2024年3月18日(月)

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18日(月) 13:30 ~ 14:30 A1456(14号館 [5階] 1456)

[A1456-1pm] 01. 化学教育・化学史

座長：今井 泉、中川 徹夫

日本語
13:30 ~ 13:50
[A1456-1pm-01]

加藤セチ・その業績の再評価

○吉祥 瑞枝[1] (1. サイエンススタジオ・マリー)

日本語
13:50 ~ 14:10
[A1456-1pm-02]

マイクロスケール実験に基づく簡易ヨードメトリー法の開発～普通校と特別支援学校の遠隔合同授業で行った実践事例～

○山田 一幸[1]、片岡 久美子[2]、荻野 和子[3] (1. 筑波大学附属桐が丘特別支援学校、2. 清泉女学院中学高等学校、3. 東北大学大学院理学研究科)

日本語
14:10 ~ 14:30
[A1456-1pm-03]

安価な手作りウェルプレートを用いたアルカリ土類金属塩の沈殿生成反応に関するマイクロスケール実験

○中川 徹夫[1] (1. 神戸女学院大学)

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18日(月) 13:00 ~ 15:20 A1441(14号館 [4階] 1441)

[A1441-1pm] 04. 物理化学—物性

座長：五月女 光、佐々木 陽一

英語
13:00 ~ 13:20
[A1441-1pm-01]

4-ニトロフェニル部位を有する電荷移動型化合物群の蛍光ソルバトクロミック特性と非蛍光過程

○三輪 真梨乃[1]、伊藤 亮孝[1] (1. 高知工大院工)

英語
13:20 ~ 13:40
[A1441-1pm-02]

複数の立体異性体を持つ種々のトリアジン誘導体の励起状態ダイナミクス解明

○笠 僚宏[1]、西郷 将生[1]、小川 知弘[1]、宮田 潔志[1]、土屋 陽一[2]、中野谷 一[2]、Arvydas Ruseckas[3]、Ifor Samuel[3]、安達 千波矢[2]、恩田 健[1] (1. 九大院理、2. 九大OPERA、3. セントアンドリュース大学)

日本語
13:40 ~ 14:00
[A1441-1pm-03]

光走査トンネル顕微鏡による単一分子内における励起子生成・消滅過程の実空間計測

○今井 みやび[1,2]、今田 裕[1]、金 有洙[1,3] (1. 理研、2. JSTさきがけ、3. 東大)

英語
14:20 ~ 14:40
[A1441-1pm-04]

多孔性金属錯体中における一重項分裂により生じた五重項状態の室温コヒーレンス

○山内 朗生[1]、田中 健太郎[1]、婦木 正明[2,3]、藤原 才也[4]、君塚 信夫[1]、笠 僚宏[1]、西郷 将生[1]、恩田 健[1]、楠本 遼太[2]、上野 那美[2]、佐藤 春実[2]、小堀 康博[2,3]、宮田 潔志[1,3]、楊井 伸浩[1,3,5] (1. 九大、2. 神大、3. JST-CREST、4. 理研、5. JST 創発)

英語
14:40 ~ 15:00
[A1441-1pm-05]

Dimeric scaffold for circularly polarized delayed luminescence

○Marine Louis[1], Yuki Yamashita[1], Yugo Tsuji[1], Chigusa Goto[1], Takuya Nakashima[3], Katsuyuki Shizu[2], Yo Shimizu[1], Hironori Kaji[2], Tsuyoshi Kawai[1] (1. Nara Institute of Science and Technology, 2. Kyoto University, 3. Osaka Metropolitan University)

英語
15:00 ~ 15:20
[A1441-1pm-06]

Effects of Monomer in Ionic Nanospheres on Sensitized Luminescence from Terbium(III) Ion

○Nikita Madhukar[1], Taizo Misato[1], Akitaka Ito[1] (1. Kochi Univ. of Tech.)

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18日(月) 9:00 ~ 11:30 A1444(14号館 [4階] 1444)

[A1444-1am] 07. 無機化学

座長：米里 健太郎、湊 拓生

英語
9:00 ~ 9:20
[A1444-1am-01]

多座ポリオキソメタレートで保護した超安定・高活性なコロイド金ナノ粒子触媒

○夏 康[1]、谷田部 孝文[1]、米里 健太郎[1]、矢部 智宏[1]、鈴木 康介[1]、山口 和也[1] (1. 東大)

英語
9:20 ~ 9:40
[A1444-1am-02]

物理蒸着を用いた伝導性MOFの薄膜合成における溶媒蒸気アニール効果

○中山 亮[1]、CHON Seoungmin[2]、岩本 俊太[2]、小林 成[1]、清水 亮太[1]、一杉 太郎[1,2] (1. 東大院理、2. 東工大物質理工)

英語
9:40 ~ 10:00
[A1444-1am-03]

Keggin型ポリオキソメタレートを基盤とした多孔性イオン結晶を利用した小核銀クラスターのサイズ選択な合成

○原口 直哉[1]、黒﨑 大誠[1]、内田 さやか[1] (1. 東大院総合)

英語
10:00 ~ 10:20
[A1444-1am-04]

金属–有機構造体の配位不飽和金属部位における幾何構造の変化によるπ逆供与の制御とその室温水素貯蔵への応用

○薮内 祐人[1,2,3]、古川 博康[1,2,3]、Kurtis Carsch[1,3]、Ryan Klein[4,5]、Nikolay Tkachenko[1,2]、Adrian Huang[1,2,3]、Craig Brown[5,6]、Martin Head-Gordon[1,2]、Jeffrey Long[1,2,3] (1. カリフォルニア大学バークレー校、2. ローレンス・バークレー国立研究所、3. 脱炭素材料研究所、4. 国立再生エネルギー研究所、5. アメリカ国立標準技術研究所、6. デラウェア大学)

英語
10:30 ~ 10:50
[A1444-1am-05]

一次元鎖状モリブデン酸化物の合成と構造制御

○湊 拓生[1]、宮本 美里[1]、石川 理史[2]、日吉 範人[3]、定金 正洋[1] (1. 広島大学、2. 神奈川大学、3. 産業技術総合研究所)

英語
10:50 ~ 11:10
[A1444-1am-06]

プレイスラー型ポリオキソメタレートにおける分子分極緩和の圧力制御

○栗原 英駿[1]、藤林 将[2]、加藤 智佐都[1]、Cosquer Goulven[3,4]、井上 克也[1,3,4,5]、西原 禎文[1,4,5,6] (1. 広島大学院先進理工、2. 宇部高専、3. 広島大キラルノット超物質拠点、4. 広島大キラル国際拠点、5. 広島大先進セ、6. JSTさきがけ)

英語
11:10 ~ 11:30
[A1444-1am-07]

シラノール基を有するかご型シロキサンと金属種の縮合反応による多孔質触媒の合成

○疋野 拓也[1]、松野 敬成[1,2]、黒田 一幸[1,2]、下嶋 敦[1,2] (1. 早大先進理工、2. 早大材研)

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18日(月) 15:55 ~ 17:15 A1444(14号館 [4階] 1444)

[A1444-1vn] 07. 無機化学

座長：宮川 雅矢、山本 瑛祐

日本語

15:55 ~ 16:15

[A1444-1vn-01]

分子シミュレーションによる有機モンモリロナイトにおける吸着サイトの決定因子の探究

○宮川 雅矢[1]、濤崎 啓吾[1]、高羽 洋充[1] (1. 工学院大学)

英語

16:15 ~ 16:35

[A1444-1vn-02]

Atomic cation vacancy engineering of NiFe-LDH nanosheets towards oxygen evolution reaction

○Huanran Li[1,2], Renzhi Ma[1,2], Yoshiyuki Sugahara[2], Takayoshi Sasaki[1] (1. NIMS, 2. Waseda Univ.)

英語

16:35 ~ 16:55

[A1444-1vn-03]

Synthesis of CoNiFe hydroxide nanosheets and composites as bifunctional oxygen electrocatalysts for Zn-air batteries

○Zihan Zhang[1,2], Renzhi Ma[1,2], Yoshiyuki Sugahara[2], Takayoshi Sasaki[1] (1. NIMS, 2. Waseda Univ.)

日本語

16:55 ~ 17:15

[A1444-1vn-04]

界面活性剤結晶を活用したアモルファスナノシートの精密合成

○山本 瑛祐[1]、栗本 大輝[1]、伊東 健太郎[1]、小林 亮[1]、長田 実[1] (1. 名大)

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18日(月) 13:00 ~ 15:40　F1231(12号館 [3階] 1231)

[F1231-1pm] 09. 錯体化学・有機金属化学

座長：三澤（鈴木） 智世、竹澤 浩気

日本語
13:00 ~ 13:20
[F1231-1pm-01]

嵩高い配位子とヒドリドで保護された[Fe$_{55}$][Fe$_{6}$]イオン対の結晶構造決定と電子構造解析

○田中 奏多[1]、大石 峻也[2]、川本 晃希[2]、高畑 遼[1]、志賀 拓也[3]、山添 誠司[4]、Zihan Zhang[5]、唯 美津木[2]、吉川 総一[4]、寺西 利治[1]、二瓶 雅之[3]、Karsten Meyer[5]、檜垣 達也[1]、大木 靖弘[1] (1. 京大化研、2. 名大院理・名大物質国際研、3. 筑波大院数物、4. 都立大理、5. Dept of Chem & Pharm, FAU Erlangen-Nürnberg.)

日本語
13:20 ~ 13:40
[F1231-1pm-02]

かさ高いCp配位子を有する[Mo$_3$S$_4$M] (M = Rh, Ir)クラスターの合成とC-Hボリル化反応への応用

○伊豆 仁[1]、下山 さやか[1]、谷藤 一樹[1]、大木 靖弘[1] (1. 京大化研)

日本語
13:40 ~ 14:00
[F1231-1pm-03]

剛直なトリプチセン三座配位子を用いたヘテロ金属酸化物クラスターの精密合成

○福井 智也[1,2]、伊藤 圭亮[1,2]、嘉藤 幹也[1,2]、福島 孝典[1,2] (1. 東工大化生研、2. 東工大物質理工)

英語
14:00 ~ 14:20
[F1231-1pm-04]

電子伝導性 を示す[Fe$_4$S$_4$]から構成される有機金属高分子の合成

○門田 健太郎[1]、Carl Brozek[2] (1. 京都大学、2. オレゴン大学)

日本語
14:20 ~ 14:40
[F1231-1pm-05]

共有結合形成による金属錯体八面体表面の事後修飾

○立石 友紀[1]、徳田 駿[1]、古川 修平[1] (1. 京都大学)

英語
14:40 ~ 15:00
[F1231-1pm-06]

光配位子置換反応による多核ルテニウム錯体の合成経路開拓

○平原 将也[1]、本田 拓真[1]、平化 匠[1] (1. 大阪工業大学)

英語
15:00 ~ 15:20
[F1231-1pm-07]

低対称銀(I)カプセル錯体から成る多核銀(I)ナノビーズ高次構造体の階層的自己集合

○山田 慶彦[1]、田代 省平[1]、塩谷 光彦[1] (1. 東大院理)

英語

15:20 ~ 15:40

[F1231-1pm-08]

シアノ金属錯体からなる発光性有機無機ハイブリッドの相制御

○岩井 優大[1]、大谷 亮、大場 正昭 (1. 九州大学)

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18日(月) 13:00 ~ 15:30 F1232(12号館 [3階] 1232)

[F1232-1pm] 09. 錯体化学・有機金属化学

座長：伊東 忍、桑田 繁樹

日本語

13:00 ~ 13:20

[F1232-1pm-01]

プロトン共役電子移動を指向したピリジン部位を有するコバルトセン誘導体の合成と反応性

○大塚 滉喜[1]、荒芝 和也[1]、西林 仁昭[1] (1. 東京大学大学院工学系研究科)

日本語

13:20 ~ 13:40

[F1232-1pm-02]

Co錯体触媒を用いたカチオン添加による高効率CO_2電解還元反応

○佐藤 俊介[1]、関澤 佳太[1]、白井 聡一[1]、坂本 直柔[1]、森川 健志[1] (1. 豊田中央研究所)

日本語

13:40 ~ 14:00

[F1232-1pm-03]

アルカリ光水素生成反応を高速駆動するCo-NHC錯体触媒の電子状態制御

○河村 佳央理[1]、山内 幸正[1]、酒井 健[1] (1. 九大)

英語

14:00 ~ 14:20

[F1232-1pm-04]

コバルト二核錯体$(Co_2L_2)(NO_3)_2$(HL=3,5-bis(2′-pyridyl)pyrazole)の合成とその電気化学二酸化炭素還元特性

○潘 雲逸[1]、堂ノ下 将希[2]、山内 美穂[1,2,3,4,5] (1. 九大院理、2. 九大先導研、3. 九大I2CNER、4. 九大K-NETs、5. 東北大AIMR)

英語

14:30 ~ 14:50

[F1232-1pm-05]

Co-NHC錯体触媒による水からの電気化学的水素生成に対する触媒回転頻度の精査

○管 昌権[1]、山内 幸正[1]、酒井 健[1] (1. 九大)

日本語

14:50 ~ 15:10

[F1232-1pm-06]

Coポルフィリン触媒修飾TiO_2カソードとポリピリジルルテニウム光増感剤修飾TIO_2フォトアノードを用いた光電気化学的CO_2還元反応

○合屋 祐輝[1]、Yan Xin[1]、酒井 健[1]、小澤 弘宜[1] (1. 九大)

日本語

15:10 ~ 15:30

[F1232-1pm-07]

アニオン添加で加速する二酸化炭素還元光触媒反応

○木原 咲穂[1]、下地 浩希[2]、前田 大光[3]、森本 樹[1] (1. 東京工科大学大学院、2. 東京工科大学、3. 立命館大学)

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18日(月) 13:00 ~ 15:30 F1233(12号館 [3階] 1233)

[F1233-1pm] 09. 錯体化学・有機金属化学

座長：高橋 仁徳、長尾 祐樹

英語
13:00 ~ 13:20
[F1233-1pm-01]

光誘起多段階イオン伝導度スイッチング材料の構築と機構解明

○青木 健太郎[1]、長尾 祐樹[1] (1. 北陸先端科学技術大学院大学)

日本語
13:20 ~ 13:40
[F1233-1pm-02]

レドックスフロー電池正極液用のターピリジン鉄錯体の溶解度向上

○岡澤 厚[1]、角地 貴行[1]、赤堀 圭祐[1]、川合 航右[1]、大久保 將史[1] (1. 早稲田大学)

英語
13:40 ~ 14:00
[F1233-1pm-03]

デヒドロベンゾアヌレンをビルディングブロックとする導電性金属有機構造体の構築

○大久保 円造[1]、相澤 直矢[1]、中山 健一[1]、鈴木 充朗[1] (1. 阪大)

日本語
14:00 ~ 14:20
[F1233-1pm-04]

パドルホイール型錯体を用いたd-π複合電子系単分子素子の設計指針に関する理論研究

○甘水 君佳[1]、西田 光博[1]、岸 亮平[1,2,3,4]、北河 康隆[1,2,3,4,5] (1. 阪大院基礎工、2. 阪大QIQB、3. 阪大RCSEC、4. 阪大ICS-OTRI、5. 阪大SRN-OTRI)

英語
14:30 ~ 14:50
[F1233-1pm-05]

Stable Neutral Iridium & Rhodium-Radical Species with an N-confused Tetrapyrrane That Exhibits Near-infrared Absorption

○ANINDA GHOSH[1], Ken-ichi Sugiura[1], Masatoshi Ishida[1] (1. TOKYO METROPOLITAN UNIVERSITY)

英語
14:50 ~ 15:10
[F1233-1pm-06]

単純なプロトンワイヤーで連結された金属ジチオレン錯体とカリックスアレーンの水素結合共結晶の電子構造と物性

○林 幹大[1] (1. 長崎大学)

英語
15:10 ~ 15:30
[F1233-1pm-07]

一次元πスタッキングを有する有機無機ハイブリッド結晶の創製と機能

○増田 峻也[1]、楠本 壮太郎[1]、小出 芳弘[1] (1. 神奈川大学)

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18日(月) 13:00 ~ 15:30 F1234(12号館 [3階] 1234)

[F1234-1pm] 09. 錯体化学・有機金属化学

座長：太田 俊、南保 正和

日本語
13:00 ~ 13:20
[F1234-1pm-01]

ホスフィン配位子の修飾に利用される嵩高い置換アリール基の立体的/電子的パラメータの定量化

○政岡 翔[1]、脇岡 正幸[2]、大木 靖弘[3]、小笠原 正道[1] (1. 徳島大学、2. 相模中央研究所、3. 京都大学)

日本語
13:20 ~ 13:40
[F1234-1pm-02]

ゲルマベンゼニルゲルミレン–ルイス塩基錯体の反応性

○西野 龍平[1]、時任 宣博[1]、山田 容子[1]、水畑 吉行[1] (1. 京大化研)

日本語
13:40 ~ 14:00
[F1234-1pm-03]

2位に2価ゲルマニウムを有する1,2,3-トリゲルマビシクロ[1.1.0]ブタンの合成とその骨格変換

○内田 大地[1]、水畑 吉行[1]、時任 宣博[1]、山田 容子[1]、行本 万里子[2] (1. 京大化研、2. 富山大)

英語
14:00 ~ 14:20
[F1234-1pm-04]

Synthesis, characterization, and reactivity of a novel di(μ-hydrido) dirhodium(II) complex bearing a reduced macrocyclic PDI ligand

○Liping YAN[1], Yuma MORIMOTO[1], Makoto YAMASHITA[1] (1. Nagoya University)

英語
14:30 ~ 14:50
[F1234-1pm-05]

^{1}H-NMRスペクトル上での環電流効果に着目した*tert*-Butylcalix[4]thiacrown-5－水銀(Ⅱ)錯体の結合能の評価と結合サイトの特定

○瀧本 竜哉[1]、橋本 悠[1]、井上 元[1]、高橋 弘樹[2]、津江 広人[2]、日置 和人[1]、佐々木 秀明[1]、袁 德其[1] (1. 神院大、2. 京大院)

日本語
14:50 ~ 15:10
[F1234-1pm-06]

配位子保護金ナノクラスターにおける位置選択的な配位子脱離反応

○鈴木 航[1]、髙畑 遼[2,3]、寺西 利治[2,3]、梅山 有和[1] (1. 兵庫県大院工、2. 京大化研、3. 京大院理)

英語
15:10 ~ 15:30
[F1234-1pm-07]

Sterically Demanding N-Heterocyclic Carbene Results in Selective Formation and Isolation of an Au_8Pt Nanocluster

〇Joseph Felix DeJesus[1], Yoshitaka Aramaki[2], Samuel I. Jacob[1], Quan Manh Phung[1,4], Takashi Ooi[1,2], Masakazu Nambo[1,4], Cathleen M. Crudden[1,3] (1. Institute of Transformative Bio-Molecules, 2. Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, 3. Department of Chemistry, Queen's University, 4. Department of Chemistry, Graduate School of Science, Nagoya University)

