.8 のケイ酸ソーダを使用し、酸性条件下でのシリカ骨格の形成過程について検討した。

純水で希釈したケイ酸ソーダ水溶液を希硫酸中に注ぎ、pH が 4 になるよう調製した。ゲル化点 ( $t_{\text{sg}}$ ) をレオロジー測定より得られた貯蔵弾性率  $G'$  と損失弾性率  $G''$  の交点の時間に決定し、サンプルの測定時間  $t$  は  $(t - t_{\text{sg}})/t_{\text{sg}}$  として規格化した (Fig. 1)。

FT-IR スペクトルを非負値行列因子分解 (NMF) からスペクトル分解した結果より、 $(t - t_{\text{sg}})/t_{\text{sg}} = 0$  までは脱水縮合反応によりシロキサン結合が増えていくが、 $(t - t_{\text{sg}})/t_{\text{sg}} = 0$  以降はほぼ変化しないことが明らかとなった。さらに講演では、小角 X 線散乱 (SAXS) 測定から得られた結果も併せて報告する。

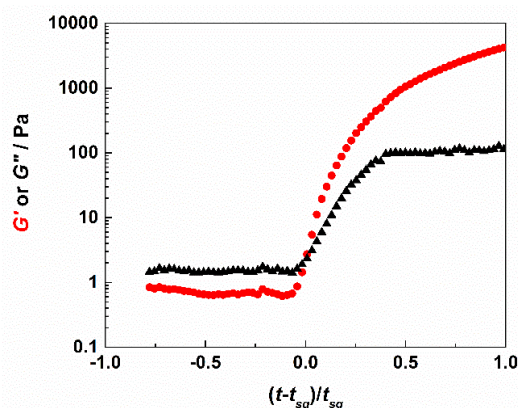


Fig. 1. Storage ( $G'$ , ●) and loss modulus ( $G''$ , ▲) of sodium silicate solutions before/after gelation at 298 K.



## インジウムアンチモン量子ドットの湿式合成と短波長赤外フォトダイオードへの応用

(NIMS<sup>1</sup>・北大院<sup>2</sup>・中大院<sup>2</sup>) ○白幡 直人<sup>1,2,3</sup>・チャタジー スバスリ<sup>1,2</sup>

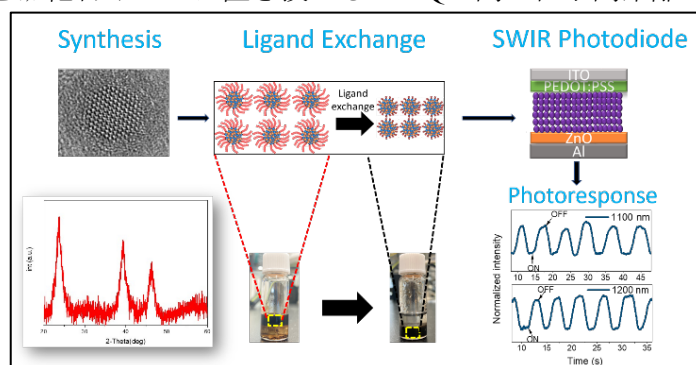
Solution-Processed InSb Quantum Dot Photodiodes for Short-Wave Infrared Light Detection  
(<sup>1</sup>Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, <sup>2</sup>Graduate School of Chemical Sciences and Engineering, Hokkaido University, <sup>3</sup>Department of Physics, Chuo University)

Solution-processed colloidal III-V semiconductor quantum dot photodiodes (QPDs) have potential applications in short-wavelength infrared (SWIR) imaging due to their tunable spectral response range and operation at 0-V bias voltage. Here we report on ligand engineering of InSb CQDs to enhance the optical response of self-powered SWIR QPDs. Specifically, by replacing the conventional ligand (i.e., oleylamine) with sulfur ions, the interparticle distance between the CQDs was shortened  $5.0 \pm 0.5$  nm to  $1.5 \pm 0.5$  nm, leading to improved carrier mobility for high photoresponse speed to SWIR light. The interparticle distance of the sulfur-liganded QDs was shorter than that of bromine-liganded counterparts. Furthermore, the use of sulfure ligands resulted in a low dark current density ( $\sim$ nA/cm<sup>2</sup>) with improving an EQE of 18.5 %, suggesting its potential for use over toxic-based infrared image sensors.

**Keywords :** Quantum dots; Indium antimonide; Solution-processed photodiodes; SWIR

溶液プロセスで作製したコロイド状 III-V 族半導体量子ドット (CQD) フォトダイオードは、受光波長を QD サイズで連続的に制御できることに加え、光起電力型の駆動が可能である。InAs や InSb は短波長赤外 (SWIR) イメージングへの応用が期待されている。本研究では、臭化物前駆体から湿式合成した InSb CQD が SWIR のフォトダイオードの活性層に資する光学特性を有することを初めて明らかにした<sup>1)</sup>。さらに、従来の配位子を硫黄イオンに置き換えることでフォトダイオード向上した。例示すると、オレイルアミンリガンドを硫化物イオンに置き換えると CQD 間の粒子間距離が  $5.0 \pm 0.5$  nm から  $1.5 \pm 0.5$  nm へ短縮した。その結果、膜内のキャリア移動度が向上し SWIR 光に対して高い光応答速度、低い暗電流密度 ( $\sim$ nA/cm<sup>2</sup>)、高い外部量子効率 (EQE=18.5%) が得られた<sup>2)</sup>。

- 1) Solution-processed InSb quantum dot photodiodes for short-wave infrared sensing. S. Chatterjee, K. Nemoto, B. Ghosh, H. T. Sun, N. S. Shirahata, *ACS Appl. Nano Mater.* **2023**, 6, 20389.
- 2) Sulfur-modified capping layer for enhancing carrier mobility in self-powered InSb quantum dot-based SWIR photodiode. S. Chatterjee, K. Nemoto, H. T. Sun, N. Shirahata, submitted for publication.



## サイズに依存した CdTe ナノ粒子の発光性能への欠陥の影響

(京大化研<sup>1</sup>・京大院理<sup>2</sup>・都立大院理<sup>3</sup>) ○高畑 遼<sup>1,2</sup>・猿山 雅亮<sup>1</sup>・山添 誠司<sup>3</sup>・寺西 利治<sup>1,2</sup>

Effect of Defects on Photoluminescent Properties of CdTe Nanoparticles Depending on Sizes (<sup>1</sup>Institute for Chemical Research, Kyoto University, <sup>2</sup>Graduate School of Science, Kyoto University, <sup>3</sup>Graduate School of Science, Tokyo Metropolitan University)

○Ryo Takahata,<sup>1,2</sup> Masaki Saruyama,<sup>1</sup> Seiji Yamazoe,<sup>3</sup> Toshiharu Teranishi<sup>1,2</sup>

Cadmium telluride nanoparticle (CdTe NP) is a good candidate for various optical functional materials because of their highly efficient photoluminescence (PL) and energy conversions in the visible to near IR region. In this study, we developed a size separation of CdTe NPs using polyacrylamide gel electrophoresis. CdTe NPs, separated depending on their sizes, were classified into PL-active and PL-silent fractions at a diameter of ~1.5 nm. X-ray absorption fine structure analysis indicated that this suppression of PL was attributed to the elution of Te<sup>2-</sup>. Furthermore, the quantum yield of PL-active CdTe NPs has been improved by annealing under basic conditions. This suggests that the surface deformations of CdTe NPs have been eliminated through this annealing process.

**Keywords :** CdTe Nanoparticles; Size Separation; Photoluminescent properties; Defects

テルル化カドミウム (CdTe) ナノ粒子は、可視から近赤外域で高効率に発光することから、広く光学材料応用が期待されている。この光物性は、CdTe ナノ粒子のサイズや化学組成に大きく影響されることから、さまざまな合成手法が開発されてきた[1,2]。本研究では、液相合成した CdTe ナノ粒子を、ポリアクリルアミドゲル電気泳動 (PAGE) を用いてサイズ分離し、その光物性を調べた。サイズ分離した CdTe ナノ粒子は、泳動距離が長くなるに従い、エキシトニックピークと発光ピークの波長が短波長シフトしており、コアサイズによる CdTe ナノ粒子の分離を確認した。また、分離後の CdTe ナノ粒子の発光量子収率を調べたところ、~1.5 nm の粒径を境に CdTe ナノ粒子で発光量子収率が 10 分の 1 以下まで減少した。泳動距離ごとに分画した CdTe ナノ粒子の X 線吸収微細構造解析から、非発光性の CdTe ナノ粒子では発光性の CdTe ナノ粒子より Cd-Te の結合数が減少していることがわかった (Fig. 1)。この結果から、非発光性の CdTe ナノ粒子では Te 欠損が多数存在し、強く消光されたと考えられる。また、発光性の CdTe ナノ粒子をさらに塩基性条件下でアニールすることで、発光量子収率が~3 倍程度に増強することがわかった。これは、欠陥の中でも表面の歪みが解消し、これに起因する消光が抑えられたためであると予想される。

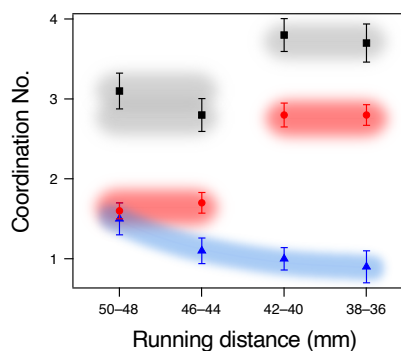


Fig.1 Plot of coordination number vs. running distances of CdTe NPs determined by X-ray absorption fine structure analysis.

1) Rogach, A. L. *et al.*, *J. Phys. Chem. C* **2007**, *111*, 14628. 2) Lensyak, V. *et al.*, *Chem. Soc. Rev.* **2013**, *42*, 2905.

## Multilayer superlattice of organic-inorganic hybrid dendrimer with Au nanoparticles and quantum dots

(<sup>1</sup>IMRAM, Tohoku Univ., <sup>2</sup>SRIS, Tohoku Univ., <sup>3</sup>NIT, Sendai college, <sup>4</sup>RIES, Hokkaido Univ., <sup>5</sup>IMCE, Kyushu Univ.) ○Rina Sato,<sup>1</sup> Takehiro Yachi,<sup>1</sup> Masaki Matsubara,<sup>2,3</sup> Megumi Suyama,<sup>1</sup> Hideyuki Mitomo,<sup>4</sup> Yuto Kajino,<sup>5</sup> Kaoru Tamada,<sup>5</sup> Atsushi Muramatsu,<sup>1,2</sup> Kiyoshi Kanie<sup>1,2</sup>

**Keywords:** organic-inorganic hybrid materials; binary superlattice; Langmuir-Schaefer method; multilayer

Inorganic nanoparticles (NPs) show exceptional properties when they form assembled structures. Formation of “NPs superlattice” is crucial for developing the unexplored properties of NP assembly and the NP-based functional materials. Here, the binary multilayer NP superlattices of Au NPs (**A**) and CdS quantum dots (QDs) have been built up by the Langmuir-Schaefer method. The optical properties of formed superlattices were also investigated. First, multilayers of 1-dodecanethiol-modified Au NPs (**A**) and CdS QDs (**Q**) were formed by depositing the dispersions of **A** and **Q** on the water surface and transferring their monolayers multiple times onto the hydrophobic substrate. Dendron-modified Au NPs (**DA**) and CdS QDs (**DQ**)<sup>[1,2]</sup> were also prepared by modification of the surface of Au NPs and CdS QDs with liquid-crystalline dendron molecule (Fig. 1) to observe an effect of such bulky and dendritic organic ligands on the structural and optical properties of superlattice. Multilayers of **DA** and **DQ** were likewise prepared. TEM observation revealed that these NPs were hexagonally arranged in their monolayers (Fig. 2). The intersurface distances in the monolayers of **DA** and **DQ** were expanded to 6.6 and 5.3 nm, respectively, compared to those of **A** and **Q** due to the thick, bulky dendron layers. On the other hand, according to the results of grazing-incidence small-angle X-ray scattering measurement and STEM images, multilayer of **A** and **Q** formed a NaCl-type structure where **A** and **Q** were closely packed. These differences in the structural feature significantly affected on the optical properties of multilayers such as local plasmon resonance effects of Au NPs and photoluminescence of QDs.

[1] K.Kanie, M. Matsubara, X. Zeng, F. Liu, G. Ungar, H. Nakamura, A. Muramatsu, *J. Am. Chem. Soc.*, **2012**, 134, 808.

[2] M. Matsubara, W. Stevenson, J. Yabuki, X. Zeng, H. Dong, K. Kojima, S. F. Chichibu, K. Tamada, A. Muramatsu, G. Ungar, K. Kanie, *Chem*, **2017**, 2, 860-876.

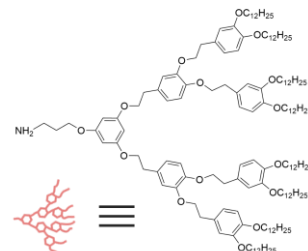


Fig. 1 A structure of dendron molecule.

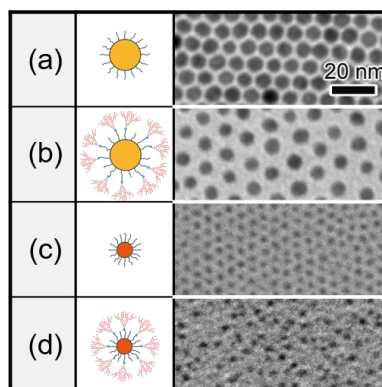


Fig. 2 Schematics and TEM images of (a) **A**, (b) **Q**, (c) **DA**, (d) **DQ** monolayer. The scale bar is common to all images.

アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2024年3月20日(水) 9:30 ~ 11:20 会場 A1443(14号館 [4階] 1443)

**[A1443-3am] 19. コロイド・界面化学**

座長：上田 貴洋、二村 竜祐

## ◆ 日本語

9:30 ~ 9:50

[A1443-3am-01]

水素発生反応ナノ構造触媒電極の活性評価

○佐藤 大樹<sup>1</sup>、田尾 和花子<sup>2</sup>、福島 知宏<sup>3</sup>、村越 敬<sup>3</sup> (1. 北大院総化、2. 北大理、3. 北大院理)

## ◆ 日本語

9:50 ~ 10:10

[A1443-3am-02]

電子移動反応速度における強結合状態形成の影響

林 峻大<sup>1</sup>、○福島 知宏<sup>2</sup>、村越 敬<sup>2</sup> (1. 北大院総化、2. 北大院理)

## ◆ 英語

10:10 ~ 10:30

[A1443-3am-03]

Fabrication of Titanium Dioxide Nanocatalyst within Carbon nanotubes for High Thermal Stability and UV/Visible light Photocatalytic Activity

○Smita Dnyandeo Takawane<sup>1</sup>, Masatoshi Miyamoto<sup>1</sup>, Takumi Watanabe<sup>1</sup>, Tomonori Ohba<sup>1</sup> (1. Chiba University)

10:30 ~ 10:40

休憩

## ◆ 日本語

10:40 ~ 11:00

[A1443-3am-04]

匂い分子のリン脂質膜への吸着脱離に基づく動的応答

○四元 まい<sup>1</sup>、松尾 宗征<sup>2,1</sup>、中田 聡<sup>1</sup> (1. 広島大学、2. 東京大学)

## ◆ 日本語

11:00 ~ 11:20

[A1443-3am-05]

単層カーボンナノチューブによる皮膚からのCO<sub>2</sub>の非侵襲・選択的検出Preety Ahuja<sup>1</sup>、Sanjeev Ujjain<sup>1</sup>、瓜田 幸幾<sup>2</sup>、森口 勇<sup>2</sup>、古瀬 あゆみ<sup>1</sup>、○金子 克美<sup>1</sup> (1. 信州大学先端材料研究所、2. 長崎大学工学部)

## 水素発生反応ナノ構造触媒電極の活性評価

(北大院総化<sup>1</sup>・北大理<sup>2</sup>・北大院理<sup>3</sup>)

○佐藤大樹<sup>1</sup>・田尾和花子<sup>2</sup>・福島知宏<sup>3</sup>・村越敬<sup>3</sup>

Investigation of surface molecular process of hydrogen evolution reaction in plasmonic conversion system (*Department of Chemistry, Faculty of Science, Hokkaido University*.<sup>3</sup>)

○Daiki Sato, Wakako Tao, Tomohiro Fukushima, Kei Murakoshi

In this study, we utilized well-defined nanostructures for electrochemical HER by the observation of hydrogen bubble generation. The formation and growth process of hydrogen bubbles were monitored with microscope under electrochemical potential control. We discuss the effects of nanostructure on the hydrogen evolution process.

**Keywords :** *Hydrogen evolution reaction, nanostructure, micro bubble, isotope effect*

【序論】電気化学水素発生反応(HER)は多電子多プロトン反応であり、3つの反応素過程で記述されるが、電極—電解質界面における水和構造が関与する為その理解は困難である。我々はこれまでに特定の金属ナノ構造電極において水素同位体選択的なHERが発現することを見出している。この選択性は電極への電位印加時における金属ナノ構造特有の分極状態及びエネルギー状態とHERの中間体が選択的な相互作用をすることにより発現していると考えている。本研究ではサイズの異なる複数種類のAgナノ構造を有する電極を用いてHERを進行させ、気泡形成動画観測から金属ナノ構造に依存したHER活性を評価した。

【実験】直径400 nmから800 nm、厚さ100 nmのAgナノディスク配列構造をグラッシ—カーボン電極上に作製し、作用極とした。Au線を擬似参照電極および対極として、75 MPaの静水圧条件下、0.25 M Na<sub>2</sub>SO<sub>4</sub>を電解質としてHERを進行させ、正立配置のカメラで1秒間に60フレーム記録を行った。取得した動画を画像解析することにより電位に依存した気泡形成、成長挙動を定量化した。

【結果と考察】Fig.にHER条件下における電極上からの気泡観察の結果を示す。Agナノ構造の局在表面プラズモンに共鳴特性を反映し、異なる色調が発現しているが、このAgナノ構造に応じて水素気泡の生成量が異なることが確認された。また電解質溶液として重水を用いた際には通常と同位体効果では観測されないナノ構造依存性が発現した。気泡解析により見かけの電位—電流依存性を定量化し、平滑電極で約0.1 V dec.<sup>-1</sup>となったターフェル線の傾きが約0.03 V dec.<sup>-1</sup>となるナノ構造群を確認した。

傾き変化から速度論的解釈より素過程のVolmer ( $M + H_2O + e^- \rightarrow MH + OH^-$ )及びHeyrovsky ( $MH + H_2O + e^- \rightarrow M + H_2 + OH^-$ )過程が加速していることが示唆された。以上の検討に基づき非触媒金属電極におけるナノ構造によるHER触媒活性発現の可能性を議論する。

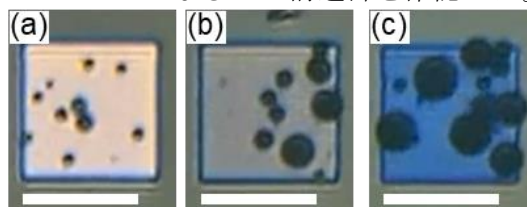


Fig. A snapshot for hydrogen bubble formation on nano-structured Ag electrode 0.25 M Na<sub>2</sub>SO<sub>4</sub> at -1.11 V vs. RHE. Scale bar = 50  $\mu$ m. Diameter of nano-disk was (a) 400 nm (b) 600 nm (c) 800 nm.

