2024年3月19日(火)

アカデミックプログラム［Ｂ講演］ | 01. 化学教育・化学史：口頭Ｂ講演

2024年3月19日(火) 14:10 ~ 15:10 A1456(14号館 [5階] 1456)

[A1456-2pm] 01. 化学教育・化学史

座長：伊藤 眞人、福本 晃造

日本語

14:10 ~ 14:30

[A1456-2pm-01]

菜種油の迅速けん化法とその授業実践

○小原 孝昭[1]、酒井 権一[2]、網本 貴一[3] (1. 有限会社NSコスメ、2. 香川県立三本松高等学校、3. 広島大院人間社会科学)

日本語

14:30 ~ 14:50

[A1456-2pm-02]

教員養成用実験学習プログラム:反応速度に関する概念の理解

○細江 剛史[1]、生尾 光[2]、國仙 久雄[2] (1. 東京学芸大学大学院連合学校教育学研究科、2. 東京学芸大学教育学部)

日本語

14:50 ~ 15:10

[A1456-2pm-03]

中等教育としての高専の一般教育理科実験－化学系学科の改組とグローバル教育－

○内山 弘美[1] (1. 茗渓学園高等学校 科学研究指導員)

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19日(火) 13:00 ~ 15:30 H937(9号館 [3階] 937)

[H937-2pm] 02. 理論化学・情報化学・計算化学

座長：吉田 悠一郎、堀 優太

英語
13:00 ~ 13:20
[H937-2pm-01]

第一原理計算を用いたプロトン伝導分子性結晶中のプロトン移動と分子運動の解析

○堀 優太[1]、小倉 浩樹[3]、出倉 駿[2]、森 初果[3]、重田 育照[1] (1. 筑波大学、2. 東北大学、3. 東京大学)

英語
13:20 ~ 13:40
[H937-2pm-02]

Comparison between a superconducting-type quantum computer and a trapped-ion-type quantum computer by the simulation of spin dynamics

Erik Lötstedt[1], ○Kaoru Yamanouchi[1,2] (1. School of Science, The Univ. of Tokyo, 2. Institute for Attosecond Laser Facility, The Univ. of Tokyo)

英語
13:40 ~ 14:00
[H937-2pm-03]

Time-dependent rovibronic wavefunction of H_2^+ by multiconfiguration theory

○Erik Lötstedt[1], Tsuyoshi Kato[1], Kaoru Yamanouchi[1,2] (1. School of Science, The University of Tokyo, 2. Institute for Attosecond Laser Facility, The University of Tokyo)

日本語
14:10 ~ 14:30
[H937-2pm-04]

効率的な量子計算に向けた短鎖長ポリエンの拡張ハバード模型構築

○吉田 悠一郎[1]、竹森 那由多[1,2]、水上 渉[1,3] (1. 阪大QIQB、2. 理研CEMS、3. 阪大院基礎工)

英語
14:30 ~ 14:50
[H937-2pm-05]

Electrolyte adsorption study on the different types of layered cathode surfaces of lithium-ion batteries with computational chemistry methods

○Attila Taborosi[1], Michihisa Koyama[1], Nobuyuki Zettsu[1] (1. Shinshu University)

英語
14:50 ~ 15:10
[H937-2pm-06]

可逆な化学反応ネットワークにおける準不可逆性の発現と経路選択

○高橋 聡[1]、阿部 司[1]、佐藤 啓文[2,3]、平岡 秀一[1] (1. 東京大学大学院総合文化研究科、2. 京都大学大学院工学研究科、3. 京都大学福井謙一記念研究センター)

英語
15:10 ~ 15:30
[H937-2pm-07]

改良型３次元離散コサイン変換と最大エントロピー法によるMg_3BN_3高圧相の精密電子密度分布解析についての研究

○平口 英夫[1] (1. （公）日本技術士会)

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19日(火) 13:00 ~ 15:40 🏛 A1452(14号館 [5階] 1452)

[A1452-2pm] 03. 物理化学—構造

座長：佐藤 和信、山添 誠司

🏷 日本語
13:00 ~ 13:20
[A1452-2pm-01]

Pd/Cu(111)単原子合金モデル触媒におけるCO_2水素化反応の準大気圧*in-situ*分光研究

○長田 渉[1]、尾崎 文彦[1]、堀尾 眞史[1]、田中 駿介[1]、向井 孝三[1]、小板谷 貴典[2]、山本 達[3]、松田 巌[1]、吉信 淳[1] (1. 東京大学物性研究所、2. 京都大学、3. 東北大学)

🏷 日本語
13:20 ~ 13:40
[A1452-2pm-02]

二成分イオン液体/電極界面におけるアニオン吸脱着の過電圧要因の研究

○岩橋 崇[1]、周 尉[2]、Kim Doseok[3]、大内 幸雄[1] (1. 東京工業大学、2. 上海大学、3. Sogang大学)

🏷 日本語
13:40 ~ 14:00
[A1452-2pm-03]

オペランドマルチモーダル計測による燃料電池Pt電極触媒上の吸着酸素種の挙動解明

○三輪 寛子[1]、吉田 健文[2]、金子 拓真[3]、佐々木 岳彦[4]、東 晃太朗[3]、坂田 智裕[1]、関澤 央輝[3]、宇留賀 朋哉[1,3]、岩澤 康裕[1] (1. 電通大学、2. 和歌山大学、3. 高輝度光科学研究センター、4. 東大)

🏷 日本語
14:20 ~ 14:40
[A1452-2pm-04]

インジウムナノ粒子による深紫外域局在プラズモンと吸着分子の相互作用

長塚 直樹[1]、松口 諒斗[1]、奥山 弘[1]、安池 智一[2]、小板谷 貴典[1]、○渡邊 一也[1] (1. 京都大学、2. 放送大学)

🏷 日本語
14:40 ~ 15:00
[A1452-2pm-05]

クラウンエーテル環状分子膜を使ったフェロセン単分子STM観察と二次元結晶成長

○山田 豊和[1] (1. 千葉大学)

🏷 日本語
15:00 ~ 15:20
[A1452-2pm-06]

氷よりも疎な疎水性空間中の微小水に対するトポロジカル解析からの構造決定

○杉山 泰啓[1]、中野 智康[2]、飯山 拓[3]、二村 竜祐[3] (1. 信州大院医理工、2. ㈱アドール、3. 信大理)

🏷 日本語
15:20 ~ 15:40
[A1452-2pm-07]

[有機1次元細孔物質-ビタミンE]包接体型分子カプセルの物理化学的性質

○小林 広和[1]、本多 英彦[1]、山本 雅人[1]、岩堀 史靖[2]、野口 真理子[2]、藤森 裕基[2]、小田中 友紀[3]、荻野 玲奈[4]、柴田 陽[4] (1. 昭和大学富士吉田教育部、2. 日本大学文理学部、3. 昭和大学薬学部、4. 昭和大学歯学部)

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19日(火) 10:00 ~ 11:40 A1441(14号館 [4階] 1441)

[A1441-2am] 04. 物理化学—物性

座長：出倉 駿、小松 徳太郎

英語
10:00 ~ 10:20
[A1441-2am-01]

プルシアンブルー磁性薄膜における磁気ドメインと磁化反転の直接観察

○長島 俊太郎[1]、矢作 祐士[1]、大越 慎一[2]、所 裕子[1,2] (1. 筑波大学、2. 東京大学)

日本語
10:20 ~ 10:40
[A1441-2am-02]

スキャホールド材料への応用を目指したTTF誘導体とF4TCNQ錯体からなる分子性ナノコイルの作成と電磁特性

○帯刀 陽子[1]、南 豪[2]、西原 禎文[3,4]、芥川 智行[5]、中村 貴義[6] (1. 農工大、2. 東大生研、3. 広島大学、4. JST さきがけ、5. 東北大多元研、6. 北大電子研)

日本語
10:40 ~ 11:00
[A1441-2am-03]

ポリアセン結晶の電子構造と安定性

○小松 徳太郎[1] (1. 日本大学)

英語
11:00 ~ 11:20
[A1441-2am-04]

量子スピン液体候補κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{Au}(\mathrm{CN})_2]\mathrm{Cl}$の低温物性

○田中 優輝[1]、前里 光彦[1]、留野 慎也[1]、吉田 幸大[1]、清水 康弘[2]、北川 宏[1] (1. 京都大学大学院理学、2. 名古屋大学大学院)

英語
11:20 ~ 11:40
[A1441-2am-05]

New Functionalities in Pseudohalide-Based Complexes

○Olaf Stefanczyk[1], Guanping Li[1], Kunal Kumar[1], Kenta Imoto[1], Koji Nakabayashi [1], Shin-ichi Ohkoshi [1] (1. The Univ. of Tokyo)

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19日(火) 9:00 ~ 11:10 A1454(14号館 [5階] 1454)

[A1454-2am] 05. 物理化学—反応

座長：石橋 千英、倉持 光

日本語
9:00 ~ 9:20
[A1454-2am-01]

銅フタロシアニン単一ファイバーのフェムト秒ナノ分光

白石 悠人[1]、森田 水由宇[1]、○石橋 千英[1]、朝日 剛[1] (1. 愛媛大学)

日本語
9:20 ~ 9:40
[A1454-2am-02]

凝集誘起発光特性を有するジベンゾイルメタンフッ化ホウ素錯体の固体状態の励起状態ダイナミクス

○藤本 悠史[1]、石橋 千英[2]、朝日 剛[2]、伊藤 冬樹[1,3] (1. 信州大院総合理工、2. 愛媛大院理工、3. 信州大教育)

英語
9:40 ~ 10:00
[A1454-2am-03]

レチナール光異性化酵素ロドプシンの吸収波長特性と可逆的光反応

森本 直也[1]、○永田 崇[1]、井上 圭一[1] (1. 東京大学)

日本語
10:10 ~ 10:30
[A1454-2am-04]

フェムト秒過渡吸収スペクトル測定によるヘミインジゴの光異性化反応ダイナミクスの追跡

○長澤 裕[1]、東 岳斗[1]、邨井 孝行[1]、木原 優[1]、小島 理沙[1]、寺本 高啓[2,3] (1. 立命館大学、2. 京都大学、3. 大阪大学)

日本語
10:30 ~ 10:50
[A1454-2am-05]

TCNQの励起状態：熱活性化遅延蛍光、電荷移動状態、および対称性の破れ

Ahatashamul Islam[1]、春藤 健介[1]、○飯森 俊文[1] (1. 室蘭工業大学)

日本語
10:50 ~ 11:10
[A1454-2am-06]

液体の超高速光電子分光におけるスペクトル回復法の開発と水溶液中のOHの構造拡散を伴う電荷再結合ダイナミクスの解明

○山本 遥一[1]、鈴木 俊法[1] (1. 京都大学)

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19日(火) 13:00 ~ 14:50 A1455(14号館 [5階] 1455)

[A1455-2pm] 05. 物理化学—反応

座長：深堀 信一、野々瀬 真司

日本語

13:00 ~ 13:20

[A1455-2pm-01]

高強度レーザー場における非対称コマ水分子のイオン化

○深堀 信一[1,2]、菊池 勇[1]、長谷川 宗良[1,2] (1. 東大院総文、2. 東大先進機構)

英語

13:20 ~ 13:40

[A1455-2pm-02]

真空中の蒸発冷却による水液滴の均質凍結：液滴径変化の光測定と相転移挙動の高速画像観察

○飯田 岳史[1]、荒川 雅[1]、堀尾 琢哉[1]、寺嵜 亨[1] (1. 九州大学)

英語

13:40 ~ 14:00

[A1455-2pm-03]

ニッケル金属原子内包シリコンケージナノクラスターのサイズ依存性と化学的特性

○佐々木 綾香[1]、市川 琢己[1]、中嶋 敦[1] (1. 慶應義塾大学)

英語

14:10 ~ 14:30

[A1455-2pm-04]

ジベンゾクラウンエーテルのアルカリ金属イオン錯体における異性化反応速度のゲストイオン依存性

○伊藤 亮佑[1]、大下 慶次郎[1]、美齊津 文典[1] (1. 東北大院理)

日本語

14:30 ~ 14:50

[A1455-2pm-05]

気相生体分子イオンのプロトン移動反応

○野々瀬 真司[1]、豊見山 蒼樹[1]、石井 空雅[1]、笹野 光紀[1]、吉野 壮悟[1] (1. 横浜市立大学)

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19日(火) 13:00 ~ 15:30 A1453(14号館 [5階] 1453)

[A1453-2pm] 06. 分析化学

座長：佐藤 雄介、川井 隆之

日本語

13:00 ~ 13:20

[A1453-2pm-01]

“ナノギャップ１分子計測法による生体分子検出・解析法の開発”

○大城 敬人[1]、小本 祐貴[1]、谷口 正輝[1] (1. 大阪大学)

日本語

13:20 ~ 13:40

[A1453-2pm-02]

細胞内生体分子の多色検出に向けた超高輝度ラマンプローブ合成

○古屋 圭惟[1]、西山 諒[1]、Phillip McCann[1]、Laura Kacenauskaite[1,2]、Bo Laursen[3]、Amar Flood[4]、丁 天本[1]、平松 光太郎[1,5]、合田 圭介[1,6,7] (1. 東大、2. スタンフォード大学、3. コペンハーゲン大、4. インディアナ大、5. 九大、6. UCLA、7. 武漢大)

英語

13:40 ~ 14:00

[A1453-2pm-03]

ラマン内視鏡を用いた生体内での肝グリコーゲン定量法の開発

○松下 昇平[1]、上田 善文[1]、吉村 英哲[1]、島田 林太郎[2]、小澤 岳昌[1] (1. 東京大学、2. 青山学院大学)

英語

14:10 ~ 14:30

[A1453-2pm-04]

時間領域分子振動解析による高速・多色ラマンタグ定量法

○西山 諒[1]、平松 光太郎[1,2]、古屋 圭惟[1]、河村 伸太郎[3]、闐闐 孝介[3]、Min Wei[4]、丁 天本[1]、袖岡 幹子[3]、合田 圭介[1,5,6] (1. 東京大学、2. 九州大学、3. 理化学研究所、4. コロンビア大学、5. カリフォルニア大学ロサンゼルス校、6. 武漢大学)

英語

14:30 ~ 14:50

[A1453-2pm-05]

Ultra-sensitive SERS at single-protein level via a new delivery technique for analytes into hotspots

○Tianxu Gao[1], Hideyuki Mitomo[2], Xu Shi[3], Yusuke Yonamine[2], Kuniharu Ijiro[2] (1. Grad. Sch. Life Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ., 3. CRIS, Hokkaido Univ.)

英語

14:50 ~ 15:10

[A1453-2pm-06]

生体深部におけるタンパク質間相互作用および細胞融合の近赤外発光検出法の開発

○李　伶[1]、河村 玄気[1]、李 喬婧[1]、小澤 岳昌[1] (1. 東京大学 理学系研究科 化学専攻)

英語

15:10 ~ 15:30

[A1453-2pm-07]

新しいオプトジェネティックシステムによる深層組織でのインスリンシグナル制御

○DONG QI[1]、遠藤 瑞己[1]、小澤 岳昌[1] (1. 東京大学)

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19日(火) 15:55 ~ 17:15 A1444(14号館 [4階] 1444)

[A1444-2vn] 07. 無機化学

座長：秋吉 一孝、神戸 徹也

英語
15:55 ~ 16:15
[A1444-2vn-01]

Tunable Optical Properties of Newly Developed Ag-Mn-Sn-S Quantum Dots through Precise Composition Control

○Chang Jiang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Naoki Banno[1], Hiroshi Yukawa[1], Yoshinobu Baba[1], Tsukasa Torimoto[1] (1. Nagoya Univ.)

英語
16:15 ~ 16:35
[A1444-2vn-02]

Tert-butoxy基を有するspiro-5型分子をプリカーサーとして用いたアルミノシリケート構築

○今泉 暁[1]、本田 暁紀[1]、横井 俊之[2]、張 浩徹[1] (1. 中央大学、2. 東京工業大学)

英語
16:35 ~ 16:55
[A1444-2vn-03]

Frustrated Lewis Pair reactivities of phosphino-phosphenium cations

○Hyehwang Kim[1], Douglas Wade Stephan[1] (1. University of Toronto)

英語
16:55 ~ 17:15
[A1444-2vn-04]

配位子保護Auクラスター合成におけるデンドリマー鋳型効果の分析

○村松 央教[1]、神戸 徹也[1,2]、塚本 孝政[1,2]、今岡 享稔[1,2]、山元 公寿[1,2] (1. 東京工業大学、2. JST-ERATO)

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19日(火) 15:55 ~ 16:35 A1457(14号館 [5階] 1457)

[A1457-2vn] 08. 触媒

座長：近藤 敏啓、清野 智史

日本語

15:55 ~ 16:15

[A1457-2vn-01]

放射線を利用した樹脂板へのPdナノ粒子固定化法のポリイミド樹脂への適用と無電解めっきへの応用

○上垣 直人[1]、清野 智史[1]、佐藤 陸弥[1]、大久保 雄司[1]、石黒 文康[1]、中川 貴[1] (1. 大阪大学)

英語

16:15 ~ 16:35

[A1457-2vn-03]

ステップ方向制御に向けたアニリン溶液浸漬によるTiO_2(110)単結晶表面の異方的エッチング

○高張 真美[1]、五島 大河[2]、吉本 惣一郎[2]、近藤 敏啓[1] (1. お茶の水女子大学、2. 熊本大学)

英語

[A1457-2vn-02]

講演取り下げ

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19日(火) 15:55 ~ 17:15 A1458(14号館 [5階] 1458)

[A1458-2vn] 08. 触媒

座長：山口 友一、西村 俊

日本語
15:55 ~ 16:15

[A1458-2vn-01]

カチオン性Zr有機金属多面体のポリ酸との集積化と光増感能

○末田 悠太[1]、Benjamin Le Ouay[1]、大谷 亮[1]、大場 正昭[1] (1. 九州大学)

日本語
16:15 ~ 16:35

[A1458-2vn-02]

ZnSナノ結晶を用いたパーフルオロアルキル化合物の光分解メカニズムの解明

○豊田 悠斗[1]、岡安 祥徳[1]、永井 邑樹[1]、小林 洋一[1,2] (1. 立命館大、2. JSTさきがけ)

英語
16:35 ~ 16:55

[A1458-2vn-03]

分析データからの特徴抽出による機械学習を用いた種々の光アノードの光電流密度の予測

○永井 優也[1]、潘 振華[1]、片山 建二[1] (1. 中央大学)

英語
16:55 ~ 17:15

[A1458-2vn-04]

畳み込みニューラルネットワークを用いた電子顕微鏡画像からの電流ー電圧曲線の予測-バナジン酸ビスマスを例に

○片山 建二[1]、林 祐太[1]、永井 優也、潘 振華 (1. 中央大学)

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19日(火) 15:55 ~ 17:15 F1232(12号館 [3階] 1232)

[F1232-2vn] 09. 錯体化学・有機金属化学

座長：亀尾 肇、小林 厚志

英語

15:55 ~ 16:15

[F1232-2vn-01]

Photocatalytic CO_2 Reduction Using Binary Metal-Porphyrins as Photosensitizer and Catalyst Units

○Sunghan Choi[1], Sebastian Nybin Remello[1], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

英語

16:15 ~ 16:35

[F1232-2vn-02]

Electrocatalytic Reduction of Low Concentration CO_2 by Iron Porphyrins

○Sebastian Nybin Remello[1,3], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology , 2. Hiroshima University, 3. Cochin University of Science and Technology)

日本語

16:35 ~ 16:55

[F1232-2vn-03]

鉄ジシリル錯体を用いた炭素−ヘテロ二重結合切断反応

○菅 雄翔[1]、砂田 祐輔[1,2] (1. 東大院工、2. 東大生研)

英語

16:55 ~ 17:15

[F1232-2vn-04]

An Iron Porphyrin-Based Framework Catalyst for Highly Efficient Photocatalytic CO_2 Reduction

○XIANJUN LI[1], Kento KOSUGI[2], Maho IMAI[2], Yutaka SAGA[2], Tetsuya KAMBE[2], Shigeyuki MASAOKA[2], Mio KONDO[1,2,3] (1. Tokyo Institute of Technology, 2. Osaka University, 3. JST PRESTO)

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19日(火) 15:55 ~ 17:15 F1233(12号館 [3階] 1233)

[F1233-2vn] 09. 錯体化学・有機金属化学

座長：小林 洋一、堀内 新之介

英語

15:55 ~ 16:15

[F1233-2vn-01]

キラルベンジルアミン配位子修飾シリカ表面への固定化による発光性Tb錯体のキラリティー誘起

○白井 そら[1]、松井 久宣[2]、郁次 智[1]、中井 英隆[2]、唯 美津木[1,3] (1. 名大院理、2. 近畿大院総理工、3. 名大物国セ)

英語

16:15 ~ 16:35

[F1233-2vn-02]

四角酸と硝酸エルビウムから合成された3種の錯体における構造と磁気特性

○高野 莉奈[1]、益田 晃希[2]、北河 康隆[2]、石田 尚行[1] (1. 電気通信大学、2. 大阪大学)

日本語

16:35 ~ 16:55

[F1233-2vn-03]

β-ジケトナート配位子の光分解過程の理解と希土類錯体の光耐久性の向上

○岡安 祥徳[1]、小林 洋一[1,2] (1. 立命館大学、2. JST さきがけ)

日本語

16:55 ~ 17:15

[F1233-2vn-04]

新規ペンタキス（*β*-ジケトン）型コラニュレン配位子による多核Eu(III)錯体形成

○山田 美穂子[1]、松本 大河[1]、加納 春華[1]、河合 壯[1] (1. 奈良先端科学技術大学院大学)

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19日(火) 15:55 ~ 17:15 F1234(12号館 [3階] 1234)

[F1234-2vn] 09. 錯体化学・有機金属化学

座長：細野 暢彦、日下 心平

英語
15:55 ~ 16:15

[F1234-2vn-01]

芳香環カプセルの等方的空間拡大と多分子内包能

○角田 瑠輝[1]、名畑 瑠斗[1]、吉沢 道人[1] (1. 東工大・化生研)

英語
16:15 ~ 16:35

[F1234-2vn-02]

C_1対称性大環状配位子からなる二次元金属有機構造体の構築および機能性小分子の層間集積制御

○中川 慶一[1]、田代 省平[1]、横森 創[2]、松下 信之[2]、塩谷 光彦[1] (1. 東大院理、2. 立教大理)

英語
16:35 ~ 16:55

[F1234-2vn-03]

Green Synthesis of a Flexible Metal-Organic Framework [Cu(BF$_4$)$_2$(4,4´-bipyridine)$_2$] (ELM-11) for Selective CO$_2$ Adsorption

○Shivakumar Kilingaru Ishwara[1], Shin-ichiro Noro[1] (1. Hokkaido University)

英語
16:55 ~ 17:15

[F1234-2vn-04]

ヨウ化銅(I)クラスターを含むピリジル型有機金属骨格を用いたC5炭化水素混合物からのイソプレンの高選択的分離.

○キム ジュンシク[1]、パベル ユーソフ[1]、和田 雄貴[1]、大津 博義[1]、松本 隆也[1,2]、河野 正規[1] (1. 東京工業大学、2. ENEOS Corporation)

アカデミックプログラム［Ｂ講演］ | 10. 有機化学—有機金属化合物：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 16:55 E1111(11号館 [1階] 1111)

[E1111-2vn] 10. 有機化学—有機金属化合物

座長：渕辺 耕平

英語

15:55 ~ 16:15

[E1111-2vn-01]

低原子価ニオブ錯体を触媒とするアルキンとシクロプロペンの [2+2+1]-環化付加反応による多置換シクロペンタジエン誘導体の合成

○秋山 拓弥[1]、真島 和志[2]、草本 哲郎[1]、劒 隼人[1] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院薬学研究科)

英語

16:15 ~ 16:35

[E1111-2vn-02]

Enantioselective [3+2] Annulation of Aromatic Aldimines with Alkynes via C−H Activation by Half-Sandwich Scandium Catalyst

○Aniket Mishra[1], Masayoshi Nishiura[1], Zhaomin Hou[1] (1. RIKEN CSRS)

英語

16:35 ~ 16:55

[E1111-2vn-03]

Efficient and Selective Synthesis of Sterically Hindered Secondary Amines by Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

○Zhou Sun[1,2], Murahashi Nishiura[2], Feng Xue Cong[2], Tetsuro Murahashi[1], MIn Zhao Hou[2] (1. Tokyo Institute of Technology, 2. Riken)

アカデミックプログラム［Ｂ講演］ | 10. 有機化学—有機金属化合物：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 16:35 E1112(11号館 [1階] 1112)

[E1112-2vn] 10. 有機化学—有機金属化合物

座長：岩本 貴寛

英語

15:55 ~ 16:15

[E1112-2vn-01]

金触媒による環化—スルホニル転位による４－スルホニルインドールの選択的合成

○Chunbo JIA[1]、寺田 眞浩[1]、中村 達[1] (1. 東北大学)

英語

16:15 ~ 16:35

[E1112-2vn-02]

活性イソニトリルの銀触媒不斉アルドール反応および不斉Michael反応

○酒井 聡史[1]、内山 渓[1]、矢藤 千菜[1]、今井 浩児[1]、東田 皓介[2]、清水 洋平[1,3]、澤村 正也[1,3] (1. 北大理、2. 京大院理、3. WPI-ICReDD)

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19日(火) 15:55 ~ 17:15 E1113(11号館 [1階] 1113)

[E1113-2vn] 11. 有機化学—構造有機化学

座長：松井 康哲、田中 一生

日本語

15:55 ~ 16:15

[E1113-2vn-01]

縮環型アゾベンゼンガリウム錯体の合成と光学特性評価

○堀田 千有希[1]、中村 将志[1]、権 正行[1]、田中 一生[1] (1. 京都大学)

英語

16:15 ~ 16:35

[E1113-2vn-02]

外部環境に依存する感圧化学センサー：ヘリカルアントラセン二量体の圧力誘起蛍光シグナル変化

○木下 智和[1]、渡邊 公太[1]、鶴巻 英治[1]、豊田 真司[1]、福原 学[1] (1. 東工大)

英語

16:35 ~ 16:55

[E1113-2vn-03]

スクアリン骨格をもつ正孔回収単分子膜材料の開発とペロブスカイト太陽電池への応用

○平 翔太[1]、チョン ミンアン[1]、中村 智也[1]、マーディー リチャード[1]、若宮 淳志[1] (1. 京都大学 化学研究所)

日本語

16:55 ~ 17:15

[E1113-2vn-04]

極性結晶を基盤とする有機トリボルミネッセンス材料の開発

○大垣 拓也[1]、松井 康哲[1]、池田 浩[1] (1. 阪公大)

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19日(火) 15:55 ~ 17:15 E1121(11号館 [2階] 1121)

[E1121-2vn] 11. 有機化学—構造有機化学

座長：羽毛田 洋平、澤田 知久

日本語
15:55 ~ 16:15

[E1121-2vn-01]

炭素•炭素一電子結合：存在の実証とその性質

○島尻 拓哉[1]、川口 聡貴[1]、鈴木 孝紀[1]、石垣 侑祐[1] (1. 北海道大学)

英語
16:15 ~ 16:35

[E1121-2vn-02]

機械学習を用いた固体混合比の予測と化学反応分析への応用

○白倉 逸人[1]、佐野 太一[1]、井手 雄紀[2]、Sheng Hu[2]、瀧川 一学[2,3]、猪熊 泰英[1,2] (1. 北大院工、2. 北大 WPI-ICReDD、3. 京大 CIREDS)

英語
16:35 ~ 16:55

[E1121-2vn-03]

A Coordination Cage as a Crystalline Sponge

○Wei He[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The Univ. of Tokyo, 2. Institute for Molecular Science)

日本語
16:55 ~ 17:15

[E1121-2vn-04]

ペンタキス（アームドサイクレン）による金属イオンに対する位置選択的な配位と位置選択的な金属イオン置換：分子オセロ

○堀田 拓希[1]、池田 茉莉[2]、桑原 俊介[1]、幅田 揚一[1] (1. 東邦大、2. 千葉工大)

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19日(火) 13:00 ~ 15:30 E1123(11号館 [2階] 1123)

[E1123-2pm] 12. 有機化学―有機結晶・超分子化学

座長：加藤 研一、山科 雅裕

日本語
13:00 ~ 13:20
[E1123-2pm-01]

巨大熱膨張を実現するアントラセン結晶の創製

○樋野 優人[1]、松尾 匠[2]、是永 大樹[3]、関 朋宏[4]、林 正太郎[2] (1. 高知工大院工、2. 高知工大理工、3. 静大院総合科学、4. 静大理)

日本語
13:20 ~ 13:40
[E1123-2pm-02]

柔軟性アントラセン分子混晶の設計と組成制御：FRET型低損失光導波路の実現

○池田 浩貴[1]、松尾 匠[1]、林 正太郎[1] (1. 高知工科大学)

日本語
13:40 ~ 14:00
[E1123-2pm-03]

フッ素化π共役系分子結晶：光物性と機械特性の解析

○矢野 圭悟[1]、松尾 匠[2]、林 正太郎[2] (1. 高知工大院工、2. 高知工大理工)

英語
14:10 ~ 14:30
[E1123-2pm-04]

ボウル状分子の合成に基づく巨大π系の積層現象の研究

○尾仲 柚香[1]、池本 晃喜[1]、磯部 寛之[1] (1. 東京大学)

日本語
14:30 ~ 14:50
[E1123-2pm-05]

準安定なPd(II)環状錯体の速度論自己集合

○真田 直樹[1]、阿部 司[1]、竹内 啓介[1]、平岡 秀一 (1. 東大)

日本語
14:50 ~ 15:10
[E1123-2pm-06]

6位修飾α-CDからの超分子構造体の作製と脂肪酸エステルに対する選択的抽出能

○石田 遥也[1]、宮坂 萌々香[1]、Justine Kalaw、重光 孟[1]、木田 敏之[1] (1. 大阪大学)

英語
15:10 ~ 15:30
[E1123-2pm-07]

A Friedel–Crafts acylation way towards multi-bridge-functionalized large pillar[*n*]arenes

○Tanhao Shi[1], Shunsuke Ohtani[1], Kenichi Kato[1], Tomoki Ogoshi[1,2] (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-NanoLSI, Kanazawa Univ.)

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19日(火) 13:00 ~ 15:10 E1131(11号館 [3階] 1131)

[E1131-2pm] 12. 有機化学—有機結晶・超分子化学

座長：重光 孟、堀内 新之介

日本語

13:00 ~ 13:20

[E1131-2pm-01]

トリスポルフィリンとゲスト分子の多成分自己集合により制御される分子配列

○久野 尚之[1]、児玉 知輝[1,2]、灰野 岳晴[1,2] (1. 広島大院先進理工、2. 広島大 持続可能性に寄与するキラルノット超物質拠点)

英語

13:20 ~ 13:40

[E1131-2pm-02]

Controlling the helicity of dynamic helical tricobalt(III) cryptands by tuning the diamine chain length at the aperture

○Sk Asif Ikbal[1], Shigehisa Akine[1,2] (1. WPI-Nano Life Science Institute, Kanazawa University, 2. Graduate School of Natural Science and Technology, Kanazawa University)

日本語

13:40 ~ 14:00

[E1131-2pm-03]

液相・固相でのカゴ状金属酸化物{Mo_{132}}内部空間へのゲスト捕捉

○中宿 朱里[1]、申 栽燮[1]、村田 千夏[1]、七分 勇勝[1,2]、小西 克明[1,2] (1. 北大院環境、2. 北大院地球環境)

英語

14:10 ~ 14:30

[E1131-2pm-04]

球状錯体の一義空間を用いたタンパク質の単分子包接

○海老原 梨沙[1]、中間 貴寛[1]、守島 健[2]、杉山 正明[2]、矢木 真穂[3]、藤田 誠[1,3,4] (1. 東京院工、2. 京都大学複合原子力科学研究所、3. 分子科学研究所、4. 東大国際高等研)

英語

14:30 ~ 14:50

[E1131-2pm-05]

ゲスト分子による箱型自己集合カプセルの構造異性の再配列とその構造変換

○陳 弘燁[1]、堀内 新之介[1]、平岡 秀一[1] (1. 東大院総合文化)

英語

14:50 ~ 15:10

[E1131-2pm-06]

アミドの水素結合を利用した位置選択的Diels-Alder反応系の開発

○倪 汪斌[1]、木原 伸浩[1] (1. 神奈川大学)

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19日(火) 13:00 ~ 15:10 E1132(11号館 [3階] 1132)

[E1132-2pm] 13. 有機化学―反応機構・光化学・電気化学

座長：恩田 健、楊井 伸浩

日本語
13:00 ~ 13:20

[E1132-2pm-01]

サイクレン中心環状ペンタセン多量体の分子内一重項分裂

〇酒井 隼人[1]、水野 しおん[1]、羽曾部 卓[1] (1. 慶大理工)

日本語
13:20 ~ 13:40

[E1132-2pm-02]

二つの炭化水素置換基あるいはラジカル基をもつ安定発光ラジカルの発光特性

〇服部 陽平[1]、北島 稜大[2]、馬場 温[2]、山本 航平[2]、内田 欣吾[2] (1. 奈良先端大、2. 龍谷大)

日本語
13:40 ~ 14:00

[E1132-2pm-03]

テトラセノチオフェン連結体の合成と一重項分裂

〇岡本 大河[1]、酒井 隼人[1]、羽曾部 卓[1] (1. 慶大理工)

英語
14:10 ~ 14:30

[E1132-2pm-04]

C-F Functionalization by Defluorinative Coupling of Trifluoromethyl Compounds

〇Chung-Yang Dennis Huang[1], Amit Kumar Jaiswal[1], Priya Saha[1] (1. Hokkaido University)

日本語
14:30 ~ 14:50

[E1132-2pm-05]

フォノンの放出・吸収過程としての無輻射遷移

〇大田 航[1,2]、上島 基之[3]、春田 直毅[1,2]、佐藤 徹[1,2] (1. 京都大学福井謙一記念研究センター、2. 京都大学大学院工学研究科、3. 株式会社MOLFEX)

日本語
14:50 ~ 15:10

[E1132-2pm-06]

近赤外フェムト秒時間分解発光測定によるポルフィリンアレー自己集積化膜における励起ダイナミクスの研究

篠崎 建矢[1]、中村 美南海[2]、森末 光彦[2]、岩村 宗高[1]、〇野崎 浩一[1] (1. 富山大院理工、2. 京繊大院工芸)

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19日(火) 15:55 ~ 17:15 E1133(11号館 [3階] 1133)

[E1133-2vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：奥田 靖浩、内山 洋介

英語

15:55 ~ 16:15

[E1133-2vn-01]

ヒ素配位子を組込んだ発光性１次元配位高分子の開発

○菊池 一槙[1]、井本 裕顕[1]、中 建介[1] (1. 京工繊大院工芸)

英語

16:15 ~ 16:35

[E1133-2vn-02]

チオフェン類で縮巻したアルシニンの合成と構造・芳香族及び反応性の調査

○隅田 滉史[1]、井本 裕顕[1]、中 建介[1] (1. 京工繊大院工芸)

英語

16:35 ~ 16:55

[E1133-2vn-03]

2点型ハロゲン結合供与体によるクロライドの捕捉における架橋構造の影響

○加藤 雅之[1,2]、大塚 尚哉[1,2]、西岡 雪奈[1]、鈴木 敏泰[1]、椴山 儀恵[1,2] (1. 分子研、2. 総研大)

英語

16:55 ~ 17:15

[E1133-2vn-04]

全フッ素ハロゲン化ナフタレンの合成・結晶構造・分子間相互作用

○大塚 尚哉[1,2]、大田 陽野[1,2]、杉浦 聡[1]、杉山 晴紀[1,2]、鈴木 敏泰[1]、椴山 儀恵[1,2] (1. 分子研、2. 総研大)

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19日(火) 15:55 ~ 17:15 E1142(11号館 [4階] 1142)

[E1142-2vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：岩田 隆幸、高橋 慎太郎

英語
15:55 ~ 16:15
[E1142-2vn-01]

新規5-5縮環ヘテロ芳香環ビルディングブロックの開発

〇宮﨑 龍也[1]、髙田 郁人[1]、菊池 拓成[1]、大黒 裕哉[2]、鎌田 信[2]、湯川 猛史[2]、武藤 慶[1]、山口 潤一郎[1] (1. 早稲田大学、2. 武田薬品工業)

英語
16:15 ~ 16:35
[E1142-2vn-02]

高い安定性を有するヘキサキスピラゾリルエタンの合成と配位挙動

〇武政 雄大[1]、野崎 京子[1] (1. 東京大学大学院工学系研究科)

英語
16:35 ~ 16:55
[E1142-2vn-03]

窒素－ヘテロ原子結合への亜鉛カルベノイドの挿入による環拡大反応の開発

〇津田 正仁[1]、盛田 大輝[1,2]、中村 浩之[1,2] (1. 東工大生命理工、2. 東工大化生研)

英語
16:55 ~ 17:15
[E1142-2vn-04]

多環式インドール誘導体合成を指向したCO_2ラジカルアニオンによる不活性アルケンの触媒的アリールカルボキシル化

〇Suvankar Debbarma[1,2]、Saeesh R. Mangaonkar[1,2]、林 裕樹[1,2]、神名 航[3]、前田 理[1,2,3]、美多 剛[1,2] (1. 北大WPI-ICReDD、2. JST-ERATO、3. 北大院理)

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19日(火) 13:00 ~ 14:50 H933(9号館 [3階] 933)

[H933-2pm] 16. 天然物化学・ケミカルバイオロジー

座長：岡野 健太郎、吉田 将人

英語
13:00 ~ 13:20
[H933-2pm-01]

竹節人参エキスからの中枢神経系保護活性をもつモノグルコシルギンセノシド類であるG-Rh_2の効率的単離・精製法

○大島 禎生[1,2]、古山 浩子[1,3]、小縣 綾[2,4]、池沼 宏[2]、木村 泰之[1,2]、加藤 隆司[1,2]、鈴木 正昭[2,3] (1. 岐阜大学　大学院連合創薬医療情報研究科、2. 国立長寿医療研究センター、3. 岐阜大学　工学部、4. 岐阜医療科学大学)

英語
13:20 ~ 13:40
[H933-2pm-02]

カルバゾマイシンＡ–Ｄのグラムスケール合成

○馮 宇軒[1]、岡野 健太郎[1]、森 敦紀[1,2] (1. 神戸大院工、2. 神戸大膜セ)

日本語
13:50 ~ 14:10
[H933-2pm-03]

新規ヒドロインドール骨格の合成法の開発と全合成への応用

○堤 大洋[1]、山上 龍威[1]、早川 一郎[1] (1. 日大院総合基)

日本語
14:10 ~ 14:30
[H933-2pm-04]

Cristaxenicin A の合成研究

○城内 航[1]、角田 祐子[1]、加藤 港介[1]、谷野 圭持[2] (1. 北大院総化、2. 北大院理)

英語
14:30 ~ 14:50
[H933-2pm-05]

海洋シアノバクテリア由来天然物Lagunamide C の合成による構造訂正

○萩元 海月[1]、照屋 俊明[2]、吉田 将人[1]、木越 英夫[1] (1. 筑波大院　数理物質、2. 琉球大学　理工学研究科)

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19日(火) 13:00 ~ 15:40 H935(9号館 [3階] 935)

[H935-2pm] 16. 天然物化学・ケミカルバイオロジー

座長：大神田 淳子、堀 雄一郎

日本語

13:00 ~ 13:20

[H935-2pm-01]

天然変性領域のケミカルリデザインによる植物ホルモン関連転写因子の選択的阻害剤の開発

○高岡 洋輔[1]、劉 瑞琦[1]、李 奇[1]、上田 実[1,2] (1. 東北大院理、2. 東北大院生命科学)

英語

13:20 ~ 13:40

[H935-2pm-02]

無洗浄生細胞イメージングが可能な光スイッチング蛍光分子の開発

○鳥井 健司[1]、Benson Sam[4]、Vendrell Marc[4]、堀 雄一郎[2]、菊地 和也[1,3] (1. 大阪大学、2. 九州大学、3. 大阪大学免疫学フロンティア研究センター、4. エディンバラ大学)

英語

13:50 ~ 14:10

[H935-2pm-03]

生細胞イメージングのための疎水性バイオイソスター結合型蛍光プローブの開発

○上川 拓也[1]、橋本 明莉[2]、山崎 のぞみ[2]、足立 惇弥[1]、菊地 和也[2,3]、堀 雄一郎[1] (1. 九大院理、2. 阪大院工、3. 阪大免フロ)

英語

14:10 ~ 14:30

[H935-2pm-04]

Synthesis of *Alcaligenes faecalis* Lipid A Conjugates with Tumor-Associated Carbohydrate Tn Antigen Towards the Develoment of Self-Adjuvanting Vaccine

○Davie Kenneth[1], Yusuke Yamanaka[1], Atsushi Shimoyama[1,2], Koichi Fukase[1,2] (1. Department of Chemistry, Graduate School of Science, Osaka University, 2. Forefront Research Centre (FRC), Graduate School of Science, Osaka University)

英語

14:40 ~ 15:00

[H935-2pm-05]

分子内アザ電子環状反応を利用したがん細胞現地での天然物誘導体合成研究

○寺島 一輝[1]、プラディプタ アンバラ[1]、田中 克典[1,2] (1. 東京工業大学・物質理工学院・応用化学系、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室)

英語

15:00 ~ 15:20

[H935-2pm-06]

化学反応により生きた動物の体内を移動する糖鎖クラスター分子の開発

○山田 健士郎[1]、向峯 あかり[2]、中村 亜希子[2]、草苅 百合子[2]、プラディプタ アンバラ[1]、張 宗哲[1]、田中 克典[1,2] (1. 東京工業大学・物質理工学院・応用化学系、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室)

日本語

15:20 ~ 15:40

[H935-2pm-07]

抗がん活性ジテルペン配糖体はリン酸化依存的な天然変性蛋白質間相互作用を安定化する

〇荻野 菜々美[1]、室井 誠[2]、長田 裕之[2]、松本 健[2]、吉田 稔[2]、喜井 勲[1]、大神田 淳子[1] (1. 信州大学学術研究院 (農学系)、2. 理化学研究所　環境資源科学研究センター)

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19日(火) 9:00 ~ 11:30 H932(9号館 [3階] 932)

[H932-2am] 17. 生体機能関連化学・バイオテクノロジー

座長：愛場 雄一郎、岡村 秀紀

日本語

9:00 ~ 9:20

[H932-2am-01]

認識領域をずらしたparallel型PNAによる2本鎖DNAへのインベージョン

○望月 直哉[1]、柴田 将成[1]、愛場 雄一郎[1]、伊藤 公太[1]、有安 真也[1]、荘司 長三[1] (1. 国立大学法人東海国立大学機構名古屋大学)

日本語

9:20 ~ 9:40

[H932-2am-02]

ホスト–ゲスト相互作用を利用した遺伝子発現制御法の開発

○矢尾 健行[1,2]、岡村 秀紀[1,2]、永次 史[1,2] (1. 東北大多元研、2. 東北大院理)

英語

9:40 ~ 10:00

[H932-2am-03]

環状化オリゴDNAによる擬ロタキサン形成とその形成加速へのアプローチ

○桑原 和貴[1,2]、鬼塚 和光[1,2]、矢島 さやか[1,2]、山野 雄平[1]、永次 史[1,2] (1. 東北大多元研、2. 東北大院理)

英語

10:10 ~ 10:30

[H932-2am-04]

ボラノホスフェートDNAのブロック合成法の確立

○高橋 裕平[1]、加藤 樹[1]、佐藤 一樹[1]、和田 猛[1] (1. 東京理科大学)

英語

10:30 ~ 10:50

[H932-2am-05]

人工核酸L-*α*TNAの長鎖伸長反応を目指したケミカルライゲーションの反応機構解析

○沖田 ひかり[1]、村山 恵司[1]、浅沼 浩之[1] (1. 名大院工)

英語

10:50 ~ 11:10

[H932-2am-06]

New Data Science in Nucleic Acids Chemistry (10): Quantitative analysis for factors affecting i-motif formation in living cells estimated by the pseudo-cellular system

○Kun Chen[1], Hisae Tateishi-Karimata[1], Naoki Sugimoto[1,2] (1. Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, 2. Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University)

英語

11:10 ~ 11:30

[H932-2am-07]

核酸化学のNew Data Science (11): G-四重らせんとi-モチーフ構造の形成を介したがん細胞内における転写制御機構の解明

○建石 寿枝[1]、川内 敬子[2]、凌 一葦[3]、奥田 修二郎[3,4]、杉本 直己[1,2] (1. 甲南大学　先端生命工学研究所（FIBER)、2. 甲南大学　フロンティアサイエンス研究科(FIRST)、3. 新潟大学医学部メディカルAIセンター、4. 新潟大学医歯学総合)

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19日(火) 9:00 ~ 11:00 H936(9号館 [3階] 936)

[H936-2am] 17. 生体機能関連化学・バイオテクノロジー

座長：秋葉 宏樹、村岡 貴博

日本語
9:00 ~ 9:20
[H936-2am-01]

立体構造情報に基づいた抗原テンプレート反応の開発

○秋葉 宏樹[1,2]、西山 健太郎[1]、永田 諭志[2]、津本 浩平[2,3]、鎌田 春彦[1,2]、大野 浩章[1,2] (1. 京大院薬、2. 医薬健栄研、3. 東大院工)

日本語
9:20 ~ 9:40
[H936-2am-02]

光操作のための小分子光スイッチ結合性人工抗体の創製

○宮崎 友輝[1]、藤野 公茂[2]、吉井 達之[1]、舟根 守[2]、村田 直哉[2]、キムグエン チュン[2]、田原 海[1]、吉川 優[1]、深谷 菜摘[1]、長門石 曉[4]、津本 浩平[4]、林 剛介[2]、村上 裕[2,3]、築地 真也[1] (1. 名工大院工、2. 名大院工、3. 名大未来ナノ、4. 東大院工)

英語
9:40 ~ 10:00
[H936-2am-03]

環状ポリアミン配位子を有するジスルフィド化合物を利用した酸化的タンパク質フォールディング

○森 圭太[1]、村岡 貴博[1,2] (1. 農工大院工、2. KISTEC)

日本語
10:00 ~ 10:20
[H936-2am-04]

アントラニル酸骨格を有するPAI-1阻害剤の合成、阻害活性評価と蛍光特性の利用

○濱田 悠菜[1]、川口 真一[1]、小川 昭弥[2]、宮田 敏男[3] (1. 佐賀大、2. 大阪公立大、3. 東北大)

日本語
10:20 ~ 10:40
[H936-2am-05]

ランタノイドイオン存在下における*Methylosinus trichosporium* OB3bのグリセロールによる毒性メカニズム

○椎名 渉[1]、伊藤 栄紘[1]、蒲池 利章[1] (1. 東京工業大学)

英語
10:40 ~ 11:00
[H936-2am-06]

Dramatic enhancement of cytochrome c catalytic activity associated with a Rh coordination cage

○Benjamin Le Ouay[1], Yuri Kanzaki[1], Purna Kanta Boruah[1], Masaaki Ohba[1] (1. Kyushu University)

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19日(火) 15:55 ~ 16:55 H931(9号館 [3階] 931)

[H931-2vn] 17. 生体機能関連化学・バイオテクノロジー

座長：中田 栄司、那須 雄介

日本語
15:55 ~ 16:15

[H931-2vn-01]

細胞内代謝を可視化するバイオセンサーの開発

○那須 雄介[1,2]、上條 由貴[1]、ロバート キャンベル[1] (1. 東京大学、2. 科学技術振興機構)

日本語
16:15 ~ 16:35

[H931-2vn-02]

チオールを用いたカップルドアッセイに基づく血液中１分子エステラーゼ活性計測技術の開発

請川 達也[1]、○小松 徹[1]、箕田 麻弥乃[1]、浦野 泰照[1] (1. 東京大学)

英語
16:35 ~ 16:55

[H931-2vn-03]

DNAナノ構造体で構築した人工コンパートメントでの酵素カスケード反応

○林 鵬[1]、楊 輝[2]、Zhang Shiwei[1]、中田 栄司[1]、森井 孝 (1. 京大 エネルギー理工学研究所、2. 京大 大学院エネルギー科学研究科)

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19日(火) 15:55 ~ 17:15 H934(9号館 [3階] 934)

[H934-2vn] 17. 生体機能関連化学・バイオテクノロジー

座長：上田 善文、仲本 正彦

日本語
15:55 ~ 16:15
[H934-2vn-01]

可視光応答性アゾベンゼンを有するハイドロゲル足場の作製とインテグリンを起点とした三次元メカノトランスダクションへの応用

○本間 健太[1]、宮国 樹[1]、松崎 典弥[1] (1. 阪大院工)

日本語
16:15 ~ 16:35
[H934-2vn-02]

高分子間生体直交性反応による膜型酵素多価リガンドのin situ合成とがん細胞増殖阻害

○仲本 正彦[1]、坂本 蓮太郎[1]、木場 勇希[1]、松崎 典弥[1] (1. 阪大院工)

日本語
16:35 ~ 16:55
[H934-2vn-03]

ホスファチジルイノシトール3,4,5-三リン酸(PIP3)を光制御するツールの開発と応用

○上田 善文[1] (1. 国立感染症研究所)

日本語
16:55 ~ 17:15
[H934-2vn-04]

ゴースト赤血球を利用した化学反応場の構築

○越山 友美[1]、坂本 大芽[1] (1. 立命館大学)

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19日(火) 15:55 ~ 17:15 D341(3号館 [4階] 341)

[D341-2vn] 18. 高分子

座長：岸本 直樹、呉羽 拓真

日本語

15:55 ~ 16:15

[D341-2vn-01]

ボトルブラシ様ポリマーを架橋した高分子ゲルの構造物性制御

難波 恵汰[1]、西 太一[1]、若山 佑香[1]、平泉 冴響[1]、○呉羽 拓真[1] (1. 弘前大学大学院)

英語

16:15 ~ 16:35

[D341-2vn-02]

酸化インジウムスズ電極上に生やしたポリ（４-ビニルピリジンービオロゲン）共重合体ブラシによる電気化学的濡れ性制御

○周 泓遥[1]、李 浩睦[1]、山田 鉄兵[1] (1. 東京大学)

英語

16:35 ~ 16:55

[D341-2vn-03]

量子化学計算と分子動力学シミュレーションの統合：有機金属触媒による熱硬化性ポリマー形成のための新しいアプローチ

○白 玉焜[1]、岸本 直樹[1]、菊川 豪太[2] (1. 東北大院理、2. 東北大流体研)

英語

16:55 ~ 17:15

[D341-2vn-04]

Mild Catalytic Degradation of Crystalline Polyethylenes in Solid State Assisted by Carboxylic Acid Groups

○Bin Lu[1], Kohei Takahashi[1], Jian Zhou[2], Shintaro Nakagawa[2], Naoko Yoshie[2], Kyoko Nozaki[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo, 2. Inst. of Industrial Sci., The Univ. of Tokyo)

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19日(火) 15:55 ~ 17:15 A1443(14号館 [4階] 1443)

[A1443-2vn] 19. コロイド・界面化学

座長：吉原 栄理佳、金原 数

日本語

15:55 ~ 16:15

[A1443-2vn-01]

硬水を利用した内部オレフィンスルホン酸塩のベシクル形成

○菅原 規[1]、市橋 春奈[1]、津村 加奈[1]、宮崎 敦史[1]、坂井 隆也[1] (1. 花王（株）)

英語

16:15 ~ 16:35

[A1443-2vn-02]

塩橋により形成されたベシクル型人工組織の運動性

○小島 知也[1]、野口 雄太郎[1]、朝倉 浩一[1]、伴野 太祐[1] (1. 慶應義塾大学)

英語

16:35 ~ 16:55

[A1443-2vn-03]

糖ペプチドの*in situ*合成を応用した超分子ヒドロゲルの創製とその生体応用

○杉浦 進太郎[1]、新谷 勇喜[1]、東 小百合[2]、池田 将[1,3,4] (1. 岐阜大院連合創薬、2. 岐阜大高等研究院、3. 岐阜大COMIT、4. 岐阜大iGCORE)

英語

16:55 ~ 17:15

[A1443-2vn-04]

液晶性を示す安息香酸フェニル誘導体で形成した有機ゲルの分光学と計算化学的手法による構造解析

○松本 健太[1]、山口 潤也[1]、金只 晃太郎[1]、遠藤 唯[1]、初田 優里[1]、森田 由紀[1]、岡本 浩明[1] (1. 山口大学)

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19日(火) 15:55 ~ 17:15 🏛 C442(4号館 [4階] 442)

[C442-2vn] 20. 材料化学—基礎と応用

座長：吉尾 正史、中西 尚志

英語

15:55 ~ 16:15

[C442-2vn-01]

キラルなアルキル–π分子液体を媒体とする高濃度πゲル

○竪山 瑛人[1,2]、山中 正道[3]、中西 尚志[1,2] (1. 北大、2. 物質・材料研究機構、3. 明治薬大)

日本語

16:15 ~ 16:35

[C442-2vn-02]

フルオレノン系ドナー・アクセプター・ドナー分子からなる刺激応答性超分子ゲル

○山田 翔太[1]、鈴木 真緒[1]、関 淳志[1,2]、青木 健一[1,2] (1. 東理大院、2. 東理大)

日本語

16:35 ~ 16:55

[C442-2vn-03]

ゲル-ゲル界面のデザインによる新奇異方性ハイドロゲルの開発

○髙橋 知大[1]、佐野 航季[1,2] (1. 信州大、2. JSTさきがけ)

日本語

16:55 ~ 17:15

[C442-2vn-04]

イオン伝導液晶ゲルの作製とアクチュエータ機能

○吉尾 正史[1,2,3]、諏訪 俊一[3,1] (1. 国立研究開発法人物質・材料研究機構、2. JSTさきがけ、3. 北海道大学大学院)

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19日(火) 15:55 ~ 17:15 C443(4号館 [4階] 443)

[C443-2vn] 20. 材料化学—基礎と応用

座長：大山 陽介、武藤 克也

日本語

15:55 ~ 16:15

[C443-2vn-01]

ビナフチル架橋ジベンゾオキセピノイミダゾール二量体の逆フォトクロミズム

○八木 詩織[1]、阿部 二朗[1] (1. 青山学院大)

日本語

16:15 ~ 16:35

[C443-2vn-02]

ヘキサアリールビイミダゾールとターアリーレンの特徴を有する新規フォトクロミック分子の開発

○武藤 克也[1]、中嶋 琢也[1] (1. 大阪公立大学)

英語

16:35 ~ 16:55

[C443-2vn-03]

熱閉環反応を示すアザジアリールエテンのフォトクロミック反応挙動

○濱谷 将太[1]、北川 大地[1]、小畠 誠也[1] (1. 阪公大院工)

日本語

16:55 ~ 17:15

[C443-2vn-04]

D-A型ピリジニウム色素のオルガノハロゲノクロミズムに及ぼすカウンターアニオンの影響

○小塚 訓平[1]、今任 景一[1]、大山 陽介[1] (1. 広大院先進理工)

アカデミックプログラム［Ｂ講演］｜22. 資源利用化学・環境・グリーンケミストリー：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 16:55 A1455(14号館 [5階] 1455)

[A1455-2vn] 22. 資源利用化学・環境・グリーンケミストリー

座長：佐川 拓矢、大久保 敬

日本語

15:55 ~ 16:15

[A1455-2vn-01]

異性化による*N*-アセチルマンノサミンの合成とその触媒的変換反応

○佐川 拓矢[1]、長田 侑大[1]、橋詰 峰雄[1] (1. 東京理科大学)

日本語

16:15 ~ 16:35

[A1455-2vn-02]

バイオガスに含まれるメタンの二酸化塩素光酸化によるギ酸・メタノール合成

○大久保 敬[1,2]、平松 久美子[2]、板橋 勇輝[2] (1. 阪大高等共創研、2. 阪大先導的学際研)

日本語

16:35 ~ 16:55

[A1455-2vn-03]

有機酸によるリグノセルロースの可溶化における水の影響

○中川 由佳[1,2]、橋爪 知弘[1,2]、渡辺 隆司[1,3] (1. 京都大学バイオマスプロダクトツリー産学共同研究部門、2. 株式会社ダイセル、3. 京都大学生存圏研究所)

アカデミックプログラム［Ｂ講演］｜01. 化学教育・化学史：口頭Ｂ講演

2024年3月19日(火) 14:10 ~ 15:10 A1456(14号館 [5階] 1456)

[A1456-2pm] 01. 化学教育・化学史

座長：伊藤 眞人、福本 晃造

日本語

14:10 ~ 14:30

[A1456-2pm-01]

菜種油の迅速けん化法とその授業実践

○小原 孝昭[1]、酒井 権一[2]、網本 貴一[3] (1. 有限会社NSコスメ、2. 香川県立三本松高等学校、3. 広島大院人間社会科学)

日本語

14:30 ~ 14:50

[A1456-2pm-02]

教員養成用実験学習プログラム:反応速度に関する概念の理解

○細江 剛史[1]、生尾 光[2]、國仙 久雄[2] (1. 東京学芸大学大学院連合学校教育学研究科、2. 東京学芸大学教育学部)

日本語

14:50 ~ 15:10

[A1456-2pm-03]

中等教育としての高専の一般教育理科実験－化学系学科の改組とグローバル教育－

○内山 弘美[1] (1. 茗渓学園高等学校 科学研究指導員)

菜種油の迅速けん化法とその授業実践

㈲NS コスメ[1]・香川県立三本松高等学校[2]・広島大院人間社会科学[3]）○小原孝昭[1]・酒井権一[2]・網本貴一[3]

Rapid Saponification of Rapeseed Oil and its Practical Application in the Classroom

([1]*NS COSME CO., LTD*, [2]*Kagawa Prefectural Sanbonmatsu High School,* [3]*Graduate School of Human and Social Sciences, Hiroshima University*) ○Takaaki Obara,[1] Ken-ichi Sakai,[2] Kiichi Amimoto[3]

In general, the reaction rate of fat and oil saponification is slow, while using dipropylene glycol as a solvent accelerated the reaction up to 500 times faster than without the use of dipropylene glycol. In this work, we describe the soap preparation from rapeseed oil using this rapid saponification method, and also report the results of a practical class at a senior high school.

Keywords：Saponification; Fat and Oil; Dipropylene Glycol; Classroom Practice

高等学校化学において，反応速度を高める因子として，温度，濃度（圧力），溶媒親和性，および触媒が取り上げられている 1)。油脂（菜種油）に対する水酸化物イオン OH^- によるけん化反応では，上記のうちの温度を上昇させることで菜種油と OH^- とを衝突させて反応速度を高めるが，菜種油と OH^- を含む水溶液との混和性がよくないため反応速度が一般に遅く，加熱を開始して 1 時間を経過しても液体状の粘性物のままである（Fig. 1 左）。他方，菜種油と 50%水酸化ナトリウム水溶液の双方を溶かすことのできるジプロピレングリコール（DPG）を少量加えることで，溶媒親和性を高めてけん化反応を行うと，室温でも菜種油と OH^- との衝突現象が常に起きるため，発熱しながら反応が迅速に完結し，20 分程度で固形の生成物が得られた（Fig. 1 右）2)。この迅速けん化法を用いることで，通常の条件の 500 倍に匹敵するけん化反応の加速効果が得られ，加熱に伴う飛散などを避けて石けんを安全に作製することができる。

Fig. 1 けん化反応生成物の状態。(左) DPG を添加せずに加熱開始 1 時間経過後，(右) DPG を添加して 20 分撹拌後。

迅速けん化法による石けん作製の教育現場での適用性を検討する目的で，高等学校での授業実践を行った。生徒実験では，石けんを 1 時限内に得ることができて，通常授業の中で行うことのできる実験としての本教材の有用性が示された。また，化学に対する興味・関心に関するアンケート調査において，好感度が授業実践の前後で大きく向上したことからも，本教材の有効性がうかがえた（Fig. 2）。

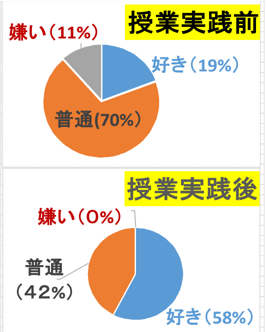


Fig. 2 授業実践の前後における化学に対する興味・関心の変容。

1) 辰巳敬ほか，化学，数研出版(2023).
2) 小原孝昭，石鹸の製造方法，Patent No. 7038271 (2020).

教員養成用実験学習プログラム：反応速度に関する概念の理解

（学芸大院教育[1]・学芸大教育[2]）〇細江 剛史[1]・生尾 光[2]・國仙 久雄[2]

Experimental Learning Program for Pre-service Teacher Education: A conceptual understanding of reaction rate

([1]*The United Graduate School of Education, Tokyo Gakugei University,* [2]*Faculty of Education, Tokyo Gakugei University*) 〇Takashi Hosoe[1], Akira Ikuo[2], Hisao Kokusen[2]

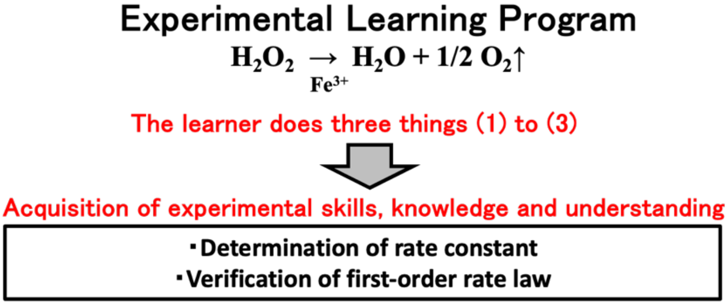
We are trying to develop the experimental learning program[1)] for teacher training on hydrogen peroxide decomposition reaction. There are (1) a plan of an appropriate experimental procedure to obtain the reaction rate, (2) obtain the time course of hydrogen peroxide concentration by titration, and calculation of its reaction rate, (3) calculation of apparent activation energy by experiment with changing temperature.

The program was practiced and conducted a survey on the degree of comprehension of the concept of "apparent activation energy". Based on the results, when trying to improve the text using the image diagram, the degree of comprehension became high. Students who took physics and chemistry in high school science tended to have a higher level of understanding than those who took biology and chemistry. In the learners' understanding of the reaction rate derivation of the activation energy, a connection with mathematical skills was seen.

Keywords: pre-service teacher education; experimental learning program; reaction rate; hydrogen peroxide

過酸化水素分解反応を題材とした教員養成用実験学習プログラム [1)]の開発を行っている．学習者は(1)反応速度を求めるための適切な実験方法の計画, (2)滴定による過酸化水素濃度の経時変化の測定および反応速度の算出, (3)温度を変えた実験による見かけの活性化エネルギーの算出を行う．

プログラム試行後，反応速度に関する概念「見かけの活性化エネルギー」に対する理解度について調査を行った．イメージ図を用いたテキストの改善により理解度が高まった．高等学校理科において物理・化学を履修した学生の方が，生物・化学を履修した学生よりも理解度が高い傾向が示された．活性化エネルギーの導出に対する学習者の概念の理解において，数学の技能との関連が窺われた．



Experimental Learning Program

$$\mathrm{H_2O_2} \xrightarrow[\mathrm{Fe^{3+}}]{} \mathrm{H_2O} + 1/2\ \mathrm{O_2}\uparrow$$

The learner does three things (1) to (3)

Acquisition of experimental skills, knowledge and understanding

・Determination of rate constant
・Verification of first-order rate law

1) Design of Chemistry Laboratory Course. I. Instruction of "Reaction Rate" Experiment. Teratani, S., *Bull. Tokyo Gakugei Univ. Sect.4.* **1990**, *42*, 35-59.

日本化学会 第104春季年会 (2024)

中等教育としての高専の一般教育理科実験
ー化学系学科の改組とグローバル教育ー

（茗渓学園高等学校科学研究指導員[1]）〇内山　弘美[1]

Practical Report of Science Experiment as General Education in Secondary Education of Kosen
-Reform of Department of Chemistry and Global Education-

([1] *Meikei High school*)　○Hiromi Uchiyama[1]

National Kosen is consist of 3years technical high school (secondary education) and 2years technical school(post-secondary education). This presentation focuses on the secondary education of Kosen, and reports the science experiment as general education (outside of technical education).Department of Chemistry in that school was integrated with other departments by reform, and the science experiment for 1st year chemical students was closed. The reporter discoverd that experiment ,and teach it using English.This is Kosen's first attempt as global education, and students responses were good.

Keywords：　Reform of Department of Chemistry, Secondary Education, Science Experiment, Global Education

国立工業高等専門学校（以下、高専）は、3 年間の工業高等学校（中等教育）と 2 年間の工業専門学校（中等後教育）から構成されている。本報告では、中等教育に着目して、グローバル教育の視点を加えた、専門教育以外（一般教育）の理科教育実験の実践報告を行う。

高専の中等教育の課題は、①学習指導要領に準拠せず、②教員免許を持たない教員が教えていることである。そのため、物理・化学以外の一般教育理科（生物基礎・地学基礎）を、専門外の工学系教員（茨城高専では、原子力工学・材料工学等）が教えている。現代では、生物学は多くの工学分野に関連しており、生物基礎をきちんと学ぶことが必要である。この課題を解決するために、報告者は生物基礎の授業に、(1) 教科書と (2) 実験（顕微鏡観察）を導入した。

顕微鏡観察は、旧物質工学科 1 年生の実験でなされていたが、2017 年の改組で他学科との統合を機に、廃止された。報告者はその実験を掘り起こし、グローバル教育の視点から、英語で実践した。具体的には、1）準備教育：高校「生物」の発展的内容を含めた細胞、及び顕微鏡を、英語の専門用語で説明した。生物学の英語は難しく、居眠りする学生は殆どいなかった。生物学への興味を喚起させるために、生物専門の教員（化学系）にゲストとして、顕微鏡の使い方を英語で説明して頂いた。2) 実験当日：化学系の実験室の壁の掲示・黒板の説明、スライド・プリントを、英語で作成した。英語を学びながら、各グループで実験が行われた。

当該実験は、グローバル教育として、高専初の試みである。実験後のアンケートでは、「英語で顕微鏡の観察をして、面白かった。」という感想が多く、学生の反応は良好であった。また生物基礎教育の重要性が認識され、前述の生物専門の教員（化学系）が、次年度から生物基礎を担当することになった。本実験は、一般教育人材の発掘という点でも、大きな貢献をした。

1）理系学生のための教養教育としての科学リテラシーと社会リテラシー　―化学系科目を中心に―,
内山弘美・ 久保田真理・西村秀雄・立川明, 大学研究教育フォーラム京大要旨集, 2018
2）大学の教養教育における科学リテラシー - 化学教育を中心に - , 内山弘美・杉本孝作, 日本化学会春季大会要旨集, 2020
3）Global Life Science, 内山他, 茨城高専シラバス 2022 年度
4）高等教育政策研究から留学生教育・支援システムの構築をめざして, 内山弘美, 高専だより, 令和４年６月号
5）大学の教養教育及び高校「生物基礎」における生物学史の実践報告, 内山弘美, 生物学史研究, 2023

謝辞：本実験を実施する上で、大変お世話になりました茨城高専の化学系の教職員の方々に感謝致します。

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19日(火) 13:00 ~ 15:30 H937(9号館 [3階] 937)

[H937-2pm] 02. 理論化学・情報化学・計算化学

座長：吉田 悠一郎、堀 優太

英語

13:00 ~ 13:20

[H937-2pm-01]

第一原理計算を用いたプロトン伝導分子性結晶中のプロトン移動と分子運動の解析

○堀 優太[1]、小倉 浩樹[3]、出倉 駿[2]、森 初果[3]、重田 育照[1] (1. 筑波大学、2. 東北大学、3. 東京大学)

英語

13:20 ~ 13:40

[H937-2pm-02]

Comparison between a superconducting-type quantum computer and a trapped-ion-type quantum computer by the simulation of spin dynamics

Erik Lötstedt[1], ○Kaoru Yamanouchi[1,2] (1. School of Science, The Univ. of Tokyo, 2. Institute for Attosecond Laser Facility, The Univ. of Tokyo)

英語

13:40 ~ 14:00

[H937-2pm-03]

Time-dependent rovibronic wavefunction of H_2^+ by multiconfiguration theory

○Erik Lötstedt[1], Tsuyoshi Kato[1], Kaoru Yamanouchi[1,2] (1. School of Science, The University of Tokyo, 2. Institute for Attosecond Laser Facility, The University of Tokyo)

14:00 ~ 14:10

休憩

日本語

14:10 ~ 14:30

[H937-2pm-04]

効率的な量子計算に向けた短鎖長ポリエンの拡張ハバード模型構築

○吉田 悠一郎[1]、竹森 那由多[1,2]、水上 渉[1,3] (1. 阪大QIQB、2. 理研CEMS、3. 阪大院基礎工)

英語

14:30 ~ 14:50

[H937-2pm-05]

Electrolyte adsorption study on the different types of layered cathode surfaces of lithium-ion batteries with computational chemistry methods

○Attila Taborosi[1], Michihisa Koyama[1], Nobuyuki Zettsu[1] (1. Shinshu University)

英語

14:50 ~ 15:10

[H937-2pm-06]

可逆な化学反応ネットワークにおける準不可逆性の発現と経路選択

○高橋 聡[1]、阿部 司[1]、佐藤 啓文[2,3]、平岡 秀一[1] (1. 東京大学大学院総合文化研究科、2. 京都大学大学院工学研究科、3. 京都大学福井謙一記念研究センター)

🏷 英語

15:10 ~ 15:30

[H937-2pm-07]

改良型３次元離散コサイン変換と最大エントロピー法によるMg_3BN_3高圧相の精密電子密度分布解析についての研究

○平口 英夫[1] (1. （公）日本技術士会)

第一原理計算を用いたプロトン伝導分子性結晶中のプロトン移動と分子運動の解析

（筑波大学 [1]・東北大学 [2]・東京大学 [3]）○堀 優太 [1]・小倉 浩樹 [3]・出倉 駿 [2]・森 初果 [3]・重田 育照 [1]

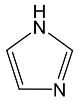
Theoretical analysis of proton transfer and molecular motion in proton-conducting molecular crystals using first-principle calculations

([1]*University of Tsukuba*, [2]*Tohoku University*, [3]*The University of Tokyo*) ○Yuta Hori,[1] Hiroki Ogura,[3] Shun Dekura,[2] Hatsumi Mori,[3] Yasuteru Shigeta[1]

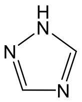
Some molecular crystals comprising acid–base pairs exhibit relatively high proton conductivities despite their crystalline nature; thus, the proton conduction mechanism of these crystals has garnered significant attention. We performed first-principles calculations to investigate the proton conduction mechanism in imidazolium succinate (Im-Suc) crystals and found that (1) the acid–base hydrogen bond structure, (2) rotational motion of molecules, and (3) intermolecular proton transfer contribute to the proton conduction.[1)] In this study, to understand the general proton conduction mechanism in acid-base molecular crystals, we performed first-principles calculations on imidazolium and 1,2,4-triazolium methanesulfonates. The analysis revealed that proton conduction occurs by rotational motion of molecules and intermolecular proton transfer as in Im-Suc. It was also suggested that the difference in pK_a between the acid and base affects the stability of the crystals, intermolecular proton transfer, and molecular rotational motion.

Keywords : Proton Conduction; First-Principles Calculation; Imidazole; Triazole; Methanesulfonic acid

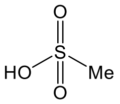
酸・塩基で構成される分子性結晶の中で、結晶でありながら比較的高いプロトン伝導性を示すものが報告されており、そのプロトン伝導機構に興味が持たれている。これまでに、コハク酸イミダゾリウム(Im-Suc)結晶中のプロトン伝導機構を調べるために第一原理計算による解析を行っており、(1)酸-塩基水素結合構造、(2)分子の回転運動、(3)分子間のプロトン移動がプロトン伝導に寄与していることを明らかにしている [1)]。本研究ではさらに酸塩基分子性結晶中のプロトン伝導機構の統一的な理解を目指すために、メタンスルホン酸イミダゾリウムおよび 1,2,4-トリアゾリウム中のプロトン伝導機構の考察に向け、第一原理計算による解析を行った。解析結果及び実験との比較により、Im-Suc 中と同様に分子の回転運動と分子間プロトン移動によりプロトン伝導が生じることが示された。また、酸塩基間の pK_a の差が結晶の安定性や分子間プロトン移動障壁、分子回転障壁に影響を与えていることが示唆された。



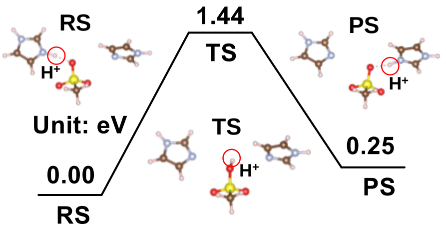
Imidazole



1,2,4-Triazole



Methanesulfonic acid



1) Y. Hori, S. Dekura, Y. Sunairi, T. Ida, M. Mizuno, H. Mori, and Y. Shigeta, *J. Chem. Phys. Lett.*, **2021**, *12*, 5390.

Comparison between a superconducting-type quantum computer and a trapped-ion-type quantum computer for the simulation of spin dynamics

([1]*School of Science, The University of Tokyo*, [2]*Institute for Attosecond Laser Facility, The University of Tokyo*) Erik Lötstedt,[1] ○Kaoru Yamanouchi[1,2]

Keywords: Quantum simulation, NISQ device, Heisenberg spin model

While accurate quantum computing of large molecules requires fault-tolerant quantum computers, there are already several types of noisy intermediate-scale quantum computers available to researchers. Given the many alternatives for practical quantum computing, it is worthy to compare the performances of different quantum computers.

We have simulated the time evolution of a three-site spin chain described by the Heisenberg XXX Hamiltonian[1] using two types of quantum computers: IBM's *ibm_prague*,[2] a superconducting-qubit type quantum computer having a prototype Heron processor, and Quantinuum's H1-1,[3] a trapped-ion type quantum computer. The time evolution is accomplished by the Suzuki-Trotter approximation,

$$|\psi(t)\rangle \approx \prod_{n=1}^{N} \exp\left(-i\frac{tH}{\hbar N}\right)|\psi(0)\rangle, \qquad (1)$$

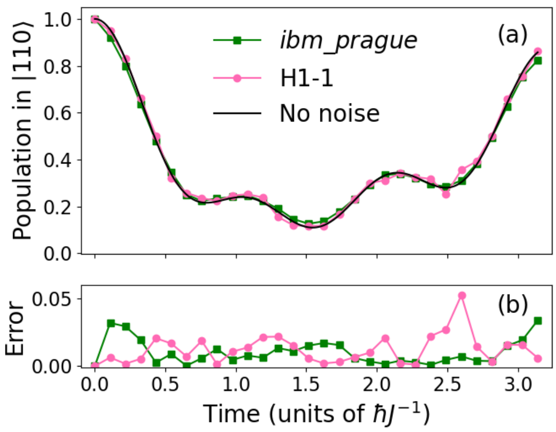


Figure 1. (a) Time-dependent population in the $|110\rangle$ state. (b) Error defined as $E = |p_{110} - p_{110}(\text{No noise})|$.

where H is the Hamiltonian, $|\psi(0)\rangle = |110\rangle$ is the initial state corresponding to the spin state $|{\downarrow\downarrow\uparrow}\rangle$ and $N = 8$ is the number of the Suzuki-Trotter steps. The short-time propagator, $\exp(-itH/\hbar N)$, is implemented as a quantum circuit having six CNOT gates. The time-dependent population $p_{110}(t) = |\langle 110|\psi(t)\rangle|^2$ in the state $|110\rangle$ is shown in Fig. 1. The curve for *ibm_prague* was obtained by applying the error suppression techniques of Pauli twirling, dynamical decoupling, and spurious-state discarding, while only spurious-state discarding was applied for H1-1. We can see in Fig. 1(a) that accurate spin-state populations can be obtained using both types of quantum computers. The error, defined as the averaged difference between the simulated population and the ideal and noise-free population is smaller than 0.05 for both devices as can be seen in Fig. 1(b). We conclude that both superconducting type and trapped-ion type quantum computers are promising devices for the simulation of time-dependent quantum systems.

References: 1) E. Lötstedt and K. Yamanouchi, *Chem. Phys. Lett.* **836**, 140975 (2024). 2) ibm.com/quantum, 3) quantinuum.com

Time-dependent rovibronic wavefunction of H_2^+ by multiconfiguration theory

([1]*School of Science, The University of Tokyo*, [2]*Institute for Attosecond Laser Facility, The University of Tokyo*) ○Erik Lötstedt,[1] Tsuyoshi Kato,[1] Kaoru Yamanouchi[1,2]

Keywords: Time-dependent multiconfiguration methods; Laser-molecule interaction

When molecules are exposed to an intense laser pulse, electronic, vibrational and rotational excitations as well as ionization proceed simultaneously. However, there are no efficient theoretical methods where all the electronic, vibrational, and rotational degrees of freedom are included in the simulation.

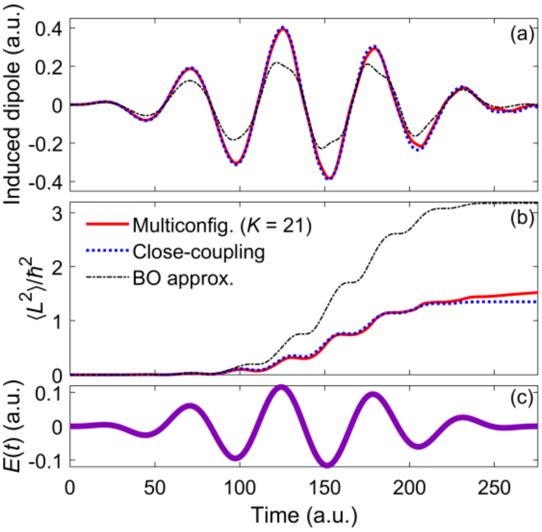


Figure 1. (a) Induced dipole moment, (b) expectation value of the total angular momentum squared, and (c) the laser field adopted in the simulation.

Here we show that the complete time-dependent rovibronic wave function of a molecule, including the three-dimensional motion of both electrons and nuclei, can be simulated using a time-dependent multiconfiguration method.[1] We apply the multiconfiguration method to H_2^+ and write the time-dependent wave function as

$$\Psi(\mathbf{r},\mathbf{R},t)=\sum_{i,j=1}^{K} C_{ij}(t)\phi_i(\mathbf{r},t)\chi_j(\mathbf{R},t) \qquad (1)$$

in the spherical coordinate system, where **r** is the electronic coordinate, **R** is the separation vector of the two protons, ϕ_i and χ_j are time-dependent orbitals, and C_{ij} are time-dependent expansion coefficients. We simulate the interaction of H_2^+ with an intense ultrashort laser pulse (2.4 fs, 400 nm, 5×10^{14} W/cm^2). As shown in Fig. 1, the curves for the induced dipole moment and the expectation value of the squared total angular momentum $\langle L^2\rangle/\hbar^2$ obtained by the multiconfiguration method agree well with those obtained by a reference close-coupling method.[2] On the other hand, as can also be seen in Fig. 1, when the standard two-state Born-Oppenheimer (BO) approximation is adopted, in which only the two lowest electronic $^2\Sigma_g^+$ and $^2\Sigma_u^+$ states are included, the induced dipole moment is suppressed in the peak regions of the laser field amplitude and $\langle L^2\rangle/\hbar^2$ is largely overestimated. These discrepancies can be ascribed to the omission of higher-lying excited states in the BO approximation. Our results show that time-dependent multiconfiguration methods are promising for the simulation of the simultaneous electronic, vibrational, and rotational excitation of molecules irradiated with an intense laser pulse.