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18日(月) 13:00 ~ 15:40 E1111(11号館 [1階] 1111)

[E1111-1pm] 10. 有機化学—有機金属化合物

座長：高橋 講平、兒玉 拓也

英語
13:00 ~ 13:20
[E1111-1pm-01]

Pd触媒によるブロモアレーンの脱芳香族的二官能基化と不斉反応への展開

○加藤 弘基[1]、山口 滋[2]、武藤 慶[1]、山口 潤一郎[1] (1. 早稲田大学、2. 理研CSRS)

英語
13:20 ~ 13:40
[E1111-1pm-02]

Nickel-Catalyzed $C(sp^3)$–O Hydrogenolysis via a Remote Concerted Oxidative Addition and its Application to Degradation of a Bisphenol A-Based Epoxy Resin

○Yumeng Liao[1], Kohei Takahashi[1], Kyoko Nozaki[1] (1. The University of Tokyo)

英語
13:40 ~ 14:00
[E1111-1pm-03]

触媒的炭素ー水素結合活性化による含七員環ナノカーボンの合成

○山田 圭悟[1]、Iain Stepek[1]、松岡 和[1]、伊藤 英人[1]、伊丹 健一郎[1] (1. 名大)

英語
14:20 ~ 14:40
[E1111-1pm-04]

パラジウムフィッシャー型カルベン中間体を経るアシルシランとイミンと一酸化炭素との反応による触媒的β—ラクタム合成

○稲垣 徹哉[1]、兒玉 拓也[1,2]、鳶巣 守[1,2] (1. 阪大院工、2. ICS-OTRI)

英語
14:40 ~ 15:00
[E1111-1pm-05]

Nickel-Catalyzed Cross-Coupling of Allyl Ethers with Organoboron Reagents: A Remarkable Effect of Pyrimidine

○Thakun Chen[1], Takanori Iwasaki[1], Kyoko Nozaki[1] (1. The University of Tokyo)

英語
15:00 ~ 15:20
[E1111-1pm-06]

配向基を導入したポリエーテルエーテルケトン誘導体の合成とニッケル触媒による炭素–酸素結合切断を経るモノマーへの制御分解

○小川 敏史[1]、徐 于懿[1]、宇山 浩[1]、鳶巣 守[1,2] (1. 阪大院工、2. ICS-OTRI)

英語
15:20 ~ 15:40
[E1111-1pm-07]

Enantiospecific Cross-coupling of Cyclic Alkyl Sulfones

○Roberto Nolla Saltiel[1,2], Zachary T. Ariki[2], Stefanie Schiele[2], Jana Alpin[2], Yasuyo Tahara[1], Masakazu Nambo[1,4], Cathleen M. Crudden[2,1,3] (1. Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa,

Nagoya, Aichi 464-8601, Japan., 2. Department of Chemistry, Queen’s University, Chernoff Hall, Kingston Ontario, Canada., 3. Carbon to Metal Coating Institute, Queen’s University, Kingston, Ontario, K7L 3N6, Canada., 4. Department of Chemistry, Graduate School of Science, Nagoya University; Furo, Chikusa, Nagoya, Aichi, 464-8601, Japan.)

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18日(月) 13:00 ~ 15:40 E1112(11号館 [1階] 1112)

[E1112-1pm] 10. 有機化学—有機金属化合物

座長：伊藤 繁和、山本 武司

日本語
13:00 ~ 13:20
[E1112-1pm-01]

動的らせん高分子骨格を有するキラリティ可変ホスホロアミダイト配位子の開発

○松本 祐輔[1]、藤江 峻也[1]、山本 武司[1]、杉野目 道紀[1] (1. 京都大学)

英語
13:20 ~ 13:40
[E1112-1pm-02]

銅触媒を用いた1-トリフルオロメチルチオアルケンのヒドロホウ素化およびヒドロアリル化

○小島 有貴[1]、平野 康次[1] (1. 阪大院工)

英語
13:40 ~ 14:00
[E1112-1pm-03]

高い酸化力を有する銅光酸化還元触媒によるスチレンの逆マルコフニコフ型水和反応

○奥 直樹[1]、福家 啓仁[2]、山崎 賢[2]、松井 康哲[3]、池田 浩[3]、三浦 智也[2] (1. 京大院工、2. 岡山大院環境生命自然、3. 阪公大院工)

英語
14:20 ~ 14:40
[E1112-1pm-04]

電子不足CpIr(III)触媒を利用した位置選択的なC-H官能基化の研究

○平田 裕己[1,3]、木邨 俊介[2]、東田 皓介[3]、吉野 達彦[1]、松永 茂樹[3,1] (1. 北大院薬、2. 京大理、3. 京大院理)

英語
14:40 ~ 15:00
[E1112-1pm-05]

Rh/ルイス酸性金属協働触媒による$C(sp^3)$–O 結合の還元的シリル化反応

○関 凜[1]、城戸 春香[1]、黄 嘉名[2]、井元 郁[2]、三浦 大樹[2]、中尾 佳亮[1] (1. 京都大学　、2. 東京都立大学)

英語
15:00 ~ 15:20
[E1112-1pm-06]

Rh触媒を用いた[2+2+2]環化付加反応による含フッ素四置換不斉炭素の構築

○濱田 慎太郎[1]、小宮 由信[1]、鈴木 俊介[1]、野上 純太郎[1]、佐藤 悠[1]、永島 佑貴[1]、田中 健[1] (1. 東工大物質理工)

英語
15:20 ~ 15:40
[E1112-1pm-07]

ロジウム錯体触媒存在下、*N*-メトキシベンズアミドと *in situ* で発生したヨードニウムイリドとの連続反応によるイソクマリンおよびイソキノロン誘導体の化学選択的合成法の開発

○金 東映[1]、三浦 理紗子[1]、木村 祐[1]、近藤 輝幸[1] (1. 京大)

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18日(月) 15:55 ~ 17:15 🏛 E1121(11号館 [2階] 1121)

[E1121-1vn] 11. 有機化学―構造有機化学

座長：猪熊 泰英、福井 識人

🏷 日本語
15:55 ~ 16:15
[E1121-1vn-01]

環状BODIPYの超酸耐性

○稲葉 佑哉[1]、米田 友貴[1]、井手 雄紀[2]、猪熊 泰英[1,2] (1. 北大院工、2. 北大WPI-ICReDD)

🏷 日本語
16:15 ~ 16:35
[E1121-1vn-02]

シクロパラフェニレンと共役した環状カルベニウムイオンの合成とメビウス芳香族性

○茅原 栄一[1]、鳥越 優河[1]、山子 茂[1] (1. 京大化研)

🏷 英語
16:35 ~ 16:55
[E1121-1vn-03]

カテナン形成を鍵とするシクロパラフェニレンの非共有結合修飾

○石橋 弥泰[1]、Manuel Rondelli[1]、周戸 大季[1]、前川 健久[2]、伊藤 英人[1]、水上 輝市[3]、君塚 信夫[3]、八木 亜樹子[1,4]、伊丹 健一郎[1,2,4] (1. 名古屋大学、2. 中央研究院化学研究所、3. 九州大学、4. トランスフォーマティブ生命分子研究所)

🏷 日本語
16:55 ~ 17:15
[E1121-1vn-04]

架橋部位に窒素原子を導入したPillar[6]areneの合成と電荷移動型発光特性

○大谷 俊介[1]、中口 風斗[1]、加藤 研一[1]、生越 友樹[1,2] (1. 京都大学大学院工学研究科、2. 金沢大WPI-NanoLSI)

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18日(月) 13:00 ~ 15:10 E1123(11号館 [2階] 1123)

[E1123-1pm] 12. 有機化学—有機結晶・超分子化学

座長：関谷 亮、山内 光陽

英語
13:00 ~ 13:20
[E1123-1pm-01]

キラルなレゾルシンアレーンカプセルを用いた第二級アルコールの速度論的光学分割

○原田 健太郎[1]、関谷 亮[1]、灰野 岳晴[1,2] (1. 広島大学、2. 持続可能性に寄与するキラルノット超物質拠点)

日本語
13:20 ~ 13:40
[E1123-1pm-02]

芳香環ミセル：多孔性高分子の内包による水溶性多空間ホストの構築

○青山 慎治[1]、Lorenzo Catti、吉沢 道人 (1. 東工大・化生研)

日本語
13:40 ~ 14:00
[E1123-1pm-03]

ジスルフィドステープルの酸化還元を駆動力としたα-ヘリカルペプチドの可逆的な静的/動的らせん変換

○逢坂 直樹[1]、Mark J MacLachlan[1,2]、秋根 茂久[1,3] (1. 金沢大 NanoLSI、2. ブリティッシュコロンビア大、3. 金沢大院自然)

英語
14:10 ~ 14:30
[E1123-1pm-04]

多座配位子内の二面角変化による自己集合性金属錯体のコントロール

○阿部 司[1]、平岡 秀一[1] (1. 東京大学)

英語
14:30 ~ 14:50
[E1123-1pm-05]

Donor-Appended Pyrazinacenes - Switching Absorption and Fluoresence from Visible to Near Infrared Region Through a Simple REDOX Process.

○Gary James Richards[1], Keita Aoki[1], Kou Kanehisa[1], Kazushi Nakada[1], Ryo Nakamura[1], Jonathan P. Hill[2], Akiko Hori[1] (1. Shibaura Institute of Technology, 2. National Institute of Materials Science)

日本語
14:50 ~ 15:10
[E1123-1pm-06]

前駆体法を利用した水素結合性ベンゾポルフィリン集合体の基板上形成と薄膜トランジスタへの展開

○上野 創[1]、山内 光陽[1]、松尾 恭平[1]、水畑 吉行[1]、山田 容子[1] (1. 京大化研)

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18日(月) 13:00 ~ 15:30 E1131(11号館 [3階] 1131)

[E1131-1pm] 12. 有機化学—有機結晶・超分子化学

座長：阿南 静佳、桶谷 龍成

日本語

13:00 ~ 13:20

[E1131-1pm-01]

低対称トリカルボン酸による水素結合性はしご型多孔質構造体の構築

○田中 那樹[1]、鈴木 悠斗[1]、桶谷 龍成[1]、久木 一朗[1] (1. 阪大院基礎工)

日本語

13:20 ~ 13:40

[E1131-1pm-02]

水素結合性固溶体フレームワークの構築と成分比に依存した構造転移挙動

○橋本 泰利[1]、桶谷 龍成[1]、久木 一朗[1]、間下 以大[2] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院情報科学研究科)

日本語

13:40 ~ 14:00

[E1131-1pm-03]

トリス(フェニルイソオキサゾリル)ベンゼンの分子結晶中に現れる多孔性と選択的分子吸着

○小野 雄大[1]、平尾 岳大[1]、灰野 岳晴[1,2] (1. 広島大、2. 広島大 WPI-SKCM²)

英語

14:10 ~ 14:30

[E1131-1pm-04]

Development of Catenane-based Supramolecular Mechanophores

○Fazil Thuluvanchery Salim[2], Nobuyuki Tamaoki[2], Yoshimitsu Sagara[1] (1. Tokyo Institute of Technology, 2. Hokkaido University)

英語

14:30 ~ 14:50

[E1131-1pm-05]

sp^2-およびsp^3-ナノカーボン分子を複合した結晶性分子ピーポッド

○寺崎 成哉[1]、小谷 祐希[1]、勝野 亮祐[1]、福永 隼也[1]、松野 太輔[1]、磯部 寛之[1] (1. 東京大学)

英語

14:50 ~ 15:10

[E1131-1pm-06]

o-カルボラン誘導体におけるπ積層構造に基づく多刺激応答特性

○油原 和公[1]、田中 一生[1] (1. 京大院工)

日本語

15:10 ~ 15:30

[E1131-1pm-07]

ジアリール置換した縮環ブタジエン類の固体発光および結晶構造

○長岡 朋希[1]、南 春彦[1]、曽 思悦[1]、松井 康哲[1]、大垣 拓也[1]、池田 浩[1] (1. 阪公大)

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18日(月) 13:00 ~ 15:30 E1132(11号館 [3階] 1132)

[E1132-1pm] 13. 有機化学—反応機構・光化学・電気化学

座長：池田 浩、嶌越 恒

英語

13:00 ~ 13:20

[E1132-1pm-01]

電子供与/求引性の置換基導入に基づく羽ばたく分子の二重発光特性の制御

○須賀 健介[1]、齊藤 尚平[1] (1. 京大)

英語

13:20 ~ 13:40

[E1132-1pm-02]

Substitution Effect on Photorelease Reaction of Alcohols from Photolabile Molecules Based on 1,4-Naphthoquinone and Its Mechanism

○Beta Achromi Nurohmah[1], Motonori Washisaka[1], Tsumoru Morimoto[1], Tsuyoshi Kawai[1] (1. Nara Inst. Sci. Technol.)

英語

13:40 ~ 14:00

[E1132-1pm-03]

可視光からUVB光へのフォトン・アップコンバージョンに向けた新規発光体材料の開発

○宇治 雅記[1]、Moghtader Julian[2]、Roy Bibhisan[3]、楊井 伸浩[1,4] (1. 九大院工、2. Johannes Gutenberg Univ. Mainz、3. H.N.B. Garhwal Univ.、4. JST CREST)

英語

14:10 ~ 14:30

[E1132-1pm-04]

ラジカル連鎖機構によるスルホニル/ハロアレーンを用いる含ヘテロ原子脂肪族の光および電気化学的直接 α-アリール化反応

○青木 航平[1]、室岡 茉里[1]、西田 智哉[1]、江島 渉[1]、池田 佑子[1]、繁田 愛美[1]、田中 勝大[1]、米倉 恭平[1]、白川 英二[1,2] (1. 関西学院大生命環境、2. JST CREST)

英語

14:30 ~ 14:50

[E1132-1pm-05]

CO_2を用いたアルケンの可視光駆動３成分アシルカルボキシ化反応

○渡部 太登[1]、ロールウォンカモル プリナット[1]、小杉 健斗[1]、嵯峨 裕[1]、神戸 徹也[1]、近藤 美欧[2,1,3]、正岡 重行[1] (1. 阪大院工、2. 東工大院理、3. JSTさきがけ)

英語

14:50 ~ 15:10

[E1132-1pm-06]

光照射による電子操作を鍵とするアリール金属反応剤とハロゲン化アリール/アリールトリフラートの電子触媒クロスカップリング反応

○太田 優輝[1]、向井 渓斗[1]、大倉 圭翔[1]、水澤 冴碩[1]、正木 脩[1]、米倉 恭平[1]、白川 英二[1,2] (1. 関西学院大生命環境、2. JST CREST)

日本語

15:10 ~ 15:30

[E1132-1pm-07]

光アップコンバージョン系におけるエネルギー捕集過程の過渡吸収スペクトル解析

○松井 康哲[1]、高橋 拓海[1]、大垣 拓也[1]、池田 浩[1] (1. 阪公大)

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18日(月) 15:55 ~ 17:15 E1123(11号館 [2階] 1123)

[E1123-1vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：佐藤 隆章、中 建介

英語

15:55 ~ 16:15

[E1123-1vn-01]

ワンポット3成分反応による硫黄官能基の合成

○齋藤 文登[1]、David Austrup[1]、Simon Euteneuer[1]、Marc Fimm[1] (1. ルートヴィヒ・マクシミリアン大学ミュンヘン)

英語

16:15 ~ 16:35

[E1123-1vn-02]

光励起を利用したニトロアレーン還元法の開発とニトロソDiels-Alder反応への応用

○岡村 俊孝[1]、金子 泰己[1]、伊藤 凛[1]、佐藤 隆章[1] (1. 慶應義塾大学)

英語

16:35 ~ 16:55

[E1123-1vn-03]

ホスファボラタトリプチセン骨格を有するホスホニウムベタインの観測とその反応

○内山 洋介[1]、山岸 正太郎[1]、安川 拓哉[1] (1. 北里大学)

日本語

16:55 ~ 17:15

[E1123-1vn-04]

アミノ(ホスフィニル)アレーンの一電子還元によるパイ拡張カルバゾールの化学選択的合成

○奥田 靖浩[1]、森 まつり[1]、今田 裕二[1]、松永 夏旺[1]、折田 明浩[1] (1. 岡山理大)

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18日(月) 15:55 ~ 17:15 E1141(11号館 [4階] 1141)

[E1141-1vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：盛田 大輝、武藤 慶

英語
15:55 ~ 16:15

[E1141-1vn-01]

Non-electronic activation on anthracene ring by steric repulsion between substituents

○Annisa Indah Reza[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

英語
16:15 ~ 16:35

[E1141-1vn-02]

鉄触媒による自己酸化イミンのアザ環化π拡張反応

○張 岩[1]、福間 翔太[1]、尚 睿[1]、中村 栄一[1] (1. 東京大学)

英語
16:35 ~ 16:55

[E1141-1vn-03]

ベンザインと窒素置換アルキンの新奇な分子内環化付加反応の開発

○田渡 司[1]、坂上 峻哉[1]、伊藤 琢磨[2]、原渕 祐[3,4]、前田 理[3,4,5]、高須 清誠[1]、瀧川 紘[1] (1. 京大院薬、2. 北大院総化、3. 北大WPI-ICReDD、4. JST-ERATO、5. 北大院理)

日本語
16:55 ~ 17:15

[E1141-1vn-04]

シクロドデシプチセンの合成

○兵頭 瑞樹[1]、岩田 隆幸[2]、新藤 充[2] (1. 九大院総理工、2. 九大先導研)

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

2024年3月18日(月) 13:00 ~ 15:40 E1142(11号館 [4階] 1142)

[E1142-1pm] 15. 有機化学—脂肪族・脂環式化合物，新反応技術

座長：荒巻 吉孝、太田 英介

英語
13:00 ~ 13:20
[E1142-1pm-01]

gem-ジフルオロシクロプロパン誘導体の双方向性均等開裂の制御によるレジオ分岐型[3+2]環化付加反応

○内田 裕貴[1]、Tobias Schirmer[1]、Julian Kürschner[2]、田浦 悠也[1]、荒巻 吉孝[1]、大井 貴史[1] (1. 名大院工・ITbM、2. ミュンスター大)

英語
13:20 ~ 13:40
[E1142-1pm-02]

アニオン性8π系電子環状反応による7員環β-ケトエステル誘導体の合成

○加藤 蘭丸[1]、斎藤 優輝[1]、谷野 圭持[2] (1. 北大院総化、2. 北大院理)

英語
13:50 ~ 14:10
[E1142-1pm-03]

ヘテロ芳香族エステルを用いたケトンとエステルの結合交換反応

○中原 輝[1]、一色 遼大[1]、山口 潤一郎[1] (1. 早稲田大学)

英語
14:10 ~ 14:30
[E1142-1pm-04]

亜鉛触媒を用いた亜リン酸ジエステル合成

○松永 晃[1]、齋藤 由樹[1]、小林 修[1] (1. 東京大学)