## 電子移動反応速度における強結合状態形成の影響

(北大院総化<sup>1</sup>・北大院理<sup>2</sup>) 林峻大<sup>1</sup>・○福島知宏<sup>2</sup>・村越敬<sup>2</sup>

Effect of strong coupling states on the electron transfer reaction rates (*Department of Chemistry, Faculty of Science, Hokkaido University*) Takahiro Hayashi, ○Tomohiro Fukushima, Kei Murakoshi

The molecules can be correlated by the formation of polaritons via vacuum field. We have developed the use of the structured electrodes for the enhanced electron transfer activity at the electrode-electrolyte interface. Here, we propose a theoretical description under the strong coupling. The electron transfer behavior can be described with the classical electron transfer parameters such as interaction of adsorbate, reorganization energy. In addition, the resonator energies and molecular correlation can be used as the descriptor for the light-matter interaction for the enhanced electron transfer reaction.

**Keywords :** Strong coupling; Electron transfer; Theoretical description

【序論】分子と共振場が真空場を介して強結合状態を形成することにより、分子物性に変調することが知られている。当研究グループにおいても、ナノ構造電極と反応中間体が相互作用することによって、特異な電子移動反応の加速が観測されている。本講演においては、既報の理論をもとに、強結合条件下でのナノ構造電極における電子移動反応加速に関して検討を行った。

【理論】既報<sup>1</sup>の電子移動反応に対して (式 1)、電極—電解質界面での電子移動反応に関して検討を行うために、状態密度、Fermi-Dirac 分布を導入した (式 2)。電極反応速度でのモード体積( $V$ )、協同分子数( $N$ )から、電気化学界面における電子移動反応の強結合効果を検討した。

$$k_{sc} \approx \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi\lambda k_B T}} \left\{ |H|^2 \exp \left[ -\frac{(-\Delta G_0 - \lambda)^2}{4\lambda k_B T} \right] + |E_{vac} \cdot \mu|^2 \exp \left[ -\frac{(-\Delta G_0 - \lambda - \hbar\omega_{cav})^2}{4\lambda k_B T} \right] \right\} \quad (1)$$

$$k_{\text{Electrode}} = \int \delta V_e D(\epsilon) f(\epsilon - \epsilon_F + \Delta G_0) k_{sc} d\epsilon \quad (2)$$

$k_{sc}$ : 強結合下での速度定数、 $\hbar$ : Planck 定数、 $\lambda$ : 再配列エネルギー、 $k_B$ : ボルツマン定数、 $T$ : 絶対温度、 $H$ : 電子カップリング行列要素、 $\Delta G_0$ : 自由エネルギー差、 $E_{vac}$  ( $= \sqrt{e\hbar\omega_{cav}/(2\epsilon_0 V)}$ ): 真空場強度、 $e$ : 電気素量、 $\omega_{cav}$ : 共振器周波数、 $\epsilon_0$ : 真空の誘電率、 $\mu$ : 遷移双極子、 $k_{ET}$ : 強結合下での電子移動速度定数、 $\delta$ : 電極反応に関与可能距離、 $V_e$ : 電極反応に関与可能な電子体積、 $D(\epsilon)$ : 電子状態密度、 $f$ : Fermi-Dirac 分布

【結果と考察】強結合下での電子移動反応において、特定の共振周波数 ( $\omega_{cav}$ ) ならびに  $N/V$  に依存して電子移動反応速度 ( $k_{ET}$ ) が増大することがわかった。古典的な電子移動反応速度解析では、再配列エネルギーと吸着分子結合エネルギーに依存した Marcus 限界が示されるが、強結合系では特定のナノ構造電極にて仮想励起状態を介した電子移動数の増大により反応が加速されることが期待される。以上の検討に基づき電子移動反応の強結合効果を議論する。

参考文献: 1) A. Semenov and A. Nitzan, *J. Chem. Phys.* **2019**, *150*, 174122.

## Fabrication of Titanium Dioxide Nanocatalyst within Carbon nanotubes for High Thermal Stability and UV/Visible light Photocatalytic Activity

(Graduate School of Science, Chiba University) ○ Smita D. Takawane<sup>1</sup>, Masatoshi Miyamoto<sup>1</sup>, Takumi Watanabe<sup>1</sup>, Tomonori Ohba<sup>1</sup>

**Keywords:** Titanium dioxide nanocatalyst; Visible light Photocatalytic activity; Carbon nanotubes; Anatase Stability

Titanium dioxide, a representative photocatalyst with three crystal phases—namely, anatase, rutile, and brookite, demonstrates superior catalytic performance in its anatase phase, where it irreversibly transforms to rutile at 800K; despite anatase's metastable nature, it maintains high catalytic efficiency owing to enhanced charge-carrier mobility.<sup>1</sup> The anatase phase has been maintained at elevated temperatures using various strategies, including metal-cation doping, non-metal anion doping, and coating; still, these methods cause harmful effects on photocatalytic activity.<sup>2</sup> However, achieving a highly stable anatase phase without dopants is a significant challenge. We employ a methodology wherein, TiO<sub>2</sub> nanocatalysts are synthesized within carbon nanotubes (CNTs), and subsequently, their thermal stability and photocatalytic activity are evaluated.

Transmission electron microscopy images supported the existence of TiO<sub>2</sub> within CNT pores. The thermal stability of TiO<sub>2</sub> nanocatalysts was assessed by heating them for 3h at 600K-1400K under argon gas. The bulk TiO<sub>2</sub> anatase transformed rutile between 600–800 K, consistent with previous findings. In contrast, TiO<sub>2</sub> nano catalysts within 1, 3, and 7 nm carbon nanotubes (CNTs) maintained the anatase structure up to 1200 K, with a rapid decrease in anatase ratios above this temperature.

The photocatalytic performance of TiO<sub>2</sub> nanocatalysts was investigated using the decomposition of Methylene Blue (MB) under Visible and UV-light irradiation. Changes in MB concentrations over time were monitored by measuring light absorbance. TiO<sub>2</sub> nanocatalysts within CNTs led to a decrease in MB concentration even in the absence of UV irradiation because CNTs effectively adsorbed MB. Subsequently, a notable decrease in MB concentration occurred following both visible and UV irradiation. The TiO<sub>2</sub> nanocatalysts demonstrated accelerated reaction rates compared to bulk TiO<sub>2</sub>, emphasizing the superior photocatalytic activity of the TiO<sub>2</sub> nanocatalysts. The high photocatalytic activity of the TiO<sub>2</sub> nanocatalysts within CNTs is attributed to the maintenance of small crystal sizes and the synergistic effect between the nanocatalysts and the CNTs.<sup>3</sup> Overall, this work represents a significant advancement in the development of highly stable and efficient TiO<sub>2</sub> nanocatalysts, with promising potential for various practical applications.

1) Hanaor, D.A.H.; Sorell C.C., *J. Mater. Sci* **2011**, 46, 855-874. 2) Periyat P, Naufal, B, Ullattil, S.G., *Mater. Sci. Forum* **2016**, 855, 78-93. 3) Takumi Watanabe, Smita Takawane, Yuki Baba, Jun Akaiwa, Atsushi Kondo, and Tomonori Ohba, *J. Phys. Chem. C* **2023**, 127,16861-16869.



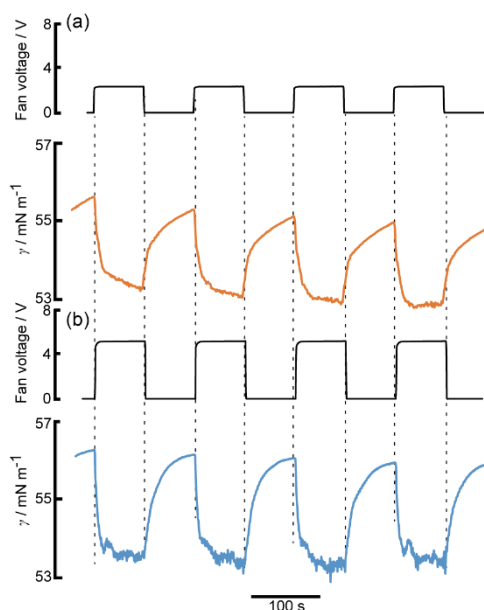
## 匂い分子のリン脂質膜への吸着脱離に基づく動的応答

(広大院統合生命<sup>1</sup>) ○四元 まい<sup>1</sup>・松尾 宗征<sup>1</sup>・中田 聡<sup>1</sup> Dynamic responses based on adsorption and desorption of odor molecules onto phospholipid molecular layers (<sup>1</sup>*Graduate School of Integrated Sciences of Life, Hiroshima University*) ○Mai Yotsumoto,<sup>1</sup> Muneyuki Matsuo,<sup>1</sup> Satoshi Nakata,<sup>1</sup>

We perform sniffing when we smell an odor. In this study, we artificially reproduced sniffing and measured the surface tension of a 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) molecular layer when the odor stimuli were supplied periodically. We found that time-variation of surface tension was characteristically changed depending on the odor species.<sup>[1]</sup> 1-octanol was recursively supplied onto DPPC molecular layers, resulting that the surface tension increased and decreased while the fan was running and stopped, respectively (Fig. 1a). The dynamic response was changed depending on the amplitude of fan voltage, i.e., the amplitude of flow rate (Fig. 1b). In addition to 1-octanol, 1-octanal, 1-hexanol, and 1-hexanal will be examined and the relationship between flow rate and dynamic surface tension responses will be discussed in terms of the interaction between phospholipid molecules and each odor molecule.

**Keywords :** Sniffing; Surface tension; Phospholipid molecular layer

我々は匂いを嗅ぐ際に鼻からリズムカルに空気を吸ったり吐いたりする行動である sniffing を行う。我々は人工 sniffing 系として、リン脂質分子膜に対して周期的に匂い刺激を与えたところ、匂い分子種に特異的な動的表面張力応答を見出した。<sup>[1]</sup> 本研究ではこの系の応用として、周期的なにおい刺激の流量と動的応答との関係を明らかにするために、ファン電圧の振幅を変えて実験した。1,2-Dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) 分子膜に 1-octanol を周期的に吹き付けた場合、ファンが回転している間は表面張力が上昇し、静止している間は低下した (Fig. 1a)。また、ファン電圧を上昇させ流量を増加させた場合、動的表面張力応答の振幅が増大した (Fig. 1b)。1-octanol に加え、1-octanal, 1-hexanol, 1-hexanal についても検討し、リン脂質分子と各匂い分子の相互作用の観点から、流量と動的表面張力応答との関係について議論する。



**Fig. 1** DPPC 分子膜に対し 1-octanol を異なる流量で周期的に吹き付けた場合の表面張力経時変化。(a) Fan voltage = 0~2 V、(b) Fan Voltage = 0~5 V.

[1] M.Yotsumoto, *et al.*, *ACS Sens.* **2023**, 8, 4494-4503.



## 単層カーボンナノチューブによる皮膚からの CO<sub>2</sub> の非侵襲・選択的検出

(信州大先鋭材料研<sup>1</sup>・長崎大工<sup>2</sup>) Preety Ahuja<sup>1</sup>・Sanjeev Ujjain<sup>1</sup>・瓜田幸幾<sup>2</sup>・森口勇<sup>2</sup>・古瀬あゆみ<sup>1</sup>・○金子克美<sup>1</sup>

Noninvasive and selective detection of skin CO<sub>2</sub> with single wall carbon nanotube

(<sup>1</sup>*Research Initiative for Supra-Materials, Shinshu University*, <sup>2</sup>*School of Engineering, Nagasaki University*) Preety Ahuja<sup>1</sup>・Sanjeev Ujjain<sup>1</sup>・Koki Urita<sup>2</sup>・Isamu Moriguchi<sup>2</sup>・Ayumi Furuse<sup>1</sup>・○Katsumi Kaneko<sup>1</sup>

Existing noninvasive methods are inadequate owing to the rigidity of hard-wired devices, insubstantial gas permeability and high operating temperature. Here, we report a cost-effective transcutaneous CO<sub>2</sub> sensing device comprising elastomeric sponges impregnated with oxidized single-walled carbon nanotubes (oxSWCNTs)-based composites. The proposed device features a highly selective CO<sub>2</sub> sensing response (detection limit ~70 ppb) in atmosphere, excellent permeability and reliability under a large deformation. A follow-up prospective study not only offers measurement equivalency to existing clinical standards of CO<sub>2</sub> monitoring but also provides important additional features. This new modality allowed for skin-to-skin care in neonates and room-temperature CO<sub>2</sub> monitoring as compared with clinical standard monitoring system operating at high temperature to substantially enhance the quality for futuristic applications.

**Keywords:** Stretchable sensor, single wall carbon nanotube, polyaniline, CO<sub>2</sub> sensor

皮膚からの CO<sub>2</sub> は体内代謝の状況を反映しており、その迅速かつ簡便な計測は健康管理に役立つだけでなく、現医療にも大いに必要とされている。しかし、大気中の CO<sub>2</sub> 濃度は 240 ppm 程度もあり、1ppm レベルの皮膚からの CO<sub>2</sub> 計測は極度に困難である。現在は電気化学センサを耳に取り付け加温して、炭酸イオンにして検出しているが、その検出感度は十分ではない。本研究では単層カーボンナノチューブ (SWCNT) にポリアニリンをコートし、ポリアニリンが水蒸気と CO<sub>2</sub> 共存下で、電気伝導体に転移することを利用して、超高感度 CO<sub>2</sub> センサを試作した。ポリアニリンをコートした SWCNT をマクロ細孔性 PDMS にドープして、迅速応答性を確保している。電気伝導度検出であるが、検出リミットは 70 ppb 程度であり、大気中でも選択的に検出可能である。このセンサ機能は可逆的である。センサ感度は PDMS にドープした状態で 60% ほど延ばすと、検出感度が 2 倍程度増加する。その場ラマン分光法によれば、CO<sub>2</sub> からの電荷移動が認められている。PDMS にポリアニリンをコートした SWCNT をドープしたセンサは捩じれや引っ張りに対する優れた機械的耐性を有する。

1) P. Ahuja, S. K. Ujjain, R. Kukobat, K. Urita, I. Moriguchi, A. Furuse, Y. Hattori, K. Fujimoto, K. Kaneko, *Chem. Eng. J.* **2023**, 457, 14126(1-12)

アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2024年3月20日(水) 13:00 ~ 15:30 会場 A1442(14号館 [4階] 1442)

**[A1442-3pm] 19. コロイド・界面化学**

座長：今岡 享稔、佐藤 良太

## ◆ 英語

13:00 ~ 13:20

[A1442-3pm-01]

Enhancing Photoluminescence of  $\text{Ag}_8\text{GeS}_6$  Quantum Dots through Controlled ZnS Shell Thickness for Near-IR *In Vivo* Bioimaging○Nurmanita Rismaningsih<sup>1</sup>, Junya Kubo<sup>1</sup>, Tatsuya Kameyama<sup>1</sup>, Norikazu Fujihira<sup>2</sup>, Hiroshi Yukawa<sup>1</sup>, Yoshinobu Baba<sup>1</sup>, Tsukasa Torimoto<sup>1</sup> (1. Graduate School of Engineering, Nagoya University, 2. Murata Manufacturing Co., Ltd.)

## ◆ 日本語

13:20 ~ 13:40

[A1442-3pm-02]

高分子コーティングをテンプレートした $\text{CeO}_2$ 粒子を用いた球状のコロイド結晶の作製及び評価○姜 楊楠<sup>1</sup>、竹岡 敬和<sup>1</sup>、大貫 良輔<sup>2</sup>、吉岡 伸也<sup>2</sup>、白井 綾野<sup>3</sup>、桑折 道済<sup>3</sup> (1. 名古屋大学大学院工学研究科、2. 東京理科大学創域理工学研究科、3. 千葉大学大学院工学研究院)

## ◆ 日本語

13:40 ~ 14:00

[A1442-3pm-03]

微粒子界面における核酸塩基光反応を利用した刺激応答性カプセルの合成

○北山 雄己哉<sup>1</sup>、堂阪 あかり<sup>1</sup>、芝 向日葵<sup>1</sup>、弓場 英司<sup>1</sup>、原田 敦史<sup>1</sup> (1. 阪公大)

14:00 ~ 14:10

休憩

## ◆ 日本語

14:10 ~ 14:30

[A1442-3pm-04]

裁断化ナノファイバーからなる新規異方性分散体の創製と凝集比濁用担体への応用

○横瀬 颯人<sup>1</sup>、市原 直弥、岡村 陽介<sup>1,2</sup> (1. 東海大院工、2. 東海大マイクロ・ナノ研)

## ◆ 日本語

14:30 ~ 14:50

[A1442-3pm-05]

無機ナノシートの自発的集合による超分子的ポリマーの作製と機能探索

上野 夏子<sup>1</sup>、海老名 保男<sup>2</sup>、佐々木 高義<sup>2</sup>、○佐野 航季<sup>1,3</sup> (1. 信州大、2. 物材機構、3. JSTさきがけ)

## ◆ 日本語

14:50 ~ 15:10

[A1442-3pm-06]

一次元ナノコロイドの配向・自己組織化による無機超分子ナノシート

○小川 大輔<sup>1</sup>、佐野 航季<sup>1,2</sup> (1. 信州大、2. JSTさきがけ)

## ◆ 日本語

15:10 ~ 15:30

[A1442-3pm-07]

コロイド結晶をモデルとしたエントロピー生成最大原理の実験的検証

○對馬 琴梨<sup>1</sup>、伴 貴彦<sup>2</sup>、並河 英紀<sup>3</sup> (1. 山大院理工、2. 阪大院理工、3. 山形大理)

---

## Enhancing Photoluminescence of $\text{Ag}_8\text{GeS}_6$ Quantum Dots through Controlled ZnS Shell Thickness for Near-IR *In Vivo* Bioimaging

(<sup>1</sup>Graduate School of Engineering, Nagoya University, <sup>2</sup>Murata Manufacturing Co., Ltd.)