1) T. Kato and K. Yamanouchi, *J. Chem. Phys.* **131**, 164118 (2009). 2) J. Feist et al., *Phys. Rev. A* **77**, 043420 (2008).

効率的な量子計算に向けた短鎖長ポリエンの拡張ハバード模型構築

（阪大 QIQB[1]・理研 CEMS[2]・阪大院基礎工[3]）○吉田 悠一郎[1]・竹森 那由多[1,2]・水上 渉[1,3]

Constructing extended Hubbard models of short polyenes toward efficient quantum computing

([1]*Center for Quantum Information and Quantum Biology, Osaka University*, [2]*Center for Emergent Matter Science, RIKEN,* [3]*Graduate School of Engineering Science, Osaka University*) ○Yuichiro Yoshida,[1] Nayuta Takemori,[1,2] Wataru Mizukami,[1,3]

A quantum computer is expected to reveal the electronic structure of a molecule that is challenging to unveil using its classical counterpart. The computation of excited states is relatively not easier than that of the ground state and maybe a meaningful task for a quantum computer. It can be considered that it is important to reduce the electronic structure Hamiltonian to the simple form as much as possible to utilize a quantum computer in the developing stage. In this research, toward efficient quantum computation, we construct extended Hubbard models of polyenes with short conjugation lengths using the *ab initio* downfolding method. As a result, the vertical excitation energies of our models are in good agreement with the experimental values and the results of the precise quantum chemical computations. We also discuss the quantum computational cost using our models and classically simulate the quantum computation of the excited states.

Keywords： *Quantum Chemistry; Quantum Computing; Conjugated System*

分子の電子状態には、現在のコンピュータでも計算が難しいものが多く存在する。量子コンピュータは、この問題に対する新たな手段として期待されている。中でも、励起状態計算は基底状態計算と比べ一般に難易度が高く、量子コンピュータの優位性が出やすい課題であると考えられている。一方で、開発途上の量子コンピュータは、ノイズの影響により複雑な演算を正確に行うことが難しく、量子ビット数にも制限がある。このため、分子の第一原理ハミルトニアンを直接扱うことは、単純な例を除き、現実的ではない。

この問題へのアプローチとして、分子の電子ハミルトニアンを、より単純な形式のモデルハミルトニアンへと還元する方法が考えられる。そこで本研究では、効率的な量子計算の実現に向けて、第一原理ダウンフォールディング法[1,2]の分子系への応用を試みた。対象系として短鎖ポリエン分子を選び、拡張ハバード模型を第一原理的に構築した。基底状態と励起状態の数値計算を通じて、このアプローチの有用性を検証した。

モデルハミルトニアンの厳密対角化により得られた励起エネルギーは、実験値や高精度量子化学計算の結果と概ね良く一致した。また、構築したモデルハミルトニアンを用いた場合の量子計算コストの評価や、量子計算のエミュレーションも行った。

[1] F. Aryasetiawan et al., *Phys. Rev. B* **2004**, *70*, 195104.
[2] K. Nakamura et al., *Comput. Phys. Commun.* **2021**, *261*, 107781.

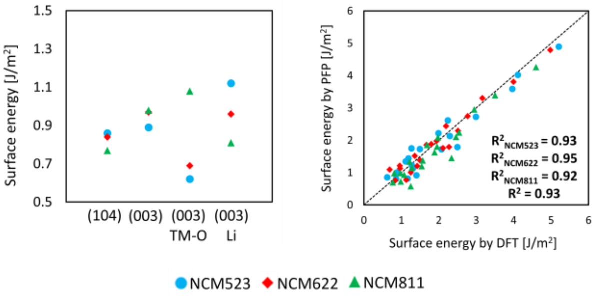
Electrolyte adsorption study on the different types of layered cathode surfaces of lithium-ion batteries with computational chemistry methods

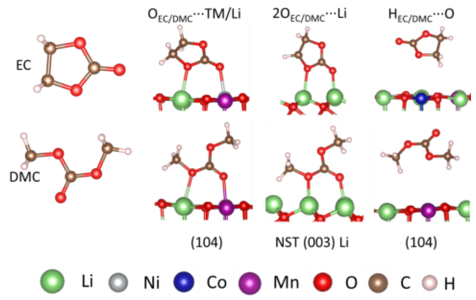
([1]*Research Initiative for Supra-Materials, Shinshu University*) ○ Attila Taborosi,[1] Michihisa Koyama,[1] Nobuyuki Zettsu,[1]

Keywords: lithium-ion batteries, layered cathode material, electrolyte adsorption, cathode electrolyte interface, computational chemistry

One of the most promising cathode materials for lithium-ion batteries (LIBs) is $LiNi_xMn_yCo_zO_2$ (NCM) with different composition of Ni, Co, and Mn in the transition metal (TM) layer. The performance of LIBs is strongly influenced by the properties of the solid electrolyte interface (SEI), which is formed by the reaction between the electrolyte and electrode surface. Understanding the first step of SEI formation, thus the adsorption of different electrolyte molecules either on the cathode or anode surface is crucial in the later examination of the decomposition of electrolyte and formation of SEI.

In our study we compared and analyzed the effect on the surface energies through changing the Ni content in the TM layer of NCM going from low to high Ni content (523, 622, 811) and to define the energetically preferable surface planes considering the synthetic conditions and stoichiometric (ST) and non-stoichiometric (NST) terminations with the usage of density functional theory (DFT). Considering the limitations during the electrolyte adsorption of the DFT method we applied Universal Neural Network Potential (UNNP), where the recreation of NNPs and datasets of each structure of interest is not necessary. We validated the UNNP based on the results of DFT such as the surface energies and TM/Li-O distances in the surface layers. We extended the investigation space and studied several initial adsorption structures of ethylene carbonate (EC) and dimethyl carbonate (DMC) for the energetically most preferable surfaces and the effect of Ni content and delithation on these adsorption configurations with UNNP method.





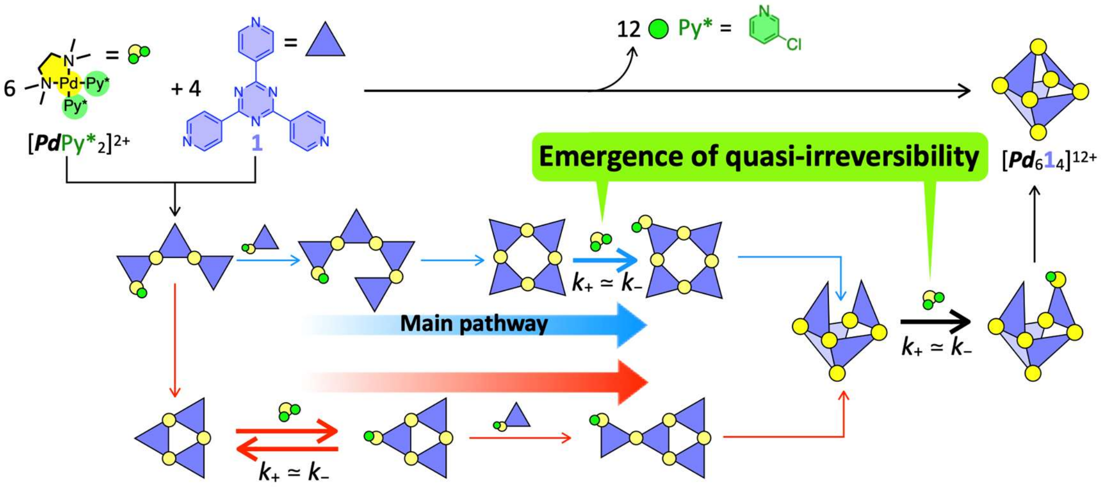
This work was supported by JST, CREST Grant Number JPMJCR21B3, Japan.

Emergence of Quasi-Irreversibility and Pathway Selection in Fully Reversible Chemical Reaction Networks

([1]*Graduate School of Arts and Sciences, The University of Tokyo*, [2]*Graduate School of Engineering, Kyoto University,* [3]*Fukui Institute for Fundamental Chemistry, Kyoto University*)
〇Satoshi Takahashi,[1] Tsukasa Abe,[1] Hirofumi Sato,[2,3] Shuichi Hiraoka[1]
Keywords: Molecular Self-Assembly; Chemical Master Equation; Kinetic Control

Consequence of chemical reactions represented with the network composed only of reversible elementary reactions is governed by thermodynamics, and thus kinetics and pathway selection have not been discussed well. However, in nature, unexpected metastable species called kinetic traps can be obtained, as in protein folding and molecular self-assembly. Understanding of their formation has been mainly explained by the kinetic stability of themselves, but in the cases with reversible elementary reactions alone, the direction to which each reaction proceeds is determined via adaptation to the surrounding environment, and the general idea of what principle is used to select the reaction pathway has not yet been established. In this study, we have clarified through numerical simulations that the emergence of quasi-irreversibility is the key to the pathway selection in fully reversible chemical reaction networks.

To see how the emergence of quasi-irreversibility leads to reaction pathway selection, we performed simulations in the network for $[\boldsymbol{Pd}_6\mathbf{1}_4]^{12+}$ truncated tetrahedron complex, whose self-assembly pathways can be classified into two groups. Pathway analysis revealed the main reaction pathway, showing an appearance of quasi-irreversibility in spite of almost the same rate constants for forward and backward processes ($k_+ \simeq k_-$). The elementary reaction on the other path with the same parameters behaved reversibly, with the direction reversed over time. It was found that the behavior of each elementary reaction is determined by the network structure, not by the rate constant alone.[1]



1) S. Takahashi, T. Abe, H. Sato, S. Hiraoka, *Chem* **2023**, *9*, 2971–2982. 10.1016/j.chempr.2023.06.015.

Electron Density Distribution analysis of Mg_3BN_3 High Pressure Phase via Modified Three-Dimensional Discrete Cosine Transform and Maximum Entropy Method

([1]The Institution of Professional Engineers, Japan) ○Hideo Hiraguchi [1]

Keywords: Mg_3BN_3 (H), Modified Discrete Cosine Transform, Maximum Entropy Method

In the previous research, it turned out that the electron density distribution of Mg_3BN_3(H)[1)-3)] (Orthorhombic *Pmmm*) could be calculated via the Maximum Entropy method (ME method[5),6)]) incorporating the normal 3 dimensional Discrete Cosine Transform (3D-DCT)[7)] for the crystal having both symmetrical planes and an center of symmetry. Therefore, in this paper, the ME method incorporating the 3D-Modified DCT (3D-MDCT) [4)] for the crystal having both a glide plane and a center of symmetry was prepared. Then a comparison between the maps (73×73×145) via the ME method incorporating the 3D-DCT (Fig.1) and 3D-MDCT (Fig.2) was performed. As a result, the obtained maps of Fig.1 and Fig.2 are almost the same with each other (Starting map : Normal DCT map replacing negative values for 0.1 /Å, Constraint function *C* : 4.0). However, in Table 1, $F_{\text{DCT-ME}}(hkl)$ and $F_{\text{MDCT-ME}}(hkl)$ were partially different in spite of the same *C*.

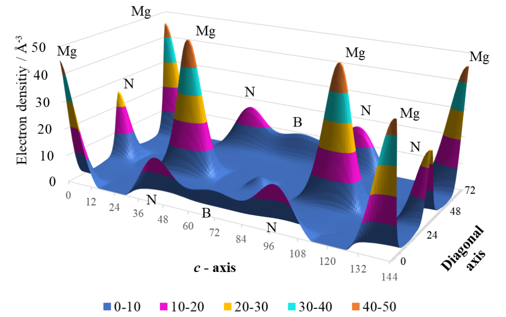


Fig. 1 An Electron density distribution map calculated by Maximum Entropy method incorporationg normal 3D-DCT

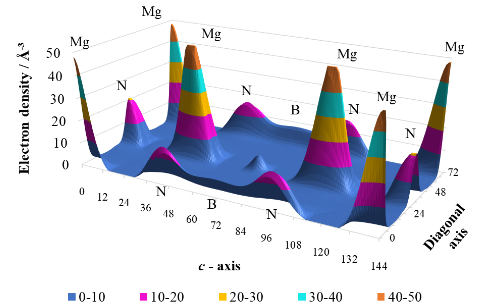


Fig. 2 An Electron density distribution map calculated by Maximum Entropy method incorporationg 3D-Modified DCT

Table 1 Comparison between original cyrstal structure factors [$F_{\text{org}}(hkl)$], DCT-ME crystal structure factors [$F_{\text{DCT\_ME}}(hkl)$] and Modified DCT-ME crystal structure factors [$F_{\text{MDCT\_ME}}(hkl)$]

	$F(hkl)$	$F_{\text{org}}(hkl)$ (B=1) Software:VESTA	$F_{\text{DCT\_ME}}(hkl)$	$F_{\text{MDCT\_ME}}(hkl)$	
1	F(000)	62.00	62.00	62.00	
2	F(001)	4.90	6.37	4.38	▲
3	F(002)	-6.72	-4.47	-7.87	▲
4	F(010)	-1.04	2.80	-1.05	▲ *
5	F(100)	-1.07	2.78	-1.08	▲ *
6	F(011)	-1.38	-0.62	-1.32	▲
7	F(101)	-1.33	-0.59	-1.08	▲
8	F(003)	24.84	21.74	24.09	▲
9	F(012)	18.26	16.10	13.88	◆
10	F(102)	18.22	16.11	13.85	◆
11	F(110)	38.55	38.60	37.82	◆
12	F(004)	24.60	20.72	20.04	◆
13	F(113)	18.42	15.63	17.17	▲
14	F(020)	29.97	34.04	32.46	▲
15	F(200)	29.63	33.85	32.31	▲
16	F(114)	20.07	15.88	15.06	◆

▲ : $F_{\text{MDCT\_ME}}(hkl)$ is nearer than $F_{\text{DCT\_ME}}(hkl)$. * : phase mismach.

◆ : $F_{\text{DCT\_ME}}$(hkl) is nearer than $F_{\text{MDCT\_ME}}$(hkl). Each σ is set as 5% of Forg.

1) H.HIRAGUCHI, O.SAKATA, H.HASHIZUME, A.TAKENAKA, O.FUKUNAGA.(1990). *J. Cryst. Soc.Jp*. OB-11, 32. 2) H. HIRAGUCHI, H. HASHIZUME, O. FUKUNAGA, A. TAKENAKA, M. SAKATA.(1991). *J. Appl. Cryst.* 24. 3) H. HIRAGUCHI, H. HASHIZUME, S. SASAKI, S. NAKANO, O. FUKUNAGA. (1993). *Acta Cryst.* B49. 4)H. HIRAGUCHI, (2021).*J.Appl.Cryst.* 5) M. Sakata & M. Sato, *Acta Cryst*. A46, 263-270, 1990. 6) M. Sakata, R. Mori, S. Kumazawa, M. Takata & H. Toraya, *J. Appl. Crvst.* 23, 526-534, 1990. 7) H.Hiraguchi, IUCr2023 in Melbourne.

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19日(火) 13:00 ~ 15:40 A1452(14号館 [5階] 1452)

[A1452-2pm] 03. 物理化学—構造

座長：佐藤 和信、山添 誠司

日本語
13:00 ~ 13:20

[A1452-2pm-01]
Pd/Cu(111)単原子合金モデル触媒におけるCO_2水素化反応の準大気圧*in-situ*分光研究

○長田 渉[1]、尾崎 文彦[1]、堀尾 眞史[1]、田中 駿介[1]、向井 孝三[1]、小板谷 貴典[2]、山本 達[3]、松田 巌[1]、吉信 淳[1] (1. 東京大学物性研究所、2. 京都大学、3. 東北大学)

日本語
13:20 ~ 13:40

[A1452-2pm-02]
二成分イオン液体/電極界面におけるアニオン吸脱着の過電圧要因の研究

○岩橋 崇[1]、周 尉[2]、Kim Doseok[3]、大内 幸雄[1] (1. 東京工業大学、2. 上海大学、3. Sogang大学)

日本語
13:40 ~ 14:00

[A1452-2pm-03]
オペランドマルチモーダル計測による燃料電池Pt電極触媒上の吸着酸素種の挙動解明

○三輪 寛子[1]、吉田 健文[2]、金子 拓真[3]、佐々木 岳彦[4]、東 晃太朗[3]、坂田 智裕[1]、関澤 央輝[3]、宇留賀 朋哉[1,3]、岩澤 康裕[1] (1. 電通大学、2. 和歌山大学、3. 高輝度光科学研究センター、4. 東大)

14:00 ~ 14:20

休憩

日本語
14:20 ~ 14:40

[A1452-2pm-04]
インジウムナノ粒子による深紫外域局在プラズモンと吸着分子の相互作用

長塚 直樹[1]、松口 諒斗[1]、奥山 弘[1]、安池 智一[2]、小板谷 貴典[1]、○渡邉 一也[1] (1. 京都大学、2. 放送大学)

日本語
14:40 ~ 15:00

[A1452-2pm-05]
クラウンエーテル環状分子膜を使ったフェロセン単分子STM観察と二次元結晶成長

○山田 豊和[1] (1. 千葉大学)

日本語
15:00 ~ 15:20

[A1452-2pm-06]
氷よりも疎な疎水性空間中の微小水に対するトポロジカル解析からの構造決定

○杉山 泰啓[1]、中野 智康[2]、飯山 拓[3]、二村 竜祐[3] (1. 信州大院医理工、2. ㈱アドール、3. 信大理)

日本語
15:20 ~ 15:40

[A1452-2pm-07]

[有機1次元細孔物質-ビタミンE]包接体型分子カプセルの物理化学的性質

○小林 広和[1]、本多 英彦[1]、山本 雅人[1]、岩堀 史靖[2]、野口 真理子[2]、藤森 裕基[2]、小田中 友紀[3]、荻野 玲奈[4]、柴田 陽[4] (1. 昭和大学富士吉田教育部、2. 日本大学文理学部、3. 昭和大学薬学部、4. 昭和大学歯学部)

In-situ spectroscopic study of CO_2 hydrogenation on the Pd/Cu(111) single atom model catalyst under near-ambient conditions

([1]*The Institute for Solid State Physics, The University of Tokyo*, [2]*Kyoto University,* [3]*Tohoku University*) ○Wataru Osada[1], Fumihiko Ozaki[1], Masafumi Horio[1], Shunsuke Tanaka[1], Kozo Mukai[1], Takanori Koitaya[2], Susumu Yamamoto[3], Iwao Matsuda[1], Jun Yoshinobu[1]

Keywords: Carbon dioxide; Hydrogen; Single atom alloy catalysts; Methanol synthesis

Chemical recycling of carbon dioxide (CO_2) into valuable chemical feedstocks is one of the promising strategies to realize a sustainable society. Methanol synthesis via CO_2 hydrogenation is an attractive reaction because of its high versatility in the modern chemical industry. The reaction process is typically operated at 220-300 °C and 50-100 bar using Cu-Zn-based catalysts.[1] Because of its exothermic reaction($\Delta H = -49.5$ kJ mol^{-1}), operation at lower temperatures is favorable. Thus, developing highly effective catalysts for CO_2 hydrogenation has been demanded. The current Cu-based catalysts show a low activity for hydrogen dissociation, although atomic hydrogen is always involved in any hydrogenation steps on the catalyst surface. Several recent studies have revealed that single atom alloy catalysts (SAACs), where active metal atoms are highly dispersed and isolated from each other on an inert metal substrate, show high activity for H_2 dissociation and hydrogenation reactions.[2] In this study, we investigated the chemical processes of CO_2 and H_2 on the single atom alloy model catalyst Pd/Cu(111) under millibar conditions.

Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) was performed at SPring-8 BL07LSU. C 1s and O 1s spectra showed that carbonate (C 1s: 288.4 and 289.0, O 1s: 531.1 eV) and atomic oxygen (529.3 and 529.8 eV) species were formed under 1 mbar of CO_2 at room temperature, indicating that dissociation and disproportion of CO_2 occurred.[3] When H_2 was added to the reactant gas (total pressure increased up to 3.4 mbar), the components of formate (C 1s: 287.7 eV) and methoxy (C 1s: 285.8, O 1s: 530.8 eV) appeared.[4] Heating to 380 K, these species are further developed. The chemical shift of Pd $3d_{5/2}$ indicates that the single atom Pd site acts as an H_2 dissociation site.[5] Thus, we concluded that H_2 was dissociated at the Pd site and the hydrogen atoms spilled over onto the Cu substrate to promote CO_2 hydrogenation even at room temperature. The present results may provide a guiding principle for the low-temperature synthesis of methanol.

1) J. Zhong *et al.*, *Chem. Soc. Rev.* **2020**, *49*, 1385. 2) R. T. Hannagan *et al.*, *Chem. Rev.* **2020**, *120*, 12044. 3) T. Koitaya *et al.*, *Top. Catal.* **2016**, *59*, 526. 4) I. Orozco *et al.*, *J. Phys. Chem. C* **2021**, *125*, 558. 5) W. Osada *et al.*, *Phys. Chem. Chem. Phys.* **2022**, *24*, 21705.

二成分イオン液体/電極界面におけるアニオン吸脱着の過電圧要因の研究

（東工大物質理工 [1]・上海大化学系 [2]・Sogang 大物理 [3]）○岩橋 崇 [1]・周 尉 [2]・Kim Doseok[3]・大内 幸雄 [1]

Excess Potential of Anion Adsorption/desorption at Binary Ionic Liquid/electrode Interfaces

([1]*Dept. Mater. Sci. Eng., Tokyo Tech.*, [2]*Dept. Chem., Shanghai Univ.*, [3] *Dept. Phys., Sogang Univ.*) ○Takashi Iwahashi,[1] Wei Zhou,[2] Doseok Kim[3], Yukio Ouchi[1]

Room temperature ionic liquids (RTILs), salts in a liquid phase at room temperature, provide the characteristic electrochemical properties and reactions. The RTIL/electrode interfaces exhibit the hysteresis behavior in the ion adsorption/desorption; the applied potential response of ion adsorption/desorption differs with respect to the potential sequence direction. This indicates that the ion adsorption/desorption requires an excess potential, which is needed to overcome the activation energy for ion desorption. In this study, we examined the anion adsorption/desorption at the RTIL/Pt electrode interface by infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy. The hysteretic potential response at the neat RTIL/Pt interface was compared with that at the binary RTIL/Pt interface to elucidate the factors determining the excess potential for anion desorption/adsorption.

Keywords : Ionic Liquid; Hysteresis; Electric Double Layer; Electrode Interface

常温で液相を呈する塩のイオン液体と電極との界面において、イオン吸脱着の電位応答ヒステリシス、すなわち電位の変更履歴に依存してイオン吸脱着挙動が異なる現象が見出された [1]。これは、イオン吸脱着がゼロ電荷電位では生じず、過剰な電圧（過電圧）を要することを示す。我々はイオン液体/電極界面におけるイオン吸脱着の過電圧要因の理解を目的として、界面敏感な振動分光法の赤外-可視和周波発生振動分光（infrared-visible sum-frequency generation vibrational spectroscopy; IV-SFG）を用い、二成分イオン液体/電極界面のアニオン吸脱着挙動を追跡した。

カチオンが共通の 1-butyl-3-methylimidazolium （$[C_4mim]^+$）、アニオンが bis(trifluoromethanesulfonyl)amide （$[TFSA]^-$）、trifluoromethanesulfonate（$[OTf]^-$）と異なる二種のイオン液体を、モル比 99:1 で混合した二成分イオン液体/Pt 界面における、アニオン由来の SF シグナルの電位応答を図 1 に示す。$[TFSA]^-$と$[OTf]^-$とで吸脱着挙動が変化する単成分イオン液体/Pt 界面と異なり [1]、二成分イオン液体/Pt 界面では$[TFSA]^-$と$[OTf]^-$とで同様の吸脱着挙動を示す。これは、アニオン吸脱着挙動がアニオン吸着種のみに依存するわけではないことを示唆する。詳細は当日議論する。

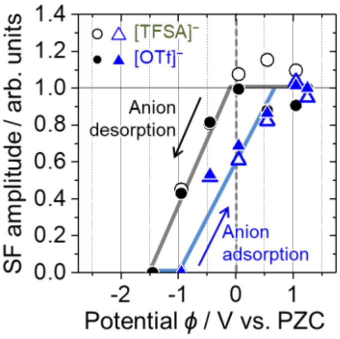


Fig. 1. Potential response of SF signals from $[TFSA]^-$ and $[OTf]^-$ (open and filled symbols).

---

1) Hysteretic potential response of anion ads./des. has been reported. W. Zhou et al., *Electrochem. Commun.* **2010,** *12,* 672.

Operando Multimodal Measurements of Oxygen Species on Pt Nanoparticles at Pt/C Cathode in Practical Polymer Electrolyte Fuel cell

([1]*Innovation Research Center for Fuel Cells, The University of Electro-Communication*, [2] *Faculty of Systems Engineering, Wakayama University,* [3]*Japan Synchrotron Radiation Research Institute,* [4]*Graduate School of Frontier Sciences, The University of Tokyo*) ○Hiroko Ariga-Miwa,[1] Takefumi Yoshida,[2] Tomoya Uruga,[1,3] Takehiko Sasaki,[4] Takuma Kaneko,[3] Tomohiro Sakata,[3] Kotaro Higashi,[3] Oki Sekizawa,[2] Yasuhiro Iwasawa, [1]

Keywords: Polymer Electrolyte Fuel cell (PEFC); Pt nanoparticle; HERFD-XANES; DFT calculation

Polymer Electrolyte Fuel Cell (PEFC) is one of the most promising power sources especially for heavy-duty vehicles to achieve low or even zero emissions. Cost, performance and durability of cathode electrocatalysts usually composed of Pt or Pt-based nanoparticles dispersed on carbon are crucial problems to be solved for a wide range of commercialization of PEFC systems. Thus, obtaining atomistic insights of platinum nanoparticle catalysts during PEFC operation condition are strongly required. Nevertheless, the nature and behavior of the Pt electrocatalysts during practical PEFC operating conditions are still not clear. Thus, we have conducted sequential multimodal measurements, including High Energy Resolution Fluorescence Detected X-ray Absorption Near-Edge Structure (HERFD-XANES), Resonant Inelastic X-ray Scattering (RIXS), Quick X-ray Absorption Fine Structure (QXAFS), and X-ray Diffraction (XRD), for Pt/C cathode electrocatalysts in membrane-electrode assembly (MEA) of PEFC under voltage operating conditions at BL36XU beamline constructed by us in SPring-8. Figure 1 shows two-dimensional maps of HERFD-XANES difference spectra (b) and RIXS difference spectra (c) during CV (a), and XRD Pt(111) peak intensities during CV (a) are also shown in Figure 1 (d). The presence of four different oxygen adsorbed species in the voltage range of 0.4–1.0–0.4 V is suggested by the two-dimensional HERFD-XANES map, and the decrease in the XRD intensity near 1.0 V implies surface reconstruction due to strong oxygen adsorption, whereas adsorbed oxygen species below 0.9 V did not bring about any surface reconstruction. The Pt-O bonding state for the oxygen species at 1.0 V was observed around 3.0 eV below Fermi level by means of RIXS (Figure 1 (c)).

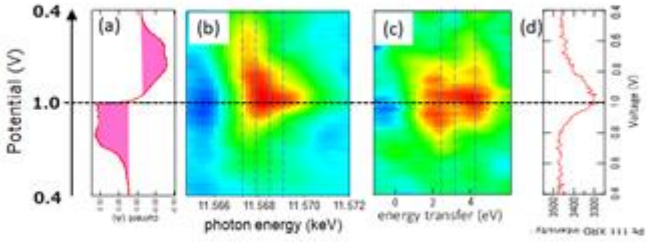


Figure. (a) CV, (b) 2D HERFD-XANES map, (c) 2D RIXS map, and (d) XRD Pt(111) intensity change. (b–d): during the CV. Difference spectra at Pt L_{III}-edge: against the spectrum at 0.4 V.

インジウムナノ粒子による深紫外域局在プラズモンと吸着分子の相互作用

（京大院理[1] 放送大教養[2]）長塚 直樹[1]・松口 諒斗[1]・奥山 弘[1]・安池 智一[2]・小板谷 貴典[1]・○渡邊 一也[1]

Interaction between deep-UV plasmon of indium nanoparticles and adsorbed molecules

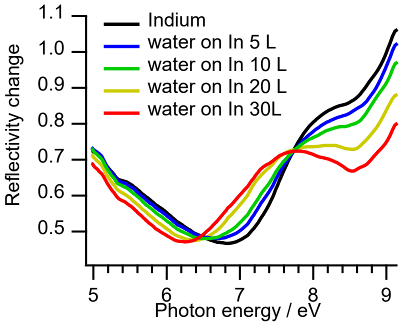
([1]*Graduate School of Science, Kyoto University*, [2]*Faculty of Liberal Arts, The Open University of Japan*) Naoki Nagatsuka,[1] Ryoto Matsuguchi,[1] Hiroshi Okuyama,[1] Tomokazu Yasuike,[2] Takanori Koitaya,[1] ○Kazuya Watanabe[1]

We study the plexciton formation in the vacuum ultraviolet region under ultrahigh vacuum conditions by using indium (In) clusters. Indium deposition on graphene sheet supported on a Rh(111) single crystal leads to a strong absorption band at 6 – 7 eV. This is due to the localized plasmon of In clusters with a diameter of a few tens of nanometers confirmed by scanning tunneling microscopy. Adsorption of water molecules on the In clusters at 145 K results in the spectral changes depicted in the figure and the features can be explained by theoretical model calculations in which the plexciton coupling is approximated by a dipole-dipole coupling.

Keywords: metal clusters, localized surface plasmon, light-matter strong coupling

金属ナノ構造体による局在プラズモンと吸着分子の電子遷移の相互作用による結合状態（plexciton）を形成する試みが多数報告されているが 1)、これまでの研究のほとんどは、金や銀を用いた可視光以下の光子エネルギー領域での研究に限られていた。これに対し我々は真空紫外領域での plexciton 形成を目指し、超高真空下でのインジウムナノクラスターを用いた研究を行っている。

ロジウム単結晶上に作製したグラフェン上に室温でインジウムを蒸着し、真空紫外域の反射率変化を計測したところ、6〜7 eV に強い吸収を示すことがわかった。走査トンネル顕微鏡により、数 10 nm サイズのインジウムクラスターが生成していることがわかり、古典電磁気学による数値シミュレーションからこの吸収はインジウムクラスターによる局在プラズモンに帰属された。145 K で水分子を吸着させて真空紫外域の反射率変化を計測したところ、図に示す反射率スペクトルの変化が観測され、局在プラズモンの遷移と水分子の電子遷移（$^1B_1 \leftarrow {}^1A_1$）の結合を遷移双極子間の相互作用で考慮したモデル計算でその変化の様子を説明することができた。これは、真空紫外域での plexciton 形成をはじめて観測したものと考えている。



インジウムクラスターに水を共吸着した場合の反射率スペクトル。水の曝露量は図中に示した。

1) P Törmä and W L Barnes, *Rep. Prog. Phys.* **2015**, *78*, 013901.

クラウンエーテル環状分子膜を使ったフェロセン単分子 STM 観察と二次元結晶成長

（千葉大院工 [1]・千葉大キラ研 [2]・台湾清華大 [3]）○山田 豊和 [1,2], 堀江 正樹 [3]

STM imaging of Ferrocene single molecules on crown ether films and 2D crystal growth

([1]*Graduate School of Engineering, Chiba Univ.*, [2]*Chiral Research Center, Chiba Univ.,* [3]*Taiwan Tsing Hua Univ.*) ○Toyo Kazu Yamada[1,2] and Masaki Horie[3]

Ferrocene has a unique structure consisting of two cyclopentadienyl rings bound to a central iron (Fe) atom, showing redox property (Fe2+/Fe3+). Although it has been challenging to image single Ferrocene (Fc) molecules on atomically flat noble metal substrates, Fc decomposed on the surface at 300 K or formed two-dimensional films even at cryogenic temperatures. In this study, we succeeded in direct visualization of Fc single molecules at 300 K using a crown ether ring molecular film. All experiments used a home-built ultrahigh vacuum low-temperature scanning tunneling microscopy (STM) setup. An ordered array of crown ether ring molecules (4,4',5,5'-tetrabromodibenzo[18]crown-6 ether (BrCR)) was prepared on Cu(111) at room temperature in ultrahigh vacuum (UHV) 1). Because of the pliable ring, the BrCR could trap guest atoms or molecules 2). We succeeded in trapping single Ferrocene molecules using the BrCR and also followed the growth of the 2D crystal.

Keywords：*Ferrocene; Crown Ether; Scanning Tunneling Microscopy*

フェロセンは、五員環で鉄原子をサンドイッチした構造を持つ。電荷移動により Fe 二価が三価へ酸化還元する。これまで、貴金属表面上にフェロセンが吸着すると、壊れたり二次元結晶膜となり単分子観察は不可能であった。しかし、クラウンエーテル環状膜を使うことで単分子観察に成功した。吸着量を徐々に増すことで単分子から二次元結晶膜への成長過程の可視化に成功した。臭素終端クラウンエーテル(BrCR)分子は、炭素原子と酸素原子からなる環を中心に持ち、その両脇にベンゼン環二個を持つ。この BrCR 分子を超高真空内で Cu(111)表面に室温で吸着すると、二次元自己組織化単層膜ができる 1)。Br-CR は中心に環を持ちゲスト原子分子をトラップできる 2)。この BrCR 規則配列にフェロセンアンモニウム塩をゲスト分子として吸着した。BrCR ホスト分子のトラップ機能により、フェロセン分子を固定し単分子 STM 観察に成功した。さらに、単分子から二次元結晶への成長過程をとらえることに成功した。本研究は全て自作の超高真空・低温・走査トンネル顕微鏡(STM)装置を用いて実施した。

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

2) On-Surface Growth of Transition-Metal Cobalt Nanoclusters Using 2D Crown-Ether Array. T. K. Yamada, R. Nemoto, F. Nishino, T. Hosokai, C. H. Wang, M. Horie, Y. Hasegawa, S. Kera, and P. Krüger, *Journal of Materials Chemistry C* **2024**, DOI: 10.1039/D3TC03339B.

Topological analysis for revealing the structure of water confined in sub-nanospaces

([1]*Graduate School of Science and Technology, Shinshu University*, [2]*AD'ALL Co.,LTD*, [3]*Faculty of Science, Shinshu University*) ○Yasuhiro Sugiyama[1], Tomoyasu Nakano[2], Taku Iiyama[3], Ryusuke Futamura[3]

Keywords: *Water; Adsorption; Porous carbon; X-ray scattering; Topological analysis*

Water, the most familiar liquid on the Earth, is called a "complex liquid" because of its numerous anomalies related to the unique hydrogen bonding nature. In addition to bulk water, the behaviors of water confined in nanospace are also of interests since the physical and chemical properties are markedly different from those of bulk. It is also important to elucidate the behaviors of water adsorbed on nanoporous materials from the viewpoints of the industrial uses for gas storage and molecular separation under humid conditions.

We have previously reported that the density of water confined in sub-nanometer pores (*i.e.,* pore width, $w < 1$ nm) of an activated carbon (A7, AD'ALL Co.) is sparser ($\rho = 0.72$ g cm^{-3}) than that of bulk ice ($\rho = 0.92$ g cm^{-3}) even at room temperature from *in-situ* small angle X-ray scattering (SAXS) measurements[1, 2]. In this study, we performed Hybrid Reverse Monte Carlo (HRMC) Simulation-aided wide angle X-ray scattering in order to determine the detailed intermolecular structure of the "sparse water" formed in the sub-nanospace. Furthermore, we applied Persistent Homology (PH) analysis[3] for the 3D structure which we obtained from HRMC simulation to extract the information of medium-range ordered structure.

Fig. 1 shows a comparison between the X-ray structure factor (balck) and the calculated one (red) from HRMC simulation for water confined in A7 pores at room temperature. The fairly good agreements between the experiment and the simulation ensure the validity of the detailed structural interpretation from the following topological analysis. The PH analysis for the confined water revealed that water molecules form a mixture of the six-membered rings as in Ice-$\mathrm{I_h}$ and of the triangular configuration with interpenetrating hydrogen bonds as in ice-VI of high-pressure phase (Fig. 1 inset), resulting in the low packing density in the sub-nanometer pores.

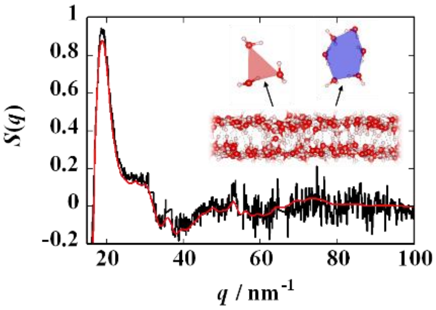


Fig. 1 Experiment (black) and simulated (red) X-ray structure factors of confined water in A7 at 298 K. (inset) A snapshot of the confined water which is composed by six-membered rings and triangular configuration.

1) R. Futamura, *et. al.*, *Phys. Chem. Chem. Phys.* **2012**, *14*, 981-986
2) Y. Sugiyama, R. Futamura, T. Iiyama, *Chem. Lett.* **2022**, *51*, 760-764
3) Obayashi I *et. al.*, *J Phys Soc Japan.,* **2022**;91:091013.

[有機 1 次元細孔物質-ビタミン E]包接体型分子カプセルの物理化学的性質

(昭和大教[1]・日大文理[2]・昭和大薬[3]・昭和大歯[4]) ○小林 広和[1]・本多 英彦[1]・山本 雅人[1]・岩堀 史靖[2]・野口 真理子[2]・藤森 裕基[2]・小田中 友紀[3]・田中 玲奈[4]・柴田 陽[4]

Physicochemical Properties of Inclusion-compound-type Molecular Capsule Using 1D Organic Nanochannels and Vitamin E ([1]*Faculty of Arts and Sciences at Fujiyoshida, Showa University,* [2]*College of Humanities and Sciences, Nihon University,* [3]*Department of Pharmaceutical Sciences, Division of Bioanalytical Chemistry, Showa University School of Pharmacy,* [4]*Department of Biomaterials and Engineering, Showa University School of Dentistry*) ○ Hirokazu Kobayashi,[1] Hidehiko Honda,[1] Masato Yamamoto,[1] Fumiyasu Iwahori,[2] Mariko Noguchi,[2] Hiroki Fujimori,[2] Yuki Odanaka,[3] Reina Tanaka,[4] Yo Shibata[4]

Inclusion compounds (ICs) have the potential to act as drug carriers. In this study, an IC of (±)-*α*-tocopherol (vitamin E; VE) incorporated into 2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine (CLPOT) was synthesized. The inclusion of VE into CLPOT nanochannels was confirmed using thermogravimetry-differential thermal analysis (TG-DTA) and solid-state ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The results suggest that CLPOT could be used as a stable microscopic carrier of biomaterials, even for oily biomaterials such as VE.

Keywords : Inclusion Compound; Solid-state ^{13}C MAS NMR; TG-DTA; Drug Delivery System; Vitamin E

2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine (CLPOT)の結晶がもつ 1 次元ナノチャンネルに acetaminophen などの薬剤が包接可能であることが TG-DTA などから示されている1)。本研究では CLPOT ナノチャンネルに (±)-*α*-tocopherol（ビタミン E; VE）が包接可能であることを、X 線構造解析、TG-DTA、^{1}H と ^{13}C 溶液 NMR、および固体 ^{13}C MAS NMR などで確認した([CLPOT-VE]包接体)。この結果、CLPOT がオイル状の VE 分子を安定に包接でき、キャリアーとして用いることができることが明らかになった。当日詳細を述べる。

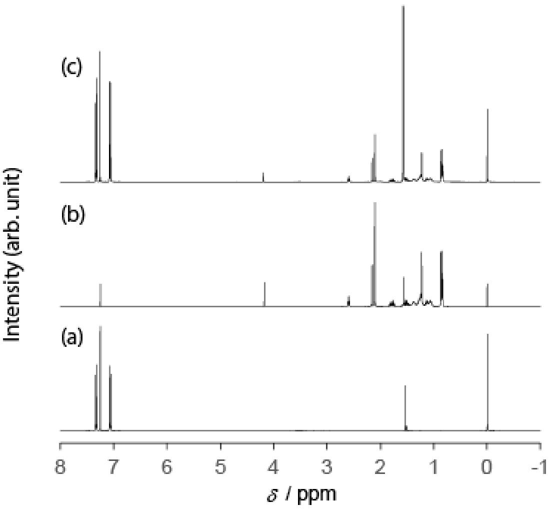


図　(a)ゲストフリーCLPOT、(b)VE、および[(CLPOT)$_2$-(VE)$_{0.49}$]包接体の溶液 ^{1}H NMR。

1) TG-DTA of IC of acetaminophen incorporated into 1D nanochannels of 2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine has been reported. H. Kobayashi, *et al.*, *Thermochim. Acta* **2021**, *702*, 178981.

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19日(火) 10:00 ~ 11:40 A1441(14号館 [4階] 1441)

[A1441-2am] 04. 物理化学—物性

座長：出倉 駿、小松 徳太郎

英語
10:00 ~ 10:20
[A1441-2am-01]
プルシアンブルー磁性薄膜における磁気ドメインと磁化反転の直接観察

〇長島 俊太郎[1]、矢作 祐士[1]、大越 慎一[2]、所 裕子[1,2] (1. 筑波大学、2. 東京大学)

日本語
10:20 ~ 10:40
[A1441-2am-02]
スキャホールド材料への応用を目指したTTF誘導体とF4TCNQ錯体からなる分子性ナノコイルの作成と電磁特性

〇帯刀 陽子[1]、南 豪[2]、西原 禎文[3,4]、芥川 智行[5]、中村 貴義[6] (1. 農工大、2. 東大生研、3. 広島大学、4. JST さきがけ、5. 東北大多元研、6. 北大電子研)

日本語
10:40 ~ 11:00
[A1441-2am-03]
ポリアセン結晶の電子構造と安定性

〇小松 徳太郎[1] (1. 日本大学)

英語
11:00 ~ 11:20
[A1441-2am-04]
量子スピン液体候補κ-(ET)$_2$Cu[Au(CN)$_2$]Clの低温物性

〇田中 優輝[1]、前里 光彦[1]、留野 慎也[1]、吉田 幸大[1]、清水 康弘[2]、北川 宏[1] (1. 京都大学大学院理学、2. 名古屋大学大学院)

英語
11:20 ~ 11:40
[A1441-2am-05]
New Functionalities in Pseudohalide-Based Complexes

〇Olaf Stefanczyk[1], Guanping Li[1], Kunal Kumar[1], Kenta Imoto[1], Koji Nakabayashi [1], Shin-ichi Ohkoshi [1] (1. The Univ. of Tokyo)

Direct observation of magnetic domain and magnetization reversal on prussian blue-based magnetic films

([1]*University of Tsukuba,* [2]*The University of Tokyo*) ○S. Nagashima,[1] Y. Yahagi,[1] S. Ohkoshi,[2] H. Tokoro[1]

Keywords: Molecule-based magnet, Magnetic domain, Magnetic force microscopy

Introduction: Molecule-based magnets have interesting characteristic to design magnetic functionalities.[1] While magnetic domains are fundamental to magnetic materials, the magnetic domains in molecule-based magnets have not been studied. Herein, we study the surface magnetization of two iron/chromium hexacyanidochromate $Fe_xCr_{1-x}[Cr(CN)_6]_{2/3}\cdot 5H_2O$ ($x = 0$ for **1** and $x = 0.2$ for **2**).[2,3]

Experiment: The target samples were prepared by electrochemically reducing aqueous solutions containing $FeCl_3$, $CrCl_3$, and $K_3[Cr(CN)_6]$, and then deposited as thin films on SiO_2-coated grass electrodes. Magnetic properties were measured by a SQUID magnetometer and surface magnetization was observed using magnetic force microscopy (MFM).

Result: The magnetization vs temperature curve of **1** showed Curie temperature (T_C) of 244 K. From MFM measurement, **1** revealed a magnetic domain below T_C with a maze pattern, and the magnetic domain exhibited a size of 0.67 ± 0.35 μm in width and 2.50 ± 0.72 μm in length. The magnetization vs temperature curve of **2** showed T_C = 222 K and the compensation temperature (T_{comp}) of 134 K (Fig. 1a). MFM measurement revealed that positive magnetic polarization appears below T_C, and magnetization becomes zero at a particular temperature (T_p = 146 K), changing magnetic polarization to negative (Fig. 1b). Monte Carlo calculations implied that T_p is T_{comp}, indicating temperature-induced magnetization reversal was achieved through a gradual change from positive to demagnetization and finally to negative. At 114 K, the magnetic domain of **2** exhibited a width of 0.61 ± 0.27 μm and a length of 2.12 ± 1.13 μm. They were slightly smaller than the sizes of **1** due to stronger thermal fluctuations in **2** compared to **1**.

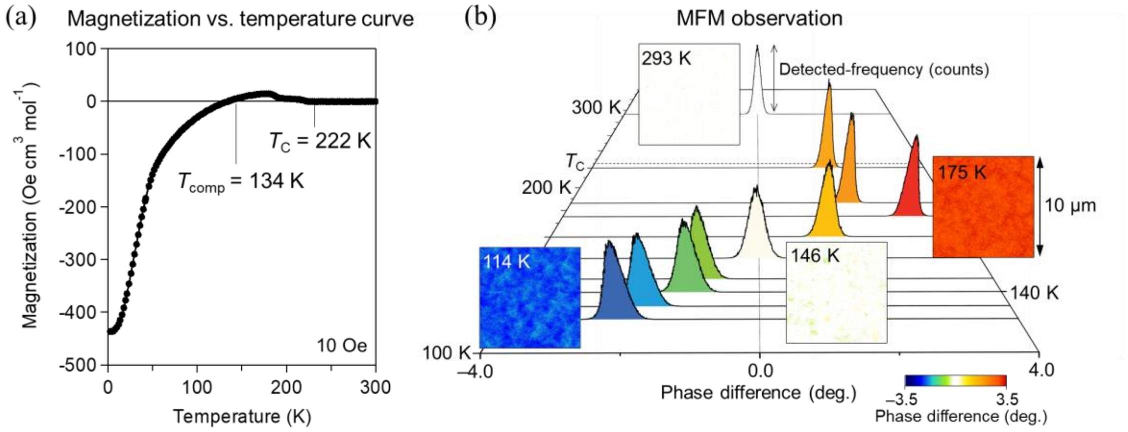


Fig. 1 (a) Magnetization vs temperature curve of **2**. (b) MFM observation for **2**. Insets are the MFM images measured at various temperatures.

References: (1) S. Ohkoshi, K. Nakagawa, K. Imoto, H. Tokoro, Y. Shibata, K. Okamoto, Y. Miyamoto, M. Komine, M. Yoshikiyo, A. Namai, *Nature Chem.*, **12**, 338 (2020). (2) S. Ohkoshi, A. Fujishima, K. Hashimoto, *J. Am. Chem. Soc.*, **120**, 5349 (1998). (3) S. Nagashima, Y. Yahagi, M. Nishino, T. Yamaoka, K. Nakagawa, J. Wang, S. Ohkoshi, H. Tokoro, *J. Am. Chem. Soc.*, **145**, 22934 (2023).

スキャホールド材料への応用を目指したTTF誘導体とF4TCNQ錯体からなる分子性ナノコイルの作成と電磁特性

（農工大院工 [1]・東大生研 [2]・広島大院理 [3]・東北大多元研 [4]・北大電子研 [5]）
○帯刀 陽子 [1]、南 豪 [2]、西原 禎文 [3]、芥川智行 [4]、中村貴義 [5]

Preparation and Electromagnetic Properties of Molecular Nanocoils Composed of TTF Derivatives and F4TCNQ Complexes for Application in Scaffold.

([1]*Tokyo University of Agriculture and Technology*, [2]*The Univ. of Tokyo,* [3]*Hiroshima University,* [4]*Tohoku University,* [5]*Hokkaido University*) ○Yoko Tatewaki[1], Tsuyoshi Minami[2], Sadafumi Nishihara[3], Tomoyuki Akutagawa[4], Takayoshi Nakamura[5]

Research on low-dimensional materials composed of organic conductive derivatives has been carried out in a large number of studies. On the other hand, the development of multifunctional scaffold materials is required in research in the field of regenerative medicine and engineering. In this study, we prepared a new scaffold material that promote cell proliferation efficiently composed of molecular nanocoils of charge transfer complexes obtained by mixing TTF derivatives (*S*-, *R*-TTF-4UM) and acceptors. The molecular nanocoils were formed on a mica substrate, and showed semiconducting conducting behavior. They also generated an induced electromotive force of 1.4 mV under the application of a magnetic field, and this electromagnetic property was used to culture osteoblasts (Saos-2) (Fig. 1). After 24 hours of culture with the magnetic field induced, the cell proliferation rate was approximately doubled compared to that without the magnetic field.

Keywords : Nanocoils; Charge Transfer Complexes; Electromagnetic properties; Scaffold

電荷移動錯体を用いた低次元材料の開発が国内外において盛んに行われている。一方、再生医工学分野の研究において、必要な細胞を効果的に機能させるスキャホールド材料の開発が求められている。スキャホールド自体が細胞に働きかけ、細胞培養を補助するためには、多孔質性・大表面積といった構造的特徴が必須となる。さらに、電気や磁気等の外部刺激が細胞増殖過程に影響を与え、細胞の増殖が促進されることが既に報告されている。そこで本研究では、TTF誘導体(*S*-、*R*-TTF-4UM)とアクセプターを混合することで得られた電荷移動錯体からなる分子性ナノコイルを用いて、効率的に細胞増殖を促す新規スキャホールド材を作製した。分子性ナノコイルはマイカ基板上において安定に形成し、高さ20、幅100、ピッチ100 nmを有しており、半導体的な伝導挙動を示した。また、磁場印加下において1.4 mVの誘導起電力を生じることが明らかとなったことから、この電磁特性を利用して骨芽細胞(Saos-2)を培養した(図1)。24時間磁場を印可し培養を進めたところ、磁場を印可しない場合と比較して、細胞増殖率が約2倍へと向上することが分かった。以上のことからスキャホールドが生じる誘導起電力が細胞増殖過程に有用な刺激となることが明らかとなった。

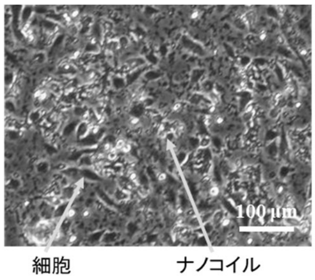


図1　分子性ナノコイルスキャホールド上における骨芽細胞の光学顕微鏡像

ポリアセン結晶の電子構造と安定性

（日大医）〇小松 徳太郎
Stability and Electronic Structure of Polyacene Crystals (*School of Medicine, Nihon University*)〇Komatsu, Tokutaro

The prediction that polyacene (PA) may be a 1000 K - class superconductor1) has attracted many theoretical chemists.2) As successful synthesis of PA has been reported in 2023 3), PA-based organic conductor / superconductor becomes much realistic. Since the theoretical studies have been limited to one PA chain, stability and the electric structure of aggregated PA are wanted to realistic design of PA-based conductors. DFT calculations on a single PA reproduced the band structure of non-magnetic semimetal1,2), however, antiferromagnetic semiconductor was more stable. Therefore, isolated PA will not show metallic conductivity. A stable structure derived from 20 candidates is shown in Fig. 1, with the band dispersion and the density of states. In addition to the details of the calculation, results of modified PA will be presented.

Keywords : density-functional theory, polyacene, electronic structure, stability

ポリアセン(PA)は、1000 K オーダーの高い超伝導転移温度を示すとの予想が出されたことをきっかけに1)、精力的に理論的研究が行われてきた2)。2023 年に多孔質配位高分子を用いた合成法が報告され3)、有機導体／超伝導体としての PA の利用が視野に入ってきた。これまでの理論研究は孤立した PA に限られていたため、集合体としての安定性と電子構造を密度汎関数法により調べた。孤立した PA について非磁性の場合の予備計算を行ったところ、以前の報告 1,2)にあった半金属的バンドが再現できた。しかしながら、スピン分極した半導体の方が安定であり、孤立した PA は金属的導電性を示さないと予想される。20 種の候補構造を最適化した結果、数種の安定構造候補を得た。安定構造の一つについて、分子配置とバンド構造、状態密度を図 1 に示す。計算の詳細と合わせて、当日は分子修飾の効果についても発表する。

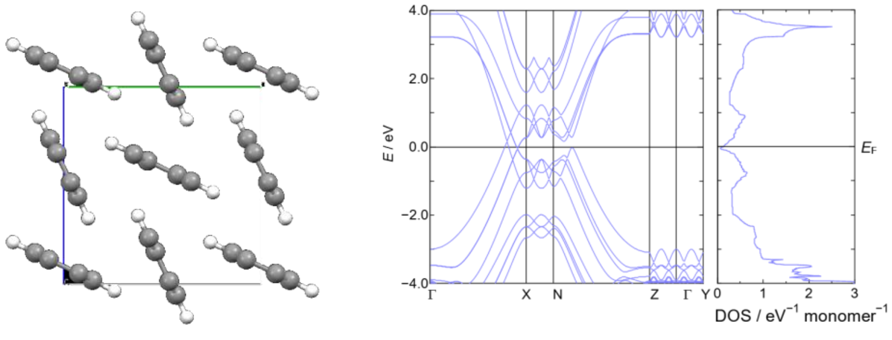


図 1：ポリアセンの安定構造（左図）、エネルギー分散（中）と状態密度（右）。

1) S. Kivelson *et al*, *Phys. Rev. B* **1983**, *28*, 7236.
2) A. Mishima *et al.*, *Synt. Met.* **1985**, *11*, 75., Y. Otsuka et al., *J. Phys. Soc. Jpn.* **2009**, *78*, 024713., G. Karakonstantakis *et al.*, *Phys. Rev. B* **2013**.
3) T. Kitao *et al.*, *Nat. Synth.* **2023**, *2*, 848.

Low temperature physical properties of quantum spin liquid candidate κ-$(ET)_2Cu[Au(CN)_2]Cl$

([1]*Graduate School of Science, Kyoto University*, [2]*Graduate School of Science, Nagoya University*) ○Yuki Tanaka,[1] Mitsuhiko Maesato,[1] Shinya Tomeno,[1] Yukihiro Yoshida,[1] Yasuhiro Shimizu,[2] Hiroshi Kitagawa[1]

Keywords: ET; Quantum spin liquid; Transport measurements; ESR; Frustration

Quantum spin liquids (QSLs) have attracted much attention because they are exotic quantum states of matter where long-range magnetic ordering is suppressed by strong spin frustration even at low temperature. Several QSL candidates with triangular lattice have been reported in organic conductors so far.[1,2] However, all the reported organic QSL candidates have some disorders in their crystal structures. In addition, recent research pointed out the influence of magnetic impurity in QSL.[3] Although such structural disorders and impurities have been discussed as one of the key factors for realizing QSL, the intrinsic role of them remains elusive.

Here we report the recent investigation of the QSL candidate κ-$(ET)_2Cu[Au(CN)_2]Cl$. This salt has a nearly regular triangular lattice (t'/t=1.19) and is considered as the first organic QSL candidate with disorder-free polyanion layers (Fig).[4] To reveal the ground state of this material, we have performed the detailed study of ESR at low temperatures. The spin susceptibility obtained by ESR shows the absence of spin gap at least down to 4 K, indicating a gapless QSL. The ^{1}H NMR spectra also show no magnetic transition down to 0.45 K, which is more than two orders of magnitude lower than the exchange interaction J/k_B = 210 K estimated by SQUID. On the other hand, the existence of magnetic impurity Cu^{2+} is revealed by ESR. It was found that π spins on ET dimers are influenced by Cu^{2+} spins. We will discuss the effect of magnetic impurity on a gapless QSL.

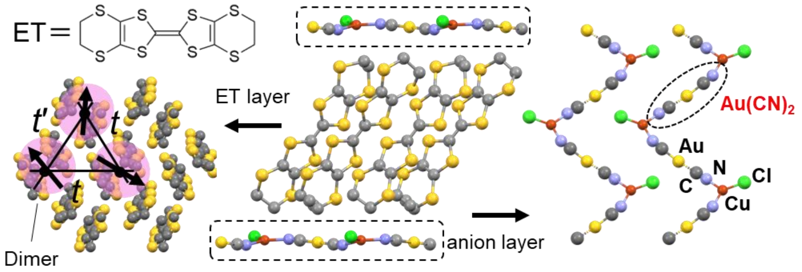


Fig. Crystal structure and magnetic susceptibility of κ-$(ET)_2Cu[Au(CN)_2]Cl$

1) Y. Zhou, K. Kanoda, T. Ng, *Rev. Mod. Phys.*, **2017**, *89*, 025003.
2) M. Maesato, Recent Topics on Organic Spin Liquid Candidates. In: Nishimura K., Murase M., Yoshimura K. (eds) *Creative Complex Systems. Creative Economy*, **2019**, Springer, Singapore.
3) B. Miksch, *et al*., *Science*, **372**, 276 (2021).
4) S. Tomeno *et al*., *Inorg. Chem*., **2020**, *59*, 8647.

New Functionalities in Pseudohalide-Based Complexes

([1]*Dept. of Chemistry, School of Science*, *The Univ. of Tokyo*) ○Olaf Stefanczyk,[1] Guanping Li,[1] Kunal Kumar,[1] Kenta Imoto,[1] Koji Nakabayashi,[1] Shin-ichi Ohkoshi[1]

Keywords: Functional Materials; Terahertz Absorption; Raman Scattering; Thermometric Properties; Nanolayers

Thiocyanate- and selenocyanate-bridged materials provide increased stability, versatile coordination modes, and unique redox properties compared to cyanide-bridged materials due to stronger metal-pseudohalide bonds, diverse coordination modes, and sulfur/selenium involvement in redox processes. These differences provide advantages in durability, design flexibility, and specialized functions, making SCN/SeCN-bridged materials attractive for a variety of scientific and technological applications.[1-5] The choice between these materials ultimately depends on the specific needs of different fields, taking into account their different properties and functionalities.

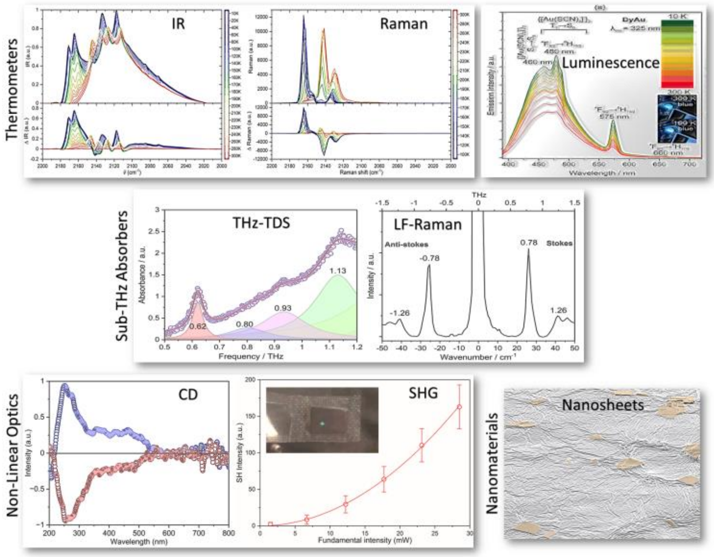


Fig. 1. Functionalities in pseudohalide-based complexes.

In this presentation, the current research on sub-THz absorption and low-frequency (LF) Raman scattering,[1] and non-linear optical effects of second harmonic generation (SHG) and circular dichroism (CD) activity in *L*-Fe-[Hg(ECN)$_4$] systems (*L* = organic ligand; E = S and Se),[2] Raman and visible/near-infrared luminescence thermometers based on Ln-[Au(ECN)$_2$] compounds,[3] and IR, Raman and optical thermometers constructed of *L*-Fe-[Hg(ECN)$_4$] will be presented (Fig. 1).[4] Moreover, the perspectives in the mechanical exfoliation of nanosheets on an example of *L*-Fe-[Hg(SCN)$_4$] systems will be discussed as a step forward in 2D materials.[5]

1) G. Li, O. Stefanczyk, K. Kumar, Y. Mineo, K. Nakabayashi, S. Ohkoshi, *Angew. Chem., Int. Ed.* **2023**, *62*, e202214673. 2) G. Li, O. Stefanczyk, K. Kumar, K. Nakabayashi, S. Ohkoshi, *Inorg. Chem.* **2023**, *62*, 3278. 3) K. Kumar, O. Stefanczyk, S. Chorazy, K. Nakabayashi, S. Ohkoshi, *Adv. Opt. Mater.* **2022**, *10*, 2201675. 4) G. Li, O. Stefanczyk, K. Kumar, K. Imoto, K. Nakabayashi, S. Ohkoshi, *Chem. Mater.* **2023**, *35*, 9613. 5) G. Li, O. Stefanczyk, F. Jia, S. Nagashima, K. Kumar, K. Imoto, H. Tokoro, S. Ohkoshi, *J. Phys. Chem. Lett.* **2023**, *14*, 10420.

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19日(火) 9:00 ~ 11:10 A1454(14号館 [5階] 1454)

[A1454-2am] 05. 物理化学—反応

座長：石橋 千英、倉持 光

日本語
9:00 ~ 9:20
[A1454-2am-01]
銅フタロシアニン単一ファイバーのフェムト秒ナノ分光

白石 悠人[1]、森田 水由宇[1]、○石橋 千英[1]、朝日 剛[1] (1. 愛媛大学)

日本語
9:20 ~ 9:40
[A1454-2am-02]
凝集誘起発光特性を有するジベンゾイルメタンフッ化ホウ素錯体の固体状態の励起状態ダイナミクス

○藤本 悠史[1]、石橋 千英[2]、朝日 剛[2]、伊藤 冬樹[1,3] (1. 信州大院総合理工、2. 愛媛大院理工、3. 信州大教育)

英語
9:40 ~ 10:00
[A1454-2am-03]
レチナール光異性化酵素ロドプシンの吸収波長特性と可逆的光反応

森本 直也[1]、○永田 崇[1]、井上 圭一[1] (1. 東京大学)

10:00 ~ 10:10
休憩

日本語
10:10 ~ 10:30
[A1454-2am-04]
フェムト秒過渡吸収スペクトル測定によるヘミインジゴの光異性化反応ダイナミクスの追跡

○長澤 裕[1]、東 岳斗[1]、郄井 孝行[1]、木原 優[1]、小島 理沙[1]、寺本 高啓[2,3] (1. 立命館大学、2. 京都大学、3. 大阪大学)

日本語
10:30 ~ 10:50
[A1454-2am-05]
TCNQの励起状態：熱活性化遅延蛍光、電荷移動状態、および対称性の破れ

Ahatashamul Islam[1]、春藤 健介[1]、○飯森 俊文[1] (1. 室蘭工業大学)

日本語
10:50 ~ 11:10
[A1454-2am-06]
液体の超高速光電子分光におけるスペクトル回復法の開発と水溶液中のOHの構造拡散を伴う電荷再結合ダイナミクスの解明

○山本 遥一[1]、鈴木 俊法[1] (1. 京都大学)

銅フタロシアニン単一ファイバーのフェムト秒ナノ分光

（愛媛大院理工）白石悠人・森田水由宇・○石橋千英・朝日　剛

Femtosecond nanospectroscopy of single copper phthalocyanine fiber (*Graduate School of Science and Engineering, Ehime University*) Yuto Shiraishi, Miyu Morita, ○Yukihide Ishibashi, and Tsuyoshi Asahi

Recently, we have separately fabricated copper phthalocyanine fibers (CuPc-Fs, 1-5 μm in length and 40 nm in width) with different crystalline phases of β- and η-forms with the laser ablation method. This study examined the exciton relaxation process of β- and η-CuPc-Fs at a single particle level using a femtosecond transient absorption microspectroscopy. As a result, the rate of bimolecular annihilation in η-CuPc-F, which strongly correlated with the exciton diffusion rate, was statistically faster than that in β-CuPc-F. At the presentation, we will present the detailed exciton diffusion process, including the results of the size effect.

Keywords：*Exciton dynamics; Transient microspectroscopy; Copper phthalocyanine fibers*

これまでに我々は液中レーザーアブレーション法により結晶相の異なるβおよびη型の銅フタロシアニンファイバー（CuPc-F、長さ１～５μm、幅 40 nm）の作り分けに成功した（Figure 1a）。本研究では、βおよびη型の CuPc-F の励起子緩和を、単一粒子レベルで、研究室自作の後方散乱光をプローブ光としたフェムト秒顕微過渡吸収分光法により調べた結果について報告する。

Figure 1b に、１本のβ型 CuPc-F の高励起光強度条件下での観測波長 530 nm における励起状態吸収の時間変化を示す。この励起状態吸収の時間変化には、低励起光強度条件では観測されなかった励起子—励起子消滅過程による緩和が主な成分であり、消滅過程の速度定数が、ファイバーごとにばらついていることがわかる。一方、η型 CuPc-F に対して同様の励起光強度依存性の測定を行った結果（Figure 1c）、励起子—励起子消滅過程に由来する迅速な緩和過程が観測されたが、やはりその緩和速度定数は、ファイバーごとに異なることがわかった。βおよびη型の CuPc-F における励起子—励起子消滅の速度定数に対するヒストグラムから、β型よりもη型の方が、全体的に励起子消滅過程が迅速に起こることがわかった。また、どちらも消滅速度定数は幅広く分布しており、これはファイバーのサイズ（長さ）が相関していると考えられる。発表では、サイズ依存性の結果も含めて励起子拡散について報告する。

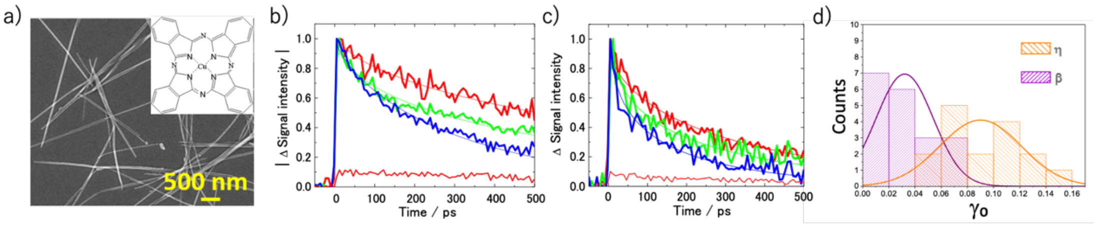


Figure 1. a) Molecular structure of copper phthalocyanine (CuPc) and SEM image β-CuPc-Fs fabricated with the laser ablation method in liquid. Similar shapes of η-CuPc-Fs was observed (image are not shown). b) and c) Representative time profiles of the transient absorption at 530 nm of single β- and η-CuPc-F, respectively. Excitation intensity was set to 2.2 pJ/pulse. The thin red line in each figure was the time profile obtained at low excitation intensity of 0.23 pJ/pulse. d) Histograms of the bimolecular annihilation rate constants of β- and η-CuPc-Fs.

凝集誘起発光特性を有するジベンゾイルメタンフッ化ホウ素錯体の固体状態の励起状態ダイナミクス

(信州大院総合理工 [1]・愛媛大院理工 [2]・信州大教育 [3]) ○藤本 悠史 [1]・石橋 千英 [2]・朝日 剛 [2]・伊藤 冬樹 [1,3]

Excited State dynamics of Solid-states of Dibenzoylmethanato Boron Difluoride Complex with Aggregation-Induced Emission ([1]*Graduate School of Science and Technology, Shinshu University*, [2]*Graduate School of Science and Engineering, Ehime University*, [3]*Institute of Education, Shinshu University*) ○Yushi Fujimoto,[1] Yukihide Ishibashi,[2] Tsuyoshi Asahi,[2] Fuyuki Ito[1,3]

The understanding of the excited-state dynamics of organic molecules in the solid state is important to improve their photophysical properties significantly for application as organic solid-state luminescent materials. Many organic luminescent molecules exhibit strong luminescence in the solution state, but weak luminescence in the solid state. Therefore, organic molecules with aggregation-induced emission (AIE) properties have attracted much attention in the field of solid-state light-emitting materials. This study focused on a dibenzoylmethanatoboron difluoride complex derivative ($2amBF_2$) with AIE properties. We evaluated the excited-state dynamics of $2amBF_2$ in the crystalline state by using time-resolved microspectroscopy.

Keywords : Dibenzoylmethanato boron difluoride, Aggregation-induced emission, excited-state dynamics, time-resolved microspectroscopy

有機分子固体の励起状態ダイナミクスを詳細に理解することは, 光機能性材料への応用展開のために重要である．凝集誘起発光（AIE）分子は，凝集起因消光を示す多くの有機分子とは異なり，固体状態でのみ強い発光を示す．本研究では，時間分解顕微分光測定により, 凝集誘起発光特性を有するジベンゾイルメタンフッ化ホウ素錯体誘導体（$2amBF_2$）の固体状態（結晶状態）の励起状態ダイナミクスを評価した．

結晶の蛍光減衰曲線は，τ_1 = 0.85 およびτ_2 = 2.0 ns の時定数をもつ 2 成分指数関数減衰で再現されたことより，結晶中での 2 種の発光種の存在を示唆している．高分子薄膜中に単分散させた $2amBF_2$ の蛍光寿命は 1 ns 程度であったことから，τ_1 は結晶中のモノマー発光に帰属した．結晶構造解析より，τ_2 は結晶中のダイマー発光に帰属した．また，観測波長の長波長化にともないτ_1 の成分比は減少し，一方τ_2 のそれは増加した. さらに, 時間分解蛍光スペクトルでは, 時間経過にともない蛍光ピーク波長は, 数 ns の間に 480 nm から 505 nm へと長波長にシフトした．以上のことは，モノマーからダイマーへの励起エネルギー移動の存在を示唆している（Fig. 1）．当日は，微結晶の顕微過渡吸収分光測定の結果も踏まえて，AIE 分子 $2amBF_2$ の固体状態の励起状態ダイナミクスについて議論する．

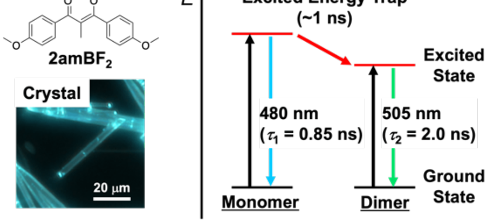


Fig. 1. Schematic representation of the excited-state relaxation of crystalline AIE molecule $2amBF_2$.

レチナール光異性化酵素ロドプシンの吸収波長特性と可逆的光反応

（東大物性研 [1]）森本 直也 [1]・〇永田 崇 [1]・井上 圭一 [1]

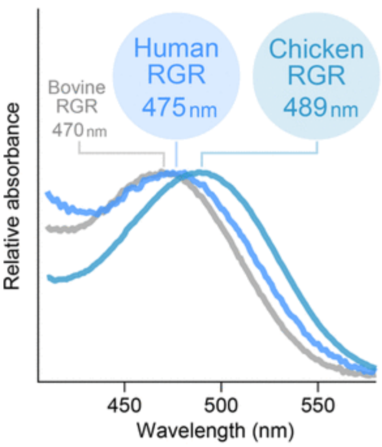
Absorption-wavelength characteristics and reversible photoreaction of retinal photo-isomerase rhodopsins

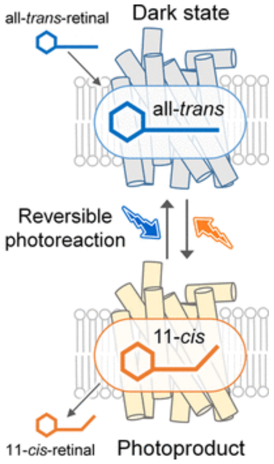
([1]*The Institute for Solid State Physics, The University of Tokyo*)
Naoya Morimoto[1], 〇Takashi Nagata[1], Keiichi Inoue[1]

Rhodopsin, a photo-sensitive membrane protein, binds retinal as a chromophore. In vertebrate visual rhodopsin, light absorption induces isomerization from 11-*cis*-retinal (11cR) to all-*trans*-retinal (atR). Subsequently, rhodopsin releases atR and binds new 11cR to receive light repeatedly. Hence, the supply of 11cR is critical for the function of visual rhodopsin. Recently, Retinal G-Protein-Coupled Receptor (RGR) was shown to function as a retinal photo-isomerase that converts atR to 11cR in the eye. However, the absorption spectra have only been investigated in bovine RGR. To understand the common properties and diversity of RGRs, in this study, we newly investigated the absorption characteristics of six RGRs and found that most of them are blue-absorbing pigments. We also found that RGRs exhibit reversible photoreactions1). In the presentation, the relevance of these properties of RGRs to their photo-isomerase function will be discussed.

Keywords : photoisomerization; photo-sensitive protein; rhodopsin; vision; retinal

光受容膜タンパク質・ロドプシンは、発色団としてレチナールを結合する。脊椎動物の視覚ロドプシンでは光を受容すると 11-*cis*-retinal（11cR）から all-*trans*-retinal（atR）への光異性化が生じる。その後 atR を遊離し 11cR を再結合することで繰り返し光を受容することが可能となるため、視覚機能の維持のためには 11cR の供給が必要である。近年、Retinal G-Protein-Coupled Receptor (RGR)が眼の中で atR を 11cR へ光異性化する光異性化酵素として機能していることが明らかとなった。一方、吸収分光特性などが調べられているのはウシの RGR に限られていた。今回、我々は RGR の共通の性質や多様性を理解するため、ヒト RGR を含め新たに６種類の RGR について吸収特性を調べ、ほとんどが青色光受容体であることを明らかにした。また RGR が可逆的な光反応を示すことも見出した 1)。発表では RGR の光異性化酵素としての機能との関連性について議論する。





1) N. Morimoto, T. Nagata, K. Inoue, *Biochemistry*, **2023**, *62*, 1429.

フェムト秒過渡吸収スペクトル測定によるヘミインジゴの光異性化反応ダイナミクスの追跡

（立命館生命 [1]・京大エネルギー科学 [2]・阪大レーザー研 [3]）○長澤 裕 [1]・東 岳斗 [1]・邨井 孝行 [1]・木原 優 [1]・小島 理沙 [1]・寺本 高啓 [2,3]

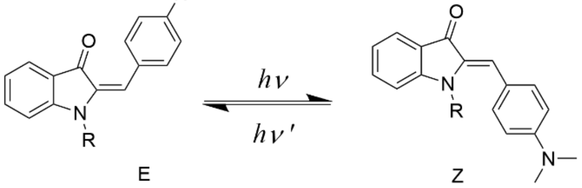
Tracking the Photoisomerization Dynamics of Hemiindigo by Femtosecond Transient Absorption Spectroscopy

([1]*Life Sciences, Ritsumeikan University*, [2]*Energy Science, Kyoto University,* [3]*Radiation Sciences, Osaka University*) ○Yutaka Nagasawa,[1] Yamato Higashi,[1] Takayuki Murai,[1] Yu Kihara,[1] Risa Kojima,[1] Takahiro Teramoto[2,3]

Hemiindigo is a photochromic dye, that exhibits *E-Z* isomerization by visible light irradiation, with a structure in which half indigo and half stilbene are connected together (See the figure below). In the case of indigo derivatives, the two carbonyl groups face each other in the *cis*-form, resulting in electrostatic repulsion that causes the *cis*-form to be unstable, that naturally returns to the *trans*-form even in the dark (T-type photochromism). In the case of hemiindigo with only one carbonyl group both the *E* and *Z*-forms are stable (P-type photochromism). In this study, femtosecond transient absorption (TA) spectra were measured in order to compare and examine these photoisomerization dynamics. As a result, it was found that hemiindigo, like indigo derivatives, exhibits a characteristic strong TA band derived from the indoxyl group at 600-750 nm[1]. However, this absorption band became unclear in methanol solution, suggesting the influence of hydrogen bonding with the solvent.

Keywords : Photoisomerization; Photochromism; Hemiindigo, Ultrafast Spectroscopy; Transient Absorption Spectroscopy

ヘミインジゴは可視光照射によりE-Z異性化を示すフォトクロミック色素であり、下図のようにインジゴとスチルベンを半分ずつ結合した構造をしている。インジゴ誘導体の場合、シス体では２つのカルボニル基が向き合うため静電的反発が強くシス体は不安定で暗所でも自然にトランス体に戻る T 型フォトクロミズムを示す。ヘミインジゴの場合、カルボニル基は１つしかないため、そのような反発はなくE体もZ体もともに安定なP型フォトクロミズムを示す。本研究では、これらの光異性化ダイナミクスを比較検討するため、フェムト秒過渡吸収スペクトル測定を行った。その結果、ヘミインジゴは、インジゴ誘導体と同様に600～750 nmにかけてindoxyl基由来の特徴的な強い過渡吸収を示すことが判明した[1]。ところが、メタノール溶液中ではこの吸収帯が不明瞭となり、溶媒との水素結合の影響が示唆された。



1) Y. Kihara, et al., *J. Phys. Chem. B* **2022**, 126, 3539.

TCNQ の励起状態：熱活性化遅延蛍光、電荷移動状態、および対称性の破れ

（室蘭工大院工）Ahatashamul Islam・春藤健介・○飯森俊文

Excited states of TCNQ : Thermally activated delayed fluorescence, charge transfer state, and symmetry breaking (*Department of Sciences and Informatics, Graduate School of Engineering, Muroran Institute of Technology*) Ahatashamul Islam, Kensuke Syundo, ○Toshifumi Iimori

A family of tetracyanoquinodimethane (TCNQ) analogues has been recognized as part of the important molecules in a fertile field of organic electronics and materials chemistry. TCNQ is the simplest molecule in the family of TCNQ analogues and can be regarded as the model system for them. We have reported the fluorescence spectra and solvatochromism of TCNQ in a variety of solvents. Here, the electroabsorption spectroscopy and quantum chemical calculations have been employed to characterize the dark nonemissive state which is responsible for the observed photophysical properties. The nonemissive state was assigned to the intramolecular charge transfer state which was produced through the symmetry breaking.

Keywords : Symmetry Breaking; Stark Spectroscopy; Photochemical Reaction Dynamics; Tetracyanoquinodimethane; Quinodimethane

キノジメタン類はジラジカル性と高い電子親和力を示すことが知られており、分子磁性体や有機エレクトロニクスへの応用が期待される化合物群である。テトラシアノキノジメタン(TCNQ)は幅広く利用される重要な電子アクセプター分子であり、キノジメタン類のなかで最もシンプルな構造を持つ安定な分子であることから、モデル分子とみなされる。我々の最近の研究により、TCNQ が溶媒中で青色蛍光を示し、蛍光量子収率が溶媒の極性に応答して鋭敏に変化すること 1-3)、熱活性化遅延蛍光を示すこと 4)、気相中でおよそ 200 ns の異常に長い蛍光寿命を示すこと 5,6)、などが明らかにされている。さらに時間分解蛍光測定およびフェムト秒過渡吸収スペクトル測定により、励起状態には蛍光性の局所励起状態と非蛍光性の電子状態が存在し、２つの電子状態のあいだで起きるフェムト秒～ピコ秒の反応ダイナミクスとその溶媒依存性を明らかにしている 4)。本研究では、電場吸収分光法を用い、励起状態の電子構造について深く理解することを目的とした。非蛍光性の電子状態は電気双極子モーメントを有する分子内電荷移動(ICT)状態であり、励起状態において分子の対称性が低下する Symmetry-breaking が生じていることが明らかになった 7,8)。量子化学計算により、局所励起状態は $^1B_{3u}$ 状態、ICT 状態は $^1B_{1g}$ 状態であることがわかった 7)。

1) H. Tamaya, H. Nakano, T. Iimori, *J. Lumin.* **2017**, *192*, 203-207.; 2) H. Tamaya, Y. Torii, T. Ishikawa, H. Nakano, T. Iimori, *ChemPhysChem* **2019**, *20*, 2531-2538.; 3) T. Iimori, et al., *Chem. Phys. Lett.* **2020,** *738*, 136911-136915.; 4) T. Iimori, Y. Torii, T. Ishikawa, N. Tamai, *J. Phys. Chem. B* **2020**, *124*, 7918-7928.N.; 5) Chaki, et al., *ChemPhysChem* **2019,** *20*, 996-1000.; 6) S. Muramatsu, et al., *RSC Advances* **2021**, *11*, 22381-22389.; 7) T. Iimori, *Comput. Theor. Chem.* **2021**, *1199*, 113211.; 8) A. Islam, K. Syundo, T. Iimori, *Phys. Chem. Chem. Phys.* **2023**, *25*, 21317-21323.