英語
14:30 ~ 14:50
[E1142-1pm-05]

Catalytic phosphonylation of alcohols with bis(2,2,2-trifluoroethyl) phosphite for the synthesis of phosphite diesters

○Dario Mrdovic[1], Yuki Saito[1], Shu Kobayashi[1] (1. The University of Tokyo)

日本語
15:00 ~ 15:20
[E1142-1pm-06]

金ナノ粒子触媒を用いたカルボニル化合物の直接シリルエノールエーテル化

○町田 陸[1]、浅尾 直樹[1] (1. 信州大院総理工)

日本語
15:20 ~ 15:40
[E1142-1pm-07]

活性メチレンおよびメチン化合物の不活性アルケンによる光アルキル化反応

○山下 恭弘[1]、小林 修[1] (1. 東京大学)

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

2024年3月18日(月) 13:00 ~ 15:40 E1143(11号館 [4階] 1143)

[E1143-1pm] 15. 有機化学—脂肪族・脂環式化合物，新反応技術

座長：安藤 吉勇、美多 剛

日本語
13:00 ~ 13:20
[E1143-1pm-01]
新規ビタミンD誘導体の合成と活性
○伊部 公太[1]、掘田 稜二[1]、中田 春樹、大上 真由、岡本 専太郎[1] (1. 神奈川大)

英語
13:20 ~ 13:40
[E1143-1pm-02]
グリーンものづくり：ファインバブル法によるフェアリー化合物の合成
○Arun Kumar Manna[1]、佐藤 浩平[1]、鳴海 哲夫[1]、間瀬 暢之[1] (1. 静大院)

日本語
13:40 ~ 14:00
[E1143-1pm-03]
H/D同位体性キラル分子の速度論的分割
○内田 竜也[1,2]、中川 雄太[1]、渡 直樹[1] (1. 九大、2. 科学技術振興機構)

英語
14:10 ~ 14:30
[E1143-1pm-04]
Nickel-Iridium Dual Catalyzed Buchwald-Hartwig-Type Amination Reaction of Aryl Chlorides under Microwave and Visible Light Dual Irradiation
○Abhijit Sen[1], Bukhanko Valerii[1], Heeyoel Baek[1], Aya Ohno[1], Atsuya Muranaka[1], Yoichi M. A. Yamada[1] (1. RIKEN, Center for Sustainable Resource Science)

日本語
14:30 ~ 14:50
[E1143-1pm-05]
量子化学計算に基づくアミンと二酸化炭素からのアルケンの触媒的アミノカルボキシル化：気液フローシステムへの展開
○神名 航[1]、原渕 祐[2,3]、林 裕樹[2,3]、髙野 秀明[2,3]、小塚 智貴[4]、櫻井 大斗[4]、間瀬 暢之[4]、前田 理[2,3,5]、美多 剛[2,3] (1. 北大院総化、2. 北大WPI-ICReDD、3. JST-ERATO、4. 静岡大工、5. 北大院理)

日本語
15:00 ~ 15:20
[E1143-1pm-06]
独自に合成した多孔性塩基性樹脂による連続フローHenry反応
○降矢 裕一[1]、石谷 暖郎[1]、小林 修[1] (1. 東京大学)

日本語
15:20 ~ 15:40
[E1143-1pm-07]
安定化高分子パラジウム触媒を用いた連続フロー式鈴木-宮浦反応の開発
○Zhang Zhenzhong[1]、大野 綾[1]、山田 陽一[1] (1. 理化学研究所)

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18日(月) 9:00 ~ 11:30 H932(9号館 [3階] 932)

[H932-1am] 17. 生体機能関連化学・バイオテクノロジー

座長：永次 史、和田 健彦

日本語
9:00 ~ 9:20
[H932-1am-01]

Ru錯体を利用した部位特異的DNA光架橋法の開発

○樫田 啓[1]、東 秀憲[1]、五月女 光[2]、宮坂 博[2]、浅沼 浩之[1] (1. 名大院工、2. 阪大院基礎工)

日本語
9:20 ~ 9:40
[H932-1am-02]

光応答性核酸塩基を導入したXNA三重鎖によるナノ構造体形成

○村山 恵司[1]、平野 桂人[1]、浅沼 浩之[1] (1. 名大)

日本語
9:40 ~ 10:00
[H932-1am-03]

光酸化によるDNA中のAbasic site生成反応の解析

○山野 雄平[1]、鬼塚 和光[1,2]、アルタン オーカン[1]、佐々木 まどか[1,2]、アーメド アブデルハーディ[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
[H932-1am-04]

核酸化学のNew Data Science (1): 細胞内の核酸構造安定性を予測できる新規の最近接塩基対パラメータの開発

○杉本 直己[1,2]、ゴッシュ サトパティ[1]、ディパニタ バナジー[1]、大山 達也[1]、遠藤 玉樹[1]、高橋 俊太郎[1]、建石 寿枝[1] (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))

英語
10:30 ~ 10:50
[H932-1am-05]

核酸化学のNew Data Science (2): 最近接塩基対パラメータとAIを用いたリボザイムの機能予測

○高橋 俊太郎[1]、Saptarshi Ghosh[1]、建石 寿枝[1]、福永 津嵩[3]、浜田 道昭[3]、杉本 直己[1,2] (1. 甲南大FIBER、2. 甲南大FIRST、3. 早稲田大)

英語
10:50 ~ 11:10
[H932-1am-06]

核酸化学のNew Data Science (3): 最近接塩基対パラメータ、擬似細胞システム、AIを用いたRNAの構造安定性予測

○Dipanwita Banerjee[1]、建石 寿枝[1]、高橋 俊太郎[1]、福永 津嵩[2]、浜田 道昭[3,4]、杉本 直己[1,5] (1. 甲南大学　先端生命工学研究所（FIBER)、2. 早稲田大学高等研究所、3. 早稲田大学 理工学術院、4. 産総研・早大 生体システムビッグデータ解析オープンイノベーションラボラトリ、5. 甲南大学　フロンティアサイエンス研究科)

英語
11:10 ~ 11:30
[H932-1am-07]

Staple核酸の合理的な設計を志向した化学的パラメーターの算出

〇木田 朋輝[1]、勝田 陽介[1]、北村 裕介[1]、井原 敏博[1] (1. 熊大院)

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18日(月) 9:00 ~ 11:30 H936(9号館 [3階] 936)

[H936-1am] 17. 生体機能関連化学・バイオテクノロジー

座長：安部 聡、藤枝 伸宇

英語
9:00 ~ 9:20
[H936-1am-01]

ミオグロビンを利用した人工金属酵素の新規触媒機能拡張：アルドキシム脱水反応によるニトリル合成

○阿部 美笛[1]、加藤 俊介[1]、林 高史[1] (1. 大阪大学大学院)

英語
9:20 ~ 9:40
[H936-1am-02]

野生型シトクロムP450BM3発現大腸菌によるプロパンからプロパノールへの生体変換

○須貝 友紀[1]、唐澤 昌之[1]、児玉 侑朔[1]、米村 開[1]、有安 真也[1]、愛場 雄一郎[1]、荘司 長三[1] (1. 名古屋大学)

英語
9:40 ~ 10:00
[H936-1am-03]

細胞内結晶化タンパク質ケージの結晶・溶液構造の解析

○田中 潤子[1]、安部 聡[1]、金丸 周司[1]、横山 武司[2]、鉄鎗 潘 [1]、永間 美咲[1]、上野 隆史[1] (1. 東工大、2. 東北大)

日本語
10:10 ~ 10:30
[H936-1am-04]

緑膿菌のヘム獲得機構の制御を志向したペプチド修飾ヘム

○松井 弘季[1]、愛場 雄一郎[1]、渡邉 菜々花[1]、有安 真也[1]、荘司 長三[1] (1. 名古屋大学)

英語
10:30 ~ 10:50
[H936-1am-05]

Redox Tuning of Myoglobin by Cofactor Replacement to Enhance Cyclopropanation Reactivity

○Yoshiyuki Kagawa[1], Koji Oohora[1], Tomoki Himiyama[2], Akihiro Suzuki[3], Takashi Hayashi[1] (1. Osaka University, 2. AIST, 3. NIT Ibaraki College)

日本語
10:50 ~ 11:10
[H936-1am-06]

人工非ヘム銅タンパク質が触媒する立体選択的ヘテロDiels-Alder反応

○松本 隆聖[1]、吉岡 紗穂[2]、森田 能次[1]、藤枝 伸宇[1,2] (1. 大阪公大院農、2. 大阪府大院生命)

英語
11:10 ~ 11:30
[H936-1am-07]

トリスルフィド架橋フェレドキシン二量体の構築とその生成機構

○真島 剛史[1]、田中 萌奈実[1]、Nur Afiqah binti Azmi[1]、山中 優[1]、緒方 英明[2]、廣田 俊[1] (1. 奈良先端大、2. 兵庫県立大)

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18日(月) 13:00 ~ 15:30 H931(9号館 [3階] 931)

[H931-1pm] 17. 生体機能関連化学・バイオテクノロジー

座長：Arivazhagan Rajendran、遠藤 玉樹

英語
13:00 ~ 13:20
[H931-1pm-01]

アルギニンに富んだペプチドとグアニン四重らせん構造によって誘起される液液相分離を制御する因子の検討

○シル シュミット[1]、鶴田 充生[1]、川内 敬子[1]、三好 大輔[1] (1. 甲南大学)

英語
13:20 ~ 13:40
[H931-1pm-02]

核酸のグアニン四重らせん構造標的分子を用いたテロメア長―TERRA発現量相関の制御

○橋本 佳樹[1]、川内 敬子[1]、三好 大輔[1] (1. 甲南大学)

英語
13:40 ~ 14:00
[H931-1pm-03]

グアニン四重らせん構造のトポロジー依存的な液液相分離

○鶴田 充生[1]、取井 猛流[1]、川内 敬子[1]、杉本 直己[1]、三好 大輔[1] (1. 甲南大学)

日本語
14:10 ~ 14:30
[H931-1pm-04]

リン酸骨格およびダイナミクスに着目したミスマッチDNA-低分子複合体のNMR解析

○櫻林 修平[1,2]、古板 恭子[1]、山田 剛史[2]、藤原 敏道[1]、中谷 和彦[2]、児嶋 長次郎[1,3] (1. 阪大蛋白研、2. 阪大産研、3. 横国大)

英語
14:30 ~ 14:50
[H931-1pm-05]

Chemical ligation of staple nicks in DNA origami

○Arivazhagan Rajendran[1], Kirankumar Krishnamurthy[1], Eiji Nakata[1], Takashi Morii[1] (1. Kyoto University)

英語
14:50 ~ 15:10
[H931-1pm-06]

核酸化学のNew Data Science (8): ハイスピード共焦点イメージングを利用した生細胞内での核酸構造変化の解析

○遠藤 玉樹[1]、建石 寿枝[1]、筒井 啓太[2]、深谷 陽子[2]、築地 真也[2]、杉本 直己[1,3] (1. 甲南大 FIBER、2. 名工大院工、3. 甲南大 FIRST)

英語
15:10 ~ 15:30
[H931-1pm-07]

New Data Science in Nucleic Acids Chemistry (9): Conformational transition of nucleic acids with virus genome sequences inside cell-like nanoconfinements

〇Sunipa Sarkar[1], Hisae Tateishi-Karimata [1], Kazunori Matsuura[2,3], Tamaki Endoh[1], Naoki Sugimoto[1,4] (1. Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, 2. Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 3. Centre for Research on Green Sustainable Chemistry, Tottori University, 4. Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan 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18日(月) 13:00 ~ 15:30 H934(9号館 [3階] 934)

[H934-1pm] 17. 生体機能関連化学・バイオテクノロジー

座長：山村 昌平、小澤 岳昌

日本語
13:00 ~ 13:20
[H934-1pm-01]

細胞膜固定化材料の作製と生体材料としての特性解析

○岡本 行広[1,2]、Xuehui Rui[1]、渡邊 望美[1]、馬越 大[1] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院基礎工学研究科未来ラボ)

日本語
13:20 ~ 13:40
[H934-1pm-02]

脂質複合化 DNA ブラシに吸着した金ナノ粒子の溶媒による集合変化

○与那嶺 雄介[1]、石 雅麗[2]、三友 秀之[1]、居城 邦治[1] (1. 北大電子研、2. 北大院生命)

英語
13:40 ~ 14:00
[H934-1pm-03]

ペプチドナノファイバーを基盤とした光応答性人工細胞骨格の創製

○梁 応冰[1]、稲葉 央[1]、松浦 和則[1] (1. 鳥取大学大学院)

英語
14:00 ~ 14:20
[H934-1pm-04]

Surface coating of an algal cell with elongated DNA strands to control the loading and releasing of cationic materials.

○YINGQI MU[1], Yuseke Yonamine[2], Hideyuki Mitomo[2], Kuniharu Ijiro[2] (1. Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University (RIES, Hokkaido Univ.))

日本語
14:30 ~ 14:50
[H934-1pm-05]

遺伝子変異がん細胞の検出のためのペプチド核酸プローブと1細胞マイクロアレイチップ技術の開発

○重藤 元[1]、北松 瑞生[2]、大槻 高史[3]、飯塚 明[4]、秋山 靖人[4]、山村 昌平[1] (1. 産総研、2. 近畿大、3. 岡山大、4. 静岡がんセンター)

英語
14:50 ~ 15:10
[H934-1pm-06]

概日時計同調時におけるNADPHオキシダーゼの役割を解明するための発光プローブの開発

○河村 玄気[1]、田丸 輝也[2]、小澤 岳昌[1] (1. 東京大学、2. 東邦大学)

英語
15:10 ~ 15:30
[H934-1pm-07]

光制御と数理モデルを用いたAktアイソフォーム活性化の時間的ダイナミクスと下流シグナル伝達の定量的解析

〇関根 由佳[1]、河村 玄気[1]、小澤 岳昌[1] (1. 東大院理・化学)

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

2024年3月18日(月) 15:55 ~ 16:55 H936(9号館 [3階] 936)

[H936-1vn] 17. 生体機能関連化学・バイオテクノロジー

座長：大嶋 孝志、李 秀栄

英語

15:55 ~ 16:15

[H936-1vn-01]

原子間力顕微鏡によるpH応答性リボン状タンパク質の構造とダイナミクスの解析

〇Xin Li[1]、Thuc Toan PHAM[1]、菊池 幸祐[1]、伊達 弘貴[1]、鱒村 颯太[1]、上野 隆史[1] (1. 東京工業大学　生命理工学院)

日本語

16:15 ~ 16:35

[H936-1vn-02]

ペプチド阻害剤設計における動的構造の影響

〇李 秀栄[1]、水口 賢司[1,2]、本多 優作[3]、高橋 大輔[3,4]、矢崎 亮[3]、大嶋 孝志[3] (1. 医薬基盤・健康・栄養研究所、2. 大阪大学蛋白質研究所、3. 九州大学大学院薬学研究院、4. 崇城大学薬学部)

日本語

16:35 ~ 16:55

[H936-1vn-03]

ヒト型抗体(T99wt)を抗体酵素に変換したときの立体構造変化の静的及び動的解析

〇宇田 泰三[1,6]、加藤 龍一[2]、重田　育照[3]、廣田 俊[4,5]、一二三　恵美[6] (1. 九州先端研、2. 高エネルギー加速器研究機構、3. 筑波大学、4. 奈良先端科学技術大学院大学、5. CREST、6. 大分大学)

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18日(月) 13:00 ~ 14:40 D341(3号館 [4階] 341)

[D341-1pm] 18. 高分子

座長：稲木 信介、相見 順子

日本語
13:00 ~ 13:20
[D341-1pm-01]

共有結合性有機構造体の電極表面への間接電解合成とその応用

○佐藤 宏亮[1]、白倉 智基[1]、稲木 信介[1] (1. 東京工業大学)

日本語
13:20 ~ 13:40
[D341-1pm-02]

電荷蓄積高分子を用いて溶液プロセスで作製する有機トランジスタメモリ

○相見 順子[1] (1. 物質・材料研究機構)

英語
13:40 ~ 14:00
[D341-1pm-03]

Tailoring Electrochromic Properties through Ru-Carbon Covalent Bonds: Design and Synthesis of Metallosupramolecular Polymers

○BANCHHANIDHI PRUSTI[1], Takasi Sato[1], Ritsuko Nagahata[2], Masayoshi Higuchi[1] (1. National Institute for Materials Science, 2. National Institute of Advanced Industrial Science and Technology)

英語
14:00 ~ 14:20
[D341-1pm-04]

Image Data Analysis of Electrochromic Display Devices for Improvement of the Durability

○Shifa Sarkar[1,2], Masayoshi Higuchi[1,2] (1. National Institute for Materials Science, 2. Osaka University)

英語
14:20 ~ 14:40
[D341-1pm-05]

大気安定性の高いn型化学ドーピングによる高分子半導体ダイオードの電子注入特性向上

○山下 侑[1,2]、刑部 永祥[2]、田嶋 陽子[2]、Stephen Barlow[3]、Seth Marder[3]、渡邉 峻一郎[2]、竹谷 純一[1,2] (1. 物材機構、2. 東大、3. コロラド大ボルダー校)

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18日(月) 15:55 ~ 16:55 D342(3号館 [4階] 342)

[D342-1vn] 18. 高分子

座長：細野 暢彦、飯田 拡基

日本語
15:55 ~ 16:15

[D342-1vn-01]

多孔性金属錯体を用いたポリアルキルチオフェンの頭尾結合の識別と分離

○高島 優[1]、澤山 拓[2]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工、2. 東大院新領域)

英語
16:15 ~ 16:35

[D342-1vn-02]

ダブルネットワーク化と無機染色によるハイドロゲル中の荷電ポリマーネットワークの実空間可視化

○野口 真司[1]、木山 竜二[1]、吉田 匡宏[1]、樫村 尚宏[1]、忠永 清治[1]、龔 剣萍[1]、野々山 貴行[1] (1. 北海道大学)

日本語
16:35 ~ 16:55

[D342-1vn-03]

超分子架橋による有機-無機高分子の複合化

山下 尚樹[1]、○山岡 賢司[1]、以倉 崚平[1]、高島 義徳[1] (1. 大阪大学)

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18日(月) 9:00 ~ 11:30 C443(4号館 [4階] 443)

[C443-1am] 20. 材料化学―基礎と応用

座長：加藤 雄一、小林 浩和

英語
9:00 ~ 9:20
[C443-1am-01]

In situ structure characterization of graphene-valve mediated carbons

〇Wang Shuwen[1]、Fernando Vallejos-Burgos[2]、Furuse Ayumi [1]、Marco-Lozar Juan P. [3]、Otsuka Hayato[1]、Nagae Miu[1]、Kawamata Yuma[1]、Kanoh Hirofumi[4]、Urita Koki[5]、Notohara Hiroo[5]、Moriguchi Isamu[5]、Tanaka Hideki[1]、Silvestre-Albero Joaquín[6]、Hayashi Takuya[7]、Kaneko Katsumi[1] (1. 信州大学先鋭材料研究所、2. Morgan Advanced Materials, State College, USA. 、3. G2MTech, Alicante, Spain.、4. 千葉大学理学部、5. 長崎大学工学部、6. Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, Spain.、7. 信州大学水環境・土木工学科)