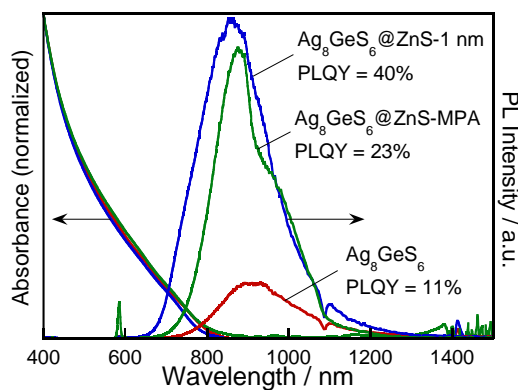
○Nurmanita Rismaningsih,<sup>1</sup> Junya Kubo,<sup>1</sup> Tatsuya Kameyama,<sup>1</sup> Norikazu Fujihira,<sup>2</sup> Hiroshi Yukawa,<sup>1</sup> Yoshinobu Baba,<sup>1</sup> and Tsukasa Torimoto<sup>1</sup>

**Keywords:** quantum dots, photoluminescence, I-IV-VI semiconductor, near-IR responsivity, bioimaging

Quantum dots (QDs) with unique photochemical properties are promising for near-IR LEDs and biomedical imaging. Binary II-VI and IV-VI QDs ( $\text{CdSe}$ ,  $\text{CdTe}$ ,  $\text{PbS}$ ) face practical use limitations due to their toxicity. In contrast, less toxic alternatives like  $\text{Ag}_2\text{ZnSnS}_4$ ,  $\text{Ag}_8\text{SnS}_6$ , and  $\text{Ag}_8\text{GeS}_6$  are gaining attention for their excellent properties, but few studies reported controlling their photochemical properties through the size quantization. This study reports the synthesis of  $\text{Ag}_8\text{GeS}_6$  QDs and the enhancement of their optical properties with a ZnS shell coating.

$\text{Ag}_8\text{GeS}_6$  QDs were synthesized through thermal decomposition of  $\text{Ge}(\text{gly})_2(\text{H}_2\text{O})_2$ ,  $\text{AgDDTC}$  and thiourea in a mixture solution of oleylamine and dodecane thiol. A ZnS shell layer was deposited on the QD surface. The ligand exchange of the QDs with 3-mercaptopropionic acid (MPA) enabled to uniformly disperse in an aqueous solution for the application to *in vivo* bioimaging.

The energy gap of  $\text{Ag}_8\text{GeS}_6$  QDs slightly decreased from 1.50 eV to 1.37 eV with an increase in the  $\text{Ge}/(\text{Ge}+\text{Ag})$  ratio of the precursor. TEM measurements revealed the formation of spherical  $\text{Ag}_8\text{GeS}_6$  QDs with an average size of 4.5 nm. The XRD pattern showed that the obtained QDs had an orthorhombic  $\text{Ag}_8\text{GeS}_6$  crystal structure. **Figure 1** shows PL spectra of  $\text{Ag}_8\text{GeS}_6$  QDs. The QDs with  $\text{Ge}/(\text{Ge}+\text{Ag}) = 0.82$  exhibited a PL peak at 920 nm with a PLQY of ca. 11%. Surface coating with ZnS shell of 1 nm in thickness remarkably enhanced the PL intensity: thus-obtained  $\text{Ag}_8\text{GeS}_6@\text{ZnS}$  QDs exhibited a PL peak at 910 nm with a PLQY of ca. 40%. The PL intensity decreased after ligand exchange with MPA slightly, but obtained MPA-modified QDs,  $\text{Ag}_8\text{GeS}_6@\text{ZnS-MPA}$ , maintained a relatively high QY, ca. 23%, which was higher than those for multinary QDs in aqueous solutions reported in our previous studies, 6.2% for  $\text{Ag-In-Ga-Se}$  and 19% for  $\text{Ag-In-Ga-S-Se}$  QDs<sup>[1,2]</sup>. The  $\text{Ag}_8\text{GeS}_6@\text{ZnS-MPA}$  QDs were successfully applied for *in vivo* bioimaging by injecting them into the back of mouse.



**Fig. 1.** Absorption and PL spectra of  $\text{Ag}_8\text{GeS}_6$  QDs,  $\text{Ag}_8\text{GeS}_6@\text{ZnS}$  QDs, and  $\text{Ag}_8\text{GeS}_6@\text{ZnS-MPA}$  QDs.

[1] T. Kameyama, *et al.*, *ACS Appl. Nano Mater.*, **3**, 3275-3287 (2020). [2] N. Rismaningsih, *et al.*, *J. Mater. Chem. C*, **9**, 12791-12801 (2021).

## 高分子コーティングをテンプレートした CeO<sub>2</sub> 粒子を用いた球状のコロイド結晶の作製及び評価

(名大院工<sup>1</sup>、理科大創域理工<sup>2</sup>、千葉大院工<sup>3</sup>) ○姜 楊楠<sup>1</sup>、竹岡 敬和<sup>1</sup>、大貫 良輔<sup>2</sup>、吉岡 伸也<sup>2</sup>、白井 綾乃<sup>3</sup>、桑折 道済<sup>3</sup>

Preparation and Evaluation of Spherical Colloidal Crystals Using CeO<sub>2</sub> Particles Templated by Polymer Coating (<sup>1</sup> Graduate School of Engineering Nagoya University, <sup>2</sup> Graduate School of Science and Technology, Tokyo University of Science, <sup>3</sup> Graduate School of Engineering, Chiba University) Kensuke Kiyokawa,<sup>1</sup> ○Yangnan Jiang<sup>1</sup>, Yukikazu Takeoka<sup>1</sup>, Ryosuke Ohnuki<sup>2</sup>, Shinya Yoshioka<sup>2</sup>, Ayano Shirai<sup>3</sup>, Michinari Kohri<sup>3</sup>

Using polydopamine (PDA), the surface of distorted CeO<sub>2</sub> core particles was coated and the surface gaps were filled. By using spherical CeO<sub>2</sub> particles, an emulsion of water-in-oil type was templated to create spherical colloidal crystals. It was found that the obtained spherical colloidal crystals have less angle dependence compared to spherical colloidal crystals made of silica particles. Furthermore, by sintering the polymer on the surface of the spherical colloidal crystals, it was discovered that the colloidal crystal structure is maintained even conditions without black materials.

**Keywords :** Structure color; Cerium oxide; Colloidal crystal; Coating; Angular dependence

本研究では、鮮やかな色相で角度依存性が抑えられた球状コロイド結晶（フォトニックボール）を作製するために、安全で屈折率が高い CeO<sub>2</sub> 粒子を用いた。しかし、CeO<sub>2</sub> 粒子は形状が真球ではなく、鮮やかな構造色を発現するのに必要な粒子の長距離秩序を有する配列性が悪いため、得られたフォトニックボールの光学特性低下の原因となっていた。そこで、CeO<sub>2</sub> 粒子を真球化するために、高分子であるポリドーパミン（PDA）のコーティング技術を参考にし、CeO<sub>2</sub>@PDA コアシェル粒子を合成した。その結果、CeO<sub>2</sub>@PDA 粒子が規則正しく配列したフォトニックボールを作製できた。得られたフォトニックボールは、SiO<sub>2</sub> 粒子からなるフォトニックボールより角度依存性が抑えられることがわかった。ただし、CeO<sub>2</sub> 粒子の表面に PDA が存在するために、CeO<sub>2</sub> 粒子のみの場合と比較すると、有効屈折率が低下する。そこで、作製したフォトニックボールを高温焼結し、PDA を取り除いたところ、PDA が無くとも、高い屈折率を有する CeO<sub>2</sub> 粒子がコロイド結晶の形状を保ち、鮮やかな構造発色性を示すことを発見した。

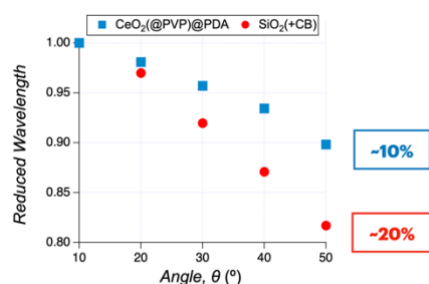


Fig.1 各フォトニックボールの角度依存性

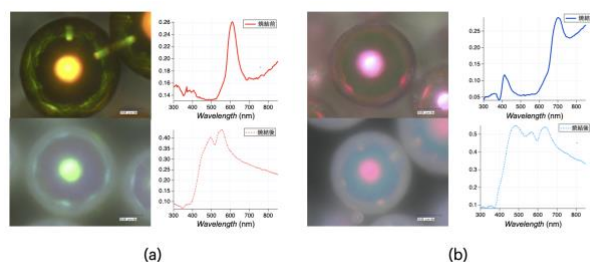


Fig.2 コア粒子CeO<sub>2</sub>の粒子径(a)184 nmと(b)200 nmの場合からなるフォトニックボールは焼結前後の光学特性の変化

- 1) Effect of the Polydopamine Composite Method on Structural Coloration: Comparison of Binary and Unary Assembly of Colloidal Particles. Iwasaki, T.; Harada, S.; Okoshi, T.; Moriya, M.; Kojima, T.; Kishikawa, K.; Kohri, M., *Langmuir* **2020**, 36 (40), 11880-11887.

## 微粒子界面における核酸塩基光反応を利用した刺激応答性カプセルの合成

(阪公大院工) ○北山 雄己哉・堂阪 あかり・芝 向日葵・弓場 英司・原田 敦史

Stimuli-Responsive Capsules Fabricated by Interfacial Photoreaction of Nucleobases

(<sup>1</sup> Department of Applied Chemistry, Graduate School of Engineering, Osaka Metropolitan University) Yukiya Kitayama, Akali Dosaka, Himari Shiba, Eiji Yuba, Atsushi Harada

Hollow and capsule polymer particles have a great potential for use in various applications such as coatings, microreactors, and drug delivery systems. The strategy of interfacial photocrosslinking of spherical polymer particles is promising for creating a wide range of functional hollow and capsule particles. Herein, polystyrene-based particles possessing nucleobases in polymer side chains were prepared and the nucleobase groups were applied to the interfacial photocrosslinking as photoreactive groups. Utilizing the interfacial photocrosslinking using nucleobase photodimerization, hollow and capsule particles were successfully prepared. Furthermore, we have demonstrated the pH-responsive release of the encapsulated molecule from the thymine-functionalized polymer capsules.

**Keywords :** Capsule particles; Interfacial photocrosslinking; Nucleobase; Polymer particles; Stimuli responsive

種々の機能性分子を封入したカプセル粒子は、蓄熱材やインキなどの産業で用いられるだけでなく、内包物の放出制御能を付与することでドラッグデリバリーシステムやマイクロリアクターなどへ応用が期待できる機能性微粒子材料として発展する。既報において、我々は光反応性側鎖をもつ高分子微粒子に対し、水分散状態で光照射を行うことで、微粒子界面近傍限定的に光二量化反応に基づく架橋反応が進行する現象（界面光架橋反応）を見出した。さらに、界面光架橋粒子から未架橋ポリマーを除去することにより、真球状高分子微粒子から中空高分子微粒子を直接調製できることを明らかにした[1,2]。

本研究では、生体分子の一種である核酸塩基を界面光架橋反応における光反応性部位および刺激応答性部位として利用した刺激応答性カプセル粒子の調製を試みた。具体的には、ピリミジン塩基である Thymine 構造を側鎖に有する高分子を合成し、この微粒子に対して界面光架橋反応による中空粒子の調製を試みた。さらに、内包物封入によるカプセル化と核酸塩基構造の pH 応答性を利用した内包物の制御放出能について評価した。

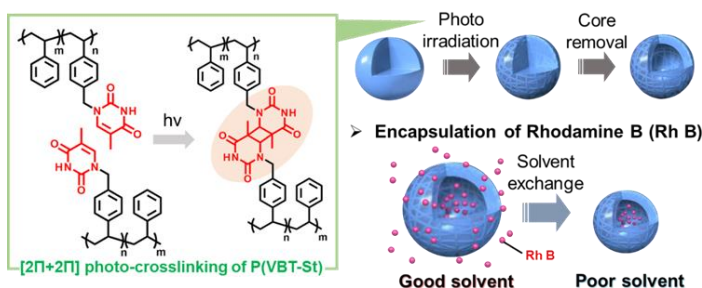


図1 微粒子界面における核酸塩基の二量化反応を利用した中空・カプセル粒子調製

1) Kitayama, Y.; Yoshikawa, K.; Takeuchi, T., *Langmuir* 2016, 32 (36), 9245-9253, 2).Kitayama, Y.; Harada, A., *ACS Appl. Mater. Interfaces* 2021, 13 (8), 10359-10375.

## 裁断化ナノファイバーからなる新規異方性分散体の創製と凝集比濁用担体への応用

(東海大院工<sup>1</sup>・東海大マイクロ・ナノ研<sup>2</sup>) ○横瀬 颯人<sup>1</sup>・市原 直弥<sup>1</sup>・岡村 陽介<sup>1,2</sup>  
Fabrication of Novel Anisotropic Dispersion Composed of Fragmented Nanofibers for Carriers of Turbidimetric Immunoassay. (<sup>1</sup>*Graduate School of Engineering, Tokai University,* <sup>2</sup>*Micro/Nano Technology Center, Tokai University*) ○ Hayato Yokose,<sup>1</sup> Naoya Ichihara,<sup>1</sup> Yosuke Okamura<sup>1,2</sup>

Polymeric particles with anisotropic shape express various unique properties. For example, disk-shaped anisotropic microparticles have been reported to have properties such as improved adhesion to interfaces, increased viscosity of dispersions, and enhanced aggregation reactions due to the plane shape they possess<sup>1)</sup>. We focused on polymer nanofibers, which have nanoscale in diameter, as a new anisotropic dispersion. In this study, we propose a fabrication procedure of fragmenting nanofibers as a novel carrier for the turbidimetric immunoassay.

Polystyrene nanofibers were prepared by electrospinning and fragmented using an ultra-high-speed homogenizer. Scanning electron microscopic observation revealed that the fragmented nanofibers possess a curved rod-like short fiber. Next, bovine serum albumin (BSA) was physically adsorbed on the surface of the nanofibers, and the amino group of BSA was used as a target for antibody modification by chemical cross-linking. The fragmented nanofibers were mixed with antigen solution in a microplate to induce specific aggregation by antigen-antibody reaction. The results showed that the fragmented nanofibers aggregated significantly in antigen concentration range of 10-fold lower and wider than microspheres with the same volume, and the antigen was detectable by visual inspection.

**Keywords:** *Polymeric nanofibers, Anisotropic nanomaterials, Aggregation and dispersion, Turbidimetric immunoassay*

高分子微粒子を異方性形状に加工すると、ユニークな特性が新たに発現する。例えば円盤状の異方性微粒子は、面を有する形状に起因して、界面への接着力の増大や分散液の粘性の上昇、凝集反応の促進などの特性が報告されている<sup>1)</sup>。我々は、新たな異方性微粒子の材料として、ナノレベルの直径を有した繊維材料である高分子ナノファイバーに着目した。本研究では、ナノファイバーを機械的に裁断することで、新規異方性微粒子を調製する方法を提案する。更に、その形状に由来する凝集特性を活かし、凝集比濁法の新たな担体としての応用を目指す。

電界紡糸法によってポリスチレンナノファイバーを調製し、超高速ホモジナイザーを用いて裁断した。裁断したナノファイバーは、電顕像より湾曲した棒状短繊維であることを確認した。次に、ナノファイバー表面にウシ血清アルブミン(BSA)を物理吸着させ、更に、BSAが持つアミノ基を標的として化学架橋にて抗体を修飾した。マイクロプレート内にて抗体結合裁断化ナノファイバーと抗原溶液を混合し、抗原抗体反応による特異的な凝集を惹起した。その結果、裁断化ナノファイバーは同体積の真球状微粒子と比較して、10倍程度低濃度かつ広い抗原濃度範囲にて著しく凝集し、目視判定にて抗原を検出可能であることを見出した。

1) Zhang H. *et al. ACS Appl. Polym. Mater.* 2, 3355-3364 (2020).

## 無機ナノシートの自発的集合による超分子的ポリマーの 作製と機能探索

(信州大繊維<sup>1</sup>・物材機構 MANA<sup>2</sup>・JST さきがけ<sup>3</sup>)

上野 夏子<sup>1</sup>・海老名 保男<sup>2</sup>・佐々木 高義<sup>2</sup>・○佐野 航季<sup>1,3</sup>

Development and function of supramolecular polymers by self-assembly of colloidal inorganic nanosheets

(<sup>1</sup>*Faculty of Textile Science and Technology, Shinshu University*, <sup>2</sup>*NIMS MANA*, <sup>3</sup>*JST PRESTO*)

Natsuko Ueno,<sup>1</sup> Yasuo Ebina,<sup>2</sup> Takayoshi Sasaki,<sup>2</sup> ○Koki Sano<sup>1,4</sup>

Supramolecular polymers are one-dimensionally self-assembled structures of monomers via non-covalent interactions, and they can be generally synthesized by using organic units. Here, we found that inorganic nanosheet monomers colloidally dispersed in water can one-dimensionally self-assemble in a face-to-face manner at room temperature to form a new type of supramolecular polymers by controlling the interaction between the nanosheets.