液体の超高速光電子分光におけるスペクトル回復法の開発と水溶液中の OH の構造拡散を伴う電荷再結合ダイナミクスの解明

（京大院理）○山本　遥一・鈴木　俊法

Development of spectral retrieval method for ultrafast photoelectron spectroscopy of liquids and elucidation of charge recombination dynamics via structural diffusion of aqueous OH

(*Graduate School of Science, Kyoto University*) ○Yo-ichi Yamamoto, Toshinori Suzuki

UV ultrafast photoelectron spectroscopy of liquids is one of the best methods to study electron dynamics in liquids, while spectral distortions by electron inelastic scattering hinder extracting complete information of the dynamics. We have developed spectral retrieval (SR) method to remove the distortion and applied it to charge transfer reaction of OH$^-$ in an aqueous solution. SR method enabled us to discuss the geminate recombination, solvation of the excess electrons, and solvent relaxation, which revealed an exceptionally fast recombination dynamics compared with similar reactions in halide anion solutions. The results were consistent with an ultrafast geminate recombination mechanism with “structural diffusion” of OH radical which is facilitated by H-atom transfer between OH radical and solvent water.

Keywords : Ultrafast Photoelectron Spectroscopy of Liquids; Spectral Retrieval; Charge Recombination; Structural Diffusion; Hydroxide

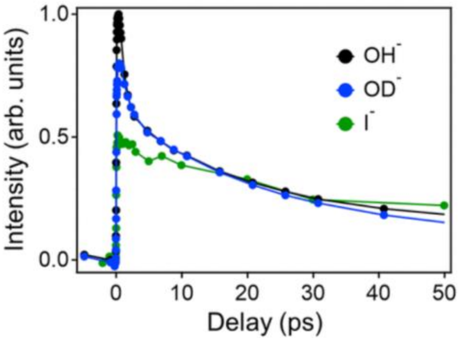


Figure 1. Photoelectron intensity as a function of pump-probe delay time.

溶液中で起こる超高速な電子移動過程や電子緩和過程を検出する目的で、我々は液体の超高速光電子分光法を開発した。紫外光をイオン化検出光に用いた場合、信号量が大きく高い感度が得られるが、紫外光で生成する低エネルギー光電子は溶液中で非弾性散乱を受けスペクトルが歪むという問題があった。[1]この問題を克服するために、我々はスペクトルの線形変換により歪みを除去するスペクトル回復（SR）法を開発した。そして、水溶液中における OH$^-$から水への電子移動反応の研究に応用した。H$_3$O$^+$や OH$^-$は水溶液中で高速に構造拡散することが知られるが、こうした構造拡散と電子ダイナミクスの因果関係は明らかではなかった。[2] Figure 1 に示すように、3 種類の異なる溶質から溶媒の水に電子移動する場合、OH$^-$や OD$^-$では I$^-$には見られない顕著な高速再結合過程が観測される。また、対応するサブピコ秒の時定数は OH$^-$と OD$^-$で異なり、同位体効果が認められる。以上のことから、この特異的な高速再結合は、負イオンから電子脱離した後の水素原子移動による OH ラジカルの構造拡散と、拡散した OH に対する電子再結合によるものと結論される。

1) Y. Yamamoto, T. Suzuki, *J. Phys. Chem. A* **2023**, 127, 2440– 2452. 2) H. Iglev, S. K. Kolev, H. Rossmadl. P. St. Petkov, G. N. Vayssilov, *J. Phys. Chem. Lett.* **2015**, 6, 986– 992.

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19日(火) 13:00 ~ 14:50 A1455(14号館 [5階] 1455)

[A1455-2pm] 05. 物理化学—反応

座長：深堀 信一、野々瀬 真司

日本語

13:00 ~ 13:20

[A1455-2pm-01]

高強度レーザー場における非対称コマ水分子のイオン化

○深堀 信一[1,2]、菊池 勇[1]、長谷川 宗良[1,2] (1. 東大院総文、2. 東大先進機構)

英語

13:20 ~ 13:40

[A1455-2pm-02]

真空中の蒸発冷却による水液滴の均質凍結：液滴径変化の光測定と相転移挙動の高速画像観察

○飯田 岳史[1]、荒川 雅[1]、堀尾 琢哉[1]、寺嵜 亨[1] (1. 九州大学)

英語

13:40 ~ 14:00

[A1455-2pm-03]

ニッケル金属原子内包シリコンケージナノクラスターのサイズ依存性と化学的特性

○佐々木 綾香[1]、市川 琢己[1]、中嶋 敦[1] (1. 慶應義塾大学)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[A1455-2pm-04]

ジベンゾクラウンエーテルのアルカリ金属イオン錯体における異性化反応速度のゲストイオン依存性

○伊藤 亮佑[1]、大下 慶次郎[1]、美齊津 文典[1] (1. 東北大院理)

日本語

14:30 ~ 14:50

[A1455-2pm-05]

気相生体分子イオンのプロトン移動反応

○野々瀬 真司[1]、豊見山 蒼樹[1]、石井 空雅[1]、笹野 光紀[1]、吉野 壮悟[1] (1. 横浜市立大学)

Ionization of asymmetric top water molecule in an intense laser field

([1] *Graduate School of Arts and Sciences, The Univ. of Tokyo*, [2] *Komaba Institute for Science, The Univ. of Tokyo*) ○Shinichi Fukahori,[1,2] Isamu Kikuchi,[1] Hirokazu Hasegawa,[1,2]

Keywords: Ionization in an intense laser field; Rotational wave packet; Asymmetric top molecules; Water

When molecules are irradiated with an intense laser field, ionization is induced by electron emission dominantly from the highest occupied molecular orbital (HOMO).[1] Recently, we recorded the yield of H_2O^+ as a function of the delay time between pump and probe femtosecond laser pulses when a rotational wave packet of H_2O is created by the pump pulse and H_2O is ionized by the probe pulse.[2] We found that ionization of H_2O is enhanced when the molecular *c* axis, which is perpendicular to the molecular plane of H_2O, is parallel to the laser polarization direction and that the photoelectrons are emitted dominantly from the $1b_1$ HOMO of H_2O in the C_{2v} geometry. In the present study, on the basis of theoretical simulation on the time evolution of the rotational wave packet of asymmetric top H_2O, we discuss the contribution from the electron emission from the lower-lying orbitals of H_2O.[3]

We numerically calculated the time evolution of the rotational wave packet of H_2O by solving the time-dependent Schrödinger equation for the interaction between H_2O (25 K) and the pump laser pulse (35 TW/cm^2, 130 fs).[2,3] Figure 1(a) shows the Fourier transform (FT) spectra of the time variation of the expectation values of $\cos^2\theta_{Zb}$ and $\cos^2\theta_{Zc}$ after the pump laser irradiation, where θ_{Zb} is angle between the laser polarization *Z* axis and the molecular *b* axis (C_2 symmetry axis) and θ_{Zc} is angle between the *Z* and *c* axes. We found that the spectrum for the *b* axis exhibits the peak at 38 cm^{-1} assigned to 2_{12}-1_{10} while that for the *c* axis does not exhibit this peak. As shown in Fig. 1(b), the FT spectrum of the delay dependent H_2O^+ yield recorded previously[2] exhibits only a small peak at 38 cm^{-1}, indicating that the angular dependence of the ionization probability of H_2O is close to $\cos^2\theta_{Zc}$ and that electrons are emitted from the $1b_1$ HOMO. However, the relative intensities of two peaks around 112 cm^{-1} are different between the FT spectrum for the *c* axis and that of the H_2O^+ yield. This discrepancy can be explained by the small contribution from the ionization induced by the electron emission from the $3a_1$ HOMO−1, whose angle-dependent probability is close to $\cos^2\theta_{Zb}$.

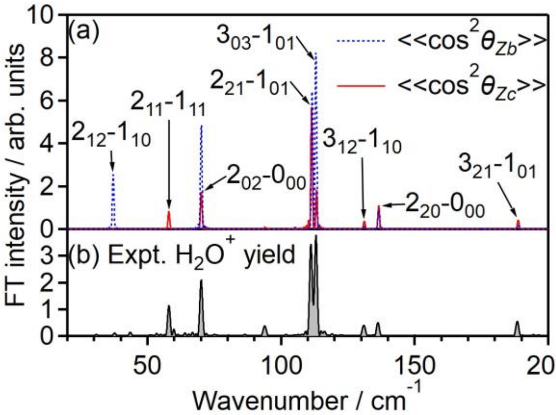


Fig. 1 Fourier transform (FT) spectra of (a) time variation of expectation values of $\cos^2\theta_{Zb}$ (blue dotted) and $\cos^2\theta_{Zc}$ (red solid) and (b) delay dependent H_2O^+ yield.

1) D. Pavicic, K. F. Lee, D. M. Rayner, P. B. Corkum and D. M. Villeneuve, *Phys. Rev. Lett.* **2007**, *98*, 243001. 2) I. Kikuchi, S. Fukahori and H. Hasegawa, *Phys. Rev. A* **2023**, *108*, 013101. 3) S. Fukahori, I. Kikuchi and H. Hasegawa, *Chem. Phys. Lett.* **2023**, *833*, 140912.

真空中の蒸発冷却による水液滴の均質凍結：液滴径変化の光測定と相転移挙動の高速画像観察

（九大院理）○飯田　岳史・堀尾　琢哉・荒川　雅・寺嵜　亨

Evaporative cooling and freezing of water droplets in vacuum in the homogeneous freezing regime (*Graduate School of Science, Kyushu University*) ○ Takefumi Handa, Masashi Arakawa, Takuya Horio, Akira Terasaki

The size of water droplets during evaporative cooling was probed by the whispering gallery modes observed in the OH stretching band of the Raman scattering spectrum. The droplet size as a function of time showed damping oscillation of quadrupolar distortion and shrinkage due to evaporation. Subsequent freezing events were monitored by a high-speed camera, which enabled discussion on the homogeneous nucleation rate and the ice-crystal growth process. Fragmentation of water droplets was induced even for sizes as small as 50 μm.

Keywords :Homogeneous ice nucleation, supercooled water, whispering gallery mode, water droplet

真空中で急速に蒸発冷却される微小な水液滴は、−40℃まで液相を保持する[1]。大気中では到達が困難な低温部の過冷却状態の探索および現象理解のため、本研究では、ラマン散乱スペクトルのOH伸縮振動領域に現れるwhispering gallery mode (WGM)を検出し、初期直径40 μmの水滴のサイズ変化を測定した。真空中に射出した水滴に波長532 nmのナノ秒パルスを照射し、水滴外周に共鳴する一連のWGMsの波長から、Mie理論に基づく解析により水滴径を算出した(Fig. 1)。WGMの周回面を固定した光学配置で実験を行ったため、1,000 μs以下では水滴生成時に誘起された四重極振動がサイズ変動に現れた。高速カメラで取得した画像からアスペクト比を定量的に解析し、振動の減衰時間から粘性を、振動数から表面張力をそれぞれ評価した。1,000 μs以降の水滴径の単調減少からは蒸発速度が得られた。4000 μs以降の凍結過程ではレーザー光散乱の画像解析により樹状結晶の形成時刻を測定し、過冷却深部(~234 K)で支配的な[2]、均質凍結核生成速度を算出した。凍結時の水滴分裂が、大気中の観測で予想される臨界サイズ(50 μm)[3]よりも小さい40 μmでも起きることが新たに確認され、その分裂確率は80%であった。

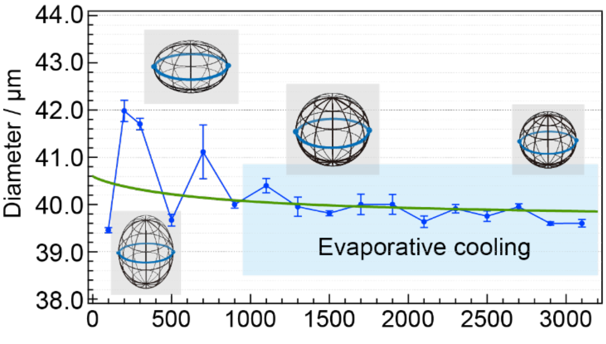


Fig. 1. Droplet size as a function of time in vacuum. Error bar represents the standard error. The solid curve shows prediction by the Knudsen theory.

[1] C. Goy et al. *Phys. Rev. Lett.* **120**, 015501 (2018).
[2] H. Laksmono et al., *J. Phys. Chem. Lett.* **6**, 2826 (2015).
[3] S. Wildeman et al. *Phys. Rev. Lett.*, **118**, 084101 (2017).

Size-dependent chemical reactivity of Ni encapsulating Si nanoclusters deposited on organic surfaces

([1]*Facalty of Science and Technology, Keio University*) ○Ayaka Sasaki,[1] Takumi Ichikawa,[1] Atsushi Nakajima[1]

Keywords: Nanoclusters; Silicon; Nickel; Superatom; Metal-atom encapsulation

Encapsulation of transition metal atoms stabilizes pure silicon nanoclusters which are chemically reactive. Using various transition metal atoms as the central metal in M@Si_n nanoclusters allows for the tailored design of their chemical and physical properties. From an experimental point of view, M@Si_{16} nanoclusters containing group 3 to 5 metal atoms exhibit superatomic behavior depending on various factors, such as electronic characteristics of the deposition substrate, changes in the total number of valence electrons, and the atomic radius of the central metal atom1). Although it is supposed to be less stable as the atomic radius of the central metal atom becomes smaller, Ni@Si_{16} becomes more stable compared to other M@Si_{16} nanoclusters containing iron or cobalt as the central metal atom. While it has been observed that Ta@Si_n nanoclusters deposited on a C_{60} substrate exhibit size-dependent oxidative stability2), there is little experimental evidence for metal-encapsulating silicon nanoclusters containing later group transition metal such as Ni. It remains unclear that the correlation between the stability of Ni@Si_n nanoclusters and the variation in the number of silicon atoms.

In this study, Ni@Si_n (n = 10-13, 16) nanoclusters were deposited onto organic substrates and exposed to O_2 gas. The size-dependent oxidative reactivity of Ni@Si_n was explored using X-ray photoelectron spectroscopy (XPS). Figure 1 shows the relative oxidative reactivities, depicting XPS peak changes of Si 2p for Ni@Si_n (n = 10-13, 16) on a C_{60} substrate before and after exposing 10000 Langmuir (L; 1L = 1.00×10^{-6} Torr × 1s = 1.33×10^{-4} Pa × 1s) O_2 gas. It has been revealed that Ni@Si_{12} exhibits relatively higher stability compared to the others. This can be attributed to both the geometric packing and the electronic stability (58 electron shell closing). This study also indicates that oxidative reactivities can be controlled by changing the type of deposition substrate.

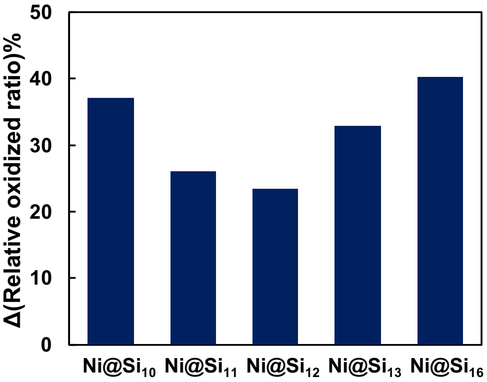


Fig. 1. The XPS peak difference of Si 2*p* between 0 L and 10000 L O_2 exposure for Ni@Si_n (*n* = 10-13, 16) on C_{60}.

1) Kamoshida, T., Shibuta, M., Ohta, T., Eguchi, T., & Nakajima, A., *J. Phys. Chem. C*, **2022**, *126*, 10889.

2) Shibuta, M., Huber, M., Kamoshida, T., Terasaka, K., Hatanaka, M., Niedner-Schatteburg, G., & Nakajima, A., *J. Phys. Chem.* C, **2022**, *126*, 4423.

Guest Ion Dependence of Isomerization Reaction Rate in Dibenzo-Crown Ether Complexes with Alkali Metal Ions

(*Graduate School of Science, Tohoku University*)
○Ryosuke Ito, Keijiro Ohshimo, Fuminori Misaizu

Keywords: Crown Ether; Isomerization Reaction; Ion Mobility–Mass Spectrometry

Crown ethers play an important role in host-guest chemistry owing to their ability to encapsulate guest ions efficiently and selectively. Previously, we studied the conformations of dibenzo-24-crown-8 (DB24C8) complexes with K^+, Rb^+, and Cs^+ ions using ion mobility–mass spectrometry (IM-MS) and confirmed the coexistence of two conformers with long and short distances between the two benzene rings in a molecule.[1] Besides, isomerization between these conformers of the K^+(DB24C8) was observed in our previous study with variable temperature cryogenic IM-MS.[2] Among the studies on these complexes, the ultraviolet photodissociation spectroscopy revealed that only the open conformer has a long benzene-benzene distance in the K^+ complex, whereas the open and boat conformers (Fig. 1) have such structures in the Rb^+ and Cs^+ complexes.[3] In this study, we investigate the guest ion dependence of the isomerization reaction rate in DB24C8 complexes with K^+, Rb^+, and Cs^+ ions.

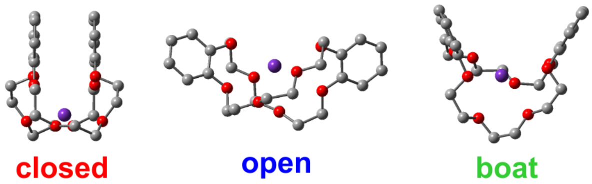


Fig 1. The most stable closed, open, and boat conformers of Rb^+(DB24C8) obtained by M05-2X/6-311++G(d,p) level with the Stuttgart RLC ECP for the Rb atom. Hydrogen atoms are not shown for clarity.

Fig. 2 shows the arrival time distributions (ATDs) of M^+(DB24C8) measured at 86 K. The bands with short and long arrival times correspond to the conformers with short and long benzene-benzene distances, respectively. Ions between the two bands observed in the K^+ complex indicates the multiple isomerization processes within about 2 ms. In contrast, fewer ions were observed between the two bands in the Rb^+ complex. This means that the isomerization rate in the Rb^+ complex was slower than that in the K^+ complex. This rate difference was due to the fact that the open and boat conformers coexist in the Rb^+ complex, while the open conformer is predominant in the band with longer arrival time in the ATD of the K^+ complex.

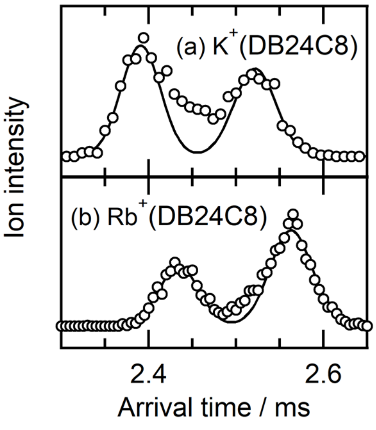


Fig 2. ATDs of M^+(DB24C8) (M = K and Rb) at 86 K.

1) K. Ohshimo, X. He, R. Ito, K. Tsunoda, S. Tainaka, F. Misaizu, *EPJ Tech. Instrum.* **2023**, *10*, 11.
2) R. Ito, X. He, K. Ohshimo, F. Misaizu, *J. Phys. Chem. A* **2022**, *126*, 4359.
3) M. Kida, T. Ujihira, M. Kubo, S. Muramatsu, T. Ebata, Y. Inokuchi, *J. Phys. Chem. A* **2023**, *127*, 3210.

気相生体分子イオンのプロトン移動反応

(横市大院生命ナノ [1]) ○野々瀬真司 [1]・豊見山蒼樹 [1]・石井空雅 [1]・笹野光紀 [1]・吉野壮悟 [1]

Proton Transfer Reactions of Bimolecular Ions in Gas Phase

([1]*Graduate School of Nanobioscience, Yokohama City University, Japan*)
○Shinji Nonose, [1] Soju Tomiyama, [1] Kuga Ishii, [1] Koki Sasano, [1] Sogo Yoshino[1]

Time-, temperature-, and OPIG-DC voltage-resolved proton transfer reactions of multiply-protonated biomolecular ions to 1,5-pentanediamine (Peda) were examined in the gas phase. Pressure of buffer gas in the collision cell, He or Ne, was also changed. Absolute reaction rate constants for proton transfer were determined from intensities of precursor and product ions in the mass spectra. With changes of direct current (DC) voltage to put octapole ion guide (OPIG) in the collision cell, V_{DC}, remarkable change was observed for distribution of the ions and reaction rate constants of proton transfer. The results indicate that conformation changes on ions at OPIG-DC voltage range, which relate with complex formation. An issue that is attracting considerable attention is their conformations might resemble structural evolution that originated from internal energy in the gas phase.

Keywords: Biomolecular ion; Proton transfer reaction; OPIG-DC; Pressure of buffer gas

気相中で生体分子の多電荷イオンと 1,5-pentanediamine (Peda)とのプロトン移動反応に関して研究した。プロトン移動の反応速度を指標として、反応温度、反応時間、およびオクタポールイオンガイド(OPIG)の直流電圧(OPIG-DC)である V_{DC} を変化させた。さらに、衝突反応セル内のバッファーガスである He あるいは Ne の圧力を変化させた。これらのパラメータの変化によって、イオンの立体構造と反応に関して検討した。図 1 に cytochrome c イオン、$[\mathrm{M}+13\mathrm{H}]^{13+}$と Peda とのプロトン移動反応の V_{DC} 依存性に関する質量スペクトルを示す。図の(A)は ESI によってイオンを生成した場合、(B)は$[\mathrm{M}+13\mathrm{H}]^{13+}$のみを選別した場合、(C)～(H)は衝突反応セルに Peda を導入して、プロトン移動反応を誘起した場合をそれぞれ表す。(C)から(H)への順で V_{DC} が増加している。V_{DC} の値が増加するのに伴って、プロトン移動反応の各生成物イオンの強度が大きく変化した。これはイオンの立体構造の変化に伴って、プロトン移動の反応速度が変化したことに起因すると考えられる。

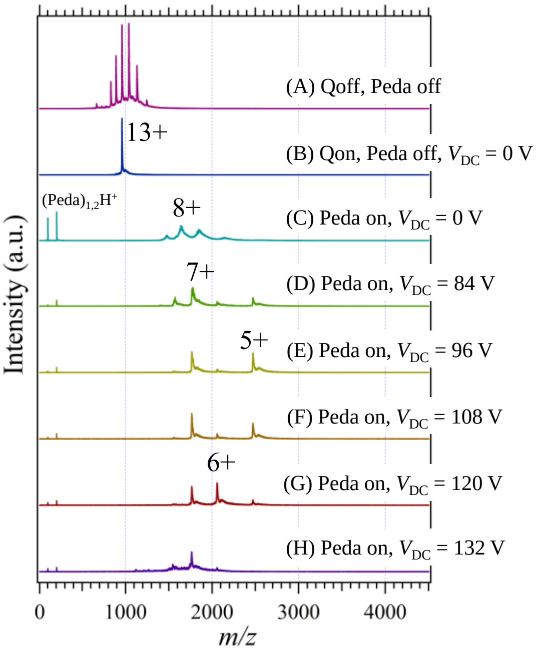


Figure 1. Mass spectra of cytochrome c ion, $[\mathrm{M}+13\mathrm{H}]^{13+}$, reacted with Peda in various V_{DC}.

1) Temperature-Resolved Proton Transfer Reactions of Biomolecular Ions, S. Nonose, *Mass Spectrometry*, **2020**, 9, A0083.

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19日(火) 13:00 ~ 15:30 A1453(14号館 [5階] 1453)

[A1453-2pm] 06. 分析化学

座長：佐藤 雄介、川井 隆之

日本語
13:00 ~ 13:20
[A1453-2pm-01]
“ナノギャップ１分子計測法による生体分子検出・解析法の開発”

〇大城 敬人[1]、小本 祐貴[1]、谷口 正輝[1] (1. 大阪大学)

日本語
13:20 ~ 13:40
[A1453-2pm-02]
細胞内生体分子の多色検出に向けた超高輝度ラマンプローブ合成

〇古屋 圭惟[1]、西山 諒[1]、Phillip McCann[1]、Laura Kacenauskaite[1,2]、Bo Laursen[3]、Amar Flood[4]、丁 天本[1]、平松 光太郎[1,5]、合田 圭介[1,6,7] (1. 東大、2. スタンフォード大学、3. コペンハーゲン大、4. インディアナ大、5. 九大、6. UCLA、7. 武漢大)

英語
13:40 ~ 14:00
[A1453-2pm-03]
ラマン内視鏡を用いた生体内での肝グリコーゲン定量法の開発

〇松下 昇平[1]、上田 善文[1]、吉村 英哲[1]、島田 林太郎[2]、小澤 岳昌[1] (1. 東京大学、2. 青山学院大学)

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30
[A1453-2pm-04]
時間領域分子振動解析による高速・多色ラマンタグ定量法

〇西山 諒[1]、平松 光太郎[1,2]、古屋 圭惟[1]、河村 伸太郎[3]、闐闐 孝介[3]、Min Wei[4]、丁 天本[1]、袖岡 幹子[3]、合田 圭介[1,5,6] (1. 東京大学、2. 九州大学、3. 理化学研究所、4. コロンビア大学、5. カリフォルニア大学ロサンゼルス校、6. 武漢大学)

英語
14:30 ~ 14:50
[A1453-2pm-05]
Ultra-sensitive SERS at single-protein level via a new delivery technique for analytes into hotspots

〇Tianxu Gao[1], Hideyuki Mitomo[2], Xu Shi[3], Yusuke Yonamine[2], Kuniharu Ijiro[2] (1. Grad. Sch. Life Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ., 3. CRIS, Hokkaido Univ.)

英語
14:50 ~ 15:10
[A1453-2pm-06]
生体深部におけるタンパク質間相互作用および細胞融合の近赤外発光検出法の開発

〇李　伶[1]、河村 玄気[1]、李 喬婧[1]、小澤 岳昌[1] (1. 東京大学 理学系研究科 化学専攻)

英語

15:10 ~ 15:30

[A1453-2pm-07]

新しいオプトジェネティックシステムによる深層組織でのインスリンシグナル制御

〇DONG QI[1]、遠藤 瑞己[1]、小澤 岳昌[1] (1. 東京大学)

ナノギャップ１分子計測法による生体分子検出・解析法の開発

（阪大産研[1]）大城 敬人[1]、小本 祐貴[1]、谷口 正輝[1]

Development of single molecule detection method for methylation-modified microRNA analysis

([1]*Osaka University*, *ISIR*) ○Takahito Ohshiro[1], Yuki Komoto[1], Masateru Taniguchi[1]

In this study, we developed a biomolecule detection and analysis technique using the nano-gap single-molecule measurement method. This approach, utilizing precision microfabrication technology, detects the unique electronic states of single molecules through electrical properties across a nano-gap. The nano-gap generates unique signals based on the properties of molecules passing through it. This allows for the individual identification and detailed analysis of biomolecules such as DNA, RNA, amino-acid, proteins, and so on. The technique has potential applications in medical diagnostics, biosensors, and molecular biology research, enabling high sensitivity and precision in biomolecule detection.

Keywords : DNA; Amino acid, Single-Molecule Detection;Tunnel-Current; Epigentics

これまで、ナノギャップを活用した一分子計測法による生体分子の検出・解析技術を開発してきた。微細加工技術により作成されたナノギャップを通過する各分子の電子物性に基づき、高感度高速に電流シグナルを検出することで、DNA やタンパク質などの生体分子を個別に識別し、詳細に解析することが可能である。本研究では、生体分子の後天的修飾に注目し、これらの網羅的な検出・識別を機械学習法によって検討した。

試料となる分子としては核酸塩基モノマーおよび修飾塩基の含む水溶液、アミノ酸 20 種およびその光学異性体、アセチル化・メチル化などの修飾アミノ酸水溶液について 100nM～1uM の濃度に調整し、室温・大気圧下で計測を行った。計測に用いる nano-MCBJ デバイスにより電極間距離をトンネル電流測定可能な距離に制御し、電気計測を行った。得られたシグナルは、分子の持つ特徴的なコンダクタンスプロファイルを反映しているため、特徴量を抽出して機械学習を行い、学習器の評価を行った。

その結果、生体分子の核酸塩基と修飾塩基の識別、アミノ酸と修飾アミノ酸の識別が高い識別能を持つことが示された。これは、特定のマイクロ RNA のメチル化修飾状態を評価でき、疾患の診断への応用可能性を示唆している。この技術は、医療診断やバイオセンサー、分子生物学研究など、多岐にわたる応用が期待されるものである。本研究により、微細な生体分子の変化を高感度かつ高速に検出することが可能になり、将来的にはより精密なバイオマーカーの同定や、疾患の早期発見に貢献することが期待される。また、この技術の進展は、生体分子の微細な差異を検出することによって、個別化医療の発展にも寄与が期待できる。

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

細胞内生体分子の多色検出に向けた超高輝度ラマンプローブ合成

（東大院理[1]・スタンフォード大[2]・コペンハーゲン大[3]・インディアナ大[4]・九大[5]・UCLA[6]・武漢大[7]）○古屋 圭惟[1]・西山 諒[1]・Phillip Mccann[1]・Laura Kacenauskaite[1,2]・Bo Laursen[3]・Amar H. Flood[4]・丁 天本[1]・平松 光太郎[1,5]・合田 圭介[1,6,7]

Synthesis of ultra-bright Raman probes for multicolor detection of intracellular biomolecules

([1]*The Univ. of Tokyo*, [2]*Stanford Univ.,*[3]*Univ. of Copenhagen,* [4]*Indiana Univ.,* [5]*Kyushu Univ.,* [6]*UCLA,* [7]*Wuhan Univ.*) ○ Kei Furuya,[1] Ryo Nishiyama,[1] Phillip Mccann,[1] Laura Kacenauskaite,[1,2] Bo Laursen,[3] Amar H. Flood,[4] Tianben Ding,[1] Kotaro Hiramatsu, [1,5] Keisuke Goda[1,6,7]

Chemical probes enable the specific detection of various biomarkers by binding to biomolecules in cells. In recent years, Raman probes have attracted attention for their capability of multicolor measurement, surpassing fluorescent probes in the detection of biomolecules in cells. However, Raman probes exhibit significantly weaker signal intensities compared to fluorescent probes, making the enhancement of their brightness a crucial challenge for effective biomolecule detection. To address this, we have synthesized MERdot (Macrocycle-enhanced Raman dot), an ultra-bright Raman tag consisting of Raman dyes and cyclic molecules encapsulated in polystyrene particles of several tens nm1). The Raman signal intensity of MERdot was over three times stronger than that of conventional Raman tags (Fig. 1) 1). In this presentation, I will describe the synthesis method of MERdot, its measurement results, and the progress in developing a Raman probe using MERdot for intracellular biomolecular measurements.

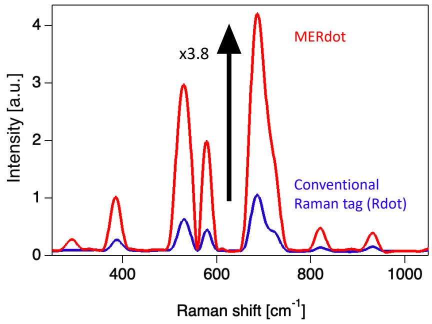


Figure 1. Raman spectra of MERdots and conventional Raman tags at the same dye concentration.

Keywords : Raman Spectroscopy; Molecular Spectroscopy; Chemical Probe; Multi-Mode Measurement; High-Sensitivity Measurement

化学プローブは、細胞内の生体分子に結合させることにより、様々なバイオマーカーの特異的な検出を可能とする。近年では、細胞中の生体分子の検出において、蛍光プローブを超える多色測定の応用が可能なラマンプローブが注目されている。しかし、ラマンプローブは蛍光プローブと比較して信号強度が著しく弱いため、生体分子の検出に用いるためにはプローブの輝度上昇が課題となる。そこで我々はラマン色素および環状分子を数十 nm のポリスチレン粒子に封入した超高輝度ラマンタグであるMERdot (Macrocycle-enhanced Raman dot)を合成した。MERdot のラマン測定を行ったところ、その信号強度は従来のラマンタグの 3 倍以上の信号強度を示した(Fig. 1)1)。本講演では MERdot の合成手法および測定結果、さらに細胞内生体分子測定に向けた MERdot を用いたラマンプローブ開発の取り組みについて述べる。

1) R. Nishiyama, K. Furuya, P. McCann, et al. Boosting the Brightness of Raman Tags Using Cyanostar Macrocycles. *Analytical Chemistry*, 2023, 95.34: 12835-12841.

In vivo quantification of hepatic glycogen by Raman endoscopy

([1] *Department of Chemistry, School of Science, The University of Tokyo*, [2] *Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama Gakuin University*) ○Shohei Matsushita,[1] Yoshibumi Ueda,[1] Hideaki Yoshimura,[1] Rintaro Shimada,[2] Takeaki Ozawa [1]

Keywords: Raman spectroscopy; Endoscopy; Glycogen; Multivariate analysis;

Glycogen plays a vital role in regulating glucose metabolism homeostasis and serves as an energy reservoir in organs such as liver and muscles. Dysregulation of these processes is closely linked to diabetes. Developing a method to quantify temporal changes in glycogen levels in living organisms could provide valuable insights for understanding and diagnosing diseases like diabetes. Conventional methods, such as biochemical assays, however, are not applicable to the real-time monitoring of glycogen in living organisms because of their destructive nature. MRI, which enables in vivo measurements, faces limitations due to expensive equipment and low selectivity. In contrast, Raman spectroscopy offers non-destructive and molecule-specific quantitative analysis. In addition, Raman spectroscopy can be mounted on endoscopes to measure the spectra inside living organisms. This research aimed to develop a novel method for monitoring hepatic glycogen in living mice by combining endoscopy with Raman spectroscopy.

Five samples of homogenized mice livers were prepared with different glycogen concentrations. Raman spectra of each sample were measured and analyzed using Singular Value Decomposition (SVD) and Independent Component Analysis (ICA). One of the obtained component spectra matched the Raman spectrum of glycogen, and its weights correlated linearly with glycogen concentration. Based on the weights, a calibration curve of glycogen concentration and the weights was created. Next, an analysis of the glycogen concentration of non-destructive liver samples was performed. Liver tissues were extracted from mice under different feeding conditions, and Raman spectra were measured on the liver surface. The weights of the glycogen component extracted by the multivariate analysis were plotted on the calibration curve to estimate glycogen concentration. The calculated glycogen concentration showed a linear relationship with glycogen quantities in paste samples, demonstrating the potential of Raman endoscopy for the surface measurements. Also, comparison of the results from Raman endoscopy and those from a colorimetric assay of glycogen showed a linear relationship, indicating comparable quantitative ability. Finally, we conducted glycogen quantification using Raman endoscopy in living mice. Under glucagon administration, depletion of glycogen was detected, consistent with its role in promoting glycogen breakdown.

In conclusion, a Raman endoscopy system was established, which has the potential to monitor glycogen changes quantitatively in the liver of living mice. The quantitative ability of the Raman endoscopy system is comparable to existing biochemical colorimetry. Using this system, the physiological phenomena of glucagon-induced glycogenolysis were monitored by glycogen depletion. This new method opens opportunities for studying glycogen-related metabolism in vivo at high temporal resolution and high quantitative ability.

High-speed, multiplex Raman tag quantification enabled by time-domain molecular vibration analysis

([1]*The University of Tokyo*, [2]*Kyushu University,* [3]*RIKEN,* [4]*Columbia University,* [5]*UCLA,* [6]*Wuhan University*) ○ Ryo Nishiyama[1], Kotaro Hiramatsu[1,2], Kei Furuya[1], Shintaro Kawamura[3], Kosuke Dodo[3], Wei Min[4], Ding Tianben[1], Mikiko Sodeoka[3], Keisuke Goda[1,5,6]

Keywords: Raman spectroscopy; Chemical probe; Flow cytometry; Imaging; Raman tag

Recently, Raman tags have attracted considerable interest as a molecular label capable of multicolor measurements in imaging [1] and flow cytometry [2], surpassing those of fluorescent tags. This stems from the fact that Raman spectra exhibit narrower line widths compared to fluorescence spectra, facilitating the differentiation between various tags. However, a notable challenge with Raman tags is their relatively weaker signal intensity compared to fluorescent tags, which has hindered their widespread applications.

In this study, we synthesized bright Raman tags by encapsulating resonance-enhanced Raman-active dyes in polymer nanoparticles. Their molecular vibration signal in the time domain were measured with a Fourier-transform coherent anti-Stokes Raman scattering (FT-CARS) spectroscopy [3], aiming to achieve rapid and highly sensitive detection of these tags (see Fig. 1a). The obtained time-domain signal (see Fig. 1b) was fit with reference time-domain signal obtained from the Raman tags as a basis set, demonstrating a higher Raman tag quantification accuracy and a potential high-speed Raman tag detection capability, which is applicable for high-speed super-multiplex imaging and flow cytometry.

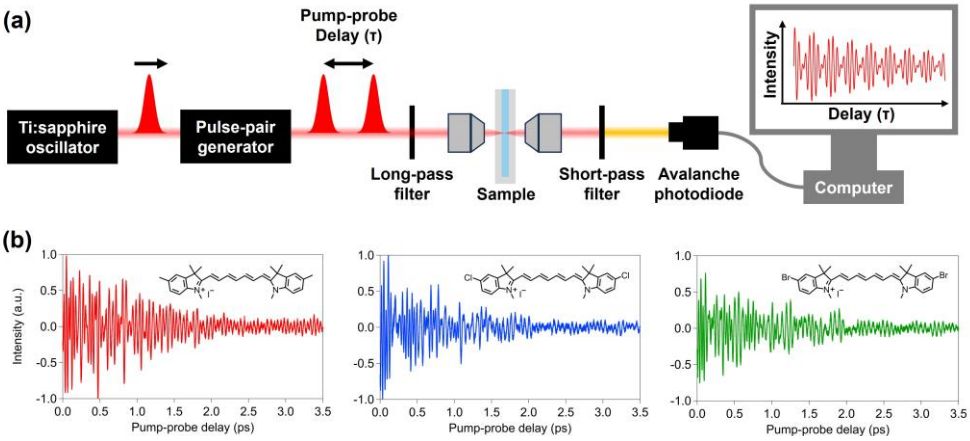


Figure 1. Schematic and measurement results for time-domain molecular vibration signals. (a) Schematic of the FT-CARS spectrometer for time-domain vibration signal acquisition. (b) FT-CARS measurement results for 3 different resonance-enhanced dye species.

1) L. Wei et al. *Nature* **544**, 465–470 (2017). 2) R. Nishiyama et al. *PNAS Nexus*. **2**, pgad001 (2023). 3) K. Hiramatsu et al. *Science Advances* **5**, eaau0241 (2019).

Ultra-sensitive SERS at Single-protein Level via a New Delivery Technique for Analytes into Hotspots

([1]*Graduate School of Life Science, Hokkaido University*, [2]*RIES, Hokkaido University,* [3]*CRIS, Hokkaido University*) ○ Tianxu Gao,[1] Hideyuki Mitomo,[2] Xu Shi,[3] Yusuke Yonamine,[2] Kuniharu Ijiro[2]

Keywords: Surface-enhanced Raman spectroscopy; Localized surface plasmon resonance; Tunable structure; Protein detection; Stimuli-responsive hydrogel

The surface-enhanced Raman spectroscopy (SERS) is a powerful tool in sensitive analyte detection, with the localized-enhanced optical near field (hotspot) in a narrow gap area. However, normal SERS active structures are unsuitable for detecting proteins, as protein's large volume hinders their approach to narrow hotspots. Based on our previous researches,[1-3] in this study, we fabricated an Au nanoTriangle plate Arrangement on Gel (AuTAG) as a gap distance tunable SERS substrates with gold nanotriangle plates (AuNTs) and thermo-responsive poly(N,N-diethylacrylamide) (pDEAA) hydrogel. A novel strategy was further proposed for better delivery of analyte proteins to hotspots.

The AuTAG substrates were fabricated by transferring a packed AuNT monolayer onto pDEAA surface (Fig. 1a). Due to the thermo-sensitivity of pDEAA, the shrinkage or swelling of hydrogel changed inter-AuNT distance under the temperature control. In particular, AuNTs were coated with ligands to prevent non-specific protein adsorption on particle surfaces. The Gel Filter Trapping (GFT) method was designed to deliver proteins into the hotspots specifically for highly sensitive SERS (Fig. 1b). In GFT method, a local water flow generated by water adsorption of the hydrogel that delivers proteins into nanogap areas in AuNT arrays. After nanogaps were closed by heating, SERS measurements were performed. Significant signals of proteins (e.g. hemoglobin) were identified until their single-molecule level concentration (10^{-9} mg/ml), indicating the fact that proteins were effectively delivered into the hotspots. These results demonstrate the ultra-sensitivity of AuTAG substrates with GFT method in protein detection.

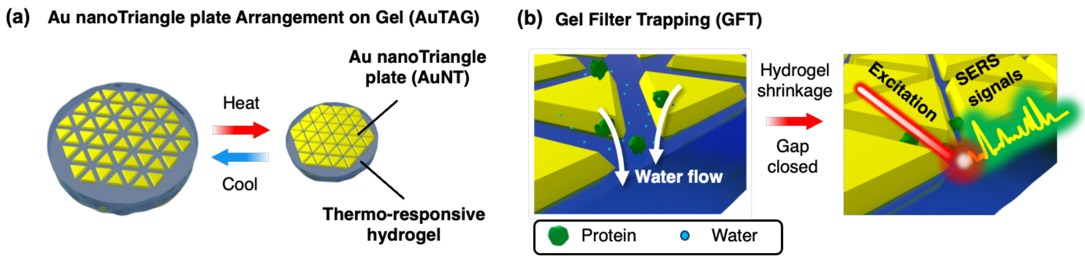


Fig. 1 (a) Structure of AuTAG substrate and its inter-particle distance tuning process. (b) illustration of GFT method.

1) Y. Osada, *Adv. Mater.,* **2012**, 24, 5243–5248. 2) H. Mitomo, K. Ijiro, *Adv. Optical Mater.,* **2016**, 4, 259–263. 3) H. Mitomo, K. Ijiro, *Nanoscale Adv.,* **2019**, 1, 1731–1739

Development of a near-infrared luminescence method for detecting protein-protein interaction and cell fusion events in deep tissues

([1]*Analytical Chemistry, Department of Chemistry, School of Science, The University of Tokyo*)
○Yiling Li[1], Genki Kawamura[1], Qiaojing Li[1], Takeaki Ozawa[1]

Keywords: *Akaluc, Near-infrared light, Split luciferase reconstitution, Protein-protein interaction, Cell fusion*

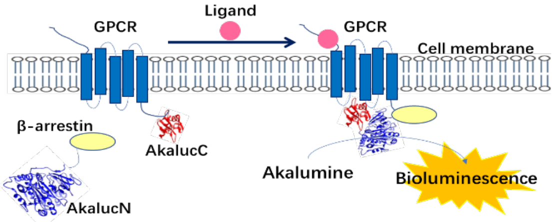


Fig. 1. Scheme of detecting GPCR/β-arrestin interaction by split Akaluc complementation.

【Introduction】 Akaluc is an artificial mutant of firefly luciferase (Fluc), that emits near-infrared light which can penetrate biological tissues efficiently.[1] This study aims to develop a near-infrared luminescence detection method for detecting cellular events in deep tissues using Akaluc-based split luciferase complementation[2], demonstrated by GPCR/β-arrestin interactions and myogenic cell fusion events as examples.

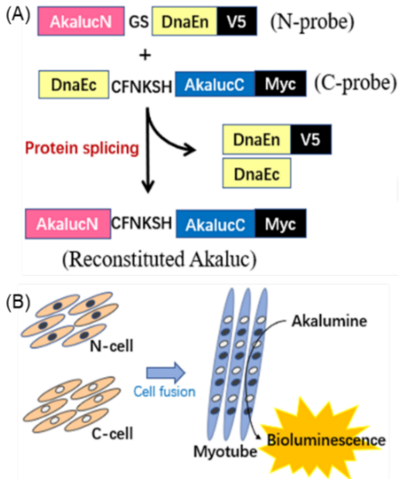


Fig. 2. Design of the myogenesis assay system. (A) Process of protein trans-splicing-based split Akaluc complementation. (B) The principle for monitoring cell fusion events.

【Results and discussion】 To observe the GPCR/β-arrestin interaction, the N- and C-terminal fragments of Akaluc (AkalucN and AkalucC) are fused with β-arrestin and GPCR, respectively. The ligand-induced GPCR/β-arrestin interaction was detected via the bioluminescence generated by split Akaluc complementation (**Fig. 1**). Increased luminescence was confirmed using stable cell lines expressed GPCR-AkalucC and AkalucN-β-arrestin.

For the myogenic cell fusion observation, myogenic cell fusion indicators (N-probe and C-probe) were developed based on trans-splicing-based split luciferase complementation using split Ssp DnaE inteins (**Fig. 2A**). The cell fusion among the mixture of the N- and C-cell, that respectively express N- and C-probe, were detected through the bioluminescence generated by the Akaluc reconstitution (**Fig. 2B**). The spontaneous Akaluc reconstitution was confirmed by the luminescence intensity correlated with myogenesis progression.

In conclusion, split Akaluc reconstitution provides a valuable method to detect GPCR/β-arrestin interaction and cell fusion events. Moreover, it will be a bioengineered analytical method to spur scientific, medical, and industrial applications.

1) Iwano S et al. *Science*. 359: 935-9. 2018. 2) Misawa N et al. *Anal Chem*. 82: 2552-60. 2010.

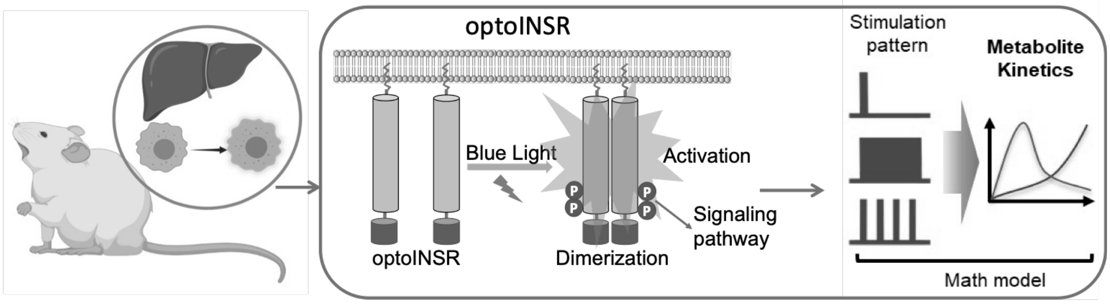
Novel Optogenetic System to Achieve Deep Tissue Insulin Signaling Control in Living Animals

([1]*Graduate School of Science, The University of Tokyo*)
○Qi Dong,[1] Mizuku Endo,[1] Takeaki Ozawa[1]

Keywords: Optogenetics; Insulin Receptor; In vivo

Insulin and insulin receptor (INSR) play a key role in the hormonal regulation system to maintain glucose homeostasis.[1] Secreted by the pancreatic islet beta cells, insulin is released into the bloodstream in several different temporal patterns.[2] To date, the detailed functional role regards to insulin secretion patterns are yet to be confirmed due to the constraint of the conventional methods. In this work, we report an opto-insulin receptor (optoINSR) system that enables the optical activation of insulin signaling using blue light illumination in vivo.

Activation of the insulin signaling cascade begins with the binding of insulin to the α subunits of INSR. Subsequently, the structural rearrangement brings the β subunit close together to activate downstream signaling cascades. Simulating this process, optoINSR consists of the β subunit of the INSR that is connected to the photoreceptorAureochrome1a (AU1) from Vaucheria frigida.[3] Upon blue light illumination, AU1 will bring the fused β subunit closer together mimicking the action of insulin binding to INSR. To confirm the activation of optoINSR upon light stimulation, mammalian cells transiently expressing optoINSR were illuminated with blue LED light (~440 nm, 10 s min-1). The western blotting analysis demonstrated an increase in phosphorylation of downstream molecules upon illumination, which confirmed the activation of optoINSR by light. To further apply optoINSR in *in vivo* mouse model, adenovirus harboring optoINSR gene was injected into BALB/c mice. The liver of infected mice was exposed and illuminated with blue LED light then subsequently excised and homogenized for western blotting analysis. Results demonstrated the increase in phosphorylation of downstream molecules upon illumination. Taken altogether, optoINSR controls the insulin-mediated signaling by blue light illumination both in cultured cells and in living mouse liver.



1) C.J. Hedeskov, *Physiol. Rev.* **1980**, *60* (2), 442–509. 2) H. Kubota, *Cell Syst.* **2018**, *7* (1), 118-128. 3) F. Takahashi, *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104* (49), 19625–19630.

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19日(火) 15:55 ~ 17:15 A1444(14号館 [4階] 1444)

[A1444-2vn] 07. 無機化学

座長：秋吉 一孝、神戸 徹也

英語

15:55 ~ 16:15

[A1444-2vn-01]

Tunable Optical Properties of Newly Developed Ag-Mn-Sn-S Quantum Dots through Precise Composition Control

〇Chang Jiang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Naoki Banno[1], Hiroshi Yukawa[1], Yoshinobu Baba[1], Tsukasa Torimoto[1] (1. Nagoya Univ.)

英語

16:15 ~ 16:35

[A1444-2vn-02]

Tert-butoxy基を有するspiro-5型分子をプリカーサーとして用いたアルミノシリケート構築

〇今泉 暁[1]、本田 暁紀[1]、横井 俊之[2]、張 浩徹[1] (1. 中央大学、2. 東京工業大学)

英語

16:35 ~ 16:55

[A1444-2vn-03]

Frustrated Lewis Pair reactivities of phosphino-phosphenium cations

〇Hyehwang Kim[1], Douglas Wade Stephan[1] (1. University of Toronto)

英語

16:55 ~ 17:15

[A1444-2vn-04]

配位子保護Auクラスター合成におけるデンドリマー鋳型効果の分析

〇村松 央教[1]、神戸 徹也[1,2]、塚本 孝政[1,2]、今岡 享稔[1,2]、山元 公寿[1,2] (1. 東京工業大学、2. JST-ERATO)

Tunable Optical Properties of Newly Developed Ag-Mn-Sn-S Quantum Dots through Precise Composition Control

([1]*Graduate School of Engineering, Nagoya University*) ○Chang Jiang,[1] Kazutaka Akiyoshi,[1] Tatsuya Kameyama,[1] Naoki Banno,[1] Hiroshi Yukawa,[1] Yoshinobu Baba,[1] Tsukasa Torimoto[1]

Keywords: Quantum dots; Colloidal synthesis; Composition-dependent optical properties

$\mathrm{I_2}$–II–IV–$\mathrm{VI_4}$ semiconductors comprised of abundant and less toxic elements, such as Cu_2ZnSnS_4, have attracted attention as photovoltaic materials owning to their suitable bandgap and high absorption coefficient (10^4 $\mathrm{cm^{-1}}$). Another recent focus involves Ag_2MnSnS_4 (AMTS), which exhibits comparable optical properties with Cu_2ZnSnS_4. The energy gap of bulk AMTS was reported to ca. 2.0 eV[1], making them suitable for solar light conversion systems. Moreover, it is expected that Mn doping imparts magnetic properties derived from unpaired 3d electrons in Mn ions. On the other hand, intensive research has been conducted to decrease the size of semiconductor particles to the nanoscale for the preparation of quantum dots (QDs), offering controllable optoelectronic properties based on size and composition. In this study, we report the colloidal preparation of AMTS QDs by a heating-up method and their optical properties depending on their chemical composition.

The precursors of Ag(OAc), $Mn(OAc)_2$, $Sn(OAc)_4$, and sulfur powder dissolved in oleylamine (OLA)/1-dodecanethiol (DDT) solution were reacted at 250 °C for 10 min under N_2 atmosphere. The resulting solution was subjected to centrifugation to remove large precipitates. Thus-obtained AMTS QDs were isolated from the supernatant by adding methanol as a non-solvent. The Ag/metal ratio in the precursors was changed from 0.50 to 0.05.

The optical bandgap determined from the absorption onset monotonously decreased from 2.4 eV to 2.0 eV with a decrease in the Ag/metal ratio (Fig 1a). The electronic energy structure of AMTS QDs was determined by the photoemission yield spectroscopy in air (PYSA). The change in the QD composition resulted in the shift of conduction band minimum from –3.5 eV to –3.1 eV (Fig 1b). Furthermore, by coating QDs with a ZnS shell followed by the ligand exchange with 3-mercaptopropionic acid, the resulting hydrophilic AMTS@ZnS QDs were uniformly dispersed in aqueous solutions without changing their optical properties and chemical composition. These findings open up the possibilities for utilizing ATMS QDs in various applications such as photocatalysis and bioimaging in aqueous media.

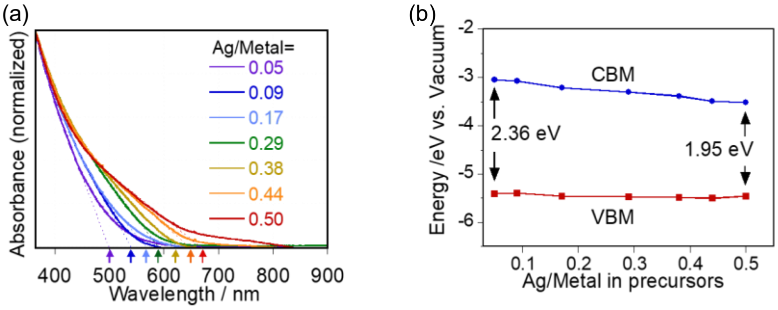


Fig 1. (a) UV-vis absorption spectra of AMTS QDs prepared with different Ag/metal ratio. (b) Electronic energy structure of AMTS QDs.

1) F. N. Keutsch, et al., *Mineral. Mag.*, **2019**, 83, 2.

Aluminosilicate Construction from Spiro-5-Type Molecular Precursors with *tert*-Butoxy Group

(*[1]Graduate School of Science and Engineering, Chuo University*, *[2]Faculty of Science and Engineering, Chuo University*, *[3]Institute of Innovative Research, Tokyo Institute of Technology*) ○Akira Imaizumi,[1] Akinori Honda,[2] Toshiyuki Yokoi,[3] Ho-Chol Chang[2]

Keywords: Molecular Precursor; Aluminosilicate; Solid Acid Catalyst; Pore; *tert*-Butoxide

Construction of aluminosilicates from structurally and compositionally well-defined molecular precursors (MPs) is a promising and stoichiometric method contrary to the conventional processes using discrete Al and Si sources. However, the MP method often suffer from several drawbacks such as the decomposition of a core structure in the presence of solvent, acid, or base during the activation of leaving groups. Herein we present the synthesis of novel spiro-5-type MPs with Si–O^{t}Bu bonds, which can be thermally converted to Si–OH bonds,[1] **C^+[AlSi$_4$]$^-$** (C^+ = PyH^+ and Na^+), and its conversion into aluminosilicate solid acid catalysts by direct heating or solvothermal treatment (Fig. a).

PyH^+[AlSi$_4$]$^-$ showed steep weight loss from 100 °C in its TG diagram under a flow of N_2, and the total weight loss upon heating to 180 °C reached 60%, which is almost consistent with the theoretical value (59%) for the desorption of the pyridine and 8 equivalents of isobutene (Fig. b). **Na^+[AlSi$_4$]$^-$** exhibited the elimination of solvated H_2O below 100 °C, accompanied by a steep weight loss of 51% upon heating to 300 °C. IR spectra of the heated product of **Na^+[AlSi$_4$]$^-$** to 300 °C showed a disappearance of vibrational bands at 2900 cm^{-1} and an increase at 3500 cm^{-1} (Fig. c), supporting the conversion of Si–O^{t}Bu into Si–OH bonds. Noteworthily, heated products to 700 °C showed good catalytic activity toward a ring-opening reaction of styrene oxide (> 80% yield), indicating the introduction of MP-derived Al–OH–Si acid sites. Solvothermal conversion of the MPs into aluminosilicates will also be discussed.

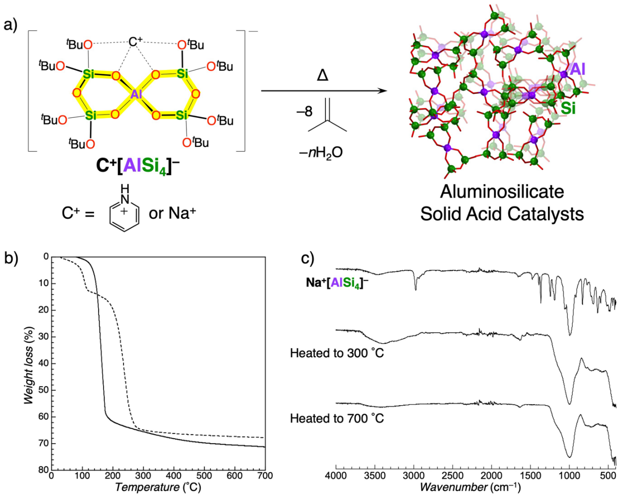


Figure. a) Molecular structure of spiro-5-type **C^+[AlSi$_4$]$^-$** (C^+ = PyH^+ and Na^+) and a plausible scheme of its conversion into aluminosilicates, b) TG diagram of **C^+[AlSi$_4$]$^-$** (C^+ = PyH^+: solid, Na^+: dotted), and c) IR spectra of **Na^+[AlSi$_4$]$^-$** and its heated products.

References 1) Fujdala, K. L.; Tilley, T. D. *J. Catal.* **2003**, *216*, 265.

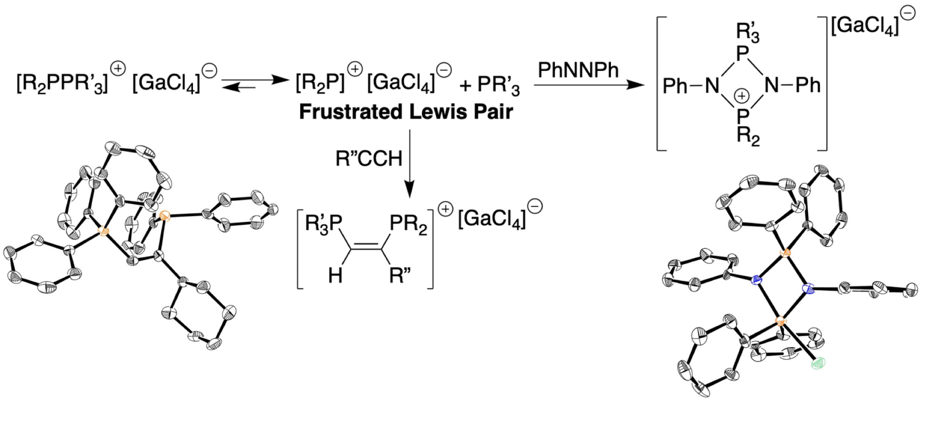
Frustrated Lewis Pair reactivities of phosphino-phosphenium cations

([1]*Department of Chemistry, University of Toronto*) ○Hyehwang Kim,[1] Douglas W. Stephan[1]

Keywords: Phosphorus; Frustrated Lewis Pairs; Phosphenium

The field of frustrated Lewis pair (FLP) chemistry began in 2006 with the Stephan group's landmark report on reversible H_2 activation by a main group compound.[1] Since then, the field has grown immensely by showing how main group compounds can activate small molecules such as CO_2 and CO.[2] FLPs are principally based on Lewis acids and bases that are sterically precluded from adduct formation. Recently, FLP chemistry has also been demonstrated from equilibrium access to the free Lewis acid and base, thus showing that it is not necessary for the Lewis acid and base to be sterically "frustrated".[3]

With this in mind, we present our work on the FLP chemistry of phosphino-phosphenium cations (PPCs) of the forms $[R_2PClPR'_2]^+$ and $[R_3PPR'_2]^+$. Intrigued by reports of these cations undergoing phosphine exchange,[4] we proposed that the labile dative bond in phosphino-phosphenium cations would provide access to the Lewis basic phosphine and Lewis acidic phosphenium moieties in FLP chemistry. In the first part of this presentation, we report the reactions of PPCs with terminal alkynes which resulted in FLP addition products. This methodology was adapted for the synthesis of several dissymmetric *cis*-olefin-linked bidentate phosphines, thus avoiding the conventional use of radicals, transition metals, or pyrophoric lithium reagents. In the second part, we report the cleavage of N=N double bonds in azobenzene using PPCs as FLPs, and the functionalization of the resulting four-membered phosphorus-nitrogen heterocycles.



1) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124. 2) D. W. Stephan, *Science* **2016**, *354*, aaf7229. 3) T. C. Johnstone, G. N. J. H. Wee, D. W. Stephan, *Angew. Chem. Int. Ed.* **2018**, *57*, 5881. 4) N. Burford, T. S. Cameron, P. J. Ragogna, *J. Am. Chem. Soc.* **2001**, *123*, 7947.

Analysis of dendrimer template effect in ligand-protected Au cluster synthesis

([1]*Tokyo Institute of Technology*, [2]*JST-ERATO*) ○Hisanori Muramatsu[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2]

Keywords: cluster; gold; dendrimer; Ligand protection

Metal clusters, which consist of several to dozens of metal atoms, have discrete electron configurations, unlike bulk bodies. Therefore, metal clusters may exhibit properties different from those of bulk states or nanoparticles. In recent years, Au clusters have attracted attention as superatoms that can be synthesized not only in the gas phase but also in the liquid phase. In particular, various reports of Au clusters have been reported since Brust and Schiffrin et al. reported a liquid phase synthesis method for thiol-protected Au clusters.[1] Furthermore, many examples of combinations of different elements have been studied, and various combinations of different elements, mainly noble metals such as Pd, Pt, Cu, Ni, Ag, Cd, and Hg, have been reported. Though Au clusters and those with different elements can be synthesized with high-yields, those require many steps and a lot of derived from etching and exchange reactions. [2,3]

On the other hand, there is a method for liquid phase synthesis of metal clusters that uses dendrimers as templates. This method allows direct synthesis because the elements clustered into the dendrimer can be collected in advance. Recently, $Au_{25}(SR)_{18}$ has been synthesized using the dendrimers (TPM G4)[4].

We verified the effect of the dendrimer by changing the number of Au salts accumulated in TPM G4 (Fig.1). It was suggested that the tendency may differ depending on the number of imine generations in the dendrimer. In the case of different element combinations, the $MAu_{24}(SR)_{18}$ synthesis was confirmed from MS spectra and STEM/EDS for many of the elements studied. Details of the results will be reported on the day.

1) Brust, M.; Schiffrin, D. J.; *et al.*, *J Chem Soc Chem Commun,* **1994**, *0*, 801–802.
2) Zhu, M.; *et al.*, *J. Am. Chem. Soc.,* **2008**, *130*, 5883–5885.
3) Dharmaratne, A. C.; *er al.*, *J. Am. Chem. Soc.,* **2009**, *131* (38), 13604–13605.
4) **Muramatsu, H**.; Kambe, T.; Yamamoto, K. *et al.*, *Molecules*, **2022**, *27*, 3398. **(Cover article)**

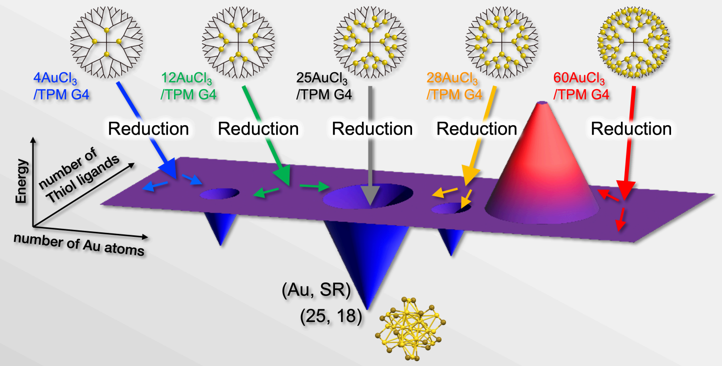


Fig. 1. Image of the difference in the number of clusters produced by the number of nuclei of Au precursors that accumulate in TPM G4. (Note: This image differs from the actual one.)

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19日(火) 15:55 ~ 16:35 A1457(14号館 [5階] 1457)

[A1457-2vn] 08. 触媒

座長：近藤 敏啓、清野 智史

日本語

15:55 ~ 16:15

[A1457-2vn-01]

放射線を利用した樹脂板へのPdナノ粒子固定化法のポリイミド樹脂への適用と無電解めっきへの応用

○上垣 直人[1]、清野 智史[1]、佐藤 陸弥[1]、大久保 雄司[1]、石黒 文康[1]、中川 貴[1] (1. 大阪大学)

英語

16:15 ~ 16:35

[A1457-2vn-03]

ステップ方向制御に向けたアニリン溶液浸漬によるTiO_2(110)単結晶表面の異方的エッチング

○高張 真美[1]、五島 大河[2]、吉本 惣一郎[2]、近藤 敏啓[1] (1. お茶の水女子大学、2. 熊本大学)

英語

[A1457-2vn-02]

講演取り下げ

放射線を利用した樹脂板へのPdナノ粒子固定化法のポリイミド樹脂への適用と無電解めっきへの応用

（阪大院工）○上垣 直人・清野 智史・佐藤 陸弥・石黒 文康・大久保 雄司・中川 貴

Immobilization of Pd nanoparticles on polymer substrates by the method using radiation applied to polyimide resins and its application to electroless plating

(*Graduate School of Engineering, Osaka University*) ○Naoto Uegaki, Satoshi Seino, Rikuya Sato, Fumiyasu Ishiguro, Yuji Ohkubo, Takashi Nakagawa

Pd nanoparticles can be immobilized on various substrates by the method using radiation[1]. Electroless plating film was obtained by using immobilized Pd nanoparticles as catalysts. In this study, we examined its application to polyimide (PI) as substrate materials for flexible printed circuit boards. PI film was enclosed in aqueous solutions of Pd ion. The solution was irradiated and Pd nanoparticles were immobilized. The obtained samples were characterized by SEM, ICP-AES, XPS and so on. Figure 1 shows SEM image of prepared resin plate surface. It was observed that the Pd nanoparticles were immobilized on the PI film. The amount of Pd immobilized on the PI film surface was 54 ng-Pd/mm^2-PI, which was comparable to that of ABS used as the polymer substrates. In addition, the immobilized Pd nanoparticles showed activity as an electroless plating catalyst. The relationship between the surface morphology and chemical state of the obtained samples and the adhesion of the plating film were discussed.

Keywords：Radiation, Nanoparticles, Polyimide, Electroless Plating

放射線を利用した手法により、Pd ナノ粒子を様々な樹脂基板に固定化できることが報告されている[1]。既往研究ではABS樹脂においては固定化したPdナノ粒子を触媒として、密着性の高い無電解めっき膜が得られている。本研究ではフレキシブルプリント配線板の基板材料に用いられているポリイミド（PI）樹脂への適用を検討した。Pd イオン水溶液に浸漬したPI フィルムに放射線を照射し、Pd ナノ粒子を固定化した。得られた試料はSEM、ICP-AES、XPSなどで分析した。得られた試料表面のSEM像をFigure 1に示す。PIフィルム上にPdナノ粒子が固定化されている様子が観察された。PIフィルム表面のPd担持量は54 ng-Pd/mm^2-PIであり、樹脂基材としてABS樹脂を用いた場合と同程度であった。また、固定化したPdナノ粒子は無電解めっき触媒として活性を示した。得られた試料の表面形状および化学結合状態とめっき膜の密着性との関係について議論する。

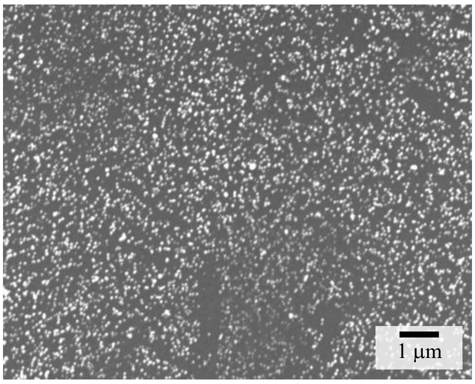


Figure 1. SEM image of prepared Pd nanoparticles on PI film.

1) N. Uegaki et al., *Nanomaterials.* **2022**, *12*, 4106.

Anisotropic Etching of TiO_2(110) Single-Crystal Surface with Aniline Solution Immersion for Step Direction Control

([1]*Graduate School of Humanities and Sciences, Ochanomizu University*, [2]*Graduate School of Science and Technology, Kumamoto University*, [3]*Institute of Industrial Nanomaterials, Kumamoto University*) ○Mami Takahari,[1] Taiga Goto,[2] Soichiro Yoshimoro,[3] Toshihiro Kondo,[1]

Keywords: Aniline (AN); TiO_2(110) Single-Crystal Surface; Solution Immersion; Step direction control; Photocatalytic reaction

TiO_2(110) single-crystal surface have been used as a model surface for photocatalytic reactions. It is important to control of a step direction on TiO_2(110) surface because photocatalytic reactions depend on the step direction. However, there are few reports to control. In this study, we found TiO_2(110) surface was etched and a uniform step structure in the [001] direction formed after immersing of the clean TiO_2(110) single-crystal substrate in an ethanol solution containing aniline.

It is known that AN is uniformly adsorbed on the TiO_2(110) surface when it was vacuum deposited. However, AN was not adsorbed on the TiO_2(110) surface from the solution. Nevertheless, its surface morphology was significantly different before and after the immersion into the ethanol solution containing AN (Fig. 1). Zigzag steps in the $[\bar{1}12]$ direction with many kinks were observed in the sample prepared by immersion into the solution without AN (sample Et), whereas linear $[001]$ direction steps were observed when the sample was immersed in the solution containing AN (sample AN). Since Ti was detected in the solution after immersion, it was concluded that the etching was promoted by the formation of TiO_2-AN complex and its desorption as a result of adsorption of AN to step edged Ti.

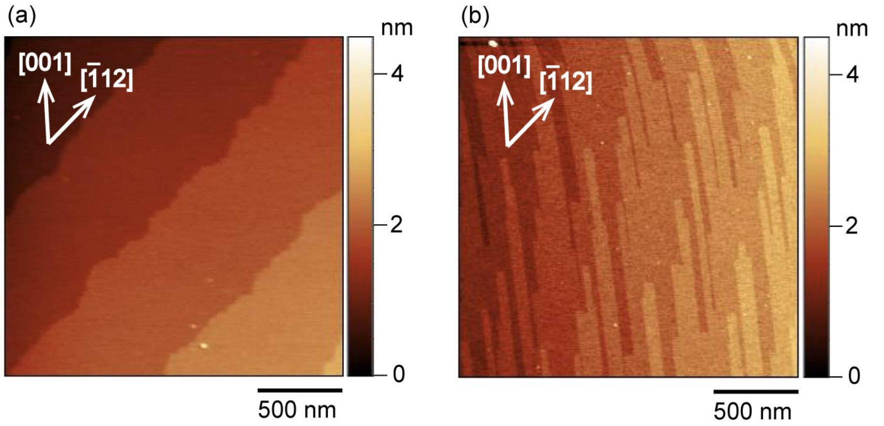


Figure 1 AFM images of (a) sample Et and (b) sample AN (2 μm × 2 μm) [1)].

1) M. Takahari, T. Goto, S. Yoshimoto, T. Kondo, *Chem. Lett.* **2023**, *52*, 823.

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19日(火) 15:55 ~ 17:15 A1458(14号館 [5階] 1458)

[A1458-2vn] 08. 触媒

座長：山口 友一、西村 俊

日本語

15:55 ~ 16:15

[A1458-2vn-01]

カチオン性Zr有機金属多面体のポリ酸との集積化と光増感能

○末田 悠太[1]、Benjamin Le Ouay[1]、大谷 亮[1]、大場 正昭[1] (1. 九州大学)

日本語

16:15 ~ 16:35

[A1458-2vn-02]

ZnSナノ結晶を用いたパーフルオロアルキル化合物の光分解メカニズムの解明

○豊田 悠斗[1]、岡安 祥徳[1]、永井 邑樹[1]、小林 洋一[1,2] (1. 立命館大、2. JSTさきがけ)

英語

16:35 ~ 16:55

[A1458-2vn-03]

分析データからの特徴抽出による機械学習を用いた種々の光アノードの光電流密度の予測

○永井 優也[1]、潘 振華[1]、片山 建二[1] (1. 中央大学)

英語

16:55 ~ 17:15

[A1458-2vn-04]

畳み込みニューラルネットワークを用いた電子顕微鏡画像からの電流ー電圧曲線の予測-バナジン酸ビスマスを例に

○片山 建二[1]、林 祐太[1]、永井 優也、潘 振華 (1. 中央大学)

カチオン性 Zr 有機金属多面体のポリ酸との集積化と光増感能

（九大院理 [1]）〇末田 悠太 [1]・ルウェ バンジャマン [1]・大谷 亮 [1]・大場 正昭 [1]

Cationic Zr-based Coordination Cages as Photosensitizers for Polyoxometalate-based Catalysis

([1]*Graduate School of Science, Kyushu University*) 〇Yuta Sueda,[1] Benjamin Le Ouay,[1] Ryo Ohtani,[1] Masaaki Ohba[1]

Polyoxometalates are industrially important catalysts and widely used for organic synthesis. However, most of noble-metal free POMs have wide band gap and therefore need high energy to be photo-excited and low accessibility hinder the use as heterogeneous catalysts. We prepared a cationic Zr-based coordination cage with light absorption maximum at 390nm and significant absorption in the visible domain. Self-assembly of the cationic cages with anionic POMs resulted in porous composites, with cages and POMs in close proximity allowing a transfer of excitation. The composite acted as a potent photocatalyst for the decomposition of Rhodamine B in water, thanks to the combination of efficient transfer of photo-excitation, high accessibility to the POM surface, and dye accumulation in the pore network.

Keywords : Metal-Organic Polyhedra; Polyoxometalates; Self-assembly; photocatalysis

Keggin 型構造に代表されるヘテロポリ酸は、工業的に重要な触媒として有機合成などに利用されている。しかし、貴金属を含まないポリ酸はバンドギャップが広いために可視光領域では励起されず、さらに不均一触媒として用いた場合にはアクセス性に欠けるという欠点がある。本研究では、390 nm に吸収帯を有するカチオン性有機金属多面体 $[Zr_{12}(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_{12}(Cp)_{12}(BDC\text{-}NH_2)_6]^{4+}$ ($BDC\text{-}NH_2^{2-}$ = 2-aminobenzene-1,4-dicarboxylate) (**ZrBDC-NH$_2$**) を光増感スペーサーとして Keggin 型ポリ酸 $SiW_{12}O_{40}^{4-}$ (**SiW$_{12}$**) と集積させることで、可視光駆動型の多孔性不均一触媒の開発を目指した。

得られた集積体 **[ZrBDC-NH$_2$][SiW$_{12}$]** はアモルファスであるが多孔性を保持しており、水中に懸濁して可視光を照射することで、物理吸着および光分解の 2 つの作用により有機染料であるローダミン B (RhB) を効率よく除去した (Figure 1)。サイクリックボルタンメトリーおよび時間分解発光測定により **ZrBDC-NH$_2$** から **SiW$_{12}$** への光誘起電子移動が確認され、反応過程において高活性な **SiW$_{12}$** の一電子および二電子還元種がスーパーオキシドラジカル $\cdot O_2^-$ を生成している可能性が示された。当日は、他の有機染料の分解や触媒の再利用性についても議論する。

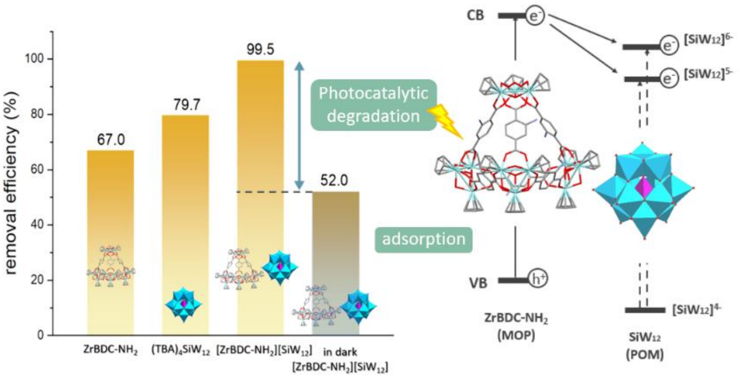


Figure 1. Photocatalytic removal of RhB under visible light irradiation and dark condition.

ZnS ナノ結晶を用いたパーフルオロアルキル化合物の光分解メカニズムの解明

（立命館大生命科学[1]・JST さきがけ[2]）○豊田 悠斗[1]・岡安 祥徳[1]・永井 邑樹[1]・小林 洋一[1,2]

Elucidation of the Photodecomposition Mechanism of Perfluoroalkyl Substances by ZnS Nanocrystals

([1]*Ritsumeikan Univ.*, [2]*PRESTO JST*) ○Yuto Toyota,[1] Yoshinori Okayasu,[1] Yuki Nagai,[1] Yoichi Kobayashi[1,2]

Perfluoroalkyl substances (PFAS) are practically used in various industries. On the other hand, their extremely high stability causes serious environmental persistence and bioaccumulation, and no practical decomposition method has been established. In this study, we report that PFAS can be decomposed into fluoride ions using near-UV LED light irradiation to zinc sulfide nanocrystals (ZnS NCs) at room temperature under atmospheric pressure. Irradiation of 365-nm LED light to the aqueous solution containing ZnS NCs, perfluorooctanesulfonic acid (PFOS, Fig 1a), and triethanolamine (TEOA) results in 99% of PFOS removal efficiency after 72 hours (Fig. 1b).

Keywords : Organic Fluoride Compounds; Zinc Sulfide; Perfluorooctanesulfonic Acid; Semiconductor Nanocrystals; Photocatalysts

パーフルオロアルキル化合物（PFAS）は高い撥水性・撥油性、高い耐熱性・耐薬品性などの優れた性質を有することから、さまざまな産業分野で応用されている。一方、その高い安定性のため、分解には過激な条件が必要であり、環境残留性や生体蓄積性が高いという問題がある。

本研究では、銅イオンをドープした硫化亜鉛ナノ結晶（ZnS NCs）と近紫外 LED 光を用いて、パーフルオロオクタンスルホン酸（PFOS, Fig.1a）の分解に成功したので報告する。

PFOS、正孔捕捉剤としてトリエタノールアミン（TEOA）、ZnS NCs を加えた水溶液に近紫外光（365 nm, 10 W cm^{-2}）を照射し、液体クロマトグラフィー質量分析およびイオンクロマトグラフィーを用いて水溶液中の PFOS 除去率およびフッ化物イオン濃度を経時的に分析した。光照射にともない徐々に PFOS が分解し、室温常圧下で最終的に PFOS が 99%分解した（Fig.1b）。また、全 C-F 結合中 64%がフッ化物イオンまで分解されており、残りはより低分子量の PFAS として存在していることがわかった。

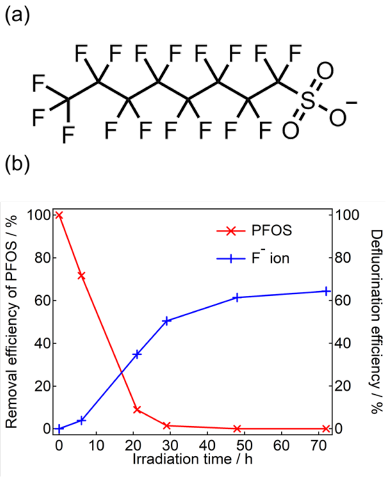


Fig. 1 (a) Molecular structure of PFOS, (b) PFOS decomposition by 365-nm UV light irradiation (690 mW, 10 W/cm^2) to 1 mol% Cu-doped ZnS NCs.