日本語
9:20 ~ 9:40
[C443-1am-02]

カーボンナノチューブ用分散剤フラビンの10-N位-直鎖アルキル側鎖長が昇華性に与える影響

〇加藤 雄一[1]、杉野 卓司[1]、物部 浩達[1] (1. 国立研究開発法人産業技術総合研究所)

英語
9:40 ~ 10:00
[C443-1am-03]

層状複水酸化物を触媒前駆体として用いたカーボンナノチューブの合成に関する研究

〇千田 知香[1]、横山 渓[2]、熊谷 陸駆[2]、會澤 純雄[1]、桑 静[1]、平原 英俊[1]、木村 寛恵[2]、二葉 ドン[3] (1. 岩手大学、2. 一関高専、3. 産総研)

日本語
10:00 ~ 10:20
[C443-1am-04]

高速充放電可能な電気二重層キャパシタのカーボンナノチューブ電極作製に向けたシンプルな”ブレンド”アプローチ

〇清水 太陽[1]、小橋 和文[1]、中島 秀朗[1]、室賀 駿[1]、山田 健郎[1]、岡崎 俊也[1]、小久保 研[1]、畠 賢治[1] (1. 国立研究開発法人産業技術総合研究所)

英語
10:30 ~ 10:50
[C443-1am-05]

テンプレート反応による無機ナノチューブの単層合成と構造多様性

〇中西 勇介[1]、古澤 慎平[1]、佐藤 雄太[2]、加藤 俊顕[3]、宮田 耕充[1] (1. 都立大、2. 産総研、3. 東北大)

英語
10:50 ~ 11:10
[C443-1am-06]

超音波処理による無機炭素源からカーボンナノオニオンの室温合成

〇ヨウ ロンウェン[1]、長谷部 靖[2]、内田 正哉[3] (1. 埼玉工業大学 工学研究科　情報システム専攻、2. 埼玉工業大学 生命環境化学科、3. 埼玉工業大学　先端科学研究所)

日本語
11:10 ~ 11:30

[C443-1am-07]

バイポーラ電気化学反応による黒鉛からの化学修飾グラフェン合成

金野 裕太[1]、下豊留 慧[1]、○沖本 治哉[1] (1. 山形大学)

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18日(月) 13:00 ~ 15:10 C442(4号館 [4階] 442)

[C442-1pm] 20. 材料化学—基礎と応用

座長：山内 美穂、田代 啓悟

日本語

13:00 ~ 13:20

[C442-1pm-01]

超分子ゲルを用いたTiO_2ナノ結晶のフォトドーピング制御

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

英語

13:20 ~ 13:40

[C442-1pm-02]

優れたプロトン伝導性を持つ蔗糖由来の酸化層炭素

○Liu Xinyao[1] (1. 熊本大学)

日本語

13:40 ~ 14:00

[C442-1pm-03]

アルキル基修飾POSSの耐原子状酸素特性

○行松 和輝[1,2]、横山 創一[2]、後藤 亜希[1]、丸山 幹人[2]、木本 雄吾[1]、家 裕隆[2] (1. 宇宙航空研究開発機構、2. 阪大産研)

日本語

14:10 ~ 14:30

[C442-1pm-04]

細孔サイズが制御されたCeO_2の細孔内担持ルテニウム触媒によるアンモニア合成

○滝本 皓也[1]、田代 啓悟[1]、里川 重夫[1] (1. 成蹊大学)

日本語

14:30 ~ 14:50

[C442-1pm-05]

極性勾配反応場を利用したスピロピランの光誘起型CO_2捕捉能制御

○田代 啓悟[1]、大鳥 誠生[1]、里川 重夫[1] (1. 成蹊大学)

英語

14:50 ~ 15:10

[C442-1pm-06]

Nacre-Inspired Graphene Oxide Bulk Materials Produced by Multiscale Interface Crosslinking

○Xuke Tang[1], Ke Chen[2], Binbin Jia[2], Cezhou Chao[2], Yan Wei[3], Junyu Hou[2], Leiting Dong[2], Xuliang Deng[3], Ting-Hui Xiao[1,6], Keisuke Goda[1,4,5], Lin Guo[2] (1. The Univ. of Tokyo, 2. Beihang Univ., 3. Peking Univ., 4. Wuhan Univ., 5. Univ. of California, 6. Zhenzhou Univ.)

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18日(月) 13:00 ~ 15:30 A1455(14号館 [5階] 1455)

[A1455-1pm] 22. 資源利用化学・環境・グリーンケミストリー

座長：吉川 聡一、大嶋 孝志

英語
13:00 ~ 13:20
[A1455-1pm-01]

ホルモース反応ネットワークの構造理解を通した反応選択性の制御

○西島 弘晃[1]、近谷 元大[1]、石原 菜々子[1]、藤本 泰成[1]、田畑 裕[1]、長谷 陽子[1,2]、中西 周次[1] (1. 阪大院基礎工、2. (株）豊田中央研究所)

英語
13:20 ~ 13:40
[A1455-1pm-02]

Multicomponent Adsorption Equilibria Modeling of Phenol and Ciprofloxacin on Differently Prepared Polyethylene Terephthalate Microplastics

○Christian Ebere Enyoh[1], Qingyue Wang[1] (1. Graduate School of Science and Engineering, Saitama University, Japan)

英語
13:40 ~ 14:00
[A1455-1pm-03]

ジアミンを二酸化炭素吸収材とする高効率Direct Air Capture

○曹 芙蓉[1]、吉川 聡一[1]、山添 誠司[1] (1. 東京都立大学)

日本語
14:00 ~ 14:20
[A1455-1pm-04]

ジアミンのCO_2吸脱着特性評価

○八木原 陸矢[1]、吉川 聡一[1]、山添 誠司[1] (1. 東京都立大学)

日本語
14:30 ~ 14:50
[A1455-1pm-05]

プルシアンブルー類似体を用いた水蒸気を含むガスおよび水中からのメタノール吸着

○首藤 雄大[1]、川本 徹[1]、高橋 顕[1] (1. 産業技術総合研究所)

日本語
14:50 ~ 15:10
[A1455-1pm-06]

作業環境測定での活性炭・シリカゲル捕集剤と有機溶剤抽出効率

○安彦 泰進[1] (1. 独立行政法人 労働者健康安全機構)

日本語
15:10 ~ 15:30
[A1455-1pm-07]

ヘテロジトピックレセプターを用いた塩化リチウムの選択的固-液抽出

○三室 翼[1]、平澤 学[2,1]、近藤 慎一[1] (1. 山形大理、2. レゾナック)

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18日(月) 15:55 ~ 16:55 A1454(14号館 [5階] 1454)

[A1454-1vn] 22. 資源利用化学・環境・グリーンケミストリー

座長：磯崎 勝弘、川口 真一

日本語

15:55 ~ 16:15

[A1454-1vn-01]

資源循環を目指した塩化リンフリーなリン酸エステルの製造とリン含有バイオマスの活用

○浅尾 和弥[1]、森 康貴[2]、松本 星奏[3]、早川 康之[4]、佐々木 猛[4]、平田 直也[4]、川口 真一[1,2,3] (1. 佐賀大学 農学部附属アグリ創生教育研究センター、2. 佐賀大学大学院 先進健康科学研究科、3. 佐賀大学農学部 生物資源科学科、4. 日本コンクリート工業株式会社)

日本語

16:15 ~ 16:35

[A1454-1vn-02]

エチレンジアミンによるPET繊維へのアミノ基の導入とメイラード反応による着色

○大江 猛[1]、吉村 由利香[1] (1. 大阪技術研)

日本語

16:35 ~ 16:55

[A1454-1vn-03]

再生樹脂添加用アルデヒド捕捉剤の開発

○須藤 幸徳[1]、木佐貫 紗也佳[1]、鈴木 孝生[1] (1. 東ソー株式会社)

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18日(月) 13:30 ~ 14:30 A1456(14号館 [5階] 1456)

[A1456-1pm] 01. 化学教育・化学史

座長：今井 泉、中川 徹夫

日本語
13:30 ~ 13:50
[A1456-1pm-01]
加藤セチ・その業績の再評価

○吉祥 瑞枝[1] (1. サイエンススタジオ・マリー)

日本語
13:50 ~ 14:10
[A1456-1pm-02]
マイクロスケール実験に基づく簡易ヨードメトリー法の開発～普通校と特別支援学校の遠隔合同授業で行った実践事例～

○山田 一幸[1]、片岡 久美子[2]、荻野 和子[3] (1. 筑波大学附属桐が丘特別支援学校、2. 清泉女学院中学高等学校、3. 東北大学大学院理学研究科)

日本語
14:10 ~ 14:30
[A1456-1pm-03]
安価な手作りウェルプレートを用いたアルカリ土類金属塩の沈殿生成反応に関するマイクロスケール実験

○中川 徹夫[1] (1. 神戸女学院大学)

加藤セチ・その業績の再評価

（サイエンススタジオ・マリー）○吉祥 瑞枝
Sechi KATO, her accomplishments (*Science Studio Marie*) ○Mizue Y. Kissho

Sechi KATO (1893-1989) was awarded a Doctor of Science from the Kyoto Imperial University on a study on acetylene polymerization. She was the 3rd female scientist following to Kono YASUI, and Chika KURODA. She was the first female Chief Scientist of RIKEN, who developed spectrometric analysis of organic compounds in Japan. She organized "Science Seminar" for 15 years after retirement, and nominated the 1st Chemistry Education Award of CSJ in 1976. Her accomplishments should be thoroughly reviewed.

Keywords : Sechi KATO ; Tokyo Women's Higher Normal School; Japan's 3rd Woman Scientist; Riken's 1st Woman Chief Scientist; Spectrometric analysis of organic compounds;

女性の STEM 分野への選択は元来 低く、女性活躍が期待されている。加藤セチは 1931 年アセチレンの重合で、京都帝国大学より学位が授与された。日本初の女性理学博士の保井コノは 1927 年、黒田チカは 1929 年につぐ三番目である 1)。

加藤セチ 2, 3, 4)は 1893 年 10 月 2 日山形県田川郡押切村(現三川町)に誕生した。庄内平野の中央で、出羽三山の一つ羽黒山を背にした大地主で豪農家であった。ところが翌年庄内地震で生家は倒壊焼失して母兄姉を失った。大型酪農の失敗で父は失意のうちに逝去した。後添えの母キンの勧めもあり、苦学の中で東京女子高等師範学校理科を卒業後、札幌の女学校に勤務。北海道帝国大学農学部の女子学生第 1 号となる。1922 年東京の理化学研究所に女性研究生となる。研究分野も農芸化学から化学化学分析へ、量子力学が脚光を浴びる時代となり、分子分光学の勃興期にスペクトル吸収を追究した。1931 年京都帝国大学より学位が授与されて、「庄内のキュウリー夫人」と世評高い。1953 年 4 月理化学研究所で初の女性主任研究員となり、理化学研究所に定年制が施行され、二度の定年延長措置の後 1955 年 3 月末に退職(解職)した。私立大学で教鞭をとった。2 児の母親だったが、長男は 1945 戦死。夫は 1959 年逝去した。加藤セチは 1968 年山形県三川町名誉町民第 1 号称号を贈られて、これを生涯最大の喜びとし, 誇りにしていた。95 歳東京の自宅で倒れ、故郷三川町の耕福寺に埋葬される。加藤セチは 80 歳まで 15 年間にわたり女性教員の人材育成のための科学勉強会『理科ゼミ』を催し, 日本化学会の第 1 回昭和 51 年度(1976 年)化学教育賞推薦候補 5)であった。加藤セチの業績 2, 3, 4, 6)はより高く評価されるべきである。

1) 吉祥瑞枝, 日本初の女性理学博士は誰か？－保井コノについて－, 研究技術計画学会第 25 回年次 学術大会, 2116, (2010)
2) 理化学研究所百年史, 編集委員会企画・編集, 理化学研究所 第 1 部, 1-22 (2018)
3) 前田侯子, 加藤セチ博士の研究と生涯～スペクトルの物理化学的解明を目指して,お茶の水女子大学ジェンダー研究センター年報, 第 7 巻, 87-110, (2004)
4) 山本美穂子, 科学は女性にとって何物にも優る美服である:女性科学者の先駆者加藤セチ, 北海道大学 大学文書館年報, 12, 53-63 (2017)
5) お茶の水女子大学歴史資料館 C9 斎正子「理科ゼミ」閲覧 (2023/9/15)
6) 東北大学史料館（広報・記念事業）, 東北大学附属図書館 (2023/12/22)

マイクロスケール実験に基づく簡易ヨードメトリー法の開発 ～普通校と特別支援学校の遠隔合同授業で行った実践事例～

(筑波大桐が丘特支 [1]・清泉女学院中高 [2]・東北大院理 [3])
○山田 一幸 [1]・片岡 久美子 [2]・荻野 和子 [3]

Development of a simple microscale iodometry method ~The practice carried out jointly in a regular school and a special needs school~

([1]Kirigaoka School for the Physically Challenged, University of Tsukuba, [2]Seisen Junior and Senior High School, [3]Graduate School of Science, Tohoku University) Kazuyuki Yamada[1], Kumiko Kataoka[2], Kazuko Ogino[3]

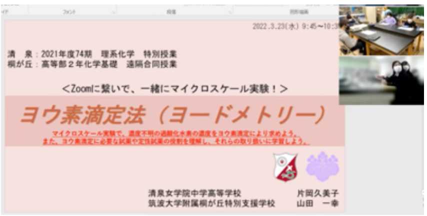
The iodometry is a back titration method that measures the concentration of an unknown reducing agent using an aqueous potassium iodide solution, and is often used as a reference in basic chemistry. However, redox reactions using the back titration method are also covered in problem sets and university entrance exam problems. In order to enhance the understanding of high school students on iodometry, we have been working on development of a simple microscale iodometry. In this presentation, we report on the practice carried out jointly in a regular school and a special needs school.

Keywords：Microscale, Iodometry, Inclusive Education, Redox Reaction

ヨウ素滴定法（ヨードメトリー）は，ヨウ化カリウム水溶液とチオ硫酸ナトリウム水溶液を使用して未知の還元剤の濃度を測定する逆滴定の手法で，高等学校の化学基礎では参考程度に取り上げられている。しかし，ヨードメトリーのような逆滴定の手法を用いた酸化還元反応は，入試問題でも扱われている。この逆滴定の手法を高校生に理解してもらうために，簡易なマイクロスケールのヨードメトリーの開発に取り組んできた。本発表は，開発した方法と普通校と特別支援学校の遠隔合同授業で実践した事例について併せて報告する。

【実験操作】詳細は口頭発表で説明

1. 濃度未知の過酸化水素水の入った点眼瓶の質量を，電子天秤で測る。
2. サンプル瓶に濃度未知の過酸化水素水を 5 滴加えた後，点眼瓶の質量を電子天秤で測る。
3. サンプル瓶に 0.5 mol/L の硫酸 3 滴を加える。
4. サンプル瓶に 0.10 mol/L のヨウ化カリウム水溶液を 10 滴加え,しばらく放置する。
5. 0.10 mol/L のチオ硫酸ナトリウム水溶液の入った点眼瓶を、電子天秤で質量を測る。
6. 点眼瓶でチオ硫酸ナトリウム水溶液を加えて攪拌し，茶褐色が薄くなったところでデンプン溶液を 1 滴加え，滴定の感度を高める。さらにチオ硫酸ナトリウム水溶液を加え、青紫色が消失した後に，点眼瓶の質量を測る。



2022.3.23(水) 9:45~10:3

清　泉：2021年度74期　理系化学　特別授業
桐が丘：高等部２年化学基礎　遠隔合同授業

＜Zoomに繋いで、一緒にマイクロスケール実験！＞

ヨウ素滴定法（ヨードメトリー）

清泉女学院中学高等学校　片岡久美子
筑波大学附属桐が丘特別支援学校　山田　一幸

安価な手作りウェルプレートを用いたアルカリ土類金属塩の沈殿生成反応に関するマイクロスケール実験

（神戸女学院大人間科学）○中川 徹夫
Microscale Experiments on Precipitation Formation of Alkaline Earth Metal Salts using Low-cost Handmade Well Plate (*School of Human Sciences, Kobe College*) ○Tetsuo Nakagawa

In high school chemistry lessons, both enthalpy change ΔH and entropy change ΔS in chemical reactions are taught. Furthermore, the introduction of Gibbs energy change ΔG is useful because the spontaneity of chemical reactions can be understood. In this study, we focus on the precipitation formation of alkaline earth metal salts ($MgCO_3$, $CaCO_3$, $SrCO_3$, $MgSO_4$, $CaSO_4$ and $SrSO_4$) where chemical reactions occur rapidly. First, we estimated ΔH, ΔG and ΔS for the formation of these salts in aqueous solutions at 10^5 Pa and 298.15 K using CRC handbook[1]. Except for $MgSO_4$, all ΔG values were negative (See Table 1). Next, we carried out microscale experiments on the precipitation formation reaction of these salts using inexpensive handmade well plates[2]. The results showed the formation of white precipitates other than $MgSO_4$, consistent with the negative ΔG values.

Table 1. ΔH, ΔG and ΔS *for* Precipitation Formation of Alkaline Earth Metal Salts in Solutions (298.15 K)

	ΔH / kJ	ΔG / kJ	ΔS / JK^{-1}
$MgCO_3(s)$	48.2	–29.5	261
$MgSO_4(s)$	91.3	28.7	210
$CaCO_3(s)$	12.3	–47.7	202
$CaSO_4(s)$	17.6	–23.9	140
$SrCO_3(s)$	2.8	–52.8	187
$SrSO_4(s)$	2.0	–36.9	130

Keywords :Microscale Experiment; Low-cost Handmade Well Plate; Alkaline Earth Metal Salt; Precipitation; Gibbs Energy Change

高等学校化学の授業では、化学変化に伴うエンタルピー変化ΔHやエントロピー変化ΔSについて指導される。加えてギブズエネルギー変化ΔGを導入すれば、化学変化の自発性に関する知見が得られ有用である。本研究では、化学反応が迅速に生じるアルカリ土類金属塩（$MgCO_3$、$CaCO_3$、$SrCO_3$、$MgSO_4$、$CaSO_4$および$SrSO_4$）の沈殿生成反応に注目した。まず、CRC ハンドブック[1]を用いて、10^5 Pa、298.15 K における水溶液中での塩生成に伴うΔH、ΔGおよびΔSを算出した。$MgSO_4$を除きΔGの値は全て負であった。続いて安価な手作りウェルプレート[2]を用いてこれらの塩の沈殿生成に関するマイクロスケール実験を実施した。$MgSO_4$以外はすべて白色沈殿が生成し、負のΔGの値との整合性が認められた。

本研究は、JSPS 科研費 17K00991 の助成を受けたものである。

1) *CRC Handbook of Chemistry and Physics*, 100th Edition, CRC Press, Boca Raton, **2019**.
2) T. Nakagawa, *School Science Review,* **2021**, 103(382), 23.