**Keywords :** *Inorganic nanosheet; 2D material; Self-assembly; Supramolecular polymer*

超分子ポリマーは、主に有機物のモノマーユニットが水素結合などの非共有結合的な相互作用によって自発的に集合した一次元状構造体である。モノマー同士が比較的弱い相互作用で結合していることから、優れたリサイクル性や自己修復性などの特性が期待される。従来の超分子ポリマーは概して、有機物ユニット間に働く相互作用によって形成されるが、もし、有機物ユニットに頼ることなく無機モノマー同士を精緻に結合することができれば、新しいタイプの超分子的ポリマーの創成に繋がるのが期待される。今回我々は、水に分散した無機ナノシート<sup>[1-6]</sup>を無機モノマーとして利用することで、無機物質のみからなる超分子的ポリマーの作成を目指した。

本研究では、無機モノマーとして、水中で負電荷を帯び、高いアスペクト比(厚さ: 0.75 nm、横サイズ: 数 μm)を有する酸化チタンナノシートを利用した。水に分散する酸化チタンナノシート間に働く相互作用を制御したところ、ナノシートは室温で一次的に自発集合し、超分子的ポリマーを形成した。種々の構造解析により、得られた超分子的ポリマーは無機ナノシートの方向も重心位置も揃っており、「従来のナノシートの液晶<sup>[1-6]</sup>」とは異なるナノシートの集合構造だということが示唆された。本発表では、構造解析の詳細や機能探索についても議論を行う予定である。

[1] T. Sasaki *et al.* *J. Am. Chem. Soc.* **118**, 8329–8335 (1996).

[2] K. Sano *et al.* *Nat. Commun.* **7**, 12559 (2016).

[3] K. Sano *et al.* *Angew. Chem. Int. Ed.* **57**, 12508–12513 (2018).

[4] K. Sano *et al.* *Nat. Commun.* **11**, 6026 (2020).

[5] K. Sano *et al.* *Nat. Commun.* **12**, 6771 (2021).

[6] Y.-Y. Zhan *et al.* *Angew. Chem. Int. Ed.* **62**, e202311451 (2023).



## 一次元ナノコロイドの配向・自己組織化による 無機超分子ナノシート

(信州大繊維<sup>1</sup>・JST さきがけ<sup>2</sup>)

○小川 大輔<sup>1</sup>・佐野 航季<sup>1,2</sup>

Inorganic supramolecular nanosheets self-assembled from spontaneously oriented 1D nanocolloids (<sup>1</sup>*Faculty of Textile Science and Technology, Shinshu University*, <sup>2</sup>*JST PRESTO*)

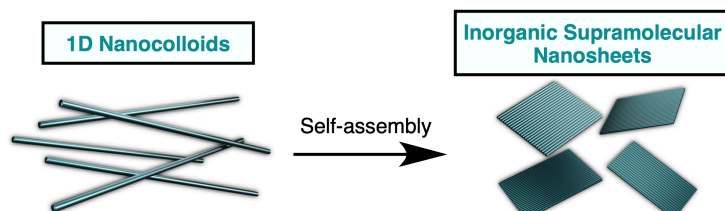
○Daisuke Ogawa,<sup>1</sup> Koki Sano<sup>1,2</sup>

Inorganic nanosheets find various applications due to their unique properties different from bulk materials. Generally, most inorganic nanosheets can be synthesized by the top-down approach such as exfoliation of layered materials. In contrast, the bottom-up approach by self-assembly of inorganic nanocolloids has recently attracted much attention because it enables the synthesis of highly designable nanosheets. Here, we report that novel inorganic supramolecular nanosheets can be self-assembled from spontaneously oriented one-dimensional nanocolloids.

**Keywords:** 1D nanocolloid; 2D material; Supramolecular nanosheet; Self-assembly

無機ナノシートは、バルク材料にはないユニークな物性を示すことから様々な分野への応用が期待されている。多くの無機ナノシートは、層状化合物の単層剥離に代表されるトップダウン的手法によって作製することができる<sup>[1]</sup>。これに対して近年、無機ナノコロイドの二次元状自己組織化による無機ナノシートのボトムアップ的な合成方法が報告されており、組成や形状を自在にデザインできる革新的手法として注目されている<sup>[2]</sup>。これまで、合成・制御が比較的容易な球状のナノコロイドがビルディングブロックとして主に利用されてきたが、もし、異方性ナノコロイドを利用できれば、無機ナノシートの設計戦略を拡張することが期待される。

今回我々は、正に帯電し高いアスペクト比を有した一次元ナノコロイドの水分散液を利用することで、無機超分子ナノシートを作製できることを見出した (Figure)。種々の顕微鏡観察の結果から、得られた無機超分子ナノシートは水中に安定に分散しており、一次元ナノコロイドが一軸配向を保ちながら二次元状に自己組織化した新しいタイプの無機ナノシートであることが明らかとなった。本発表では、構造解析、形成メカニズム、機能探索の詳細に関しても議論を行う予定である。



[1] T. Sasaki *et al.* *J. Am. Chem. Soc.* **118**, 8329–8335 (1996).

[2] W. Cheng *et al.* *J. Am. Chem. Soc.* **141**, 1725–1734 (2019).

## コロイド結晶をモデルとしたエントロピー生成最大原理の実験的検証

(山形大院理工<sup>1</sup>・阪大院基工<sup>2</sup>・山形大理<sup>3</sup>) ○對馬琴梨<sup>1</sup>・伴貴彦<sup>2</sup>・並河英紀<sup>3</sup>  
 Experimental Verification of the Maximum Entropy Production Principle Using Colloidal Crystals as a Model (<sup>1</sup>Graduate School of Science and Engineering, Yamagata University, <sup>2</sup>Graduate School of Engineering, Science, Osaka University, <sup>3</sup>Faculty of Science, Yamagata University) ○Kotori Tsushima<sup>1</sup>, Takahiko Ban<sup>2</sup>, Hideki Nabika<sup>3</sup>

Colloidal crystals (CC) undergo an entropy-driven structural transition, the Alder transition, which has a structure selection rule that depends on the volume fraction ( $\phi$ )<sup>1</sup>. However, the relationship between entropy and the Alder transition has not yet been experimentally verified. On the other hand, a  $\phi$ -dependent selection law has also been observed in  $\text{NH}_4\text{Cl}$  crystals and follows the "Maximum Entropy Production Principle: MEPP," which stipulates that the system spontaneously selects an organization that maximizes the entropy production rate  $\sigma$  of the system<sup>2</sup>. In this study, we clarify the correlation between the Alder transition and  $\sigma$ . A polystyrene colloidal dispersion with a particle size of 140 nm, which had been deionized for one month, was diluted with ultrapure water to a predetermined concentration, and the reflection spectra were measured in-situ. In this system, two types of CC were obtained, one is primary growth structure and the other is secondary growth structure. While the  $k$  of  $\text{NH}_4\text{Cl}$  varies linearly with  $\phi$ , it varies nonlinearly in CC (Fig. 1). This is because  $\text{NH}_4\text{Cl}$  crystallizes directly from solution, whereas CC changes to a face-centered cubic via a body-centered cubic. In the presentation, we will report the results of the analysis of  $\sigma$  based on  $k$  calculated from the approximation by the rate equation for sequential reactions.

**Keywords :** colloidal crystal, Maximum Entropy Production Principle, structural color

エントロピー最大化を駆動力とした構造転移である Alder 転移を誘起するコロイド結晶 (CC) には体積分率 $\phi$ に依存的な構造選択律がある<sup>1</sup>が、エントロピー生成と Alder 転移の相関性の実験的検証例は未だない。一方、 $\text{NH}_4\text{Cl}$  結晶でも $\phi$ 依存的な構造選択律が確認されており<sup>2</sup>、系のエントロピー生成速度 $\sigma$ が最大となる組織化を自発的に選択することを定めた「エントロピー生成速度最大原理」に従う。両者の類似性に基づき、本研究では CC の反射スペクトルの

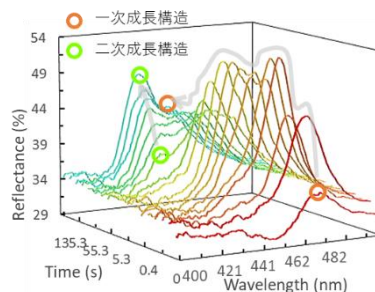


図 1.  $\phi = 0.029$  における反射スペクトルの経時変化.

in-situ 測定から結晶化速度定数  $k$  および  $\sigma$  を求め、Alder 転移と  $\sigma$  の相関を明らかにする。一ヶ月脱イオン化した粒径 140 nm のポリスチレンコロイド分散液を超純水で所定濃度へ希釈し、反射スペクトルの in-situ 測定を行った。本系では先に成長する一次成長構造と後から成長する二次成長構造の 2 つが共存した CC が得られた (図 1)。 $\text{NH}_4\text{Cl}$  の  $k$  が  $\phi$  に対し線形的に変化するのに対し、CC では非線形的に変化したが、これは  $\text{NH}_4\text{Cl}$  が溶液から直接結晶になるのに対し、CC は体心立方格子を経由して面心立方格子に変化する為であり、このような逐次反応を考慮した解析が必要である。発表では、逐次反応速度式による近似から算出した  $k$  に基づいた  $\sigma$  の解析結果を報告する。

1) Adrian, H., *NATURE*, **348**, 426-428 (1990) .2) Chiho. K. et al., *Int. J. Microgravity Sci.*, **32** (2) 320205 (2015).

アカデミックプログラム [B講演] | 20. 材料化学—基礎と応用：口頭B講演

📅 2024年3月20日(水) 9:00 ~ 11:30 📍 C443(4号館 [4階] 443)

**[C443-3am] 20. 材料化学—基礎と応用**

座長：竹谷 純一、齋藤 健一

## ◆ 日本語

9:00 ~ 9:20

[C443-3am-01]

難燃剤の組合せ効果解析法及びそれを用いた難燃性高分子設計法

○倉地 育夫<sup>1</sup> (1. 株式会社ケンシュウ)

## ◆ 英語

9:20 ~ 9:40

[C443-3am-02]

Establishment of a universal functional tuning strategy via homogeneous alkyl- $\pi$  liquid blending○Zhenfeng Guo<sup>1,2</sup>, Chengjun Pan<sup>3</sup>, Akira Shinohara<sup>2</sup>, Takashi Nakanishi<sup>1,2</sup> (1. Hokkaido University, 2. National Institute for Materials Science (NIMS), 3. Shenzhen University)

## ◆ 英語

9:40 ~ 10:00

[C443-3am-03]

プロトン共役電子移動を用いた有機半導体キャリア密度の精密制御

○石井 政輝<sup>1,2</sup>、山下 侑<sup>2,3</sup>、渡邊 峻一郎<sup>3</sup>、竹谷 純一<sup>2,3</sup>、有賀 克彦<sup>1,2,3</sup> (1. 東理大、2. 物材研究機構、3. 東大)

## ◆ 英語

10:00 ~ 10:20

[C443-3am-04]

Temporarily Controllable Dual-Emission from Gold(I)-NHC Complex with Flexible Alkoxy Chain.

○Arushi Rawat<sup>1</sup>, Siddhant Kumar<sup>1</sup>, Kohsuke Matsumoto<sup>1</sup>, Ganesan Prabusankar<sup>2</sup>, Osamu Tsutsumi<sup>1</sup> (1. Ritsumeikan University, 2. Indian Institute of Technology Hyderabad)

10:20 ~ 10:30

休憩

## ◆ 日本語

10:30 ~ 10:50

[C443-3am-05]

キラル側鎖を有するドナー・アクセプター連結分子の機能評価

○関 淳志<sup>1,2</sup>、土井 早雲<sup>2</sup>、青木 健一<sup>1,2</sup> (1. 東理大、2. 東理大院)

## ◆ 英語

10:50 ~ 11:10

[C443-3am-06]

色素ドーブ液晶の非線形分子配向変化：液晶分子構造に依存した高感度光応答

○横田 純輝<sup>1</sup>、相沢 美帆<sup>1,2</sup>、久野 恭平<sup>1</sup>、久保 祥一<sup>1</sup>、山口 留美子<sup>3</sup>、穴戸 厚<sup>1</sup> (1. 東工大化生研、2. JSTさきがけ、3. 秋田大院理工)

🇯🇵 日本語

11:10 ~ 11:30

[C443-3am-07]

SOFT法によるDonor-Acceptor型共役系ポリマーの配向膜作製：*in-situ*時間分解分光による配向ダイナミクス

○廣田 天丸<sup>1</sup>、坂田 俊樹<sup>2</sup>、齋藤 健一<sup>1,2,3</sup> (1. 広島大院先進理工、2. 広島大院理、3. 広島大自然セ)

---

## 難燃剤の組合せ効果解析法及びそれを用いた難燃性高分子設計法

((株)ケンシュー) 倉地育夫

Combination effect analysis method of flame retardants and flame retardant polymer design method using the same

(KENSYU &co.,Ltd) Yasuo Kurachi

*Considering the physical properties and economic efficiency of flammable polymer, it is desirable to reduce the amount of flame retardant used. For this purpose, when developing the effective combinations of flame retardants, statistical methods or methods of describing and evaluating flame retardant factors using mathematical models are used to evaluate the effectiveness. Multivariate analysis is useful when evaluating small amounts of data. Similarly, the Taguchi method is the most convenient because it can reveal the combination effect and at the same time determine the optimal conditions.*

*Keywords : flame retardant polymer, Combination effect analysis method, Multivariate analysis , Taguchi method*

可燃性高分子の物性や経済性を考慮すると難燃剤の使用量を少なくしたい。この目的で、減量効果を期待して添加剤の組み合わせによる難燃剤システムを開発する時に、その効果評価法には統計手法あるいは数理モデル、深層学習などデータサイエンスが使われる。1970年代から使用されてきた多変量解析は、少数のデータでも解析評価でき、その結果を基に材料設計までできるので便利である。

ChatGPTなど第3次AIブームとなり、老若男女誰でも容易に深層学習の手法を活用できる時代となった。ホスファゼン変性ポリウレタンフォーム<sup>1)</sup>の解析結果から導き出された、燃焼時の熱で無機高分子を生成し揮発しやすいオルソリン酸を効果的に活用できる組み合わせ難燃剤システム<sup>2)</sup>について多変量解析と深層学習の手法でどちらが材料設計に適しているか検討した。条件を揃えるために同一プログラムの中で同一データを用いて評価する手法で、線形性が期待される現象では多変量解析が優位という結果が出た。

一方、1990年代から普及が始まった数理モデルの1種タグチメソッドは、組み合わせ効果を明らかにすると同時に最適条件まで求めることができるので最も便利である。制御因子に組み合わせ効果を配置した実験計画の結果を一例として示す。

- 1) Y.Kurachi, T.Okuyama and T.Oohasi, "Synthesis and properties of urethane foams having a  $N_3P_3$  ring compound", J.Materials Science, 24, p2761 (1989)
- 2) 特開昭58-136615 (この手法から高分子前駆体を用いた高純度SiC製造法の基本特許 (特開昭60-220406) が生まれている。)

## Establishment of a universal functional tuning strategy via homogeneous alkyl- $\pi$ liquid blending

(<sup>1</sup>*Division of Soft Matter, Graduate School of Life Science, Hokkaido University*, <sup>2</sup>*Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS)*, <sup>3</sup>*Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University*) ○Zhenfeng Guo,<sup>1,2</sup> Chengjun Pan,<sup>3</sup> Akira Shinohara,<sup>2</sup> Takashi Nakanishi,<sup>1,2</sup> \*

**Keywords:** Alkyl- $\pi$  liquids; Homogeneous blending; Precise property control; Full-color fluorescence tuning; Rheology

Alkyl- $\pi$  functional molecular liquids (FMLs) refer to a class of room-temperature soft materials that have gained attention due to their distinctive properties and potential applications, such as electret devices for energy harvesters<sup>[1]</sup>. These materials feature a specific structure—a  $\pi$ -conjugated core surrounded by covalently attached, bulky yet flexible alkyl side chains. Despite the availability of conventional methods for tailoring their properties, such as specific chemical modifications and solid-liquid blending, these approaches face limitations<sup>[2]</sup>. Chemical modification is a meticulous and time-intensive procedure involving the synthesis of individual molecules. On the other hand, solid-liquid blending often results in uneven distribution and solid precipitation over time.

Our study adopted a homogeneous liquid blending approach for FMLs to overcome these challenges effectively. As depicted in Fig. 1, we focused on synthesizing bis-phenylene derivatives (**R**, **G**, and **B**). A series of blending experiments with varying ratios yield stable and miscible liquid blends at room temperature. The miscibility and homogeneity of these blends, which DSC cannot determine due to nearly identical glass transition temperatures, were verified by full-color fluorescence tuning and rheological analysis. In conclusion, we establish a universal methodology for controlling properties through the homogeneous blending of FMLs.

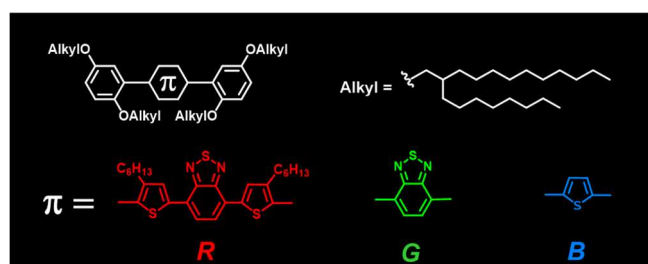


Fig.1 Chemical structure of alky- $\pi$  liquids **R**, **G**, and **B**.

1) R. K. Gupta, M. Yoshida, A. Saeki, Z. Guo, T. Nakanishi, *Mater. Horiz.*, **2023**, *10*, 3458-3466. 2) F. Lu, K. Hagiwara, M. Yoshizawa, K. Nagura, S. Ishihara, T. Nakanishi, *J. Mater. Chem. C*, **2019**, *7*, 2577-2582.

## Precise control of carrier densities in organic semiconductors through proton-coupled electron transfer

(<sup>1</sup>Graduate School of Science and Technology, Tokyo University of Science, <sup>2</sup>Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, <sup>3</sup> Graduate School of Frontier Sciences, The University of Tokyo) ○Masaki Ishii,<sup>1,2</sup> Yu Yamashita,<sup>2,3</sup> Shun Watanabe,<sup>3</sup> Jun Takeya,<sup>2,3</sup> Katsuhiko Ariga<sup>1,2,3</sup>

**Keywords:** organic semiconductor; chemical doping; proton-coupled electron transfer; control of carrier density; semicrystalline semiconducting polymer

Precise control of carrier densities in organic semiconductors (OSCs) is required to fabricate advanced electronic devices through chemical impurity doping, which is generally achieved by redox reaction between OSC and dopant molecules. However, control of doping levels at a thermal energy scale of 25 meV at RT has been challenging by choosing dopant with proper energy levels. In addition, conventional dopants are especially unstable in air because of their reactivity with water or oxygen, which further decreases the precision of the doping levels. Low precision in doping levels and the need for an inert environment have been bottlenecks in the development and manufacturing of advanced OSC devices.