Prediction of photocurrent density of various photoanodes using machine learning with feature extraction from analytical data.

([1]*Chuo University*) ○Yuya Nagai,[1] Zhenhua Pan,[1] Kenji Katayama[1]

Keywords: Machine learning, Photoanode, Photocurrent

Photoanodes are promising for solar-driven hydrogen evolution, yet their performance (photocurrent) varies despite identical preparation conditions. This suggests that the unidentified factors could affect the photocurrent of the photoanodes. To clarify the factors, we have developed a scheme to predict the material performance using machine learning (ML) from analytical data, including X-ray diffraction (XRD), Raman spectroscopy, UV/Vis absorption spectroscopy, and photoelectrochemical impedance spectroscopy (PEIS). The analytical data provided features, such as peak intensities or positions, which were used to predict photocurrent values. Then, the ML process identified the dominant factors for performance. This scheme was applied to hematite and bismuth vanadate photoanodes.[1,2] Additionally, we adjusted the operational parameter for the sample preparation based on the dominant factors through ML to enhance the photoanode activity.[3]

In our previous studies, we were unable to determine the contributions of the dominant descriptors to the performance because we used various ML methods. In addition, the use of multiple ML functions could negatively impact the robustness of our scheme when applied to various material data with target values. To address these issues, we have developed a comprehensive and robust approach that encompasses data preprocessing, ML computations, descriptor selection, and importance analysis of the dominant descriptors. The accompanying figure illustrates our recent ML methodology. In this presentation, we explain the calculation scheme and present the results of its application to hematite, bismuth vanadate, and various photoanodes.

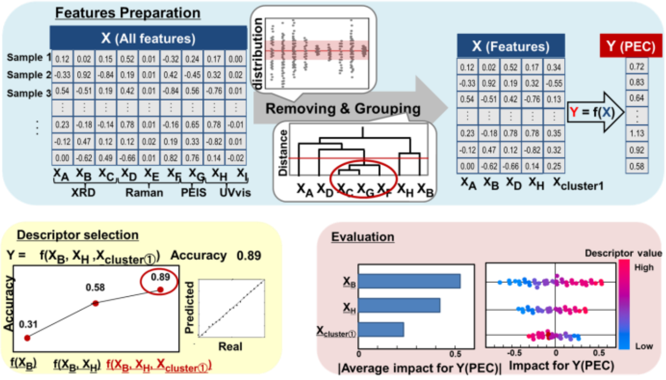


Figure. Overall ML scheme for descriptor selection and contribution analysis are shown.

1) Y. Nagai, et al. *The Analyst*, **2022**, *147*, 1313. 2) K. Kobayashi, et al. *J. Photochem. Photobiol. Chem.*, **2023**, *440*, 114651. 3) T. Idei, et al. *ACS Appl. Mater. Interfaces*, **2023**, *15*, 55644.

Convolutional Neural Network Prediction of the photocurrent−voltage curve directly from scanning electron microscopic image for BiVO4

(*Chuo University*) ○Kenji Katayama, Yuta Hayashi, Yuya Nagai, Zhenhua Pan

Keywords: CNN, BiVO4

In the race for efficient and sustainable energy conversion, the development of high-performance photocatalytic devices holds great promise. These devices rely on a critical characteristic called the photocurrent density vs applied voltage (JV) curve, which provides essential insights into their functionality and performance. In this study, we present an exciting breakthrough in predicting the JV curve for a promising photoanode material, $BiVO_4$, **using convolutional neural networks (CNNs). The CNN was trained solely on conventional scanning electron microscopy (SEM) images, making it an accessible and cost-effective method. Our optimized methodology achieved an impressive curve match ratio of 98.9%**, paving the way for significant advancements in solar energy conversion.

Fabricating materials and devices takes a long time, and typically only dozens of samples can be produced on a lab scale. Our method provided the good prediction of the photoelectrochemical (PEC) performance only from dozens of data, even by using CNNs. It is surprizing that the photocatalytic performance can be predicted only from a single SEM image, which is a very common measurement in the study of photocatalysis. If we could find the performance only from an image, the burden for the development/finding new photocatalytic materials/devices could be potentially much reduced and would be a transition of the research method.

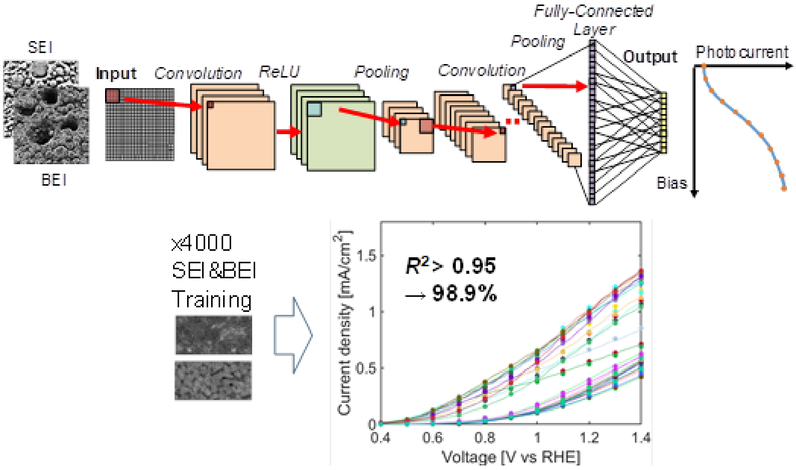


Figure Scheme of this resaerch. The combination of SEM images (SEI and BEI) were used for the prediction of the current − voltage curve using the convolutiona neural network. The prediction accuracy for the test data reached 98.9 %.

1) Y. Hayashi, et al. *J. Mater. Chem. A* **2023**, 11, 22522-22532.

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19日(火) 15:55 ~ 17:15 F1232(12号館 [3階] 1232)

[F1232-2vn] 09. 錯体化学・有機金属化学

座長：亀尾 肇、小林 厚志

英語

15:55 ~ 16:15

[F1232-2vn-01]

Photocatalytic CO_2 Reduction Using Binary Metal-Porphyrins as Photosensitizer and Catalyst Units

〇Sunghan Choi[1], Sebastian Nybin Remello[1], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

英語

16:15 ~ 16:35

[F1232-2vn-02]

Electrocatalytic Reduction of Low Concentration CO_2 by Iron Porphyrins

〇Sebastian Nybin Remello[1,3], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology , 2. Hiroshima University, 3. Cochin University of Science and Technology)

日本語

16:35 ~ 16:55

[F1232-2vn-03]

鉄ジシリル錯体を用いた炭素−ヘテロ二重結合切断反応

〇菅 雄翔[1]、砂田 祐輔[1,2] (1. 東大院工、2. 東大生研)

英語

16:55 ~ 17:15

[F1232-2vn-04]

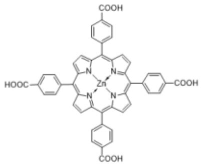
An Iron Porphyrin-Based Framework Catalyst for Highly Efficient Photocatalytic CO_2 Reduction

〇XIANJUN LI[1], Kento KOSUGI[2], Maho IMAI[2], Yutaka SAGA[2], Tetsuya KAMBE[2], Shigeyuki MASAOKA[2], Mio KONDO[1,2,3] (1. Tokyo Institute of Technology, 2. Osaka University, 3. JST PRESTO)

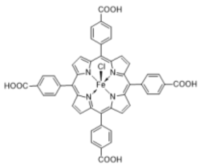
Title: Photocatalytic CO_2 Reduction Using Binary Metal-Porphyrins as Photosensitizer and Catalyst units

Sunghan CHOI, Sebastian Nybin Remello, Osamu Ishitani*

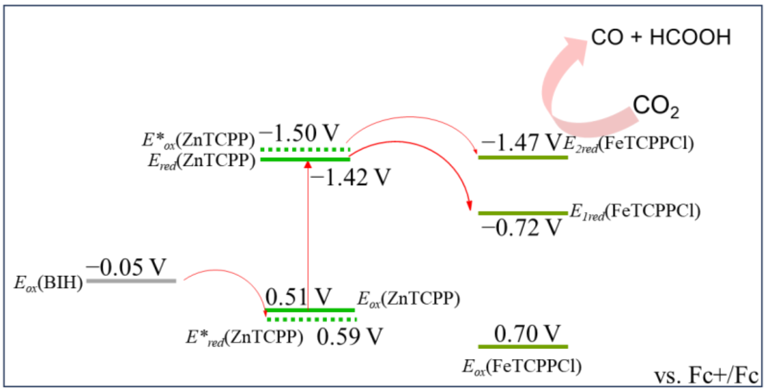
Photocatalytic CO_2 reduction consisting of both ZnTCPP and FeTCPP efficiently proceeded due to optimized electron transfer within their close distance. Furthermore, employing a metal-organic framework (MOF) containing ZnTCPP, FeTCPP linkers, and ZrO clusters exhibited substantial CO_2 reduction capabilities.



ZnTCPP



FeTCPP



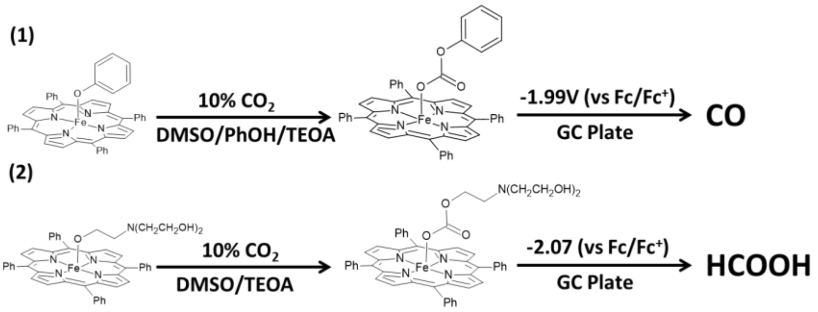
Electrocatalytic Reduction of Low Concentration CO_2 by Iron Porphyrins

([1]*Tokyo Institute of Technology*, [2]*Hiroshima University,* [3]*Cochin University of Science and Technology*) ○Sebastian Nybin Remello,[1,3] Osamu Ishitani[1,2]

Keywords: Low Concentration CO_2 Reduction; Iron Porphyrin; Electrocatalytic reaction

Transition Metal Complexes are one of the effectively utilized systems for the selective conversion of CO_2 with high efficiency, and most of these catalyst systems can function effectively under electrochemical and photochemical conditions. For the practical realization of these systems for the direct conversion of CO_2 in the flue gas, the catalyst should work under low concentrations of CO_2.[1] The Re(I) complexes with a deprotonated triethanolamine are efficient catalysts for direct reduction of low-concentration CO_2; the versatility of this system is attributed to the fast CO_2 insertion reaction to the Re-O bond.[2] However, considering the elemental strategy, we should identify other efficient catalysts based on earth-abundant elements that can work under low CO_2 concentrations.

Porphyrin complexes of iron are efficient catalysts for CO_2 reduction under electrochemical and photochemical conditions. Selective electrochemical reduction of CO_2 to CO is observed in most iron porphyrin-based catalyst systems under pure CO_2 atmosphere when a Brønsted acid is employed as an additive or prepositioned near the catalyst by ligand modification.[3] In this report, we could successfully observe CO formation using the commercially available iron porphyrin catalyst Fe(III) tetraphenyl porphyrin (FeTPP), under 10% CO_2 concentration with a 91% faradic yield and 23 TON in the presence of phenol and TEOA (trace,) indicating the possibility phenyl carbonate formation with FeTPP-Phenol system (eq. 1). The formation of Fe-CO_2-OPh was confirmed using FTIR by observing the C=O stretching upon CO_2 bubbling to the FeTPP-OPh complex. Another aspect is the possibility of low-concentration CO_2 reduction in the presence of triethanolamine (TEOA); the reaction produced HCOOH as the major product with a 52% faradic yield and 12 TON, in this case also, the CO_2 inserted complex, Fe-CO_2TEOA was observed using FTIR (eq. 2).



(1) Yamazaki, Y. and Ishitani, O. et al., *J. Am. Chem. Soc.* **2022**, 144, 6640-6660. (2) Kumagai, H. and Ishitani, O. et al., *Chem. Sci.* **2019**, 10, 1597-1606. (3) Costentin, C. and Savéant J. M. et al., *Science* **2012**, 338 (6103), 90-94.

鉄ジシリル錯体を用いた炭素−ヘテロ二重結合切断反応

（東大院工 [1]・東大生産研 [2]） ○菅 雄翔 [1]・砂田 祐輔 [1,2]

Cleavage of Carbon–Heteroatom Double Bonds by Iron Disilyl Complexes

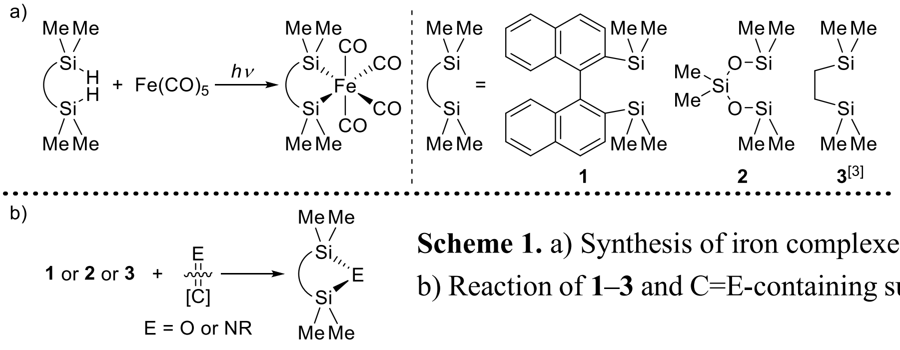
([1]*Graduate School of Engineering and* [2]*Institute of Industrial Science, The University of Tokyo*)
○Yuto Suga[1], Yusuke Sunada[1,2]

Transition metal complexes bearing organosilyl ligands exhibit unique reactivity reflecting the chemical properties of silicon moieties. For instance, coordinatively unsaturated and electron-rich metal complexes could be facilely synthesized by introducing the organosilyl ligands due to their strong electron donating properties as well as strong *trans*-influence. In addition, oxophilic property of silicon moiety led to the effective activation of oxygen-containing molecules such as carbonyl compounds.[1]

Herein, we synthesized a series of iron complexes **1**–**3** bearing bridging disilyl ligands (Scheme 1-a). We found that **1**–**3** could cleave the C=E (E = O, NR) double bonds of the substrates to afford cyclic compounds bearing silicon–heteroatom bonds (Scheme 1-b). A similar reaction using **3** was previously reported by Nakazawa and Gladysz, but the applicable substrates were limited to aldehydes.[2] In contrast, both ketones and imines could be used in our system. For instance, C=O double bond of cyclopropenone was facilely cleaved by iron complexes, giving cyclic siloxane in good yield. It should be emphasized here that an iron complex bearing cyclopropenyl-1-ylidene ligand could also be isolated.

Keywords : Iron, Silicon, Carbene, Double Bond Cleavage

有機ケイ素配位子を持つ遷移金属錯体は、ケイ素配位子の強い電子供与性や親酸素性などの特性を反映した種々の興味深い性質を示す[1]。今回我々はまず、架橋ジシリル配位子を有する鉄錯体 **1**–**3** (Scheme 1-a) を合成した。さらに、**1**–**3** が基質の C=E (E = O, NR) 二重結合を切断し、環状 Si–E–Si 化合物を与えることを見出した (Scheme 1-b)。同様の反応が Nakazawa, Gladysz らによって報告されているが、基質はアルデヒドに限られている[2]。一方、我々の系ではケトンやイミンも基質として適用可能であった。さらに、シクロプロペノンを基質として用いた際には、環状ジシロキサンに加えてシクロプロペニリジン配位子を有する鉄錯体が得られた。



Scheme 1. a) Synthesis of iron complexes **1**–**3**. b) Reaction of **1**–**3** and C=E-containing substrates.

[1] M. T. Whited, B. L. H. Taylor, *Comments Inorg. Chem.* **2020**, *40*, 217.
[2] H. Nakazawa, D. L. Johnson, J. A. Gladysz, *Organometallics* **1983**, *2*, 1846.
[3] L. Vancea, W. A. G. Graham, *Inorg. Chem.* **1974**, *13*, 511.

An Iron Porphyrin-Based Framework Catalyst for Highly Efficient Photocatalytic CO_2 Reduction

([1]*Tokyo Institute of Technology*, [2]*Osaka University*, [3]*JST PRESTO*) ○Xianjun Li[1], Kento Kosugi[2], Maho Imai[2], Yutaka Saga[2], Tetsuya Kambe[2], Shigeyuki Masaoka[2], Mio Kondo[1,3]

Keywords: CO_2 Reduction; Photochemical Reaction; Iron Porphyrin; Self-Assembly; Heterogeneous catalyst

To address both challenges of global warming and energy scarcity, visible-light driven CO_2 reduction (e.g., $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$) can be a viable solution, and the development of catalytic systems for the reaction is widely studied.

In this work, we aimed to construct a novel catalytic system for photochemical CO_2 reduction. An iron porphyrin complex bearing carboxyl groups (-COOHs) at its peripheral positions (Fe(III) meso-tetra(4-carboxyphenyl) porphyrin chloride), **[FeCl(H_4P)]**, Figure 1) was employed as the basic unit.

Self-assembly of **[FeCl(H_4P)]** afforded a framework catalyst, **[Fe(H_2P)]$_n$** (Figure 2), which possesses fixed carboxylate groups and free carboxyl groups with a multifunctional environment. **[Fe(H_2P)]$_n$** shows very high catalytic activity for a photocatalytic CO_2 reduction to form CO at under visible-light irradiation in a CO_2-saturated acetonitrile (MeCN) solution containing $Ir(ppy)_3$ (Hppy = 2-phenylpyridine, 20 μM) as a photosensitizer, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH, 0.2 M) as a sacrificial electron donor, and trifluoroethanol (TFE, 0.2 M) as a proton source. During a 3-hours of photocatalytic experiment, the amount of CO increased extremely fast while H_2 evolution was negligible (Figure 3). An average production rate of CO reached 1.8×10^6 /μmol g^{-1} h^{-1} with 100% of selectivity. This rate is new record among molecule-based heterogeneous photocatalytic systems for CO_2 reduction to produce CO reported up to now.

In the presentation, we will also show the detailed results of robustness tests, gas adsorption results and investigation of proton conductivity.

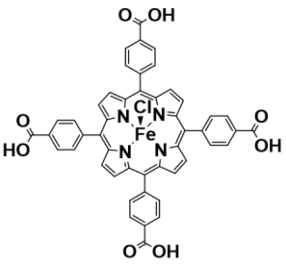


Figure 1. Chemical structure of **[FeCl(H_4P)]**

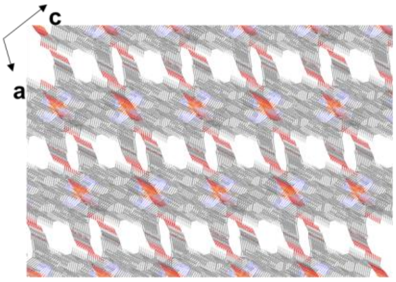


Figure 2. Crystal packing structure of **[Fe(H_2P)]$_n$**

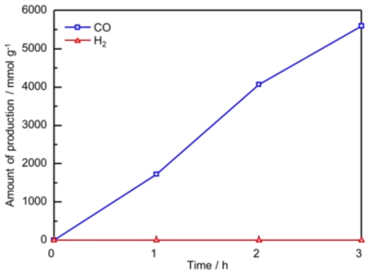


Figure 3. Production amounts of CO and H_2 generated from CO_2 saturated MeCN solution, which contained 16 μg **[Fe(H_2P)]$_n$**, 20 μM $Ir(ppy)_3$, 0.2 M BIH and 0.2 M TFE, being irradiated with a Xe lamp (400 ≤ λ ≤ 750 nm) over 3 h at 20 °C.

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19日(火) 15:55 ~ 17:15 F1233(12号館 [3階] 1233)

[F1233-2vn] 09. 錯体化学・有機金属化学

座長：小林 洋一、堀内 新之介

英語

15:55 ~ 16:15

[F1233-2vn-01]

キラルベンジルアミン配位子修飾シリカ表面への固定化による発光性Tb錯体のキラリティー誘起

○白井 そら[1]、松井 久宜[2]、郡次 智[1]、中井 英隆[2]、唯 美津木[1,3] (1. 名大院理、2. 近畿大院総理工、3. 名大物国セ)

英語

16:15 ~ 16:35

[F1233-2vn-02]

四角酸と硝酸エルビウムから合成された3種の錯体における構造と磁気特性

○高野 莉奈[1]、益田 晃希[2]、北河 康隆[2]、石田 尚行[1] (1. 電気通信大学、2. 大阪大学)

日本語

16:35 ~ 16:55

[F1233-2vn-03]

β-ジケトナート配位子の光分解過程の理解と希土類錯体の光耐久性の向上

○岡安 祥徳[1]、小林 洋一[1,2] (1. 立命館大学、2. JST さきがけ)

日本語

16:55 ~ 17:15

[F1233-2vn-04]

新規ペンタキス（*β*-ジケトン）型コラニュレン配位子による多核Eu(III)錯体形成

○山田 美穂子[1]、松本 大河[1]、加納 春華[1]、河合 壮[1] (1. 奈良先端科学技術大学院大学)

Chirality Induction of Luminous Tb Complexes on Silica Surface Functionalized with Chiral Benzylamine Ligands

(*[1]Dept. Chem. Grad. Sch. Sci., Nagoya Univ.*, *[2]Dept. Energy Mater. Grad. Sch. Sci. Eng., Kindai Univ. [3]RCMS, Nagoya Univ.*)
○Sora Shirai,[1] Hisaki Matsui,[2] Satoshi Muratsugu,[1] Hidetaka Nakai,[2] Mizuki Tada[1,3]

Keywords: Terbium Complex; Chirality; Chiral Ligand; Silica Surface; Circularly Polarized Luminescence

Immobilization of chiral metal complexes on solid surfaces produces chiral metal complexes on solid materials, which are applied to chiral sensors and heterogeneous asymmetric catalysts etc. The preparation of new chiral molecular structures on SiO$_2$ surface was investigated by the attachment of an achiral Tb complex on a SiO$_2$ surface modified with chiral moieties and the chirality induction of an achiral Tb complex ($\mathbf{^{Ph}1_{Tb}}$) on a SiO$_2$ surface with chiral benzylamine ligands ($\mathbf{L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$) was successfully achieved.

A chiral ligand ($\mathbf{L_{NHBoc}(\mathit{R}/\mathit{S})}$), whose amine moiety was protected with a *t*-butoxycarbonyl (Boc) group, was newly synthesized and characterized by ^{1}H NMR, FT-IR, and ESI-MS. $\mathbf{L_{NHBoc}(\mathit{R}/\mathit{S})}$ was attached to a SiO$_2$ surface, and the Boc group was finally deprotected to prepare $\mathbf{L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$ (Figure 1). Solid-state CD spectra of $\mathbf{L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$ showed inverted CD peaks derived from the surface-attached chiral benzylamine moieties, suggesting the formation of a homo-chiral SiO$_2$ surface with chiral benzylamine.

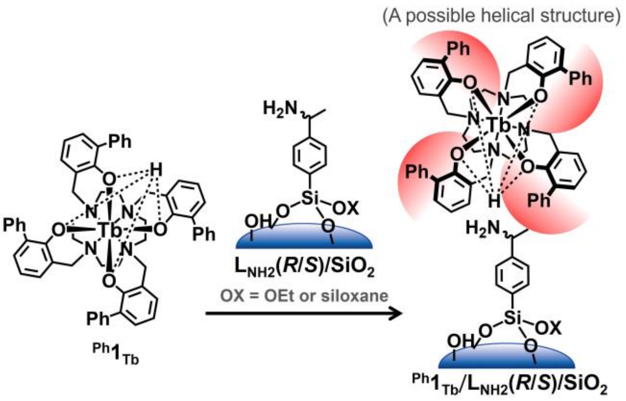


Figure 1. Preparation of $\mathbf{^{Ph}1_{Tb}/L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$.

An achiral Tb complex with a tetraazacyclododecane-based tetrakis-(2-phenylphenoxide) ligand ($\mathbf{^{Ph}1_{Tb}}$) was immobilized on $\mathbf{L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$ (Figure 1). Tb L_{III}-edge EXAFS of $\mathbf{^{Ph}1_{Tb}/L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$ were similar to that of $\mathbf{^{Ph}1_{Tb}}$, indicating that the coordination structure of the precursor $\mathbf{^{Ph}1_{Tb}}$ was maintained on the SiO$_2$ surface (Figure 2). Solid-state CPL spectra of $\mathbf{^{Ph}1_{Tb}/L_{NH2}(\mathit{R}/\mathit{S})/SiO_2}$ showed inverted CPL peaks derived from f-f emissions of $\mathbf{^{Ph}1_{Tb}}$, strongly suggesting that the chirality of $\mathbf{^{Ph}1_{Tb}}$ was successfully induced on the attached SiO$_2$ surface with the chiral benzylamine ligands.

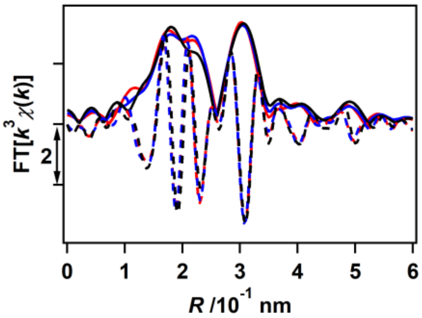


Figure 2. k^3-weighted Tb L_{III}-edge EXAFS Fourier transforms (k = 30－105 nm^{-1}) of $\mathbf{^{Ph}1_{Tb}}$ (black), $\mathbf{^{Ph}1_{Tb}/L_{NH2}(\mathit{R})/SiO_2}$ (blue), and $\mathbf{^{Ph}1_{Tb}/L_{NH2}(\mathit{S})/SiO_2}$ (red) (at 20 K). Solid lines: magnitude; dotted lines: imaginary parts.

Structures and Magnetic Properties of Three Types of Complexes Prepared from Squarate and Erbium Nitrate

([1]*The University of Electro-Communications*, [2]*Osaka University*) ○Rina Takano,[1] Koki Masuda,[2] Yasutaka Kitagawa,[2] Takayuki Ishida[1]

Keywords: Heavy Lanthanide Ions; Multi Nuclear Complexes; Magnetic Properties; Computation Chemistry

Single ion magnets are expected to show high-performance magnetic properties. To develop such magnets, it is necessary to characterize the properties of each single ion, such as the crystal field and electronic environment. Squaric acid (H_2sq) is well known as a versatile ligand to produce several types of complexes from mononuclear to polymer[1-4)]. We obtained three types of structures from erbium(III) nitrate and squaric acid by means of hydrothermal synthesis. Oxalate (ox^{2-}) appeared as a decomposed product from squarate. The structures of $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$, $[Er_2(sq)_3(H_2O)_8]_n$,[1)] $[Er_2(sq)_2(ox)\ (H_2O)_4]_n$ were confirmed to be discrete mononuclear (Fig. (a)), double-layer two-dimensional polynuclear, and three-dimensional polynuclear (Fig. (b)), respectively.

DC magnetic results indicate negligible magnetic interaction among lanthanide ions. In the AC magnetic measurements, all the compounds showed frequency dependence when a bias-field was applied. From the Arrhenius plots, the magnetization relaxation barriers were determined as 27(2), 14(1), and 20.6(9) K for $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$ (Fig. (c)), $[Er_2(sq)_3(H_2O)_8]_n$, and $[Er_2(sq)_2(ox)(H_2O)_4]_n$, respectively. The CASSCF calculations are ongoing by using the crystal structures determined. The relationship between magnetic properties and crystal structure will be discussed.

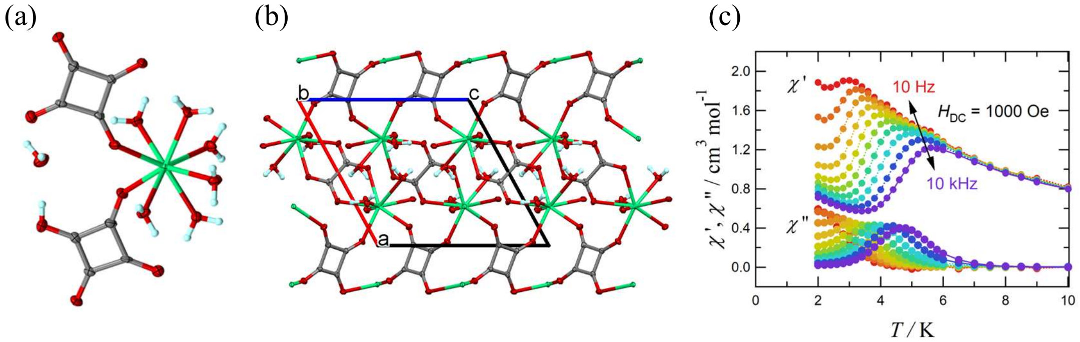


Fig. (a) Crystal structures of $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$ and (b) $[Er_2(sq)_2(ox)(H_2O)_4]_n$ viewed along the *b* axis. (c)AC magnetic susceptibility result of $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$.

Ref. 1) R. Takano et al., *Dalton Trans*. **2023**, *52*, 8873. 2) J. F. Petit et al, *Inorg. Chim. Acta* **1990**, *167*, 51. 3) S. Biswas et al., *Inorg. Chem*. **2013**, *53*, 3926. 4) L. Wang et al., *Aust. J. Chem*. **2011**, *64*, 1373.

β-ジケトナート配位子の光分解過程の理解と希土類錯体の光耐久性の向上

（立命館大生命科学 [1]・JST さきがけ [2]）岡安 祥徳 [1]・小林 洋一 [1,2]

Understanding of photodecomposition mechanisms of β-diketonate ligand and improving the photodurability of lanthanide complexes

([1]*College of Life Sciences, Ritsumeikan Univ.*, [2]*PRESTO JST*)○Yoshinori Okayasu,[1] Yoichi Kobayashi[1,2]

Suppression of photodegradation is important for applications in sensors and organic light-emitting devices. Although energy transfer processes from ligands to lanthanide ions have been extensively studied in recent years, more detailed investigations of the excited-state dynamics are necessary for unveiling the photodegradation mechanism. In this study, we synthesized mono- and dinuclear Eu(III) complexes with β-diketonate ligands ($Eu(PhDK)_3$ and $Eu_2(BTP)_3$) and investigated the excited state dynamics in detail using femtosecond to millisecond time-resolved spectroscopic measurements.

The sub-millisecond transient absorption spectra of $Eu(PhDK)_3$ in acetonitrile show a positive signal at 320 nm immediately after the excitation. This signal was not observed for $Y(PhDK)_3$, suggesting that it originated from electron transfer from the ligand to the Eu(III) ion. $Eu(PhDK)_3$ is more decomposed than $Y(PhDK)_3$, and the electron transfer process promotes photodecomposition.

Keywords: *Lanthanide complex; β-diketonate ligand; Photostability; Photodegradation; Time-resolved spectroscopy*

特徴的な光学特性を示す希土類錯体は、配位子から希土類イオンへのエネルギー移動過程が詳細に研究されている一方、光分解過程においては未解明な部分が多く、光耐久性の高い分子設計は確立されていない。光分解過程の詳細な理解は分解の抑制につながり、その知見は希土類錯体を用いたセンサーや発光デバイスにおいて重要である。

本研究では、β-ジケトナート配位子を有する単核および二核Eu(III)錯体 ($Eu(PhDK)_3$, $Eu_2(BTP)_3$)を合成し(Fig. 1a)、フェムト秒からミリ秒の時間分解分光測定を行い、分解メカニズムを詳細に検討したので報告する。

窒素雰囲気下、$Eu(PhDK)_3$ のアセトニトリル溶液に 355 nm のナノ秒レーザーを照射すると、励起直後から 320 nm に正のシグナルが観測された(Fig.1b)。このシグナルは電子移動の起こらない $Y(PhDK)_3$ では観測されず、配位子から Eu(III)イオンへの電子移動に由来することが示唆された。また、$Eu(PhDK)_3$の方が$Y(PhDK)_3$よりも分解反応が進行するため、電子移動過程が分解を促進することがわかった。

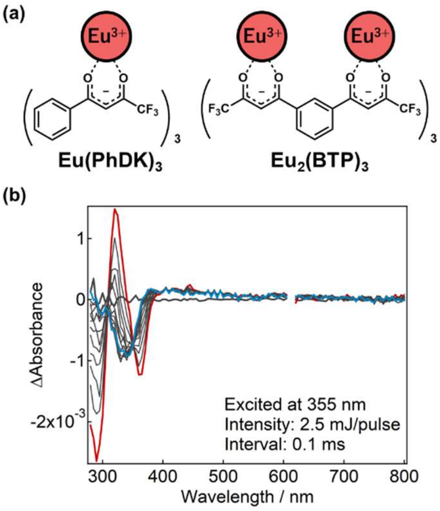


Fig.1 (a) Chemical structure of the Eu(III) complexes. (b) Transient absorption spectra of $Eu(PhDK)_3$ in acetonitrile (10 μM) on sub-millisecond timescales with a 355 nm nanosecond laser pulse (2.5 mJ $pulse^{-1}$) under a nitrogen atmosphere at room temperature.

新規ペンタキス(β-ジケトン)型コラニュレン配位子による多核Eu(III)錯体形成

（奈良先端大物質 [1]）○山田 美穂子 [1]・松本 大河 [1]・加納 春華 [1]・河合 壯 [1]

Formation of Multinuclear Europium(III) Complexes with a New Pentakis(β-diketone)-Type Corannulene Ligand

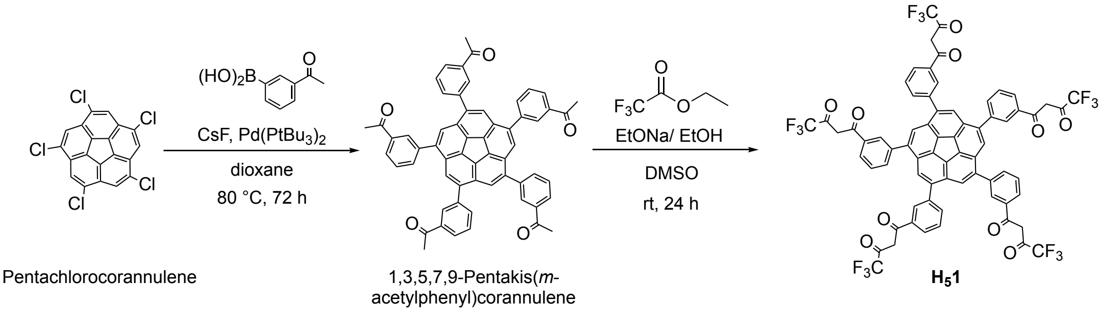
([1]*Division of Materials Science, Nara Institute of Science and Technology*)
○Mihoko Yamada,[1] Taiga Matsumoto,[1] Haruka Kano,[1] Tsuyoshi Kawai[1]

Emission of Eu complex is enhanced by the antenna effect of the ligands having large absorption coefficient. C_5-Symmetric curved aromatic corannulene with a large absorption coefficient is a promising motif for enhancement of emission of Eu(III) complexes. It has been found that Eu(III) complex, which has a large diversity of coordination geometries, is effectively stabilized by forming the closed structure. In this work, focusing on the stability of the closed structure and the charge balance, we studied formation behavior of multinuclear Eu(III) complexes with a new pentakis(β-diketone)-type ligand having a corannulene skeleton.

Keywords : Europium Complex; Corannulene; Multinuclear Complex; Closed Structure; Emission

Eu(III)錯体はシャープな発光特性を示すことから、発光材料への応用のために、発光強度や効率向上を目指した研究が行われてきた。C_5 対称の湾曲状芳香族コラニュレンは大きなモル吸光係数を有し、光アンテナ効果による Eu(III)錯体の発光増強が期待できる。近年、柔軟性の高い Eu(III)錯体の配位構造制御に向けて閉殻かご状構造の適用が検討されている1)。本研究では、発光効率向上と錯体の多核化による機能制御を目指し、新規ペンタキス(β-ジケトン)型コラニュレン配位子の多核 Eu(III)錯体形成挙動を検討した。

まず、ペンタクロロコラニュレンから 2 段階で、5 つの β-ジケトン配位部位とコラニュレン骨格を有する新規配位子 $\mathbf{H_51}$ を合成した。得られた $\mathbf{H_51}$ を DMSO 中で過剰量の Eu(III)と反応させたところ、613 nm に Eu(III)錯体に特徴的な発光バンドが観測され、Eu(III)錯体の形成が示唆された。この発光は顕著な O_2 消光効果を示したことから、配位子の T_1 準位を経由するものと推定された。配位子 $\mathbf{H_51}$ と Eu(III)による滴定実験の分光測定と ESI-MS 測定から、Eu(III):$\mathbf{1}^{5-}$=4:2 錯体が安定に得られることが示唆された。当日は、閉殻構造と電荷バランスに注目し、錯体の構造についても議論する。



1) Y. B. Tan, *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 17653–17661.

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19日(火) 15:55 ~ 17:15 🏛 F1234(12号館 [3階] 1234)

[F1234-2vn] 09. 錯体化学・有機金属化学

座長：細野 暢彦、日下 心平

🏷 英語
15:55 ~ 16:15
[F1234-2vn-01]
芳香環カプセルの等方的空間拡大と多分子内包能

○角田 瑠輝[1]、名畑 瑠斗[1]、吉沢 道人[1] (1. 東工大・化生研)

🏷 英語
16:15 ~ 16:35
[F1234-2vn-02]
C_1対称性大環状配位子からなる二次元金属有機構造体の構築および機能性小分子の層間集積制御

○中川 慶一[1]、田代 省平[1]、横森 創[2]、松下 信之[2]、塩谷 光彦[1] (1. 東大院理、2. 立教大理)

🏷 英語
16:35 ~ 16:55
[F1234-2vn-03]
Green Synthesis of a Flexible Metal-Organic Framework [Cu(BF$_4$)$_2$(4,4´-bipyridine)$_2$] (ELM-11) for Selective CO$_2$ Adsorption

○Shivakumar Kilingaru Ishwara[1], Shin-ichiro Noro[1] (1. Hokkaido University)

🏷 英語
16:55 ~ 17:15
[F1234-2vn-04]
ヨウ化銅(I)クラスターを含むピリジル型有機金属骨格を用いたC5炭化水素混合物からのイソプレンの高選択的分離.

○キム ジュンシク[1]、パベル ユーソフ[1]、和田 雄貴[1]、大津 博義[1]、松本 隆也[1,2]、河野 正規[1] (1. 東京工業大学、2. ENEOS Corporation)

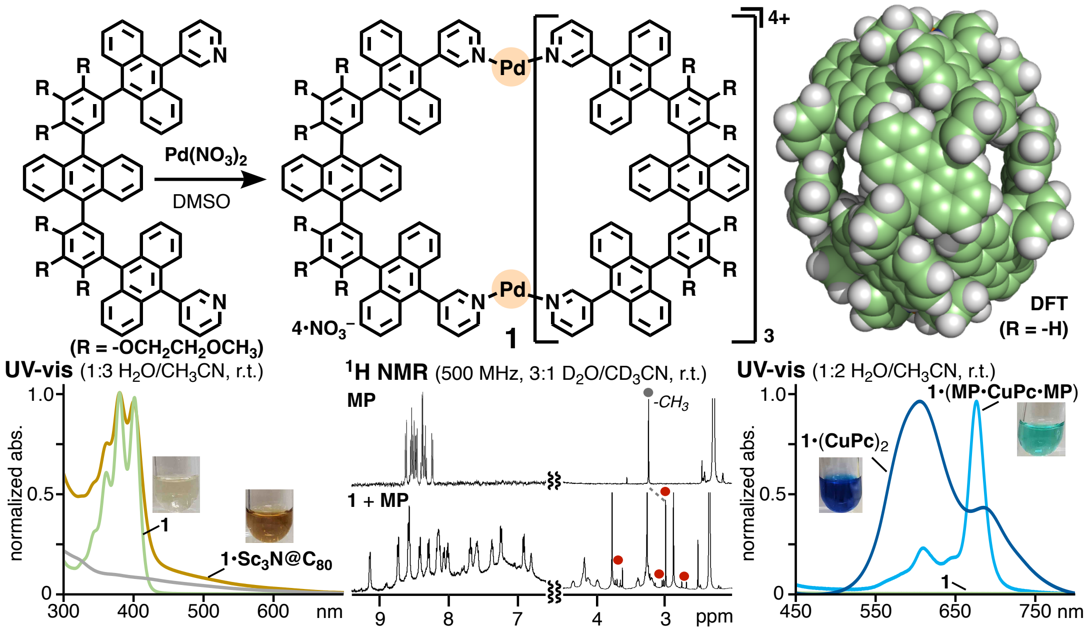
Isotropic Expansion of a Polyaromatic Capsule and its Multi-Guest Binding Ability

(Lab. for Chem. & Life Sci., Tokyo Tech) Ryuki Sumida, Ryuto Nabata, Michito Yoshizawa

Keywords: Polyaromatic capsule; Isotropic expansion; Large cavity; Binding ability; Pairwise encapsulation

Higher fullerenes, which are expanded analogues of fullerene C_{60}, provide closed, large polyaromatic cavities. Whereas the isotropic expansion of spherical M_nL_{2n} cages has been achieved using metal ions and elongated wire-like ligands, its host properties remain unclear because of large openings.[1] Here we report the synthesis of an isotropically expanded polyaromatic capsule and its binding abilities.

Expanded capsule **1** was obtained by the treatment of Pd(II) ions and tri-anthracene-based bent ligand **2** in DMSO (Figure, top). When capsule **1** and higher fullerene **$Sc_3N@C_{80}$** were stirred in 1:3 H_2O/CH_3CN at 80 °C, the solution color was changed from pale yellow to brown (Figure, bottom left), due to the quantitative formation of 1:1 host-guest complex **1•$Sc_3N@C_{80}$**. In the similar way, capsule **1** quantitatively bound four 1-methylpyrene (**MP**) molecules in the cavity of **1** (Figure, bottom middle). In addition, capsule **1** encapsulated two Cu(II)-phthalocyanines (**CuPc**) to give a blue solution of **1•(CuPc)$_2$**. The combination of **1•(CuPc)$_2$** and **MP** gave rise to **1•(MP•CuPc•MP)** as a bluish green solution (Figure, bottom right). UV-visible, ESI-TOF MS, and theoretical studies indicated the selective formation of an unusual sandwich-like stack **MP•CuPc•MP** within **1**.



[1] K. Harris, D. Fujita, M. Fujita, *Chem. Commun.* **2013**, *49*, 6703–6712.

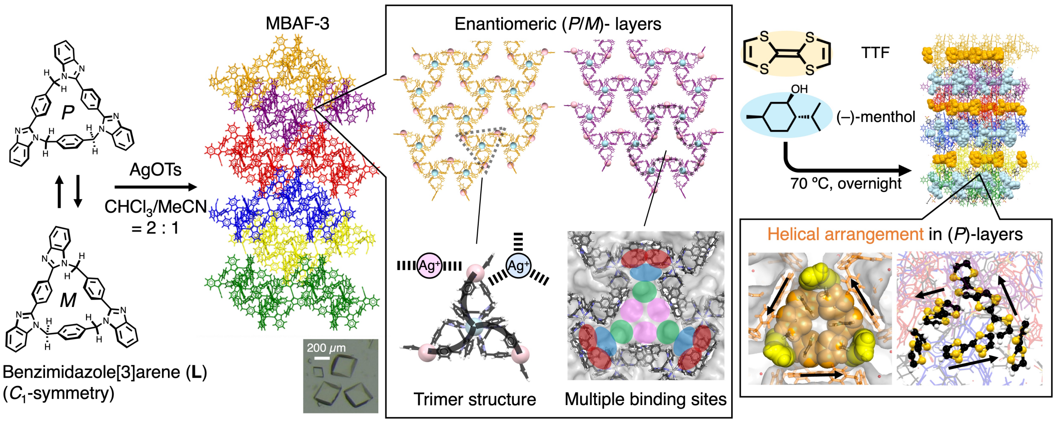
Construction of a two-dimensional metal-organic framework composed of C_1-symmetric macrocyclic ligands and interlayer arrangement control of functional small molecules

([1]*Graduate School of Science, The University of Tokyo*, [2]*College of Science, Rikkyo University*) ○Keiichi NAKAGAWA,[1] Shohei TASHIRO,[1] So YOKOMORI,[2] Nobuyuki MATSUSHITA,[2] Mitsuhiko SHIONOYA[1]

Keywords: Porous crystal; Molecular recognition; Metal-organic framework; Macrocycle; Molecular arrangement

Metal-organic frameworks (MOFs) exhibit highly excellent molecular adsorption capacity due to their high porosity and molecular recognition ability. In particular, 2D MOFs have attracted much attention because their dimensionally restricted arrangement of guest molecules allows them to be applied to various functions such as template synthesis, separation, and sensing. For precise arrangement of guest molecules, it is important to construct multiple binding sites on the 2D MOFs. However, it remained difficult because conventional MOFs use simple, flat-shaped ligands to control their dimensionality, providing only a few interaction points for molecular recognition.

In this study, a 2D MOF with multiple guest binding sites, metal-benzimidazole[3]arene framework-3 (MBAF-3, $[Ag_{1.17}\mathbf{L}](OTs)_{1.17}$), was developed based on a C_1-symmetric macrocyclic ligand ((*P*/*M*)-benzimidazole[3]arene, **L**) and AgOTs. In the crystal structure of MBAF-3, three (*P*)- or (*M*)-**L** molecules are tricoordinated with two Ag^+ ions, forming homochiral trimers $[Ag_2((P/M)\text{-}\mathbf{L})_3]^{2+}$. These are further connected with two-coordinate Ag^+ to form enantiomeric (*P*)- and (*M*)-layers, which are stacked alternately to form a crystal. Crystallographic analysis revealed that the enantiomeric layers with multiple binding sites enable helical and diastereoselective arrangement of TTF (= tetrathiafulvalene) using (–)-menthol as a chiral auxiliary. (–)-Menthol was only introduced into the (*M*)-layers of MBAF-3 by hydrogen bonding, and TTF molecules were adsorbed to the (*P*)-layers to form a right-handed helical cluster.



Green Synthesis of a Flexible Metal-Organic Framework [Cu(BF_4)$_2$(4,4´-bipyridine)$_2$] (ELM-11) for Selective CO_2 Adsorption

(*Faculty of Env. Earth Sci.*, *Hokkaido Univ.*) ○Kilingaru I. Shivakumar, Shin-ichiro Noro

Keywords: Green Chemistry; Metal-Organic Framework; CO_2 Capture; Gas Separation

Developing cost-effective and eco-friendly adsorbents is crucial for reaching the 2050 carbon neutrality goal. Elastic Layer-structured Metal-organic framework-11 (ELM-11), a flexible MOF with the formula [Cu(BF_4)$_2$(bpy)$_2$] (bpy = 4,4´-bipyridine), exhibits energy-efficient carbon capture potential with high working capacity and intrinsic thermal management.[1] However, the conventional synthesis of its precursor, pre-ELM-11 [Cu(BF_4)$_2$(bpy)(H_2O)$_2$]·bpy, involves organic solvents in addition to H_2O. In this research, we achieved pre-ELM-11 synthesis using only H_2O at room temperature and studied the CO_2 adsorption and CO_2/N_2 gas separation behaviors of its dehydrated form ELM-11.

The pre-ELM-11 was synthesized in 85-87% yield at 25 °C using only H_2O as the reaction solvent and as the washing solvent during filtration. The CO_2 uptake of H_2O-synthesized ELM-11 was 78 cm^3(STP)$\cdot g^{-1}$ at 298 K, slightly lower than 85 cm^3(STP)$\cdot g^{-1}$ for MeOH/H_2O-synthesized ELM-11 (**Fig. 1a**). Both samples exhibited high selectively for CO_2 adsorption over N_2 at 298 K under mixed CO_2/N_2 gas condition (**Fig. 1b**). Moreover, the H_2O-synthesized ELM-11 showed a slightly lower gate-opening pressure compared to MeOH/H_2O-synthesized ELM-11 (**Fig. 1a**). Our synthetic method is economical and environmentally friendly for scalable, real-world CO_2 sequestration applications.

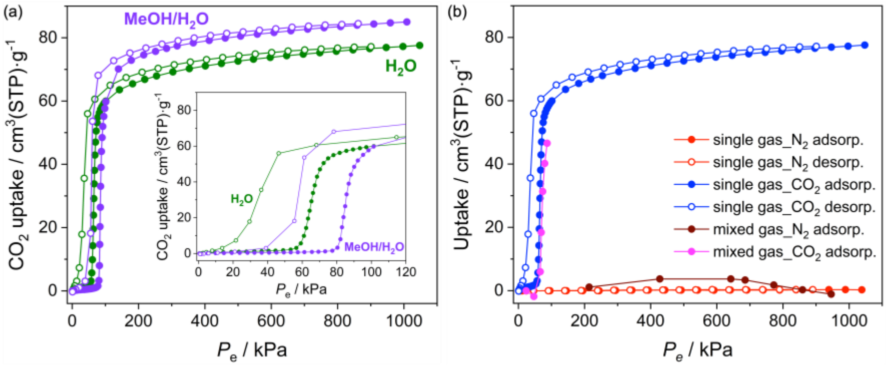


Fig. 1 (a) CO_2 sorption isotherms measured at 298 K for ELM-11 samples synthesized from MeOH/H_2O and H_2O. (b) Single gas (CO_2 and N_2) and mixed gas (CO_2:N_2 = 1:9) sorption isotherms measured at 298 K for ELM-11 sample synthesized from H_2O.

1) a) D. Li, K. Kaneko, *Chem. Phys. Lett.* **2001**, *335*, 50. b) A. Kondo, H. Noguchi, S. Ohnishi, H. Kajiro, A. Tohdoh, Y. Hattori, W.-C. Xu, H. Tanaka, H. Kanoh, K. Kaneko, *Nano Lett.* **2006**, *6*, 2581. c) S. Hiraide, Y. Sakanaka, H. Kajiro, S. Kawaguchi, M. T. Miyahara, H. Tanaka, *Nat. Commun.* **2020**, *11*, 3867.

Highly Selective Separation of Isoprene from C5 Hydrocarbons Mixture Using Pyridyl-based Metal-Organic Frameworks containing copper(I) iodide cluster

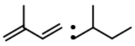
([1]*School of Science, Tokyo Institute of Technology*, [2]*ENEOS Corporation*) ○Joonsik Kim,[1] Pavel M Usov,[1] Yuki Wada,[1] Hiroyoshi Ohtsu,[1] Takaya Matsumoto,[1,2] Masaki Kawano[1]

Keywords: Metal-organic frameworks; Hydrocarbon separation; X-ray crystallography, Structural optimization calculations

Unsaturated hydrocarbons are widely used in industry as raw materials, but they typically require the use of extractive distillation processes for purification, which consume large amounts of energy. To address this challenge, several metal-organic frameworks (MOFs) based on copper iodide were developed.[1] The presence of accessible pores inside these frameworks could be used for separating and isolating specific molecules from hydrocarbon mixtures. However, there have not been many studies on the separation of olefin mixtures, especially including diene. Therefore, several pyridyl-based ligands were employed for MOF formation, providing promising candidates with high selectivity for olefins.

Three pyridyl-based (3- and 4-pyridyl) metal-organic frameworks (MOF) with copper(I) iodide cluster were used to selectively separate three structurally related C5 hydrocarbons (isoprene, 2-methyl-1-butene and 2-methylbutane). The separation is especially challenging due to close similarity of the molecules geometric shapes and have not been investigated in detail in the past. One of those MOF displayed over 3267 times higher selectivity for adsorption of isoprene over 2-methylbutane making it a promising candidate for industrial scale separation. Structural optimization calculations using Matlantis software, an atomistic simulator, revealed the reason of the high affinity for isoprene.

Table 1. Guest uptake and selectivity of each MOFs.

Material	Isoprene uptake, mmol/g	IAST Selectivity at 50 kPa	Reference
		 IP : 2MB	
MOF1	1.7	**3267 : 1**	This work
MOF2	0.65	327 : 1	Previous work
MOF3	1.4	9.5 : 1	Previous work
MIL-125	4.4	1.1 : 1	2
NH_2-MIL-125	4.6	1.1 : 1	2

1) R. Robson, *J. Am. Chem Soc*. **1989**, *111*, 5962-5964.
2) S. Kim, W. Ahn, *Catalysis Today*. **2013**, *204*, 85-93.

アカデミックプログラム［Ｂ講演］ | 10. 有機化学—有機金属化合物：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 16:55 E1111(11号館 [1階] 1111)

[E1111-2vn] 10. 有機化学—有機金属化合物

座長：渕辺 耕平

英語

15:55 ~ 16:15

[E1111-2vn-01]

低原子価ニオブ錯体を触媒とするアルキンとシクロプロペンの [2+2+1]-環化付加反応による多置換シクロペンタジエン誘導体の合成

〇秋山 拓弥[1]、真島 和志[2]、草本 哲郎[1]、劒 隼人[1] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院薬学研究科)

英語

16:15 ~ 16:35

[E1111-2vn-02]

Enantioselective [3+2] Annulation of Aromatic Aldimines with Alkynes via C−H Activation by Half-Sandwich Scandium Catalyst

〇Aniket Mishra[1], Masayoshi Nishiura[1], Zhaomin Hou[1] (1. RIKEN CSRS)

英語

16:35 ~ 16:55

[E1111-2vn-03]

Efficient and Selective Synthesis of Sterically Hindered Secondary Amines by Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

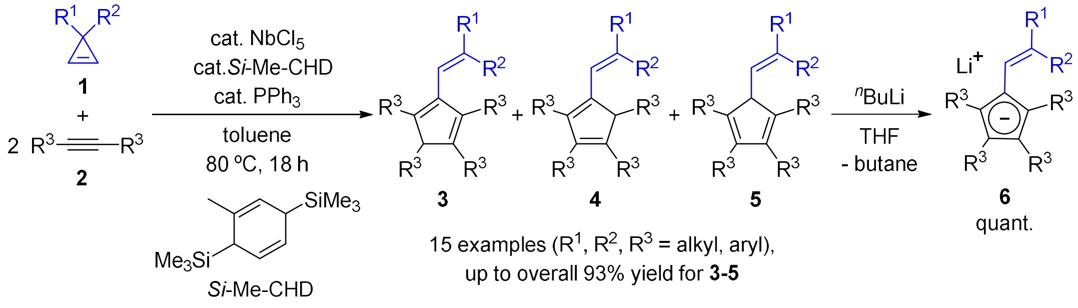
〇Zhou Sun[1,2], Murahashi Nishiura[2], Feng Xue Cong[2], Tetsuro Murahashi[1], MIn Zhao Hou[2] (1. Tokyo Institute of Technology, 2. Riken)

Synthesis of Multi-substituted Cyclopentadiene Derivatives from 3,3-Disubstituted Cyclopropenes and Internal Alkynes Catalyzed by Low-valent Niobium Complexes

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Pharmaceutical Science, Osaka University*) ○Takuya Akiyama,[1] Kazushi Mashima,[2] Tetsuro Kusamoto,[1] Hayato Tsurugi[1]

Keywords: Niobium; Cyclopentadiene; Cycloaddition; Alkyne Complex; Cyclopropene

Cyclopentadienes are the important class of carbocyclic compounds due to their applicability as cyclopentadienyl (Cp) ligands for organometallic complexes. Transition metal-catalyzed [2+2+1]-cycloaddition reactions of two simple alkynes and one carbene precursor are a powerful tool for synthesizing a wide variety of multi-substituted cyclopenadienes in atom- and step-economical manners, though suitable carbene precursors are still limited in this catalytic transformation.[1] Herein, we report an unprecedented [2+2+1]-cycloaddition reaction of 3,3-disubstituted cyclopropenes **1** and two equiv. of dialkyl/diarylacetylenes **2** leading to multi-substituted cyclopentadienes **3**－**5** as an isomeric mixture of the cyclopentadiene moiety, where a combination of an *in situ*-generated low-valent niobium species and PPh_3 exhibits high catalytic activity. ^1H NMR monitoring of the reaction products during the cyclopentadiene formation revealed that the reaction provides **4** and **5** as initial products, and subsequent proton migration *via* 1,5-sigmatropic hydrogen shift results in a thermodynamically controlled ratio of **3**/**4**/**5** in the reaction mixture. An isolated mixture of **3**－**5** is converted to lithium cyclopentadienide **6** as a sole product by treating with *n*-butyllithium in THF. The reaction mechanism of this unprecedented catalytic reaction was clarified by DFT calculation. The initial step is a formation of cyclopropane-fused metallacyclopentenes *via* 1,2-insertion of **1** into (η^2-alkyne)niobium species, and subsequent ring-opening of the fused cyclopropene ring provides niobium dienylcarbene species. Enyne metathesis of the niobium dienylcarbene species with the second alkyne forms metallacyclohexadiene whose reductive elimination after or without 1,5-proton transfer gives **4** or **5** as the products. We will disclose an applicability of the lithium cyclopentadienide for (cyclopentadienyl)metal complexes.



15 examples (R^1, R^2, R^3 = alkyl, aryl), up to overall 93% yield for **3-5**

---

1) Frei, A. *Chem. Eur. J.* **2019**, *25*, 7074.

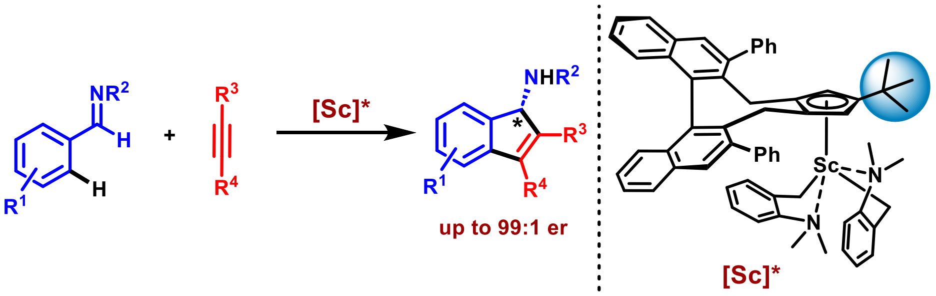
Enantioselective [3+2] Annulation of Aromatic Aldimines with Alkynes via C−H Activation by Half-Sandwich Scandium Catalyst

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science*)
○Aniket Mishra,[1] Masayoshi Nishiura,[1] Zhaomin Hou[1]

Keywords: C–H activation, Annulation, Scandium, Rare-earth-metal, Asymmetric synthesis

Chiral 1-aminoindenes and its derivatives are important components in a wide array of natural products, pharmaceuticals, bioactive molecules, and functional materials. Therefore, the development of efficient protocols for the asymmetric synthesis of chiral 1-aminoindenes bearing a stereodefined amino functionality is of great interest and much importance. Ideally, formal asymmetric [3+2] annulation of aldimines with alkynes *via* the catalytic C–H activation represents the most straightforward and 100% atom-efficient route for the construction of densely functionalized chiral 1-aminoindenes. However, such an approach has remained unsuccessful, presumably due to the lack of suitable chiral catalysts. Recently, we have found that half-sandwich rare-earth-alkyl complexes can serve as efficient catalysts for the [3+2] annulation of aldimines and alkenes via C–H activation.[1] These studies invoked us to examine the feasibility of the asymmetric annulation of aldimines with alkynes by using chiral half-sandwich rare-earth-alkyl catalyst.

Herein, we report for the first time the enantioselective [3+2] annulation of a wide range of aldimines with internal alkynes via *ortho*- aryl C(sp^2)–H activation by a novel chiral half-sandwich scandium complex derived from a *tert*-butyl substituted chiral binaphthyl-bearing Cp. This protocol offers an efficient and selective route for the synthesis of a new family of chiral 1-aminoindenes in high yields with high regio- and enantioselectivity. Intriguingly, attractive noncovalent interaction such as C–H···π interaction plays a crucial role for determining the high level of enantioselectivity in an unprecedented manner, established by the DFT studies.



1) (a) X. Cong, G. Zhan, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2020**, *143*, 5531. (b) A. Mishra, X. Cong, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2023**, *145*, 17468.

Efficient and Selective Synthesis of Sterically Hindered Secondary Amines by Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, [2]Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako, Saitama 351-0198*) ○Zhou Sun[1], Masayoshi Nishiura[1,2], Xuefeng Cong[1], Zhaomin Hou[1,2]

Keywords: *C-H alkylation, aldimines, rare-earth catalyst, hydrosilylation*

Sterically Hindered Secondary Amines are an important class of compounds that constitute the major body of bioactive natural products and pharmaceuticals[1]. The catalytic imidoyl C-H alkylation of aldimines with alkenes is an effective way to construct diverse sterically hindered ketimines which after hydrosilylation reaction can be converted to corresponding secondary amines. However, such transformation has remained a challenge to date because of the lack of suitable catalysts[2-3]. Here we report for the first time sequential imidoyl C-H alkylation of aldimines with alkenes followed by hydrosilylation of aldimines by half-sandwich rare-earth catalysts.

This protocol offers a straightforward and step-economical route for the synthesis of a series of sterically hindered secondary amines from easily accessible aliphatic or aromatic aldimines and alkenes (Fig.1). When R= secondary alkyl or aryl, R^1=secondary alkyl, imidoyl C-H alkylation of aldimines with styrenes exclusively afforded corresponding ketimines through the 2,1-insertion of a styrene unit by half-sandwich scandium catalysts and then after yttrium catalyzed reduction reaction can convert to different sterically hindered secondary amines, featuring excellent yields (70%-86%), broad substrate scope, high chemo- and regioselectivity under simple reaction conditions.

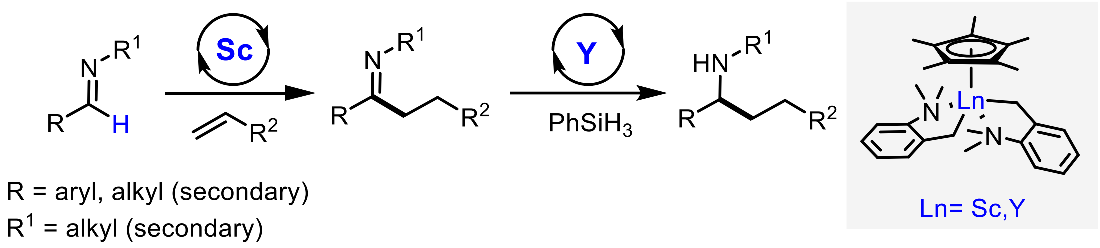


Fig.1 Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

References:

[1] R. N. Salvatore, C. H. Yoon, K. W. Jung, *Tetrahedron* **2001**, *57*, 7785 – 7811.

[2] X. Cong, Q. Zhuo, N. Hao, Z. Mo, G. Zhan, M. Nishiura, Z. Hou. J. Am. Chem. Soc., **2022**, *61*, e202

[3] Dixneuf. P. H. et al*, ACS Catal.* **2011**, 1, 122.

アカデミックプログラム［Ｂ講演］ | 10. 有機化学—有機金属化合物：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 16:35 E1112(11号館 [1階] 1112)

[E1112-2vn] 10. 有機化学—有機金属化合物

座長：岩本 貴寛

英語

15:55 ~ 16:15

[E1112-2vn-01]

金触媒による環化—スルホニル転位による４－スルホニルインドールの選択的合成

〇Chunbo JIA[1]、寺田 眞浩[1]、中村 達[1] (1. 東北大学)

英語

16:15 ~ 16:35

[E1112-2vn-02]

活性イソニトリルの銀触媒不斉アルドール反応および不斉Michael反応

〇酒井 聡史[1]、内山 渓[1]、矢藤 千菜[1]、今井 浩児[1]、東田 皓介[2]、清水 洋平[1,3]、澤村 正也[1,3] (1. 北大理、2. 京大院理、3. WPI-ICReDD)

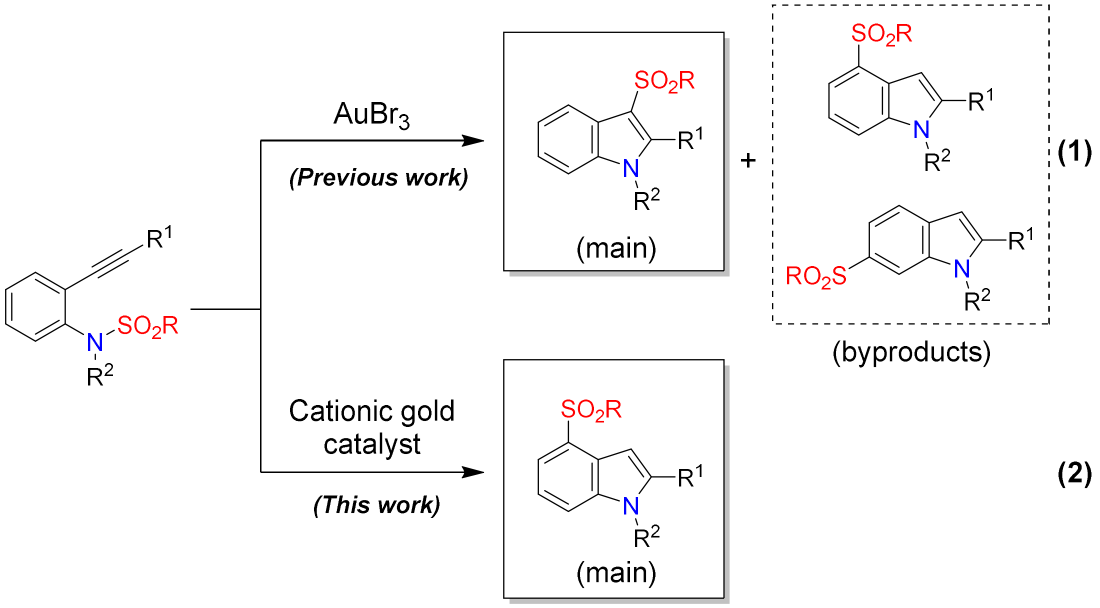
Selective Synthesis of 4-Sulfonylindoles by Gold-catalyzed Consecutive Cyclization-Sulfonyl Migration

([1]*Graduate School of Science, Tohoku University*)
○Chunbo Jia,[1] Masahiro Terada,[1] Itaru Nakamura[1]

Keywords: Gold catalyst; Indole; Rearrangement; Cyclization; Alkyne

π-Lewis acid-catalyzed cyclization reactions of *ortho*-alkynylanilines have been widely used to synthesize indole derivatives that are difficult to be synthesized by direct electrophilic substitution of indole substrates.[1-4] Previously, our group reported $AuBr_3$-catalyzed cycloisomerization reactions of *ortho*-alkynyl-*N*-sulfonylanilines to form 3-sulfonylindoles with high efficiency,[5] along with small amounts of 4- and 6- sulfonylated byproducts (Scheme 1). The presence of 4-sulfonylindoles aroused our interest, because 4-substituted indole skeleton is presented in various bioactive molecules, while it is hard to synthesize due to poor electron density at C4 position and generally requires additional directing groups to accomplish.[6]

In this work, we report that 4-sulfonylindole can be obtained as the main product by using cationic gold catalyst and controlling reaction conditions (Scheme 2). Factors influencing the product selectivity and a mechanism based on DFT calculations and control experiments will be discussed.



1) C. Praveen, K. Karthikeyan and P. T. Perumal, *Tetrahedron*, **2009**, *65*, 9244-9255. 2) A. Fürstner and P. W. Davies, *J. Am. Chem. Soc.*, **2005**, *127*, 15024-15025. 3) T. Shimada, I. Nakamura and Y. Yamamoto, *J. Am. Chem. Soc.*, **2004**, *126*, 10546-10547. 4) S. Cacchi, G. Fabrizi and L. Moro, *Tetrahedron Lett.*, **1998**, *39*, 5101-5104. 5) I. Nakamura, U. Yamagishi, D. Song, S. Konta and Y. Yamamoto, *Angew. Chem. Int. Ed.*, **2007**, *46*, 2284-2287. 6) J. Kalepu, P. Gandeepan, L. Ackermann and L. T. Pilarski, *Chem. Sci*, **2018**, *9*, 4203-4216.

Silver-Catalyzed Asymmetric Aldol Reaction and Michael Reaction of Activated Isocyanides

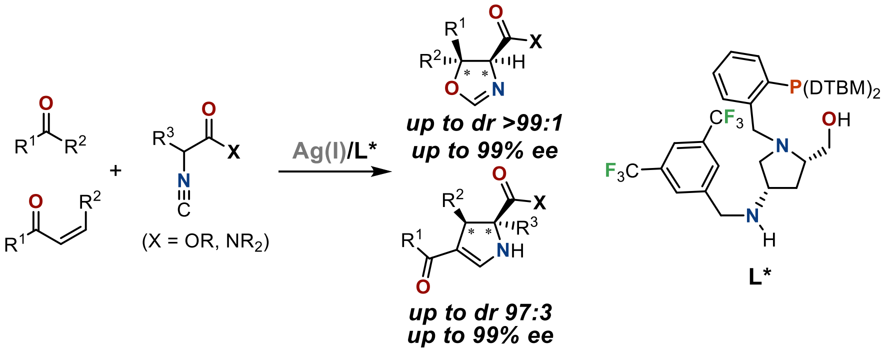
([1] *Department of Chemistry, Faculty of Science, Hokkaido University*, [2] *Department of Chemistry, Graduate School of Science, Kyoto University,* [3] *WPI-ICReDD*) ○Satoshi Sakai,[1] Kei Uchiyama,[1] Kazuna Yato,[1] Koji Imai,[1] Kosuke Higashida,[2] Yohei Shimizu,[1,3] Masaya Sawamura[1,3]

Keywords: Silver Catalysis; Isocyanide; Asymmetric Aldol Reaction; Asymmetric Michael Addition Reaction; DFT Calculation

Asymmetric aldol reactions are powerful carbon-carbon bond formation reactions. Especially, the asymmetric aldol reactions of isocyanoacetic acid derivatives proceed with successive cyclization to produce chiral oxazolines, which can be transformed into β-hydroxy-α-amino acids by hydrolysis. While the reactions using aryl ketones or sterically accessible dialkyl ketones were reported,[1] the reaction using sterically and electronically unbiassed ketones was elusive.

Our original chiral prolinol-phosphine ligands enable promotion and stereocontrol of aldol reactions with aldehydes by forming multiple hydrogen bonds with the carbonyl group of the substrates.[2] The newly developed ligands bearing a secondary amino group showed excellent performance in the asymmetric aldol reactions of isocyanoacetoamides with various ketones. In particular, bulky dialkyl ketones such as pinacolone were competent giving the products in highly diastereo- and enantioselective manner. Furthermore, the same catalytic system can be applied to the asymmetric Michael reactions of α-substituted isocyanoacetates with α,β-unsaturated ketones, affording the cyclized products with high stereoselectivity.

Computational analysis suggested that multiple hydrogen bonds and dispersive interactions between the ligand and substrates contribute to stabilization of the transition states to increase the reactivity and stereoselectivity.



1) a) R. Campa, I. Ortin, D. J. Dixon, *Angew. Chem. Int. Ed.* **2015**, *127*, 4977. b) P. Martinez-Pardo, G. Blay, M. C. Munoz, J. R. Pedro, A. Sanz-Marco, C. Vila, *Chem. Comuun.* **2018**, *54*, 2862.

2) Sakai, S.; Fujioka, A.; Imai, K.; Uchiyama, K.; Shimizu, Y.; Higashida, K.; Sawamura, M. *Adv. Synth. Catal.* **2022**, *364*, 2333.

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19日(火) 15:55 ~ 17:15 E1113(11号館 [1階] 1113)

[E1113-2vn] 11. 有機化学―構造有機化学

座長：松井 康哲、田中 一生

日本語

15:55 ~ 16:15

[E1113-2vn-01]

縮環型アゾベンゼンガリウム錯体の合成と光学特性評価

○堀田 千有希[1]、中村 将志[1]、権 正行[1]、田中 一生[1] (1. 京都大学)

英語

16:15 ~ 16:35

[E1113-2vn-02]

外部環境に依存する感圧化学センサー：ヘリカルアントラセン二量体の圧力誘起蛍光シグナル変化

○木下 智和[1]、渡邊 公太[1]、鶴巻 英治[1]、豊田 真司[1]、福原 学[1] (1. 東工大)

英語

16:35 ~ 16:55

[E1113-2vn-03]

スクアリン骨格をもつ正孔回収単分子膜材料の開発とペロブスカイト太陽電池への応用

○平 翔太[1]、チョン ミンアン[1]、中村 智也[1]、マーディー リチャード[1]、若宮 淳志[1] (1. 京都大学 化学研究所)

日本語

16:55 ~ 17:15

[E1113-2vn-04]

極性結晶を基盤とする有機トリボルミネッセンス材料の開発

○大垣 拓也[1]、松井 康哲[1]、池田 浩[1] (1. 阪公大)

日本化学会 第104春季年会 (2024)

縮環型アゾベンゼンガリウム錯体の合成と光学特性評価

（京大院工）○堀田千有希・中村将志・権正行・田中一生

Synthesis and Optical Evaluation of Gallium-Fused Azobenzene Complexes

(*Graduate School of Engineering, Kyoto University*) ○Chiaki Hotta, Masashi Nakamura, Masayuki Gon, Kazuo Tanaka

Azobenzene is known as a non-emissive molecule due to its highly efficient photoisomerization, and therefore luminescent materials based on the azobenzene moiety have been hardly reported. Kawashima *et al.* found that the coordination of boron atom to the azobenzene scaffold suppressed the photoisomerization and permitted the electronic transitions, resulting in excellent fluorescence. We have developed typical element complexes with the ring-fused structure based on the tridentate azobenzene ligand. These complexes exhibited unique electronic states and fluorescent properties originating from heteroatom-specific structures. Boron-fused azobenzene complexes showed unique solid state luminescence derived from the four-coordinated tetrahedron structure. In addition, tin-fused complexes expressed the outstanding narrow energy gap originating from 3c–4e bond and Sn–N coordination, and exhibited vapochromic luminescence triggered by alteration of the coordination number from five to six at the tin atom. In this work, we focus on gallium, one of the high periodic elements of the group 13, and will explain the synthesis and optical property of the luminescent gallium-fused azobenzene complex.

Keywords : Gallium; Azobenzene; Fluorescence; π-Conjugated system

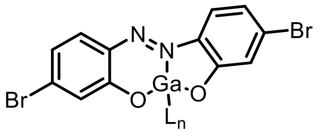


Figure 1. Chemical structure of a gallium-fused azobenzene complex.

アゾベンゼンはその高効率な光異性化のために非発光性であることが知られており、発光性の π 共役系骨格としての検討は進んでいない。一方川島らは、アゾベンゼンにホウ素を配位させることで、光異性化の抑制及び電子遷移の許容化に基づき、発光性分子となることを報告した 1)。当研究室では、アゾベンゼン三座配位子を用いた縮環構造を有する典型元素錯体を設計し、ヘテロ元素特有の構造に由来する機能性発光材料の創出に取り組んできた。13 族元素のホウ素を導入すると、四配位四面体構造に基づく特異な固体発光性を示すことを見出した 2)。また、14 族高周期元素の Sn を導入し、五配位三方両錐型の超原子価結合による狭エネルギーギャップ性や、スズ原子の配位数変化に伴うベイポクロミズム特性を明らかにした 3)。13 族高周期元素は未開拓であるが、ホウ素錯体と類似した固体発光性、及びスズと類似した高周期元素特有の光学物性の発現が期待される。そこで本研究では、13 族高周期元素の一つであるガリウムに注目し、縮環型アゾベンゼンガリウム錯体を創出した。発表では化合物の合成及び光学特性について詳述する。

1) J. Yoshino, N. Kano and T. Kawashima, *Chem. Commun.* **2007**, 559–561.
2) M. Gon, K. Tanaka, Y. Chujo, *Angew. Chem. Int. Ed.* **2018**, *57*, 6546–6551.
3) M. Gon, K. Tanaka, Y. Chujo, *Chem. – Eur. J.* **2021**, *27*, 7561–7571.

Solvent-directed, pressure-controllable chemosensor: A case of helical anthracene dimer

([1]*Department of Chemistry, Tokyo Institute of Technology*) ○Tomokazu Kinoshita,[1] Kota Watanabe,[1] Eiji Tsurumaki,[1] Shinji Toyota,[1] Gaku Fukuhara[1]

Keywords: Pressure-Responsive Chemosensor; Hydrostatic Pressure Spectroscopy; Anthracene

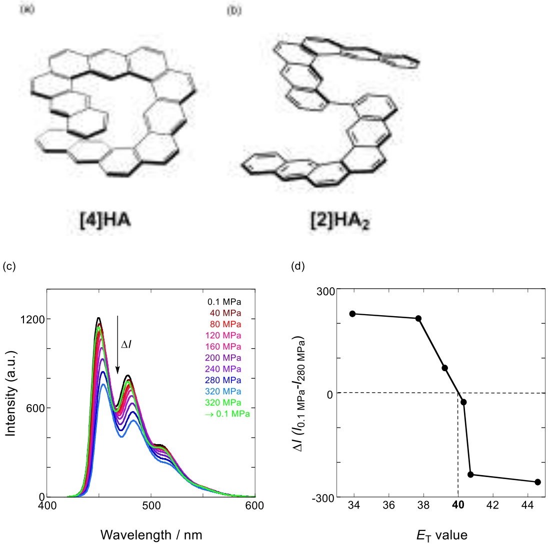


Figure 1. Chemical structures of helical anthracenes ((a) **[4]HA** and (b) **[2]HA$_2$**). (c) Fluorescence spectra of **[2]HA$_2$** in dichloromethane (λ_{ex} 412 nm, 57 μM) at room temperature, measured in a high-pressure cell. (d) Hydrostatic pressure-induced ΔI ($I_{0.1MPa}$ - I_{280MPa}).

The exploration of a pressure-responsive chemosensor is of particular significance in current multidisciplinary chemistry from the viewpoints of mechanoscience. So far, we have developed such chemosensors that are susceptible to hydrostatic pressure in solutions.[1] Of these, an anthracene-fused helicene, **[4]HA** (Fig. 1a), shows ratiometric pressure-responsive fluorescence changes upon the hydrostatic pressurization. The ratiometry in **[4]HA** is caused by the [4+4] photocyclodimerization of the intramolecularly π-π stacked anthracenes.[2] In this study, we focused on a pseudo-helicene dimer, **[2]HA$_2$** (Fig 1b) that is linked with two fused anthracene skeletons (**[2]HA**) via a single bond, which is believed to exhibit a solvation-dependent pressure sensitivity. Interestingly, as shown in Fig. 1c, **[2]HA$_2$** showed a distinctive pressure-induced fluorescence response. The fluorescence responses in some solvents are strongly dependent on solvent polarity estimated by E_T value; the response sign (ΔI) inverted at the border of E_T as 40 kcal mol^{-1}, shown in Fig. 1d. The excited-state dynamics (k_f and k_{nr}) of **[2]HA$_2$** under hydrostatic pressures supports the origins controlling pressure-induced solvation-driven transition states. It should be therefore noted that such interesting chemosensory responses are originated from the excited-state dynamics greatly involving pressure-induced microenvironmental polarities.

1) Mizuno, H.; Fukuhara, G. *Acc. Chem. Res.* **2022**, *55*, 1748–1762. 2) Kinoshita, T.; Fujise, K.; Tsurumaki, E.; Toyota, S.; Fukuhara, G. *Chem. Commun.* **2022**, *58*, 3290–3293.