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18日(月) 13:00 ~ 15:20 A1441(14号館 [4階] 1441)

[A1441-1pm] 04. 物理化学—物性

座長：五月女 光、佐々木 陽一

英語

13:00 ~ 13:20

[A1441-1pm-01]

4-ニトロフェニル部位を有する電荷移動型化合物群の蛍光ソルバトクロミック特性と非蛍光過程

〇三輪 真梨乃[1]、伊藤 亮孝[1] (1. 高知工大院工)

英語

13:20 ~ 13:40

[A1441-1pm-02]

複数の立体異性体を持つ種々のトリアジン誘導体の励起状態ダイナミクス解明

〇笠 僚宏[1]、西郷 将生[1]、小川 知弘[1]、宮田 潔志[1]、土屋 陽一[2]、中野谷 一[2]、Arvydas Ruseckas[3]、Ifor Samuel[3]、安達 千波矢[2]、恩田 健[1] (1. 九大院理、2. 九大OPERA、3. セントアンドリュース大学)

日本語

13:40 ~ 14:00

[A1441-1pm-03]

光走査トンネル顕微鏡による単一分子内における励起子生成・消滅過程の実空間計測

〇今井 みやび[1,2]、今田 裕[1]、金 有洙[1,3] (1. 理研、2. JSTさきがけ、3. 東大)

14:00 ~ 14:20

休憩

英語

14:20 ~ 14:40

[A1441-1pm-04]

多孔性金属錯体中における一重項分裂により生じた五重項状態の室温コヒーレンス

〇山内 朗生[1]、田中 健太郎[1]、婦木 正明[2,3]、藤原 才也[4]、君塚 信夫[1]、笠 僚宏[1]、西郷 将生[1]、恩田 健[1]、楠本 遼太[2]、上野 那美[2]、佐藤 春実[2]、小堀 康博[2,3]、宮田 潔志[1,3]、楊井 伸浩[1,3,5] (1. 九大、2. 神大、3. JST-CREST、4. 理研、5. JST 創発)

英語

14:40 ~ 15:00

[A1441-1pm-05]

Dimeric scaffold for circularly polarized delayed luminescence

〇Marine Louis[1], Yuki Yamashita[1], Yugo Tsuji[1], Chigusa Goto[1], Takuya Nakashima[3], Katsuyuki Shizu[2], Yo Shimizu[1], Hironori Kaji[2], Tsuyoshi Kawai[1] (1. Nara Institute of Science and Technology, 2. Kyoto University, 3. Osaka Metropolitan University)

英語

15:00 ~ 15:20

[A1441-1pm-06]

Effects of Monomer in Ionic Nanospheres on Sensitized Luminescence from Terbium(III) Ion

〇Nikita Madhukar[1], Taizo Misato[1], Akitaka Ito[1] (1. Kochi Univ. of Tech.)

Fluorescent Solvatochromic Behaviors and Nonfluorescence Processes of Charge-Transfer-Type Compounds with A 4-Nitrophenyl Moiety

([1]*Graduate School of Engineering, Kochi University of Technology*) ○Marino Miwa,[1] Akitaka Ito[1]

Keywords: Nitro Group; Fluorescent Solvatochromism; Charge-Transfer Transition; Nonfluorescence Process; Intersystem Crossing

Owing to its strong electron-withdrawing ability, an introduction of a nitro group(s) can extend charge-transfer character in an electronic transition. Most compounds with a nitro group(s) are, however, nonemissive[1] and, therefore, effects of the presence of a nitro group(s) on the excited-state properties are not necessarily clear. In this work, we synthesized a series of compounds with a 4-nitropheny moiety (**1**–**3**, Figure) and evaluated their spectroscopic/photophysical properties.

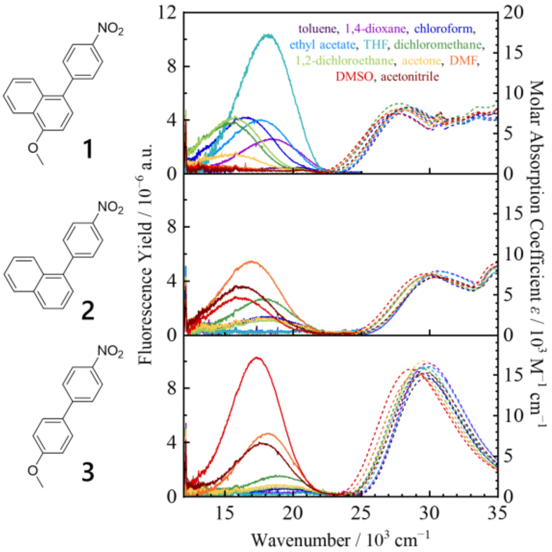


Figure. Chemical structures and absorption/ fluorescence spectra of **1**–**3** in various solvents.

1–**3** showed large fluorescent solvatochromism and, especially, fluorescence maximum energy ($\tilde{\nu}_\mathrm{f}$) of **1** drastically decreased from 20000 cm^{-1} to 16000 cm^{-1} with increasing the solvent polarity (Figure). Large fluorescent solvatochromism of **1**–**3** is explainable by large excited-state electric dipole moments being 9.7 (**1**), 7.0 (**2**) and 8.7 D (**3**) determined by the solvent dependences on the absorption/fluorescence maxima. Furthermore, nonfluorescence rate constants (k_d) of the compounds exhibited an identical trend, irrespective of the compound and solvent. In the region being $\tilde{\nu}_\mathrm{f} < 17500$ cm^{-1}, k_d decreased with increasing $\tilde{\nu}_\mathrm{f}$, as expressed by the energy gap law. On the other hand, in the >17500-cm^{-1} region, k_d increased with the fluorescence energy. The latter reverse energy gap dependence of k_d originates from intersystem crossing to a triplet excited state as evaluated by transient absorption measurements and TD-DFT calculations.

1) a) M. C. Chen, D. G. Chen, P.-T. Chou, *ChemPlusChem* **2021**, *86*, 11. b) Y. M. Poronik, G. V. Baryshnikov, I. Deperasinska, E. M. Espinoza, J. A. Clark, H. Agren, D. T. Gryko, V. I. Vullev, *Commun. Chem.* **2020**, *3*, 190.

Elucidation of the excited-state dynamics of various triazine derivatives with stereo-structural isomers

([1]*Graduate School of Science, Kyushu University*, [2]*OPERA, Kyushu University,* [3]*School of Physics and Astronomy, University of St Andrews*) ○Tomohiro Ryu [1], Masaki Saigo [1], Tomohiro Ogawa [1], Kiyoshi Miyata [1], Youichi Tsuchiya [2], Hajime Nakanotani [2], Arvydas Ruseckas [3], Ifor D. W. Samuel [3], Chihaya Adachi [2], Ken Onda [1]

Keywords: Time-resolved Photoluminescence Spectroscopy; Transient Absorption Spectroscopy; Dual Emission

Donor-acceptor (D-A) type organic luminescent molecules are paid attention to for applications to organic light-emitting diodes (OLEDs)[1]. For achieving high-efficiency OLEDs, a comprehensive understanding of the emission mechanism of D-A molecules is essential. However, the high flexibility of the D-A dihedral angle of some D-A molecules leads to complex emission mechanisms. For example, phenothiazine-triphenyltriazine (PTZ-TRZ) has dual emission derived from two types of structures in the excited state because of the flexibility[2]. We have already elucidated the excited-state dynamics of PTZ-TRZ[3]. In this study, we investigated various D-A molecules to establish the general model of the excited-state dynamics.

In addition to PTZ-TRZ, we selected the two molecules, dimethyldihydroacridine-TRZ (DMAC-TRZ) and phenoxazine-TRZ (PXZ-TRZ) (Fig. 1a), which exhibit single emission on steady-state photoluminescence (PL) spectra. Time-resolved PL (TR-PL) spectra revealed dual emission for DMAC-TRZ and PXZ-TRZ on a picosecond time scale (Fig. 1b). These results indicate that DMAC-TRZ and PXZ-TRZ possess two stable structures in the excited state due to the flexibility of the dihedral angle. Moreover, transient absorption (TA) spectra showed spectral changes in DMAC-TRZ and PXZ-TRZ, suggesting a structural change due to the rotation of D-A dihedral angles (Fig. 1c,d). From these measurements, the complicated excited-state dynamics, including the previously overlooked effects of D-A dihedral angle rotations, have been elucidated.

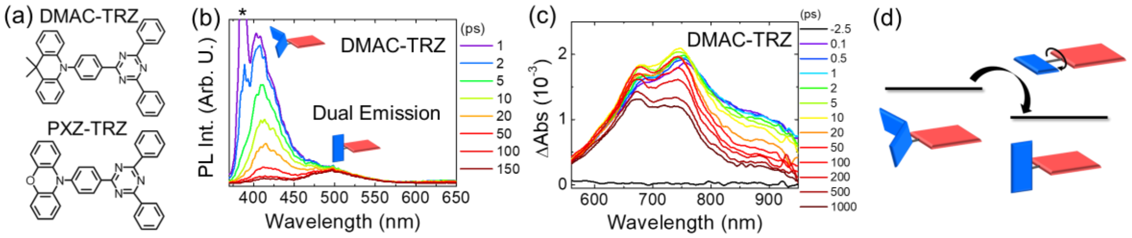


Fig. 1 (a) Structure of DMAC-TRZ and PXZ-TRZ. (b) TR-PL spectra of the DMAC-TRZ, schematic of the two structures of DMAC-TRZ, and their emission attribution. (c) TA spectra of DMAC-TRZ, (d) Schematic of the structural changes due to D-A dihedral angle rotation.

[1] A. Endo *et al. Appl. Phys. Lett.* **98**, 083302 (2011), [2] H. Tanaka *et al. J. Phys. Chem. C* **118**, 15985−15994 (2014), [3] T. Ryu *et al. Chem. Phys. Lett.* **809**,140155 (2022).

光走査トンネル顕微鏡による単一分子内における励起子生成・消滅過程の実空間計測

（理研[1]・JST さきがけ[2]・東大[3]）○今井　みやび[1,2]・今田　裕[1]・金 有洙[1,3]

Real-space observation of exciton formation and annihilation processes in a single molecule by Photon-scanning tunneling microscopy

([1]*RIKEN*, [2]*PRESTO, JST,* [3]*Univ. Tokyo*) ○Miyabi Imai-Imada,[1,2] Hiroshi Imada,[1] Yousoo Kim,[1,3]

The creation and annihilation of an exciton induced by electron dynamics, such as transition in a molecule or transfer between a molecule and an electrode, play crucial roles in optoelectronic energy conversion. However, the correlation between the exciton and electron dynamics in a molecule is yet to be thoroughly described, mainly because the spatial resolution of conventional techniques is not enough to resolve individual molecules. Recently, we have developed Photon-STM (Figure) by combining low-temperature scanning tunneling microscope with laser irradiation and photo detection systems, and realized to investigate the exciton dynamics in a single molecule 1-3). In this presentation, we report Photon-STM study of the electron dynamic processes that drive exciton creation and annihilation, including electroluminescence, photoluminescence, and photocurrent generation, in a free-base phthalocyanine single molecule adsorbed on the NaCl thin film grown on the Ag(111) substrate.

Keywords : single molecule; scanning tunneling microscope; exciton; electron

分子内において励起子が生成・消滅される過程は、光電変換デバイスにおいて極めて重要な役割を果たしている。この過程は、電子遷移や電子移動によって引き起こされるが、励起子と電子ダイナミクスの相関は一分子レベルでは解明されていない。この理由の一つとして、従来の計測手法の空間分解能が個々の分子を判別できるほど十分でないことが挙げられる。近年、我々は原子分解能の走査トンネル顕微鏡に光照射・検出機構を融合した光走査トンネル顕微鏡（Photon-STM、図）を開発し、単一分子内で生じる励起子ダイナミクスを観測することに成功した 1-3)。本講演では、Photon-STM を用いて、NaCl/Ag(111)基板に吸着したフタロシアニン単一分子の電子と励起子ダイナミクスを原子分解能で観測した結果について報告し、発光や光電流生成といった励起子消滅過程がどのような電子ダイナミクスによって引き起こされるのか議論する。

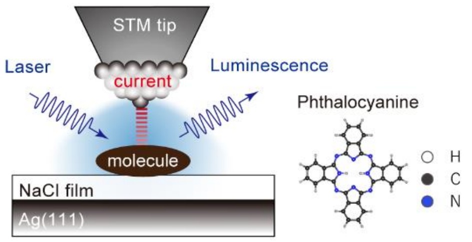


Figure: Schematics of Photon-STM and Phthalocyanine molecule

1) M. Imai-Imada et al., *Phys. Rev. B* **98**, 201403(R) (2018).
2) M. Imai-Imada *et al.*, *Nature* **603**, 829 (2022).
3) H. Imada, M. Imai-Imada *et al.*, *Science* **373**, 95 (2021).

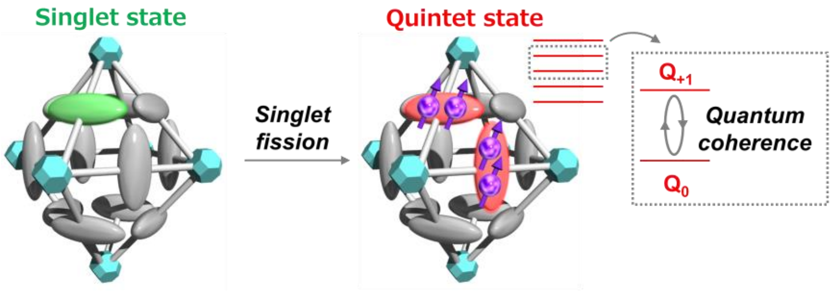
Room-temperature quantum coherence of quintet state generated through singlet fission in a metal-organic framework

([1]*Kyushu University*, [2]*Kobe University*, [3]*CREST, JST*, [4]*RIKEN*, [5]*FOREST, JST*) ○Akio Yamauchi,[1] Kentaro Tanaka,[1] Masaaki Fuki,[2,3] Saiya Fujiwara,[4] Nobuo Kimizuka,[1] Tomohiro Ryu,[1] Masaki Saigo,[1] Ken Onda,[1] Ryota Kusumoto,[2] Nami Ueno,[2] Harumi Sato,[2] Yasuhiro Kobori,[2,3] Kiyoshi Miyata,[1,3] Nobuhiro Yanai[1,3,5]

Keywords: Singlet fission; Quintet state; Qubit; Quantum coherence; Metal-organic framework

A quantum bit (qubit) that expands a concept of bit to a two-level quantum state, is a basic building block of quantum information science to realize quantum technologies such as quantum computing and quantum sensing.[1] Qubits based on electron spins of molecules has several advantages such as a high controllability of qubit properties by chemical modifications. Among the molecular qubit, quintet state generated through singlet fission (SF) has unique feature of being consisted by four spins, which enables advanced qubit operations.[2] To utilize the quintet state as a qubit, the generation of the quantum spin coherence in the quintet sublevels are required. However, there were no reports about the quantum coherence at room temperature.

Here we reports the first observation of the room-temperature quantum coherence of the quintet state generated though SF in a metal-organic framework (MOF).[3] A typical SF molecule, pentacene was modified and loaded as the ligand. The existence of SF and the quintet state in the MOF (Pn-MOF) was confirmed by transient absorption spectroscopy and time-resolved electron paramagnetic resonance (EPR). Nutation measurement with pulsed EPR shows the quantum coherence of the quintet state. The simulation based on the results indicate the suppressed motion in the densely packed MOF contributes the generation of the quintet state with keeping its quantum coherence.



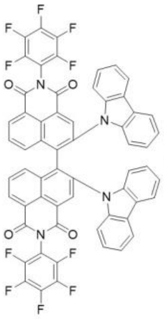
1) C. L. Degen, F. Reinhard, P. Cappellaro *Rev. Mod. Phys*. **2017**, *89*, 035002. 2) R. M. Jacobberger, Y. Qiu, M. L. Williams, M. D. Krzyaniak, M. R. Wasielewski, *J. Am*., *Chem*. *Soc*. **2022**, *144*, 2276. 3) A. Yamauchi et al., *Sci. Adv.* **2024**, *10*, eadi3147.

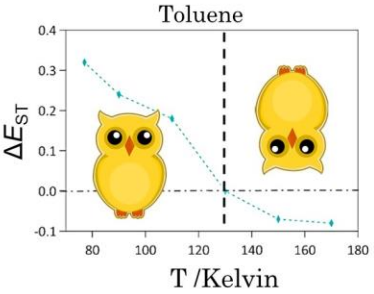
Dimeric scaffold for circularly polarized delayed luminescence

([1] *Division of Materials Science, Nara Institute of Science and Technology,* [2] *Kyoto University,* [3] *Osaka Metropolitan University*)
○Marine Louis[1], Yuki Yamashita[1], Yugo Tsuji[1], Chigusa Goto[1], Takuya Nakashima[3], Katsuyuki Shizu[2], Yo Shimizu[1], Hironori Kaji[2], Tsuyoshi Kawai[1]

Keywords: *delayed emission, circularly polarized luminescence, Self-assemblies.*

Significant research efforts have been dedicated to the development of efficient circularly polarized luminescent (CPL) emitters. Such derivatives have proven to be of use in countless applications including organic light-emitting diodes. [1,2] We report an original binaphthalimide chiral scaffold. [3] Monomeric achiral variants are compared to dimeric targets. This study highlights the design of new thermally activated delayed fluorescence (TADF) emitters relying on Davydov splitting (DS) effect to induce small singlet-triplet energy gap which is supported by theoretical calculations. Time-dependent and temperature-dependent spectroscopic analyses revealed that the nature of the acceptor can lead to an inversion of fluorescence and phosphorescence emission which were observed in both toluene around 170 K and at room temperature in PMMA films. The dimers being chiral emitters, CPL was also measured. The enantiomers exhibited expected CPL at room and low temperature with a dissymmetry factor up to 6×10^{-3} for TADF at room temperature and 5.2×10^{-2} for phosphorescence at 77 K. To boast those performances, the targets were modified and used as dopants in liquid crystals media.





1) Kanj, A. B.; Bürck, J.; Vankova, N.; Mutruc, D.; Chandresh, A.; Hecht, S.; Heine T.; Heinke, L. J. Am.Chem. Soc., 2021, 143, 7059-7068. 2) Singh, R.; Unni, k. N. N.; Solanki A.; Deepak, Optical Mater., 2012, 34, 716-723. 3) Tsuji, Y.; Kanno, N.; Goto, C.; Katao, S.; Okajima, Y.; Reine, P.; Imbrasas, P.; Reineke, S.; Shizu, K.; Nakashima, T.; Kaji, H.; Kawai, T.; Louis, M. J. Mat. Chem. C. 2023, 11, 5968-5978.