In this study, doping levels of OSCs were controlled reproducibly and precisely under ambient conditions.<sup>1</sup> We demonstrated precise control of carrier densities in a spin-coated thin film of polymer semiconductor PBTTT via proton-coupled electron transfer (PCET) reaction (Fig. a). The employed PCET-type redox couple, BQ/HQ, shows a pH-controlled electrochemical potential with a slope of 59 meV/pH, which enables precise control of the doping levels (Fig. b). The BQ/HQ redox reactions and intercalation of hydrophobic anion TFSI<sup>-</sup> occur cooperatively to achieve chemical doping of the OSCs. Our method controls the doping level of OSCs with a high degree of precision within a few hundred meVs around the band edge, which will contribute to reliable and scalable device fabrication.

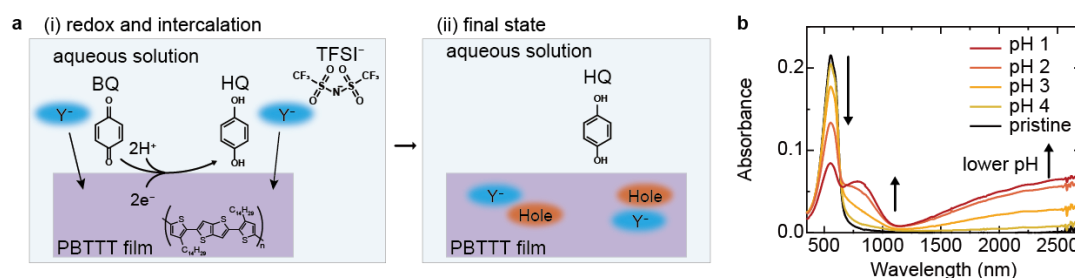


Figure (a) Schematic illustrations of our chemical doping method. (i) High proton concentration promotes oxidation of PBTTT through PCET reaction of BQ/HQ redox couple. Simultaneously, dopant anions get intercalated into the charged PBTTT. (ii) The final state of doping process. (b) UV-vis-NIR spectra of PBTTT thin films immersed into aqueous solutions with BQ/HQ and LiTFSI at pH 1-4.

1) M. Ishii, Y. Yamashita, S. Watanabe, K. Ariga, J. Takeya, *Nature* **2023**, 622, 285.

## Temporally Controllable Dual Emission from Gold(I)-NHC Complexes with Flexible Alkoxy Chain

(<sup>1</sup>Department of Applied Chemistry, Ritsumeikan University, <sup>2</sup>Department of Chemistry, Indian Institute of Technology Hyderabad) ○Arushi Rawat,<sup>1</sup> Kumar Siddhant,<sup>1</sup> Kohsuke Matsumoto,<sup>1</sup> Ganesan Prabusankar,<sup>2</sup> Osamu Tsutsumi<sup>1</sup>

**Keywords:** Aggregation-Induced Emission, Delayed Emission; Liquid Crystal; Room Temperature Phosphorescence.

Organic luminophores have been reported to show excellent luminescence in solution. However, the luminescence is quenched at higher concentrations, and in condensed phases, like crystal, due to Aggregation Caused Quenching (ACQ) effect prevalent in plethora of such organic luminophores. Because of ACQ effect, the application of these materials in optoelectronic devices is inhibited. In contrast to this quenching effect, Tang et al. reported enhanced luminescence in condensed phase for hexaphenylsilole molecule in 2001, and this effect is now commonly known as Aggregation Induced Emission (AIE) behavior.<sup>1</sup> This development paved way for the development of AIE-active materials among which gold (I) complexes have been recognized to show aurophilic interactions, and therefore enhanced luminescence and room temperature phosphorescence in solid phase, wherein luminescence can be controlled by controlling the aggregated structures.<sup>2</sup>

In the present work, we report a gold (I) complex with *N*-heterocyclic carbene (NHC) ligand bearing a flexible alkoxy chain. The photophysical properties of the material investigated in crystals revealed a unique dual luminescence behavior, showing blue emission under UV-irradiation and a green delayed luminescence. Apart from this, the complex was found to form distinct blue and green emissive crystals under different recrystallization conditions, implying the presence of polymorphic behavior.

- 1) J. Luo *et al.*, *Chem. Commun.* **2001**, *11*, 1740.
- 2) A. Sathyanarayana *et al.*, *Sci. China Chem.* **2018**, *61*, 957.

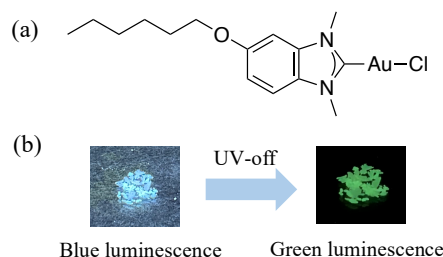


Figure 1 (a) Molecular structure of gold complex, (b) dual luminescence behavior in crystal.

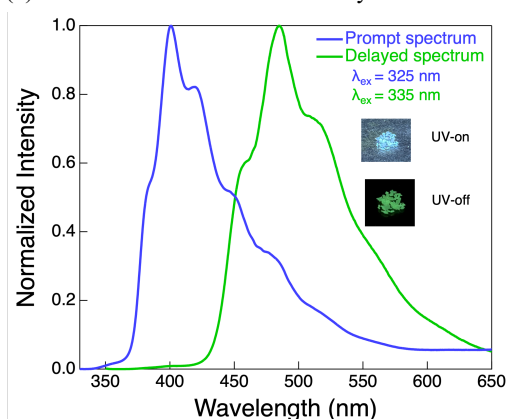


Figure 2. Prompt and delayed luminescence spectra of the complex in crystal.



## キラル側鎖を有するドナー・アクセプター連結分子の機能評価

(東理大<sup>1</sup>・東理大院<sup>2</sup>) ○関 淳志<sup>1,2</sup>・土井 早雲<sup>2</sup>・青木 健一<sup>1,2</sup>

Functional evaluation of donor-acceptor molecules bearing chiral side (<sup>1</sup>Tokyo University of Science, <sup>2</sup>Graduate School of Science, Tokyo University of Science) ○Atsushi Seki,<sup>1,2</sup> Sou-un Doi,<sup>2</sup> Ken'ichi Aoki<sup>1,2</sup>

Ferroelectric  $\pi$ -conjugated liquid crystals possibly exhibit a ferroelectric bulk photovoltaic effect (FPVE) in the polar aggregated states induced by the electrical poling treatment. The FPVE is a characteristic phenomenon which is different from conventional photovoltaic effect based on the p-n heterojunctions because the output voltage is independent of the bandgaps of the active materials. However, the open-circuit voltages and energy conversion efficiencies achieved thus far have been unsatisfactory. We are currently addressing the improvement of the output characteristics of FPVE. In this study, we focus on donor-acceptor molecules that cause intramolecular charge transfer so that the visible light absorption efficiency is improved. Several chiral  $\pi$ -conjugated compounds were synthesized and investigated their liquid crystallinity, absorption properties, and electrical functionalities.

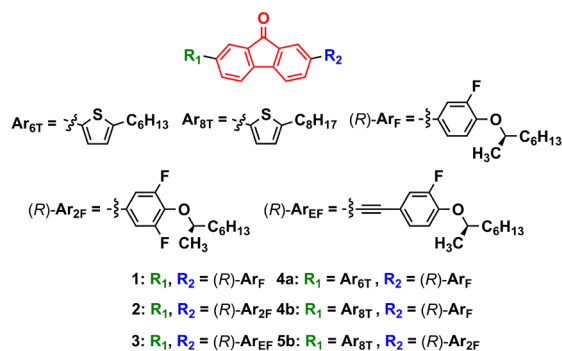
**Keywords :** Molecular Chirality; Donor-Acceptor Molecules, Intramolecular Charge Transfer; Bulk Photovoltaic Effects

強誘電性  $\pi$  共役液晶は、分極処理により形成される極性の液晶状態において、強誘電性バルク光起電力効果 (FPVE) を示す可能性を有する。FPVE の出力電圧は活物質のバンドギャップとは独立であり、FPVE は p-n ヘテロ接合に基づく従来の光起電力効果とは異なる特異な現象である。これまでに FPVE を示す強誘電性  $\pi$  共役液晶が報告されてきたが、

十分な出力特性を得るには至っていない<sup>[1,2]</sup>。このような背景から、我々は、現在、FPVE の出力特性の改善に取り組んでいる。本研究では、分子内電荷移動 (ICT) を生じ、可視光の吸収効率向上が期待できるドナー・アクセプター分子に注目した。複数のキラル  $\pi$  共役化合物 (Figure 1) を合成し、それらの機能について検討した。

合成した化合物はいずれもキラルスメクチック液晶相を発現した。各化合物の紫外可視吸収スペクトルでは、局所励起 (LE) 状態への電子遷移を示唆する紫外域の吸収に加えて、長波長側に ICT 由来のブロードな吸収帯が認められた。D-A 型芳香族部位をメソゲンコアに用いることで従来系よりも可視光に対する吸光感度が向上した。強誘電性も含めた物性の詳細は、当日、報告予定である。

[1] M. Funahashi, *Symmetry* **2021**, 13, No.672; [2] A. Seki et al. *Bull. Chem. Soc. Jpn.* **2023**, 96, 1224.



**Figure 1.** Chemical structures of chiral D-A type fluorenone derivatives.

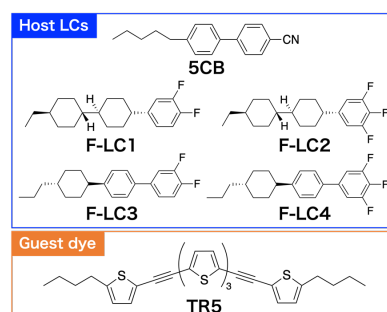
## Nonlinear Molecular Reorientation of Dye-doped Liquid Crystals: Highly Sensitive Optical Response Depending on Liquid Crystal Molecular Structures

(<sup>1</sup>Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, <sup>2</sup>PRESTO, JST, <sup>3</sup>Akita University) ○Junki Yokota,<sup>1</sup> Miho Aizawa,<sup>1,2</sup> Kyohei Hisano,<sup>1</sup> Shoichi Kubo,<sup>1</sup> Rumiko Yamaguchi,<sup>3</sup> Atsushi Shishido<sup>1</sup>

**Keywords:** Nonlinear Optical Effect; Liquid Crystal; Dye; Molecular Reorientation; Transmittance Change

Nonlinear optical materials whose optical properties depend on the incident light intensity have attracted much attention. Liquid crystals (LCs) exhibit large optical nonlinearity due to their high optical anisotropy in coincidence with molecular reorientation parallel to the polarization direction of the incident laser beam. Molecular reorientation occurs only by irradiation with a high-intensity beam above a certain threshold intensity; thus, it can be applied to optical switching and light dimming. We decreased the threshold intensity by adding oligothiophene dyes<sup>1-4</sup> and further reported enhancement of sensitivity by polymer stabilization<sup>1,2</sup> and the assistance of an electric field.<sup>4</sup> On the other hand, high-performance molecular design is a remaining challenge in dye-doped LCs, including elucidation of the molecular structure-property relationship. In this study, we investigated the effect of the host LC structures and physical properties on the molecular reorientation behavior.

The molecular structures of host LCs and a guest dye are shown in Figure 1. Host LCs were prepared by adding fluorinated LCs to 5CB with 25 mol% concentration. An oligothiophene dye was doped into the host LCs. Then, the mixtures were injected into glass cells whose surfaces had been treated with a homeotropic alignment layer. When a laser beam was incident on the cells, diffraction rings appeared based on the molecular reorientation, and transmittance decreased. The addition of F-LC2 or F-LC4 with three fluorine substituents to 5CB reduced the threshold light intensity of molecular reorientation. We found a positive relationship between the elastic constant ( $K_{33}$ ) value of the host LCs and the threshold intensity of molecular reorientation.<sup>5</sup>



**Figure 1.** Chemical structures of the sample used in this study.

1) Y. Aihara, A. Shishido, *et al.*, *Adv. Opt. Mater.* **2013**, *1*, 787. 2) K. Matsumoto, A. Shishido, *et al.*, *Mol. Cryst. Liq. Cryst.* **2020**, *713*, 46. 3) M. Yaegashi, T. Ikeda, *et al.*, *Chem. Mater.* **2005**, *17*, 4304. 4) K. Usui, A. Shishido, *et al.*, *ACS Appl. Mater. Interfaces* **2021**, *13*, 23049. 5) J. Yokota, A. Shishido, *et al.*, *Materials* **2022**, *15*, 4125.

## SOFT 法による Donor-Acceptor 型共役系ポリマーの配向膜作製： in-situ 時間分解分光による配向ダイナミクス

(広島大院先進理工<sup>1</sup>・広島大院理<sup>2</sup>・広島大自然セ<sup>3</sup>) 廣田 天丸<sup>1</sup>・○坂田 俊樹<sup>2</sup>・齋藤 健一<sup>1,3</sup>

Orientation Films of Donor-Acceptor Conjugated Polymer Prepared by SOFT Method: Orientation Dynamics by in-situ Time-Resolved Spectroscopy (<sup>1</sup>Graduate School of Advanced Science and Engineering, Hiroshima University, <sup>2</sup>Graduate School of Science, Hiroshima University, <sup>3</sup>Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University) ○Temmaru Hirota,<sup>1</sup> Toshiki Sakata,<sup>2</sup> Ken-ichi Saitow<sup>1,3</sup>

Orientations of conductive polymer have improved optoelectronic properties of polymer film. Recently, a new method to prepare an oriented film of conductive polymer, “SOFT”, was developed<sup>1)</sup>. In our previous study, an oriented film of a conjugated polymer, PFO composed of a monomer F8 unit (Fig.1a), was prepared by the SOFT method, and its orientation mechanism was investigated by in-situ time-resolved spectroscopy<sup>2)</sup>. However, the orientation mechanism of other conjugated polymers has not been understood so far.

In this study, we investigated the orientation and its dynamics of donor-acceptor (D-A) type conjugated polymer using in-situ time-resolved spectroscopy. The D-A type polymer of F8BT (Fig. 1b) we chosen had the same unit (i.e., F8 donor unit) to the PFO, which was no D-A type conjugated polymer. Thus, detail orientation mechanisms with or without D-A unit could be understood by comparing with each result. Details of the structural change and dynamics of the F8BT and PFO polymer chains before and after orientations will also be presented.

**Keywords :** *conjugated polymers; conductive polymers; orientation films; Raman spectroscopy*

導電性高分子は配向により光・電子物性が変化する。近年、新規な導電性高分子配向膜の作製法「SOFT 法」が開発された<sup>1)</sup>。これまでの研究で、単一のモノマーユニット(F8, 図 1 a)が重合した PFO の SOFT 法における詳細な配向ダイナミクスを報告してきた<sup>2)</sup>。しかし、他の系での配向の詳細なメカニズムは不明であった。

本研究では D-A 型導電性高分子である F8BT(図 1b) の SOFT 法における配向ダイナミクスや主鎖の構造変化等を in-situ 時間分解分光により明らかにした。この系は上述した先行研究の PFO に BT ユニットが加わっており、先行研究における配向度、配向ダイナミクスの結果と比べることにより、両者の配向メカニズムを比較検討できる。当日は配向前後における F8BT と PFO の主鎖の構造変化とそのダイナミクスの詳細を報告する。

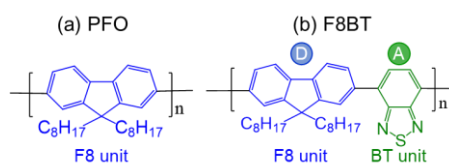


図 1 a) PFO と b) F8BT のモノマーユニットの構造

- 1) Cellulose-Templated Stable Foldable Oriented Films with Polarized RGB Luminescence. M. Takamatsu, T. Sakata, D. Kajiya, K. Saitow., *Chem. Mater.* **2022**, 34, 1052–1064.
- 2) Cellulose Templating for  $\pi$ -Conjugated Polymer Orientation: An In Situ Time-Resolved Spectroscopy Exploration. T. Sakata, T. Hirota, K. Saitow., *ACS Appl. Polym. Mater.* **2022**, 4, 8166–8179.