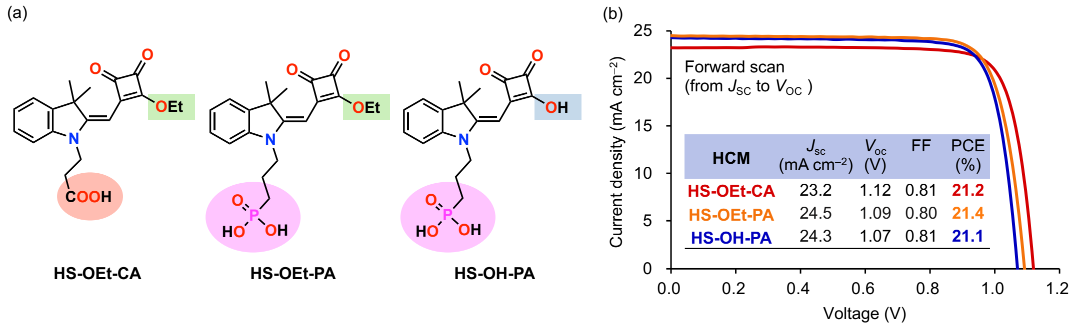
Development of Squaraine-Based Hole-Collecting Monolayer Materials for Perovskite Solar Cells

([1]*Institute for Chemical Research, Kyoto University*) ○Shota Hira,[1] Minh Anh Truong,[1] Tomoya Nakamura,[1] Richard Murdey,[1] Atsushi Wakamiya[1]

Keywords: Perovskite Solar Cell; Hole-Collecting Material; Monolayer; Squaraine; Chemisorption

Recently, chemically adsorbed hole-collecting monolayers (HCMs) with their ease of processing and high performance, have attracted great attention in order to further improve the performance of perovskite solar cells (PSCs).[1,2]

In this study, we designed and synthesized a series of half-squaraine derivatives (**HS-OEt-CA**, **HS-OEt-PA**, and **HS-OH-PA**, Figure 1a) as HCM materials. The cyclic voltammetry measurements in DMF solution revealed that compared to ethoxy-substituted **HS-OEt-CA** and **HS-OEt-PA**, hydroxyl-contained **HS-OH-PA** shows a lower oxidation potential, indicating the existence of an anionic form generated from the deprotonation of the squaric acid moiety. These molecules were found to adsorb on the surface of transparent conductive metal oxide electrodes to form a monolayer. According to photoelectron yield spectroscopy, the ionization potentials of **HS-OEt-CA**, **HS-OEt-PA**, and **HS-OH-PA** adsorbed ITO were estimated to be 5.54, 5.50, and 5.33 eV, respectively, which are shallower than the valence band (VB) of the perovskite material ($Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$, VB = 5.56 eV). PSCs using these half-squaraine derivatives as HCMs were fabricated and evaluated. All devices showed high power conversion efficiencies of over 21% (Figure 1b). **HS-OEt-CA**-based devices exhibit suppressed interfacial non-radiative recombination and higher open-circuit voltage (V_{OC}) than devices using phosphonic acid-substituted HCMs. In this presentation, molecular design, characterization, and device evaluation will be discussed in detail.



HCM	J_{sc} (mA cm⁻²)	V_{oc} (V)	FF	PCE (%)
HS-OEt-CA	23.2	1.12	0.81	**21.2**
HS-OEt-PA	24.5	1.09	0.80	**21.4**
HS-OH-PA	24.3	1.07	0.81	**21.1**

Figure 1. (a) Chemical structures of the half-squaraine derivatives. (b) *J*–*V* curves of the perovskite solar cells using the half-squaraine derivatives.

1) A. Al-Ashouri, S. Albrecht et al., *Science* **2020**, *370*, 1300.
2) M. A. Truong, A. Wakamiya et al., *J. Am. Chem. Soc.* **2023**, *145*, 7528.

極性結晶を基盤とする有機トリボルミネッセンス材料の開発

（阪公大院工）〇大垣 拓也・松井 康哲・池田 浩

Development of Organic Triboluminescence Materials Based on Polar Crystals

(*Grad. Sch. of Eng., Osaka Metro. Univ.*) 〇Takuya Ogaki, Yasunori Matsui, Hiroshi Ikeda

Triboluminescence (TL) is a luminescent phenomenon induced by mechanical stimuli. TL materials require both highly-luminescent properties in the solid state and organic polar crystals with a spontaneous polarization. However, it is difficult to rationally design such organic materials. To overcome the difficulty, we have developed organic TL polar crystals based on a host–dopant system.[1] As an alternative strategy to develop organic TL materials, in this work, we focused on the crystal symmetry and comprehensively explored organic TL materials among solid-state luminescent materials. Among various asymmetric diaryl keto-enols **1-R** (Fig. 1b), crystals of **1-*n*-Pr** with *n*-Pr group exhibit yellow TL upon mechanical stimuli (Fig. 1c) and belong to polar crystal with a space group of $P2_1$ (Fig. 1d). Moreover, TL-active polar crystals were newly found among other solid-state luminescent materials such as organoboron complexes. From these findings, it is found out that it is important to focus on both the solid-state luminescence and the crystal symmetry for developing new organic TL materials.

Keywords: Triboluminescence; Mechanoluminescence; Polar Crystals; Solid-state Luminescence; Organoboron Complexes

トリボルミネッセンス（TL，Fig. 1a）は，機械的刺激による発光現象である．有機 TL 材料には固体状態での高い発光性に加えて，自発分極をもつ有機極性結晶（Fig. 1a）が必要とされるが，そのような材料の合理的設計は一般に困難である．この問題に対して，我々は最近ホスト–ドーパント系有機 TL 材料を開発した[1]．本研究ではこれに代わる有機 TL 材料開発戦略として結晶の対称性に着目し，固体発光材料の中から TL 材料の網羅的探索を行った．その結果，非対称ジアリールケトエノール **1-R**（Fig. 1b）のうち，*n*-Pr 基を有する **1-*n*-Pr** の結晶は機械的刺激により黄色 TL を示し（Fig. 1c），$P2_1$ の空間群をもつ極性結晶に属することがわかった（Fig. 1d）．また，この他に有機ホウ素錯体などの他の固体発光材料の中からも，新たな有機 TL 材料が見つかった．これらの知見から，新たな有機 TL 材料開発には，固体発光特性と結晶の対称性の両方に着目することが重要であることがわかった．

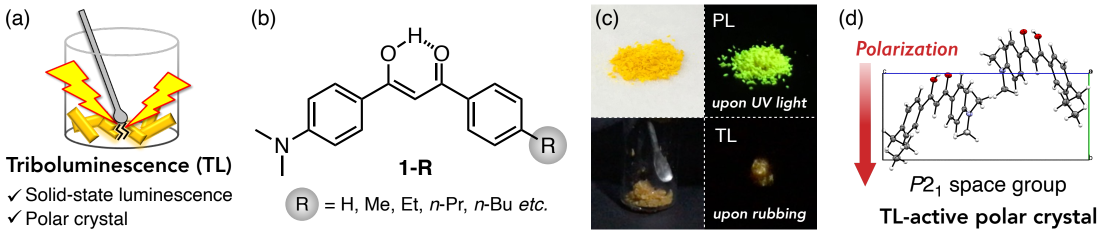


Fig. 1. (a) An illustration and fundamental requirements of organic TL materials, (b) molecular structure of **1-R**, (c) photographs of photoluminescence (PL) and TL of **1-*n*-Pr**, and (d) the packing structure of **1-*n*-Pr**.

1) 大垣，松井，池田，*日本化学会第 103 春季年会(2023) 予稿集*，K603-1pm-05，**2023**.

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19日(火) 15:55 ~ 17:15 E1121(11号館 [2階] 1121)

[E1121-2vn] 11. 有機化学—構造有機化学

座長：羽毛田 洋平、澤田 知久

日本語
15:55 ~ 16:15
[E1121-2vn-01]
炭素•炭素一電子結合：存在の実証とその性質

○島尻 拓哉[1]、川口 聡貴[1]、鈴木 孝紀[1]、石垣 侑祐[1] (1. 北海道大学)

英語
16:15 ~ 16:35
[E1121-2vn-02]
機械学習を用いた固体混合比の予測と化学反応分析への応用

○白倉 逸人[1]、佐野 太一[1]、井手 雄紀[2]、Sheng Hu[2]、瀧川 一学[2,3]、猪熊 泰英[1,2] (1. 北大院工、2. 北大 WPI-ICReDD、3. 京大 CIREDS)

英語
16:35 ~ 16:55
[E1121-2vn-03]
A Coordination Cage as a Crystalline Sponge

○Wei He[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The Univ. of Tokyo, 2. Institute for Molecular Science)

日本語
16:55 ~ 17:15
[E1121-2vn-04]
ペンタキス（アームドサイクレン）による金属イオンに対する位置選択的な配位と位置選択的な金属イオン置換：分子オセロ

○堀田 拓希[1]、池田 茉莉[2]、桑原 俊介[1]、幅田 揚一[1] (1. 東邦大、2. 千葉工大)

炭素･炭素一電子結合：存在の実証とその性質

（北大院理 [1]・北大創成研究機構 [2]・北大理 [3]）○島尻 拓哉 [1,2]・川口 聡貴 [3]・鈴木 孝紀 [1]・石垣 侑祐 [1]

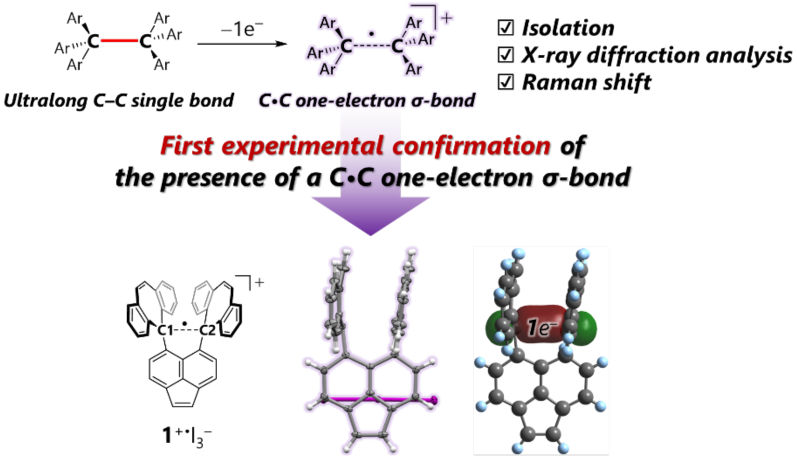
Direct evidence for a carbon•carbon one-electron σ-bond and its nature

([1,3]*Faculty of Science, Hokkaido University*, [2]*Creative Research Institution, Hokkaido University*) ○ Takuya Shimajiri,[1,2] Soki Kawaguchi,[3] Takanori Suzuki,[1] Yusuke Ishigaki[1]

As early as 1931, Pauling postulated the existence of one-electron bonds.[1] However, in striking contrast to the large body of work on electron-pair bonds, the paucity of examples with one-electron bonds is remarkable,[2-4] which is most likely due to their intrinsic weakness. In this work, we disclose the synthesis and isolation of radical cation salt with a carbon•carbon one-electron σ-bond (2.921(3) Å at 100 K). The presence of the bond was demonstrated by experimental and theoretical investigations. Such a carbon•carbon one-electron bond can induce near-infrared-absorbing properties even with just one σ-bond in contrast to common organic near-infrared-absorbing materials.

Keywords : One-electron bond; X-ray analysis; Raman spectroscopy; Near-infrared absorption

Pauling が一電子結合を提案して以来 [1]、その存在について多くの調査がなされてきた。一方で、現在まで X 線構造解析によりその存在が実証された例は極めて少なく [2-4]、中でも炭素原子間ではおよそ百年にわたって報告例がない。本研究では、炭化水素 **1** の一電子酸化により、炭素•炭素一電子結合を有するラジカルカチオン $\mathbf{1}^{\bullet+}\mathrm{I}_3^-$の合成、X 線構造解析に成功した。$\mathbf{1}^{\bullet+}\mathrm{I}_3^-$は 2.921(3) Å の近接した炭素原子間距離を有しており、ラマン測定によって C–C 対称伸縮振動に対応するラマンシフトが観測されたことから、炭素原子間における一電子結合を直接的に初めて実証した。また、この一電子結合の小さな軌道の分裂に基づいて、$\mathbf{1}^{\bullet+}\mathrm{I}_3^-$は近赤外光吸収特性を示したので、その詳細を報告する。



1) L. Pauling, *J. Am. Chem. Soc.* **1931**, *53*, 3225.; 2) G. Bertrand *et al., Science* **1998**, *279*, 2080.; 3) J. C. Peters *et al., J. Am. Chem. Soc.* **2013**, *135*, 3792.; 4) M. Wagner *et al., Angew. Chem. Int. Ed.* **2014**, *53,* 4832.

Predicting Solid Mixing Ratios Using Image-based Machine Learning and Application to Chemical Reaction Analysis

([1]*Grad. Sch. Eng., Hokkaido Univ.*, [2]*WPI-ICReDD*, *Hokkaido Univ.*, [3]*CIREDS*, *Kyoto Univ.*)
○Hayato Shirakura,[1] Taichi Sano,[1] Yuki Ide,[2] Sheng Hu,[2] Ichigaku Takigawa,[2,3] Yasuhide Inokuma[1,2]

Keywords: Machine Learning; Enantiomer Ratio; Mixing Ratio Prediction; Reaction Yield Prediction; Organic Crystal

Machine learning is recently used as a powerful tool for discovering relationships between complex chemical parameters, and enabling predictions in chemical reactions and molecular design. Our laboratory recently reported machine learning systems that instantly predicts mixing ratios of sugar and dietary salt from their images[1]. Image-based prediction has potentials to analyze objects that are difficult to identify with human eyes. In this research, we explored the practical applicability of this machine learning system for chemical research.

Crystal polymorphs are defined as different crystal structures of the same compound, and instrumental analysis methods are limited to the solid state. It was assumed that glycine with different crystalline polymorphs of α- and γ-from can be visually distinguished. Machine learning model built from 300 images of 200 mg α- and γ-glycine mixtures and their mixing ratios (training data) can predict mixing ratios from images with an error of 4.0% (**Figure 1a**). Prediction of the enantiomeric ratio of D-/L-tartaric acid was also possible, although the difference between the crystals was more difficult to distinguish with naked eyes. Furthermore, yield prediction was conducted as an application to chemical reaction. Reaction yield prediction of *m*-aminophenol obtained by solid-state decarboxylation for *p*-aminosalicylic acid was achieved with an error of 5.7% by using sample images and ^{1}H NMR yields (**Figure 1b**). As an example of more practical systems in chemical research, we attempted to predict the mixing ratios using sample solutions. The enantiomeric ratio was predicted from evaporated solid-state images of solutions containing (*R*)- or (*S*)-1,1'-binaphthyl with an error of 6.8% (**Figure 1c**).

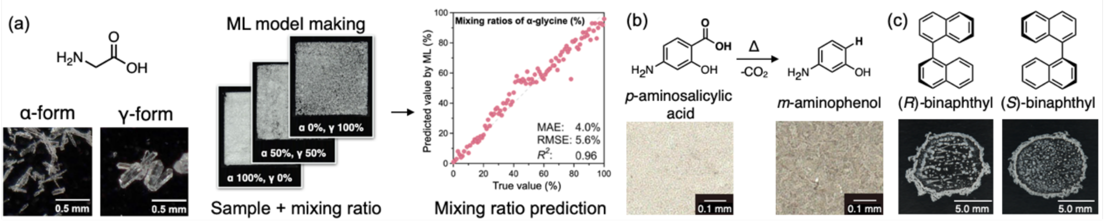


Figure 1. (a) Crystal polymorph mixing ratio prediction results from α- and γ-glycine crystal images. (b) Yield prediction using solid-state reaction images. (c) Enantiomeric ratio prediction using droplet drying images.

1) Y. Ide, H. Shirakura, T. Sano, M. Murugavel, Y. Inaba, S. Hu, I. Takigawa, Y. Inokuma, *Ind. Eng. Chem. Res.* **2023**, *62*, 13790.

A Coordination Cage as a Crystalline Sponge

(*[1]Graduate School of Engineering, The University of Tokyo, [2]Division of Advanced Molecular Science, Institute for Molecular Science, [3]UTIAS, The University of Tokyo)*
○Wei He,[1] Hiroki Takezawa,[1] Makoto Fujita[1,2,3]
Keywords: Coordination Cage, Molecular Recognition, Crystalline Sponge

The crystalline sponge (CS) method has emerged as an innovative X-ray technique for single-crystal diffraction analysis, eliminating the need for the traditional crystallization of analytes.[1] However, certain limitations persist, including constraints on the molecular size and polarity of analytes. In this study, we employ an M_6L_4 cage, a self-assembled molecular host with well-established host-guest chemistry,[2] as an enhanced CS to address the limitations of the original method. Large aromatic polysulfonates, or "*sticker*" anions, significantly facilitate the crystallization of the cage and circumvent the issue of static guest disorder encountered in crystallographic analysis by producing crystals in a low space group symmetry (typically, *P*-1). Benefiting from the large cavity of the cage coupled with its strong guest-binding properties, the enhanced CS allows for the analysis of a broader spectrum of analytes, including rare synthetic molecules, water-soluble molecules, and large amphiphilic molecules with a molecular weight up to ~1200.

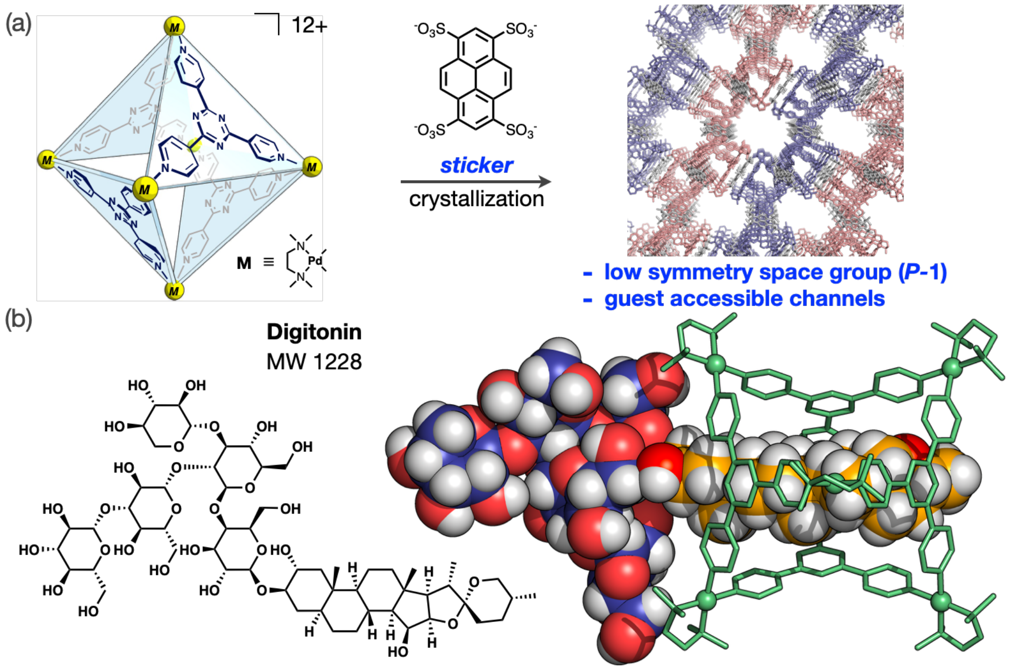


Fig.1. (a) Crystallization of an M_6L_4 cage into a potent crystalline sponge. (b) Crystal structures of guests were determined using an M_6L_4 cage as a crystalline sponge.

1) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita, *Nature*. **2013**, *496*, 461. 2) H. Takezawa, M. Fujita, *Bull. Chem. Soc. Jpn*. **2021**, *94*, 2351.

ペンタキス（アームドサイクレン）による金属イオンに対する位置選択的な配位と位置選択的な金属イオン置換：分子オセロ

（東邦大理[1]・東邦大複合物性研究セ[2]・千葉工大工[3]）○堀田拓希[1]・池田茉莉[3]・桑原俊介[1,2]・幅田揚一[1,2]

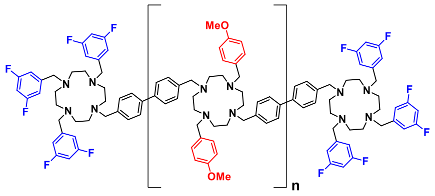
Regioselective coordination toward metal ion and regioselective metal ions exchange by Pentakis(armed-cyclen)s: Molecular Othello ([1]*Department of Chemistry and* [2]*Research Center for Materials with Integrated Properties, Toho University,* [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*) ○Hiroki Horita,[1] Mari Ikeda,[3] Shunsuke Kuwahara,[1,2] Yoichi Habata[1,2]

L1 (**Fig. 1**), which consists of three tetra-armed cyclens, coordinates regioselectively to Ag$^+$ by the electron density of the aromatic side arms.[1] In this study, we designed **L2** (**Fig. 1**) which has more cyclen moieties, and aimed to develop a molecule that exhibits unprecedented complexation behavior by regioselective coordination to Ag$^+$ and metal ions exchange.

We added metal ions to **L2** and confirmed the complexation behavior by ^{1}H and ^{19}F NMR. When Ag$^+$ was added, the central three cyclens with MeO groups formed complexes with Ag$^+$ by regioselective coordination. When Hg^{2+} was added, the cyclens at both ends that had not formed complexes coordinated to Hg^{2+} first, and metal ions exchange (Ag$^+$→Hg^{2+}) occurred in the three cyclens in the center after adding more Hg^{2+}. This behavior is similar to that of a disk's front and back sides in an Othello game, indicating that **L2** behaves as a "Molecular Othello".

Keywords: Cyclen; Regioselective Coordination; Electron Density; Silver Ion; Metal Ions Exchange

テトラアームドサイクレンを 3 個連結した配位子 **L1**（**Fig. 1**）は芳香環側鎖の電子密度を変えることで Ag$^+$に対して位置選択的に配位する．[1] 本研究では，さらに多くのサイクレンを連結した配位子 **L2**（**Fig. 1**）を設計し，Ag$^+$に対する位置選択的な配位と他の金属イオンを用いた金属イオン交換によって，これまでにない錯形成挙動を示す分子の開発を目的とした．



L1 (n = 1), **L2** (n = 3)

Figure 1. 配位子の構造.

L2 に金属イオンを添加し，^{1}H と ^{19}F NMR で錯形成挙動を確認した．まず Ag$^+$を添加すると位置選択的な配位により，4-メトキシベンジル基を持つ中央の 3 個のサイクレンが Ag$^+$と錯体を形成した．そこに Hg^{2+}を添加していくと，錯形成していない両端のサイクレンが先に Hg^{2+}と錯体を形成し，さらに加えると中央の 3 個のサイクレンで金属イオン置換（Ag$^+$→Hg^{2+}）が起こった．これはオセロゲームにおいてディスクの表と裏が入れ替わるような挙動であり，**L2** が「分子オセロ」として振る舞うことがわかった．

[1] H. Horita *et al. Inorg. Chem.*, **2023**, *62 (31)*, 12272–12282.

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19日(火) 13:00 ~ 15:30 E1123(11号館 [2階] 1123)

[E1123-2pm] 12. 有機化学―有機結晶・超分子化学

座長：加藤 研一、山科 雅裕

日本語
13:00 ~ 13:20

[E1123-2pm-01]
巨大熱膨張を実現するアントラセン結晶の創製

○樋野 優人[1]、松尾 匠[2]、是永 大樹[3]、関 朋宏[4]、林 正太郎[2] (1. 高知工大院工、2. 高知工大理工、3. 静大院総合科学、4. 静大理)

日本語
13:20 ~ 13:40

[E1123-2pm-02]
柔軟性アントラセン分子混晶の設計と組成制御：FRET型低損失光導波路の実現

○池田 浩貴[1]、松尾 匠[1]、林 正太郎[1] (1. 高知工科大学)

日本語
13:40 ~ 14:00

[E1123-2pm-03]
フッ素化π共役系分子結晶：光物性と機械特性の解析

○矢野 圭悟[1]、松尾 匠[2]、林 正太郎[2] (1. 高知工大院工、2. 高知工大理工)

14:00 ~ 14:10

休憩

英語
14:10 ~ 14:30

[E1123-2pm-04]
ボウル状分子の合成に基づく巨大π系の積層現象の研究

○尾仲 柚香[1]、池本 晃喜[1]、磯部 寛之[1] (1. 東京大学)

日本語
14:30 ~ 14:50

[E1123-2pm-05]
準安定なPd(II)環状錯体の速度論自己集合

○真田 直樹[1]、阿部 司[1]、竹内 啓介[1]、平岡 秀一 (1. 東大)

日本語
14:50 ~ 15:10

[E1123-2pm-06]
6位修飾α-CDからの超分子構造体の作製と脂肪酸エステルに対する選択的抽出能

○石田 遥也[1]、宮坂 萌々香[1]、Justine Kalaw、重光 孟[1]、木田 敏之[1] (1. 大阪大学)

英語
15:10 ~ 15:30

[E1123-2pm-07]
A Friedel–Crafts acylation way towards multi-bridge-functionalized large pillar[*n*]arenes

〇Tanhao Shi[1], Shunsuke Ohtani[1], Kenichi Kato[1], Tomoki Ogoshi[1,2] (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-NanoLSI, Kanazawa Univ.)

巨大熱膨張を実現するアントラセン結晶の創製

（高知工大院工 [1]・高知工大理工 [2]・静大院総合科学 [3]・静大理 [4]）○樋野 優人 [1]・松尾 匠 [2]・是永 大樹 [3]・関 朋宏 [4]・林 正太郎 [2]

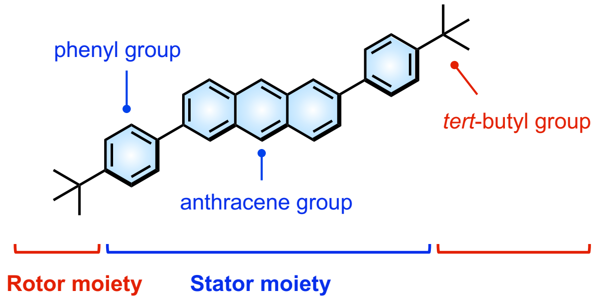
An Anthracene Crystal for Its Giant Thermal Expansion

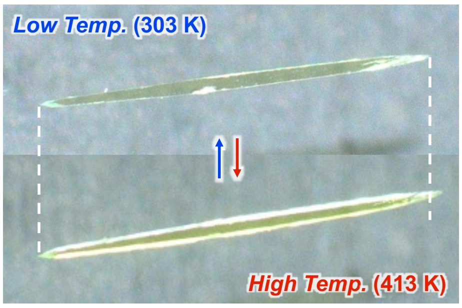
([1]*Graduate School of Engineering, Kochi University of Technology,* [2]*School of Engineering Science, Kochi University of Technology,* [3]*Graduate School of Integrated Science and Technology, Shizuoka University,* [4]*Faculty of Science, Shizuoka University*) ○Yuto Hino,[1] Takumi Matsuo,[2] Daiki Korenaga,[3] Tomohiro Seki,[4] Shotaro Hayashi[2]

The design for thermal expansion in a molecular crystal has attracted much interest in the sensors and actuators because the molecular motion in the solid state plays an important role in understanding the physical properties changes in solid materials1). Here, we designed and synthesized structurally rod-like anthracene molecules bearing phenyl group with a bulky tert-butyl substituent on the 2 and 6 positions. Interestingly, in a crystal structure, array order and disorder coexist was obtained by the stator moiety derived from the anthracene, phenyl groups, and the rotor moiety from the tert-butyl group. This molecular structure allowed giant thermal expansion and reversible stretching behavior. In this presentation, we report the detailed crystal structure and its thermal expansion observation.

Keywords : Anthracene; Molecular Rotor; Thermal Expansion; Reversible; Single-Crystal-to-Single-Crystal Phase Transition

分子結晶の熱膨張は、分子運動に基づく固体材料の物性変化を理解する上で重要な現象の一つである1)。本研究では、嵩高い *tert*-ブチル基を有するフェニル基を 2,6 位に付与したアントラセンを合成し、結晶構造と熱応答性を調査した。その結果、アントラセンとフェニル基に由来するステーター部位と *tert*-ブチル基によるローター部位によって秩序性と乱れが共存した結晶構造が得られた。結晶は温度変化に対して、ある閾値で巨大熱膨張を示し、結晶形状の可逆的な伸縮挙動を示した。本発表では、これらの詳細な結晶構造と熱膨張性について説明する。





1) (a) M. K. Panda, T. Runčevski, S. C. Sahoo, A. A. Belik, N. K. Nath, R. E. Dinnebier, P. Naumov, *Nat. Commun.* **2014**, *5*, 4811. (b) K. Kato, T. Seki, H. Ito, *Inorg. Chem.* **2021**, *60*, 10849–10856.

柔軟性アントラセン分子混晶の設計と組成制御：FRET 型低損失光導波路の実現

（高知工大院工[1]・高知工大理工[2]）○池田 浩貴[1]・松尾 匠[2]・林 正太郎[2]

Design and Composition Control of Flexible Anthracene Molecular Mixed Crystals : Realization of Low-Loss Optical Waveguides Based on FRET ([1]*Graduate School of Engineering, Kochi University of Technologe*, [2]*School of Engineering Science, Kochi University of Technology*) ○Koki Ikeda,[1]Takumi Matsuo,[2] Shotaro Hayashi[2]

Molecular crystals composed of a pitched π-stack structure show elastic bending flexibility. Fluorescent elastic molecular crystals are attracted in the application of flexible optical waveguides. However, an increased optical loss (α) because of self-absorption makes it difficult to give efficient flexible optical waveguides. Herein, we have successfully demonstrated the development of flexible and low-loss optical waveguides based on an energy transfer approach by creating flexible mixed crystals. The mixed crystals exhibited elastic deformation and highly efficient optical waveguide characteristics. In this presentation, we will also discuss other mixed crystals based on anthracene derivatives as a guest molecule.

Keywords : ; Organic Miexed Crystals, Förster Resonance Energy Transfer, Optical Waveguide, Anthracene, Elastic

我々は弾性分子結晶が分子間の pitched π–stack 構造によって実現されることを示した。一方、発光性の弾性分子結晶の場合、その柔軟な光導波路の開発が注目されている。しかし、蛍光再吸収による光損失 (α)の増加が問題となり、効率的な柔軟性光導波路の実現は困難である。そこで、我々は有機混晶 (**MC**)に注目した。**MC** はある分子に対して僅かにドーパントを加えることで光特性のみを改質できる。本研究では弾性分子結晶となる分子に対しドーパントを加えることで **MC** を作製し、柔軟かつエネルギー移動に基づく低損失光導波路の開発を達成した。

弾性分子結晶となる 9,10-dibromoanthracene **(DBA)**と 9,10-diformylanthracene **(DFA)** を用いて混晶 **(MC1)**を作製したところ **(Figure 1a)**、**MC1** は弾性変形を示し、光損失は **DBA** 結晶に比べ著しく低下した **(Figure 1b,c)**。本発表では他のアントラセン誘導体をゲスト分子とした混晶についても述べる。

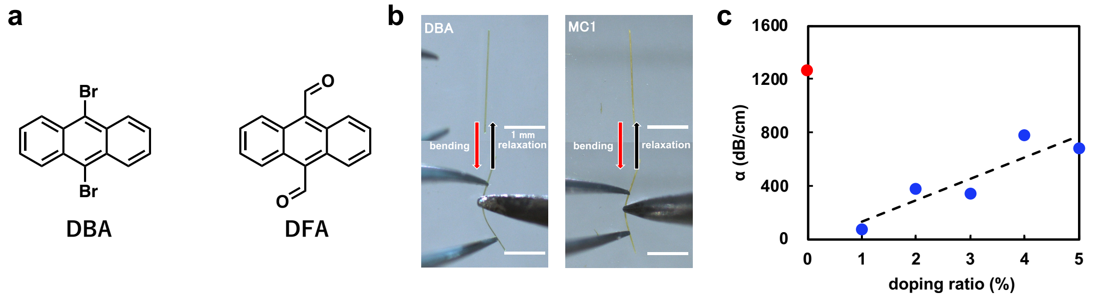


Figure 1. a) Molecular structure of **DBA** and **DFA**. b) Mechanical deformation of **DBA** crystal and **MC1**, scale bar 1 mm. c) Plot of α estimated for each doping ratio of **DFA**.

フッ素化 π 共役系分子結晶：光物性と機械特性の解析

(高知工大院工[1]・高知工大理工[2]) ○矢野 圭悟[1]・松尾 匠[2]・林 正太郎[2]

Fluorinated π-Conjugated Molecular Crystals: Detailed Investigation of Their Photophysical and Mechanical Properties.

([1]*Graduate School of Engineering, Kochi University of Technology,* [2]*Schoool of Science and Engineering, Kochi University of Technology*) ○Keigo Yano,[1] Takumi Matsuo,[2] Shotaro Hayashi[2]

Molecular crystals with flexibilities and narrow bandgap are potential materials to create flexible organic devices. We have previously developed that the repulsion-rich π-π stacking structure in crystals contributes to the elastic deformation. However, in general π-conjugated molecules forms CH–π interaction, thus; we need the molecular design toward π-π stacking. We report herein a new elastic molecular crystal of a DA–type fluorinated π-conjugated molecules, **BTFT**. The crystals were prepared by vapor diffusion process. The obtained crystals which formed a pitched π-stack structure in the crystal showed yellow-luminescence and elastic deformation.

Keywords : Elastic Deformation, Fluorinated π–conjugated Molecules, DA–Type Structure, Benzothiadiazole, Charge Transfer Interaction

分子結晶への柔軟性付与および狭バンドギャップ化はフレキシブル有機デバイスとしての応用に繋がる。これまでに、我々は結晶内の π–π スタッキング構造が分子結晶の弾性に寄与することを見出した。しかし、一般的な π 共役系分子では、CH–π 相互作用の働きにより結晶化過程にて π–π スタッキング形成が不利となる。そこで、我々は分子短軸にヘテロ原子を導入することによる pitched π–stack 構造の実現を目指した。その結果、フッ素を導入した分子設計により弾性分子結晶の創製に成功した[1]。ここでは、さらに DA 型フッ素化 π 共役系分子 **BTFT** を設計し、その光物性および機械特性を解析した。

BTFT は蒸気拡散法 (chloroform: *n*-hexane = 1:1) により黄色発光性の良質な針状結晶を与え、結晶内に pitched π–stack 構造を形成していた。この結晶は応力負荷に対して、(001) および (100) 面のいずれの面でも弾性変形を示した **(Figure 1)**。本発表では、更に各種測定にて明らかにした光物性と機械特性について定量的な議論を行う。

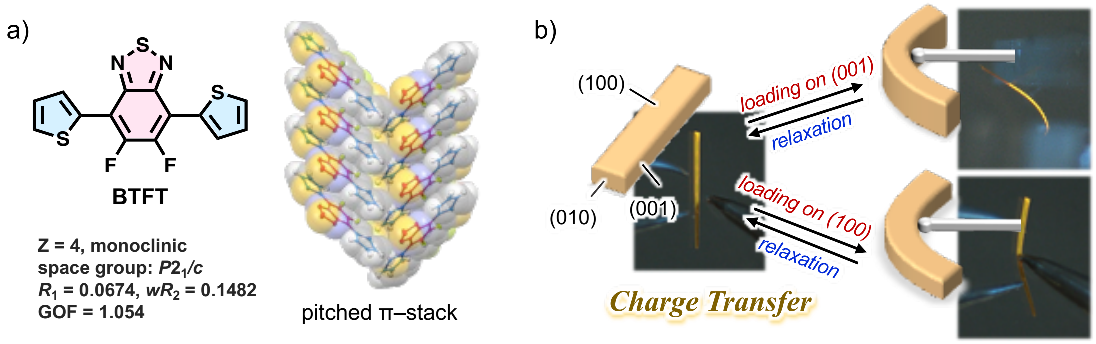


Figure 1. a) Crystal structure and b) elastic deformation of **BTFT** crystal.

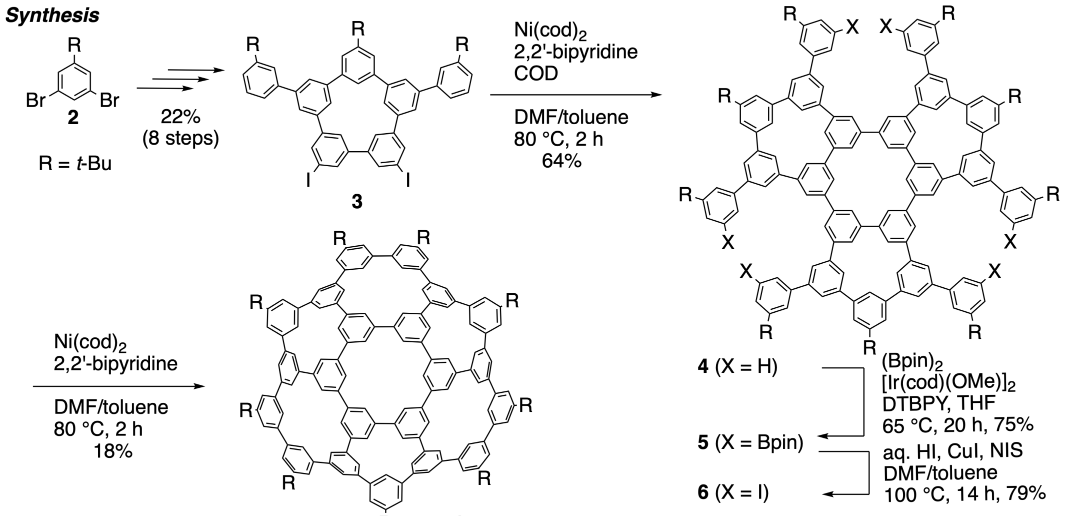
1) S. Hayashi, A. Asano, N. Kamiya, Y. Yokomori, T. Maeda, T. Koizumi, *Sci. Rep.* **2017**, 7, 9453.

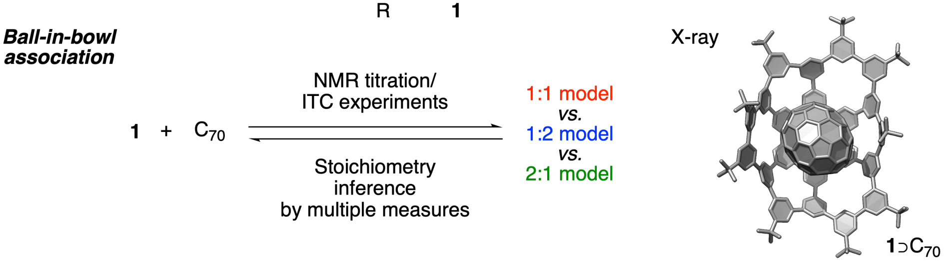
Synthesis of Bowl-Shaped Molecules for Studies of Stacked Gigantic π-Systems

([1]*Department of Chemistry, The University of Tokyo*) ○Yuzuka Onaka,[1] Koki Ikemoto,[1] Hiroyuki Isobe[1]

Keywords: Bowl-Shaped Molecule; Nanocarbon; Stacking; Stoichiometry Inference

Bowl-shaped molecules are interesting synthetic targets that can serve as hosts for supramolecular complexes. In this work, a gigantic bowl-shaped molecule, phenine tridehydrosumanene (**1**), was designed and synthesized by devising a 12-step route from a dibromobenzene derivative. Thus, a pentagonal unit **3** was synthesized from **2** in 8 steps and was subjected to macrocyclization with Yamamoto coupling. Trimerization proceeded to afford **4** in 64% yield. The macrocycle (**4**) was then furnished with iodine handles, which was closed by Yamamoto coupling to afford **1** in 18% yield. The gigantic bowl-shaped structure of **1** was found suitable to accommodate C_{70}, and the host-guest complexation was studied by NMR and ITC experiments. The host-guest system was driven by van der Waals interactions, which provided an interesting case for the stoichiometry inference studies. We introduced a novel measure to elucidate the stoichiometry for this study and found that the 1:1 complex was formed in solution. The structure of the 1:1 complex was unequivocally revealed by X-ray crystallographic analysis of a single crystal.





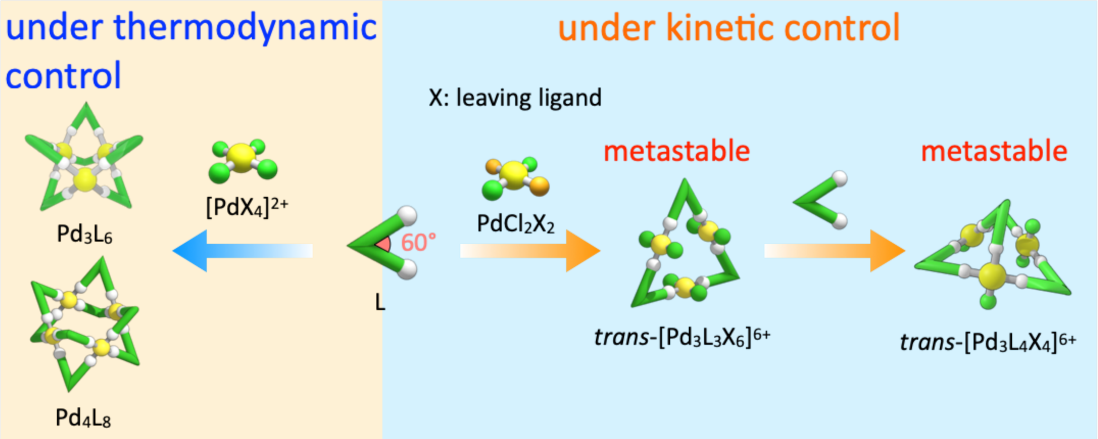
準安定な Pd(II)環状錯体の速度論自己集合

（東大院総合文化）〇真田 直樹・阿部 司・竹内 啓介・平岡 秀一
Kinetically controlled self-assembly of metastable Pd(II) ring complexes (*Graduate School of Arts and Sciences, The University of Tokyo*) 〇Naoki Sanada, Tsukasa Abe, Keisuke Takeuchi, Shuichi Hiraoka

Generally, coordination self-assembly proceeds under thermodynamic control due to reversible coordination bonds. We have recently developed a method for the formation of all six types of metastable heteroleptic $\mathrm{Pd_2L_4}$ cages under kinetic control[1]. In this research, we employed this method to prepare metastable triangular complexes (*trans*-$[\mathrm{Pd_3L_3X_6}]^{6+}$) from *trans*-$\mathrm{PdCl_2X_2}$ (X: leaving ligand) and ditopic ligand (L) with a 60° bite angle. The addition of one equivalent of L in a solution of *trans*-$[\mathrm{Pd_3L_3X_6}]^{6+}$ selectively afforded a metastable *trans*-$[\mathrm{Pd_3L_4X_4}]^{6+}$.

Keywords : coordination self-assembly; kinetic control; ring complex; supramolecule;

多くの配位自己集合は配位結合の可逆性により、熱力学支配で進行する。一方、我々は最近 Pd(II)–N 配位結合系において、速度論支配により全 6 種類の多成分 $\mathrm{Pd_2L_4}$ かご形錯体の形成手法を開発した [1]。本手法では *trans* 構造をもつ $\mathrm{Pd_2L_2}$ 環状錯体を鍵中間体として、段階的な配位子交換により準安定な集合体を形成することができる。本研究では、この手法を *trans*-$\mathrm{Pd_3L_3}$ 環状錯体へ拡張し、速度論支配による新たな準安定な集合体の形成を試みた。結合角 60°の二座配位子 L と $\mathrm{Pd^{2+}}$イオンから $\mathrm{Pd_3L_6}$ や $\mathrm{Pd_4L_8}$ double-walled ring 構造が熱力学安定種として生成するが、*trans*-$\mathrm{Pd_3L_3}$ は $\mathrm{Pd_3L_6}$ の部分構造となり得ないため、1 種類の L のみからも準安定な構造の形成が考えられる。単核 *trans*-$\mathrm{PdCl_2X_2}$ (X: 脱離配位子) と L から、準安定な三角形錯体 (*trans*-$[\mathrm{Pd_3L_3X_6}]^{6+}$) を形成したのち、1 当量の L を加えると、三角形錯体に一つの L が導入された錯体 (*trans*-$[\mathrm{Pd_3L_4X_4}]^{6+}$) が選択的に得られた。



1) T. Abe, N. Sanada, K. Takeuchi, A. Okazawa, S. Hiraoka *J. Am. Chem. Soc.* **2023**, *145*, 28061–28074.

6 位修飾α-CD による超分子構造体の作製と脂肪酸エステルの選択的抽出能

（阪大院工 [1]）○石田 遥也 [1]、Justine M. Kalaw[1]、宮坂 萌々香 [1]、重光 孟 [1]、木田 敏之 [1]

Preparation of Supramolecular Structures from 6-*O*-Modified α-CD and Their Selective Extraction Ability for Fatty Acid Esters

([1]*Graduate School of Engineering, Osaka University*)
○Haruya Ishida[1], Justine M. Kalaw[1], Momoka Miyasaka[1], Hajime Shigemitsu[1], Toshiyuki Kida[1]

Cyclodextrins (CDs) are known to encapsulate appropriate guests in their internal cavity, and adopt three types of assembly modes in the crystalline states: cage, channel, and layer types. By selectively preparing CD assemblies with regulated molecular arrangement, it is expected to precisely control the guest inclusion ability and create supramolecular structures with various morphologies. In this study, we examined the morphology of supramolecular structures formed from 6-*O*-modified α-CDs and the assembly modes of the CD molecules that compose them. We also examined the ability of these supramolecular assemblies to selectively extract *cis*- and *trans*-fatty acid esters in acetonitrile.

Keywords : cyclodextrin, methylation, self-assembly, supramolecular structure, head-to-head arrangement

シクロデキストリン(CD)はその内部空孔に適したゲストを包接することができるとともに、結晶中で、かご型、チャンネル型、層状型の 3 種の集合様式をとることが知られている。我々のグループでは最近、2 位メチル化α-CD から、その head-to-tail 型チャンネル集合体から構成される六角形ロッド状超分子構造体を選択的に作製することに成功した [1)]。本研究では、6 位水酸基すべてを修飾したα-CD から形成される超分子構造体の形態とそれを構成する CD 分子の集合様式を検討した。また、6 位修飾α-CD 超分子集合体の不飽和脂肪酸エステルに対する選択的抽出能についても検討した。

6-Me-α-CD のメタノール溶液を炭化水素系貧溶媒に滴下した時、その head-to-head 型二量体からなるひし形状超分子構造体が選択的に形成された（Figure 1A）。この構造体の形態と CD 分子の集合様式は 2 位メチル化α-CD（2-Me-α-CD）の場合とは大きく異なっており、α-CD のメチル化部位を変えることで超分子構造体の形態とそれを構成する CD 分子の集合様式を制御できることが分かった。また、アセトニトリル中の不飽和脂肪酸エステルに対する固液抽出実験により 6-Me-α-CD がシス脂肪酸エステルよりもトランス脂肪酸エステルに対して高い抽出能を示すことがわかった。

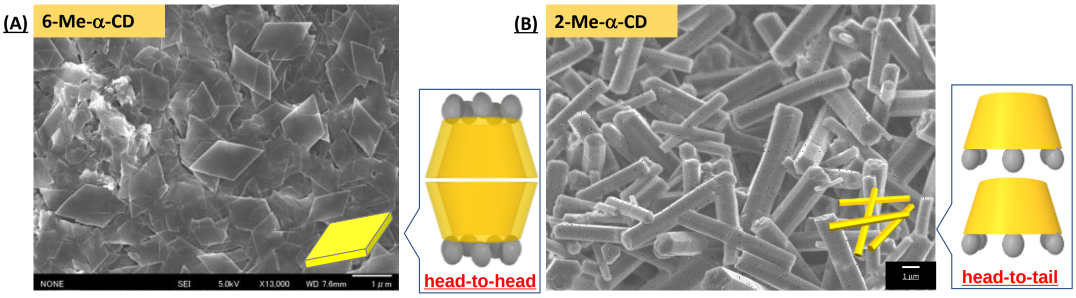


Figure 1. SEM images of supramolecular structures formed by (A) 6-Me-α-CD and (B) 2-Me-α-CD in a mixture of methanol and cyclohexane.

1) Kalaw, J. M.; Kitagawa, M.; Shigemitsu, H.; Kida, T. *Langmuir* **2022**, *38*, 5149.

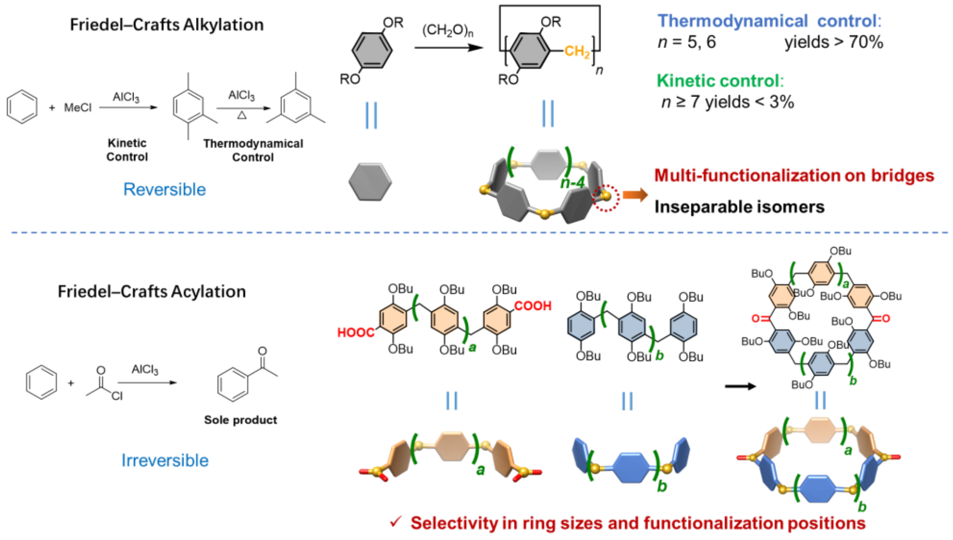
A Friedel-Crafts acylation way towards multi-bridge-functionalized large pillar[*n*]arenes

([1]*Graduate School of Engineering, Kyoto University,* [2]*WPI Nano Life Science Institute, Kanazawa University.*) ○Tanhao Shi[1], Shunsuke Ohtani[1], Kenichi Kato[1] and Tomoki Ogoshi[1,2]

Keywords: *Supramolecular chemistry; Friedel-Crafts reaction; Pillar[n]arenes; Macrocycles*

Using FC alkylation, many macrocycles have been constructed, including calix[*n*]arenes, resorcin[*n*]arenes, calix[*n*]pyrroles, cyclotriveratrylene, and pillar[*n*]arenes. These macrocycles all possess their own unique supramolecular properties. But there are limitations from the reversible alkylation strategy. For example, selective synthesis of larger pillar[*n*]arenes ($n \geq 7$), which are not thermodynamical stable under alkylation conditions, has always been a challenging task. Moreover, inert methylene bridges are introduced from the alkylation process, and the multi-functionalization of bridges have never been truly tackled.

Herein, irreversible Friedel-Crafts acylation is used to prepare pillar[*n*]arenes. Via acylation, connecting precursors bearing carboxyl acids and electron-rich arene rings results in size-exclusive formation of pillar[*n*]arenes, in which the sizes are determined by the precursor lengths. Moreover, methylene bridges have been installed with multiple carbonyl groups, which can be easily converted to other subunits to afford bridge-functionalized pillar[*n*]arenes. As many useful macrocyclic hosts are prepared from FC alkylation, we anticipate that our FC acylation strategy can also be applied in creating those host molecules, along with more delicate structures and sophisticated properties.



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19日(火) 13:00 ~ 15:10 E1131(11号館 [3階] 1131)

[E1131-2pm] 12. 有機化学—有機結晶・超分子化学

座長：重光 孟、堀内 新之介

日本語

13:00 ~ 13:20

[E1131-2pm-01]

トリスポルフィリンとゲスト分子の多成分自己集合により制御される分子配列

○久野 尚之[1]、児玉 知輝[1,2]、灰野 岳晴[1,2] (1. 広島大院先進理工、2. 広島大 持続可能性に寄与するキラルノット超物質拠点)

英語

13:20 ~ 13:40

[E1131-2pm-02]

Controlling the helicity of dynamic helical tricobalt(III) cryptands by tuning the diamine chain length at the aperture

○Sk Asif Ikbal[1], Shigehisa Akine[1,2] (1. WPI-Nano Life Science Institute, Kanazawa University, 2. Graduate School of Natural Science and Technology, Kanazawa University)

日本語

13:40 ~ 14:00

[E1131-2pm-03]

液相・固相でのカゴ状金属酸化物{Mo_{132}}内部空間へのゲスト捕捉

○中宿 朱里[1]、申 栽燮[1]、村田 千夏[1]、七分 勇勝[1,2]、小西 克明[1,2] (1. 北大院環境、2. 北大院地球環境)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[E1131-2pm-04]

球状錯体の一義空間を用いたタンパク質の単分子包接

○海老原 梨沙[1]、中間 貴寛[1]、守島 健[2]、杉山 正明[2]、矢木 真穂[3]、藤田 誠[1,3,4] (1. 東京院工、2. 京都大学複合原子力科学研究所、3. 分子科学研究所、4. 東大国際高等研)

英語

14:30 ~ 14:50

[E1131-2pm-05]

ゲスト分子による箱型自己集合カプセルの構造異性の再配列とその構造変換

○陳 弘燁[1]、堀内 新之介[1]、平岡 秀一[1] (1. 東大院総合文化)

英語

14:50 ~ 15:10

[E1131-2pm-06]

アミドの水素結合を利用した位置選択的Diels-Alder反応系の開発

○倪 汪斌[1]、木原 伸浩[1] (1. 神奈川大学)

トリスポルフィリンとゲスト分子の多成分自己集合により制御される分子配列

(広島大院先進理工 [1]・広島大 持続可能性に寄与するキラルノット超物質拠点 [2])
○久野 尚之 [1]・児玉 知輝 [1,2]・灰野 岳晴 [1,2]

Controlled molecular array in multi-component self-assembly of trisporphyrin and guests

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*, [2]*WPI-SKCM*[2], *Hiroshima University*) ○Naoyuki Hisano,[1] Tomoki Kodama,[1,2] Takeharu Haino[1,2]

Our group developed a triple-layered trisporphyrin molecule **1** possessing two cleft cavities, which encapsulated electron-deficient aromatic molecules in a negative cooperative fashion.[1] In this study, we synthesized tris(zinc-porphyrin) **2**, capturing donor and acceptor guests **L1** and **G1** driven by dative bonds and donor-acceptor interactions, respectively. Tris(zinc-porphyrin) **1** showed homotropic negative cooperativity in the guest binding of **G1** and **L1**. The homotropic negative cooperativity led to the selective formation of a ternary host-guest complex. Upon the addition of **L2** into a solution of the ternary host-guest complex, a sequence-controlled multi-component supramolecular complex **(L1•2•G1)$_2$L2** was constructed.

Keywords : Molecular Recognition; Host–Guest Complex; Porphyrin

当研究室は, クレフト型ビスポルフィリンを二つ連結したトリスポルフィリン **1** が電子不足な芳香族分子の包接に負の協同性を示すことを見出した [1)]。本研究は，亜鉛を導入したトリスポルフィリン **2** を合成し，ゲスト包接挙動を調べた。亜鉛ポルフィリンの配位サイトは一つであるため，**2** は **L1** の包接に負の協同性が発現することが予想される。**2** のゲスト包接を調べたところ，**2** は **G1** および **L1** の包接にそれぞれホモトロピックな負の協同性を示すことがわかった。また，**2** はホモトロピックな負の協同性により, **G1** および **L1** を選択的に一分子ずつ包接した三元超分子錯体 **L1•2•G1** を形成することが分かった。^{1}H NMR および DOSY 測定により，三元超分子錯体 **L1•2•G1** は **L2** を添加することで二分子の **L1•2•G1** が架橋された多元超分子錯体 **(L1•2•G1)$_2$L2** が形成されることが分かった。

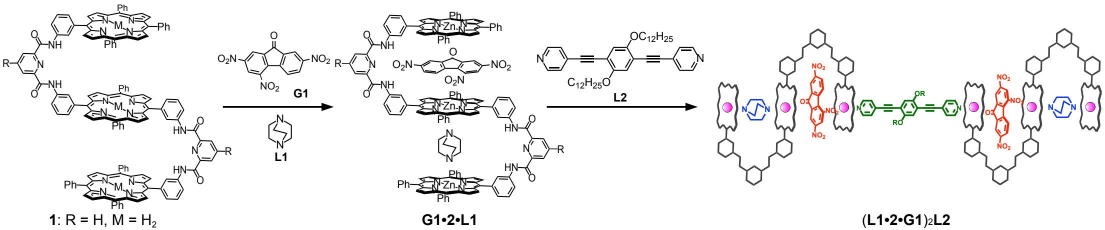


Figure 1. Molecular structures of trisporphyrin, ternary host–guest complex **G1•2•L1**, and multi-component host–guest complex (**L1•2•G1**)$_2$**L2**.

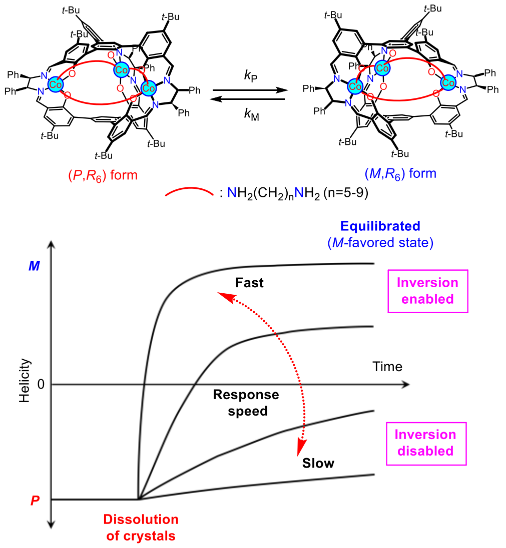
1) N. Hisano, T. Kodama, T. Haino, *Chem. Eur. J.* **2023**, *29*, e202300107.

Controlling the helicity of dynamic helical tricobalt(III) cryptands by tuning the diamine chain length at the aperture

([1]*Nano Life Science Institute*, *Kanazawa University*, [2]*Graduate School of Natural Science and Technology, Kanazawa University*) ○Sk Asif Ikbal,[1] Shigehisa Akine[1,2]

Keywords: Helicity inversion, Dynamic structure conversion, Cobalt complex, Diamine, Cryptand

Development of artificial dynamic helical molecules with controllable helix inversion rate can be useful to make chiral memory materials.[1] Most of the previous reports of stimuli-responsive chiral molecules have been focused only on the equilibrium states before and after stimulation but not on controlling the kinetics.[1] We have already demonstrated that the helicity inversion kinetics of trinickel(II) cryptands can be controlled by guest recognition in the cryptand cavity.[2,3] In this research, novel chiral tris(salen)-type tricobalt(III) cryptands with diamines introduced at the aperture were synthesized. A series of diamines with different chain length were used (short 1,5-pentanediamine to long 1,9-nonanediamine). The tricobalt(III) complex is in dynamic equilibrium between *P* and *M* isomers in solution, preferring one isomer in major concentration. However, in single crystals the complexes were stabilized in one handed isomer (*P* isomer). We have investigated the time-dependent changes in the *P*/*M* ratios by spectroscopic techniques. The details of the energy diagrams for the *P*/*M* inversion will be discussed.



Scheme 1. Controlling the speed of helicity inversion by tuning the diamine chain length at the aperture.

1) S. Akine, H. Miyake, *Coord. Chem. Rev.* **2022**, *486*, 214582. 2) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front.*, **2014**, *1*, 53. 3) S. A. Ikbal, P. Zhao, M. Ehara, S. Akine *Sci. Adv.* **2023**, *9*, eadj5536.

液相・固相でのカゴ状金属酸化物{Mo132}内部空間へのゲスト捕捉

（北大院環境 [1]・北大院地球環境 [2]）○中宿 朱里 [1]・申　栽燮 [1]・村田 千夏 [1]・七分 勇勝 [1,2]・小西 克明 [1,2]

Guest Encapsulation within Metal Oxide Cage {Mo$_{132}$} in Liquid and Solid Phases.

([1]*Grad. School of Env. Sci., Hokkaido Univ.*, [2]*Fac. of Env. Earth Sci., Hokkaido Univ.*) ○Akari Nakashuku,[1] Jaeseob Shin,[1] Chinatsu Murata,[1] Yukatsu Shichibu, [1,2] Katsuaki Konishi[1,2]

Metal oxide cluster of {Mo$_{132}$} has 20 pores on the surface and its inner wall is coordinated with acetate ligands. Previous studies demonstrated the encapsulation of guest molecules within {Mo$_{132}$} in solution phase. In this work, we performed such a guest encapsulation in solid phase. We evaluated the efficiency of solid grinding method with guest molecules through NMR measurements.

Keywords : Metal Oxide ; Guest Encapsulation; Solid State

金属酸化物クラスター$[Mo_{132}O_{372}(H_2O)_{72}(CH_3COO)_{30}]^{42-}$（以下{Mo$_{132}$}）は表面に20箇所の空孔が存在し（**Fig. 1**）[1]、水溶液中でこの空孔を通じたゲストの取り込みが報告されている[2]。当研究室でも、溶液中でベンゼン誘導体をはじめとするゲストがアニオン-π相互作用によって内部に取り込まれることを見出している[3]。一方、水への溶解性が著しく低いゲストの{Mo$_{132}$}への取り込みの報告はない。そこで本研究では、固相混合を用いて{Mo$_{132}$}へのゲスト内包を検討した。

{Mo$_{132}$}とベンゾフェノンの粉体を固相混合し、得られた粉体にD_2Oを加えてフィルターでろ過した。このろ液を^{1}H-NMRで測定するとブロードなピークが5.8 ppmに見られた。このブロードピークの拡散係数が{Mo$_{132}$}のアセテート配位子と同程度の値を示すことがDOSY NMR測定からわかり、ベンゾフェノンの内包を確認した（**Fig. 2**）。さらに、本手法によって一度{Mo$_{132}$}に取り込まれたゲストは有機溶媒下においても内包状態を維持していることがわかった。

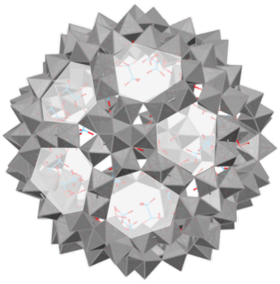


Fig. 1 Skeletal structure of {Mo$_{132}$}.

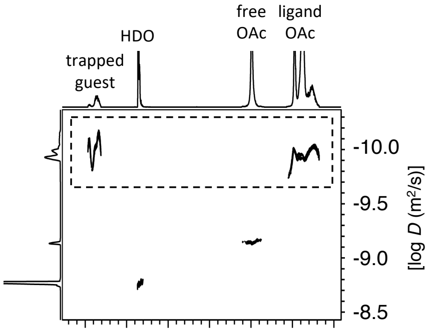


Fig. 2 ^{1}H-NMR and DOSY spectra of {Mo$_{132}$} mixed with benzophenone.

[1] A. Müller *et al.*, *Chem. Soc. Rev.* **2012**, *41*, 7431.
[2] R. Newman *et al.*, *Chem. Eur. J.* **2016**, 22, 15231.
[3] C. Murata *et al.*, *Chem. Commun.* **2023**, *59*, 2441.

球状錯体の一義空間を用いたタンパク質の単分子包接

(東大院工 [1]・京大複合研 [2]・分子研 [3]・東大国際高等研 [4]) ○海老原 梨沙 [1]・中間 貴寛 [1]・守島 健 [2]・杉山 正明 [2]・矢木 真穂 [3]・藤田 誠 [1,3,4]

Single protein encapsulation in well-defined cavities of spherical complexes ([1]*Grad. School of Engineering, The Univ. of Tokyo*, [2]*Inst. for integrated Radiation and Nuclear Science, Kyoto Univ.*, [3]*Inst. for Molecular Science*, [4]*UTIAS, The Univ. of Tokyo*) ○Risa Ebihara,[1] Takahiro Nakama,[1] Ken Morishima[2], Masaaki Sugiyama[2], Maho Yagi-Utsumi[3], Makoto Fujita[1,3,4]

Protein encapsulation within artificial hosts is useful for protein functional modulation and stabilization, but precise control of encapsulation is difficult due to the inhomogeneity of host cavities. In this work, we have reported single protein encapsulation in well-defined cavities of $M_{12}L_{24}$ cages constructed by self-assembly of bis-pyridine ligands (L) and Pd(II) ions (M)(1,2. ^{1}H diffusion-ordered spectroscopy (DOSY) NMR and analytical ultracentrifugation (AUC) verify precise protein encapsulation in a single-molecule state. By using different sizes of cages, 15 kinds of proteins with 3-6 nm diameter were encapsulated within the cage in a single-molecule state. By isolating proteins within their cavity, the interactions and aggregation of the proteins were inhibited, thus significantly stabilizing them against organic solvents.

Keywords : protein encapsulation, self-assembly, $M_{12}L_{24}$ cage, protein stabilization, nano space

人工ホストへのタンパク質包接は、安定化などタンパク質機能制御に有用だが、ホスト空間の不均一性のため精密な包接は難しい。本研究では、巨大球状錯体の一義空間へのタンパク質の単分子包接を報告する。配位子(L)と Pd(II)イオン(M)の自己集合により形成する $M_{12}L_{24}$ 中空錯体(1,2 は、配位子の設計に基づき大きさの異なる一義的な内部空間(内径 4-6 nm)を構築するため、精密なタンパク質単分子包接が可能である(Fig. 1a)。^{1}H DOSY NMR や分析超遠心(AUC)の測定から錯体へ 1 分子のタンパク質が選択的に包接されたことが示された。適したサイズの球状錯体を用いることで最大径 3-6 nm の計 15 種類のタンパク質の単分子包接を達成した(Fig. 1b)。包接されたタンパク質は、タンパク質間の相互作用・凝集が抑制されて安定性が著しく向上した。

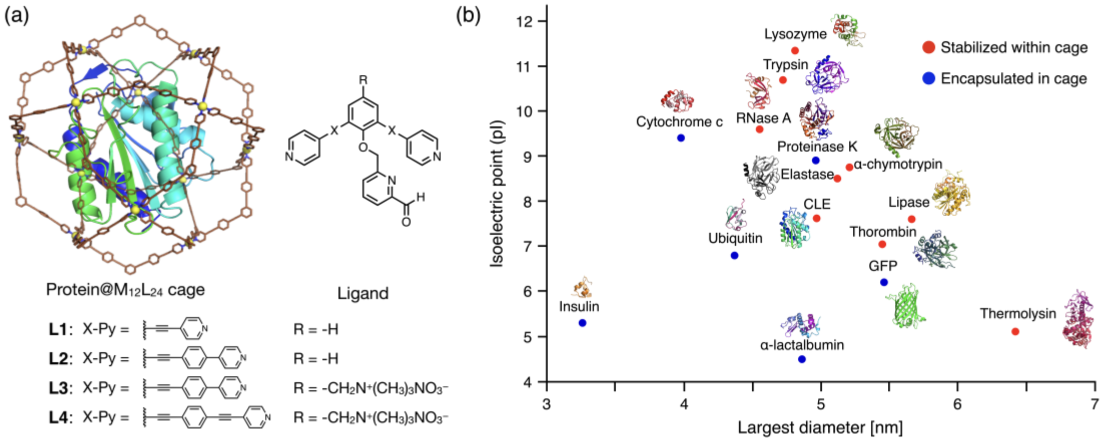


Fig. 1 (a) Protein encapsulated in $M_{12}L_{24}$ cages. (b) Scope of single protein encapsulation in the cages.

1) D. Fujita, *et al., Chem* **2021**, *7*, 2672. 2) T. Nakama, R. Ebihara, *et al.*, *Chem. Sci.* **2023,** *14,* 2910.

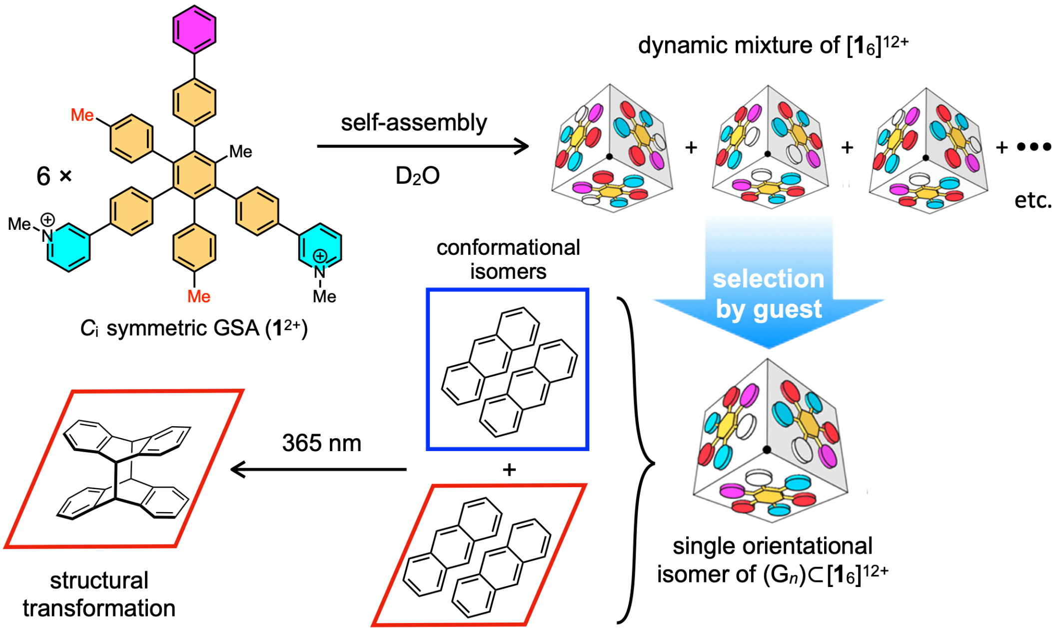
Guest-induced redistribution of conformational isomers of self-assembled box-shaped capsule and their structural transformation

([1]*Graduate School of Arts and Science, The University of Tokyo*)
○Hongye Chen,[1] Shinnosuke Horiuchi,[1] Shuichi Hiraoka,[1]

Keywords: amphiphile; self-assembly; induced-fit; structure transformation

Biological receptors such as enzymes are structurally flexible, which allows them to adapt to target molecules. In contrast, most synthetic receptors are relatively rigid because rigid building blocks are connected through strong and highly directional interactions. Previously, our group reported box-shaped water-soluble capsules, nanocube,[1] assembled from six gear-shaped amphiphiles (GSAs). Although only less directional, weak interactions exist between the six GSAs, the nanocubes are thermally very stable but show adaptive properties, responding to the size, shape, and charge state of the guest molecules in an induced-fit manner.[2]

In this study, we designed and synthesized a C_i-symmetric GSA ($\mathbf{1}^{2+}$). Because of its asymmetrical structure, the peripheral methyl groups can be placed at both the poles or the equator when it assembles into the nanocube. As a result, a D_2O solution of GSA showed a complicated ^{1}H NMR spectrum, indicating the formation of a mixture of 16 possible isomers of $[\mathbf{1}_6]^{12+}$. Upon the encapsulation of guest molecules (G), the ^{1}H NMR spectrum became sharp, indicating a single orientational isomer of $(\mathrm{G}_n)\subset[\mathbf{1}_6]^{12+}$. Upon the encapsulation of a couple of anthracenes in the nanocube, two types of conformational isomers were produced and photodimerization of the anthracenes in the nanocube induced one of the conformations.



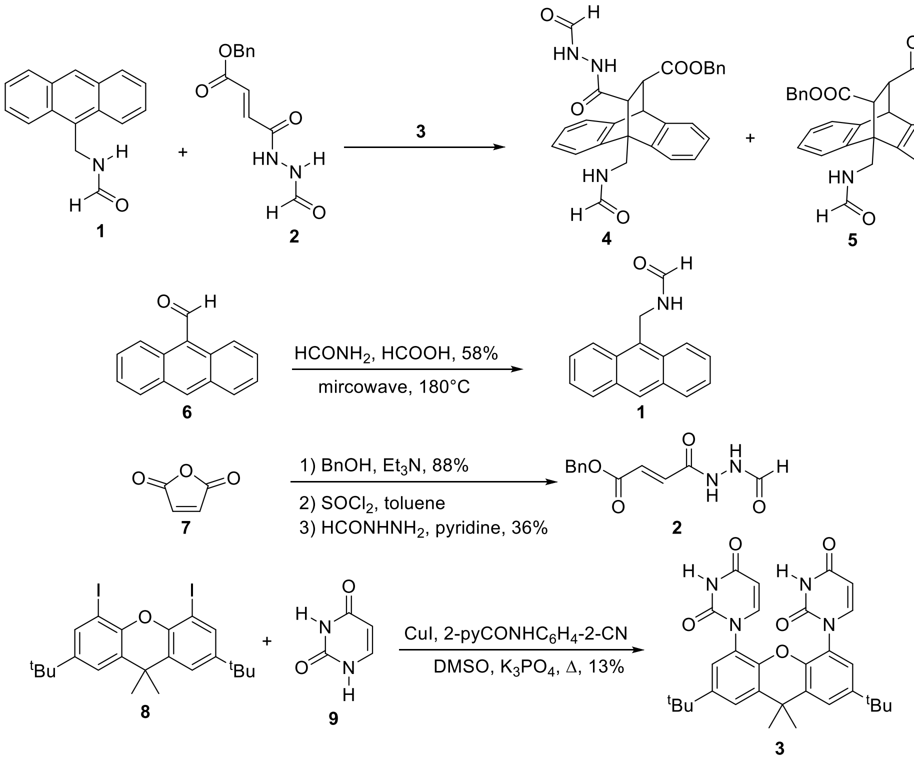
1) Y.-Y. Zhan *et al. Commun. Chem.* **2018**, *1*, 14. 2) Y.-Y. Zhan *et al. Nat. Commun.* **2018**, *9*, 4530.

Regioselective Diels-Alder reaction using hydrogen bonding of amides

(*Graduate School of Science, Kanagawa University*) ○Wang-Bin Ni, Nobuhiro Kihara

Keywords*:* Diels-Alder reaction, hydrogen bonding, regioselectivity, reaction field, molecular recognition

In the Diels-Alder reaction of a diene with an electron-donating group and a dienophile with an electron-withdrawing group, one of the two possible regioisomers is formed selectively because the overlap of frontier molecular orbitals controls the regioselectivity. Therefore, the regioselective Diels-Alder reaction of diene **1** with dienophile **2** is difficult because ester and amide functional groups in **2** exhibit similar electronic effects. When the Diels-Alder reaction is carried out in the presence of xanthene derivative **3**, a regioselective formation of **4** is expected because **1** and **2** will be aligned on **3** by the hydrogen bonding between amides. Formamide **1** was synthesized from **6** by the reductive amidation using formamide in the pressure of formic acid. Diacylhydrazine **2** was synthesized by the acylation of formhydrazide with the half ester derived from **7**. Cu(I)-catalyzed condensation of **8** and uracil **9** afforded **3**. While direct Diels-Alder reaction of **1** and **2** did not occur, regio-selective Diels-Alder reaction of **1** and **2** was investigated in the presence of **3**.



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19日(火) 13:00 ~ 15:10 E1132(11号館 [3階] 1132)

[E1132-2pm] 13. 有機化学—反応機構・光化学・電気化学

座長：恩田 健、楊井 伸浩

日本語
13:00 ~ 13:20
[E1132-2pm-01]
サイクレン中心環状ペンタセン多量体の分子内一重項分裂

○酒井 隼人[1]、水野 しおん[1]、羽曾部 卓[1] (1. 慶大理工)

日本語
13:20 ~ 13:40
[E1132-2pm-02]
二つの炭化水素置換基あるいはラジカル基をもつ安定発光ラジカルの発光特性

○服部 陽平[1]、北島 稜大[2]、馬場 温[2]、山本 航平[2]、内田 欣吾[2] (1. 奈良先端大、2. 龍谷大)

日本語
13:40 ~ 14:00
[E1132-2pm-03]
テトラセノチオフェン連結体の合成と一重項分裂

○岡本 大河[1]、酒井 隼人[1]、羽曾部 卓[1] (1. 慶大理工)

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30
[E1132-2pm-04]
C-F Functionalization by Defluorinative Coupling of Trifluoromethyl Compounds

○Chung-Yang Dennis Huang[1], Amit Kumar Jaiswal[1], Priya Saha[1] (1. Hokkaido University)

日本語
14:30 ~ 14:50
[E1132-2pm-05]
フォノンの放出・吸収過程としての無輻射遷移

○大田 航[1,2]、上島 基之[3]、春田 直毅[1,2]、佐藤 徹[1,2] (1. 京都大学福井謙一記念研究センター、2. 京都大学大学院工学研究科、3. 株式会社MOLFEX)

日本語
14:50 ~ 15:10
[E1132-2pm-06]
近赤外フェムト秒時間分解発光測定によるポルフィリンアレー自己集積化膜における励起ダイナミクスの研究

篠崎 建矢[1]、中村 美南海[2]、森末 光彦[2]、岩村 宗高[1]、○野崎 浩一[1] (1. 富山大院理工、2. 京繊大院工芸)

サイクレン中心環状ペンタセン多量体の分子内一重項分裂

（慶大理工 [1]）○酒井 隼人 [1]・水野 しおん [1]・羽曾部 卓 [1]

Intramolecular Singlet Fission of Cyclen-Centered Cyclic Pentacene Oligomers

([1]*Faculty of Science and Technology, Keio University*) ○Hayato Sakai,[1] Shion Mizuno,[1] Taku Hasobe[1]

Singlet fission (SF) is a photophysical process where two triplet excitons are generated from one-photon absorption in two nearby chromophores. Many examples of SF using dimers and oligomers have been reported, whereas the number of cyclic molecular systems is quite limited. Moreover, the relationship between substituted position and SF properties in cyclic oligomers has not yet been reported. Cyclenes, nitrogen-containing cyclic molecules, are capable of regioselective molecular modification with respect to nitrogen units, and metal insertion allows control of photophysical properties associated with structural changes. In this study, we newly synthesized cyclen-centered pentacene oligomers to examine the SF properties.