Effects of Monomer in Ionic Nanospheres on Sensitized Luminescence from Terbium(III) Ion

([1]*Graduate School of Engineering, Kochi University of Technology*) ○Nikita Madhukar,[1] Taizo Misato,[1] Akitaka Ito[1]

Keywords: f–f Transition; Photosensitization; Electrostatic Interactions; Ionic Nanosphere

Terbium(III) species have been used in a variety of applications, including sensing, photovoltaics, phosphor, bioimaging and others, owing to their high luminescence-color purity arising from narrow band shapes.[1] In contrast to such applicability, their luminescence is typically weak since both excitation and luminescence processes are Laporte-forbidden. An introduction of a photosensitizing unit(s) is one of the most popular strategies to compensate the weak absorption. In this study, we utilized ionic nanospheres, spherical ion-exchange resins with a diameter of <300 nm,[2] as solid-state media and photosensitizers for terbium(III) ion. Luminescence from terbium(III) ion was successfully sensitized upon doping in the ionic nanospheres with and without a ligating unit.

Ionic nanospheres were synthesized by copolymerizing sodium *p*-styrenesulfonate, divinylbenzene and poly(ethylene glycol)methacrylate methyl ether (M_n: 2000) in the absence and presence (1mol%) of 5-(4-vinylphenyl)-1,10-phenanthroline (vPPhen). Terbium(III) ion was doped in the ionic nanospheres (5–300 nmol/mg) by soaking the ionic nanosphere in an aqueous solution of $TbCl_3$. The terbium(III)-doped nanospheres without vPPhen exhibited several luminescence bands at 488, 544, 583 and 620 nm, which resemble to the luminescence originating in the $^5D_4 \rightarrow {}^7F_J$ (J = 3–6) transitions in terbium(III) species, upon an excitation at 260 nm (Figure).[3] In the case of the nanosphere with vPPhen, an excitation at 300 nm resulted in the similar 4f–4f luminescence. Thus, the copolymerized vPPhen would help longer-wavelength excitation as a photosensitizer along with ligating moiety. Detailed effects of the monomer unit on the luminescence from terbium(III) ion will be discussed.

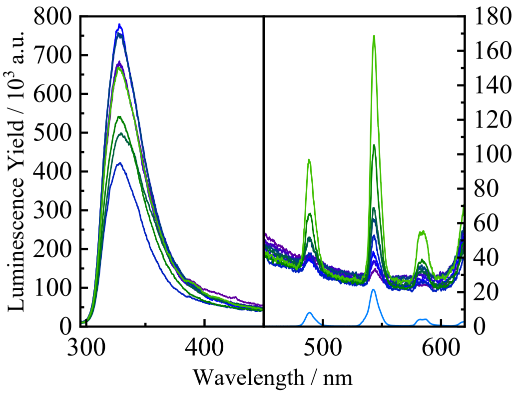


Figure. Luminescence spectra of terbium(III)-doped ionic nanospheres without vPPhen (5.04–299 nmol mg^{-1}, purple → green, λ_{ex} = 260 nm). Blue spectrum represents that of the aqueous $TbCl_3$ solution.

1) D. Sarkar, S. Ganguli, T. Samanta, V. Mahalingam, *Langmuir* **2019**, *35*, 6211. 2) H. Yamamoto, M. Taomoto, A. Ito, D. Kosumi, *J. Photochem. Photobiol. A: Chem.* **2020**, *401*, 11277. 3) N. Madhukar, T. Misato, A. Ito, submitted.

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18日(月) 9:00 ~ 11:30 A1444(14号館 [4階] 1444)

[A1444-1am] 07. 無機化学

座長：米里 健太郎、湊 拓生

英語
9:00 ~ 9:20
[A1444-1am-01]
多座ポリオキソメタレートで保護した超安定・高活性なコロイド金ナノ粒子触媒

○夏 康[1]、谷田部 孝文[1]、米里 健太郎[1]、矢部 智宏[1]、鈴木 康介[1]、山口 和也[1] (1. 東大)

英語
9:20 ~ 9:40
[A1444-1am-02]
物理蒸着を用いた伝導性MOFの薄膜合成における溶媒蒸気アニール効果

○中山 亮[1]、CHON Seoungmin[2]、岩本 俊太[2]、小林 成[1]、清水 亮太[1]、一杉 太郎[1,2] (1. 東大院理、2. 東工大物質理工)

英語
9:40 ~ 10:00
[A1444-1am-03]
Keggin型ポリオキソメタレートを基盤とした多孔性イオン結晶を利用した小核銀クラスターのサイズ選択的な合成

○原口 直哉[1]、黒﨑 大誠[1]、内田 さやか[1] (1. 東大院総合)

英語
10:00 ~ 10:20
[A1444-1am-04]
金属–有機構造体の配位不飽和金属部位における幾何構造の変化によるπ逆供与の制御とその室温水素貯蔵への応用

○薮内 祐人[1,2,3]、古川 博康[1,2,3]、Kurtis Carsch[1,3]、Ryan Klein[4,5]、Nikolay Tkachenko[1,2]、Adrian Huang[1,2,3]、Craig Brown[5,6]、Martin Head-Gordon[1,2]、Jeffrey Long[1,2,3] (1. カリフォルニア大学バークレー校、2. ローレンス･バークレー国立研究所、3. 脱炭素材料研究所、4. 国立再生エネルギー研究所、5. アメリカ国立標準技術研究所、6. デラウェア大学)

10:20 ~ 10:30

休憩

英語
10:30 ~ 10:50
[A1444-1am-05]
一次元鎖状モリブデン酸化物の合成と構造制御

○湊 拓生[1]、宮本 美里[1]、石川 理史[2]、日吉 範人[3]、定金 正洋[1] (1. 広島大学、2. 神奈川大学、3. 産業技術総合研究所)

英語
10:50 ~ 11:10
[A1444-1am-06]
プレイスラー型ポリオキソメタレートにおける分子分極緩和の圧力制御

○栗原 英駿[1]、藤林 将[2]、加藤 智佐都[1]、Cosquer Goulven[3,4]、井上 克也[1,3,4,5]、西原 禎文[1,4,5,6] (1. 広島大学院先進理工、2. 宇部高専、3. 広島大キラルノット超物質拠点、4. 広島大キラル国際拠点、5. 広島大先進セ、6. JSTさきがけ)

🏷 英語

11:10 ~ 11:30

[A1444-1am-07]

シラノール基を有するかご型シロキサンと金属種の縮合反応による多孔質触媒の合成

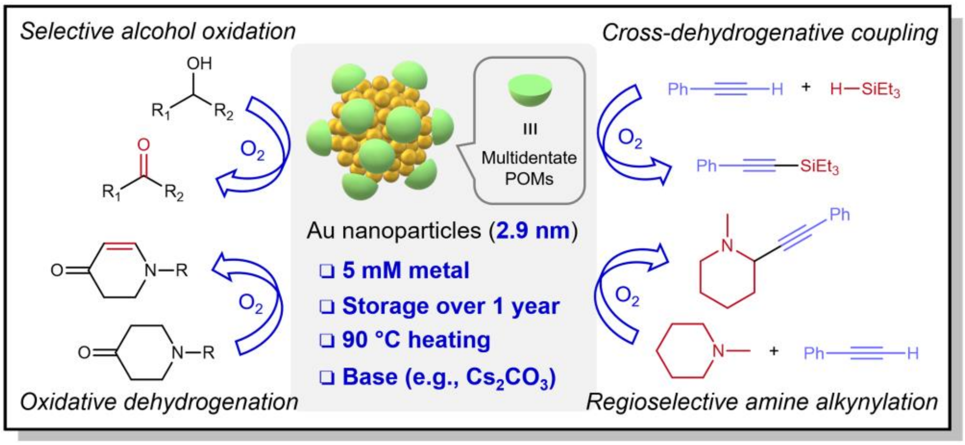
○疋野 拓也[1]、松野 敬成[1,2]、黒田 一幸[1,2]、下嶋 敦[1,2] (1. 早大先進理工、2. 早大材研)

Ultra-stable and highly reactive colloidal gold nanoparticle catalysts protected using multi-dentate polyoxometalates

(*School of Engineering, The University of Tokyo*) ○Kang Xia, Takafumi Yatabe, Kentaro Yonesato, Tomohiro Yabe, Kosuke Suzuki, Kazuya Yamaguchi

Keywords: Polyoxometalates; Gold Nanoparticles; Metal Nanoparticles; Hybrid Materials; Catalysis

Metal nanoparticles modified with polyoxometalates (POMs) have been extensively studied because these modifications can modulate their catalytic performance and achieve concerted catalysis.[1,2] Despite utilization of unique multielectron transfer and photoredox property of POMs in photo- and electro-catalysis, the inherent low stability of POM-modified metal nanoparticles has limited catalytic applications.[2] Hence, by utilization of our previous knowledges that a robust electronic interaction exists between multi-dentate POMs and Au nanoparticles,[3] we developed a feasible strategy to prepare small Au nanoparticles (~3 nm) protected using multidentate POMs in various non-polar organic solvents.[4] It is noted that they possess an extraordinary stability towards practical conditions such as high concentration, long time, temperature and addition of base, and more importantly, they can maintain notable reactivity in various oxidation reactions using O_2 as the terminal oxidant, including selective aerobic oxidation of benzyl alcohol to benzaldehyde without noticeable aggregation after the reaction, oxidative dehydrogenation of piperidone derivates, cross-dehydrogenative coupling reaction and regioselective amine alkynylation reaction. Finally, we validated that this methodology can be expanded to different metals and POM ligands.



1) Y. Wang, I. A. Weinstock, *Chem. Soc. Rev.* **2012**, *41*, 7479. 2) K. Xia, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214506. 3) K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205873. 4) K. Xia, T. Yatabe, K. Yonesato, S. Kikkawa, S. Yamazoe, R. Ishikawa, N. Shibata, R. Ikuhara, A. Nakata, K. Yamaguchi, K. Suzuki, *in revision.*

Solvent vapor annealing effects on thin film synthesis of conductive metal–organic framework using physical vapor deposition

([1]*Graduate School of Science, The University of Tokyo*, [2]*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Ryo NAKAYAMA,[1] Seoungmin CHON,[2] Shunta IWAMOTO,[2] Shigeru KOBAYASHI,[1] Ryota SHIMIZU,[1] Taro HITOSUGI[1,2]

Keywords: MOF; Thin film; Electrical conductivity; Physical vapor deposition

[Introduction] $Cu_3(HHTP)_2$ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) is a conductive metal-organic framework (MOF), and its thin-film synthesis by dry process is crucial for device applications and interfacial studies. Previously, we reported on the successful synthesis of $Cu_3(HHTP)_2$ thin films by a two-step dry process combining physical vapor deposition (PVD) with pyridine vapor annealing. [1] However, the detailed effect of solvent vapor annealing is unclear. In this study, we investigated the effect of solvent vapor annealing on the synthesis of $Cu_3(HHTP)_2$ thin films using various solvents.

[Experiments] As a first step, $Cu_3(HHTP)_2$ thin films were deposited on Al_2O_3 (0001) using infrared laser deposition. The thin films were deposited at 100 °C in a multilayer form: alternate deposition of HHTP (10 nm) and copper acetate anhydrous (8 nm) was repeated five times. As a second step, the fabricated films were annealed under solvent vapor; the deposited film and 3 μL of the mixed solvents of superdehydrated pyridine and H_2O (0–60 vol%) were separately set in a gasket-sealed cell (10.3 ml) under air. The cell was annealed at 60 °C for 24h. The structural characterization was performed by Infrared (IR) spectroscopy and X-ray diffraction (XRD).

[Results] The IR spectra of the films annealed under the vapor of mixed solvents containing more than 20 vol% H_2O showed a peak at the same position as Cu_3HHTP_2 (Fig. 1). Out-of-plane and in-plane X-ray diffraction indicate the successful fabrication of (001)-oriented $Cu_3(HHTP)_2$ film after annealing with mixed solvents containing more than 20 vol% H_2O. Additionally, solvent vapor annealing with a mixture of H_2O and other organic solvents such as methanol and N,N-dimethylformamide did not provide Cu_3HHTP_2. Thus, vapor annealing of pyridine and H_2O is essential for fabricating $Cu_3(HHTP)_2$ thin films using PVD.

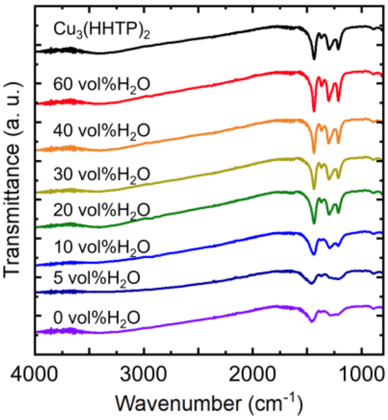


Fig. 1 IR spectra of the films annealed with the mixture of superdehydrated pyridine and H_2O.

1) Chon, Nakayama, Hitosugi *et al.*, *ACS Appl. Mater, Interfaces.*, **2023**, *15*, 56057.

Size-Selective Synthesis of Small Silver Clusters with Porous Ionic Crystals based on Keggin-Type Polyoxometalates

([1]*Graduate School of Arts and Sciences, The University of Tokyo*) ○Naoya Haraguchi,[1] Taisei Kurosaki,[1] Sayaka Uchida[1]

Keywords: Metal Clusters; Porous Crystalline Materials; Polyoxometalates

Small silver clusters consisting of a few atoms have unique catalytic and optical properties, which are not observed in the corresponding bulk samples.[1] While the properties of small silver clusters are highly dependent on their size, size-selective synthesis is still challenging because small clusters tend to aggregate. Although we have previously reported size-controlled synthesis of small silver clusters within redox-active porous ionic crystal, improving size-selectivity has remained as our next challenge.[2] In this work, we utilized $[Cr_3O(OOCH)_6L_3]_2[\alpha\text{-}XM_{11\text{-}1}M'O_{40}]$ (L = methylpyridine (mepy) or ethylpyridine (etpy), X = Si orP, M = Mo or W, M’ = Mo, W, or V, **L-XMM’**) as scaffold and investigate the effect of POM and crystal structure of size selectivity of small Ag clusters formed in PICs.

Small Ag clusters were synthesized thorough 2 step reaction. In the reaction 1, electrons were stored in the PIC scaffolds by reducing comprising POMs.

$$\textbf{L-XMM'} + Cs^+ + xe^- \rightarrow \textbf{L-XMM'}(\boldsymbol{x}) \qquad \text{……(1)}$$

In the reaction 2, Ag introduction was occurred and electrons transferred from POM to Ag^+ followed by aggregation of Ag^0 and Ag^+ to form small Ag clusters in the PIC.

$$\textbf{L-XMM'}(\boldsymbol{x}) + yAg^+ \rightarrow \textbf{L-XMM'}(\boldsymbol{x, y}) + Cs^+ \qquad \text{……(2)}$$

X-ray photoelectron spectroscopy (XPS), Photoluminescence spectroscopy (PL), and X-ray absorption fine structure (XAFS) measurements revealed that constituent elements of POMs (X and M) affect the size of Ag clusters initially formed and crystal structure affect the stability of Ag cluster formed inside PICs which results in size-selective formation.

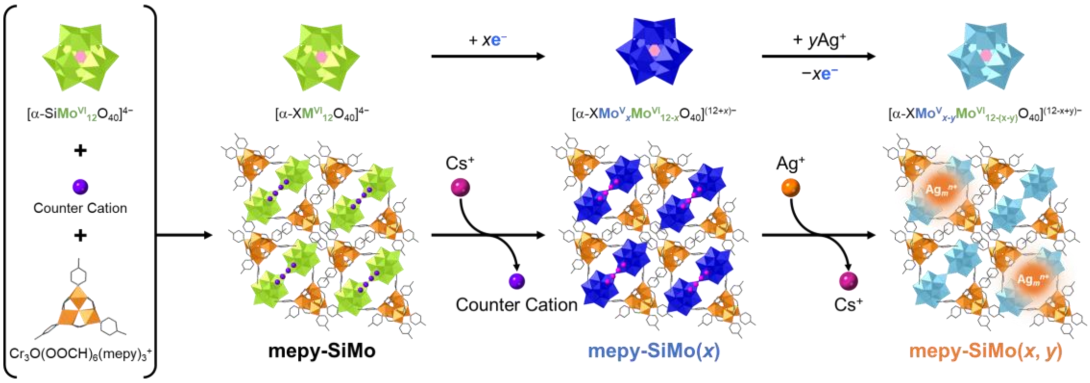


Figure 1　Ag cluster formation in PICs

1) Y. Lei *et al.*, *Science* **2010**, *328*, 224. 2) N. Haraguchi, T. Tachikawa, S. Uchida, et al., Small, 2023, 19, 2300743.

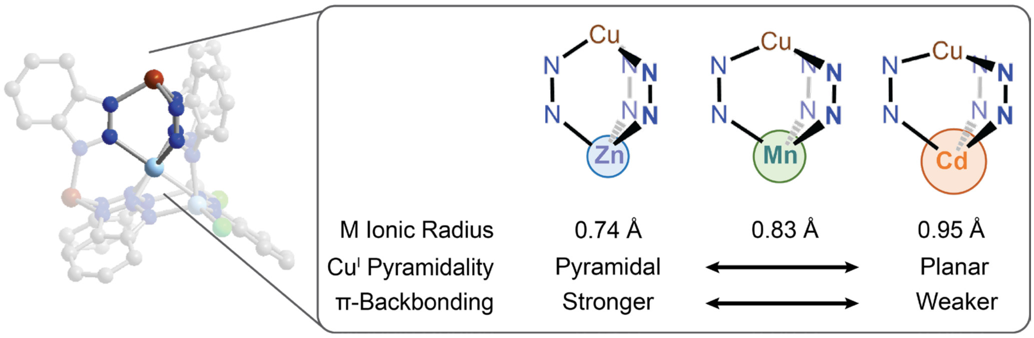
Geometric Effects of π-Basicity of Open Metal Sites in Metal–Organic Frameworks for Ambient Temperature Hydrogen Storage

([1]*University of California, Berkeley*, [2]*Lawrence Berkeley National Laboratory,* [3]*Institute for Decarbonization Materials,* [4]*National Renewable Energy Laboratory,* [5]*National Institute for Standards and Technology,* [6]*University of Delaware*) ○Yuto Yabuuchi,[1,2,3] Hiroyasu Furukawa,[1,2,3] Kurtis Carsch,[1,3] Ryan Klein,[4,5] Nikolay Tkachenko,[1,2] Adrian J. Huang,[1,2,3] Craig Brown,[5,6] Martin Head-Gordon,[1,2] Jeffrey R. Long[1,2,3]

Keywords: Metal–Organic Frameworks, Hydrogen Storage, π-Backbonding, Geometric Effects, Coordinatively Unsaturated Metal Sites

Metal–organic frameworks have been studied for hydrogen storage materials because physisorption-driven hydrogen storage in porous adsorbents is believed to offer high cyclability and facile H_2 charging/discharging kinetics without heating.1) The synthetic designability of metal–organic frameworks has been thought to realize optimal properties, such as pore volume, pore geometry, and adsorption sites, to densify hydrogen at less extreme conditions than the current physical storage systems (compression at 700 bar or liquification at 20 K) to store H_2 safely. However, hydrogen storage at ambient temperature or even sub-ambient temperature (as low as –50 °C) is challenging because typical hydrogen–framework interaction relies on weak van der Waals interaction with hydrogen adsorption enthalpy in a range of −4 to −7 kJ/mol.