アカデミックプログラム [B 講演] | 20. 材料化学—基礎と応用：口頭B講演

2024年3月20日(水) 13:00 ~ 14:40 会場 C442(4号館 [4階] 442)

**[C442-3pm] 20. 材料化学—基礎と応用**

座長：深津 亜里紗、速水 真也

## ◆ 英語

13:00 ~ 13:20

[C442-3pm-01]

液晶性コロイド前駆体を用いた自立性酸化亜鉛材料のナノ構造制御

○三上 喬弘<sup>1</sup>、加藤 利喜<sup>1</sup>、細川 済弘<sup>1</sup>、宮元 展義<sup>2</sup>、加藤 隆史<sup>1</sup> (1. 東大院工、2. 福岡工大)

## ◆ 英語

13:20 ~ 13:40

[C442-3pm-02]

原グラフェン酸化物負荷三元過渡金属硫化物量子ドットとしての新規デュアルバンド電磁波吸収体

○Cai Ze<sup>1</sup>、真也 速水<sup>1</sup>、Md. Saidul Islam<sup>1</sup> (1. 熊本大学)

## ◆ 日本語

13:40 ~ 14:00

[C442-3pm-03]

対カチオン制御による温度応答性酸化グラフェンの作製とその転移温度制御

○近藤 翔麻<sup>1</sup>、西村 智貴<sup>1</sup>、仁科 勇太<sup>2</sup>、佐野 航季<sup>1,3</sup> (1. 信州大、2. 岡山大、3. JSTさきがけ)

## ◆ 英語

14:00 ~ 14:20

[C442-3pm-04]

機械刺激応答特性を示す発光性分子材料の結晶学および力学パラメーター

○平井 悠一<sup>1</sup>、中西 貴之<sup>1</sup>、武田 隆史<sup>1</sup>、大村 孝仁<sup>1</sup> (1. 物質・材料研究機構 (NIMS))

## ◆ 日本語

14:20 ~ 14:40

[C442-3pm-05]

天然由来DNAと各種金属イオンの特異的な相互作用により架橋された多機能性ハイドロゲルの構造解析

○深津 亜里紗<sup>1</sup>、栗栖 沙理<sup>2</sup>、倉本 七夏海<sup>1</sup>、吉田 和加<sup>1</sup>、安井 伊吹<sup>1</sup>、野村 佳澄<sup>2</sup>、藤原 照巳<sup>2</sup>、岡田 健司<sup>1</sup>、高橋 雅英<sup>1</sup> (1. 大阪公立大学、2. 大阪府立大学)

## Nanostructure Control in Free-Standing Zinc Oxide Materials Using Liquid-Crystalline Colloidal Precursors

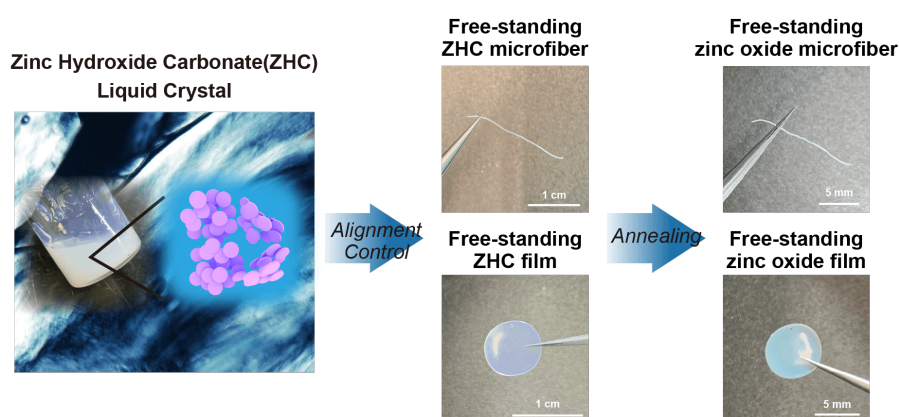
(<sup>1</sup>*School of Engineering, The University of Tokyo*, <sup>2</sup>*Fukuoka Institute of Technology*)

○Takahiro Mikami,<sup>1</sup> Riki Kato,<sup>1</sup> Yoshihiro Hosokawa,<sup>1</sup> Nobuyoshi Miyamoto,<sup>2</sup> Takashi Kato<sup>1</sup>

**Keywords:** Liquid Crystal; Self-Organization; Nanostructural Material; Zinc Oxide; Self-Assembly

Zinc Oxide (ZnO) based materials are utilized as varieties of functional inorganic materials such as photocatalysis and piezoelectric materials.<sup>1</sup> To synthesize ZnO materials with large scale orientation, physical vapor deposition methods such as sputtering and pulsed laser deposition are commonly utilized. These methods require expensive equipment and substrates such as seeded layers and pre-coated catalysts. Free-standing ZnO materials without substrates have great potential for functional materials such as piezoelectric devices and catalyst filters. However, the synthetic strategies for free-standing anisotropic materials that form oriented structures at large scales are still limited.

Herein, we report the selective synthesis of oriented free-standing ZnO materials with controlled morphologies using liquid-crystalline (LC) colloidal precursors.<sup>2</sup> LC zinc hydroxide carbonate (ZHC) nanoplates were prepared utilizing acidic synthetic macromolecules.<sup>3</sup> Alignment control of the LC ZHC nanoplates led to the formation of free-standing ZHC materials. Free-standing ZHC microfibers were formed by injecting LC colloidal dispersions into acetone solvent and drying them at room temperature. Sandwiching the LC ZHC nanoplates between fluorinated polymer sheets and subsequent drying them under ambient conditions resulted in the formation of free-standing ZHC films. Followed by subsequent annealing processes, free-standing ZnO materials were fabricated. Their crystallographic orientation and morphologies were maintained after the thermal treatment of ZHC materials.



1) S. A. Patil and M. Saxena *et al.*, *Small* **2023**, *19*, 2206063. 2) T. Mikami, R. Kato, N. Hosokawa, N. Miyamoto, T. Kato, *Small Methods* **2023**, 2300353. 3) M. Nakayama, S. Kajiyama, A. Kumamoto, T. Nishimura, Y. Ikuhara, M. Yamato, T. Kato, *Nat. Commun.* **2018**, *9*, 568.

## Reduced Graphene Oxide-Loaded Ternary Transition Metal Sulfide Quantum Dots as a Novel Dual-Band Electromagnetic Wave Absorber

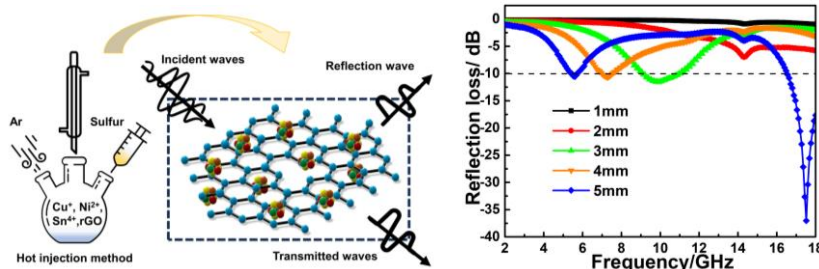
(<sup>1</sup>Graduate School of Science and Technology, Kumamoto University) ○Ze Cai,<sup>1</sup> Hayami Shinya,<sup>1</sup> Md. Saidul Islam<sup>1</sup>

**Keywords:** Ternary Transition Metal Sulfide; electromagnetic wave absorption; Quantum Dots; interface polarization; Hot injection method.

In our study, we have explored the application of the hot injection technique to grow high-purity ternary transition metal sulfide quantum dots (TTMSQDs) on the surface of graphene for the synthesis of an electromagnetic wave absorption material (EAM) capable of simultaneously absorbing electromagnetic waves in non-adjacent frequency bands. Therefore, in the current work, we have investigated a quaternary chalcogenide composite consisting of  $\text{Cu}_2\text{NiSnS}_4$  (CNTS), incorporating three transition metal atoms and sulfur atoms to enhance electromagnetic absorption (EMA).

Moreover, the hybridization of CNTS with reduced graphene oxide (rGO) is expected to induce interfacial polarization, enhancing the composite's capability for efficient absorption across dual frequency bands and extending the absorption range to include the C-band region.<sup>1,2</sup> We employed a hot injection method to achieve a uniform distribution of CNTS nanoparticles on the surface of rGO. The CNTS/rGO hybrid was systematically characterized using material dielectric loss and magnetic loss parameters to elucidate this distinctive electromagnetic wave absorption phenomenon.

Remarkably, the CNTS/rGO (50%) composite with a thickness of 5 mm demonstrates outstanding electromagnetic wave absorption properties across dual frequency bands, exhibiting an optimal absorption loss of -38.2 dB at 17.1 GHz and a broad absorption peak of -10.4 dB at 5.6 GHz. This achievement realizes simultaneous absorption of electromagnetic waves in the C and Ku frequency bands, representing non-adjacent frequency bands.



1) Cui Y, *Journal of Materials Chemistry*. **2012**;22(43):23136-40. 2) Chen, H.J., *Materials Letters*, **2016**, 166, 215-218.



## 対カチオン制御による温度応答性酸化グラフェンの作製とその転移温度制御

(信州大繊維<sup>1</sup>・岡山大 RCIS<sup>2</sup>・JST さきがけ<sup>3</sup>)

○近藤 翔麻<sup>1</sup>・西村 智貴<sup>1</sup>・仁科 勇太<sup>2</sup>・佐野 航季<sup>1,3</sup>

Synthesis of thermoresponsive graphene oxides and control of their transition temperature by tuning their counteranions (<sup>1</sup>Faculty of Textile Science and Technology, Shinshu University, <sup>2</sup>RCIS, Okayama University <sup>3</sup>JST PRESTO)

○Shoma Kondo,<sup>1</sup> Tomoki Nishimura,<sup>1</sup> Yuta Nishina,<sup>2</sup> Koki Sano<sup>1,3</sup>

Graphene oxides (GO) have attracted attention in various fields owing to their outstanding properties. Especially, thermoresponsive GO nanosheets are expected to serve as promising building blocks for the construction of smart materials. However, the strategy for their synthesis has been limited to the modification of GO surfaces with thermoresponsive polymers. Here, we succeeded in giving a thermoresponsive capability to GO themselves just by replacing their counteranions with specific cations. Additionally, we achieved to precisely control the transition temperature by mixing of some kinds of counteranions.

*Keywords: Graphene oxide; Sol-gel transition; Hydrogel; Self-assembly; Thermoresponsiveness*

酸化グラフェン (Graphene Oxide; GO) はグラファイトを酸化・剥離して得られる二次元ナノシートであり、優れた特性を有することから多様な分野での応用が期待されている<sup>[1]</sup>。特に、温度応答性を示す GO はスマートマテリアル構築のための有用なビルディングブロックであるが、GO に温度応答性を付与するためには従来、poly(*N*-isopropylacrylamide) のような温度応答性高分子を GO 表面に修飾する必要があった。この手法に対して我々は、今まで利用されてこなかった GO 表面の対カチオンに着目し、「GO 表面の対カチオン制御」を行うことで、温度応答性高分子を利用せずに GO 自体に温度応答性を付与することに成功している<sup>[2]</sup>。今回我々は、複数種類の対カチオンを利用することによって、温度応答性 GO の転移温度の制御を目指した。

本研究では、二段階の反応によって様々な種類の対カチオンを有する GO を作製し、その水分散液の温度応答挙動を精査した。その結果、特定の種類の対カチオンを有する GO が温度応答性を示し、その水分散液は可逆的なゾル-ゲル転移を示すことを見出した。さらに、異なる相転移温度を示す GO を混合し、その比率を制御することで、転移温度の精密制御が可能であることも明らかになった。本発表では、詳細な構造解析や形成メカニズムなどについても議論を行う予定である。

[1] N. Morimoto *et al.* *Chem. Mater.* **29**, 2150 (2017).

[2] S. Kondo *et al.* *ACS Appl. Mater. Interfaces*, **15**, 37837 (2023).

## Crystallographic and mechanical parameters of mechanically responsive luminescent molecular materials

(<sup>1</sup>*National Institute for Materials Science (NIMS)*) ○Yuichi Hirai<sup>1</sup>, Takayuki Nakanishi<sup>1</sup>, Takashi Takeda<sup>1</sup>, Takahito Ohmura<sup>1</sup>

**Keywords:** Solid mechanics; Stimuli-responsive luminescence; Mechanoluminescence; Molecular material; Crystal structure

Mechanically responsive luminescence of molecular materials (*i.e.* mechanochromic luminescence: MCL, mechanoluminescence: ML) has garnered considerable attention owing to its potential applications in sensors to visualise the location/magnitude of the stress and information encryption systems for anticounterfeiting technologies.<sup>[1]</sup> Since one of the primary drivers of those mechanical sensitivity is the reversible breaking and formation of non-covalent interactions,<sup>[2]</sup> understanding the fundamental principles and elucidating structure–property relationships are crucial for designing and optimising materials with tailored sensing behaviour.

To investigate these relationships, we focused on a family of pyrene-derived carboxamides with alkylsilyl groups due to their reported monomer-like purple fluorescence in solid state with half-stacking motifs, which allows fluorescence modification by increasing or decreasing the effective  $\pi$ -orbitals overlaps.<sup>[3]</sup> We studied the fluorescence responsivity including the spontaneous recovery process from a broad perspective using crystallography (cell dimensions and interactions), spectroscopy (shifts in intensities and wavelengths), and nanomechanics (Young's moduli and hardness) to guide the design and development of novel materials with enhanced MFC properties.

[1] a) K. Muthamma, D. Sunil, P. Shetty, *Mater. Today Chem.* **2020**, *18*, 100361. b) Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605–610. [2] a) Y. Sagara, H. Traeger, J. Li, Y. Okado, S. Schrettl, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2021**, *143*, 5519–5525. b) H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 10044–10045. [3] A. Wrona-Piotrowicz, M. Ciechańska, J. Zakrzewski, R. Métivier, A. Brosseau, A. Makal, *Dye. Pigment.* **2016**, *125*, 331–338.



## 天然由来 DNA と各種金属イオンの特異的な相互作用により架橋された多機能性ハイドロゲルの構造解析

(阪公大院工<sup>1</sup>・阪府大院工<sup>2</sup>) ○深津 亜里紗<sup>1</sup>・栗栖 沙理<sup>2</sup>・倉本 七夏海<sup>1</sup>・吉田 和加<sup>1</sup>・安井 伊吹<sup>1</sup>・野村 佳澄<sup>2</sup>・藤原 照巳<sup>2</sup>・岡田 健司<sup>1</sup>・高橋 雅英<sup>1</sup>  
 Structural Analysis of Multifunctional Hydrogels Crosslinked by Unique Interactions of Naturally Occurring DNA and Various Metal Ions (<sup>1</sup>Graduate School of Engineering, Osaka Metropolitan University, <sup>2</sup>Graduate School of Engineering, Osaka Prefecture University)  
 ○Arisa Fukatsu,<sup>1</sup> Sari Kurisu,<sup>2</sup> Nanami Kuramoto,<sup>1</sup> Waka Yoshida,<sup>1</sup> Ibuki Yasui,<sup>1</sup> Kasumi Nomura<sup>2</sup>, Terumi Fujiwara<sup>2</sup>, Kenji Okada,<sup>1</sup> Masahide Takahashi<sup>1</sup>

DNA, which can be extracted from biomass, is an environmentally friendly, biodegradable polymer with diverse functional groups. In addition, various functional groups in DNA form specific coordinate bonds and other interactions with various metal ions, which can be used as crosslinkers for hydrogels. In this study, hydrogels crosslinked by the interaction of DNA derived from salmon milt and various metal ions were prepared, and their structural analysis and functionalities derived from their structural properties were evaluated.

**Keywords :** DNA; Hydrogel; Biomass; Organic-Inorganic Hybrid; Coordination Bond

バイオマスから取得可能な DNA は、資源の供給と廃棄物の環境負荷の両面で環境親和性が高い生体由来材料として近年注目されている。また、DNA は様々な官能基から構成されており、多様な金属イオンと特異的に配位結合等の相互作用を示す。その一例として、白金(II)イオンは DNA 塩基のグアニン、アデニンと配位結合を形成することが知られている (Fig. 1)。このような DNA と種々の金属イオンとの相互作用をハイドロゲルの架橋点として利用することで、ハイドロゲルの物性を制御することが可能となり、様々な機能を有するハイドロゲルを作製できることを報告してきた。本研究では、サケ白子由来の DNA と種々の金属イオンとの相互作用により架橋されたハイドロゲルの構造解析およびその構造的性質に由来する機能性の評価を行った。白金(II)イオンを用いて作製したハイドロゲルを真空乾燥し、赤外吸収測定を行ったところ、DNA のグアニンやアデニン由来のピークが低波数側にシフトしたため、グアニンやアデニンと白金(II)イオンが相互作用していることが示された。一方、銅(II)イオンを用いて作製したハイドロゲルにおいては、DNA のリン酸由来のピークが低波数側にシフトしたため、銅(II)イオンは DNA の外側に位置するリン酸と相互作用していることが示された。また、構成金属種に由来する架橋構造の違いにより、ハイドロゲルが異なる物性を有することが示された。

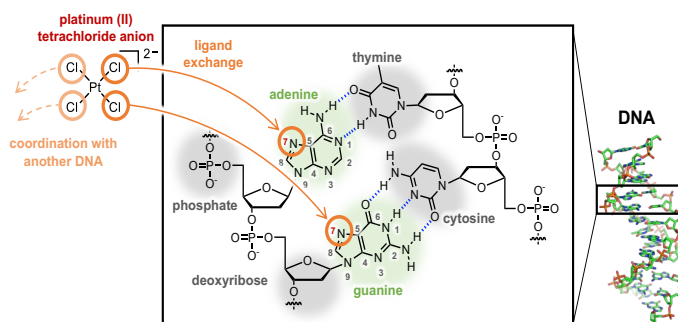


Fig. 1. Interaction of DNA and a platinum(II) ion.

アカデミックプログラム [B 講演] | 20. 材料化学—基礎と応用：口頭B 講演

2024年3月20日(水) 15:55 ~ 16:55 C443(4号館 [4階] 443)

**[C443-3vn] 20. 材料化学—基礎と応用**

座長：巢山 慶太郎、立石 友紀

## ◆ 日本語

15:55 ~ 16:15

[C443-3vn-01]

MOP-酵素複合体の高機能化に向けた混合タンパク質アプローチ

○神崎 友理<sup>1</sup>、南 良友<sup>1</sup>、ルウェ バンジャマン<sup>1</sup>、大場 正昭<sup>1</sup> (1. 九州大学)

## ◆ 英語

16:15 ~ 16:35

[C443-3vn-02]

刺激応答性粒状ゲルを利用した4Dバイオプリンティング

○中村 圭佑<sup>1</sup>、Nikolas Di Caprio<sup>1</sup>、Jason Burdick<sup>1</sup> (1. コロラド大学ボルダー校)

## ◆ 英語

16:35 ~ 16:55

[C443-3vn-03]

短鎖エラスチン様ペプチド(FPGVG)<sub>n</sub>-アゾベンゼン複合体の光照射による自己集合能の制御○巢山 慶太郎<sup>1</sup>、前田 衣織<sup>2</sup>、野瀬 健<sup>1</sup> (1. 九州大学基幹教育院、2. 九州工業大学情報工学研究院)

## MOP-酵素複合体の高機能化に向けた混合タンパク質アプローチ

(九大院理<sup>1)</sup> ○神崎 友理<sup>1</sup>・南 良友<sup>1</sup>・ルウェ バンジャマン<sup>1</sup>・大場 正昭<sup>1</sup>  
Mixed Protein Approach for High Functionalization of MOP-Enzyme Composites (<sup>1</sup>*Graduate School of Science, Kyushu University*) ○Yuri Kanzaki,<sup>1</sup> Ryosuke Minami,<sup>1</sup> Benjamin Le Ouay,<sup>1</sup> Masaaki Ohba<sup>1</sup>

We have developed an enzyme-immobilization method to construct assemblies with enzymes using cage-shaped metal complexes called MOPs as porous spacers.<sup>1</sup> Currently, however, the method requires a precise control of the MOP-to-enzyme ratio to obtain precipitates, and has thus a limited versatility. Therefore, we developed a mixed protein approach in which a feeder protein constitutes the bulk of the MOP-protein network and another enzyme is added as an active catalyst, at a controllable concentration. Assembling condition of water-soluble Rh(II)-based MOPs with ionic groups and enzyme with feeder proteins, BSA or lysozyme, was optimized. Substitution of part (2 to 20 w%) of the feeder protein by three different types of enzymes led to the easy and systematic synthesis of catalytically active composites with well-controlled content of enzyme.