Keywords : Pentacene; Cyclene; Singlet Fission; Oligomer

一重項分裂 (SF) は、近接二分子間において一光子吸収により生成した一つの一重項励起子 (S_1) から二つの三重項励起子 (T_1) を生成する多励起子生成過程である。一般に効率的な SF の発現には、隣接する色素間の電子的相互作用の精密な制御が必要である。これまで、SF は色素を共有結合で連結した二量体や直線状多量体で多数観測されているが、環状多量体における色素の修飾位置と SF を関連付けた例はない。一方、含窒素環状分子サイクレンは、窒素に対して位置選択的に分子修飾が可能である。さらに、サイクレンは骨格中心に銀イオンを包接することで分子構造を変化させることもできる。本研究では、サイクレンにペンタセン (TP) を導入した一連の誘導体 [$(TP)_n$-Cy] (Fig. 1) を合成し、置換位置の違いによる SF 特性だけでなく、金属包接に伴う構造変化による SF の制御も検討した。さらに、$(TP)_n$-Cy に対して銀イオンを包接させた錯体 $Ag^+ \subset (TP)_n$-Cy も合成し、構造変化による SF の制御も検討した。

TP 間の配向制御による SF 特性を議論するために、$(TP)_n$-Cy および $Ag^+ \subset (TP)_n$-Cy の過渡吸収スペクトルを測定した。一例として(*E*)-$(TP)_2$-Cy では、銀イオンの内包に伴い SF の速度定数が 4.1×10^7 s^{-1} から 1.4×10^8 s^{-1} と一桁加速するだけでなく、独立した T_1 の収率 (Φ_T) も大幅な上昇に成功した。本発表では、導入した TP の置換位置および銀イオンの有無に伴う励起ダイナミクス制御に関して詳細に議論する。

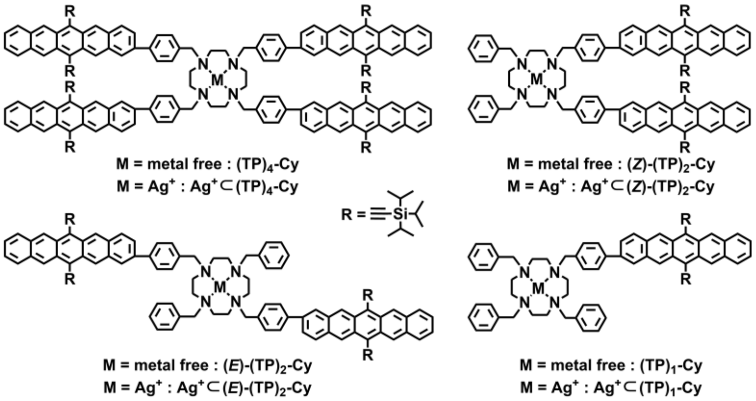


Fig. 1 Chemical structures of cyclen-centered TIPS-pentacene oligomers in the presence and absence of Ag^+ in this study.

二つの炭化水素置換基あるいはラジカル基をもつ安定発光ラジカルの発光特性

（奈良先端大 ^{1}・龍谷大 ^{2}）○服部 陽平 ^{1}・北島 稜大 ^{2}・馬場 温 ^{2}・山本 航平 ^{2}・内田 欣吾 ^{2}

Emission Properties of Stable Luminescent Radicals with Two Hydrocarbon Substituents or Radical Groups

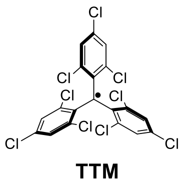
(^{1}*Nara Institute of Science and Technology*, ^{2}*Ryukoku University*) ○Yohei Hattori,^{1} Ryota Kitajima,^{2} Atsumi Baba,^{2} Kohei Yamamoto,^{2} Kingo Uchida^2

Stable luminescent radicals have attracted much attention for applications such as highly efficient OLED emitter.$^{1)}$ We study derivatives of PyBTM$^{2)}$ and F_2PyBTM$^{3)}$, which are more photostable than TTM. Suzuki-Miyaura reaction was developed to substitute chlorine atoms at the *para*-position of the benzene rings of PyBTM.$^{4)}$ Especially, when the chlorine atoms were substituted to mesityl groups, photoluminescence quantum yield of the substituted F_2PyBTM in chloroform was as much as 69%.$^{5)}$

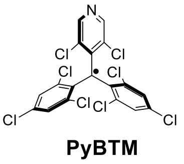
Recently we have prepared stable luminescent radical derivatives with two types of hydrocarbon substituents and diradicals with two radical units bridged by phenylene linker. We will report luminescent properties of these molecules.

Keywords : Fluorescence; Luminescence; Radical; Diradical

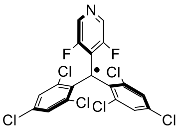
安定発光ラジカルは、高効率有機 EL の発光体等への応用で注目されている ^{1}。我々は、TTM よりも光に強い特長をもつ PyBTM$^{2)}$や、やや発光効率の良い F_2PyBTM$^{3)}$の誘導体について研究している。鈴木･宮浦カップリングの応用で、PyBTM や F_2PyBTM のベンゼン環のパラ位の塩素原子をアリール基で置換できるようになり $^{4)}$、特にメシチル基で両方の塩素原子を置換したときに、クロロホルム中で 69%と高い蛍光量子収率を示すことがわかった $^{5)}$。最近新たに 2 種類の炭化水素芳香族置換基を付けた F_2PyBTM 誘導体や、2 つのラジカルユニットを 1,4-フェニレン基で架橋した発光ジラジカルを開発した。これらの発光特性について考察し、2 つの置換基の影響や、ラジカルユニット同士の影響について考察する。



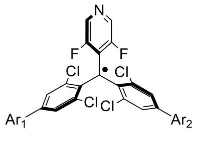
TTM

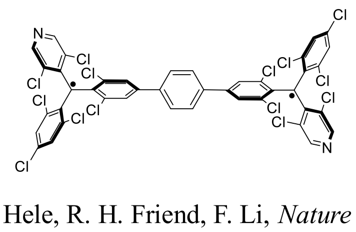


PyBTM



F_2PyBTM





1) X. Ai, E. W. Evans, S. Dong, A. J. Gillett, H. Guo, Y. Chen, T. J. H. Hele, R. H. Friend, F. Li, *Nature* **2018**, *563*, 536.

2) Y. Hattori, T. Kusamoto, H. Nishihara, *Angew. Chem. Int. Ed.* **2014**, *53*, 11845.

3) Y. Hattori, T. Kusamoto, H. Nishihara, *RSC Adv.* **2015**, *5*, 64802.

4) S. Mattiello, F. Corsini, S. Mecca, M. Sassi, R. Ruffo, G. Mattioli, Y. Hattori, T. Kusamoto, G. Griffini, L. Beverina, *Mater. Adv.* **2021**, *2*, 7369–7378.

5) Y. Hattori, R. Kitajima, W. Ota, R. Matsuoka, T. Kusamoto, T. Sato, K. Uchida, *Chem. Sci.* **2022**, *13*, 13418–13425.

日本化学会 第104春季年会 (2024)

テトラセノチオフェン連結体の合成と一重項分裂

（慶大理工）○岡本 大河・酒井 隼人・羽曾部 卓

Syntheses and Singlet Fission of Tetracenothiophene Dimers (*Faculty of Science and Technology, Keio University*) ○Taiga Okamoto, Hayato Sakai, Taku Hasobe

Singlet fission (SF) is a multi-exciton generation process, in which uncoupled two triplet excitons were generated after one-photon absorption in two nearby molecules. One of the typical chromophores for SF is pentacene and many examples of SF systems utilizing pentacene derivatives were reported, so far. On the other hand, tetracenothiophene (TTh) is one of the pentacene analogs. However, the number of reports regarding singlet fission using TTh is extremely limited as compared to pentacene. In this study, we synthesized a series of TTh dimers linked at the α and β positions of TTh units and evaluated the detail photophysical properties.

Keywords : Singlet Fission; Dimer; Tetracenothiophene

一重項分裂 (Singlet Fission: SF) とは、一光子吸収により生じた一重項励起子 (S_1) が中間体である三重項対を経由して、2 つの独立した三重項励起子 (T_1) を生じる多励起子生成過程である[1]。そのエネルギー条件として、S_1 のエネルギーが T_1 のエネルギーの 2 倍以上であることが挙げられる $[E(S_1) \geq 2E(T_1)]$。SF を発現可能な代表的な発色団として、ベンゼン環が 5 つ直線状に縮環したペンタセンが知られている $[E(S_1) = 1.9\ \mathrm{eV}, E(T_1) = 0.8\ \mathrm{eV}]$。しかし、ペンタセンは T_1 のエネルギーが低いことから、励起子利用という観点では課題が残る。

一方、アセン骨格にヘテロ環を導入することで、励起エネルギーの制御や構造制御が期待できる。実際、ペンタセン末端をチオフェンに置換したテトラセノチオフェン (TTh) はより高い T_1 のエネルギーを有しており $[E(S_1) \approx 2\ \mathrm{eV}, E(T_1) \approx 1\ \mathrm{eV}]$、二量体中で高速な SF の進行が観測されている[2]。しかしながら、チオフェン末端の連結部位に着目した報告はなされていない。

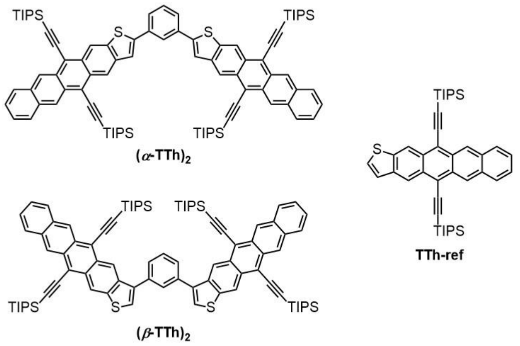


Fig. 1 本研究で用いる化合物の化学構造

本研究では、チオフェンの 2 種類の連結部位でそれぞれ繋いだ TTh 二量体を合成した (Fig. 1)。チオフェンのα位およびβ位を用いることで、新たな発色団間のカップリングの制御が期待される。分光測定の結果、いずれの二量体においても良好な SF が進行を観測されたが、SF の反応速度には 2 桁以上の大きな違いがあることが明らかとなった。

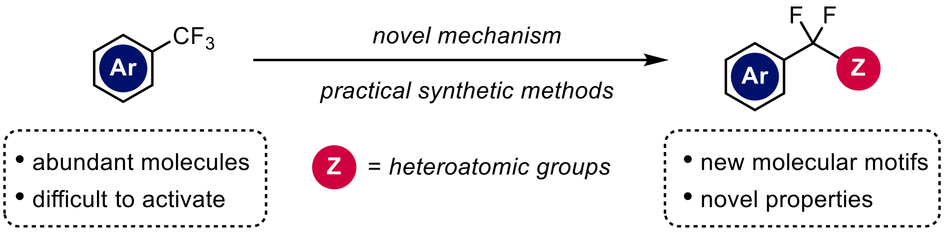
1) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891.
2) L. M. Campos, M. Y. Sfeir, et al., *J. Am. Chem. Soc.* **2023**, 145, 22058.

C−F Functionalization by Defluorinative Coupling of Trifluoromethyl Compounds

([1]*WPI-ICReDD, Hokkaido University*) ○Amit Kumar Jaiswal,[1] Priya Saha,[1] Dennis Chung-Yang Huang[1]

Keywords: Fluorine Chemistry, Photoredox Catalysis, Hydrogen Atom Transfer, Base Metal Catalysis, C−F Activation

Fluorine-containing compounds represent one of the most important classes of molecules due to their unique properties, where trifluoromethyl group remains as a prestigious motif. Recently, in the effort to expand the available chemical space, attention has been shifted to difluoromethyl moieties. Defluorinative coupling from the abundant trifluoromethyl compounds would be a natural strategy but is currently limited to a small selection of viable mechanisms. Challenges in this approach include strong C−F bonds and product selectivity regarding over-defluorination. Herein, we report two new methodologies for constructing difluoromethyl groups containing C−heteroatom bonds. The first work features a new hydrogen atom transfer (HAT) agent for hydrodefluorination reaction that enables the synthesis of a wide array of molecules containing -CF_2H moieties.[1] Mechanistic studies provided insights on the key role of HAT agent. Secondly, we developed a protocol involving base-metal photoredox catalysis that enables the direct C−F activation to afford C−heteroatom bonds. We proposed that the catalyst serves dual roles in substrate activation and bond-forging cross coupling. Overall, the new mechanism and activation mode point to novel avenue towards general C−F functionalization enabling the expansion of chemical space to unprecedented molecular structures.



1) A. K. Jaiswal, B. B. Skjelstad, S. Maeda, C.-Y. Huang *manuscript in preparation*. 2) P. Saha, C.-Y. Huang *manuscript in preparation*.

日本化学会 第104春季年会 (2024)

フォノンの放出・吸収過程としての無輻射遷移

（京大福井セ[1]・京大院工[2]・MOLFEX[3]）○大田 航[1,2]・上島 基之[3]・春田 直毅[1,2]・佐藤 徹[1,2]

Nonradiative Transitions as Phonon Emission and Absorption Processes

([1]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*MOLFEX, Inc.*) ○Wataru Ota,[1,2] Motoyuki Uejima,[3] Naoki Haruta,[1,2] Tohru Sato[1,2]

An analytical expression for the nonradiative rate constant is derived based on Fermi's golden rule within the mixed-spin crude adiabatic (CA) approximation. The mixed-spin CA basis is defined by a set of eigenstates for the electronic Hamiltonian that comprises the nonrelativistic electronic Hamiltonian and spin-orbit coupling clumped at the reference nuclear configuration. The mixed-spin basis differs from the pure-spin basis defined by a set of eigenstates for the nonrelativistic electronic Hamiltonian. The mixed-spin CA representation provides a unified view of the nonradiative transitions; both internal conversion and intersystem crossing (ISC) are regarded as vibronically induced phonon emission and absorption processes. The analytical expression enables us to determine important vibrational modes responsible for phonon emission/absorption (promoting modes) and accepting excitation energy (accepting modes) according to the selection rule of vibronic coupling. An advantage of the CA representation is that the spatial distribution of vibronic coupling is elucidated based on its density form, i.e., vibronic coupling density, which can be applied to theoretical molecular design with controlled nonradiative processes. The calculated ISC rate constant for tetracene reproduces the experimental result well.

Keywords： *Internal Conversion; Intersystem Crossing; Vibronic Coupling*

混合スピン粗断熱表現を用いたフェルミの黄金律に基づき、分子の全振動モードを考慮した無輻射速度定数の解析的表式を導出した1)。混合スピン状態は非相対論的電子ハミルトニアンにスピン軌道相互作用を加えたハミルトニアンの固有状態で定義される。これは、非相対論的電子ハミルトニアンの固有状態で定義される純粋スピン状態2)とは異なる。混合スピン粗断熱表現では、無輻射遷移を振電相互作用を駆動力としたフォノン放出、吸収過程とみなせ、内部転換と系間交差を統一的に扱うことができる。得られた解析的表式により、振電相互作用の選択則に基づきながら、振動モードをフォノン放出・吸収に関与するモード（促進モード）と電子励起エネルギーを受け取るモード（受容モード）に分類することができる。また、粗断熱表現を用いることで、振電相互作用の起源を振電相互作用密度3)により明らかにし、系間交差を制御した分子設計に応用することが可能である。計算によって得られたテトラセンの系間交差速度定数は実験値を良く再現した。

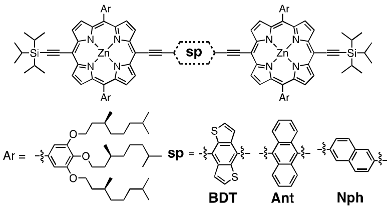
1) W. Ota, M. Uejima, N. Haruta, T. Sato, *Bull. Chem. Soc. Jpn.* in press.
2) B. R. Henry and W. Siebrand, *J. Chem. Phys.* **1971**, *54*, 1072.
3) T. Kato, N. Haruta, and T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation* (Springer, 2021).

Studies on photoexcitation dynamics in self-organized porphyrin array films by near-infrared femtosecond time-resolved emission spectroscopy

(*Grad. Sch. Sci. Eng., Univ. of Toyama,*[1] *Fac. Mol. Chem. Eng., Kyoto Inst. of Tech.*[2]) Kenya Shinozaki[1], Minami Nakamura[2], Mitsuhiko Morisue[2], Munetaka Iwamura[1], ○Koichi Nozaki[1]

Keywords: porphyrin, aggregate, near-infrared luminescence, bar-coated thin film

Arylene-linked porphyrin arrays bearing elastic 3,4,5-tri((S)-3,7-dimethyl-octyloxy)phenyl groups (Scheme 1) form amorphous molecular glasses containing a partial crystalline arrangement due to self-organization[1]. Neat films of the porphyrin arrays display a large split of the B (Soret) band at 400-500 nm and a bathochromic shift of the Q band at around 700 nm due to exciton coupling in the J-type aggregates (Figure 2). Bar-coated films of the arrays exhibit fluorescence from the Q states at 700-800 nm. Furthermore, near-infrared (NIR) emissions with maxima at 795, 895, and 960 nm were observed for the **Nph**, **BDT**, and **Ant** films, respectively. The emission quantum yields of the films were 5.8×10^{-2} (**Nph**), 1.6×10^{-4} (**BDT**), and 1.0×10^{-3} (**Ant**).



Scheme 1. Arylene-linked porphyrin arrays.

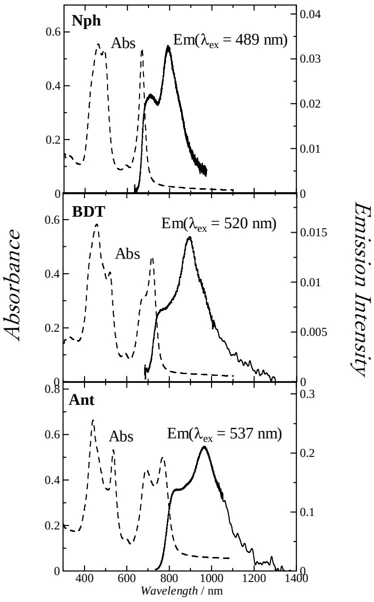


Figure 2. Absorption and emission spectra of bar-coated films of arylene-linked porphyrin arrays.

To understand the photoexcitation dynamics in the self-organized porphyrin glasses, femtosecond fluorescence up-conversion measurements were carried out for the **BDT** bar-coated films. Upon excitation into the B band at 420 nm, ultrafast B→Q internal conversion ($\tau < 0.05$ ps) was followed by relaxation within the Q states with 0.1 ps. The Q-band emission at 740 nm decayed with lifetimes of 0.1 ps(29%) and 0.55ps(55%). The NIR emission at 920 nm appeared within 0.1 ps immediately after the excitation, suggesting that the NIR-luminescent species are ascribed to excimers resulting from self-trapping of the excitons in the aggregates. The NIR emission then decayed with lifetimes of 1 ps (27%), 24 ps(59%), and 400 ps (13%).

1) M. Morisue *et al., RSC Adv.*, **2017**, *7*, 22679.

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19日(火) 15:55 ~ 17:15 E1133(11号館 [3階] 1133)

[E1133-2vn] 14. 有機化学―芳香族・複素環・ヘテロ原子化合物

座長：奥田 靖浩、内山 洋介

英語

15:55 ~ 16:15

[E1133-2vn-01]

ヒ素配位子を組込んだ発光性１次元配位高分子の開発

〇菊池 一槙[1]、井本 裕顕[1]、中 建介[1] (1. 京工繊大院工芸)

英語

16:15 ~ 16:35

[E1133-2vn-02]

チオフェン類で縮巻したアルシニンの合成と構造・芳香族及び反応性の調査

〇隅田 滉史[1]、井本 裕顕[1]、中 建介[1] (1. 京工繊大院工芸)

英語

16:35 ~ 16:55

[E1133-2vn-03]

2点型ハロゲン結合供与体によるクロライドの捕捉における架橋構造の影響

〇加藤 雅之[1,2]、大塚 尚哉[1,2]、西岡 雪奈[1]、鈴木 敏泰[1]、椴山 儀恵[1,2] (1. 分子研、2. 総研大)

英語

16:55 ~ 17:15

[E1133-2vn-04]

全フッ素ハロゲン化ナフタレンの合成・結晶構造・分子間相互作用

〇大塚 尚哉[1,2]、大田 陽野[1,2]、杉浦 聡[1]、杉山 晴紀[1,2]、鈴木 敏泰[1]、椴山 儀恵[1,2] (1. 分子研、2. 総研大)

Development of Luminescent One-Dimensional Coordination Polymers with Arsenic Ligands

([1]*Graduate School of Science and Technology, Kyoto Institute of Technology*)
○Kazuma Kikuchi,[1] Hiroaki Imoto,[1] Kensuke Naka[1]

Keywords: Coordination Polymer; Group 15 Element; Emissive Complexes; Arsenic; Copper(I) halide

Copper(I) complexes, especially copper iodide (CuI) complexes, have been extensively investigated as cost-effective luminescent materials, offering an alternative to rare-metal-based complexes. CuI complexes are notable for their varied metal clusters, which contribute to their chromic luminescence properties.[1] However, the sensitivity to slight changes in external conditions limits their application in optical devices that require emissive stability. To address this issue, there is growing interest in structurally robust complexes, particularly one-dimensional coordination polymers (1D-CPs).[2]

Recently, arsine ligands have attracted much attention in the development of luminescent CuI complexes,[3] although phosphine and sulfide ligands are the conventional choices. Arsine, a Group 15 element, not only exhibits characteristics similar to phosphine but also offers several advantages. These benefits include stable handling in air due to its high oxidation resistance, and enhanced phosphorescence owing to the heavy atom effect from Spin-Orbit Coupling parameters. In our previous work, we reported the structural and optical properties of luminescent CuI-based discrete complexes with dinuclear rhombic metal clusters, using triphenylarsine ($AsPh_3$) and *N*-heteroaromatic co-ligands.[4]

In this study, we successfully synthesized two types of CuI-based 1D-CPs with arsine ligands (Figure 1).[5] The 1D-CPs exhibited intense emission even at room temperature, and the emission efficiencies of these complexes were higher than those of the discrete complexes. In this presentation, the structures, optical properties, and external stimuli response of the 1D-CPs will be discussed in detail.

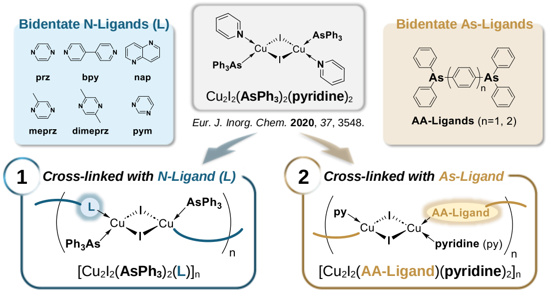


Figure 1. Two types of luminescent CuI-based 1D-CPs using arsine ligands in this work.

1) J. Troyano, F. Zamora, S. Delgado, *Chem. Soc. Rev.* **2021**, *50*, 4606. 2) a) H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka, N. Kitamura, *Inorg. Chem.* **2005**, *44*, 9667. b) W. Liu, Y. Fang, G. Z. Wei, S. J. Teat, K. Xiong, Z. Hu, W. P. Lusting, J. Li, *J. Am. Chem. Soc.* **2015**, *137*, 9400. 3) A. V. Artem'ev, Y. V. Demyanov, M. I. Rakhmanova, I. Y. Bagryanskaya, *Dalton Trans.* **2022**, *51*, 1048. 4) R. Kobayashi, H. Imoto, K. Naka, *Eur. J. Inorg. Chem.* **2020**, *37*, 3548. 5) K. Kikuchi, H. Imoto, K. Naka, *Dalton Trans.* **2023**, *52*, 11168.

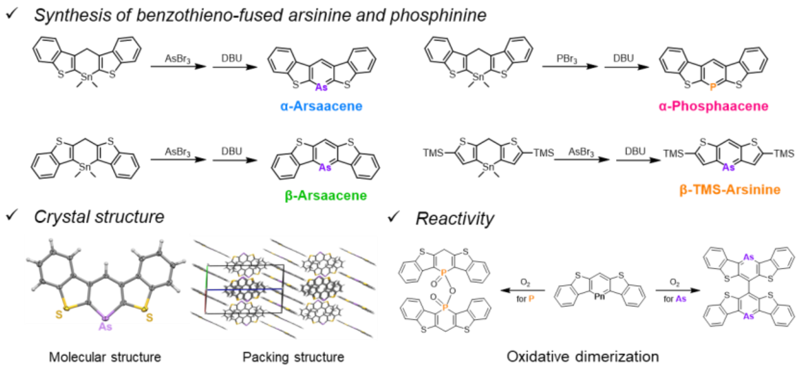
Synthesis of thieno-fused arsinines and investigation of their structure, aromaticity, and reactivity

(1Graduate School of Science and Technology, Kyoto Institute of Technology) ○Akifumi Sumida[1], Hiroaki Imoto[1], Kensuke Naka[1]

Keywords: Organoarsenic compound; Arsinine; Phosphinine; Heteroacene; Aromaticity

Aromatic compounds are among the most fundamental in organic chemistry and have been extensively investigated due to their distinctive structural and electronic properties. Among these, heterobenzenes are particularly intriguing. These are compounds in which a heteroatom has been incorporated, resulting in unique properties stemming from the presence of this atom. Typically, period II main-group elements are used in their synthesis. However, recent developments have seen the introduction of higher-period group 14 and 15 elements into these compounds. [1] Despite these advancements, the synthesis of arsenic analogs, such as arsinines, remains a challenging and unexplored area. There are only a few examples of stable, isolable arsinine compounds [2], and comprehensive studies on their structure and properties are scarce. In this study, we investigated the properties of thieno-fused arsinines.

We synthesized benzo-thieno-fused arsinines via Sn-As exchange reactions. All the arsinines were stable at room temperature. The structures of the arsinines were highly planar, with bond lengths between the As-C and As=C bonds, indicating high aromaticity in the arsinine rings. This is supported by a DFT analysis of NICS values and ACID analysis. UV-vis and luminescence spectra of the benzothieno-fused arsinines showed the absorption and fluorescence bands were longer wavelengths than those observed for phosphinines, indicating less effective conjugation. In contrast, both fluorescence bands were significantly longer in the solid state than in the solution state, attributable to J-aggregation. Finally, the reactivity of arsinines and phosphinines to oxygen was examined. For arsinines, dehydrogenative dimerization occurred at the C4 position while retaining aromaticity. In contrast, for phosphinine, oxidative dearomatization led to dimerization at the phosphorus atom. These differences are attributed to the differing oxygen affinities of the pnictogen atoms.



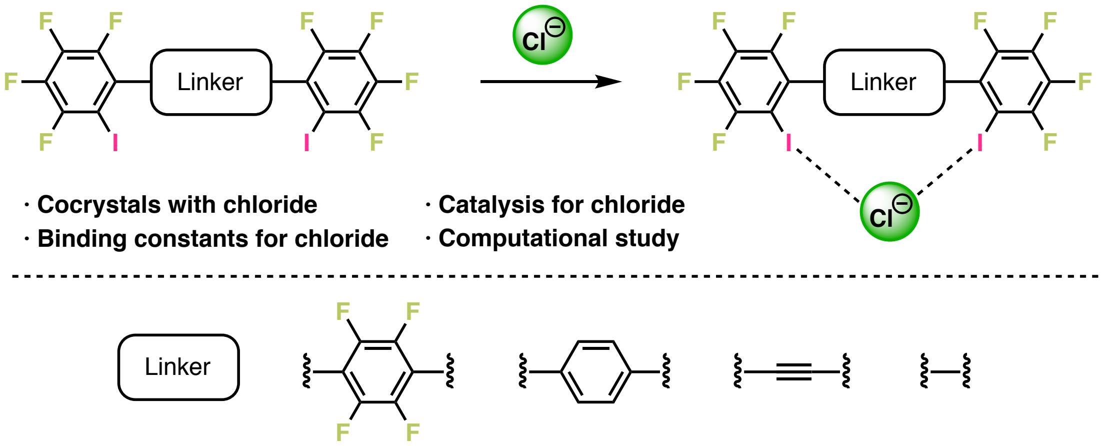
[1] (a) Wakita, K. *et al.*, *J. Am. Chem. Soc.*, **2000**, *122*, 5648. (b) N. Nakata, *et al.*, *Organometallics*, **2001**, *20*, 5507. (c) K. Matsuo, *et al.*, *Chem. Commun.*, **2022**, *58*, 13576. [2] (a) V. Kremláček, *et al.*, *Chem. Eur. J.* **2019**, *25*, 5668. (b) Dr. Dennis Rottschäfer *et al.*, *Angew. Chem. Int. Ed.* **2021** *60*, 15849.

Impact of Linker Structure on Chloride-binding by Two-point Halogen Bond Donors

([1]*Institute for Molecular Science*, [2]*SOKENDAI*) ○Masayuki Kato,[1,2] Naoya Ohtsuka,[1,2] Yukina Nishioka,[1] Toshiyasu Suzuki,[1] Norie Momiyama[1,2]

Keywords: Halogen Bonds; Perfluoroiodoarenes; Cocrystals; Catalysis; Mannich reaction

Halogen bond has been utilized in crystal engineering and currently applied in molecular recognition and organocatalysis.[1,2,3] Two- and multi-point halogen bond donors have been designed to enhance their halogen bond donor ability compared to one-point donors. In this study, we systematically investigated the effect of linker structure possessed in two-point halogen bond donors, with a focus on perfluoroiodobenzene structures. Halogen bond donors with a different linker were evaluated in binding constants K (M^{-1}) for chloride and reaction yields (%) in Mukaiyama-Mannich-type reaction of isoquinoline through chloride-binding. The two-point halogen bond donor possessing a tetrafluorophenylene linker exhibited the highest activity. Chloride-binding modes were proposed based on Job's plots and co-crystal structures with chloride. Computational study was performed to elucidate the effect of linker on the activity. Finally, the utility of the tetrafluorophenylene-linked two-point halogen bond donor was established in the Mukaiyam-Mannich-type reaction involving various isoquinolines, chloroformates, and silyl enol ethers.



[1] Corradi, E.; Meille, S. V.; Messina, M,; Metrangolo, P.; Resnati, G. *Angew. Chem. Int. Ed.* **2000**, *39*, 1782-1786. [2] Brown, A.; Beer, P. D. *Chem. Commun.* **2016**, *52*, 8645-8658. [3] Bulfield, D.; Huber, S. M. *Chem. Eur. J.* **2016**, *22*, 14434-14450.

Perfluorohalogenated Naphthalene: Synthesis, Crystal Structure, and Intermolecular Interaction

([1]*Institute for Molecular Science*, [2]*SOKENDAI*) ○Naoya Ohtsuka,[1,2] Hino Ota,[1,2] Satoshi Sugiura,[1] Haruki Sugiyama,[1,2] Toshiyasu Suzuki,[1] Norie Momiyama[1,2]

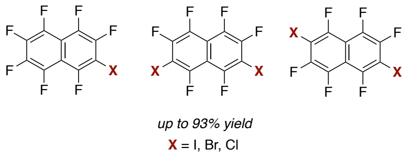
Keywords: Naphthalene, Perfluorohalogenation, σ-hole, π-hole, Crystal structure

Perfluorohalogenated arenes (PFXArs) are unique small molecules whose electronic density distributions differ not only from those of simple arenes but also from perfluoroarenes. The tip of halogen atoms (I, Br, and Cl) and the core of the aromatic ring in PFXArs carry a positive charge due to the most electronegative fluorine atom on the aromatic ring. Since 2000, non-covalent interaction associated with PFXArs have attracted significant attention and evolved into a new field of material science, such as supramolecular material and crystalline material.[1] Despite the utility of PFXArs is unveiled, the reports are limited to commercially available or readily synthesized perfluorohalogenated benzenes.

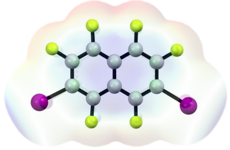
Perfluorohalogenated naphthalenes (PFXNaPs) are excellent candidates as novel perfluorohalogenated arenes due to enhanced electron-withdrawing properties by introducing a greater number of fluorine atoms onto the naphthalene ring. However, PFXNaPs are commercially unavailable and challenging to synthesis. Although Kukushkin and co-workers reported the synthesis of PFXNaPs (X = I, and Br) via C-F activation using Fe-catalyst and Grignard reagent, the yields were less than 20% yield.[2] A practical and versatile synthetic reaction is essential for yielding PFXNaPs.

We developed the synthetic protocol for PFXNaPs via halogenation reactions of electron-deficient polyfluoronaphthalenes. We revealed that metalation-halogenation sequences achieve the synthesis of PFXNaPs (X = I, Br, and Cl) in high yield. Furthermore, crystallization of PFINaPs were succeeded. X-ray diffraction analysis clarified the unique molecular arrangement. Here we report a detail of synthesis method, molecular crystal structures, and intermolecular interactions of PFXNaPs.[3]

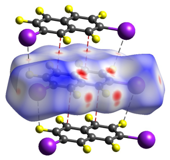
◆Synthesis of PFXNaPs



◆Crystal structure



◆Intermoleculer Interaction



[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo *Chem. Rev.* **2016**, *116*, 2478–2601. [2] A. V. Rozhkov, A. A. Eliseeva, S. V. Baykov, B. Galmés, A. Frontera, V. Y. Kukushkin *Cryst. Growth Des.* **2020**, *20*, 5908–5921. [3] N. Ohtsuka, H. Ota, S. Sugiura, S. Kakinuma, H. Sugiyama, T. Suzuki, N. Momiyama *CrystEngComm accepted (ChemRxiv:* http://dx.doi.org/10.26434/chemrxiv-2023-r2s6n-v2)

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19日(火) 15:55 ~ 17:15 E1142(11号館 [4階] 1142)

[E1142-2vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：岩田 隆幸、高橋 慎太郎

英語

15:55 ~ 16:15

[E1142-2vn-01]

新規5-5縮環ヘテロ芳香環ビルディングブロックの開発

〇宮﨑 龍也[1]、髙田 郁人[1]、菊池 拓成[1]、大黒 裕哉[2]、鎌田 信[2]、湯川 猛史[2]、武藤 慶[1]、山口 潤一郎[1] (1. 早稲田大学、2. 武田薬品工業)

英語

16:15 ~ 16:35

[E1142-2vn-02]

高い安定性を有するヘキサキスピラゾリルエタンの合成と配位挙動

〇武政 雄大[1]、野崎 京子[1] (1. 東京大学大学院工学系研究科)

英語

16:35 ~ 16:55

[E1142-2vn-03]

窒素－ヘテロ原子結合への亜鉛カルベノイドの挿入による環拡大反応の開発

〇津田 正仁[1]、盛田 大輝[1,2]、中村 浩之[1,2] (1. 東工大生命理工、2. 東工大化生研)

英語

16:55 ~ 17:15

[E1142-2vn-04]

多環式インドール誘導体合成を指向したCO_2ラジカルアニオンによる不活性アルケンの触媒的アリールカルボキシル化

〇Suvankar Debbarma[1,2]、Saeesh R. Mangaonkar[1,2]、林 裕樹[1,2]、神名 航[3]、前田 理[1,2,3]、美多 剛[1,2] (1. 北大WPI-ICReDD、2. JST-ERATO、3. 北大院理)

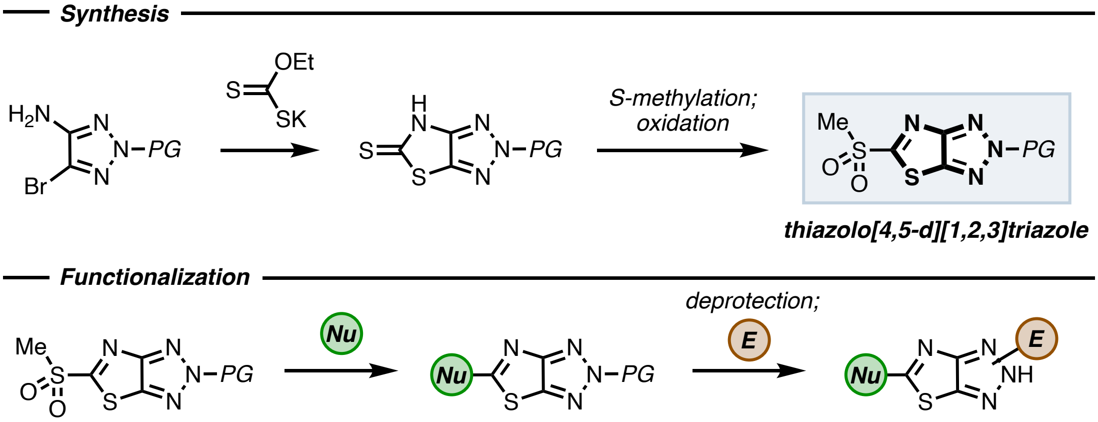
Development of A Novel 5-5 Fused Heteroaromatic Ring Building Block

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*Takeda Pharmaceutical Company*, [3]*Institute for Advanced Study, Waseda University*)
○Ryuya Miyazaki,[1] Fumito Takada,[1] Takunari Kikuchi,[1] Yuya Oguro,[2] Makoto Kamata,[2] Takahumi Yukawa,[2] Kei Muto,[3] Junichiro Yamaguchi[1]

Keywords: Heteroaromatic Ring; 5-5 Fused Aromatic Ring; Building Block; Thiazole; Triazole

Heteroaromatic rings are privileged structures frequently found in pharmaceuticals. Adopting heteroatoms in an aromatic ring would not only affect physical/chemical properties such as water solubility and polarity, but also control non-covalent interactions with a protein of interest such as hydrogen bonding. To find a better molecular scaffold, many pharmaceutical companies have developed novel heteroaromatic ring systems including bicyclic ring to replace the aromatic moiety of a certain lead compound (scaffold hopping).[1]

Herein, we have successfully synthesized thiazolo[4,5-*d*][1,2,3]triazoles as an unprecedented 5-5 fused heteroaromatic building block. This skeleton was constructed from aminobromo-1,2,3-triazoles and potassium ethylxantates, affording a desired thiazolotriazole with a methyl sulfone on the thiazole ring.[2] Toward the use of this heteroarene as a building block, we established various functionalization on the thiazole ring by using the methyl sulfone as a leaving group. It was also found that the functionalization of the triazole ring was possible.



[1] (a) Schneider, G.; Neidhart, W.; Giller, T.; Schmid, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2894–2896. (b) Sun, H.; Tawa, G.; Wallqvist, A. *Drug Discov. Today* **2012,** *17*, 310–324.

[2] Liu, L.; Zhu, N.; Gao, M.; Zhao, X.; Han, L.; Hong, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2016**, *191*, 699–701.

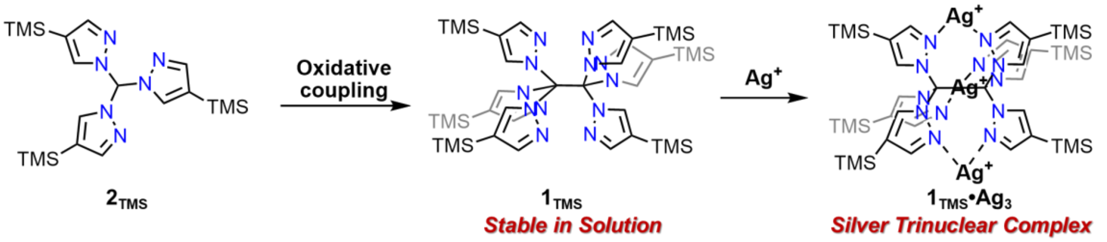
Synthesis and Coordination Behavior of Hexakispyrazolylethane with High Stability

([1]*Graduate School of Engineering, The University of Tokyo*) ○Yuta Takemasa,[1] Kyoko Nozaki[1]

Keywords: *Pyrazole, Hexaarylethane, Trityl radical, Ag complex, Polynuclear complex*

Hexaphenylethane (**HPE**) is one of the most attractive compounds with riddles many researchers have tried to solve for a long time.[1] It is known that there is an equilibrium between hexaphenylethane (α,α-dimer) and trityl radical, which dimerizes to form another isomer, thermally stable quinoidal dimer (α,*p*-dimer). To isolate the labile hexaphenylethane structure, there have been reported two strategies. As one approach, the introduction of sterically bulky substituents was successfully applied to stabilization of the α,α-dimer structure by London dispersion interactions.[2,3] Another strategy is bridging: Phenyl groups of each triarylmethyl unit were covalently connected. We envisaged a novel approach to isolate non-bridged hexaarylethane by introducing heterocycles. Herein, we report the synthesis and isolation of hexakis(4-trimethylsilylpyrazol-1-yl)ethane ($\mathbf{1_{TMS}}$) which shows much higher stability compared with other non-bridged hexaarylethanes.

$\mathbf{1_{TMS}}$ was synthesized by the oxidative dimerization of tris(4-trimethylsilylpyrazol-1-yl)methane ($\mathbf{2_{TMS}}$). Single-crystal X-ray structural analysis of 1_{TMS} showed that the ethane C–C bond (1.623(4) Å) is shorter than that in hexaphenylethane (1.67(3) Å).[3] In solution, 1_{TMS} existed as a single species, contrastive that conventional hexaphenylethanes can keep the central C–C bond only by the aid of additional bridges between the two triarylmethyl units. Theoretical calculations indicated that the stabilization of the central carbon radical is much less significant in case of pyrazolyl compared to phenyl, due to lack of delocalization. Furthermore, introduction of pyrazole groups allowed additional bridging between the two triarylmethyl moieties through metal coordination to the adjacent N atoms: 1_{TMS} exhibited unique coordination to three Ag atoms affording a hexaarylethane analog bearing three N–Ag–N bridges ($\mathbf{1_{TMS}{\bullet}Ag_3}$). In the crystal structure of $\mathbf{1_{TMS}{\bullet}Ag_3}$, the ethane C–C bond (1.73(2) Å) was elongated from 1_{TMS} by coordination.



1) J. M. Mcbride, *Tetrahedron* **1974**, *30*, 2009–2022. 2) M. Stein, W. Winter, A. Rieker, *Angew. Chem. – Int. Ed.* **1978**, *17*, 692–694. 3) B. Kahr, D. V. Engen, K. Mislow, *J. Am. Chem. Soc.* **1986**, *108*, 26, 8305–8307. 4) G. Wittig, H. Petri, *Justus. Liebigs. Ann. Chem.* **1933**, *505*, 17–41.

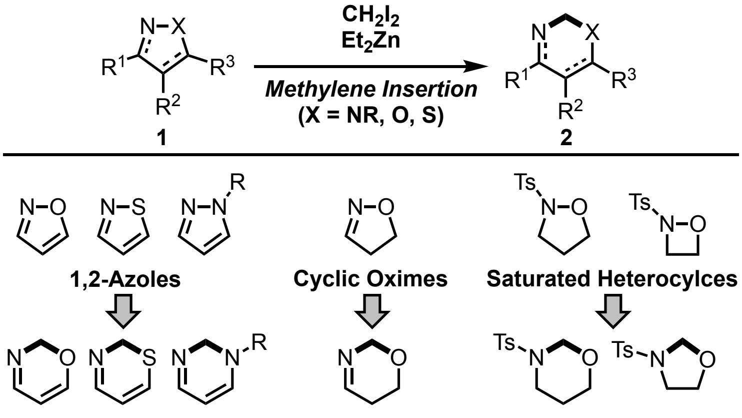
Ring Expansion of Heterocycles via Insertion of a Zinc Carbenoid to Nitrogen-Heteroatom Bonds

(*[1]School of Life Science and Technology, Tokyo Institute of Technology, [2]Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○Masato Tsuda,[1] Taiki Morita,[1, 2] Hiroyuki Nakamura[1, 2]

Keywords: 1,2-Azoles, Zinc-Carbenoid, Insertion, Ring Expansion

Recently, the skeletal transformation of heterocycles has attracted much attention because it allows us to construct scaffolds that are not readily accessible by other means. Current methods for ring-expansion via insertion into nitrogen-heteroatom bonds of 1,2-azoles rely on highly reactive species such as free carbenes[1)] or transitional metal carbenoids.[2)] Another approach is rearrangement of azolium ylides which could be prepared from azolium salts,[3)] but it requires multi-step from 1,2-azoles.

We previously found that a zinc carbenoid inserted into nitrogen-oxygen bond of an isoxazole derivative.[4)] Herein, we report the ring expansion of a wide variety of heterocycles **1** which have nitrogen-heteroatom (X = NR, O, S) bonds to produce corresponding methylene inserted products **2**. The developed reaction employing a zinc carbenoid could be applicable not only to 1,2-azoles, but also to cyclic oximes and saturated heterocycles. Furthermore, we performed DFT calculations to elucidate the reaction mechanisms, clarifying the distinct reaction paths among different types of rings.[5)]



1) Hyland, E. E.; Kelly, P. Q.; McKillop, A. M.; Dherange, B. D. I.; Levin, M. D. *J. Am. Chem. Soc.* **2022**, *144*, 19258-19264.

2) Li, L.; Ning, Y.; Chen. H.; Ning, Y.; Sivaguru, P.; Liao, P.; Zhu, Q.; Ji, Y.; de Ruiter, G.; Bi, X. *Angew. Chem. Int. Ed.* **2023**, e202313807.

3) Kashima, C.; Tsuda, Y.; Imada, S.; Nishio, T. *J. Chem. Soc. Perkin Trans I.* **1980**, 1866-1869.

4) Tsuda, M.; Morita, T.; Nakamura, H. *Chem. Commun.* **2022**, *58*, 1942-1945.

5) Tsuda, M.; Morita, T.; Morita, Y.; Takaya, J.; Nakamura, H. *Adv. Sci.* **2023**, DOI: 10.1002/advs.202307563.

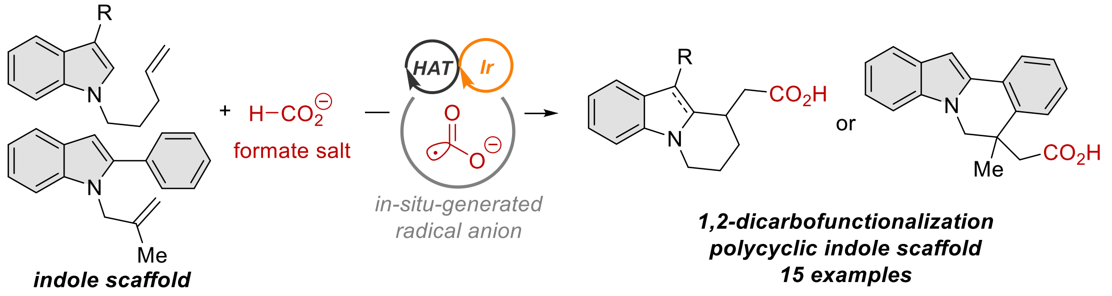
Photoredox Catalysis for the Synthesis of Polycyclic Indole Derivatives via Arylcarboxylation of Unactivated Alkenes with the CO_2 Radical Anion

([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*) ○Suvankar Debbarma,[1,2] Saeesh R. Mangaonkar,[1,2] Hiroki Hayashi,[1,2] Wataru Kanna,[3] Satoshi Maeda,[1,2,3] Tsuyoshi Mita[1,2]

Keywords: Photoredox; Metalloformates; Alkene; Arylcarboxylation; Polycyclic Indole

The arylcarboxylation of alkenes has proven to be a promising method for introducing two consecutive C–C bonds in a single transformation, providing a diverse range of substituted carboxylic acids.[1] However, the photocatalyzed carboxylation of unactivated alkenes with CO_2 presents a significant challenge, primarily attributed to the high reduction potentials of both starting materials.

Metalloformates (HCO_2M) are stand out as a renewable ore of carbon dioxide radical anion ($CO_2^{\bullet -}$), which has been utilized as a potential C1 source of valuable synthetic carboxyl intermediate.[2] Leveraging the reactive nucleophilic radical character of $CO_2^{\bullet -}$ in contemporary organic chemistry,[3] we have developed an effective and robust photochemical method for the arylcarboxylation of unactivated alkenes (reduction potential: −3.2 V). This 1,2-dicarbofunctionalization of alkenes using the indole core and CO_2 radical anion (from HCO_2K) under visible light mediated photoredox-HAT conditions, employing *fac*-[Ir(dFppy)$_3$] as photoredox catalyst and DABCO as hydrogen atom transfer (HAT) source, delivers a diverse array of polycyclic indole derivatives. Indoles bearing an alkene at an appropriate position undergo a dearomative 6-*exo-trig* radical cyclization via the arylcarboxylation pathway. *N*-Allyl substituted 2-phenylindoles and 1*H*-benzo[*g*]indole have been proven to be effective substrates for this arylcarboxylation.



1) Zhang, W.; Chen, Z.; Jiang, Y.-X.; Liao, L.-L.; Wang, W.; Ye, J.-H.; Yu, D.-G. *Nat. Commun*. **2023**, *14*, 3529. 2) Mangaonkar, S. R.; Hayashi, H.; Takano, H.; Kanna, W.; Maeda, S.; Mita, T. *ACS Catal.* **2023**, *13*, 2482−2488. 3) Alektiar, S. N.; Han, J.; Dang, Y.; Rubel, C. Z.; Wickens, Z. K. *J. Am. Chem. Soc*. **2023**, *145*, 10991−10997.

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19日(火) 13:00 ~ 14:50 H933(9号館 [3階] 933)

[H933-2pm] 16. 天然物化学・ケミカルバイオロジー

座長：岡野 健太郎、吉田 将人

英語

13:00 ~ 13:20

[H933-2pm-01]

竹節人参エキスからの中枢神経系保護活性をもつモノグルコシルギンセノシド類であるG-Rh_2の効率的単離・精製法

○大島 禎生[1,2]、古山 浩子[1,3]、小縣 綾[2,4]、池沼 宏[2]、木村 泰之[1,2]、加藤 隆司[1,2]、鈴木 正昭[2,3] (1. 岐阜大学　大学院連合創薬医療情報研究科、2. 国立長寿医療研究センター、3. 岐阜大学　工学部、4. 岐阜医療科学大学)

英語

13:20 ~ 13:40

[H933-2pm-02]

カルバゾマイシンＡ–Ｄのグラムスケール合成

○馮 宇軒[1]、岡野 健太郎[1]、森 敦紀[1,2] (1. 神戸大院工、2. 神戸大膜セ)

13:40 ~ 13:50

休憩

日本語

13:50 ~ 14:10

[H933-2pm-03]

新規ヒドロインドール骨格の合成法の開発と全合成への応用

○堤 大洋[1]、山上 龍威[1]、早川 一郎[1] (1. 日大院総合基)

日本語

14:10 ~ 14:30

[H933-2pm-04]

Cristaxenicin A の合成研究

○城内 航[1]、角田 祐子[1]、加藤 港介[1]、谷野 圭持[2] (1. 北大院総化、2. 北大院理)

英語

14:30 ~ 14:50

[H933-2pm-05]

海洋シアノバクテリア由来天然物Lagunamide C の合成による構造訂正

○萩元 海月[1]、照屋 俊明[2]、吉田 将人[1]、木越 英夫[1] (1. 筑波大院　数理物質、2. 琉球大学　理工学研究科)

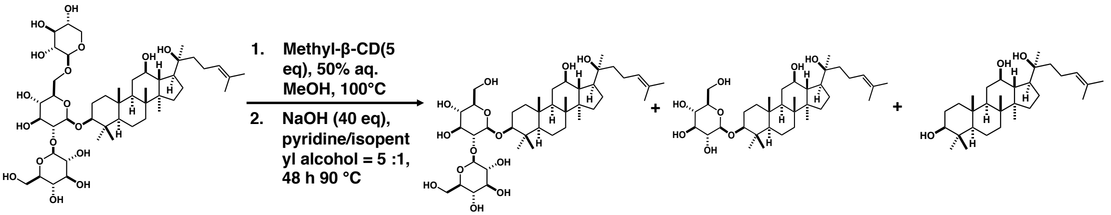
Efficient Isolation and Purification of Monoglucosyl Ginsenoside G-Rh_2 with CNS Protective Activity from an Extract of Chikusetsu Ginseng

([1]*United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University,* [2]*National Center for Geriatrics and Gerontology,* [3]*Faculty of Engineering, Gifu University,* [4]*Gifu University of Medical Science*) ○ Yoshiki Ooshima,[1,2] Hiroko Koyama,[1,3] Aya Ogata,[2,4] Hiroshi Ikenuma,[2] Yasuyuki Kimura,[1,2] Takashi Kato,[1,2] Masaaki Suzuki[2,3]

Keywords: Ginsenoside; Cyclodextrin; Hydrolysis of sugar

Ginsenosides, active components of Korean ginseng as medicinal resources in traditional Chinese medicine, have recently been considered as a potential therapy for central nervous system diseases.[1] We planned to evaluate the brain uptake of highly active metabolites, prosapogenols distinguished as Compound-K, Ginsenoside-Rh_2 (G-Rh_2) and the sapogenin 20(*S*)-protopanaxadiol (PPD) by non-invasive molecular imaging technology positron emission tomography. In this study, we attempted to synthesize and isolate enough amounts of G-Rh_2 and PPD from ginseng extract, which contains various ginsenosides, in order to synthesize the precursors for labeling.

Chikusetsusaponin III contained a three glucose residue in the structure, isolated from Japanese ginseng (Panax japonicus C.A. Meyer), was used to optimize the conditions of glucose hydrolysis. Following the reported conditions, PPD was obtained from Chikusetsusaponin III at 90% yield under NaOH (40 eq)/1-butanol conditions at 90 °C for 24 hours.[2] To selectively obtain the partial hydrolysis intermediate G-Rh_2, we controlled the reaction rate by using co-solvent of non-protonic polar solvent, and protected the resulted structure with cyclodextrin. Actually, the inclusion complex between Chikusetsusaponin III and methyl-β-cyclodextrin was reacted in the presence of NaOH (40 eq) in pyridine/isopentyl alcohol (5:1, *v*/*v*) at 90 °C for 48 hours, resulted in the selective improvement and the 61% isolation yield of objective G-Rh_2.



Chikusetsusaponin III **20(*S*)-G-Rg_3** **20(*S*)-G-Rh_2** **20(*S*)-PPD**

1) H.-J. Kim, S.-W. Jung, S.-Y. Kim, I.-H. Cho, H.-C. Kim, H. Rhim, M. Kim, S.-Y. Nah, *J. Ginseng Res.,* **2018**, *42*, 401. 2) J.-F. Cui, S. Bystroem, P. Eneroth, I. Bjoerkhem, *J. Org. Chem.*, **1994**, 59, 8251.

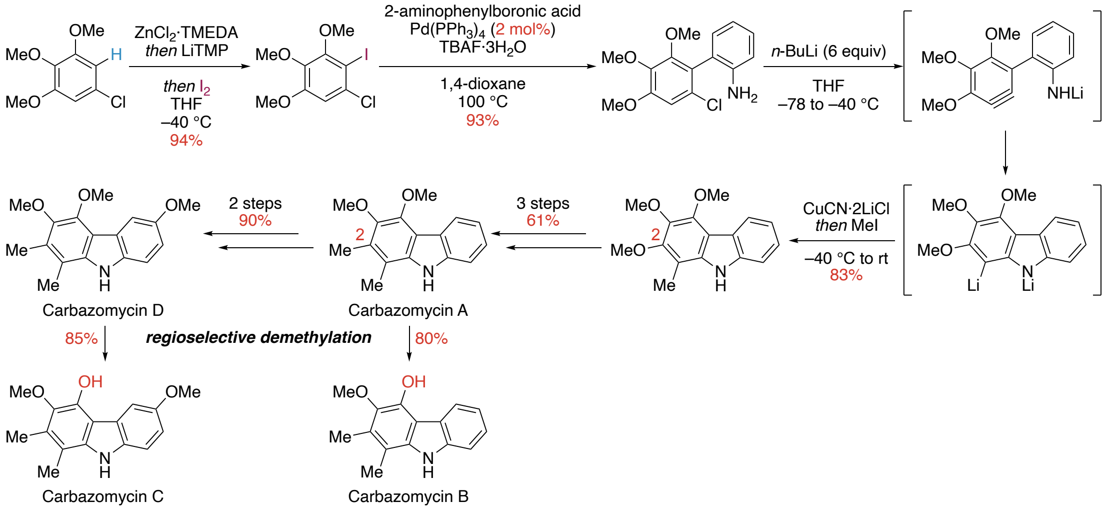
Gram-Scale Synthesis of Carbazomycin A–D

([1]*Department of Chemical Science and Engineering, Kobe University*, [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Yuxuan Feng,[1] Kentaro Okano,[1] Atsunori Mori[1,2]

Keywords: Carbazole alkaloids; Aryne intermediate; Regioselective demethylation; Protecting-group-free synthesis

Carbazomycins A–D, isolated from *Streptoverticillium ehimense* by Nakamura and co-workers in the 1980s, are the first class of antibiotics containing a carbazole framework.[1] These compounds were characterized by a highly unsymmetrical structure, in which one of the benzene rings carries four electron-donating groups to form the fully substituted aromatic ring.

Herein, we achieved the total synthesis of carbazomycins A–D on gram scales. Iodination of the symmetrical trimethoxychlorobenzene and subsequent Suzuki–Miyaura coupling sequence gave the aminobiaryl bearing the chlorine atom. Treatment of this compound with six equivalents of *n*-BuLi led to the formation of the aryne, which underwent the intramolecular nucleophilic addition with the lithium amide tether to construct the carbazole framework. The use of the carbazole dianion enabled the synthesis of 1-methylcarbazole without protecting groups. Carbazomycin A was obtained by transforming the methoxy group at the C-2 position into the methyl group over three steps.[2] Subsequently, carbazomycin D was provided via the regioselective methoxylation from carbazomycin A over two steps. Finally, total synthesis of carbazomycins B and C was achieved through the regioselective demethylation of carbazomycins A and D, respectively.



1) a) Sakano, K. -I.; Ishimaru, K.; Nakamura, S. *J. Antibiot.* **1980**, *33*, 683. b) Naid, T.; Kitahara, T.; Kaneda, M.; Nakamura, S. *J. Antibiot.* **1987**, *40*, 157. c) Knölker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303. 2) Feng, Y.; Yukioka, T.; Matsuyama, M.; Mori, A.; Okano, K. *Org. Lett.* **2023**, *25*, 3013.

新規ヒドロインドール骨格の合成法の開発と全合成への応用

（日大院総合基）○堤 大洋・山上 龍威・早川 一郎

Development of Novel Synthetic Method for Hydroindole Skeleton and Its Application for Total Synthesis of Natural Product (*Graduate School of Integrated Basic Sciences, Nihon University*) ○Tomohiro Tsutsumi, Ryui Yamagami, Ichiro Hayakawa

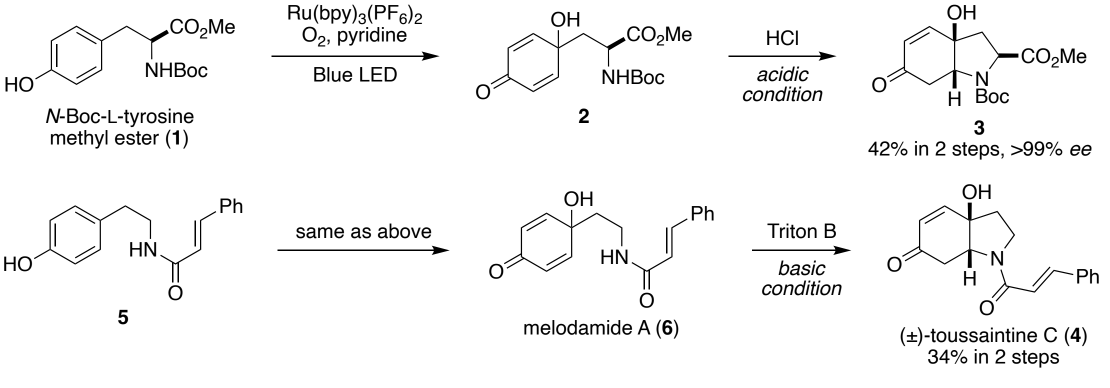
Hydroindole skeleton which contains fused six membered ring and pyrrolidine ring is usually prepared by using hypervalent iodine reagent. In this study, we developed the novel synthetic method of hydroindole skeleton by dearomatization reaction using singlet oxygen and cyclization cascade reaction. Moreover, we achieved the total synthesis of toussaintine C using our synthetic method. We will report the optimization of reaction conditions and detail of substrate scope of this synthetic method.

Keywords : Hydroindole; Dearomatization Reaction; Singlet Oxygen; Toussaintine C

ヒドロインドール骨格は六員環とピロリジン環が縮環した構造であり、フェノールに対して超原子価ヨウ素試薬を用いる合成法が報告されている[1]。本合成法は多くの研究者が利用しているが、強塩基による異性化が懸念されることから、新たなヒドロインドール骨格の合成法の開発が望まれていた。今回我々は、一重項酸素を用いた新たな手法によるヒドロインドール骨格の合成法の開発を行なったので報告する。

N-Boc-L-チロシンメチルエステル(**1**)を用いて、O_2雰囲気下、Ru錯体に対して青色LEDを照射することで[2]、一重項酸素の発生とフェノールの脱芳香族化反応が進行しジエノン**2**を得た。**2**に対して、酸性条件でアザマイケル付加反応による環化を行ったところ、光学純度を損なうことなくヒドロインドール**3**を合成することができた。

この合成法をトウサインチン C (**4**)の全合成へ適用した。すなわちチラミン誘導体**5**に対して、確立した一重項酸素を用いたフェノールの脱芳香族化反応を行うことでメロダミド A (**6**)を合成した。得られた**6**に対して、塩基性条件で環化反応を行い、ラセミ体のトウサインチン C (**4**)全合成を達成した。現在、**4**の不斉全合成を検討している。本発表では反応条件の最適化および基質適用範囲の詳細を報告する。



1) Pierce, J. G.; Kasi, D.; Fushimi, M.; Cuzzupe, A.; Wipf, P. *J. Org. Chem.* **2008**, *73*, 7807.
2) Carson, M. C.; Orzolek, B. J.; Kozlowski, M. C. *Org. Lett.* **2022**, *24*, 7250.

Cristaxenicin A の合成研究

（北大院総化 [1]・北大院理 [2]）〇城内 航 [1]・角田 祐子 [1]・加藤 港介 [1]・谷野 圭持 [2]

Synthetic Studies on Cristaxenicin A

([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Faculty of Science, Hokkaido University*) 〇Wataru Kiuchi,[1] Yuko Tsunoda,[1] Kosuke Kato,[1] Keiji Tanino[2]

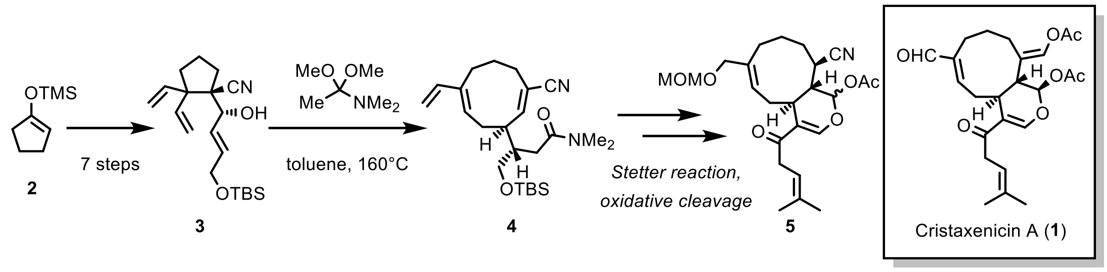
Cristaxenicin A (**1**) is a marine natural product which possesses the core structure consisting of a nine-membered carbocycle and a trans-fused dihydropyran ring. For its high antiprotozoal activity, this compound is anticipated to be a lead compound for a treatment drug against leishmaniasis. Therefore, **1** has been considered as an attractive synthetic target.

We began our synthesis with readily available silyl enol ether **2** which was converted to five-membered nitrile **3** having a geminal divinyl group. This nitrile was subjected to a sequential Claisen-Cope rearrangement reactions to afford the key nine-membered nitrile **4.** Then compound **4** was converted to dihydropyran **5** through a stereoselective construction of a 9-5 fused bicyclic skeleton by an intramolecular Stetter reaction followed by an oxidative cleavage of the five-membered ring.

Keywords： *Total synthesis, Diterpenoid, Tandem reaction*

Cristaxenicin A（**1**）は、中尾らによって軟体サンゴより単離・構造決定された海洋性ジテルペノイドであり [1)]、炭素 9 員環とジヒドロピランが縮環した xenican 骨格上に多数の酸素官能基を有する。**1** は、リーシュマニア症の原因原虫に対して高い抗原虫活性を示すことから、その治療薬のリード化合物として期待されているが、天然からの供給量は微量であり、合成研究も細川らによる 1 例があるのみある [2)]。このような背景から我々は、本化合物の合成法の確立を目指した。

市販のシリルエノールエーテル **2** から出発し、7 工程で *gem*-ジビニル基を有する 5 員環ニトリル **3** を合成した。このものをジメチルアセトアミドジメチルアセタールと共に加熱すると、Eschenmoser-Claisen 転位反応と、Cope 転位反応が連続的に進行し、アミド側鎖を有する 9 員環ニトリル **4** が得られた。さらに、分子内ステッター反応による立体選択的な 9-5 縮環骨格の構築と 5 員環の酸化的開裂を含む数工程の変換を経て、ジヒドロピラン環を有する化合物 **5** の合成に成功した。



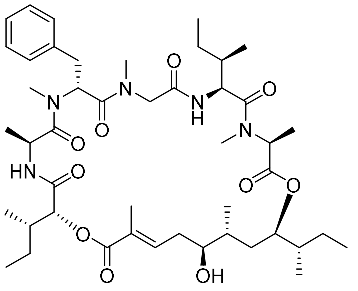
1) Ishigami, S. *et al. J. Org. Chem.* **2012**, 77, 10962.
2) Fumiyama, H. *et al. Bioorg. Med. Chem. Lett.* **2016**, *26*, 4355.

Synthesis and Structure Revision of Marine Cyanobacteria-Derived Natural Product Lagunamide C

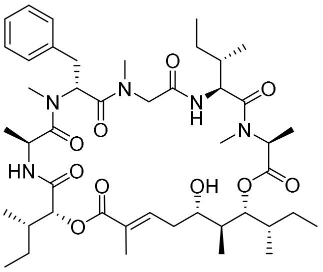
([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, [2]*Faculty of Education, University of the Ryukyus*) ○Kazuki Hagimoto,[1] Toshiaki Teruya,[2] Masahito Yoshida,[1] Hideo Kigoshi[1]

Keywords: Natural Product; Total Synthesis; Peptide; Polyketide; Cyclodepsipeptide

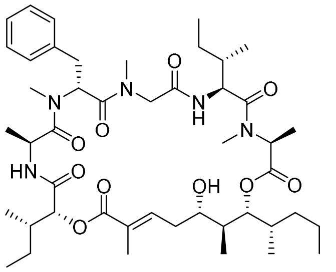
Lagunamide C, a 27-membered cyclodepsipeptide, was isolated from the marine cyanobacteria *Lyngbya majuscule* in 2011 by Tripathi et al.[1] and exhibits potent cytotoxicity against several cancer cells, comparable to that of the 26-membered analog lagunamide A.[2] The structural difference between the above compounds lies only in the presence or absence of a methylene carbon in the aliphatic acid moiety. However, it is known that the biological activity of cyclopeptides is strongly dependent on the conformation of their structure[3]. It should be interesting that the lagunamide families show comparable cytotoxicity regardless of the difference in the ring size of the cyclopeptide structure. Therefore, we planned the total synthesis of lagunamide C to elucidate its relationships between conformation and biological activity. In this presentation, we will report the total synthesis of the putative structure of lagunamide C and structure revision of lagunamide C to the related analog odoamide.



Lagunamide C (**1**, Putative structure)
IC$_{50}$ 2.4 nM against A549



Lagunamide A
IC$_{50}$ 2.9 nM against A549



Odoamide
(Revised structure of Lagunamide C)

Referrences

1) Tripathi, A.; Puddick, J.; Prinsep, M. R.; Rottmann, M.; Chan, K. P.; Chen, D. Y.; Tan, L. T. *Phytochemistry* **2011**, *72*, 2369–2375. 2) a) (Isolation) Tripathi, A.; Puddick, J.; Prinsep, M. R.; Rottmann, M.; Tan, L. T. *J. Nat. Prod.* **2010**, *73*, 1810–1814. b) (Biochemical study) Tripathi, A.; Fang, W.; Leong, D. T.; Tan, L. T. *Mar. Drugs* **2012**, *10*, 1126–1137. c) (Structure revision) Dai, L.; Chen, B.; Lei, H.; Wang, Z.; Liu, Y.; Xu, Z.; Ye, T. *Chem. Commun.*, **2012**, *48*, 8697–8699. 3) a) Kessler, H. *Angew. Chem. Int. Ed.* **1982**, *21*, 512–523. b) Weide, T.; Modlinger, A.; Kesselar, H. *Top. Curr. Chem.* **2007**, *272*, 1–50. c) Jwad, R.; Weissberger, D.; Hunter, L. *Chem. Rev.* **2020**, *120*, 9743–9789.

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19日(火) 13:00 ~ 15:40 H935(9号館 [3階] 935)

[H935-2pm] 16. 天然物化学・ケミカルバイオロジー

座長：大神田 淳子、堀 雄一郎

日本語

13:00 ~ 13:20

[H935-2pm-01]

天然変性領域のケミカルリデザインによる植物ホルモン関連転写因子の選択的阻害剤の開発

○高岡 洋輔[1]、劉 瑞琦[1]、李 奇[1]、上田 実[1,2] (1. 東北大院理、2. 東北大院生命科学)

英語

13:20 ~ 13:40

[H935-2pm-02]

無洗浄生細胞イメージングが可能な光スイッチング蛍光分子の開発

○鳥井 健司[1]、Benson Sam[4]、Vendrell Marc[4]、堀 雄一郎[2]、菊地 和也[1,3] (1. 大阪大学、2. 九州大学、3. 大阪大学免疫学フロンティア研究センター、4. エディンバラ大学)

13:40 ~ 13:50

休憩

英語

13:50 ~ 14:10

[H935-2pm-03]

生細胞イメージングのための疎水性バイオイソスター結合型蛍光プローブの開発

○上川 拓也[1]、橋本 明莉[2]、山崎 のぞみ[2]、足立 惇弥[1]、菊地 和也[2,3]、堀 雄一郎[1] (1. 九大院理、2. 阪大院工、3. 阪大免フロ)

英語

14:10 ~ 14:30

[H935-2pm-04]

Synthesis of *Alcaligenes faecalis* Lipid A Conjugates with Tumor-Associated Carbohydrate Tn Antigen Towards the Develoment of Self-Adjuvanting Vaccine

○Davie Kenneth[1], Yusuke Yamanaka[1], Atsushi Shimoyama[1,2], Koichi Fukase[1,2] (1. Department of Chemistry, Graduate School of Science, Osaka University, 2. Forefront Research Centre (FRC), Graduate School of Science, Osaka University)

14:30 ~ 14:40

休憩

英語

14:40 ~ 15:00

[H935-2pm-05]

分子内アザ電子環状反応を利用したがん細胞現地での天然物誘導体合成研究

○寺島 一輝[1]、プラディプタ アンバラ[1]、田中 克典[1,2] (1. 東京工業大学・物質理工学院・応用化学系、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室)

英語

15:00 ~ 15:20

[H935-2pm-06]

化学反応により生きた動物の体内を移動する糖鎖クラスター分子の開発

○山田 健士郎[1]、向峯 あかり[2]、中村 亜希子[2]、草苅 百合子[2]、プラディプタ アンバラ[1]、張 宗哲[1]、田中 克典[1,2] (1. 東京工業大学・物質理工学院・応用化学系、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室)

日本語

15:20 ~ 15:40

[H935-2pm-07]

抗がん活性ジテルペン配糖体はリン酸化依存的な天然変性蛋白質間相互作用を安定化する

○荻野 菜々美[1]、室井 誠[2]、長田 裕之[2]、松本 健[2]、吉田 稔[2]、喜井 勲[1]、大神田 淳子[1] (1. 信州大学学術研究院 (農学系)、2. 理化学研究所　環境資源科学研究センター)

天然変性領域のケミカルリデザインによる植物ホルモン関連転写因子の選択的阻害剤の開発

（東北大院理[1]・東北大院生命科学[2]）○高岡 洋輔[1]・劉 瑞琦[1]・李 奇[1]・上田 実[1,2]

Development of selective inhibitors for plant hormone-related transcription factors based on chemical redesigned intrinsically disordered region peptide

([1]*Graduate School of Science, Tohoku University*, [2]*Graduate School of Life Sciences, Tohoku University*) ○ Yousuke Takaoka[1], Ruiqi Liu,[1] Qi Li,[1] Minoru Ueda,[1,2]

Plant hormones regulate various responses such as plant growth, differentiation or defense by simultaneously controlling multiple transcription factors. Recent reports suggested that intrinsically disordered regions (IDR), which can interact with multiple interacting partners while changing their conformation, play important roles in these signaling pathways. We herein developed selective inhibitors for plant hormone, Jasmonate (JA)-related transcription factors based on the chemically redesigned IDR peptides.

Keywords : Plant hormone; Protein-protein interaction; Intrinsically disordered region; Transcription factor

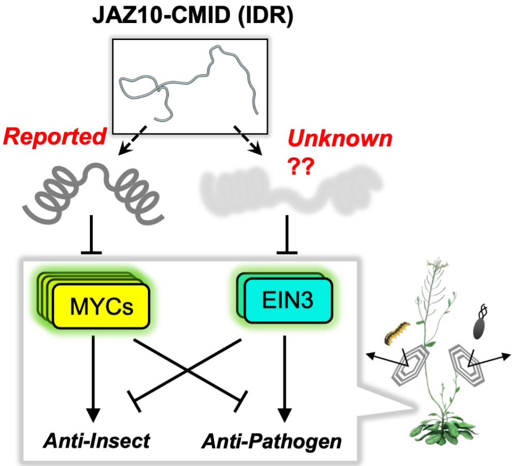


Fig 1. 天然変性領域の JAZ10-CMID が、複数の転写因子を阻害する様子.

植物防御や生長・老化などを制御するジャスモン酸（JA）は、植物体内で転写リプレッサーJAZ の分解を引き起こすことで、複数の転写因子の活性化を一挙に引き起こす。JA の下流では、虫害耐性を制御する MYC ファミリーや、病原菌耐性を制御する EIN3/EIL1 など複数の転写因子が機能しており、これらは遺伝学的に冗長的に機能したり、それぞれがクロストーク制御しあっているために、解析・制御が困難である。最近我々は、JA 応答の脱感作に関わるスプライスバリアント JAZ10.4 の MYC との結合ドメイン（CMID）1,2) が天然変性領域（IDR）であること、および MYC・EIN3 ともに同程度の強度で結合することを示唆する結果を得た（Fig 1）。そこで、CMID の MYC3 との結合フォーム 3)に化学的に構造を固定した人工ペプチドを設計したところ、MYC 活性を選択的に阻害することを見出した。開発したペプチドは、MYC 下流の応答を抑制する一方で、EIN3 下流の応答を亢進し、両者のクロストークを切り分けることに成功した。MYC ファミリーは多くの陸上植物で高度に保存されており、本ペプチド型ツールは植物種を超えて JA シグナル伝達解析に有用な化学ツールとなることが期待される。

1) Moreno, J.E. *et al. Plant Physiol.* **162**, 1006-1017 (2013). 2) Takaoka, Y. *et al. J. Biol. Chem.* **298**, 1015404 (2022). 3) Zhang, F. *et al. Proc. Natl. Acad. Sci.* **114**, 1720-1725 (2017).

Development of Photoswitchable Fluorescent Molecules for No-Wash Live Cell Imaging

([1]*Graduate School of Engineering, Osaka University*, [2]*The University of Edinburgh*, [3]*Faculty of Science*, *Kyushu University*, [4]*Immunology Frontier Research Center*, *Osaka University* ○Kenji Torii,[1] Sam Benson,[2] Marc Vendrell,[2] Yuichiro Hori,[3] Kazuya Kikuchi[1,4]

Keywords: photoswitchable fluorescent molecules, fulgimide, protein labeling, FRET, fluorogenicity

Photoswitchable fluorescent molecules (PSFMs) are valuable tools for tracking cellular dynamics and super-resolution imaging due to their photoswitching ability upon light irradiation. In recent years, photoswitchable cyanine[1] and diarylethene[2] have been applied to super-resolution imaging. However, these molecules require high concentrations of cytotoxic thiol for photoswitching or have poor cell membrane permeability, which hampers live cell applications. Despite the high demand for PSFMs that are suitable for live-cell imaging, no general method has been reported that enables reversible fluorescence control on proteins of interest in living cells.

Herein, we have established a platform to realize reversible fluorescence switching in living cells by adapting a protein labeling system. We have developed a new PSFM, named HTL-Trp-BODIPY-FF, which exhibits strong fluorogenicity upon recognition of Halo-tag protein and reversible fluorescence photoswitching in living cells (Figure 1). The fluorogenicity helps to minimize the fluorescence from unlabeled HTL-Trp-BODIPY-FF and allows no-wash labeling. As for the fluorescence photoswitching, we have used FF (furylfulgimide) as a photochromic FRET quencher[3,4]. The labeled HTL-Trp-BODIPY-FF exhibited reversible fluorescence switching upon light irradiation with higher photostability compared to the unlabeled one, assisted by the Halo-tag surface that prevents intermolecular aggregation. This is the first example of a PSFM that can be applicable to a general-purpose Halo-tag protein labeling system for no-wash live-cell imaging[4]. In this conference, we will report on the detailed molecular designs, photophysical properties, and biological experiments of HTL-Trp-BODIPY-FF.

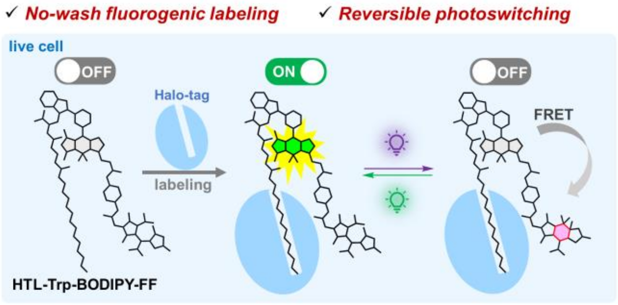


Figure 1. Schematic of this study

---

1) J. Kwon, *et al. Sci. Rep.* **2015**, *5*, 17804

2) (a) B. Roubinet, *et al. Angew. Chem. Int. Ed.* **2016**, *55*, 15429. 3. **(b)** K. Uno, *et al. J. Am. Chem. Soc.* **2019**, *141*, 16471.

3) K. Torii, *et al. Anal. Chem.* **2023**, *95*, 8834.

4) K. Torii, *et al. Chem. Sci.* **2024** (in press) DOI: 10.1039/d3sc04953a

Development of Hydrophobic Bioisostere Conjugated Fluorescent Probes for Live-Cell Imaging

([1]*Graduate School of Science, Kyushu University*, [2]*Graduate School of Engineering, Osaka University*, [3]*Immunology Frontier Research Center, Osaka University*)○Takuya Kamikawa[1], Akari Hashimoto[2], Nozomi Yamazaki[2], Junya Adachi[1], Kazuya Kikuchi[2, 3], Yuichiro Hori[1]

Keywords: Bioisostere, Fluorescent probe, Live-cell imaging, PYP-tag, Halo tag

Protein-labeling probes with membrane permeability are important tools for the visualization of intracellular protein of interests (POIs). Cationic dye derivatives that show favorable optical properties (*e.g.* high brightness and photostability) and water solubility are useful scaffolds for the protein-labeling probes. Indeed, cationic probes using the derivatives can be used as mitochondrial-targeting probes owing to their mitochondrial accumulation. However, the mitochondrial accumulation caused serious artifacts in the visualization of non-mitochondrial proteins. To suppress the artifacts, anionic groups such as carboxylate and sulfonate groups are introduced into the probes; this strategy mostly leads to the decrease of their membrane permeability. As a solution to this problem, anionic groups with relatively high hydrophobicity are expected to maintain the membrane permeability of the probes, suppressing nonspecific organelle accumulation. Based on this discussion, we focused on hydrophobic bioisosteres of carboxylic acid as the introducing group to develop membrane-permeable probes.

In this presentation, we will report a design strategy for bioisostere-conjugated probes that enable intracellular protein imaging using protein tag labeling system. We successfully developed several bioisostere-conjugated probes that show membrane permeability and suppress non-specific accumulation in the mitochondria. In addition, our design strategy can be applied to two different protein labeling systems, HaloTag and PYP-tag systems. We further demonstrate that these probes can be used for the visualization of intracellular multiple localizations of POIs in living cells.