Herein, we report a series of metal–organic frameworks with open Cu^I sites that exhibit π-backbonding to an H_2 molecule to realize H_2 binding stronger than those of typical adsorbents. We demonstrate that π-basicity of open Cu^I sites is systematically tuned with geometry (specifically, pyramidality) of open trigonal Cu^I sites by changing the identity of an interstitial metal for a tripodal scaffold for the Cu^I sites. Importantly, we realize the second-ever metal–organic framework showing optimal H_2 binding strength for ambient temperature H_2 storage with the least pyramidal Cu^I sites among the series.



1) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782–835.

Synthesis and structural control of one-dimensional molybdenum oxide chains

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*, [2] *Faculty of Engineering, Kanagawa University*, [3]*Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology*) ○Takuo Minato,[1] Misato Miyamoto,[1] Satoshi Ishikawa,[2] Norihito Hiyoshi,[3] Masahiro Sadakane[1]

Keywords: Molybdenum Oxides; One-dimensional Structures

Molybdenum oxides are known to exhibit diverse crystal structures and morphologies.[1] For example, α-MoO_3, a two-dimensional sheet-like structure, has been utilized as a catalyst material and electrode material through intercalation. However, conventional α-MoO_3 faces several issues, such as a small surface area and the absence of micropores, when employed in catalytic materials. In this study, one-dimensional chain-like structures, resembling slices of a single sheet of α-MoO_3, were successfully synthesized and crystallized (**1**). X-ray crystallographic analysis revealed that **1** was crystallized in the primitive monoclinic $P2_1/c$ with the short *a*-axis and was the bundle of unique one-dimensional MoO_3 subnanofibers along the *a*-axis (Figure 1). Each fiber was composed of two edge-sharing octahedral $\{MoO_6\}$ zigzag chains connected by corner-sharing Mo–O–Mo bonds, which was essentially the same structure obtained by cutting one layer of two-dimensional α-MoO_3 sheet into 8.0 Å wide strips along [001] direction. Importantly, O atoms of *N*,*N*-dimethylformamide molecules were coordinated to Mo atoms to prevent fibers from further condensation into two-dimensional structures. Inspired by this unique structure of **1**, α-MoO_3 was synthesized by calcination of **1** at different temperatures. Consequently, structural control of the material through calcination was possible, resulting in the preparation of unique oxidation catalysts with properties not present in conventional α-MoO_3.

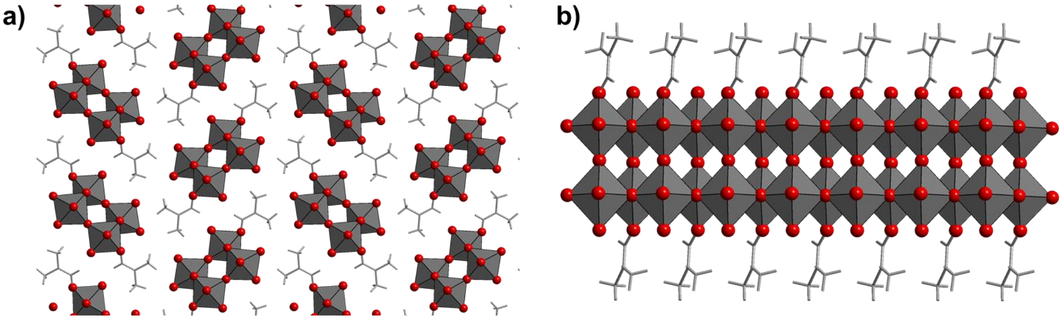


Figure 1. a) Crystal structure of **1** along *a*-axis and b) fiber structure of **1**.

1) I. A. de Castro, R. S. Datta, J. Z. Ou, A. Castellanos-Gomez, S. Sriram, T. Daeneke, K. Kalantar-zadeh, *Chem. Mater.* **2017**, *29*, 1701619.

Pressure control of polarization relaxation in Preyssler-type polyoxometalate

([1]*Grad. Sch. Adv. Sci. Eng. Hiroshima Univ.*, [2]*NIT, Ube college*, [3]*SKCM*[2], [4]*CResCent*, [5]*IAMR, Hiroshima Univ.*, [6]*PRESTO JST*) ○Hidetoshi Kurihara,[1] Masaru Fujibayashi,[2] Chisato Kato,[1] Goulven Cosquer,[3,4] Katsuya Inoue,[1,3,4,5] Sadafumi Nishihara[1,4,5,6]

Keywords: Polyoxometalate; Ferroelectric; Dielectric; Single-molecule electret; Pressure

Since long-range ordering of dipole interactions is required for ferroelectricity to develop, it was thought to be impossible to develop ferroelectricity in a single molecule. Against this background, our laboratory has found out a "single-molecule electret," a molecule that behaves like a ferroelectric material within a single molecule.[1,2] This molecule, a Preyssler-type polyoxometalate(POM) $[M^{n+}\subset P_5W_{30}O_{110}]^{(15-n)-}$, encapsulates a metal ion in its cage-like molecular framework. There are two energetically stable ionic sites in that molecule, and an energy barrier (U_E) exists between the stable sites (Fig. 1). When the energy barrier is larger than the thermal energy, the metal ion is localized to one of the stable sites and exhibit molecular polarization according to the position of the metal ion. When an external electric field is applied to a single molecule dielectric at that temperature, the position of the ions is reversed, and it exhibits polarization hysteresis characteristic of ferroelectrics.

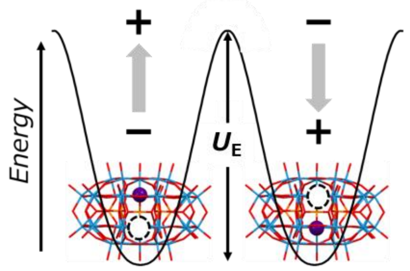


Fig. 1 Double-well type potential structure of the dipole moment in a **POM** molecule.

On the other hand, when the thermal energy is higher than the energy barrier, the molecular polarization relaxes gradually. Therefore, if the value of the energy barrier can be manipulated, it is possible to perform charging and discharging like a secondary battery using only a single-molecule electret. I chose pressurization as the method to change the value of the energy barrier. First, an external electric field was applied to the single-molecule dielectric in the high-temperature region to induce spontaneous polarization, and then the temperature was lowered to the temperature at which the polarization did not relax. I then observed that when hydrostatic pressure was applied to the single-molecule electret, it discharged. I will report on the details of the charging and discharging mechanism of the single-molecule electret on the day of the presentation.

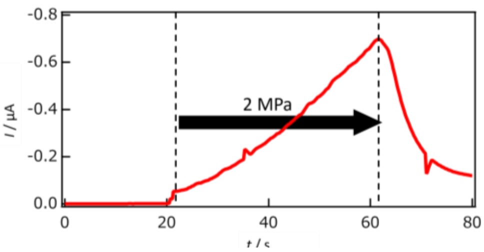


Fig. 2 Discharge current by applying constant pressure to the POM pellet.

1)C. Kato, S. Nishihara, *et. al., Angew. Chem. Int. Ed.*, 2019, 57,13429-13432.

2) S. Nishihara, *Nat. Nanotechnol.*, 15, 966-967, 2022

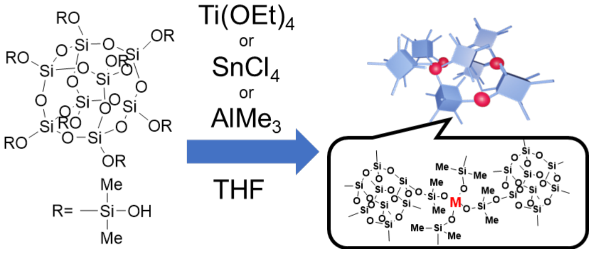
Synthesis of Porous Catalysts by Condensation Reaction of Silanol-modified Cage Siloxanes with Metal Species

([1] *School of Advanced Science and Engineering, Waseda University*, [2] *Kagami Memorial Research Institute for Materials Science and Technology, Waseda University*)
○Takuya Hikino,[1] Takamichi Matsuno,[1,2] Kazuyuki Kuroda,[1,2] Atsushi Shimojima[1,2]

Keywords: Cage Siloxane; Porous Catalysts

Silica-based porous catalysts, represented by zeolites, play a crucial role in various industrial applications.[1] Understanding their catalytic functions by controlling the environments of the active sites is an important issue. However, it is difficult to control the active sites by conventional synthesis methods including hydrothermal and aqueous sol–gel methods. We have focused on the condensation reaction between silanol groups and metal sources under non-aqueous conditions. In this study, siloxane-based porous catalysts were synthesized by the condensation reaction of silanol-modified cage siloxanes with metal species (Ti, Sn, and Al), and their catalytic activities were investigated.

Cage siloxane with dimethylsilanol groups was reacted with each of the three different metal species at the stoichiometric ratio in anhydrous THF solvent (Scheme 1). The first one is titanium ethoxide to form Si–O–Ti bonds.[2] The formation of the Si–O–Ti bonds and the isolation of TiO_4 units were confirmed by FT-IR and XAFS analysis. The second one is tin tetrachloride to form Si–O–Sn bonds. Because the Sn–Cl groups partially remained, the obtained compounds were treated with water or phosphate buffer to hydrolyze the Sn–Cl groups into Sn–OH groups. The use of phosphate buffer was effective to avoid the formation of SnO_2 and UV–Vis spectra showed that the Sn environment was isolated, although the Sn content in the sample significantly decreased. The third one is trimethylaluminum to form Si–O–Al bonds in the presence of triethylamine. ^{27}Al MAS NMR analysis confirmed that the aluminum was four-coordinated. N_2 adsorption/desorption analysis showed that all the samples had both micropores and mesopores. The catalytic reaction was investigated using the Ti-containing catalyst. The cyclohexene epoxidation reaction proceeded with a high selectivity. Thus, the reactions between silanol-modified cage siloxanes and metal precursors in the non-aqueous solvent resulted in the formation of porous networks via the Si–O–M bonds. Additionally, the isolation of the metal sites in the frameworks was achieved. This simple building block approach to preparing porous materials will contribute to the production of metalosiloxane-based catalysts with controlled metal environments.



Scheme 1 Synthesis of the metalosiloxane catalyst

1) M. E. Davis, *Nature* **2002**, *417*, 813. 2) T. Hikino *et al.*, *Chem. Lett.* **2021**, *50*, 1643.

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18日(月) 15:55 ~ 17:15 A1444(14号館 [4階] 1444)

[A1444-1vn] 07. 無機化学

座長：宮川 雅矢、山本 瑛祐

日本語

15:55 ~ 16:15

[A1444-1vn-01]

分子シミュレーションによる有機モンモリロナイトにおける吸着サイトの決定因子の探究

○宮川 雅矢[1]、濤崎 啓吾[1]、高羽 洋充[1] (1. 工学院大学)

英語

16:15 ~ 16:35

[A1444-1vn-02]

Atomic cation vacancy engineering of NiFe-LDH nanosheets towards oxygen evolution reaction

○Huanran Li[1,2], Renzhi Ma[1,2], Yoshiyuki Sugahara[2], Takayoshi Sasaki[1] (1. NIMS, 2. Waseda Univ.)

英語

16:35 ~ 16:55

[A1444-1vn-03]

Synthesis of CoNiFe hydroxide nanosheets and composites as bifunctional oxygen electrocatalysts for Zn-air batteries

○Zihan Zhang[1,2], Renzhi Ma[1,2], Yoshiyuki Sugahara[2], Takayoshi Sasaki[1] (1. NIMS, 2. Waseda Univ.)

日本語

16:55 ~ 17:15

[A1444-1vn-04]

界面活性剤結晶を活用したアモルファスナノシートの精密合成

○山本 瑛祐[1]、栗本 大輝[1]、伊東 健太郎[1]、小林 亮[1]、長田 実[1] (1. 名大)

分子シミュレーションによる有機モンモリロナイトにおける吸着サイトの決定因子の探究

（工学院大先進工[1]）○宮川 雅矢[1]・濤崎 啓吾[1]・高羽 洋充[1]

Key factor to determine adsorption site in organomontmorillonite investigated by molecular simulation

([1]*School of Advanced Engineering, Kogakuin University*) ○Masaya Miyagawa,[1] Keigo Tozaki[1], Hiromitsu Takaba[2]

Layer surface and center of interlayer are the possible adsorption sites in layered materials, and effect of organocation should not be negligible. In the present study, we investigated how the adsorption site is determined in water-immersed organomontmorillonite by molecular simulation. When the interlayer is modified with tetramethylammonium ion, the center of the interlayer is too narrow, resulting in the surface adsorption of benzene. In contrast, the center is applicable in the case of hexadecyltrimethylammonium ion, where trichlorophenol is adsorbed. However, both the surface and center play a role as the adsorption site in the benzene adsorption. Therefore, it was found that the formation of the center is dependent on the size of the organocation and the interaction between the adsorbate and layer surface significantly affects the adsorption site.

Keywords：Molecular dynamics method; Organoclay; Montmorillonite; Surface adsorption

層状化合物が示す吸着特性は層間に導入する有機カチオンの影響を強く受ける。しかし、層表面と層間中心部のどちらが吸着サイトとして機能するかを実験で決定することは難しく、有機カチオン・吸着質の組み合わせにも依存する。我々は分子シミュレーションを用いて有機粘土の層間構造を探究しており 1)、水中で層間が膨潤し有機カチオンの配向も変化することを見出している。本研究ではさまざまな含水有機モンモリロナイトについて、有機カチオン・吸着質が吸着サイトに与える影響を調べた。

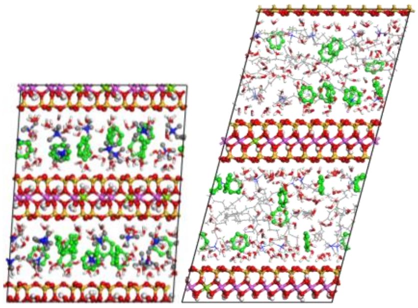


Fig. 1. Benzene-containing montmorillonite modified with TMA (left) and HDTMA (right).

Tetramethylammonium ion を含む系では含水時の層間の高さは 5.4 Å と狭いため、ベンゼンは単分子層で表面に吸着する（Fig. 1 左）。一方でアルキル鎖が長い hexadecyltrimethylammonium ion（HDTMA）を含む系では、層間の高さは 13.3 Å と広いため中心部も明確に形成され水は層間全体に分布する。このとき、トリクロロフェノール（TCP）は中心部のみに、ベンゼンは表面と中心部の両方に分布している（Fig. 1 右）。これらのことから、中心部の形成は有機カチオンのサイズで決まり、ベンゼンと層表面の van der Waals 相互作用は TCP よりも強いと考えられる。また、TCP の拡散係数は 3.23×10^{-10} m^2 s^{-1} と HDTMA（1.11×10^{-10} m^2 s^{-1}）に近いことから、HDTMA が中心部で形成するナノ細孔に強くトラップされることが明らかとなった。

1) M. Miyagawa, F. Hirosawa, H. Takaba, Langmuir, **2022**, *38*, 3514.

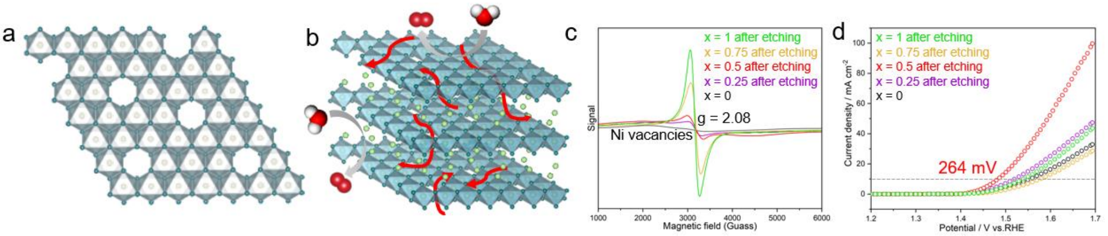
Atomic cation vacancy engineering of NiFe-LDH nanosheets towards oxygen evolution reaction

([1]*National Institute for Materials Science*, [2]*Graduate School of Advanced Science and Engineering, Waseda University*) ○ Huanran Li,[1,2] Renzhi Ma,[1,2] Yoshiyuki Sugahara,[2] Takayoshi Sasaki[1]

Keywords: Layered double hydroxide; Chemical etching; Vacancy engineering; Oxygen evolution reaction

The increasingly challenging global energy crisis and environmental issues have inspired intensive research interests in designing cost-effective and highly active electrocatalysts. It has been reported that layered double hydroxides (LDHs) based on transition metal elements such as Ni and Fe exhibit high activity in oxygen evolution reaction (OER). To further enhance the intrinsic activity and catalytic performance, several effective strategies such as morphological design[1], compositional tuning[2], and heterostructure construction[3] have been explored. Recently, vacancy engineering has emerged as a promising approach to improve the electrocatalytic activity of transition-metal-based LDHs.

In this study, $Ni_{5-x}Zn_xFe_{2.5}$-LDHs with a designated amount of Zn (x = 0, 0.25, 0.5, 0.75, 1.0) were first synthesized by a homogeneous precipitation method in the presence of hexamethylenetetramine (HMT, $C_6H_{12}N_4$) and anthraquinone-2-sulfonate (AQS, $C_{14}H_7O_5S^-$). Metal cation vacancies were created by chemical etching of Zn dopants from the LDH precursors treated in a NaOH solution. After etching, vacancy-containing monolayer nanosheets of Ni^{2+}-Fe^{3+}-LDHs (Fig. a) were produced by exfoliation in formamide. Then, the nanosheets were flocculated with carbonate ions to obtain fluffy powdered products (Fig. b). In the electron paramagnetic resonance (EPR) spectra (Fig. c), the signal became more prominent for the samples with a higher concentration of Zn, indicating that more vacancies were produced after the chemical removal of Zn.[4] The vacancy concentration may impart a significant effect on OER activity. As shown in Fig. d, the sample with a suitable concentration of vacancies, e.g., x = 0.5, exhibits an ultralow overpotential of 264 mV at 10 mA·cm^{-2} and excellent long-term stability.



1) X. Liu, *Adv. Mater.* **2012,** *24*, 2148. 2) W. Ma, *ACS Nano* **2015**, *9*, 1977. 3) P. Xiong, *Nano Lett.* **2019**, *19*, 4518. 4) Q. Xie, *Nano Res.* **2018**, *11*, 4524.