**Keywords :** Immobilization; Enzyme; Metal Organic Polyhedra; Composite; Catalyst

酵素は環境に優しい触媒として注目されている。しかし、遊離酵素は水溶性であるために工業的応用が難しく、酵素のリサイクル性や過酷な条件下での安定性の向上を目指して、酵素の固定化法が開発されてきた。当研究室では、MOP と呼ばれるカゴ状の金属錯体を多孔性スパーサーとして酵素と集積化する新しい酵素固定化法を開発してきた<sup>1</sup>。しかし、この方法では沈殿物を得るために MOP と酵素の比率を精密に制御する必要があり、汎用性に限界があった。そこで、MOP-酵素ネットワークの大部分をタンパク質で置き換えて構成し、活性触媒としての酵素を制御可能な濃度で添加する「混合タンパク質アプローチ」による酵素固定化法を開発した。(図 1)

イオン性基を持つ水溶性 Rh(II) ベース MOP と酵素、および入手しやすいタンパク質 (BSA または lysozyme) との集積化条件を最適化した。タンパク質の一部 (2~20 w%) を 3 種類の酵素で置換することにより、酵素の含有量を十分に制御した触媒活性な複合体を容易かつ系統的に合成できた。さらに、固体材料中の体積酵素濃度の影響を調べたところ、酵素濃度が低いほど基質が移動し易くなる傾向が確認された。

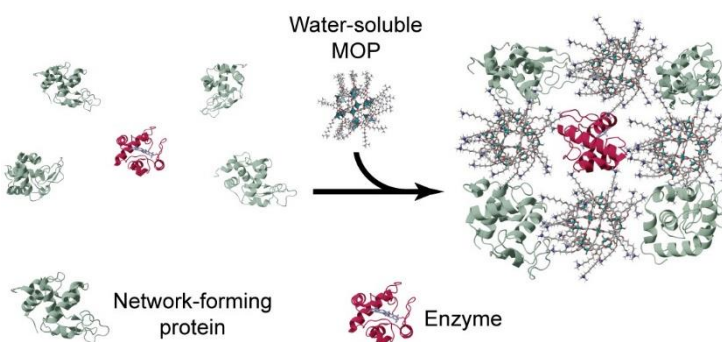


図 1 複合体形成の概要

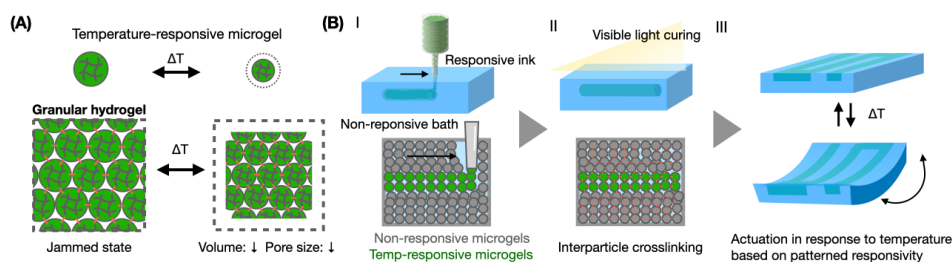
1) B. Le Ouay, M. Ohba et al., *J. Am. Chem. Soc.* **2023**, 145, 11997.

## Suspension 4D bioprinting of stimuli-responsive dynamic granular hydrogels

(<sup>1</sup>BioFrontiers Institute and Department of Chemical and Biological Engineering, University of Colorado Boulder; <sup>2</sup>Department of Bioengineering, University of Pennsylvania) ○Keisuke Nakamura,<sup>1</sup> Nikolas Di Caprio,<sup>1,2</sup> Jason A. Burdick<sup>1,2</sup>

**Keywords:** 4D printing; granular hydrogel; temperature-response; porous material

4D bioprinting is an emerging technology to fabricate dynamic cellular constructs that can change their shape and properties by external stimuli (e.g., temperature). 4D bioprinted materials are applicable to cell delivery, implants, and soft robotics; however, despite the potential, there have been limited printing approaches to fabricate multi-material structures with programmed shape changes. There are two major challenges to 4D printing: (i) designing bioinks with good responsivity, printability, and cytocompatibility; and (ii) developing printing methods to fabricate complex multi-material structures. Granular hydrogels, comprised of jammed microgels, are promising as 3D printable materials due to their shear-thinning and self-healing properties, as well as unique micropore structures that facilitate cell growth. The focus of this work was to introduce the 4<sup>th</sup> dimension into 3D printed granular hydrogels, specifically by fabricating microgels that are either non-responsive or include stimuli responsiveness (e.g., volume transitions), and then 3D printing multi-material constructs of these microgels that exhibit dynamic macroscopic and micropore structures based on temperature (Figure A). To accomplish this, we implemented a novel extrusion-based printing technique, where non-responsive granular hydrogels serve as suspension baths to receive the stimuli-responsive granular hydrogel inks, followed by interparticle crosslinking to create multi-material objects that actuate in response to temperature based on patterned responsivity (Figure B). Microgels were fabricated from norbornene-modified hyaluronic acid and crosslinked with either stable dithiothreitol or temperature-responsive dithiol-terminated poly-N-isopropylamide and patterned into granular hydrogels with suspension printing. A uniform temperature-responsive granular hydrogel postcrosslinked with light exhibited a decrease in pore sizes and macroscopic diameter when heated. 3D printing conditions for granular hydrogel inks were optimized by varying extrusion speeds and needle sizes. Multi-material granular hydrogels were then achieved with the suspension bath approach and postcrosslinking and the dynamic macroscopic behaviors of the printed materials were studied (e.g., bending or twisting based on pattern).



## Regulation of self-assembly ability of short-chain elastin-like peptide (FPGVG)<sub>n</sub>-azobenzene conjugates by light irradiation

(<sup>1</sup> Faculty of Arts and Science, Kyushu University, <sup>2</sup> Department of Physics and Information Technology, Department of Chemistry, Faculty and Graduate School of Science, Kyushu University) ○Keitaro Suyama,<sup>1</sup> Iori Maeda,<sup>2</sup> Takeru Nose<sup>1,3</sup>

**Keywords:** Elastin-like peptide; Azobenzenes; Self-assembly; Temperature-responsive molecules; Photo-responsive molecules

Elastin-like peptides (ELPs) are peptides that are artificially synthesized by mimicking the characteristic repetitive sequences of elastin. ELPs consist of characteristic repetitive sequences of amino acids, such as Val-Pro-Gly-Val-Gly (VPGVG), and exhibit temperature-dependent reversible self-assembly in solution. Previously, we developed ELPs composed of the (FPGVG) sequence,<sup>1</sup> which exhibited a strong self-aggregation ability even with short chain lengths. Owing to their excellent biocompatibility, ELPs have been utilized to develop temperature-responsive biomaterials for drug delivery. However, controlling the drug release remains challenging when such ELPs are used as drug carriers; although temperature control is required for rapid drug release from ELP coacervates, it is not always feasible to cool the affected area during treatment. To address this issue, we aimed to develop ELP analogs that could undergo controlled drug release by light irradiation in addition to temperature changes.

In this study, temperature- and photoresponsive ELP analogs were synthesized by conjugating azobenzene, the most widely used class of photoswitch, with short ELP analogs for the photocontrol of various biomolecules. Upon irradiation with UV or visible light, azobenzene can be mutually converted into *cis* and *trans* isomers. Several azobenzene-conjugated ELP analogs were synthesized by introducing (FPGVG)<sub>2</sub> to both benzene rings of azobenzene. The absorption spectra of the obtained azobenzene-conjugated ELP analogs showed strong absorption band at approximately 330–350 nm, which decreased in intensity upon irradiation with corresponding wavelength of light. These results, along with UPLC analyses, suggested that the synthesized ELP analogs could be isomerized from the *trans*-rich to the *cis*-rich state by light irradiation. From turbidimetry measurements performed before and after UV light irradiation, the self-assembly ability of ELP analogs in the *cis*-rich state was reduced compared to the *trans*-rich state. In addition, microscopic observation revealed that the synthesized ELP-azobenzene complex forms spherical aggregates in PBS solution above the phase transition temperature, which were redissolved upon irradiation with UV light. These results suggested that the azobenzene-conjugated ELP analogs could be applicable as temperature- and light-responsive drug carrier.

1) I. Maeda, I., S. Taniguchi, N. Watanabe, A. Inoue, Y. Yamasaki, T. Nose, *Protein Pept. Lett.* **2015**, 22, 934.

アカデミックプログラム [B講演] | 21. エネルギーとその関連化学, 地球・宇宙化学: 口頭B講演

2024年3月20日(水) 13:00 ~ 15:10 会場 A1454(14号館 [5階] 1454)

**[A1454-3pm] 21. エネルギーとその関連化学, 地球・宇宙化学**

座長: 栄長 泰明、神谷 和秀

## ◆ 日本語

13:00 ~ 13:20

[A1454-3pm-01]

重アルカリ金属を用いた金属空気電池の正極反応

○多々良 涼一<sup>1</sup>、藤本 竜成<sup>1</sup>、五十嵐 大輔<sup>1</sup>、保坂 知宙<sup>1</sup>、駒場 慎一<sup>1</sup> (1. 東京理科大学)

## ◆ 日本語

13:20 ~ 13:40

[A1454-3pm-02]

CO<sub>2</sub>を活物質としたレドックスフロー電池の開発○兼賀 量一<sup>1</sup>、山本 旭<sup>2</sup>、吉田 寿雄<sup>2</sup>、大平 昭博<sup>1</sup> (1. 産業技術総合研究所、2. 京都大学大学院人間・環境学研究科)

## ◆ 日本語

13:40 ~ 14:00

[A1454-3pm-03]

テトラチアフルバレンを基盤とする金属有機構造体の電子貯蔵性能

○若松 勝洋<sup>1</sup>、古野 壮一郎<sup>1</sup>、吉川 浩史<sup>1</sup> (1. 関西学院大学)

14:00 ~ 14:10

休憩

## ◆ 英語

14:10 ~ 14:30

[A1454-3pm-04]

炭酸緩衝液由来CO<sub>2</sub>の電解還元によるマルチカーボン化合物の高速・高選択合成○井上 明哲<sup>1</sup>、原田 隆史<sup>1</sup>、中西 周次<sup>1</sup>、神谷 和秀<sup>1</sup> (1. 阪大院基礎工太陽エネ研)

## ◆ 日本語

14:30 ~ 14:50

[A1454-3pm-05]

ダイヤモンド電極によるCO<sub>2</sub>の電解還元におけるファインバブルの影響○富崎 真衣<sup>1</sup>、櫻井 大斗<sup>2</sup>、間瀬 暢之<sup>2</sup>、栄長 泰明<sup>3</sup> (1. 九大I2CNER、2. 静大、3. 慶大理工)

## ◆ 日本語

14:50 ~ 15:10

[A1454-3pm-06]

10 mV/K級の熱起電力を発現する熱電キャパシタ

○堀家 匠平<sup>1,2</sup>、衛 慶碩<sup>2</sup>、桐原 和大<sup>2</sup>、向田 雅一<sup>2</sup>、小柴 康子<sup>1</sup>、石田 謙司<sup>1,3</sup> (1. 神戸大、2. 産総研、3. 九大)

## 重アルカリ金属を用いた金属空気電池の正極反応

(東理大理) ○多々良 涼一・藤本 竜成・五十嵐 大輔・保坂 知宙・駒場 慎一  
Oxygen Cathode Reactions in Rb- and Cs-based Nonaqueous Electrolytes  
(Department of Applied Chemistry, *Tokyo University of Science*)  
○Ryoichi Tatara, Ryusei Fujimoto, Daisuke Igarashi, Tomooki Hosaka, Shinichi Komaba

Alkali metal-air batteries offer a high potential energy density, yet they face challenges such as their high reactivity and the difficulty of recharging their discharge products. Nonetheless, the stability of these discharge products can differ depending on the type of alkali metal ion, with potassium-air batteries showing better reversibility compared to sodium-air ones. This study explores the reactions in air batteries that use heavier alkali metals, particularly rubidium and cesium, and conducts a thorough comparison of the reactions at the air cathodes among various alkali metal ions. **Keywords** : Air Batteries; Oxygen Batteries; Alkali Metal; Rb; Cs

大気中の酸素を活性物質として用いるリチウム空気電池は、二次電池の高エネルギー密度化の観点から実用化が期待されている<sup>1)</sup>。金属空気電池の正極反応は酸素還元反応(放電)および再酸化反応(充電)によって進行し、アルカリ金属イオンを含む非水系電解液中では、放電生成物としてアルカリ金属の超氧化物( $\text{MO}_2$ )が生成する。この超氧化物の安定性はアルカリ金属イオン( $\text{M}^+$ )と超氧化物イオン( $\text{O}_2^-$ )のイオン半径に依存すると考えられている<sup>2)</sup>。例として  $\text{LiO}_2$  は  $\text{Li}^+$  (0.76 Å) と  $\text{O}_2^-$  (1.49 Å) のイオン半径差が大きく、迅速な不均化反応( $2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$ )により  $\text{Li}_2\text{O}_2$  が生成する。生成した 2 電子還元生成物である  $\text{Li}_2\text{O}_2$  は再酸化しにくく、リチウム空気電池は充電過電圧が極めて大きいことが知られている<sup>1)</sup>。一方で  $\text{NaO}_2$  は  $\text{Na}^+$  (1.02 Å) のイオン半径が比較的大きく  $\text{NaO}_2$  として単離できるため、充電過電圧の小さいナトリウム空気電池として研究が進められている。しかし  $\text{NaO}_2$  も水分や電解液と高い反応性を示し、 $\text{Na}_2\text{O}_2$  が一部生成することが報告されている<sup>3)</sup>。さらに  $\text{K}^+$  (1.38 Å) では、そのイオン半径の大きさから  $\text{KO}_2$  が比較的安定であり、可逆性の高いカリウム空気電池が報告されている<sup>4)</sup>。本研究では Fig. 1 に示すように、 $\text{Rb}^+$  (1.52 Å)、 $\text{Cs}^+$  (1.69 Å) に注目し、その電気化学特性および、アルカリ金属イオンのイオンサイズが各電極反応に与える影響について調査した。

- 1) P. Bruce, J-M. Tarascon, et al., *Nat. Mater.*, 2012, **11**, 19-29.
- 2) L. Qin, Y. Wu, et al., *J. Am. Chem. Soc.*, 2020, **142**, 11629.
- 3) P. Hartmann, P. Adelhelm, et al., *Nat. Mater.*, 2013, **12**, 228.
- 4) X. Ren, Y. Wu, *J. Am. Chem. Soc.*, 2013, **2**, 2923.

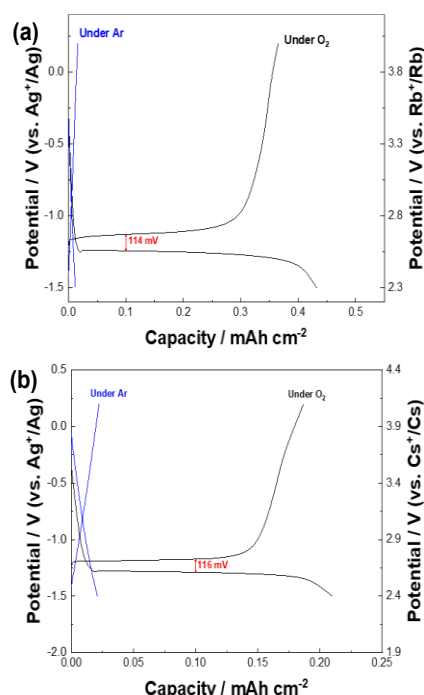


Fig. 1 Charge-discharge curves of (a) Rb- $\text{O}_2$  and (b) Cs- $\text{O}_2$  cells.



## CO<sub>2</sub> を活物質としたレドックスフロー電池の開発

(産総研<sup>1</sup>、京大人環<sup>2</sup>) ○兼賀 量一<sup>1</sup>・山本 旭<sup>2</sup>・吉田 寿雄<sup>2</sup>・大平 昭博<sup>1</sup>

Development of an aqueous redox flow battery using CO<sub>2</sub> as an active material (*National Institute of Advanced Industrial Science and Technology*<sup>1</sup>, *Graduate School of Human and Environmental Studies, Kyoto University*<sup>2</sup>) ○Ryoichi Kanega<sup>1</sup>, Akira Yamamoto<sup>2</sup>, Hisao Yoshida<sup>2</sup>, Akihiro Ohira<sup>1</sup>

H<sub>2</sub> storage system utilizing the interconversion of CO<sub>2</sub> and formate, named chemical hydrogen battery, has been proposed<sup>1)</sup>. However, in the chemical hydrogen battery, energy losses are inevitable in the conversion of electrical energy to H<sub>2</sub> as chemical energy and H<sub>2</sub> to electrical energy, resulting in a loss of more than half of the input electricity. Thus, we considered that the significant energy loss could be overcome by directly storing and generating electrical energy without using H<sub>2</sub>. The system exhibited a maximum discharge capacity of 10.5 mAh (1.5 AhL<sup>-1</sup>), capacity decay of 0.2% per cycle, and total turnover number of 2550 after 50 cycles<sup>2)</sup>.