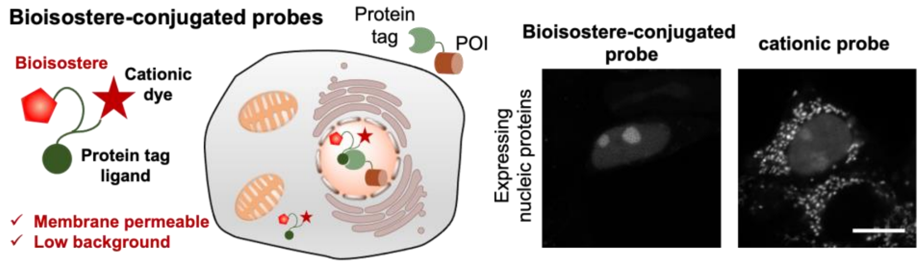


Figure (Left) Schematic illustration of the probe design strategy using a hydrophobic bioisostere for intracellular protein imaging using protein tag labeling system. (Right) Fluorescence images of HEK293T cells expressing nucleic proteins stained with bioisostere-conjugated probe and cationic probe. Scale bar 10 μm.

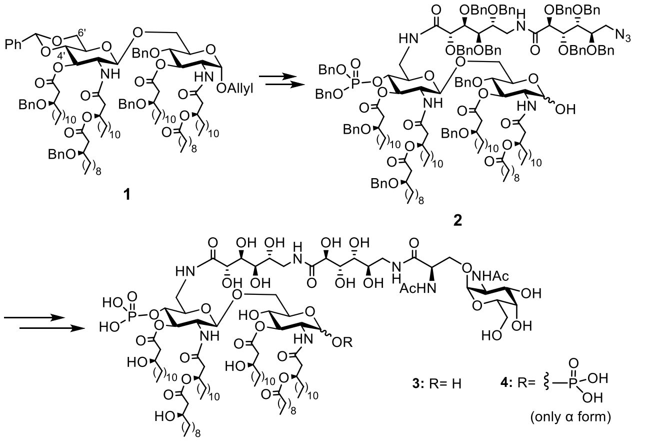
Synthesis of *Alcaligenes faecalis* Lipid A Conjugates with Tumor-Associated Carbohydrate Tn Antigen Towards the Development of Self-Adjuvanting Vaccine

(*[1]Department of Chemistry, Graduate School of Science, Osaka University; [2]Forefront Research Center (FRC), Graduate School of Science, Osaka University)* ○Davie Kenneth[1], Yusuke Yamanaka[1], Atsushi Shimoyama[1,2], Koichi Fukase[1,2]

Keywords: lipid A, adjuvant, self-adjuvanting vaccine, sugar chain mimic linker, *Alcaligenes faecalis*

Lipopolysaccharide (LPS) and its active center, lipid A, of Gram-negative bacterial outer membrane are representative innate immunostimulants which have potential to function as vaccine adjuvants. However, canonical *E. coli* LPS and lipid A induce lethal toxicity due to excessive inflammatory effects hence not safe for adjuvant utilization. We have revealed that symbiotic *Alcaligenes faecalis* LPS and synthetic *A. faecalis* lipid A (AfLA)[1] induce effective antigen-specific IgA production without toxicity[2] hence promising adjuvant candidates.

Meanwhile, self-adjuvanting vaccine strategy, in which antigen and adjuvant are covalently linked has recently been well studied especially in the development of carbohydrate-based vaccines[3,4]. The strategy enhances active and simultaneous uptake of antigen with the conjugated innate immune ligand (adjuvant) by same immune cell thereby promoting efficient antigen-specific immune responses.



On the other hand, there are only few reports of lipid A-based self-adjuvanting vaccines[4,5] because structural modifications often inactivate lipid A. Thus a simple and universal conjugation method that can retain significant lipid A activity is required. Here we conjugated *A faecalis* lipid As with tumor-associated carbohydrate Tn antigen by employing a strategy which mimics natural LPS structure; linking 6'-position of lipid A to the antigen via hydrophilic sugar-chain mimic linker based on D-mannitol. The synthetic process involved azidation of 6'-position of **1** followed by 4'-phosphorlyation and then condensation of the linker and allyl group cleavage to yield **2**. Thereafter, the condensation of Tn-antigen to **2** was followed by global deprotection to obtain conjugate **3**. Meanwhile, condensation of the Tn antigen to **2** was followed by anomeric phosphorylation and subsequently, global deprotection was performed to synthesize conjugate **4**. Both conjugates **3** and **4** showed significant IL-6 cytokine induction at the same level as the unmodified lipid As.

1) A. Shimoyama, *et al., Angew. Chem. Int. Ed.* **2021**, 60, 10023. 2) K. Yoshii, *et al., Microorganisms,* **2020***,* 8, 1102. 3) K. Fukase, *et al., Angew. Chem. Int. Ed.*, **2018**, 57, 8219. 4) Z. Guo, *et al., ACS Chem. Biol.* **2012**, *7*, 235. 5) J. Cod'ee, *et al., J. Med. Chem.* **2020**, *63*, 11691**.**

分子内アザ電子環状反応を利用したがん細胞現地での天然物誘導体合成研究

（東工大物質理工 [1]・理研 開拓研究本部 田中生体研 [2]）○寺島 一輝 [1]・プラディプタ アンバラ [1]・田中 克典 [1,2,]

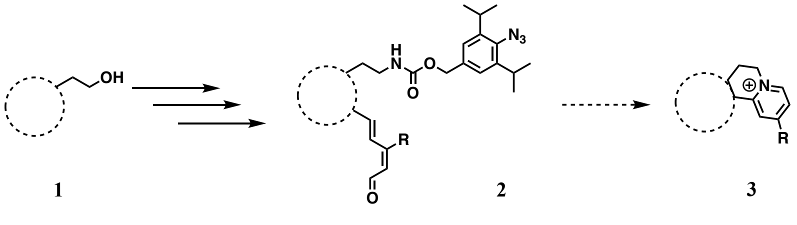
Synthetic study of natural product derivative in cancer cells via intramolecular aza electrocyclization

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Biofunctional Synthetic Chemistry Laboratory, Cluster for Pioneering Research, RIKEN,*) ○Kazuki Terashima,[1] Ambara R. Pradipta,[1] Katsunori Tanaka[1,2]

We have previously reported that cancer cells overexpress acrolein. Based on this finding, we have developed a prodrug that takes advantage of the reaction between phenyl azide and acrolein in cancer cells to deprotect the amino group on the drug molecule.[1] Our aim in the present study is to synthesize a natural product derivative **3** with a zwitterionic bicyclic backbone from an inactive precursor compound **2**. This will be achieved by deprotecting the amino group to induce a rapid intramolecular 6π-azaelectrocyclization directly in cancer cells. We expect the final products to have anticancer activity. We will be presenting further details about our findings at the symposium.

Keywords: Acrolein, Cycloaddition, Phenyl azide, In vivo synthesis, On-site synthesis

これまでに我々は、がん細胞においてアクロレインが特異的に大量発現していることを発見し、さらにフェニルアジド分子がアクロレイン分子と生体内においても選択的に反応できることを利用し、薬分子上のアミノ基を脱保護するプロドラッグの開発に成功した [1)]。そこで今回我々は、このがん細胞上でのアミノ基の脱保護を起点として分子内 6π-アザ電子環状を含む一連の分子内反応を起こすことで、不活性な前駆体化合物 **2** から一挙にがん現地で抗がん活性を持つ天然物 **3** を合成し、治療を行う計画を考えた。ここでは、市販で購入可能な化合物 **1** から前駆体化合物 **2** の合成、及び化合物 **2** から **3** への変換、化合物 **3** の細胞毒性に関して検討をおこなったのでこれらの成果について報告する。



1. A. R. Pradipta, P. Ahmadi, K. Terashima, K. Muguruma, M. Fujii, T. Ichino, S. Maeda, K. Tanaka, *Chem. Sci.* **2021**, *12*, 5438-5449.

化学反応により生きた動物の体内を移動する糖鎖クラスター分子の開発

（東工大物質理工[1]・理研 開拓研究本部 田中生体研[2]）○山田 健士郎[1]・向峯 あかり[2]・中村 亜希子[2]・草刈 百合子[2]・プラディプタ アンバラ[1]・張 宗哲[1]・田中 克典[1,2]
Development of glyco-cluster molecule translocating in living mice triggered by in vivo chemical reaction. ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Biofunctional Synthetic Chemistry Laboratory*, *Cluster for Pioneering Research, RIKEN*) ○Kenshiro Yamada,[1] Akari Mukaimine,[2] Akiko Nakamura,[2] Yuriko Kusakari,[2] Ambara R. Pradipta,[1] Tsung-che Chang,[1] Katsunori Tanaka[1,2]

N-type glycans are the biomolecules that have important role for interaction between cells and proteins.Previously we have found glycoalbumin molecules modified with *N*-glycans on albumin recognize various types of cancer cells depending on their glycan modification patterns (glycan pattern recognition). Here, we developed an innovative glycoalbumin capable of undergoing transformation and remodeling of its glycan pattern in vivo, which induced its translocation from the initial target to a second one. In this presentation, we will describe an investigation of pattern recognition remodeling by in vivo chemical reaction in living mice.

Keywords: Glycan pattern recognition; N-type glycan; In vivo synthesis

*N*型糖鎖は生体内での細胞・タンパク質間での相互作用において重要な役割を果たす生体分子である。これまでに我々は，アルブミンに*N*型糖鎖約10分子を修飾した糖鎖アルブミン分子が，がん細胞周辺に集積すること，さらに糖鎖の修飾パターンに応じて種々のがん細胞へ異なる強度の認識（パターン認識）が発現することを見出し，糖鎖アルブミン分子を用いたがん治療研究へと発展させてきた[1]。糖鎖パターン認識をさらに活用する方法として，生体内化学反応により糖鎖パターン認識を更新し，新たな標的へと向かって体内を移動する糖鎖アルブミン分子の開発を試みた。本発表では，生きたマウス体内での化学反応スイッチによるパターン認識更新の検討について述べる。

1) K. Vong, T. Tahara, S. Urano, I. Nasibullin, K. Tsubokura, Y. Nakao, A. Kurbangalieva, H. Onoe, Y. Watanabe, K. Tanaka, *Sci. Adv.*, **2021**, *7*, eabg4038.

抗がん活性ジテルペン配糖体はリン酸化依存的な天然変性蛋白質間相互作用を安定化する

（信州大農 [1]・理研 CSRS[2]）○荻野 菜々美 [1]・室井 誠 [2]・長田 裕之 [2]・松本 健 [2]・吉田 稔 [2]・喜井 勲 [1]・大神田 淳子 [1]

Antitumor diterpene glucoside stabilizes phosphorylation-dependent protein-protein interactions of intrinsically disordered proteins

([1]*Institution of Agriculture, Shinshu University*, [2] *RIKEN Center for Sustainable Resource Science, RIKEN*) ○Nanami Ogino[1], Makoto Muroi[2], Hiroyuki Osada[2], Ken Matsumoto[2], Minoru Yoshida[2], Isao Kii[1], Junko ohkanda[1]

Fusicoccin (FC) is a diterpene glucoside that stabilizes protein-protein interactions (PPIs) between 14-3-3 and phosphoproteins. While FC is inactive in cancer cells, 12-deoxy FC exhibits significant antiproliferative activity. Here, we report the details of the mechanism of action of 12-deoxy FC, which turns out to be shown to upregulate PPI between 14-3-3 and GIGYF2, a highly intrinsically disordered scaffold of a mRNA translation repression complex. 12-Deoxy FC was also found to enhance binding of GIGYF2 to a mRNA binding protein TTP, suggesting that the PPI between 14-3-3 and GIGYF2 is necessary for the formation of the repressive complex. Furthermore, the coimmunoprecipitation experiments using deletion mutants of GIGYF2 identified that pS546 as the binding site of 12-deoxy FC and 14-3-3, which locates near the TTP-binding site. These results clearly indicate that 12-deoxy FC upregulates PPI of GIGYF2 and 14-3-3, suppresses protein synthesis, and inhibits proliferation. Since TTP-dependent translational repression has been shown to be implicated in stress granules, the results shown here suggest that 14-3-3 may play general roles in the regulation of cellular stress responses. *Keywords : Transient protein-protein interactions; Fusicoccin; 14-3-3 Proteins; Intrinsically disordered proteins; posttranslational modification*

Fusicoccin (FC)は、14-3-3 と Ser/Thr リン酸化蛋白質との相互作用(PPI)を安定化するジテルペン配糖体である。天然型 FC は不活性である一方、12-deoxy FC 誘導体は低酸素環境で強い細胞増殖阻害と制癌活性を有する。本研究では、14-3-3 インタラクトーム解析により 12-deoxy FC の作用機序の詳細を明らかにしたので報告する。

14-3-3 結合蛋白質の定量的プロテオミクス解析の結果、12-deoxy FC 存在下で結合が増強する蛋白質として、mRNA 翻訳抑制複合体の足場で全長の 76%が構造を持たない天然変性蛋白質(IDR)の GIGYF2 を同定した。12-Deoxy FC は mRNA 結合蛋白質 TTP と GIGYF2 との相互作用も亢進することが判り、14-3-3 と GIGYF2 の PPI が翻訳抑制複合体を安定化させることが示唆された。これを裏付けるように、12-deoxy FC 処理により細胞の新生蛋白質量が減少し、この効果は GIGYF2 をノックダウンすると解除された。さらに GIGYF2 の欠損変異体および点変異体を用いた共免疫沈降及びリン酸化ペプチドを用いた蛍光偏光滴定試験を行った結果、TTP 結合部位近傍の S546 が作用点であることが示された。興味深いことに TTP の GIGYF2 作用部位近傍にも 14-3-3 結合配列が存在するため、2 量体である 14-3-3 が GIGYF2 と TTP の PPI を直接誘導している可能性が考えられる。以上のように、GIGYF2 と 14-3-3 の PPI の詳細を初めて解明し、12-deoxy FC によるリン酸化依存的な IDR の PPI 安定化と蛋白質合成抑制による増殖阻害作用機序を明らかにした。TTP が関わる翻訳抑制機構はストレス由来の液液相分離と関連することが示唆されており、ストレス応答における 14-3-3 の生物学的役割を示唆するものとして興味深い。

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19日(火) 9:00 ~ 11:30 H932(9号館 [3階] 932)

[H932-2am] 17. 生体機能関連化学・バイオテクノロジー

座長：愛場 雄一郎、岡村 秀紀

日本語

9:00 ~ 9:20

[H932-2am-01]

認識領域をずらしたparallel型PNAによる2本鎖DNAへのインベージョン

○望月 直哉[1]、柴田 将成[1]、愛場 雄一郎[1]、伊藤 公太[1]、有安 真也[1]、荘司 長三[1] (1. 国立大学法人東海国立大学機構 名古屋大学)

日本語

9:20 ~ 9:40

[H932-2am-02]

ホスト–ゲスト相互作用を利用した遺伝子発現制御法の開発

○矢尾 健行[1,2]、岡村 秀紀[1,2]、永次 史[1,2] (1. 東北大多元研、2. 東北大院理)

英語

9:40 ~ 10:00

[H932-2am-03]

環状化オリゴDNAによる擬ロタキサン形成とその形成加速へのアプローチ

○桑原 和貴[1,2]、鬼塚 和光[1,2]、矢島 さやか[1,2]、山野 雄平[1]、永次 史[1,2] (1. 東北大多元研、2. 東北大院理)

10:00 ~ 10:10

休憩

英語

10:10 ~ 10:30

[H932-2am-04]

ボラノホスフェートDNAのブロック合成法の確立

○高橋 裕平[1]、加藤 樹[1]、佐藤 一樹[1]、和田 猛[1] (1. 東京理科大学)

英語

10:30 ~ 10:50

[H932-2am-05]

人工核酸L-αTNAの長鎖伸長反応を目指したケミカルライゲーションの反応機構解析

○沖田 ひかり[1]、村山 恵司[1]、浅沼 浩之[1] (1. 名大院工)

英語

10:50 ~ 11:10

[H932-2am-06]

New Data Science in Nucleic Acids Chemistry (10): Quantitative analysis for factors affecting i-motif formation in living cells estimated by the pseudo-cellular system

○Kun Chen[1], Hisae Tateishi-Karimata[1], Naoki Sugimoto[1,2] (1. Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, 2. Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University)

英語

11:10 ~ 11:30

[H932-2am-07]

核酸化学のNew Data Science (11): G-四重らせんとi-モチーフ構造の形成を介したがん細胞内における転写制御機構の解明

〇建石 寿枝[1]、川内 敬子[2]、凌 一葦[3]、奥田 修二郎[3,4]、杉本 直己[1,2] (1. 甲南大学　先端生命工学研究所（FIBER)、2. 甲南大学　フロンティアサイエンス研究科(FIRST)、3. 新潟大学医学部メディカルAIセンター、4. 新潟大学医歯学総合)

日本化学会 第104春季年会 (2024)

認識領域をずらした parallel 型 PNA による 2 本鎖 DNA へのインベージョン

（名大院理 [1]）○望月 直哉 [1]・柴田 将成 [1]・愛場 雄一郎 [1]・伊藤 公太 [1]・有安 真也 [1]・荘司 長三 [1]

Recognition of Double-Stranded DNA with Multiple Pairs of Shifted Parallel PNAs

([1]*Graduate School of Science, Nagoya University*, [2]) ○Naoya Mochizuki,[1] Masanari Shibata,[1] Yuichiro Aiba,[1] Kota Ito,[1] Shinya Ariyasu,[1] Osami Shoji[1]

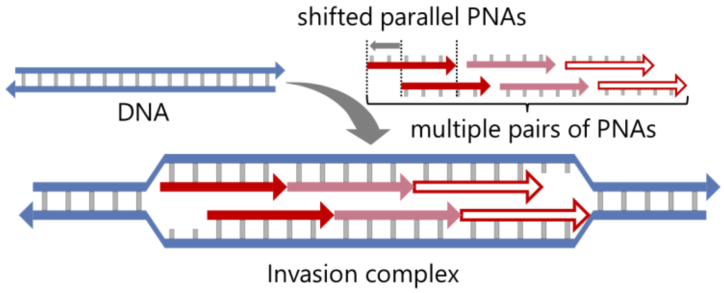
Peptide nucleic acid (PNA) [1] is a type of artificial nucleic acid in which the sugar-phosphate backbone of DNA is replaced by an *N*-(2-aminoethyl)glycine backbone. Since PNA has no negative charge on its backbone, there is no electrostatic repulsion between PNA and DNA, and PNA exhibits high DNA binding affinity. Furthermore, PNA can directly recognize the sequences in double-stranded DNA through a unique recognition called "invasion".[2]

In our laboratory, we have developed a novel invasion of parallel-stranded PNAs that does not require the modified nucleobases of PNA.[3] In this study, we aimed to make the parallel-stranded PNA invasion adoptable to a variety of applications. We confirmed that DNA recognition is possible when using multiple pairs of PNAs even in different sequence combinations. In addition, we succeeded in improving DNA recognition by shifted parallel-stranded PNAs.

Keywords : PNA; Invasion; DNA; artificial nucleic acids; genetic engineering

ペプチド核酸（PNA）[1]は、DNA の糖-リン酸骨格を *N*-(2-aminoethyl)glycine 骨格に置き換えた人工核酸である。PNA は骨格に負電荷を持たないことから、DNA と静電反発を生じず、DNA に対する高い結合力を示す。その結果、PNA が 2 本鎖中に潜り込みながら DNA を認識する「インベージョン」という結合様式が可能である。[2]

当研究室では、2 本の PNA を parallel 型で設計することで、これまでインベージョンに必要であった修飾核酸塩基を必要としない新規インベージョンの開発に成功している。[3]本研究では、この parallel 型 PNA インベージョンによる DNA 認識の適応範囲拡大を目指した。複数組の PNA を用いることで、様々な配列において DNA 認識が可能であることを明らかにした。さらに、各 PNA の認識領域を互い違いに設計することで、インベージョン効率の向上に成功した。



1) P. E. Nielsen, *et al., Science*, **1991**, 254, 1497. 2) Y. Aiba, *et al., Appl. Sci.*, **2022**, 12, 3677.
3) M. Shibata, *et al., ChemRxiv*, **2022**, doi:10.26434/chemrxiv-2022-wq3dm.

ホストーゲスト相互作用を利用した遺伝子発現制御法の開発

（東北大多元研 [1]・東北大院理 [2]）○矢尾 健行 [1,2]・岡村 秀紀 [1,2]・永次 史 [1,2]

Development of gene expression controlling system driven by host-guest interaction

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University.*, [2]*Graduate School of Science, Tohoku University*) ○Takeyuki Yao,[1,2] Hidenori Okamura,[1,2] Fumi Nagatsugi[1,2]

Artificial genes provide numerous applications ranging from elucidation of biological functions to gene expression-based therapeutics such as DNA vaccines. Lack of a methodology to control gene expression at arbitrary locations and timing is a challenge. To this end, we designed adenosine derivatives modified with cucurbit[7]uril (CB[7])-specific guest moieties; these nucleoside derivatives were expected to form a stable duplex by base-pairing with thymidine whereas in the presence of CB[7] forms a bulky host-guest complex to dissociate the duplex structure. Furthermore, we anticipated that addition of a high-affinity guest would induce guest exchange reaction to reassociate the duplex structure. By utilizing these nucleosides, we successfully demonstrated the reversible control of base pair formation and artificial gene expression control *in vitro*. In the presentation, we will report the details of molecular design and reversible control of gene expression.

Keywords : Functional nucleic acid; Host-guest interaction; Gene expression control; Supramolecular chemistry

人工遺伝子の発現を任意の場所とタイミングで制御できる方法論は、生命現象の解明のほか、合成生物学や創薬研究に有用である。本研究では、二重鎖の形成と解離を基盤とする遺伝子発現制御法の開発を目的として、ホストーゲスト相互作用によって塩基対形成を可逆的に制御できるヌクレオシド誘導体を設計した（**Fig. 1**）。本誘導体は、CB[7]の非存在下ではチミジンと塩基対を形成し安定な二重鎖を形成するが、CB[7]の存在下では、強固かつかさ高い CB[7]-ゲスト複合体形成により、二重鎖構造を解離すると考えられる。さらに、CB[7]に対してより強く結合するゲスト分子を添加することでゲスト交換が生じ、二重鎖構造の再形成を誘起できると期待した。本設計概念を検証したところ、二重鎖 DNA の解離と形成を可逆制御できることを確認した。さらに、本誘導体を用いることで、無細胞系における人工遺伝子発現の制御にも成功した。発表では、分子設計と遺伝子発現の可逆制御の詳細について議論する。

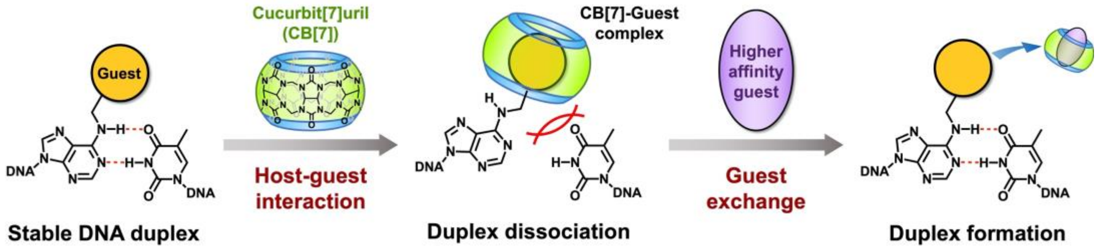


Fig. 1 ホストーゲスト相互作用による塩基対形成の可逆制御

Pseudorotaxane formation by cyclized oligo DNAs and approach to accelerating its formation

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Department of Chemistry, Graduate School of Science, Tohoku University*) ○ Kazuki Kuwahara[1,2], Kazumitsu Onizuka[1,2], Sayaka Yajima[1,2], Yuuhei Yamano[1], Fumi Nagatsugi[1,2]

Keywords: Interlocked molecule; pseudorotaxane; cyclized nucleic acids

Since interlocked molecules such as rotaxane and catenane have unique properties that are not found in ordinary covalent molecules, they have been actively applied to artificial molecular machines driven by external stimuli. In nucleic acid chemistry, interlocked and threaded molecular structures have been studied for DNA nanotechnology, topological labeling, and complex stabilization. In our laboratory, we have discovered that a pseudorotaxane structure is spontaneously formed upon mixing cyclized DNA with a complementary target nucleic acid.1) However, complexity of the synthesis of cyclized nucleic acids made further investigation difficult. In this study, we successfully simplified the synthesis of pseudorotaxane-forming oligo DNAs (rfODN) and investigated the effects of linker position and length on the formation of the pseudorotaxane structures. These rfODNs formed pseudorotaxane structure at 37 °C with high efficiency (~90%, 2 h) simply by mixing with the complementary target RNA and rfODNs with longer linker showed the more efficient formation. Interestingly, rfODN with a ring at the 5'-side was found to be highly efficient in the formation of pseudorotaxane with RNA having a complementary region at the 3'-side. In contrast, rfODN with a ring at the 3'-side forms a highly efficient pseudorotaxane with RNA having a complementary region at the 5'-side. This result suggests that the threading direction can be controlled by changing the position of the ring (Figure 1). In addition, we found that the pseudorotaxane formation was accelerated by extending the duplex from the complementary sequence. We will report on them in detail.

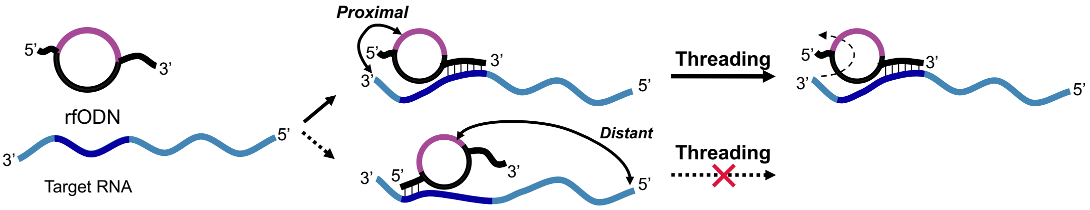


Figure 1. Schematic illustration of threading direction control.

1) K. Onizuka, T. Chikuni, T. Amemiya, T. Miyashita, K. Onizuka, H. Abe and F. Nagatsugi, *Nucleic Acids Res.* **2017**, *45*, 5036−5047.
2) K. Kuwahara, S. Yajima, Y. Yamano, F. Nagatsugi, K. Onizuka, *Bioconjugate Chem.* **2023**, *34*, 696−706.

ボラノホスフェート DNA のブロック合成法の確立

○高橋 裕平[1]、加藤 樹[1]、佐藤 一樹[1]、和田 猛[1] (1. 東京理科大学)

Development of the Convergent Synthesis of Boranophosphate DNA by an *H*-boranophosphonate Method

([1]Tokyo University of Scienece) ○Yuhei Takahashi[1], Itsuki Kato[1], Kazuki Sato[1], Takeshi Wada[1]

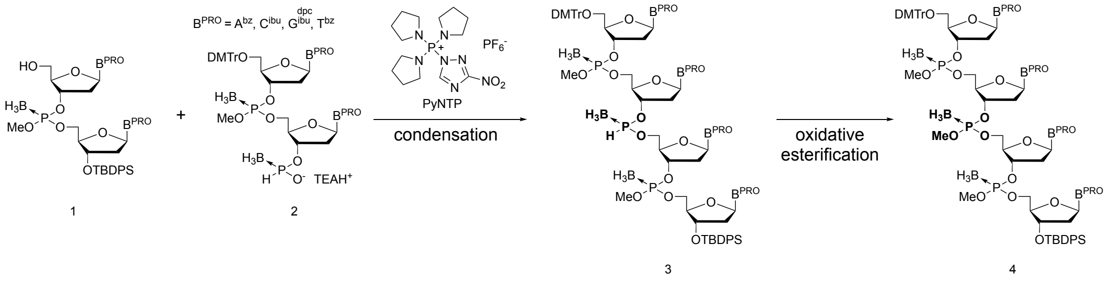
Boranophosphate DNAs (PB-DNAs), which have been suggested to be useful as antisense oligonucleotides, are difficult to synthesize by the conventional phosphoramidite method. In our laboratory, we developed the *H*-boranophosphonate method for the synthesis of boranophosphate DNAs. However, the synthesis of oligomer was conducted only by solid-phase synthesis, and large scale synthesis of PB-DNAs is remaining issue.

In this study, we apply this method to the block synthesis of boranophosphate oligonucleotides in solution by converting *H*-boranophosphonate diester **3** to the more stable boranophosphotriester **4** after condensation of *H*-boranophosphonate monoester **1** using a phosphonium type condensing reagent (PyNTP). By using this synthetic strategy, we have synthesized a boranophosphate DNA tetramer containing four nucleobases by condensation of the dimer building blocks followed by oxidative esterification of the internucleotidic bond.

Keywords : boranophosphate, H-boranophosphonate method, convergent synthesis

siRNA やアンチセンス核酸として有用であると示唆されているボラノホスフェート核酸は、一般的な核酸合成法であるホスホロアミダイト法では合成が困難である。当研究室は、*H*-ボラノホスホネート法を開発し、ボラノホスフェート核酸の合成を達成した。しかし、本手法でのオリゴマー合成は固相法に限られており、反応のスケールアップが困難であるという課題が残っている。

そこで本研究では、ホスホニウム型縮合剤を用いて化合物 **1** と *H*-ボラノホスホネートモノエステル **2** を縮合後、得られた *H*-ボラノホスホネートジエステル **3** をより安定なボラノホスホトリエステル **4** へと変換することで、本手法をブロック合成に応用し、液相にて長鎖のボラノホスフェート核酸のブロック合成を検討した。本合成戦略を用いて 2 量体のビルディングブロック同士の縮合・酸化を行うことで 4 種核酸塩基を有するボラノホスフェート核酸 4 量体の合成を達成したので、その詳細を報告する。



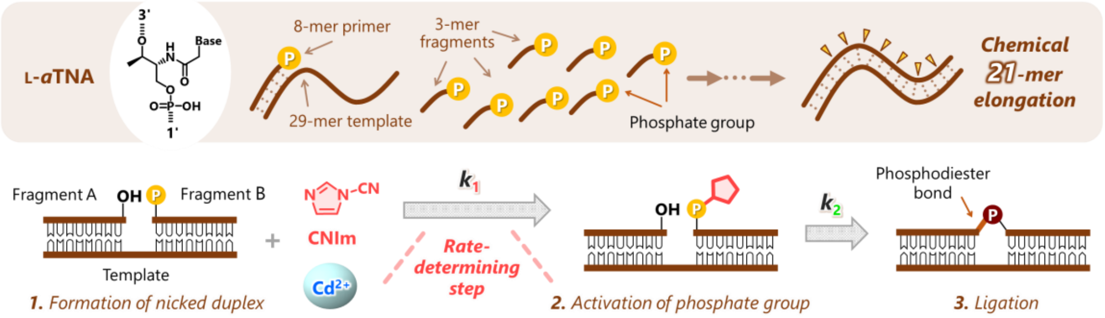
Reaction mechanism analysis of chemical ligation for long-chain elongation of L-*a*TNA

(*Graduate School of Engineering, Nagoya University*) ○Hikari Okita, Keiji Murayama, Hiroyuki Asanuma

Keywords: Chemical ligation; Artificial nucleic acid; Template-directed synthesis; DNA

DNA functions as a versatile biological tool due to its sequence specificity, but it is vulnerable to enzymatic degradations. Many artificial nucleic acids have been developed by chemical modification of DNA scaffold to provide enzyme resistivity. We have designed *acyclic* L-threoninol nucleic acids (L-*a*TNA) by changing D-ribose scaffold to acyclic scaffold. L-*a*TNA can form highly stable homo-duplex compared with DNA and it can hybridize with complementary strands of DNA and RNA.[1] However, since natural enzyme does not recognize L-*a*TNA, it cannot be a substrate of useful enzymes such as polymerase and ligase.

We have recently developed nonenzymatic pseudo-primer extension reactions by using *N*-cyanoimidazole (CNIm) and Mn^{2+} instead of enzymes, which enabled template-directed elongation of 9-mer L-*a*TNA from random trimer fragments.[2] If we achieve much efficient template-directed synthesis, design of L-*a*TNA aptamer, creation of artificial life, and nanotechnology based on L-*a*TNA will be possible. For this purpose, we focused on CNIm/M^{2+} system and ligation mechanisms were analyzed in detail to improve the efficiency of L-*a*TNA replication. It was revealed that Cd^{2+}, Ni^{2+}, and Co^{2+} dramatically increased the ligation rate more than Mn^{2+} for not only L-*a*TNA but also DNA ligations.[3] Furthermore, we performed kinetic analysis of chemical ligation of L-*a*TNA. The ligation proceeds mainly via three steps: (i) duplex formation between fragments and a template, (ii) activation by CNIm binding to phosphate group, and (iii) ligation of two fragments by generating a phosphodiester bond. We found that the activation was rate-determining step and stabilization of 3'-phopahte group of L-*a*TNA at nick site accelerated the ligation rate. Based on these results, we finally achieved elongation of 21-mer L-*a*TNA with Cd^{2+} and random trimers by reversing the elongation direction suitable for stabilizing phosphate group.[3]



1) K. Murayama *et al.*, *Chem. Commun.*, **2015**, *51*, 6500. 2) K. Murayama, H. Okita *et al.*, *Nat. Commun.*, **2021**, *12*, 804. 3) H. Okita *et al.*, *J. Am. Chem. Soc.*, **2023**, *145*, 17872.

New Data Science in Nucleic Acids Chemistry (10): Quantitative analysis for factors affecting i-motif formation in living cells estimated by the pseudo-cellular system

(*[1]Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, [2]Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University*) ○Kun Chen,[1] Hisae Tateishi-Karimata,[1] Naoki Sugimoto[1,2]

Keywords: Cancer; i-motif; Molecular crowding; Pseudo-cellular system; Living cell

The structural versatility of DNA is profoundly influenced by its surrounding environments, with the canonical duplex structure being just one facet of its dynamic conformational landscape. Beyond the conventional duplex, DNA exhibits the ability to adopt alternative structures such as triplexes, G-quadruplexes and i-motifs. The intricacies of DNA folding are further modulated by environmental factors, including the presence of cosolutes such as polyethylene glycol (PEG) and Ficoll, as well as cations like K^+ and Mg^{2+}.[1] These factors have been demonstrated to either stabilize noncanonical DNA structures or induce destabilization of short duplexes, thus adding an additional layer of complexity to the regulation of DNA stability.[2] However, molecular environment within living cells influencing i-motif structures are unknown. Intracellular environments are densely populated with an array of macromolecules, creating a highly crowding conditions and ionic strength setting for DNA structures like i-motif (Figure 1).

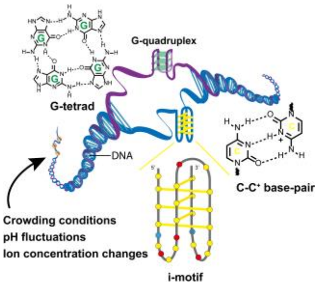


Figure 1. Scheme of intracellular environments providing conditions for i-motif formation.

The *CDH1* gene encodes E-cadherin, which is a protein responsible for cell adhesion. *CDH1* is a tumor suppressor gene, which contains many C-rich sequences that can form i-motif. In this study, as a typical example of an oncogene, we selected some C-rich sequences from *CDH1* to conduct a systematic study of pH dependence examining the relationship between intracellular conditions and i-motif dynamics in the context of cancer. Firstly, we employed biophysical techniques such as CD and UV spectroscopy to examine the stability of *CDH1*-derived C-rich sequences under varying pH and ion concentrations with cosolute mimicking cancer cell environments. Typically, we use PEG as a common cosolute. For example, i-motifs with PEG8000 is stable than in dilute solution. Our results demonstrated that i-motif stability was markedly altered in cosolute conditions, suggesting crowding conditions influences largely i-motif formation. In this presentation, we will show quantitative analysis of the determinants impacting i- motif formation within living cells, utilizing a novel pseudo-cellular system.

1) S. Takahashi, N. Sugimoto, *Chem. Soc. Rev.* **2020**, *49*, 8439. 2) H. Tateishi-Karimata, K. Kawauchi, N. Sugimoto, *J. Am. Chem. Soc.* **2018**, *140*, 642.

New Data Science in Nucleic Acids Chemistry (11): Transcriptional regulation in cancer cells induced by formation of G-quadruplexes and i-motifs

(*[1]Frontier Institute for Biomolecular Engineering Research (FIBER) Konan University, [2]Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University, [3]Graduate School of Medical and Dental Sciences, Niigata University*)
○ Hisae Tateishi-Karimata,[1] Keiko Kawauchi,[2] Yiwei Ling,[3] Shujiro Okuda,[3] Naoki Sugimoto,[1,2]

Keywords: Molecular crowding; Cancer cell; G-quadruplex; i-motif; Transcript mutation

Formation of non-canonical DNA structures in response to the environment can regulate the expression of disease-related genes. It is known that the cell shape changes during with malignant transformation (Figure 1).[1] In addition, because of the increased expression of the cytoskeleton (F-actin), the environments in malignant cancer cells are more crowded than those in normal cells (Figure 1).[1] The changes should alter the intracellular molecular environments, affecting biological reactions responses to the structure and stability of nucleic acids. We have reported that G-quadruplexes are stabilized in normal and mild cancer cells and destabilized in a malignant cancer cells,[2] and that these changes regulate transcription although the detailed mechanism is still unknown. In this study, we investigated the effects of the intracellular environments on nucleic acids associated with malignant transformation of cancer. As results, the malignancy of the cancer cells is higher, the expression level of the cytoskeleton, which creates an intracellular crowding condition, was markedly increased. Moreover, we found that G-quadruplexes formed in normal cells, while, i-motifs were shown to form in malignant cancer cells. In the presentation, we will explain the effects of formation for G-quadruplexes and i-motifs on the transcriptional mutation.

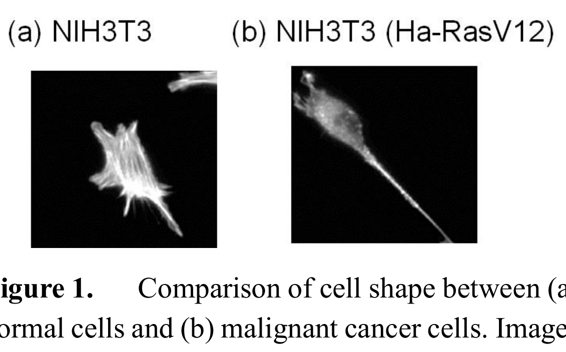


Figure 1. Comparison of cell shape between (a) normal cells and (b) malignant cancer cells. Images were taken with a confocal microscope. The cytoskeleton, which is F-actin, is shown in white.

1) S. Yamauchi, Y. Hou, A. Kunyao Guo, H. Hirata, W. Nakajima, A. Kia Yip, C. Yu, I. Harada, K. Chiam, Y. Sawada, N. Tanaka, K. Kawauchi, *J Cell Biol,* **2014**, *204*, 1191.
2) H. Tateishi-Karimata, K. Kawauchi, N. Sugimoto, *J. Am. Chem. Soc.* **2018**, *140*, 642.

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19日(火) 9:00 ~ 11:00 H936(9号館 [3階] 936)

[H936-2am] 17. 生体機能関連化学・バイオテクノロジー

座長：秋葉 宏樹、村岡 貴博

日本語
9:00 ~ 9:20
[H936-2am-01]
立体構造情報に基づいた抗原テンプレート反応の開発

○秋葉 宏樹[1,2]、西山 健太郎[1]、永田 諭志[2]、津本 浩平[2,3]、鎌田 春彦[1,2]、大野 浩章[1,2] (1. 京大院薬、2. 医薬健栄研、3. 東大院工)

日本語
9:20 ~ 9:40
[H936-2am-02]
光操作のための小分子光スイッチ結合性人工抗体の創製

○宮崎 友輝[1]、藤野 公茂[2]、吉井 達之[1]、舟根 守[2]、村田 直哉[2]、キムグエン チュン[2]、田原 海[1]、吉川 優[1]、深谷 菜摘[1]、長門石 曉[4]、津本 浩平[4]、林 剛介[2]、村上 裕[2,3]、築地 真也[1] (1. 名工大院工、2. 名大院工、3. 名大未来ナノ、4. 東大院工)

英語
9:40 ~ 10:00
[H936-2am-03]
環状ポリアミン配位子を有するジスルフィド化合物を利用した酸化的タンパク質フォールディング

○森 圭太[1]、村岡 貴博[1,2] (1. 農工大院工、2. KISTEC)

日本語
10:00 ~ 10:20
[H936-2am-04]
アントラニル酸骨格を有するPAI-1阻害剤の合成、阻害活性評価と蛍光特性の利用

○濱田 悠菜[1]、川口 真一[1]、小川 昭弥[2]、宮田 敏男[3] (1. 佐賀大、2. 大阪公立大、3. 東北大)

日本語
10:20 ~ 10:40
[H936-2am-05]
ランタノイドイオン存在下における*Methylosinus trichosporium* OB3bのグリセロールによる毒性メカニズム

○椎名 渉[1]、伊藤 栄紘[1]、蒲池 利章[1] (1. 東京工業大学)

英語
10:40 ~ 11:00
[H936-2am-06]
Dramatic enhancement of cytochrome c catalytic activity associated with a Rh coordination cage

○Benjamin Le Ouay[1], Yuri Kanzaki[1], Purna Kanta Boruah[1], Masaaki Ohba[1] (1. Kyushu University)

立体構造情報に基づいた抗原テンプレート反応の開発

（京大院薬[1]・医薬健栄研[2]）○秋葉宏樹[1,2]・西山健太郎[1]・永田諭志[2]・津本浩平[2]・鎌田春彦[1,2]・大野浩章[1,2]

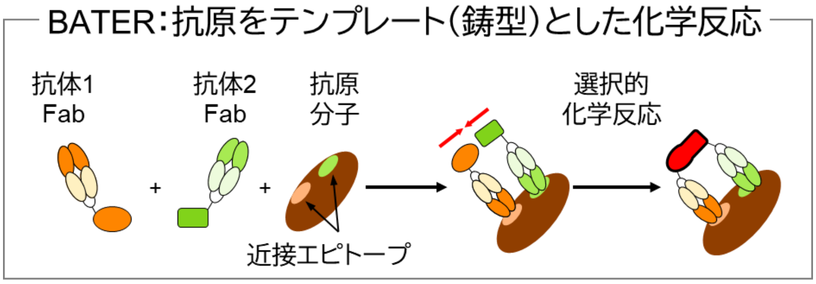
Development of antigen-templated biepitopic chemical reactions (BATER) based on structural information

([1]*Graduate School of Pharmaceutical Sciences, Kyoto University*, [2]*National Institutes of Biomedical Innovation, Health and Nutrition*) ○ Hiroki Akiba,[1,2] Kentaro Nishiyama,[1] Satoshi Nagata,[2] Kouhei Tsumoto,[2] Haruhiko Kamada,[1,2] Hiroaki Ohno[1,2]

A chemical reaction that proceeds in the presence of a specific template by utilizing the structural complementarity of biomolecules is called a template reaction. We have developed a template reaction called biepitopic antigen-templated chemical reaction (BATER) based on the interaction of two different antibodies binding to different epitopes of an antigen molecule. Using fluorogenic click reaction, we demonstrated that BATER was observed in dependence on the epitopes of a model antigen, TNFR2, recognized by the pair of antibody fragments (Fab). We also demonstrated that the linker length affected the reaction rates. Observation of the reactions in other antigen–antibody pairs suggested that the limitation of BATER was dominated by the potential frequency of collisions of reacting moieties, which can be designed by the information of tertiary structure of the antigen–antibody complexes.

Keywords : Antibody; biorthogonal reactions; template reaction; epitopes; protein-protein interaction

生体高分子などの構造相補性を利用することで、特定の鋳型（テンプレート）存在下で特異的に進行する化学反応をテンプレート反応と呼ぶ。我々は、抗原分子の異なる 2 つのエピトープに結合する抗体の抗原との相互作用をテンプレート反応の鋳型に利用したテンプレート反応（biepitopic antigen-templated chemical reaction: BATER）を開発した。TNFR2 をモデルに、異なるエピトープに結合する抗体に由来する抗原結合フラグメント（Fab）を得て、これに対して発蛍光性のクリック反応を観察するための官能基を Fab の C 末端選択的に導入した。蛍光観察によって、抗原 TNFR2 分子存在下において選択的に、抗体が認識するエピトープペアとリンカー長に依存したクリック反応が観察された1)。さらに我々は他の抗原・抗体組み合わせを利用することで、Fab の C 末端に互いに修飾された反応性官能基の分子衝突が可能な距離に 2 つの Fab が結合する設計とすれば BATER が観察されることを示した。



1) Nishiyama *et al*, *Angew. Chem. Int. Ed.* **2023,** *62,* e202306431.

光操作のための小分子光スイッチ結合性人工抗体の創製

（名工大院工[1]・名大院工[2]・名大未来ナノ[3]・東大院工[4]）○宮崎 友輝[1]・藤野 公茂[2]・吉井 達之[1]・舟根 守[2]・村田 直哉[2]・キムグエン チュン[2]・田原 海[1]・吉川 優[1]・深谷 菜摘[1]・長門石 曉[4]・津本 浩平[4]・林 剛介[2]・村上 裕[2,3]・築地 真也[1]

Artificial antibodies against a photo-switchable small molecule for optical cell manipulation

([1]*Graduate School of Engineering, Nagoya Institute of Technology*, [2]*Graduate School of Engineering,* [3]*Institute of Nano-Life-Systems, Institute of Innovation for Future Society, Nagoya University,* [4]*Graduate School of Engineering, The University of Tokyo*)○Tomoki Miyazaki[1], Tomoshige Fujino[2], Tatsuyuki Yoshii[1], Mamoru Funane[2], Naoya Murata[2], Chung Nguyen Kim[2], Kai Tahara[1], Masaru Yoshikawa[1], Natsumi Fukaya[1], Satoru Nagatoishi[4], Kouhei Tsumoto[4], Gosuke Hayashi[2], Hiroshi Murakami[2,3], Shinya Tsukiji[1]

Optical manipulation of tag-fused proteins using photo-functional synthetic molecules is a powerful approach for controlling cell functions. In this study, we developed a novel chemo-optogenetic tool for cell manipulation based on an artificial antibody–photo-switchable small molecule pair. First, we generated artificial antibodies that bind to the cis-form of azobenzene using the TRAP display. The clone #16 showed high affinity and specificity to cis-azobenzene in vitro and in cells. By fusing clone #16 to signaling proteins, we successfully demonstrated photo-reversible control of cell signaling, such as the Raf/ERK pathway, and cell migration.

Keywords: In vitro selection, Artificial antibody, Azobenzene, Tag protein, Intracellular signal transduction

細胞内のシグナル分子を光で操作する技術は、時空間分解能の高い細胞機能制御を可能にする強力なアプローチである。その一つに、HaloTag や SNAP-tag に代表される「タグタンパク質」を用いた手法がある。これらのタグタンパク質は特定の小分子と特異的に結合するため、それら小分子の光機能化（ケージド化やフォトクロミック化など）によって二種類のタグタンパク質間の相互作用を光制御する光化学遺伝学法が報告されている1,2)。一方、従来のツールは既存の「タグタンパク質－小分子ペア」に依存しているため、その種類は少ない。また、小分子の光機能化にも構造的な限界がある。そこで我々は、“任意の光機能性小分子に結合する人工抗体タグを進化分子工学により創製する”という新しい方法論に基づいた光操作ツールの開発を目指した。

本研究では、光で結合の可逆的な ON/OFF 制御が可能な人工抗体タグ－小分子ペアの確立を目指し、cis 型アゾベンゼンに特異的に結合するアンティカリン型人工抗体の in vitro セレクションを行なった。人工抗体ライブラリの作成後、TRAP 提示法3)によるセレクションを行なった結果、アゾベンゼンの trans 型には結合を示さず、cis 型に特異的に結合を示す人工抗体クローンの取得に成功した（$K_{\mathrm{d}} \approx 14$ nM）。この人工抗体は、動物細胞内に安定に発現でき、細胞内での光可逆的な結合と解離が可能であった。さらに、人工抗体に種々のシグナル分子を融合することで、脂質・キナーゼのシグナル活性や細胞運動の光可逆的な操作に成功した。

1) E. R. Ballister et al., *Nat. Commun.*, **2014**, 5, 5475. 2) T. Mashita et al., *ChemBioChem.*, **2019**, 5, 1382.
3) T. Ishizawa et al., *J. Am. Chem. Soc.*, **2013**, 14, 5433.

Oxidative Protein Folding Driven by Disulfide Compounds Containing Cyclic Polyamines Ligands

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*KISTEC*) ○Keita Mori,[1] Takahiro Muraoka[1,2]

Keywords: Protein Folding; Metal Complex; Disulfide Compound; Redox Reaction; Cyclic Polyamine Ligand

Protein folding is driven and precisely controlled by various interactions, resulting in the formation of native conformations. In particular, folding of many functional proteins is accompanied by disulfide (S–S) bonding between cysteine residues, called oxidative folding. Therefore, it has been demanded to artificially promote oxidative folding for production of therapeutic proteins and inhibition of pathological aggregates. Previously, disulfide compounds exhibiting desirable redox activity have been reported as a synthetic folding modulator.[1,2] In this study, we developed disulfide derivatives tethering cyclic polyamine ligands (cpa-SS) for efficient promotion of oxidative folding (Fig. 1a). It was expected that the cyclic polyamines can interact with substrate proteins via hydrogen bonds and metal coordination[3] to accelerate S–S introduction and suppress protein aggregation.

The designed compound cpa-SS was synthesized by conjugating cyclic polyamines with a disulfide-containing alkyl linker. Bovine Pancreatic Trypsin Inhibitor (BPTI) was used as a substrate of oxidative folding. Reverse-phase HPLC analysis revealed that cpa-SS promoted BPTI folding more efficiently than glutathione (GSSG), a typical redox-active biomolecule. The folding ability of cpa-SS became more significant when a reduced form of disulfide compounds (cpa-SH and GSH) was added to promote shuffling of S–S bonds. Furthermore, the folding efficiency was improved in the presence of transition metal ions such as Cu^{II} and Ni^{II}, which can bind to the cyclic polyamine ligands (Fig. 1b). On the other hand, GSSG hardly yielded native BPTI in the presence of Cu^{II} ions due to Cu^{II}-dependent aggregation of BPTI. These results suggested that cpa-SS have a dual effect: (i) promotion of oxidative folding and (ii) inhibition of metal-dependent protein aggregation. We will also include effects of different cyclic polyamine ligands and folding assay of other protein substrates in the presentation.

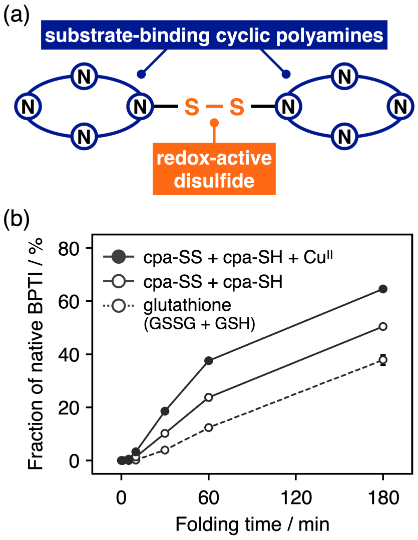


Fig. 1 (a) Disulfide compound with cyclic polyamines (cpa-SS). (b) Time-course analysis of oxidative folding of BPTI by cpa-SS.

1) J. C. Lukesh III, K. A. Andersen, K. K. Wallin, R. T. Raines, *Org. Biomol. Chem.* **2014**, *12*, 8598.
2) S. Okada, Y. Matsumoto, R. Takahashi, K. Arai, S. Kanemura, M. Okumura, T. Muraoka, *Chem. Sci.* **2023**, *14*, 7640.
3) L. O. Gerlach, J. S. Jakobsen, K. P. Jensen, M. R. Rosenkilde, R. T. Skerlj, U. Ryde, G. J. Bridger, T. W. Schwartz, *Biochemistry* **2003**, *42*, 710.

アントラニル酸骨格を有する PAI-1 阻害剤の合成、阻害活性評価と蛍光特性の利用

（佐賀大院先進[1]・佐賀大農[2]・大阪公立大院工[3]・東北大院医[4]）○濱田 悠菜[1]・川口 真一[1,2]・小川 昭弥[3]・宮田 敏男[4]

Synthesis, inhibitory activity evaluation, and utilization of the fluorescence characteristics of PAI-1 inhibitors that have anthranilic acid scaffold

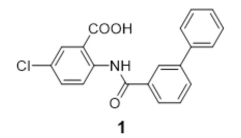
([1]*Graduate School of Advanced Health Science, Saga University*, [2]*Faculty of Agriculture, Saga University,* [3]*Graduate School of Engineering, Osaka Metropolitan University,* [4]*Graduate School of Medicine, Tohoku University*)○Yuna Hamada,[1]Shin-ichi Kawaguchi,[1, 2] Akiya Ogawa[3], Toshio Miyata[4]

Plasminogen activator inhibitor-1 (PAI-1) is an important protein which inhibits tissue type plasminogen activator (tPA) and prevents thrombolysis. Because PAI-1 level in various diseases is increased, inhibition of PAI-1 is expected. In this research, we synthesized anthranilic acid derivatives which inhibit PAI-1 and evaluated them in vitro. These derivatives also have fluorescence characteristics, so we quantified compound amount in cell with fluorescence detection HPLC.

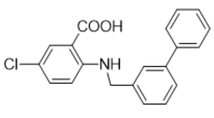
Keywords : Inhibitors; Anthranilic acid; Fluorescence molecules; Fibrinolysis system; Cells

Plasminogen activator inhibitor-1(PAI-1)は線溶系に関与するタンパク質で、tissue type plasminogen activator(tPA)を阻害して血栓溶解を妨げる。血栓症だけではなく様々な疾患で PAI-1 値が上昇することが報告されており、低分子 PAI-1 阻害剤による病状改善が期待されている。これまでにいくつかの PAI-1 阻害剤が報告されているが、いずれも上市していない。

当研究グループでは、PAI-1 阻害活性を示すジフェニルアミド誘導体（**1**）を見出し1)、**1** は臨床試験に進んでいる。また、**1** のアミド部分を還元したアントラニル酸誘導体（**2**）においても PAI-1 阻害活性を示すことが明らかになった。**2** はブラックライトの照射により蛍光を示すので、蛍光特性の利用が期待できる。

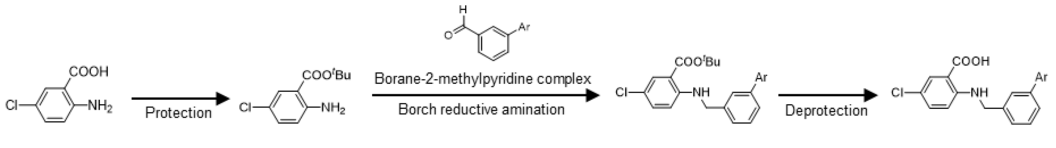


1



2

本研究では、3 段階の反応でアントラニル酸誘導体を合成した。また、PAI-1 阻害アッセイや Cell viability assay で評価した。さらに、細胞への取り込みを蛍光検出 HPLC で確認した。



1) Yamaoka, N. et al., *Bioorg. Med. Chem. Lett.*, **2018**, *28*, 809-813

ランタノイドイオン存在下における *Methylosinus trichosporium* OB3b のグリセロールによる毒性メカニズム

（東京工業大学 [1]）○椎名 渉 [1]、伊藤 栄紘 [1]、蒲池 利章 [1]

Mechanism of glycerol-induced toxicity in *Methylosinus trichosporium* OB3b cultured with lanthanide ion

([1]*Tokyo Institute of Technology*) ○Wataru Shiina[1], Hidehiro Ito[1], Toshiaki Kamachi[1]

Methanotrophs, which can utilize methane as a sole carbon source, were known to exhibit growth inhibition by glycerol 1). In our previous study 2), we revealed that glycerol causes a toxic effect on *Methylosinus trichosporium* OB3b (OB3b strain) cultured with lanthanide ions.

In this study, we revealed that the glycerol-dependent toxicity in OB3b strain was caused by the oxidation of glycerol by lanthanide-dependent methanol dehydrogenase, XoxF1. The Maillard reaction, protein modification by reactive carbonyl species, occurred in OB3b cells cultured with glycerol and lanthanide ions. We demonstrated from the Maillard reaction that XoxF1 and aldehyde were involved in glycerol-dependent toxicity. We purified XoxF1 from OB3b strain and characterized its methanol and glycerol oxidation activity. Finally, we isolated and characterized an OB3b mutant that could avoid glycerol-dependent toxicity.

Keywords：Methanotroph; Lanthanide; Methanol dehydrogenase; Glycerol

メタンを単一の炭素源として生育することができるメタン資化細菌は、グリセロールによって増殖が阻害される 1)。以前の研究において、メタン資化細菌の一種である *Methylosinus trichosporium* OB3b (OB3b 株)をランタノイドイオン存在下で培養することで、グリセロール毒性が強くなることが明らかとなっている 2)。

本研究では、OB3b 株におけるグリセロール毒性が、ランタノイド依存性メタノールデヒドロゲナーゼである XoxF1 のグリセロール酸化に起因することを明らかにした(Figure)。グリセロール存在下で培養した OB3b 株菌体内で、活性カルボニル種により誘導される Maillard 反応が起きていることを蛍光分析および SDS-PAGE により明らかにした。この Maillard 反応を手掛かりとして、グリセロール毒性に XoxF1 およびアルデヒドが関連していることを示した。さらに、OB3b 株より精製した XoxF1 のメタノールおよびグリセロール酸化活性を評価した。最後に、実験室進化によってグリセロール毒性を回避した OB3b 変異株を単離し、変異遺伝子を解析した。

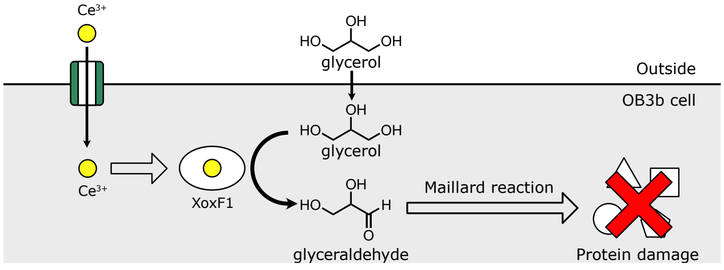


Figure Proposed mechanism of glycerol-dependent toxicity in OB3b strain.

1) Hoefman, S. *et al. PLOS ONE* **2012**, *7* (4), e34196.
2) Shiina, W. *et al. Appl. Environ. Microbiol.* **2023**, *89* (1), e01413-22.

Dramatic Enhancement of Cytochrome c Catalytic Activity Associated with a Rh Coordination Cage

([1]*Kyushu University, Graduate School of Science*) ○Benjamin Le Ouay,[1] Yuri Kanzaki,[1] Purna K. Boruah,[1] Masaaki Ohba[1]

Keywords: Cytochrome c; Peroxidase; Metal-organic Polyhedra, Coordination cage, Allosteric effect

The control of enzymes' interactions with nanosystems is a fascinating approach to regulate their catalytic performances. Recently, our group has been investigating the association of enzymes with coordination cages (also known as metal-organic polyhedra, MOPs). MOPs combine several unique features such as a nanometer-sized perfectly defined structure, a high symmetry and the coexistence of several different micro-domains on their surface, that make them very interesting materials to associate with proteins. Thanks to their intrinsic porosity and to their tunable surface properties, MOPs can act as efficient nanosized spacers for the versatile immobilization of enzymes in very mild conditions.[1] However, the influence of the local-scale structure of MOPs on their interactions with enzymes remains to be fully understood.

Here, we describe the systematic study of the influence of a rhodium-based MOP, **Rh-SO_3** (Figure 1A), on the catalytic activity of cytochrome c (**CytC**) acting as a peroxidase. Simple mixing of **Rh-SO_3** with **CytC** resulted in a dramatic enhancement of catalytic activity, up to a factor 2000 compared to that of free **CytC** at the same concentration (Figure 1B). By comparison, free ligand and Rh acetate had only a minimal influence on the activity of **CytC**, highlighting a MOP-specific effect and the importance of associating Rh metal centers and ligand functional groups in close proximity to activate the enzyme. Analysis of the **Rh-SO_3/CytC** dose-response plot suggested the formation of a 1:1 MOP-enzyme assembly as the active specie, with a high stability ($K_{\text{MOP-Enzyme}} > 10^{10}$ M^{-1}). The structural reasons explaining this dramatic activity enhancement are currently under investigation.

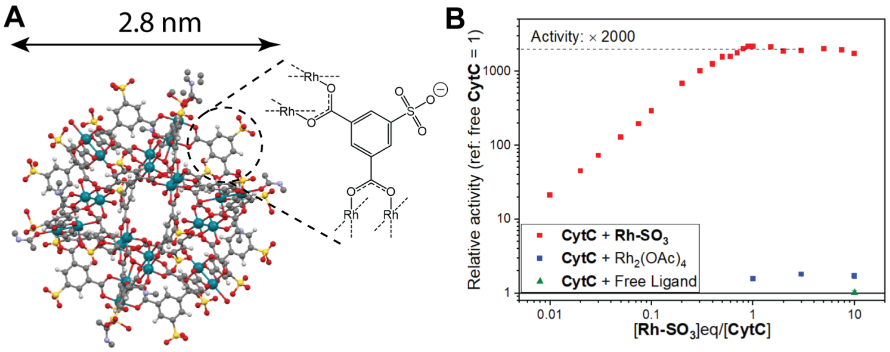


Figure 1. A: Structure of **Rh-SO_3** and of its constitutive ligand. **B**: Activity comparison for **CytC** in presence of **Rh-SO_3** or its constituents. **CytC** concentration was 1.5 µM.

[1] B. Le Ouay, R. Minami, P. K. Boruah, R. Kunitomo, Y. Ohtsubo, K. Torikai, R. Ohtani, C. Sicard, M. Ohba *J. Am. Chem. Soc.* **2023**, *145*, 11997.

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19日(火) 15:55 ~ 16:55 H931(9号館 [3階] 931)

[H931-2vn] 17. 生体機能関連化学・バイオテクノロジー

座長：中田 栄司、那須 雄介

日本語

15:55 ~ 16:15

[H931-2vn-01]

細胞内代謝を可視化するバイオセンサーの開発

○那須 雄介[1,2]、上條 由貴[1]、ロバート キャンベル[1] (1. 東京大学、2. 科学技術振興機構)

日本語

16:15 ~ 16:35

[H931-2vn-02]

チオールを用いたカップルドアッセイに基づく血液中１分子エステラーゼ活性計測技術の開発

請川 達也[1]、○小松 徹[1]、箕田 麻弥乃[1]、浦野 泰照[1] (1. 東京大学)

英語

16:35 ~ 16:55

[H931-2vn-03]

DNAナノ構造体で構築した人工コンパートメントでの酵素カスケード反応

○林 鵬[1]、楊 輝[2]、Zhang Shiwei[1]、中田 栄司[1]、森井 孝 (1. 京大 エネルギー理工学研究所、2. 京大 大学院エネルギー科学研究科)

細胞内代謝を可視化するバイオセンサーの開発

（東大院理 [1], JST さきがけ [2]）○那須 雄介 [1,2]・上條由貴 [1]・Robert E. Campbell[1]

Genetically encoded biosensors for cellular metabolism

([1]*School of Science, The University of Tokyo*, [2]*PRESTO, Japan Science and Technology Agency*) ○Yusuke Nasu,[1,2] Yuki Kamijo,[1] Robert E. Campbell[1]

Fluorescent proteins (FPs) have been proven to be versatile scaffolds for development of biosensors1). Specifically, GCaMP, a calcium ion (Ca^{2+}) biosensor, has been widely employed to monitor neural activities in live model animals. In addition to GCaMP, various FP-based biosensors for non-Ca^{2+} target have been developed. However, few sensors have sensitivity as high as GCaMP, hampering their wide application *in vivo*.

Herein, we present that directed protein evolution and extensive biosensor expression optimization can enable the engineering of FP-based biosensors for a versatile metabolite L-lactate with high sensitivity, specificity, and spatiotemporal resolution in living cultured cells and *in vivo*. L-Lactate, traditionally considered a metabolic waste product, is increasingly recognized as an important intra- and intercellular energy fuel and signaling molecule. This study provides a powerful new optical toolbox, LACCO series, for investigating the emerging roles of extracellular and intracellular L-lactate in live model animals2)–5).

Keywords：L-Lactate, Fluorescent protein, Genetically encoded biosensor

蛍光タンパク質は，標的分子依存的な蛍光バイオセンサーの足場としてよく用いられている1)．特にカルシウムイオン（Ca^{2+}）センサーであるGCaMPは，生きたモデル動物（*in vivo*）の神経活動をモニターするために広く使用されている．GCaMP以外にも様々な標的のバイオセンサーが開発されているが，GCaMPほど高い感度を持つセンサーはほとんどなく，バイオセンサーの*in vivo*での広範な利用は容易ではなかった．そこで本研究では，directed evolutionをはじめとするタンパク質工学手法により，高感度，高特異性，および*in vivo*での高時空間分解能を有する乳酸バイオセンサーの開発を目的とした．これまで代謝副産物と考えられてきた乳酸は，細胞内外のエネルギー分子およびシグナル分子として近年注目されている．本研究は，生きたモデル動物における細胞内外の乳酸の新たな役割を解明するための強力なツール（LACCOシリーズ）を提供する2)–5).

1) **<u>Nasu, Y.</u>**, Shen, Y., Kramer, L. & Campbell, R. E. “Structure- and mechanism-guided design of single fluorescent protein-based biosensors.” *Nat. Chem. Biol.* **17**, 509–518 (2021).
2) **<u>Nasu Y.</u>**, et al. “A genetically encoded fluorescent biosensor for extracellular L-lactate”, *Nature Communications*, **12**, 7058 (2021).
3) Le and Hario et al. “High performance genetically-encoded green fluorescent biosensors for intracellular L-lactate” *bioRxiv* 2022.10.19.512892 (2022).
4) **<u>Nasu Y.</u>**, et al. “A red fluorescent genetically encoded biosensor for extracellular L-lactate”, *bioRxiv* 2022.08.30.505811 (2022).
5) **<u>Nasu Y.</u>**, et al. “Lactate biosensors for spectrally and spatially multiplexed fluorescence imaging” *Nature Communications*, **14**, 6598 (2023).

チオールを用いたカップルドアッセイに基づく血液中１分子エステラーゼ活性計測技術の開発

（東大院薬[1]・東大院医[2]）請川 達也[1]・○小松 徹[1]・箕田 麻弥乃[1]・浦野 泰照[1,2]

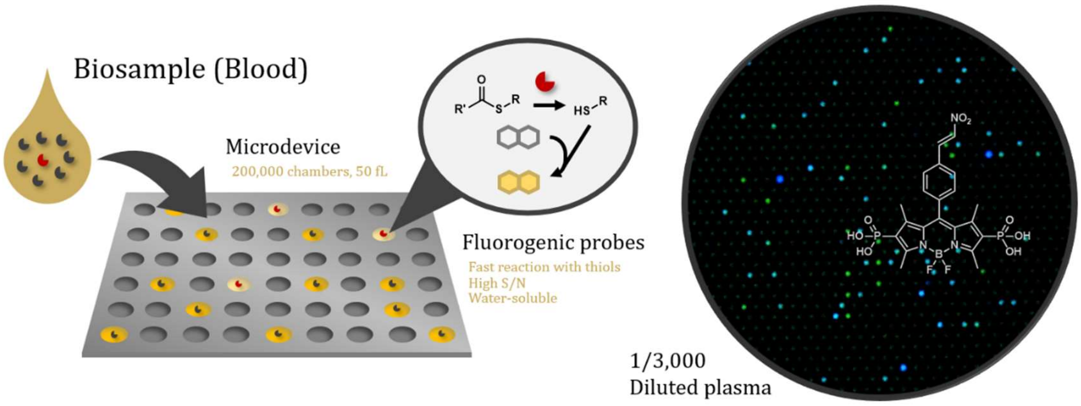
Thioester-Based Coupled Fluorogenic Assays in Microdevice for the Detection of Single-Molecule Enzyme Activities of Esterases with Specified Substrate Recognition

([1]*Graduate School of Pharmaceutical Sciences, The University of Tokyo,* [2]*Graduate School of Medicine, The University of Tokyo*) Tatsuya Ukegawa,[1] ○Toru Komatsu,[1] Mayano Minoda,[1] Yasuteru Urano[1,2]

Single-molecule enzyme activity assay is a platform that enables the analysis of enzyme activities at single proteoform level. The limitation of the targetable enzymes is the major drawback of the assay, but the general assay platform is reported to study single-molecule enzyme activities of esterases based on the coupled assay using thioesters as substrate analogues. The coupled assay is realized by developing highly water-soluble thiol-reacting probes based on phosphonate-substituted boron dipyrromethene (BODIPY). The system enables the detection of cholinesterase activities in blood samples at single-molecule level.

Keywords ：Chemical Biology; Enzymes; Liquid Biopsy; Single-molecule Analysis

血液中の１分子酵素活性計測によって, 疾患と関わる proteoform レベルのタンパク質機能異常を明らかにすることができることが期待される[1)]. １分子酵素活性計測技術は, 10 万～100 万個の微小なチャンバーが並列したマイクロデバイスに希釈した生体サンプルをロードし, 確率的に 0 または 1 分子の標的酵素が含まれる状態で蛍光基質を用いた活性検出をおこなうことで目的の活性を含む酵素が含まれるチャンバーを「数える」ことによっておこなわれる．本研究では，チオエステルの加水分解反応によって生じるチオールを boron dipyrromethene（BODIPY）を母核とした新規チオール検出プローブを用いてマイクロチャンバー内で検出するカップルドアッセイ系を設計，開発し，これにより血液中の１分子エステラーゼ活性の検出をおこなうことを可能とした[2)].



1) S. Sakamoto et al., *Sci. Adv.* **2020**, 6, eaay0888, 2) T. Ukegawa et al., *Adv. Sci.* **2023**, *in press (DOI: 10.1002/advs.202306559)*

Construction of DNA-based artificial compartments for enzyme cascade reactions

([1]*Institute of Advanced Energy, Kyoto University*, [2]*Graduate School of Energy Science, Kyoto University*) ○Peng Lin,[1] Hui Yang,[2] Shiwei Zhang,[1] Eiji Nakata,[1] Takashi Morii[1]

Keywords: DNA Scaffold; Artificial Compartments; Enzyme Cascade Reactions; Substrate Channeling; Competitive Enzyme

In cells, enzymes are spatially organized to perform specific sequential reactions within the compartments such as membrane-bound or membraneless organelles.[1] Artificial compartments have been constructed using liposomes, proteins, or polymers, but the applications of these carriers face the challenges of low enzyme loading yields and the difficulty in controlling the location and number of enzymes. With the advantages of precise addressability, DNA scaffolds provide the ideal platforms for enzyme assembly.[2] In this study, a series of DNA hexagonal prisms with different dimensions were prepared to construct the artificial compartments for enzyme reactions.

A series of scaffold systems were developed for the cascade reactions of xylose reductase (XR) and xylitol dehydrogenase (XDH) from the D-xylose metabolic pathway. The DNA scaffolds of 3D hexagonal prism (HP), medium HP (MHP), and shallow HP (SHP) were prepared by the DNA origami method.[3] XR and XDH were specifically located to the scaffold in the open state by the modular adaptor method,[4] followed by the closing process of the scaffold induced by the closing keys (short DNAs).[5] XR and XDH were encapsulated in the closed states of HP, MHP, and SHP with an estimated interenzyme distance of ~18 nm, ~10 nm, and ~4 nm, respectively. Alditol oxidase (AldO) was used as a competing enzyme for XDH to evaluate the free diffusion of intermediates (Figure 1).

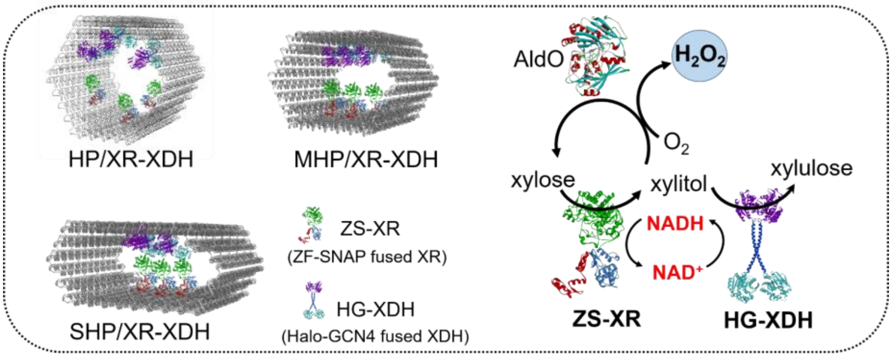


Figure 1. Cascade enzyme reactions of XR and XDH on the DNA scaffolds.

1) R. Wang, X. Liu, B. Lv, W. Sun, C. Li, *ACS Synth. Biol*. **2023**, *12*, 1378. 2) F. Hong, F. Zhang, Y. Liu, H. Yan, *Chem. Rev.* **2017**, *117*, 12584. 3) P. W. K. Rothemund, *Nature* **2006**, *440*, 297. 4) E. Nakata, H. Dinh, T. A. Ngo, M. Saimura, T. Morii, *Chem. Commun.* **2015**, *51*, 1016. 5) P. Lin, H. Dinh, Y. Morita, E. Nakata, T. Morii, *Adv. Funct. Mater.* 2**023**, *33*, 2215023.

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19日(火) 15:55 ~ 17:15 H934(9号館 [3階] 934)

[H934-2vn] 17. 生体機能関連化学・バイオテクノロジー

座長：上田 善文、仲本 正彦

日本語

15:55 ~ 16:15

[H934-2vn-01]

可視光応答性アゾベンゼンを有するハイドロゲル足場の作製とインテグリンを起点とした三次元メカノトランスダクションへの応用

〇本間 健太[1]、宮国 樹[1]、松崎 典弥[1] (1. 阪大院工)

日本語

16:15 ~ 16:35

[H934-2vn-02]

高分子間生体直交性反応による膜型酵素多価リガンドのin situ合成とがん細胞増殖阻害

〇仲本 正彦[1]、坂本 蓮太郎[1]、木場 勇希[1]、松崎 典弥[1] (1. 阪大院工)

日本語

16:35 ~ 16:55

[H934-2vn-03]

ホスファチジルイノシトール3,4,5-三リン酸(PIP3)を光制御するツールの開発と応用

〇上田 善文[1] (1. 国立感染症研究所)

日本語

16:55 ~ 17:15

[H934-2vn-04]

ゴースト赤血球を利用した化学反応場の構築

〇越山 友美[1]、坂本 大芽[1] (1. 立命館大学)

可視光応答性アゾベンゼンを有するハイドロゲル足場の作製とインテグリンを起点とした三次元メカノトランスダクションへの応用

（阪大院工 [1]）○本間 健太 [1]・宮国 樹 [1]・松崎 典弥 [1]

Construction of a Visible-Light Responsive Azobenzene-Bearing Gel Scaffold for Spatio-Temporal Regulation of Integrin-Mediated Mechanotransduction

([1]*Graduate School of Engineering, Osaka University*) ○Kenta Homma,[1] Itsuki Miyaguni,[1] Michiya Matsusaki[1]

Integrins are transmembrane proteins that anchor cells to the extracellular matrix. Integrins play vital roles in deciding cell behaviors in response to the microenvironment. Specifically, integrin-mediated mechanotransduction determines various cell functions. Designer scaffolds capable of controlling this mechanotransduction could have applications in tissue engineering.

To this aim, we sought to regulate mechanotransduction by mechanically stimulating integrins through photoisomerization of azobenzene molecules (Fig. 1a)[1]. We synthesized a visible-light responsive azobenzene monomer (PPAzo) with the cell-adhesive peptide (cRGD) directly attached to PPAzo. PPAzo was subsequently polymerized with *N*,*N*-dimethylacrylamide (DMA) to obtain a photoresponsive polymer (poly(PPAzo-*r*-DMA)). PPAzo exhibited reversible absorbance spectra changes in response to visible light (Fig. 1b). Additionally, cRGD-modified poly(PPAzo-*r*-DMA) was confirmed to be cell-adhesive through adhesion tests. We will report on its potential for a photoresponsive scaffold to control mechanotransduction.

Keywords: Mechanotransduction; Integrin; Dynamic cell scaffold; Photoisomerization

インテグリンは細胞が微小環境に応答して運命を決定する上で重要な役割を担っている。特に、インテグリンを介して足場の力学特性を認識し、細胞内シグナル伝達が誘起されるメカノトランスダクションは様々な細胞挙動を司る。従って、メカノトランスダクションを制御可能な足場が創製できれば、組織工学に資する材料となる。

本研究ではアゾベンゼンの光異性化によってインテグリンに力学刺激を印可し、メカノトランスダクションを操作することを目的とした(Fig. 1a)[1]。具体的には、細胞接着性ペプチドを担持した可視光応答性アゾベンゼン(PPAzo)を高分子鎖に修飾し、その光異性化に伴う構造変化を利用してインテグリンに微小な伸縮刺激を付与する。本発表では、PPAzo 含有ポリマーの合成およびそのキャラクタリゼーションについて報告する(Fig. 1b)。

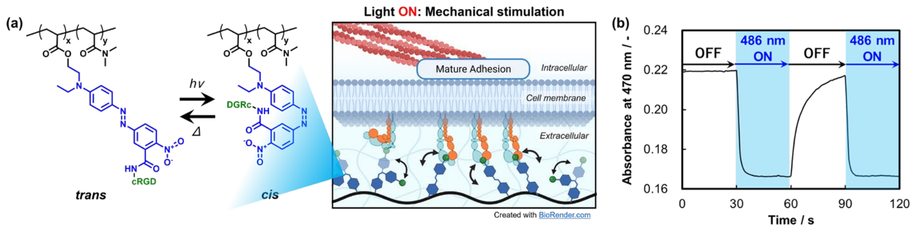


Fig. 1 (a) Conceptual illustration of this study. (b) Time-dependent absorbance of PPAzo at 470 nm.

1). L. F. Kadem, *et al., Angew. Chem. Int. Ed.* **2017**, *56*, 225.

高分子間生体直交性反応による膜型酵素多価リガンドの *in situ* 合成とがん細胞増殖阻害

（阪大院工）○仲本 正彦・坂本蓮太郎・木場勇希・松崎 典弥

In situ Synthesis of Multivalent Ligands of Membrane Enzyme by Inter-Polymer Click Chemistry for Inhibition of Cancer Cell Growth (*Graduate School of Engineering, Osaka University*) ○Masahiko Nakamoto, Rentaro Sakamoto, Yuki Koba, Michiya Matsusaki

Engineering of stimuli-responsive nanomaterials that release drug and/or recognize cells have been a promising strategy in cancer therapy and imaging. Nevertheless, insufficient selectivity due to spatio-temporal fluidity of target proteins or non-specific response is still serious problem. In this study, targeting carbonic anhydrase IX (CAIX) as a target enzyme, we report in situ synthesis of multivalent ligand of CAIX by inter-polymer biorthogonal click chemistry. Cancer cell proliferative inhibition by synthesized ligands will be also demonstrated.