**Keywords:** Redox flow battery, Ir complex, Carbon dioxide, Formate

CO<sub>2</sub> とギ酸塩の相互変換を活用した H<sub>2</sub> 貯蔵システムは、化学水素電池として提案されている。一方で、化学水素電池は、電気エネルギーを H<sub>2</sub> に変換する過程におけるエネルギー損失と H<sub>2</sub> を電気エネルギーに戻す際のエネルギー損失を避けることができない。そこで、H<sub>2</sub> を経由しない直接的な電力貯蔵ができれば、エネルギー損失を克服できると考えた。開発した新規レドックスフロー電池では、放電容量は最大で 10.5mAh に到達した。また、50 サイクル後の放電容量は初期値の 90%以上を保持し、Ir 錯体の合計の触媒回転数は 2550 であった。

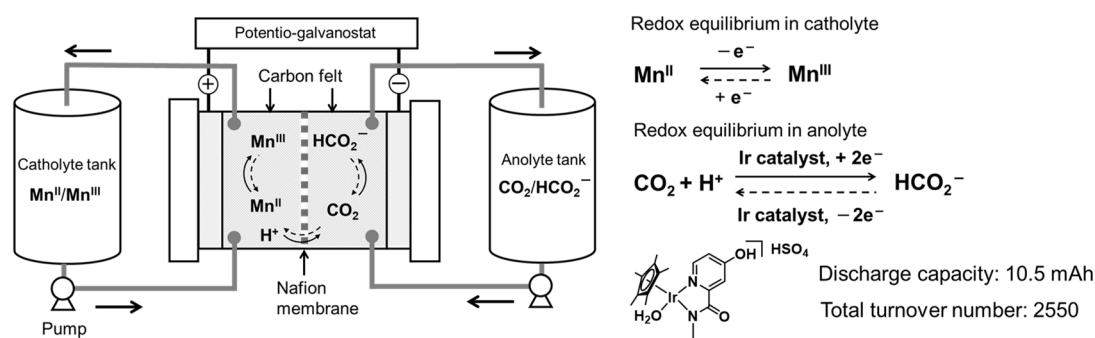


Fig. 1. Working principle of an aqueous redox flow battery using CO<sub>2</sub> as an active material with a homogeneous Ir catalyst.

1) D. Wei, R. Sang, P. Sponholz, H. Junge, M. Beller, *Nat. Energy*, **2022** 7, 438-447.

2) R. Kanega, E. Ishida, T. Sakai, N. Onishi, A. Yamamoto, H. Yasumura, H. Yoshida, H. Kawanami, Y. Himeda, Y. Sato, A. Ohira, *Angew. Chem. Int. Ed.*, **2023**, 62, e202310976.



## テトラチアフルバレンを基盤とする金属有機構造体の電子貯蔵性能

(関西学院大学工学部<sup>1</sup>・関西学院大学大学院理工学研究科<sup>2</sup>) ○若松 勝洋<sup>1</sup>・古野 壮一郎<sup>2</sup>・吉川 浩史<sup>1</sup>

Electron Storage Performance of Metal–Organic Frameworks Based on Tetrathiafulvalene (<sup>1</sup>*School of Engineering, Kwansei Gakuin University*, <sup>2</sup>*Graduate School of Science and Technology, Kwansei Gakuin University*) ○Katsuhiro Wakamatsu,<sup>1</sup> Soichiro Furuno,<sup>2</sup> Hirofumi Yoshikawa,<sup>1</sup>

**Abstract:** Redox-active and rigid tetrathiafulvalene–tetrabenzoate ( $H_4TTFTB$ ) based MOFs ( $[M_2(TTFTB)]$ ,  $M = Zn, Co$ , and  $Mn$ ) were used as a cathode active material for rechargeable lithium-ion and sodium-ion batteries. As a result, the cycle stability and battery capacity at high current densities were improved by including TTF parts in MOFs.

**Keywords:** *Lithium-ion batteries (LIBs); Sodium-ion batteries (SIBs); Cathode active materials; Metal–organic frameworks (MOFs); Tetrathiafulvalene (TTF) derivatives*

**[背景]** テトラチアフルバレン (TTF) 誘導体は、分子性導体として、これまで基礎から応用に至る多種多様な研究がなされてきた物質群である。近年では、この TTF 誘導体を配位子にすることで、一般的には絶縁体である金属有機構造体 (MOF) に、導電性を付与する研究も展開されている。MOF は、その多孔性から二次電池の電極材料としての利用が期待される物質群だが、その低い伝導性などが問題となっている。本研究では、TTF 誘導体を配位子として含む導電性 MOF に着目し、その電極特性の検討を試みた。ここでは、テトラチアフルバレン–テトラベンゾエート ( $H_4TTFTB$ ) を配位子とする MOF ( $[M_2(TTFTB)]$ ,  $M = Zn, Co, Mn$ ) [図 1] を作製し、そのリチウムイオンおよびナトリウムイオン電池 (LIB, SIB) の正極活物質としての電極特性評価を行った<sup>2)</sup>。

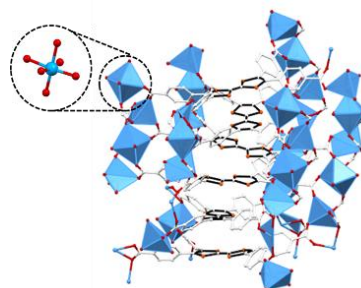


図 1、 $M_2(TTFTB)$  [ $M = Zn, Co, Mn$ ]の構造図<sup>2)</sup>

**[結果・考察]** 図 2 は、 $H_4TTFTB$  および  $M_2(TTFTB)$  [ $M = Zn, Co, Mn$ ]を正極とする SIB の放電容量のサイクル特性とレート特性である。これより、TTF を MOF に組み込むことで、サイクル特性と高電流密度での電池容量が配位子のみのときよりも向上することが明らかとなった。また、電池容量とサイクル特性について、SIB のほうが、LIB よりも大きいことも分かった。詳細については当日の発表にて報告する。

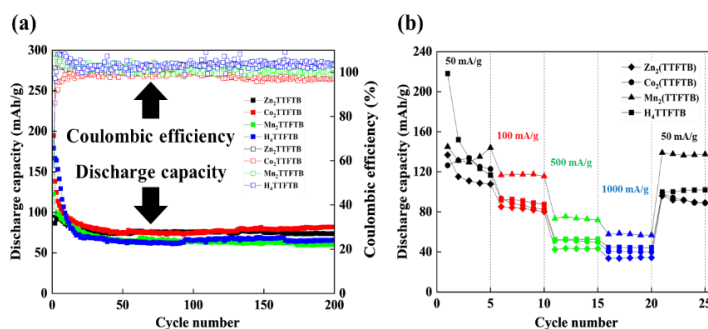


図 2、 $H_4TTFTB$  と  $M_2(TTFTB)$  [ $M = Zn, Co, Mn$ ]の(a)電流密度 100 mA/g における放電容量とクーロン効率、および(b)レート特性

**[文献]** 1) S. S. Park, E. R. Hontz, L. Sun, C. H. Hendon, A. Walsh, T. V. Voorhis, and M. Dincă, *J. Am. Chem. Soc.* **2015**, *137*, 1774–1777, 2) K. Wakamatsu, S. Furuno, Y. Yamaguchi, R. Matsushima, T. Shimizu, N. Tanifuji, and H. Yoshikawa, *ACS Appl. Energy Mater.* **2023**, *6*, 9124–9135

## 炭酸緩衝液由来 CO<sub>2</sub> の電解還元によるマルチカーボン化合物の高速・高選択合成

(阪大院基礎工太陽エネ研<sup>1</sup>) ○井上 明哲<sup>1</sup>・原田 隆史<sup>1</sup>・中西 周次<sup>1</sup>・神谷 和秀<sup>1</sup>  
 High-rate electrochemical CO<sub>2</sub> reduction reactions to multi-carbon products using bicarbonate solution. (<sup>1</sup>Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University) ○Asato Inoue,<sup>1</sup> Takashi Harada,<sup>1</sup> Shuji Nakanishi,<sup>1</sup> Kazuhide Kamiya<sup>1</sup>

Recently, electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is attracting a keen attention as an environmentally friendly technology aimed at achieving a carbon-neutral society. In this work, we aimed to synthesize multi-carbon chemicals (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, n-C<sub>3</sub>H<sub>7</sub>OH, CH<sub>3</sub>COOH) with high reaction rate (> 200 mA/cm<sup>2</sup>) and high selectivity (> 60%) using bicarbonate solution. We realized the high-rate electrolysis by generating gaseous CO<sub>2</sub> in the electrolysis cells from bicarbonate solutions and feeding the gaseous CO<sub>2</sub> to the reaction interface (Figure 1). Furthermore, we confirmed that high-rate and selective C<sub>2+</sub> formation was also possible even when O<sub>2</sub>-contaminated CO<sub>2</sub> was used as the source of the bicarbonate solution. In the presentation, we will discuss the detailed product selectivity and various benefits of this electrolysis system.

**Keywords :** CO<sub>2</sub> reduction reaction; High-rate electrolysis; Multi-carbon chemicals

再生可能エネルギー由来の電力を用いた CO<sub>2</sub> の電解還元が大きな注目を集めている。特に本技術では付加価値の高いマルチカーボン化合物(C<sub>2+</sub>化合物)を高速かつ高選択的に合成することが重要である。本研究ではアルカリ水溶液に CO<sub>2</sub> 含有ガスを溶解させることで調製した炭酸緩衝液から C<sub>2+</sub>化合物を高電流密度(> 200 mA/cm<sup>2</sup>)で合成する反応系の作成に取り組んだ(Figure 1)。本電解系ではカソードに供給した炭酸緩衝液とアノード反応によって生成したプロトン間の酸-塩基反応によってガス状の CO<sub>2</sub> が電解セル内で生成し(Reaction ①)、続いて電気化学反応によってガス状 CO<sub>2</sub> から C<sub>2+</sub>化合物が高電流密度で合成される(Reaction ②)。我々は本電解系を用いることで、O<sub>2</sub> 混入 CO<sub>2</sub> ガスを用いた条件でも高速かつ高選択的に C<sub>2+</sub>化合物を合成することに成功した。発表当日は電解活性の詳細や本電解系の種々の利点に関して議論する。

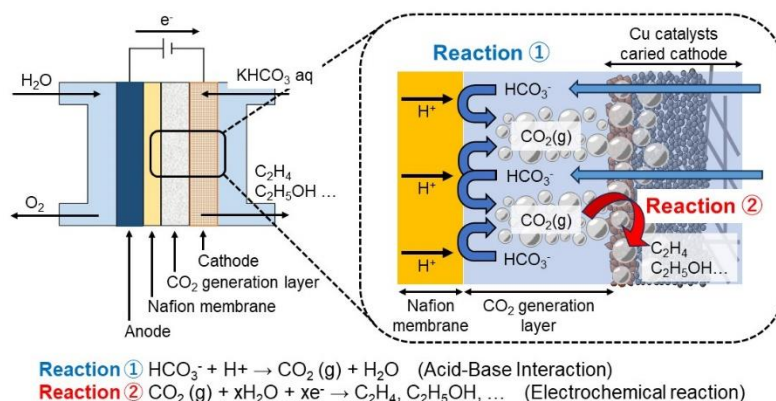


Figure 1 本研究で用いた電解セルの概略図(左)とそのカソード反応界面(右)

## ダイヤモンド電極による CO<sub>2</sub> の電解還元におけるファインバブルの影響

(九大 I<sup>2</sup>CNER<sup>1</sup>・静大<sup>2</sup>・慶大理工<sup>3</sup>) ○富崎 真衣<sup>1</sup>・櫻井 大斗<sup>2</sup>・間瀬 暢之<sup>2</sup>・栄長 泰明<sup>3</sup>

Effect of Fine Bubbles on the Electrochemical Reduction of Carbon Dioxide Using Diamond Electrodes (<sup>1</sup>*International Institute for Carbon-Neutral Energy Research, Kyushu University*, <sup>2</sup>*Shizuoka University*, <sup>3</sup>*Faculty of Science and Technology, Keio University*) ○Mai Tomisaki,<sup>1</sup> Hiroto Sakurai,<sup>2</sup> Nobuyuki Mase,<sup>2</sup> Yasuaki Einaga<sup>3</sup>

Bubbles whose diameters are less than 100 μm are called fine bubbles and have certain specific properties unlike macrobubbles<sup>1)</sup>. They have long stagnation in solutions, the high internal pressure, and charged surface. On the other hand, in electrochemical CO<sub>2</sub> reduction, there are several problems such as the use of complex catalysts, addition of mediators, or large overpotential. By using fine bubbles, the improved solubility of CO<sub>2</sub> or efficient reaction can be expected, so the electrochemical reduction of CO<sub>2</sub> on diamond electrodes using the solutions containing CO<sub>2</sub> fine bubbles were conducted.

When the solutions with CO<sub>2</sub> fine bubbles were used, applied potential shifted to the positive side (Fig. 1) and the production of carbon monoxide was promoted compared to the case without fine bubbles. CO<sub>2</sub> fine bubbles might interact with hydrated CO<sub>2</sub> molecules or CO<sub>2</sub> reduction intermediate and restrain their movement near the electrode.

**Keywords :** Fine Bubble; Electrochemical Reduction of Carbon Dioxide; Diamond Electrode

気泡の直径が 100 μm 未満のファインバブルは、溶液中での長時間の残存や高い気泡内圧力、気泡表面の帯電といった特異な性質を有する<sup>1)</sup>。一方、CO<sub>2</sub> の電解還元では、複雑な触媒の使用や、反応を仲介する化合物の添加、高い過電圧などが環境配慮や反応効率の観点から課題である。微細気泡を用いることで、CO<sub>2</sub> の溶解性の向上や反応の効率化が期待できると考え、CO<sub>2</sub> ファインバブルを含む溶液の電解還元を検討した。

CO<sub>2</sub> ファインバブルを含む電解液を用いると、ファインバブルを通気していない電解液を用いた場合と比較して、印加電位が貴側へシフトし (Fig. 1)、一酸化炭素の生成が促進された。CO<sub>2</sub> ファインバブルが、水和した CO<sub>2</sub> 分子や CO<sub>2</sub> 還元反応の中間体と電極近傍で相互作用して動きを制限し、電解反応の促進や一酸化炭素生成の増加がみられたと考えられる。

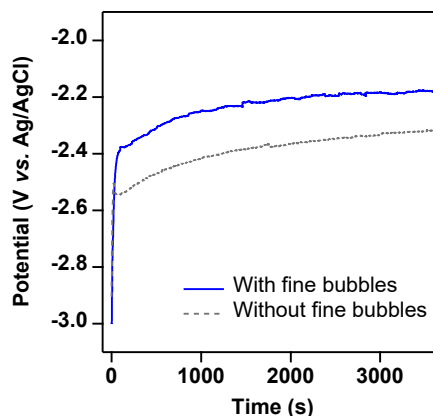


Fig. 1 Chronopotentiograms during electrochemical CO<sub>2</sub> reduction at -2 mA/cm<sup>2</sup> in the solutions with and without CO<sub>2</sub> fine bubbles.

1) M. Takahashi, *J. Phys. Chem. B* **2005**, 109, 21858-21864.

## 10 mV/K 級の熱起電力を発現する熱電キャパシタ

(神戸大院工<sup>1</sup>・神戸大先端膜工学研究センター<sup>2</sup>・神戸大環境保全推進センター<sup>3</sup>・産総研ナノ材<sup>4</sup>・九大院工<sup>5</sup>) ○堀家 匠平<sup>1,2,3,4</sup>・衛 慶碩<sup>4</sup>・桐原 和大<sup>4</sup>・向田 雅一<sup>4</sup>・小柴 康子<sup>1,2</sup>・石田 謙司<sup>1,2,5</sup>

Thermally chargeable supercapacitor with thermo-electromotive force of 10 mV/K (<sup>1</sup>Graduate School of Engineering, Kobe University, <sup>2</sup>Research Center for Membrane and Film Technology, Kobe University, <sup>3</sup>Center for Environmental Management, Kobe University, <sup>4</sup>Nanomaterials Research Institute, AIST, <sup>5</sup>Graduate School of Engineering, Kyushu University) Shohei Horike<sup>1,2,3,4</sup>, Qingshuo Wei<sup>4</sup>, Kazuhiro Kirihara<sup>4</sup>, Masakazu Mukaida<sup>4</sup>, Yasuko Koshiba<sup>1,2</sup>, Kenji Ishida<sup>1,2,5</sup>

Thermally chargeable supercapacitor (TCS) is a new class of thermoelectric devices and has a potential to be used as a power supply method for IoT sensors. We present here TCSs constructed with an ionic hydrogel based on 1-ethyl-3-methylimidazolium chloride and poly(vinyl alcohol) and metal or conducting polymer electrodes with outstanding thermo-electromotive force of up to 10 mV/K<sup>1,2</sup>. The developed TCS could induce large open circuit voltage from the supplied temperature difference, and the voltage could be repeatedly converted into electrical energy by disconnection and connection of an external load resistance. Owing to the large electromotive force induced (>1 V), the TCS module enabled intermittent powering of electric devices such as LEDs even without the use of a DC-to-DC converter, that has been one of the bottlenecks of typical semiconductor-based thermoelectric devices.

**Keywords :** *Thermally Chargeable Supercapacitor; Ionic Hydrogel; Thermoelectric; Energy Harvesting; Polarization*

熱電キャパシタはレドックスフリーの電解液を電極で挟持した単純な構造ながら、高い熱起電力を示す新規熱電素子であり、IoT センサ用の電源技術として期待される。本研究では、1-ethyl-3-methylimidazolium chloride/ポリビニルアルコールからなるハイドロゲルならびに金属あるいは導電性高分子電極を用いた熱電キャパシタにおいて、10 mV/K 級の熱起電力を見出したので報告する<sup>1,2</sup>。また、熱電キャパシタを 5–10 列、熱流に対して並列に設置し、電気的に直列に接続することで、温度差から 1 V 以上の起電力を得られ、LED 等の電子デバイスへの給電を実証した。従来の半導体熱電素子では、起電力を増幅するためのチャージポンプが必要であったが、こうした昇圧回路不要にて、少ない列数のモジュールからボルトオーダーの電圧を出力可能なことは、回路の単純化や低コスト化、材料削減につながると考えられる。

謝辞：本研究の一部は NEDO 未踏チャレンジ 2050 の支援のもと実施されました。

- 1) Outstanding Electrode-Dependent Seebeck Coefficients in Ionic Hydrogels for Thermally Chargeable Supercapacitor near Room Temperature. S. Horike, Q. Wei, K. Kirihara, M. Mukaida, T. Sasaki, Y. Koshiba, T. Fukushima, K. Ishida, *ACS Appl. Mater. Interfaces*. **2020**, *12*, 43674.
- 2) Anomalous n-type conversion of thermoelectric polarity in ionic hydrogels using PEDOT:PSS electrodes. S. Horike, Q. Wei, K. Kirihara, M. Mukaida, Y. Koshiba, K. Ishida, *J. Mater. Chem. C* **2021**, *9*, 15813.