Keywords: Cancer cell; Enzyme inhibition; Carbonic anhydrase IX; Biorthogonal click reaction; Polymeric self-assembly

刺激に応答した細胞認識が可能なナノマテリアルががん治療およびイメージング技術として注目されている。一方で、非特異的応答や標的の時空間的流動性に起因した不十分な選択性が大きな課題である。本研究では、がん細胞上で過剰発現する膜型炭酸脱水酵素 IX（CAIX）[1]を標的として、高分子自己集合体間の生体直交性クリック反応による CAIX 多価リガンドの *in situ* 合成およびがん細胞増殖阻害を報告する（Figure 1A）。末端にアジドを導入した PEG 化 CAIX 阻害剤（N_3-PEG-U）および側鎖に歪みアルキンを導入したポリグルタミン酸（DBCO-PGA）からなる二種の高分子自己集合体間のクリック反応により構造体のサイズが減少することが明らかになった（Figure 1B）。更に、クリック反応生成物（PGA-trz-PEG-U）が乳がん細胞の増殖を抑制することが示された（Figure 1C）。

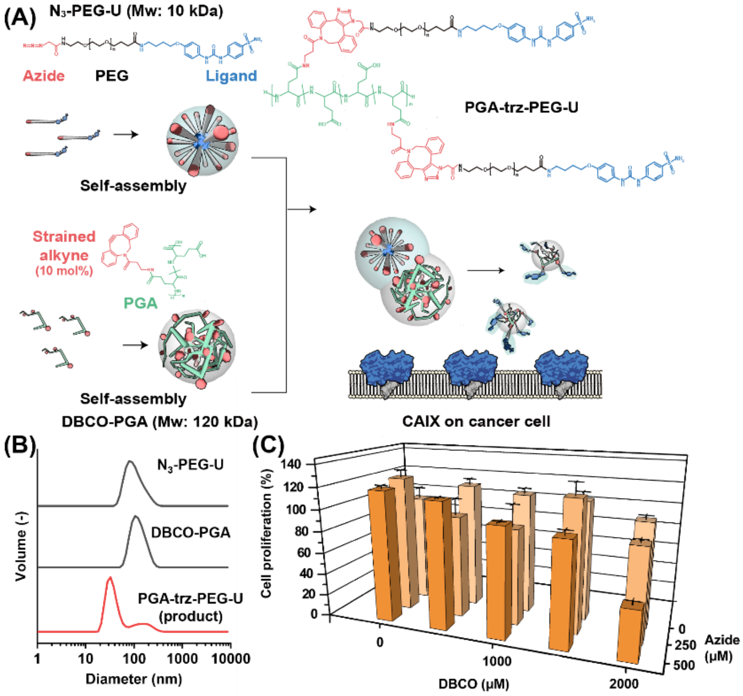


Figure 1. (A) Conceptual illustration of this study. **(B)** Hydrodynamic diameter of self-assemblies. **(C)** Cancer cell proliferative inhibition by in situ click reaction between two assemblies.

1) Y. Koba, M. Nakamoto, M. Matsusaki, *ACS Appl. Mater. Interfaces* 2022, 14, 51790.

日本化学会 第104春季年会 (2024)

ホスファチジルイノシトール 3,4,5-三リン酸(PIP3)を光制御するツールの開発と応用

（感染症研究所　品質保証・管理部 [1]）○上田　善文 [1]

Development and application of an optogenetic tool to regulate phosphatidylinositol 3,4,5-trisphosphate (PIP3)

([1]*Department of quality assurance and radiological protection, National Institute of Infectious Diseases*) ○Yoshibumi Ueda[1]

Phosphatidylinositol 3,4,5-trisphosphate (PIP3) is a functional lipid that is generated at the plasma membrane in response to extracellular stimuli such as hormones. PIP3 is involved in not only normal cellular functions including cell motility and cell differentiation but also cancer and mental disorder by abnormal accumulation. We have developed PPAP (PIP3 production by photo-activated PI3K) as optogenetic tools in order to overcome the limitation with previous methods to produce PIP3, such as inhibitors and knockdown for PIP3-producing enzymes. PPAP1 was developed based on a CRY2-CIBN module, which enabled to observe fine cell motility combined with structured illumination microscopy. Regarding PPAP2, we revealed the mechanism underlying cancer drug resistance by making the cells a cancerous state temporally using PPAP2 combined with mass spectrometry. Thus, we demonstrated that PPAP allows for producing PIP3 with high temporal resolution and aim to apply it to neurons and animals to regulate PIP3 from now on.

Keywords: Phosphatidylinositol 3,4,5-trisphosphate; optogenetics; Phototropin; Cryptochrome;

ホスファチジルイノシトール 3,4,5-三リン酸(PIP3)は、ホルモンなどの細胞外刺激によって細胞膜に産生され、細胞運動、細胞分化などの細胞機能を制御するのみならず、異常な蓄積によって、がん、精神疾患を誘導する機能性脂質分子である。従来の PIP3 産生酵素の阻害剤やノックダウンの手法ではなし得なかった時間時間分解能での PIP3 の生理的機能を探るために、光モジュール CRY2-CIBN を用いた PPAP1(PIP3 production by photo-activated PI3K (Anal. Sci. 2019))、および、PPAP1 に比べて高 PIP3 産生能力を有する PPAP2 を開発した (Cell Chem. Biol. 2022)。PPAP1 を発現させた細胞においては、超解像顕微鏡(Structured Illumination Microscopy)と組み合わせて、PIP3 産生によって誘導される詳細な細胞運動を明らかにした。PPAP2 においては、細胞に一時的ながん状態を引き起こし、その際に誘導される抗がん剤耐性因子の同定を質量分析器と組み合わせることで実現した。このように、PPAP は PIP3 およびその下流の PI3K シグナル伝達を高時間分解能で活性化することができるツールであることが証明され、今後、神経細胞や小動物への応用を目指す。

1) Membrane Dynamics Induced by a Phosphatidylinositol 3,4,5-Trisphosphate Optogenetic Tool. Ueda Y. *et. al.* Anal Sci. 2019 Jan 10;35(1):57-63.

2) Mechanistic insights into cancer drug resistance through optogenetic PI3K signaling hyperactivation. Ueda Y. *et. al.* Cell Chem Biol. 2022 Nov 17;29(11):1576-1587.e5.

ゴースト赤血球を利用した化学反応場の構築

（立命館大生命科学）○越山友美・坂本大芽

Construction of Chemical Reaction Space using Red Blood Cell Ghosts (*College of Life Sciences, Ritsumeikan University*) ○Tomomi Koshiyama, Taiga Sakamoto

In this study, we attempted to construct a chemical reaction space using red blood cell ghosts. Using the cytoskeletal structure on the internal surface of red blood cell ghosts as a scaffold, we synthesized metal nanoparticles such as gold and platinum that have catalytic ability. It was found that RBCGs deposited with Au NPs can be used for catalytic reactions of the reduction of 4-nitrophenol. Furthermore, RBCGs deposited with Pt NPs were found to catalyze photochemical hydrogen evolution reactions in the presence of photosensitizers, sacrificial reductants and electron mediators.

Keywords ：Red Blood Cell Ghost; Cytoskeleton; Catalytic Reaction; Metal Nanoparticle

近年、リポソームなどの人工脂質膜が様々な化学反応を制御する場として有用であることが報告されている。脂質膜は、界面である表面、疎水性の膜内部、親水性の内水相の性質の異なる領域を有しており、この性質の違いを利用することで親水性、疎水性の機能分子を選択的に集積可能である。しかしながら、人工脂質膜は対称性の高い膜構造を有し、機能分子の膜上での配向や配置の制御は未だ難しい。そこで我々は、新たな化学反応場として生体膜である「ゴースト赤血球（Red blood cell ghost; RBCG）」に着目した。RBCG は、溶血操作によって赤血球からヘモグロビン等の内容物を取り除いたマイクロサイズの膜空間であり、RBCG 膜の内部表面には蛋白質から成る網目状細胞骨格が存在し (Figure 1)、膜の内外で異なる構造を有する。本研究では、細

胞骨格へ金属ナノ粒子を担持した RBCG を作製し、触媒能の評価を行った。金ナノ粒子を担持した RBCG は 4-ニトロフェノールの還元を触媒し1)、白金ナノ粒子を担持した RBCG では、光増感剤、犠牲還元剤と電子伝達体を共存させることで光水素生成反応が進行することがわかった。以上のことから、RBCG は様々な触媒反応に対して有用な反応場であることが明らかとなった。

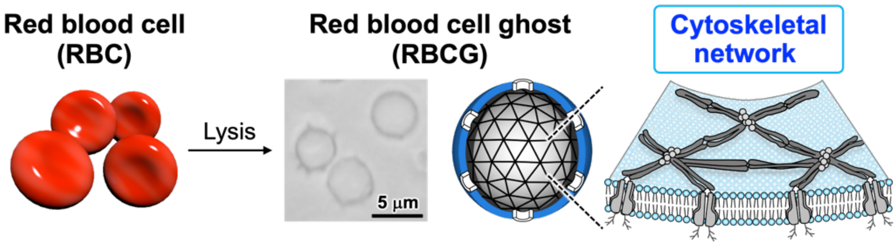


Figure 1. Schematic representation of red blood cell ghost (RBCG).

1) H. Matsumoto, K. Okuichi, H. Imamura, K. Yasuhara, M. Kato and T. Koshiyama, *Chem. Commun.*, **2022**, *58*, 12220.

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19日(火) 15:55 ~ 17:15 D341(3号館 [4階] 341)

[D341-2vn] 18. 高分子

座長：岸本 直樹、呉羽 拓真

日本語

15:55 ~ 16:15

[D341-2vn-01]

ボトルブラシ様ポリマーを架橋した高分子ゲルの構造物性制御

難波 恵汰[1]、西 太一[1]、若山 佑香[1]、平泉 冴響[1]、〇呉羽 拓真[1] (1. 弘前大学大学院)

英語

16:15 ~ 16:35

[D341-2vn-02]

酸化インジウムスズ電極上に生やしたポリ（４-ビニルピリジンービオロゲン）共重合体ブラシによる電気化学的濡れ性制御

〇周 泓遥[1]、李 浩睦[1]、山田 鉄兵[1] (1. 東京大学)

英語

16:35 ~ 16:55

[D341-2vn-03]

量子化学計算と分子動力学シミュレーションの統合：有機金属触媒による熱硬化性ポリマー形成のための新しいアプローチ

〇白 玉焜[1]、岸本 直樹[1]、菊川 豪太[2] (1. 東北大院理、2. 東北大流体研)

英語

16:55 ~ 17:15

[D341-2vn-04]

Mild Catalytic Degradation of Crystalline Polyethylenes in Solid State Assisted by Carboxylic Acid Groups

〇Bin Lu[1], Kohei Takahashi[1], Jian Zhou[2], Shintaro Nakagawa[2], Naoko Yoshie[2], Kyoko Nozaki[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo, 2. Inst. of Industrial Sci., The Univ. of Tokyo)

ボトルブラシ様ポリマーを架橋した高分子ゲルの構造物性制御

（弘前大学大学院[1]）難波 恵汰[1]・西 太一[1]・若山 佑香[1]・平泉 冴響[1]・○呉羽 拓真[1]

Control of structural properties of polymer gels crosslinked by bottle-brush-like polymers

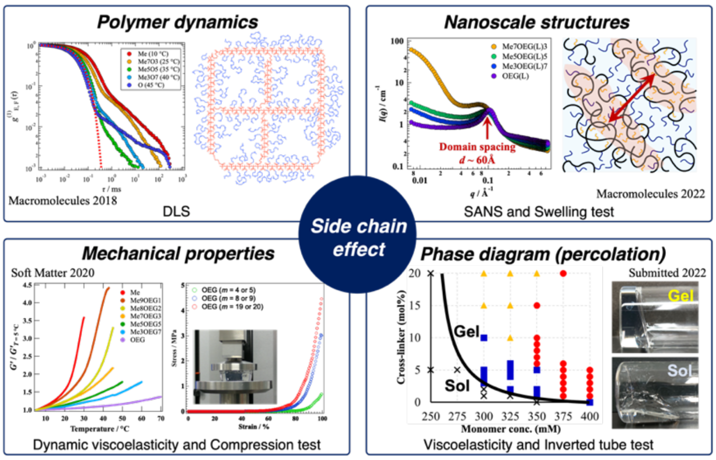
([1]Graduate School of Science and Technology, *Hirosaki University*)
Keita Namba,[1] Taichi Nishi,[1] Yuka Wakayama,[1] Sakyo Hiraizumi,[1] ○Takuma Kureha[1]

Hydrogels are smart, soft, and swellable materials with many similarities to biological systems, and have therefore attracted significant attention in various applications, including tissue and biomedical engineering, artificial organs, sensors, and actuators. In this study, we investigated the hydrogels crosslinked by bottle brush polymers, which exhibited unique properties such as mechanical properties, swelling behavior, and thermo-responsiveness. There were three main effects of long-side chains: (1) imparting hydrophilicity, (2) increasing excluded volume, and (3) suppressing entanglement of polymers due to steric hindrance in the hydrogel network. For instance, due to the side chain effects, the mechanical stability of the gels was improved.[1,2] In addition, the swelling ratio of the gels was also increased, and thus their nanoscale structures, i.e., mesh size, were changed by increasing side chain length.[3,4]

Keywords : Hydrogels; Bottle brush polymers; Swelling behavior; Stimuli responsiveness

自身の体積の約 80%が水からなるハイドロゲルは、柔らかく、その高い生体適合性や外部刺激応答性からバイオ、センサー、アクチュエータ等の応用が期待されている。本研究では、長い側鎖を有するポリマー、すなわちボトルブラシポリマーを架橋したハイドロゲルを対象に構造物性を評価してきた。これまでの研究から、側鎖長の効果は大きく 3 つあり、①親水性の付与、②排除体積の増加、③立体障害によるポリマーの絡まり合いの抑制であった。実際に、側鎖長の効果により、力学特性の向上や膨潤度の増加、ネットワークのメッシュサイズ等のナノスケール構造が大きく変わることが圧縮試験[1]や動的粘弾性測定[2]および動的光散乱法[3]や小角中性子散乱法[4]により明らかにしてきた。当日は、ボトルブラシの効果についての詳細や、ゲル材料設計にフィードバックさせた機能性ゲル合成に関しても発表し、議論する。

1) T. Kureha, K. Takahashi, M. Kino, H. Kida, T. Hirayama, *Soft Matter* **2023**, *19*, 2878.
2) T. Kureha, K. Hayashi, X. Li, M. Shibayama, *Soft Matter* **2020**, *16*, 10946.
3) T. Kureha, K. Hayashi, M. Ohira, X. Li, M. Shibayama, *Macromolecules* **2018**, *51*, 8923.
4) T. Kureha, M. Ohira, Y. Takahashi, X. Li, E. P. Gilbert, M. Shibayama, *Macromolecules* **2022**, *55*, 1844.



Electrochemical Wetting by Poly(4-vinylpyridine-*co*-viologen) Brush Grown on Indium Tin Oxide Electrode

(*Graduate School of Science, Department of Chemistry, The University of Tokyo*)
○Hongyao Zhou, Hiromu Moku, and Teppei Yamada

Keywords: Polymer Brush; Surface Wettability; Atom Transfer Radical Polymerization

Electrowetting is an emerging technology which can manipulate the shape of liquid droplets or transport the droplets at microscale, realizing ink-based digital displays and microfluidic devices.[1] Electrochemical wetting is one of the methods to electrically switch the surface wettability by controlling the surface redox state. Previous research on electrochemical wetting was demonstrated by using self-assembled monolayer (SAM) of ferrocene[2] or ferrocene-attached polymer brush,[3] however, the poor stability of ferrocene in water significantly limited their practical application.

In this study, a functional polymer brush which is stable in water and can electrochemically switch between the hydrophilic and hydrophobic states is synthesized: Poly-(4-vinylpyridyl-*N*-(*N',N"*-diethylviologen), P4VPV) was grown on a conductive transparent electrode—indium tin oxide (ITO)—using surface-initiated atom transfer radical polymerization (ATRP) of 4-vinylpyridine, followed by attachment of diethylviologen on the pyridine ring (**Figure 1a**). The P4VPV brush on ITO electrode showed fully reversible two-step redox reaction (**Figure 1b**), and the color change of the polymer brush in response to the redox state was observed by operando UV-vis spectroscopy. The electrochemical wetting was attempted by using this polymer brush for the first time.

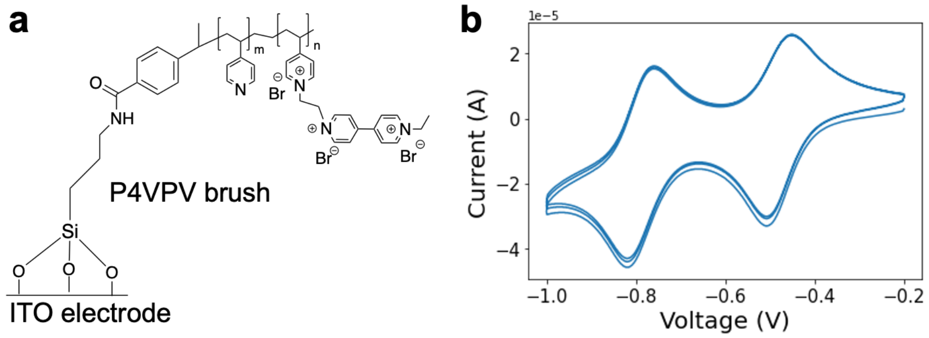


Figure 1. (a) Chemical structure of P4VPV and (b) its cyclic voltammogram (vs. Ag/AgCl, 50 mV s^{-1})

1) Papaderakis, A. A.; Dryfe, R. A. W. *Curr. Opin. Electrochem.* **2023**, *38*, 101245
2) Sondag-Huethorst, J. A. M.; Fokkink, L. G. J. *Langmuir* **1994**, *10* (11), 4380–4387.
3) Bui-Thi-Tuyet, V.; Trippé-Allard, G.; Ghilane, J.; Randriamahazaka, H. *ACS Appl. Mater. Interfaces* **2016**, *8* (42), 28316–28324.

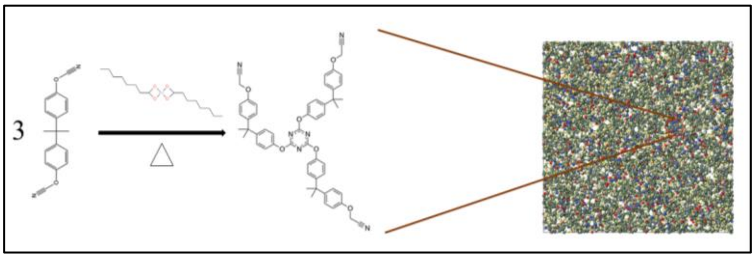
Integration of Quantum Calculation and Molecular Dynamics Simulation : A Novel Simulation Framework for Organic Metal-Catalyzed Thermosetting Polymer Formation

([1]*Graduate School of Science, Tohoku University,* [2]*Institute of Fluid Science, Tohoku University*) ○Yukun Bai,[1] Naoki Kishimoto,[1] Gota Kikugawa[2]

Keywords: Quantum Chemistry Calculation; Molecular Dynamics Simulation; Thermosetting Polymer; Cyanate Resin

Cyanate resins are an important class of thermosetting polymers known for their high glass transition temperatures (T_g), excellent physical properties, and low water uptake, making them widely used in aerospace. Cyanate groups can react to form a triazine ring structure through a crosslinking reaction, typically under heating conditions. However, without catalysts, this crosslinking reaction requires high curing temperatures. Organic-metal catalysts are considered to reduce the reaction temperature during the cyanate curing reaction and achieve a high conversion rate.[1]

In this research, we employed a simulation approach that integrates quantum chemistry calculations with molecular dynamics simulations, as used in our previous work,[2] to investigate how various organic metal catalysts affect the thermophysical properties of cyanate resins. This study used the Zn octanoate as the catalyst, and the Bisphenol A dicyanate molecule as the reactant. We first utilized the Global Reaction Route Mapping (GRRM) algorithm[3] to determine organic metal catalysts' reaction pathways, including both one- and two-step reaction pathways. Our algorithm was refined to include the effects of catalysts, considering activation energy and heat of formation between reactants and products, and using distance criteria from quantum chemistry (4.6 Å and 8.0 Å for second/third cyanate group to form triazine and 4.0 Å for catalysis). The crosslinked models of cyanate resins generated by our algorithm will be analyzed through MD simulations to assess thermophysical properties in various systems and to examine the impact of different catalysts on final polymer properties, such as the glass transition temperature et al.



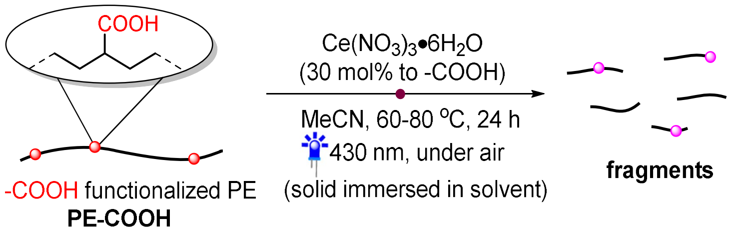
1) T. Fang, D. A. Shimp, *Prog. Polym. Sci.*, **1995**, *20*, 61-118. 2) Y. Bai, G. Kikugawa, Y. Xi, N. Kishimoto, *Polymer*, **2024**, *292*, 126606. 3) S. Maeda, K. Ohno, K. Morokuma, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 3683-3701.

Mild Catalytic Degradation of Crystalline Polyethylenes in Solid State Assisted by Carboxylic Acid Groups

([1] *Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku Tokyo 113-8656, Japan.* [2] *Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku Tokyo 153-8505, Japan*)
○Bin Lu[1], Kohei Takahashi[1], Jian Zhou[2], Shintaro Nakagawa[2], Naoko Yoshie[2], Kyoko Nozaki[1]
[1]Tel: +81-03-5841-7264, Fax: +81-03-5841-7263, E-mail: knozaki@g.ecc.u-tokyo.ac.jp

Keywords: crystalline polyethylene, photodegradation, visible light, radical decarboxylation, cerium complex

The efficient degradation of polyolefins has become an emerging hot topic, as well as a big challenge. Generally, the operating processes of the chemical recycling of polyolefins require harsh conditions (e.g. high temperature) and suffer from high viscosity problems.[1,2] Therefore, the development of the efficient degradation of polyolefins in a solid state under milder conditions is highly desirable.



- Mild conditions
- Air as an oxidant
- Nearly quantitative recovery of carbon atom
- Study of crystal morphology change

Fig. 1. This work

When irradiating the linear powdered PE-COOH (M_n = 8.3 kg/mol, M_w/M_n = 2.6 of the corresponding methyl ester copolymer; 4.8 mol% of -COOH relative to $-CH_2CH_2-$) under the standard conditions (Fig 1),[3] a significant amount of CH_2Cl_2-soluble product (18 w.t.%) was generated together with the insoluble part (80 w.t.%, M_n of insoluble part was 0.5 kg/mol; Fig. 2, black line). Consequently, the combined fragments showed a M_n of 0.3 kg/mol by GPC analysis (Fig. 2, green line). It is worth mentioning that the reaction mixture was heterogeneous during the irradiation as PE-COOH is insoluble and not even swelled in MeCN, and the success of depolymerization regardless of the heterogeneity highlights the ability of this method to degrade insoluble polymeric materials. Notably, the degradation was still effective in H_2O (48 h, M_n of insoluble part was 0.8 kg/mol; Fig. 2, blue line), further supporting the reaction progress in a solid state without swelling. Controlled experiments demonstrate the necessity of Ce salt (Fig. 2, purple line), blue light (Fig. 2, yellow line), and dioxygen in promoting degradation. The standard conditions were compatible with other powdered PE-COOH samples with lower content of -COOH group, wherein a linear-PE-COOH (-COOH content 1.2 mol%) and a more branched one (-COOH content 1.7 mol%) were similarly effective despite their less -COOH contents. A slight decrease in molecular weight was detected in the irradiating simple polyethylene lacking -COOH group. The reaction was suitable even for a PE-COOH film (thickness ~0.1 mm), and its M_n reduced from 8.3 kg/mol to 0.3 kg/mol after 96 h of irradiation. Finally, the heterogeneous feature of the reaction allowed the exploration of the behavior of the polymer crystal during the degradation.

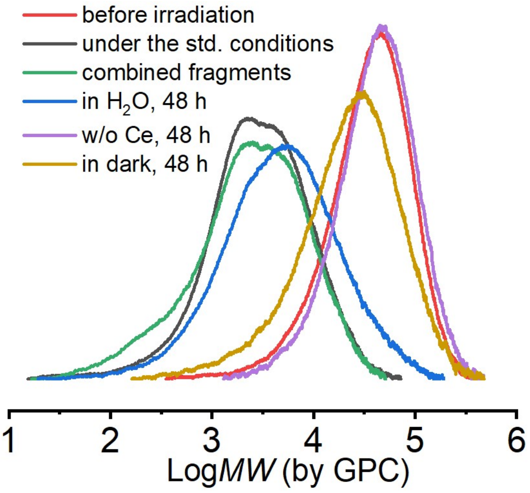


Fig. 2 GPC charts

1) Dai, L.; Zhou, N.; Lv, Y.; Cheng, Y.; Wang, Y.; Liu, Y.; Cobb, K.; Chen, P.; Lei, H.; Ruan, R. *Prog. Energy Combust. Sci.* **2022**, *93*, 101021.
2) a) Dufaud, V.; Basset, J.-M. *Angew. Chem. Int. Ed.* **1998**, *37*, 806. b) Conk, R. J.; Hanna, S.; Shi, J. X.; Yang, J.; Ciccia, N. R.; Qi, L.; Bloomer, B. J.; Heuvel, S.; Wills, T.; Su, J.; Bell, A. T.; Hartwig, J. F. *Science* **2022**, *377*, 1561.
3) Korpusik, A. B.; Adili, A.; Bhatt, K.; Anatot, J. E.; Seidel, D.; Sumerlin, B. S. *J. Am. Chem. Soc.* **2023**, *145*, 10480.

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19日(火) 15:55 ~ 17:15 A1443(14号館 [4階] 1443)

[A1443-2vn] 19. コロイド・界面化学

座長：吉原 栄理佳、金原 数

日本語

15:55 ~ 16:15

[A1443-2vn-01]

硬水を利用した内部オレフィンスルホン酸塩のベシクル形成

○菅原 規[1]、市橋 春奈[1]、津村 加奈[1]、宮崎 敦史[1]、坂井 隆也[1] (1. 花王（株）)

英語

16:15 ~ 16:35

[A1443-2vn-02]

塩橋により形成されたベシクル型人工組織の運動性

○小島 知也[1]、野口 雄太郎[1]、朝倉 浩一[1]、伴野 太祐[1] (1. 慶應義塾大学)

英語

16:35 ~ 16:55

[A1443-2vn-03]

糖ペプチドの*in situ*合成を応用した超分子ヒドロゲルの創製とその生体応用

○杉浦 進太郎[1]、新谷 勇喜[1]、東 小百合[2]、池田 将[1,3,4] (1. 岐阜大院連合創薬、2. 岐阜大高等研究院、3. 岐阜大COMIT、4. 岐阜大iGCORE)

英語

16:55 ~ 17:15

[A1443-2vn-04]

液晶性を示す安息香酸フェニル誘導体で形成した有機ゲルの分光学と計算化学的手法による構造解析

○松本 健太[1]、山口 潤也[1]、金只 晃太郎[1]、遠藤 唯[1]、初田 優里[1]、森田 由紀[1]、岡本 浩明[1] (1. 山口大学)

硬水を利用した内部オレフィンスルホン酸塩のベシクル形成

（花王（株））○菅原　規・市橋　春奈・津村　加奈・宮崎　敦史・坂井　隆也

Vesicle Formation of Internal Olefin Sulfonate Induced by Hard Water

(*Kao Corporation*) ○Tadashi Sugahara, Haruna Ichihashi, Kana Tsumura, Atsushi Miyazaki, Takaya Sakai

Vesicles are known to spontaneously form supported lipid bilayers (SLB) at solid/liquid interface, and cationic surfactants have been mainly used for the SLB formation. On the other hand, anionic surfactants have been used as base agents of detergents because they exhibit superior detergency, foamability and dispersibility of solid particles. However, common anionic surfactants such as sodium dodecyl sulfate, lose their solubilities and functions due to water hardness. Recently, we have developed anionic surfactant, internal olefin sulfonate (IOS)[1]. In this study, we investigated self-aggregation behavior of C18HAS, which is one of the main components of IOS with the alkyl chain length of C18 (Fig. 1), in $CaCl_2$ aqueous solution. The results suggested that formation of the C18HAS vesicles is induced by addition of the water hardness. We also found that the vesicles formed by C18HAS can spontaneously form the supported lipid bilayers (SLB) at solid/liquid interface. These findings lead us to predict that C18HAS can act as surface modifiers, even though it is anionic surfactants.

Keywords：Internal olefin sulfonate, Vesicle, Supported lipid bilayer, Hard water

ベシクルは固液界面に自発的に支持二分子膜(SLB)を形成することが知られており、衣類の柔軟仕上げ剤に用いられている。また、固体表面は水中で負に帯電していることが多いため、SLB 形成には主にカチオン界面活性剤が利用されてきた。一方、アニオン界面活性剤は洗浄力、起泡性、固体粒子の分散性に優れるため、洗浄剤の主基剤として使用されている。しかし、ドデシル硫酸ナトリウムのような汎用のアニオン界面活性剤は、水の硬度(Ca^{2+}や Mg^{2+})により溶解性が低下し、機能が失われてしまう。このことは、アニオン界面活性剤の長年の課題であった。近年、我々はアニオン界面活性剤である内部オレフィンスルホン酸塩(IOS)を開発した[1]。本研究では、C18 のアルキル鎖長を有する IOS の主要成分の一つである C18HAS(Fig. 1)の $CaCl_2$ 水溶液中での会合挙動を検討した。その結果、C18HAS は Ca 塩となって高分散なベシクル分散液を形成した。さらに、固体表面への自発的な SLB 形成も確認できた。以上より、C18HAS はアニオン界面活性剤であるにもかかわらず、硬度成分を有効に利用することで、表面改質剤としても機能することが期待される。

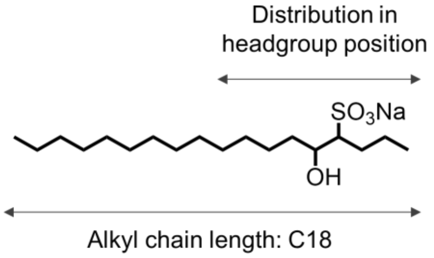


Fig. 1 Typical chemical structure of C18HAS

1) Y. Tabuchi and T. Sakai, RSC Adv. **2021**, *11*, 19836-19843.

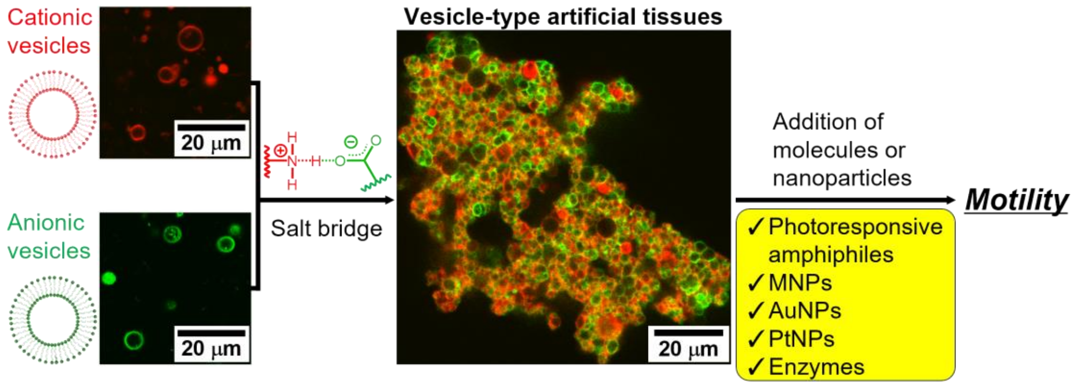
Motility of Vesicle-Type Artificial Tissues Formed by Salt Bridges

([1]*Faculty of Science and Technology, Keio University*) ○ Tomoya Kojima,[1] Yutaro Noguchi,[1] Kouichi Asakura,[1] Taisuke Banno[1]

Keywords: Vesicles; Artificial Cells; Artificial Tissues; Motility

Motility is one of the characteristics in life. Reconstitution of such motility functions into synthetic cell-like entities could lead to engineering brand-new biomimetic materials which exhibit manipulation and propulsion. Nowadays, artificial cells are focused on to be engineered as colloidal materials mimicking abilities of biological cells.[1] Among them, vesicles are considered to be artificial cells because they have boundaries between inner and outer phase, which are similar to biomembranes.[2] Inspired by multicellular organisms where multiple cells assemble into tissues, assembling multiple artificial cells could induce large-scale structures considered to be artificial tissues.[3] We previously found a formation of artificial tissues comprising multiple vesicles triggered by salt bridges.[4] In this presentation, we report how to induce motility of such vesicle-type artificial tissues.

First, addition of azobenzene-containing amphiphiles induced a contraction of tissues under UV illumination. It was estimated that a deformation of each vesicle due to photoisomerization of the amphiphiles promoted close contacts between vesicles. Second, utilizing magnetic nanoparticles (MNPs) enabled us to manipulate tissues and transport large cargoes by using a magnet. Third, in the presence of gold nanoparticles (AuNPs), phototaxis of the tissues was observed due to a photothermal effect of AuNPs. Fourth, addition of platinum nanoparticles (PtNPs) or catalase caused propulsion at a vertical direction in H_2O_2 solutions, which was due to a buoyancy of oxygen bubbles generated by decomposition of H_2O_2. These results suggest a possibility of engineering biomimetic materials comprising multiple colloids with versatile motility.



1) C. Xu, S. Hu, X. Chen, *Mater. Today* **2016**, *19*, 516. 2) A. J. Dzieciol, S. Mann, *Chem. Soc. Rev.* **2012**, *41*, 79. 3) X. Wang, H. Du, Z. Wang, W. Mu, X. Han, *Adv. Mater.* **2021**, *33*, e2002635. 4) T. Kojima, Y. Noguchi, K. Terasaka, K. Asakura, T. Banno, *under review*.

In situ construction of glycopeptide-based supramolecular hydrogels for medical-related applications

([1]*United Graduate School of Drug Discovery & Medicine Information Sciences, Gifu University*, [2]*GUiAS, Gifu University,* [3]*COMIT, Gifu University*, [4]*iGCORE, Gifu University*)
○Shintaro Sugiura[1], Yuki Shintani[1], Sayuri Higashi[2], Masato Ikeda[1,3,4]

Keywords: Glycopeptides; Supramolecular hydrogels; Lectin; Antimicrobial nanomaterials

Glycopeptide-based supramolecular materials, serving as a multivalent saccharide ligand toward lectins on the surface of self-assembled structures, can emulate the biological function of polysaccharides and glycans. They thus could lead to exploring a variety of medical-related applications, including regenerative medicine and antimicrobial therapy.[1] Nevertheless, the chemical complexity of saccharides is a massive barrier to the molecular design and synthesis of self-assembling glycopeptide monomers. Hence, straightforward strategies for developing them are highly desirable. In this study, we applied a one-pot oxyamine ligation[2] to construct a variety of self-assembling glycopeptide under aqueous conditions, which gives rise to supramolecular hydrogels capable of capturing lectin-bearing pathogens in the hydrogel matrices through lectin-saccharide interactions.

We newly designed and synthesized (*N*-methyl)aminooxy-functionalized peptide derivatives, which gave a supramolecular hydrogel even in the presence of saccharides. ^{1}H NMR spectroscopic analysis revealed the conjugation of unprotected saccharides toward these peptides. Furthermore, we conducted confocal laser scanning microscopy (CLSM) observations with fluorescent dye-labeled lectins, which revealed their colocalization with fibrous structures of glycopeptides as anticipated. The results indicate the favorable affinity of self-assembled glycopeptide nanostructures toward the lectins and their selectivity. These findings offer opportunities to develop glycopeptide-based supramolecular biomaterials with potential applications in cell culture or vaccine preparation.

1) (a) L. Su *et al.*, *Curr. Opin. Chem. Biol.*, **2022**, 69, 102171, (b) A. Brito *et al.*, *Chem*, **2021**, 7, 2943–2964.
2) T. Cheewawisuttichai *et al.*, *Org. Biomol. Chem.*, **2021**, 19, 6613–6617.

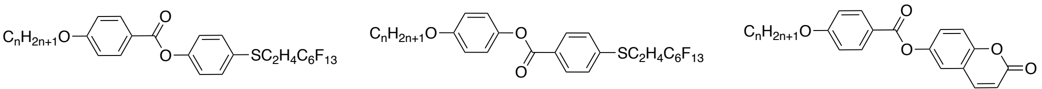
Structural Analyses with Spectroscopic and Computational Studies of Organogels Formed by Liquid-crystalline Phenyl Benzoates

([1]*Graduate School of Sciences and Technology for Innovation, Yamaguchi University,* [2]*Advanced Technology Institute, Yamaguchi University*) ○ Kenta Matsumoto,[1] Junya Yamaguchi,[1] Korato Kaetada,[1] Yui Endo,[1] Yuri Hatsuda,[1] Yuki Morita,[2] Hiroaki Okamoto[1]

Keywords: Liquid Crystal; Low-molecular Gel; Phenyl Benzoate; Fluoroalkyl Group; Coumarin

In our previous works, it has been found that some liquid-crystalline phenyl benzoates with several organic solvents can form physical gels.[1,2] While the correlation between molecular structures and gelation is not elucidated. Meanwhile, it has been reported in our publication[2] that 2-oxochromene-6-yl 4-alkoxybenzoates (Compounds **3**-n, Figure 1) with organic solvents were self-assembled by electrostatic interaction between coumarin skeletons, supporting in UV-Vis and TD-DFT.

In this work, self-assembly phenomena of gelation in organic solvents with phenyl benzoates containing a fluoroalkyl group (Compounds **1**-n and **2**-n, Figure 1) or a coumarin skeleton (Compounds **3**-n) were analyzed by spectroscopic and computational studies.



Compounds **1**-n (n = 3–12) Compounds **2**-n (n = 3–12) Compounds **3**-n (n = 3–12)

Figure 1. Chemical structures of compounds **1**-n, **2**-n, and **3**-n.

Optimized structures as a dimer for compounds **1**-8 and **2**-8, and each formation enthalpies (ΔH_f) are shown in Figure 2. The gel-sol transition enthalpies for propylene carbonate gels ($\Delta H_{\text{gel-sol}}$) with compounds **1**-8 and **2**-8 at room temperature estimated 36.6 kJ mol^{-1} and 12.5 kJ mol^{-1}, respectively. self-assembly phenomena for gelation with compounds **1**-8 and **2**-8 may be driven by π–π interaction and fluorophilic effect, respectively, since absolute value of $\Delta H_{\text{gel-sol}}$ $\Delta_f H$ are similar values.

In this presentation, effect of polar functional group on gelation, which compared with compounds **1**-n and **3**-n, analyzed by XRD and IR will be reported.

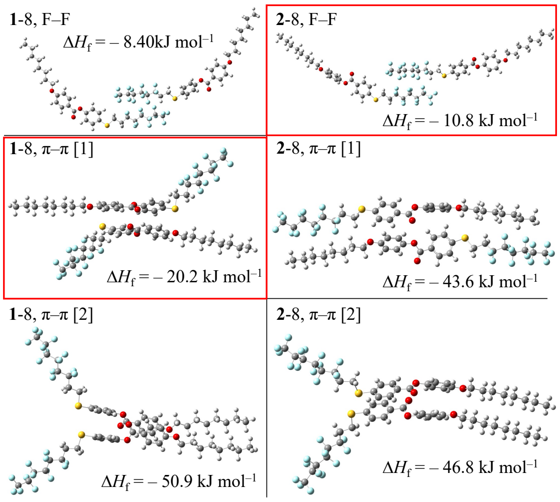


Figure 2. Optimized geometries of compounds **1**-n and **2**-n as a dimer and DFT-calculated formation enthalpy ($\Delta_f H$) using the M06/6-311G (d) level.

1) B-P. Cao, *et al.*, *J. Fluorine Chem.*, **2019**, *226*, 109348. 2) Y. Endo *et al*, *Chem. Lett.* **2023**, *52*, 337.

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19日(火) 15:55 ~ 17:15 C442(4号館 [4階] 442)

[C442-2vn] 20. 材料化学—基礎と応用

座長：吉尾 正史、中西 尚志

英語

15:55 ~ 16:15

[C442-2vn-01]

キラルなアルキル–π分子液体を媒体とする高濃度πゲル

〇竪山 瑛人[1,2]、山中 正道[3]、中西 尚志[1,2] (1. 北大、2. 物質・材料研究機構、3. 明治薬大)

日本語

16:15 ~ 16:35

[C442-2vn-02]

フルオレノン系ドナー・アクセプター・ドナー分子からなる刺激応答性超分子ゲル

〇山田 翔太[1]、鈴木 真緒[1]、関 淳志[1,2]、青木 健一[1,2] (1. 東理大院、2. 東理大)

日本語

16:35 ~ 16:55

[C442-2vn-03]

ゲル-ゲル界面のデザインによる新奇異方性ハイドロゲルの開発

〇髙橋 知大[1]、佐野 航季[1,2] (1. 信州大、2. JSTさきがけ)

日本語

16:55 ~ 17:15

[C442-2vn-04]

イオン伝導液晶ゲルの作製とアクチュエータ機能

〇吉尾 正史[1,2,3]、諏訪 俊一[3,1] (1. 国立研究開発法人物質・材料研究機構、2. JSTさきがけ、3. 北海道大学大学院)

Highly condensed π–gels based on chiral alkyl–π molecular liquids as a medium

([1]*Graduate School of Life Science, Hokkaido University*, [2]*Research Center for Materials Nanoarchitectonics, National Institute for Materials Science*, [3]*Meiji Pharmaceutical University*) ○Akito Tateyama,[1,2] Masamichi Yamanaka,[3] Takashi Nakanishi[1,2]

Keywords: π-Gels; Functional Molecular Liquids; Chirality; Low Molecular Weight Gelator

In recent years, with increasing interest in soft organic materials, fluidic and non-volatile functional liquid materials have attracted attention. By modifying a π-conjugated unit with bulky yet flexible branched alkyl chains, solvent-free functional liquids (alkyl–π liquids) have been developed[1]. Since it is necessary to adjust the elastic modulus (*G*’) over a wide range to expand the usefulness of alkyl–π liquids, we have developed new functional gel materials based on alkyl–π liquids by employing low-molecular-weight gelators.[2] The effect of the chirality on the physicochemical properties of alkyl–π liquids and their gelated materials remains largely unexplored. This study focuses on the effect of chirality for both alkyl–π liquid and low-molecular-weight gelator towards the gelation and optoelectronic properties.

In this presentation, we mainly utilize blue-fluorescent liquid carbazoles possessing a racemic (***rac*-CZL**)[3] or a (*R*)-isomeric (***R*-CZL**) branched alkyl chain (Fig. 1a). These exhibited different phase transition behaviors. As gelators, (*R,R*)- and (*S,S*)-isomer containing amide units for intermolecular hydrogen bonding (***RR*-GA** and ***SS*-GA**)[4] (Fig. 1b) were employed. By investigating the rheological and optical properties of the gels of ***rac*-CZL** or ***R*-CZL** using ***RR*-GA** or ***SS*-GA** (Fig. 2), we discuss the effect of chirality on the formation process of gelator’s fibrous assemblies and on the viscoelastic and optical properties.

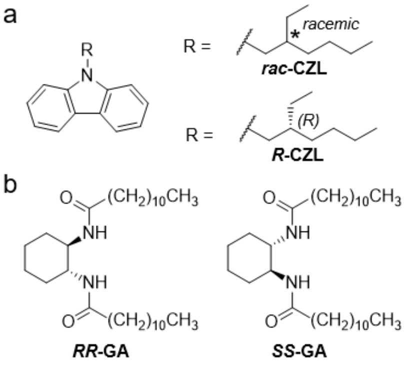


Fig. 1 Molecular structures of (a) liquid carbazoles ***rac*-CZL** and ***R*-CZL**, (b) gelators ***RR*-GA** and ***SS*-GA**.

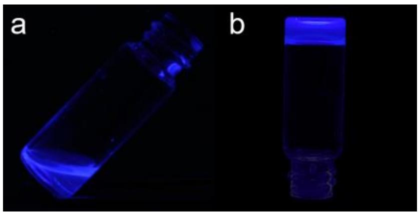


Fig. 2 Images of (a) neat liquid ***R*-CZL**, and (b) gel ***R*-CZL** with 1 wt% gelator ***RR*-GA**, under 365 nm UV irradiation.

1) A. Tateyama, T. Nakanishi, *Responsive Mater.* **2023**, *1*, e20230001. 2) A. Tateyama, M. Yamanaka, T. Nakanishi, *The 103rd CSJ Annual Meeting*, Noda, 2023.3.23, K206-2am-06. 3) Hendrickx E., et. al., *Chem. Phys.*, **1999**, *245*, 407. 4) K. Hanabusa, et al., *Angew. Chem. Int. Ed.*, **1996**, *35*, 1949.

フルオレノン系ドナー・アクセプター・ドナー分子からなる刺激応答性超分子ゲル

（東理大院[1]・東理大[2]）〇山田 翔太[1]・鈴木 真緒[1]・関 淳志[1,2]・青木 健一[1,2]

Stimuli-responsive Supramolecular Gels of Fluorenone-Based Donor-Acceptor-Donor Molecules ([1]*Graduate School of Science, Tokyo University of Science*, [2]*Tokyo University of Science*) 〇Syota Yamada,[1] Mao Suzuki,[1] Atsushi Seki,[1,2] Ken’ichi Aoki[1,2]

Electron donor-acceptor-donor (D-A-D) type molecules exhibit characteristic visible light absorption and emission properties based on intramolecular charge transfer. The electronic transitions in D-A-D type molecules are sensitive to the ambient environment, which is the basis of chromic behavior. Since supramolecular gels show reversible sol-gel transitions upon external stimuli, they can work as a platform for stimuli-responsive materials. In this study, we investigated the gelation and chemo-responsive behaviors of fluorenone-based D-A-D type molecules modified with urethane groups via linker units. The fluorenone derivatives formed supramolecular organogels, which supported by the intermolecular hydrogen bond. The organogels exhibit the chemo-responsive behaviors toward an acid or alkali metal cations.

Keywords : Supramolecular Gels, Fluorenone, Stimuli-Responsive Materials, Intramolecular Charge Transfer

電子アクセプター（A）に電子ドナー（D）を修飾したD-A-D型分子は，分子内電荷移動に基づく特徴的な可視光吸収および発光特性を示す。D-A-D型分子における電子遷移は分子の周囲環境に鋭敏であり，クロミズムの基盤となる。非共有結合性分子間相互作用を駆動力として形成される超分子ゲルは，熱などの外部刺激によって可逆的なゾル-ゲル転移を示し，刺激応答性材料のプラットフォームとして機能する。本研究では，新たな化学刺激応答性超分子ゲルの創出を目的として，フルオレノンを中心とするD-A-D型コアにリンカー部位を介して水素結合性のウレタン基を導入した分子（Figure 1）を数種類合成し，ゲル化挙動と化学刺激応答性について検討した。

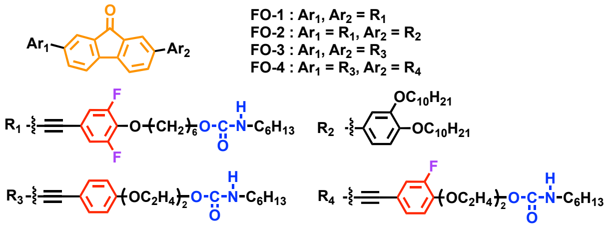


Figure 1. Chemical structures of fluorenone derivatives **FO-1**, **FO-2**, **FO-3**, and **FO-4**.

FO-1, **FO-2**, **FO-3**, **FO-4** は，ドデシルベンゼン（DB）および低分子量ポリエチレングリコール（LMW-PEG）中でオルガノゲルを形成した。それらのオルガノゲルについてFT-IRスペクトル測定を行ったところ，水素結合性のC=O伸縮振動に帰属される吸収が認められ，ウレタン基を架橋点とする分子間水素結合により，超分子ゲルを形成していることがわかった。**FO-1**, **FO-2** のDBゲルはトリフルオロ酢酸の添加により，凝集挙動の変化と吸収色の変化，蛍光の消光が生じた。また，**FO-3**, **FO-4** のLMW-PEGゲルでは，アルカリ金属カチオンの添加により，吸収色，発光色の変化が見られた。詳細については，当日報告する。

日本化学会 第104春季年会 (2024)

ゲル-ゲル界面のデザインによる新奇異方性ハイドロゲルの開発

（信州大繊維 [1]・JST さきがけ [2]）

○高橋 知大 [1]・佐野 航季 [1,2]

Development of an anisotropic hydrogel by designing its gel-gel interface

([1]*Faculty of Textile Science and Technology, Shinshu University,* [2]*JST PRESTO*)

○Tomohiro Takahashi,[1] Koki Sano[1,2]

Anisotropic hydrogels exhibit various unique functions, and therefore, are regarded as promising soft materials for biomedical and soft-robotic applications. They are typically synthesized by embedding anisotropic structures throughout the entire interior (bulk) of the hydrogel. In this study, we aimed to synthesize a new type of anisotropic hydrogel by introducing an interface, a complementary region to the bulk, in the hydrogel.

Keywords : Hydrogel; Gel-gel interface; Anisotropy; Orientation control

ハイドロゲルは三次元のゲルネットワークが水を豊富に含んだソフトマテリアルである。特に、異方性ハイドロゲルは生体に近い組成や構造を有しており、その異方的構造に由来するユニークな機能を示すことから、医用材料やソフトロボティクスなどへの応用が期待されている[1–3]。今までに多くの異方性ハイドロゲルが合成されてきたが、その設計戦略は主に「バルク（物質内部）」全体に渡って巨視的な配向構造を埋め込むという方法に頼っている[1,2]。このような従来の方法に対して、我々は「バルク」と相補的な領域である「界面」をハイドロゲルに導入することで、新しいタイプの異方性ハイドロゲルの作製を目指した。

本研究では、一般的なアクリル系モノマー、架橋剤、重合開始剤を混合した水溶液を利用したフリーラジカル重合によってハイドロゲルを作製した。意図的にゲル作製のプロセスを二段階に分けることで、ゲル-ゲル界面を内包したハイドロゲルを得ることに成功した。ゲル内部の構造解析を行ったところ、驚くべきことに、ゲル-ゲル界面近傍において、高分子ネットワークが自発的に局所配向構造を形成していることを見出した。さらに、多段階の光開始重合を利用することで、任意の形状に配向した高分子ネットワークを導入した新しいタイプの異方性ハイドロゲルの作製にも成功した。本発表では、ゲル内部の詳細な構造解析や配向構造の形成メカニズムなどについても議論する予定である。

[1] K. Sano *et al. Angew. Chem. Int. Ed.* **57**, 2532–2543 (2018).

[2] K. Sano *et al. Angew. Chem. Int. Ed.* **57**, 12508–12513 (2018).

[3] K. Sano *et al. Nat. Commun.* **11**, 6026 (2020).

イオン伝導液晶ゲルの作製とアクチュエータ機能

（物材機構 [1]・JST さきがけ [2]・北大院総合化学 [3]）○吉尾 正史 [1,2,3]・諏訪 俊一 [1,3]

Preparation of Ion-Conductive Liquid-Crystalline Gels and Their Actuator Properties

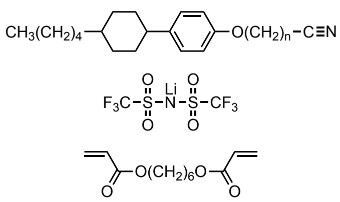
([1]*National Institute for Materials Science*, [2]*JST PREST*, [3]*Graduate School of Chem. Sci. & Eng., Hokkaido Univ.*) ○Masafumi Yoshio,[1,2,3] Shunichi Suwa[1,3]

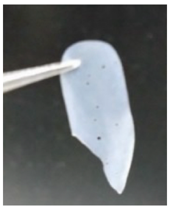
Developing high-frequency response and high-force generating electroactive polymer actuators is essential for advancing haptic human interface devices and soft robotics. In this work, we introduce novel ionic electroactive soft actuators composed of ion-conductive liquid-crystalline polymer gel electrolytes. These actuators incorporate room-temperature smectic liquid crystals containing nitrile-terminated alkyl chains groups complexed with lithium salts, which were mixed with vinyl monomers. Through in-situ photopolymerization, we successfully fabricated free-standing films showcasing microphase-separated structures comprising liquid crystals and polymers. The resulting electrolytes were integrated between layers of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS). Our trilayer device demonstrated significant bending actuation under an AC voltage of 2 V, attributed to its high ionic conductivity of up to 10^{-4} S cm^{-1} under ambient conditions.

Keywords : Actuator; Liquid Crystal; Lithium Ion; Electric Field; Haptics

ウェアラブル触覚デバイスやソフトロボットの構築において、高速応答および高出力を示す電気活性高分子アクチュエータの開発が重要である。これまでに、我々は光架橋イオン伝導性液晶高分子膜を活用した高出力アクチュエータの開発を進めてきた1)。本研究では、高速振動アクチュエータの構築を目指して、新たにリチウムイオン伝導性液晶ゲル電解質の開発を行った。

アルキル鎖末端にニトリル基を有する棒状分子を合成し、リチウムビス（トリフルオロメチルスルホニル）イミド塩と混合することで、層状構造を有する室温スメクチック液晶が得られることを見出した。この液晶と様々なビニルモノマーを複合化し、その場光重合することにより、液晶と光架橋高分子からなるミクロ相分離構造を有する自立性膜を得ることに成功した。この電解質膜と PEDOT:PSS 導電性高分子電極からなる三層構造の素子を作製し、2 V の交流電場を印加することで、素子が大きな屈曲変形を示すことを明らかにした。





1) Example of ionic electroactive actuators based on photocured ionic liquid crystals: Yoshio et al., *ACS Mater. Lett.*, **2022**, *4*, 153–158; *ACS Appl. Mater. Interfaces*, **2023**, *15*, 4495–4504; *Mater. Chem. Front.*, **2023**, *7*, 2828–2838; *J. Mater. Chem. C*, **2023**, *11*, 10154–10162; *Adv. Funct. Mater.*, **2024**, *in press*.

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19日(火) 15:55 ~ 17:15 C443(4号館 [4階] 443)

[C443-2vn] 20. 材料化学―基礎と応用

座長：大山 陽介、武藤 克也

日本語

15:55 ~ 16:15

[C443-2vn-01]

ビナフチル架橋ジベンゾオキセピノイミダゾール二量体の逆フォトクロミズム

○八木 詩織[1]、阿部 二朗[1] (1. 青山学院大)

日本語

16:15 ~ 16:35

[C443-2vn-02]

ヘキサアリールビイミダゾールとターアリーレンの特徴を有する新規フォトクロミック分子の開発

○武藤 克也[1]、中嶋 琢也[1] (1. 大阪公立大学)

英語

16:35 ~ 16:55

[C443-2vn-03]

熱閉環反応を示すアザジアリールエテンのフォトクロミック反応挙動

○濱谷 将太[1]、北川 大地[1]、小畠 誠也[1] (1. 阪公大院工)

日本語

16:55 ~ 17:15

[C443-2vn-04]

D-A型ピリジニウム色素のオルガノハロゲノクロミズムに及ぼすカウンターアニオンの影響

○小塚 訓平[1]、今任 景一[1]、大山 陽介[1] (1. 広大院先進理工)

ビナフチル架橋ジベンゾオキセピノイミダゾール二量体の逆フォトクロミズム

（青山学院大理工 [1]）○八木 詩織 [1]・阿部 二朗 [1]

Negative Photochromism of Binaphthyl-Bridged Dibenzo[2,3:6,7]oxepino[4,5-d]imidazole Dimer

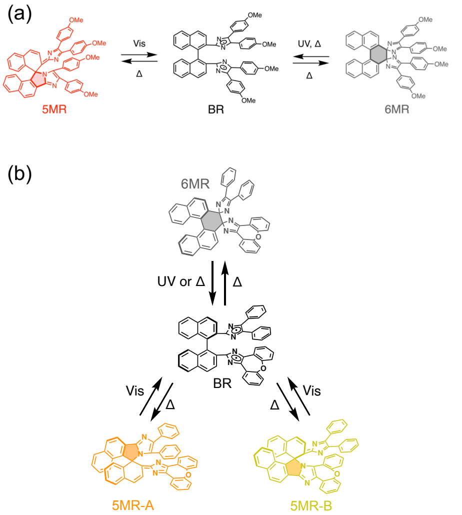
([1] *Dept. Chem., Sch. Sci. Eng., Aoyama Gakuin Univ.*) ○Shiori Yagi,[1] Jiro Abe[1]

Upon exposure of visible light, binaphthyl-bridged imidazole dimers (**BN-ImD**) exhibit negative photochromic reaction from a stable colored isomer to a metastable colorless isomer via a short-lived biradical. In this study, we have successfully synthesized novel binaphthyl-bridged imidazole dimers (**BN-DBOXPImD**) by introducing an imidazole moiety with a dibenzooxepine structure. **BN-DBOXPImD** has two colored isomers, which are isomerized to the colorless isomer upon the irradiation of visible light. This molecule exhibits not only negative photochromism but also bistable photoswitch between two colored isomers.

Keywords : Photochromism; Biradical; Imidazole Dimers

フォトクロミック分子の多くは紫外光照射によって光異性化するが、紫外光はエネルギーが大きく、材料や細胞の光劣化を引き起こすため、エネルギーが小さな可視光や近赤外光に応答するフォトクロミック分子の開発が求められている。当研究室では可視光に応答するビナフチル架橋型イミダゾール二量体（**BN-ImD**）を開発した[1]。**BN-ImD** の安定着色体（5MR）に可視光を照射すると、短寿命ビラジカル（BR）を経由して、準安定体である無色体（6MR）に光異性化する逆フォトクロミズムを示す。本研究では、**BN-ImD** にジベンゾオキセピン構造を有するイミダゾール環を導入することで、新たなビナフチル架橋イミダゾール二量体（**BN-DBOXPImD**）を合成し、その光反応特性の評価を行った。

Scheme 1. Photochromism of (a) **BN-ImD** and (b) **BN-DBOXPImD**.



BN-DBOXPImD はイミダゾール部位が非対称であることから、2 つの着色異性体（5MR-A, 5MR-B）を有する。可視光照射によって、着色異性体は短寿命のビラジカル（BR）を経由して、準安定異性体である 6MR に異性化する。5MR-B は 5MR-A よりも不安定で、熱的に 5MR-A に異性化する。**BN-DBOXPImD** は逆フォトクロミズムだけでなく、5MR-A と 5MR-B 間で双安定なフォトクロミズムを示す。

[1] S. Hatano, T. Horino, A. Tokita, T. Oshima, J. Abe, *J. Am. Chem. Soc.* **2013**, *135*, 3164.

ヘキサアリールビイミダゾールとターアリーレンの特徴を有する新規フォトクロミック分子の開発

(阪公大院理[1]) ○武藤 克也[1]・中嶋 琢也[1]

Development of a Photochromic Molecule with Characteristics of Hexaarylbiimidazole and Terarylene

([1] *Osaka Metropolitan Univ.*)○Katsuya Mutoh,[1] Takuya Nakashima[1]

Multi-state photochromism has been considered more attractive than traditional bistable photochromism because it can offer more versatility and control in photoresponsive systems. One of the attractive designs for the multi-state photochromic molecule is an efficient combination of two photochromic units. In this study, we have designed and synthesized a novel photochromic molecule (1) that consists of a hexaarylbiimidazole unit and a terarylene unit. Compound 1 shows four-state photochromic reaction upon UV light irradiation. We found that the delocalized π-radical on the closed-ring form of the terarylene is efficient to enhance the photosensitivity to the NIR-I and -II region.

Keywords : Photochromism; Hexaarylbiimidazole; Diarylethene; Radical

異種フォトクロミック分子の融合は、単一のフォトクロミック分子では実現できない多彩な光応答性を創出できる。本研究では、ヘキサアリールビイミダゾール1)とターアリーレン2)の特徴を併せ持つフォトクロミック分子（**1**）を合成し、その光応答性および光学特性を検討した。過渡吸収分光法および量子化学計算より、化合物 1 は紫外光照射により C-N 結合が均等開裂し、発色体としてラジカル（**1OR**）を生成することが明らかとなった。**1OR** に紫外光を照射するとターアリーレンの 6π 閉環反応が進行し **1CR** を生成した。**1CR** は閉環構造にラジカルが非局在化することで近赤外領域まで吸収帯が長波長シフトした。また、1CR は 500 nm を極大吸収波長とする異性体に熱的に変化した。以上のことから、化合物 **1** は 4 つの状態を経由するマルチフォトクロミック反応を示すことを明らかにした。

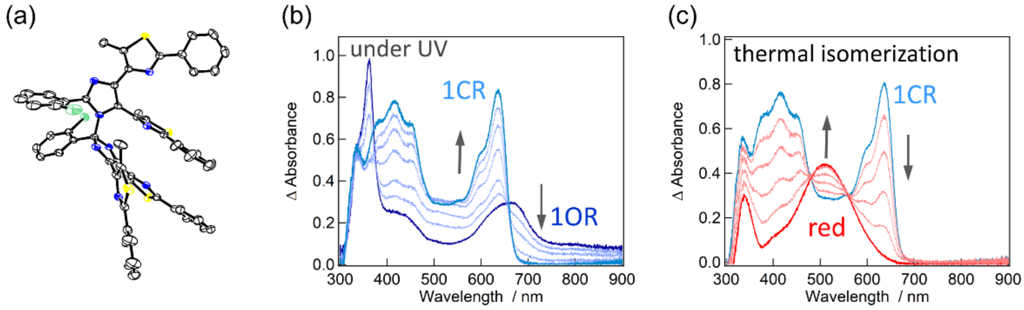


Figure 1. (a) The ORTEP representation of the molecular structure of 1 (thermal ellipsoids at 50% probability). (b, c) The transient absorption spectra of 1OR upon UV light irradiation and the thermal isomerization from 1CR.

1) T. Hayashi, K. Maeda, *Bull. Chem. Soc. Jpn.*, **1960**, *33*, 565.
2) T. Nakashima, M. Goto, S. Kawai, T. Kawai, *J. Am. Chem. Soc.*, **2008**, *130*, 14570.

Photochromic Reaction Behavior of Azadiarylethenes Exhibiting Thermal Cyclization Reaction

(*Graduate School of Engineering, Osaka Metropolitan University*) ○Shota Hamatani, Daichi Kitagawa, Seiya Kobatake

Keywords: Azadiarylethene, Thermal Cyclization, Photochromism

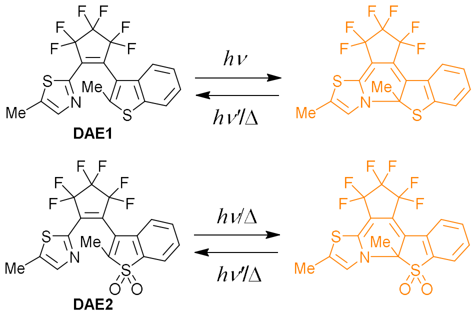


Figure 1. Molecular structure of diarylethene derivatives in this work.

Photochromic compounds are of great interest as light-driven molecular switches in research fields of material and life sciences. Diarylethene is a typical P-type photochromic molecule,[1] and the photochromic reaction is based on a 6π electrocyclic reaction between open-ring and closed-ring isomer. Recently, it has been reported that azadiarylethenes having a nitrogen atom at the reaction site exhibit fast T-type photochromism due to the disrotatory thermal cycloreversion allowed by Woodward-Hoffman rule,[2] and further development of azadiarylethenes is expected. In this work, we synthesized diarylethene derivatives **DAE1** and **DAE2**, in which a benzothiophene ring and a S,S-dioxide benzothiophene ring were introduced into the aryl group, and investigated their photochromic properties (Figure 1).

DAE1 and **DAE2** were synthesized, their properties were investigated. When **DAE1** in *n*-hexane was irradiated with ultraviolet (UV) light, it became to color yellow. When UV light irradiation was stopped, it quickly returned to its original colorless state, exhibiting fast T-type photochromism. This fast thermal cycloreversion reaction is based on a disrotatory pathway. **DAE2** in *n*-hexane was pale yellow. When irradiated with UV light, it turned a deep yellow color. When UV light irradiation was stopped, it returned to its original color. These color changes are based on photocyclization and thermal cycloreversion. Furthermore, when the solution was irradiated with visible light, it became colorless. Without visible light irradiation, it gradually returned to its original pale yellow. These results suggested that open-ring and closed-ring isomer exist in thermal equilibrium, and thermal cyclization can proceed. Thus, it was found that the cyclization reaction of azadiarylethene derivatives with S,S-dioxide benzothiophene ring proceeds not only by photochemical reactions but also by thermal reactions.

1) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.
2) S. Hamatani, D. Kitagawa, S. Kobatake, *J. Phys. Chem. Lett.* **2023**, *14*, 8277–8280.

D-A 型ピリジニウム色素のオルガノハロゲノクロミズムに及ぼすカウンターアニオンの影響

（広大院先進理工）○小塚訓平・今任景一・大山陽介

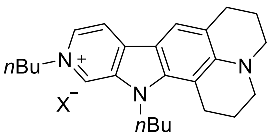
Influence of Counter Anion of D-A Type Pyridinium Dyes on its Organohalogenochromism

(*Grad. Sch. of Adv. Sci. and Eng., Hiroshima Univ.*) ○Kumpei Kozuka, Keiichi Imato, Yousuke Ooyama

Organohalogenochromism (OHC) is a photophysical phenomenon that induces a significant bathochromic or hypsochromic shift of the photoabsorption bands of organic dyes in halogenated solvents compared with those in non-halogenated solvents 1)‐3). Thus, OHC is a specific solvatochromism observed only in halogenated solvents that is different from a common solvatochromism depending on the Solvent polarity. However, there is little published research on OHC although the phenomenon is of great scientific interest and practical importance, such as the development of optical sensing technology for the detection of toxic organohalogen compounds. In this work, in order to establish new molecular design strategies for OHC dyes and elucidate the mechanism of OHC, we designed and synthesized D-A type pyridinium dyes **KK1**–**KK4** bearing various counter anions. Indeed, **KK2** bearing chloride ion as a counter anion showed bathochromic shifts of the photoabsorption band in halogenated solvents by about 20 nm compared with those in non-halogenated solvents. In this presentation, we will report the optical properties of **KK1–KK4** in various halogenated or non-halogenated solvents.

Keywords : Organohalogenochromism, Pyridinium dye, Counter anion, Photoabsorption property, Oraganic halogenated solvent.

オルガノハロゲノクロミズ（OHC）とは、ハロゲン溶媒中における有機色素の光吸収帯が非ハロゲン溶媒中のものと比べて長波長シフトあるいは短波長シフトする現象である 1)-3)。OHC はハロゲン溶媒中でのみ観測される特異的なクロミズムであり、溶媒極性の増加に伴い色素の光吸収帯がシフトするソルバトクロミズムとは異なる。OHC は学術的に興味深いだけではなく、有毒な有機ハロゲン化合物を検出するための光学センサーへの応用など実用的にも重要であるにも関わらず、OHC に関する研究はほとんど行われていない。そこで本研究では、OHC 色素の新たな分子設計指針の確立と OHC のメカニズムの解明を目的とし、種々のカウンターアニオンを有する D-A 型ピリジニウム色素を分子設計及び合成した（Fig. 1）。その結果、塩化物イオンをカウンターアニオンとして有する **KK2** の光吸収帯はハロゲン溶媒中において長波長シフトしており、OHC を発現することが観察された（Fig. 2）。本発表では、**KK1–KK4** の様々なハロゲンまたは非ハロゲン溶媒中における光学特性を評価した結果について報告する。



KK1 : X = Cl, **KK2** : X = Br
KK3 : X = I, **KK4** : X =BPh$_4$

Fig. 1 Chemical structures of **KK1–KK4**.

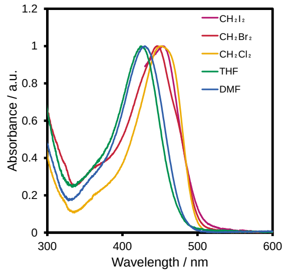


Fig. 2 Photoasorption spectra of **KK2** in various solvents.

1) Y. Ooyama, Y. Oda, T. Mizuno, J. Ohshita, *Tetrahedron*, 2013, **69**, 1755.
2) T. Higashino, Y. Ooyama, *Chem. Lett.*, 2021, **50**, 1530.
3) K. Kozuka, K. Imato, Y. Ooyama, *Mater. Adv.,* 2023, DOI: 10.1039/D3MA00671A.

アカデミックプログラム［Ｂ講演］｜22. 資源利用化学・環境・グリーンケミストリー：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 16:55 A1455(14号館 [5階] 1455)

[A1455-2vn] 22. 資源利用化学・環境・グリーンケミストリー

座長：佐川 拓矢、大久保 敬

日本語
15:55 ~ 16:15

[A1455-2vn-01]
異性化による*N*-アセチルマンノサミンの合成とその触媒的変換反応

○佐川 拓矢^{1}、長田 侑大^{1}、橋詰 峰雄^{1} (1. 東京理科大学)

日本語
16:15 ~ 16:35

[A1455-2vn-02]
バイオガスに含まれるメタンの二酸化塩素光酸化によるギ酸・メタノール合成

○大久保 敬^{1,2}、平松 久美子^{2}、板橋 勇輝^{2} (1. 阪大高等共創研、2. 阪大先導的学際研)

日本語
16:35 ~ 16:55

[A1455-2vn-03]
有機酸によるリグノセルロースの可溶化における水の影響

○中川 由佳^{1,2}、橋爪 知弘^{1,2}、渡辺 隆司^{1,3} (1. 京都大学バイオマスプロダクトツリー産学共同研究部門、2. 株式会社ダイセル、3. 京都大学生存圏研究所)

異性化による*N*-アセチルマンノサミンの合成とその触媒的変換反応

（東理大工）○佐川 拓矢・長田 侑大・橋詰 峰雄

Synthesis of *N*-Acetylmannosamine by Isomerization and Its Catalytic Conversion Reaction

(*Faculty of Engineering, Tokyo University of Science*) ○Takuya Sagawa, Yuta Osada, Mineo Hashizume

N-Acetylmannosamine (NAM) is an epimer of *N*-acetylglucosamime (NAG), which is obtained by depolymerization of chitin. In this study, to develop the further utilization of NAM, the improvement of NAM yield by isomerization of NAG and the synthesis of a bioplastic monomer, 2-acetamide-2-deoxyisomannide (ADIM), from NAM were performed. Optimizing the reaction conditions, the isomerization of NAG gave NAM with 46% HPLC yield. Furthermore, ADIM was obtained from NAM by hydrogenation and subsequent dehydration.

Keywords : Chitin; N-Acetylmannosamine; Isomerization; Dehydration

N-アセチルマンノサミン（NAM）は、キチンの解重合によって得られる*N*-アセチルグルコサミン（NAG）のエピマーである。NAMはNAGの異性化により得られるものの、その収率は非常に低い。そのためNAMは医薬品原料以外の用途には利用されていない。そこで本研究では、NAMのさらなる用途開拓を目指し、NAGの異性化におけるNAM収率の向上およびNAMの触媒的変換反応を検討した。まずNAGの異性化は、ホウ酸緩衝溶液中におけるNAMの合成[1)]を参考に条件の最適化を行った。続いてNAMの水素化により2-アセトアミド-2-デオキシマンニトール（ADM）に変換した後、酸触媒を用いた脱水縮合により、バイオプラスチック原料として期待される2-アセタミド-2-デオキシイソマンニド（ADIM）への変換を行った（Figure 1）。

ホウ酸緩衝溶液中におけるNAGの異性化は、NAGのホウ酸エステルを経由する可逆反応であり、ホウ酸の添加量および溶液のpHが平衡に影響を与えると考えられる。反応条件を最適化したところ、pH 7.5かつNAGとホウ酸のモル比が1:4のときHPLC収率46%でNAMを得た。次に、ルテニウム担持触媒を用いたNAMの水素化反応を行い、ADMを単離収率63%で得た。続いて、酸触媒を用いたADMの脱水縮合によりADIMの合成を検討した。減圧下、トリフルオロメタンスルホン酸（TfOH）を用いることで、ADIMをHPLC収率53%で得た。

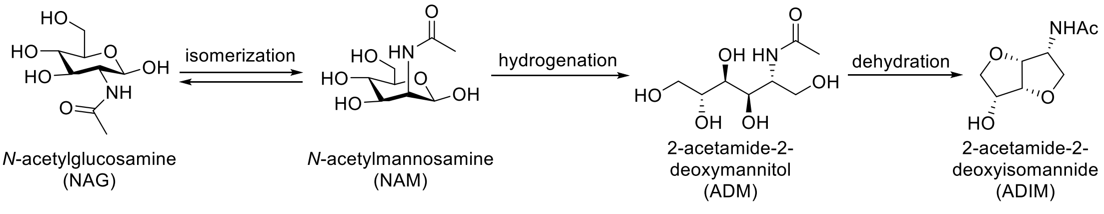


Figure 1. Synthetic route for ADIM from NAG.

1) M. Oagata, T. Hattori, R. Takeuchi, T. Usui, *Carbohudr. Res.* **2010**, *345*, 230.

バイオガスに含まれるメタンの二酸化塩素光酸化によるギ酸・メタノール合成

(阪大先導的学際研 [1]・阪大高等共創研 [2]) ○大久保 敬 [1,2]・平松 久美子 [1]・板橋 勇輝 [1]

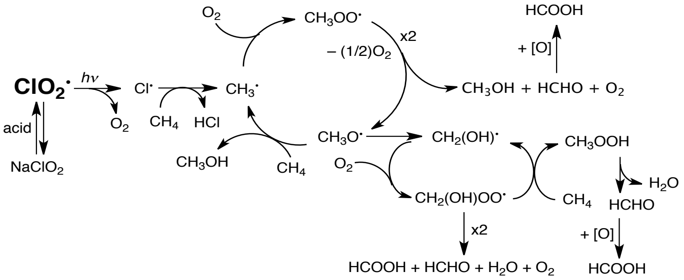
Photochemical Synthesis of Methanol and Formic Acid by Oxygenation of Methane Containing Biogas with Chlorine Dioxide

([1]*Osaka University, OTRI,* [2]*Osaka University, IACS*)
○Kei Ohkubo,[1,2] Kumiko Hiramatsu,[1] Yuki Itabashi[1]

Oxygenation of methane in biogas photochemically occurred in the presence of chlorine dioxide ($ClO_2^{\bullet}$). The yields of methanol and formic acid as products were 17% and 82%, respectively, with a methane conversion of 99% in a two-phase system comprising perfluorohexane and water under ambient conditions. Mechanistic studies revealed that the C-H bond of methane was activated in the fluorous phase by the chlorine radical generated by the photoexcitation of $ClO_2^{\bullet}$. The photochemical oxygenation of methane is initiated by generation of chlorine radical and singlet oxygen from photoexcited state of $ClO_2^{\bullet}$, leading to the final products by aerobic radical chain processes. The photochemical oxygenation of methane containing biogas using $ClO_2^{\bullet}$ reported herein could be generalized to provide novel application for usage of biogas instead of gas electric power generation in biogas plant.

Keywords : Biogas; Methane; Photochemical Reaction; Radical

100 mL マイヤーフラスコにパーフルオロ-*n*-ヘキサン（*n*-C_6F_{14}, 30 mL）にメタンと酸素を加えた溶液を調製し、その後、$ClO_2^{\cdot}$水溶液（0.1 M, 20 mL）を添加した二層反応液を準備した。次に、フルオラス溶媒の一つであるパーフルオロ-*n*-ヘキサン（*n*-C_6F_{14}）にメタンと酸素を加えた溶液を調製し、その後、$ClO_2^{\cdot}$水溶液を添加した二層反応液を準備した[1)]。次に常温・常圧条件下、LED 光（60 W, λ = 365 nm）で 15 分間の光照射を行うと、$ClO_2^{\cdot}$の黄色い吸収（λ_{max} = 350 nm）が速やかに消失した。反応後の溶液を^1H NMR およびガスクロマトグラフィーで分析するとバイオガス中のメタンは完全に消費され、導入したメタン量を基準としてメタノールとギ酸がそれぞれ 17%, 82%の収率で得られることが分かった。アクチノメーターを用いた実験より光反応の量子収率は 130%と極めて高いことが分かり、連鎖反応が関与していることが分かった（Scheme 1）[1)]。



Scheme 1. Plausible reaction mechanism for oxygenation of CH_4 into CH_3OH and formic acid with $ClO_2^{\bullet}$. *hν* means photoirradiation. [O] means autooxidation.

1) K. Ohkubo, K. Hirose, *Angew. Chem., Int. Ed.* **2018**, *57*, 2126.

有機酸によるリグノセルロースの可溶化における水の影響

（京都大学バイオマスプロダクトツリー産学共同研究部門[1]・株式会社ダイセル[2]・京都大学生存圏研究所[3]）○中川　由佳[1,2]・橋爪　知弘[1,2]・渡辺　隆司[1,3]

The Effect of Water on the Solubilization of Lignocellulose by Organic Acids

([1]*Biomass Product Tree Industry-Academia Collaborative Research Laboratory, Kyoto University,* [2]*Daicel Corporation,* [3]*Research Institute for Sustainable Humanosphere, Kyoto University*)
○Yuka Kawahara-Nakagawa, [1,2] Tomohiro Hashizume, [1,2] Takashi Watanabe[1,3]

Secondary cell walls in plants are mainly composed of cellulose, hemicellulose and lignin, which strongly bind each other through covalent and non-covalent interactions. The rigidity of secondary cell walls causes high energy consumption for biomass utilization in chemical industries. We have developed new materials such as biomass films and compressed molded products by gently dissolving wood using simple organic acids like formic acid. In this study, we investigated the effect of water on the dissolution of wood using organic acids.

Keywords : biomass, substitute for petroleum, solubilization under super-mild condition, lignocellulose

木材細胞壁中では、セルロース、ヘミセルロース、リグニンが強固な会合構造を形成しているため、木材は溶媒には容易に溶解せず、成分分離にも多大なエネルギーを要する。我々は、80 wt %のギ酸水溶液（水分率 20 wt %）が、おがくずやチップなどの木質細胞壁を室温～50℃程度の穏和な条件で、可溶化できることを見出した[1]。更に、木材溶液からバイオマスフィルムや成形物が製造できることも見出した。また、偏光観察から、木材溶液中にセルロースが結晶状態で存在することが示唆されてきた。

本研究ではまず、80 wt %のギ酸水溶液を用いてユーカリ木粉を可溶化し、次いで可溶化液を乾固して固形物を得た。これを XRD および固体 NMR 測定に供した。その結果、セルロースがⅠ型の状態で存在していることが明らかになった（Figure 1）。植物由来のセルロースは、結晶中の分子鎖が平行であるⅠ型構造を形成しており、その安定性から、溶解性が著しく低い。また、一度溶解したセルロースはⅠ型を再生しないことが知られている。従って、80 wt %のギ酸水溶液では、木材中のセルロース結晶は溶解しなかったことが分かった。一方、ギ酸を用いて同様の実験を行うと、セルロースⅠ型に由来するピークは観測されなくなり、セルロースも含めて分子レベルで溶解したことが示唆された。

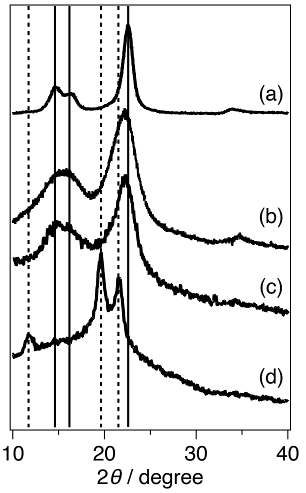


Figure 1. XRD patterns for (a) hardwood pulp (Cellulose I), (b) original Eucalyptus powder and the solvent evaporation residue of the wood dissolution solution, obtained by dissolving Eucalyptus powder in (c) aqueous formic acid (water content of 20 wt %) and in (d) formic acid.

1) Nishiwaki-Akine, Y., Watanabe, T., *Green Chem.*, **2014**, *16*, 3569.