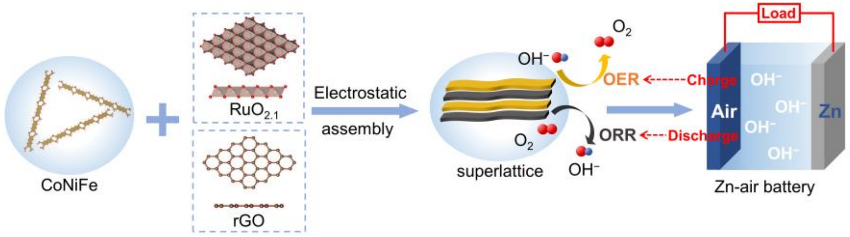
Synthesis of CoNiFe hydroxide nanosheets and composites as bifunctional oxygen electrocatalysts for Zn-air batteries

([1]*National Institute for Materials Science*, [2]*Graduate School of Advanced Science and Engineering, Waseda University*) ○Zihan Zhang,[1,2] Renzhi Ma,[1,2] Yoshiyuki Sugahara,[2] Takayoshi Sasaki[1]

Keywords: Layered transition metal hydroxide; Nanosheets; Superlattice structure; Electrocatalysts; Zn-air batteries

Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are the two core processes of rechargeable Zn-air batteries, in which highly effective and stable bifunctional electrocatalysts are required as the air electrode. In this aspect, layered transition metal hydroxides have been explored as promising low-cost electrocatalysts for energy storage and conversion. The laminar structure may provide abundant active sites and ion channels, thus promoting electrochemical reactions and enhancing catalytic performance. Typically, exfoliation into monolayer two-dimensional (2D) nanosheets can further increase the specific surface area. As an advantage, hetero-assembly of exfoliated hydroxide nanosheets with other counterpart nanomaterials as building blocks into superlattice-like composites could realize synergistic effects between different components for enhanced catalytic activity.[1-3]

Herein, layered CoNiFe hydroxides with hollow conical morphology were synthesized. The ternary composition and unique conical feature offer an ideal platform to optimize electronic structure, to enhance the electrical conductivity and improve the catalytic performance. Generally, a high Co content in layered hydroxides guarantees a high ORR performance. At the same time, doping of small amounts of Ni and Fe into the Co-based hydroxides is utilized as an effective strategy to enhance the OER performance. Furthermore, the CoNiFe hydroxide nanocones were exfoliated into 2D nanosheets and then hetero-assembled with other electrically conductive nanosheets, such as $RuO_{2.1}$ nanosheets and reduced graphene oxide (rGO), to form a superlattice-like structure. The obtained CoNiFe-$RuO_{2.1}$ and CoNiFe-rGO superlattice composites demonstrated smaller overpotential of OER and four-electron dominated pathway of ORR, superior to CoNiFe hydroxides alone, promising for uses as high-performance air electrode in Zn-air batteries.



1) X. Lu *et al.*, *ACS Appl. Mater. Inter.* **2020**, *12*, 33083. 2) P. Xiong *et al.*, *Nano Lett.* **2019**, *19*, 4518. 3) W. Ma *et al.*, *ACS Nano* **2015**, *9*, 1977.

界面活性剤結晶を活用したアモルファスナノシートの精密合成

（名大未来研[1]）○山本　瑛祐[1]・栗本 大輝[1]・伊東 健太郎[1]・小林 亮[1]・長田 実[1]

Tailored synthesis of amorphous nanosheets using surfactant crystals

([1]*Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University*) ○Eisuke Yamamoto[1], Daiki Kurimoto[1], Ito Kentaro[1], Makoto Kobayashi[1], Minoru Osada[1]

2D amorphous nanosheets have received increasing attention due to their unique properties that are distinct from those of 2D crystalline nanosheets.1) Nevertheless, synthesis of amorphous 2D nanosheets tends to be itemized and restricted to rather thick nanosheets, despite the existence of various generalized methods for designing molecularly thin crystalline nanosheet compositions. The surfactant templating method should be potentially effective technique for obtaining molecularly thin amorphous nanosheets;2) however, the conventional surfactant templating methods have difficulty on the synthesis of molecularly thin amorphous 2D nanosheets with various compositions. In this study, we present a sold-state surfactant templating strategy that allowed tailored synthesis of 10 distinct 2D amorphous metal oxides/oxyhydroxides with various metal ions (Al^{3+}, Sc^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ga^{3+}, Rh^{3+} and In^{3+}) (Fig.1).

Keywords : Nanosheet, Amorphous, Oxide, Oxihydroxide

アモルファスナノシートは、その特異な特性や構造から、結晶性ナノシートとは異なる機能を発現することが知られている。1)しかし、これまでに多様な種類が合成されてきた結晶性ナノシートと比較すると、アモルファスナノシートの合成方法は未だに各論的な手法に限定されている。界面活性剤集合体を活用したナノシート合成方法は、様々な二次元化合物を合成する有効な手法として知られている。しかし、従来の界面活性剤を鋳型とする手法では、原子数子分厚みのナノシートが得られる組成は、限られていた。2)本研究では、固体相の界面活性剤結晶を活用することで、様々な組成のアモルファスナノシート合成する新しい手法を確立した。目的とする金属イオンを含む界面活性剤結晶をアンモニア蒸気で処理することで、層間で金属酸化物/オキシ水酸化物のクラスターを形成させた。さらに、得られた界面活性剤と酸化物/オキシ水酸化物の複合体をホルムアミドに浸漬し、加熱処理をすることで 10 種類のアモルファス酸化物/オキシ水酸化物ナノシートの合成に成功した(Fig.1)。

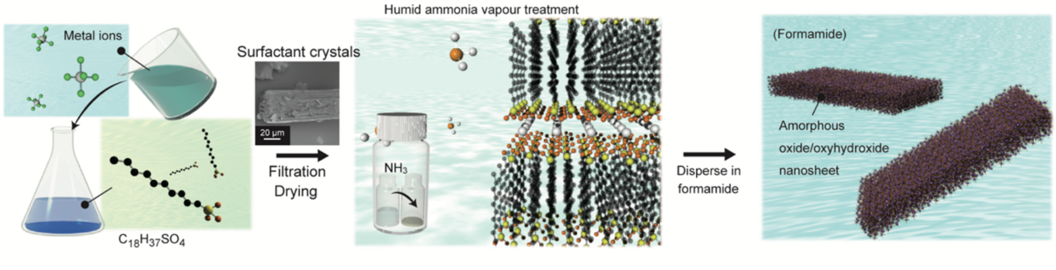


Fig. 1 Illustration of the synthesis process for molecularly thin amorphous 2D nanosheets.

1) C.-T. Toh *et al. Nature* 577, 199–203 (2020).　2) Z. Sun *et al. Nat. Commun.* 5, 4813 (2014).

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18日(月) 13:00 ~ 15:40 F1231(12号館 [3階] 1231)

[F1231-1pm] 09. 錯体化学・有機金属化学

座長：三澤（鈴木） 智世、竹澤 浩気

日本語
13:00 ~ 13:20
[F1231-1pm-01]
嵩高い配位子とヒドリドで保護された[Fe_{55}][Fe_6]イオン対の結晶構造決定と電子構造解析

〇田中 奏多[1]、大石 峻也[2]、川本 晃希[2]、高畑 遼[1]、志賀 拓也[3]、山添 誠司[4]、Zihan Zhang[5]、唯 美津木[2]、吉川 総一[4]、寺西 利治[1]、二瓶 雅之[3]、Karsten Meyer[5]、檜垣 達也[1]、大木 靖弘[1] (1. 京大化研、2. 名大院理・名大物質国際研、3. 筑波大院数物、4. 都立大理、5. Dept of Chem & Pharm, FAU Erlangen-Nürnberg.)

日本語
13:20 ~ 13:40
[F1231-1pm-02]
かさ高いCp配位子を有する[Mo_3S_4M] (M = Rh, Ir)クラスターの合成とC-Hボリル化反応への応用

〇伊豆 仁[1]、下山 さやか[1]、谷藤 一樹[1]、大木 靖弘[1] (1. 京大化研)

日本語
13:40 ~ 14:00
[F1231-1pm-03]
剛直なトリプチセン三座配位子を用いたヘテロ金属酸化物クラスターの精密合成

〇福井 智也[1,2]、伊藤 圭亮[1,2]、嘉藤 幹也[1,2]、福島 孝典[1,2] (1. 東工大化生研、2. 東工大物質理工)

英語
14:00 ~ 14:20
[F1231-1pm-04]
電子伝導性 を示す[Fe_4S_4]から構成される有機金属高分子の合成

〇門田 健太郎[1]、Carl Brozek[2] (1. 京都大学、2. オレゴン大学)

日本語
14:20 ~ 14:40
[F1231-1pm-05]
共有結合形成による金属錯体八面体表面の事後修飾

〇立石 友紀[1]、徳田 駿[1]、古川 修平[1] (1. 京都大学)

英語
14:40 ~ 15:00
[F1231-1pm-06]
光配位子置換反応による多核ルテニウム錯体の合成経路開拓

〇平原 将也[1]、本田 拓真[1]、平化 匠[1] (1. 大阪工業大学)

英語
15:00 ~ 15:20
[F1231-1pm-07]
低対称銀(I)カプセル錯体から成る多核銀(I)ナノビーズ高次構造体の階層的自己集合

○山田 慶彦[1]、田代 省平[1]、塩谷 光彦[1] (1. 東大院理)

🏷 英語

15:20 ~ 15:40

[F1231-1pm-08]

シアノ金属錯体からなる発光性有機無機ハイブリッドの相制御

○岩井 優大[1]、大谷 亮、大場 正昭 (1. 九州大学)

嵩高い配位子とヒドリドで保護された$[Fe_{55}][Fe_6]$イオン対の結晶構造決定と電子構造解析

（京大化研 [1]・名大院理・名大物質国際研 [2]・筑波大院数物 [3]・都立大理 [4]・Dept of Chem & Pharm, FAU Erlangen-Nürnberg [5]）○田中 奏多 [1]・大石 峻也 [2]・川本 晃希 [2]・高畑 遼 [1]・志賀 拓也 [3]・山添 誠司 [4]・Zihan Zhang [5]・唯 美津木 [2]・吉川 聡一 [4]・寺西 利治 [1]・二瓶 雅之 [3]・Karsten Meyer [5]・檜垣 達也 [1]・大木 靖弘 [1]

Crystal Structure Determination and Electronic Structural Analysis of a $[Fe_{55}][Fe_6]$ Ion Pair Protected by Bulky Ligands and Hydrides ([1]*Institute for Chemical Research, Kyoto Univ.*, [2]*Graduate School of Science and RCMS, Nagoya Univ.*, [3]*Dept of Chem., Univ. of Tsukuba*, [4]*Graduate School of Science, Tokyo Metropolitan Univ.*, [5]*Dept of Chem & Pharm, FAU Erlangen-Nürnberg*) ○Kanata Tanaka,[1] Shunya Oishi,[2] Koki Kawamoto,[2] Ryo Takahata,[1] Takuya Shiga,[3] Seiji Yamazoe,[4] Zihan Zhang,[5] Mizuki Tada,[2] Soichi Kikkawa,[4] Toshiharu Teranishi,[1] Masayuki Nihei,[3] Karsten Meyer,[5] Tatsuya Higaki,[1] Yasuhiro Ohki[1]

Iron clusters composed of multiple iron atoms show specific physical properties and reactivity derived from their unique geometric and electronic structures.[1] However, synthesis of Fe clusters larger than 1 nm has remained elusive. Herein, we synthesized a nanosized Fe cluster as an ion pair, $[Fe_{55}H_x(P^tBu_3)_{12}][Fe_6H_8\{N(SiMe_3)_2\}_6]$ ($x \sim 46$; $[Fe_{55}][Fe_6]$ in short) by using bulky ligands and analyzed geometric and electronic structures.

$[Fe_{55}][Fe_6]$ was synthesized from the reaction of $Fe\{N(SiMe_3)_2\}_2$ with pinacolborane in the presence of bulky P^tBu_3. X-ray crystallographic analysis revealed that $[Fe_{55}]$ has an icosahedral core protected by twelve P^tBu_3, which are located on twelve vertices of the icosahedron. The octahedral $[Fe_6]$ core is protected by six silylamides (i.e., $-N(SiMe_3)_2$), which are located on each vertex of the octahedron. Electrospray-ionization mass spectrometry (ESI-MS) analysis confirmed the chemical formulae of $[Fe_{55}][Fe_6]$. X-ray absorption fine structure (XAFS) analysis revealed the average oxidation state of Fe in $[Fe_{55}][Fe_6]$. Further characterization was performed on $[Fe_{55}][Fe_6]$ including spectroscopic analyses as well as electrochemical studies.

Keywords : Metal Clusters; Crystal Structure; Hydride; XAFS

複数の鉄原子から構成される鉄クラスターは、特異的な幾何構造や電子構造に由来する物性や反応性を示すことが知られている。[1] しかし、先行研究にて報告されているのは 1 nm よりも小さな鉄クラスターのみである。本研究では、配位子の嵩高さを利用することで 1 nm よりも大きな鉄クラスター$[Fe_{55}H_x(P^tBu_3)_{12}][Fe_6H_8\{N(SiMe_3)_2\}_6]$ ($x \sim 46$; $[Fe_{55}][Fe_6]$)をイオン対として合成し、幾何構造及び電子構造について解析を行った。

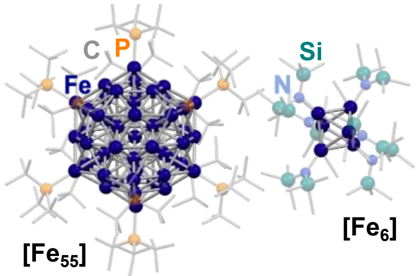


Fig.1 Crystal structure of $[Fe_{55}][Fe_6]$.

嵩高い P^tBu_3 存在下、原料の鉄アミド錯体 $Fe\{N(SiMe_3)_2\}_2$ とピナコールボランを反応させることで、$[Fe_{55}][Fe_6]$を得た。単結晶 X 線構造解析（SCXRD）により、$[Fe_{55}]$は正二十面体型コアを持ち、各頂点それぞれに P^tBu_3 が配位していること、$[Fe_6]$は正八面体型コアを持ち、各頂点それぞれにシリルアミド基（*i.e.* $-N(SiMe_3)_2$）が配位していることを確認した（**Fig. 1**）。エレクトロスプレーイオン化質量分析(ESI-MS)から、ヒドリドも含む化学組成を決定した。また、X 線吸収微細構造（XAFS）解析により、 $[Fe_{55}][Fe_6]$内の鉄の平均酸化状態を確認した。さらに、分光学的測定や電気化学的測定により$[Fe_{55}][Fe_6]$の性質を評価した。

1) Ohki, Y. *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 5596.

かさ高い Cp 配位子を有する$[\mathrm{Mo_3S_4M}]$ (M = Rh, Ir)クラスターの合成と C-H ボリル化反応への応用

（京大化研 [1]）○伊豆 仁 [1]・下山 さやか [1]・谷藤 一樹 [1]・大木 靖弘 [1]

Synthesis of $[\mathrm{Mo_3S_4M}]$ (M = Rh, Ir) Clusters Bearing Bulky Cyclopentadienyl (Cp) ligands and Their Application in C-H Borylation Reactions

([1]*Institute for Chemical Research, Kyoto University*) ○Hitoshi Izu,[1] Sayaka Shimoyama,[1] Kazuki Tanifuji,[1] Yasuhiro Ohki[1]

Selective transformations of hydrocarbons without functional groups are highly desirable to expand their utility other than solvents or fuels. One promising reaction is the C-H borylation reaction, but this reaction remains limited to laboratory settings because the catalytic turnovers are not sufficiently high under heating conditions. In this study, we designed and synthesized cubic metal-sulfur clusters $[\mathrm{Cp^{SiEt3}}_3\mathrm{Mo_3S_4M}]$ ($\mathrm{Cp^{SiEt3}} = \mathrm{C_5Me_4SiEt_3}$, M = Rh or Ir) having bulky Cp ligands to enhance the heat resistance of molecular catalysts and prevent their thermal decomposition. Our cubic clusters have the following two advantages: (i) high thermal stability due to robust M-S/Mo-S bonds and Mo-Cp bonds, and (ii) steric control to suppress dimerization that represents the major deactivation pathway. By taking advantage of these features, the synthesized clusters catalyzed the C-H borylation of arenes and demonstrated high thermal stability at 150 °C for 48 hours.

Keywords : Metal-sulfur cluster; C-H borylation reaction; cubic cluster

溶媒や燃料以外の用途に乏しい炭化水素に官能基を選択的に付与する反応は、高難度で挑戦的な分子変換反応である。特に有望な反応の 1 つとして Rh 錯体や Ir 錯体を触媒とする C-H ボリル化反応が挙げられるが、150 ºC 程度で行われる加熱条件下では分子触媒（有機金属錯体）が分解もしくは失活しやすいため反応回転数が伸びない問題がある。そこで本研究では、150 ºC 程度の反応条件で長時間分解もしくは失活しない新触媒として、かさ高い Cp 配位子を有し Rh や Ir を反応点とする金属-硫黄クラスター錯体$[\mathrm{Cp^{SiEt3}}_3\mathrm{Mo_3S_4M}]$ ($\mathrm{Cp^{SiEt3}} = \mathrm{C_5Me_4SiEt_3}$, M = Rh or Ir)を合成した(Figure)。安定な立方体構造を特徴とする$[\mathrm{Cp^{SiEt3}}_3\mathrm{Mo_3S_4M}]$は、(i) 強固な金属-硫黄結合で構成され耐熱性が高いこと、(ii) 配位子の立体制御によって主な失活過程である分子触媒の二量化を抑制できること、の 2 つの優れた特徴がある。これらの特徴を活かすことで、本研究のクラスター錯体が芳香族C-Hボリル化反応を触媒することと、150 ºC で長時間分解しないことを確認した。

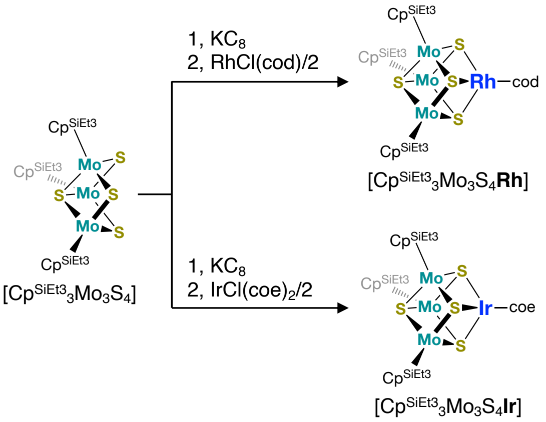


Figure Synthesis of $[\mathrm{Cp^{SiEt3}}_3\mathrm{Mo_3S_4M}]$ (M = Rh, Ir).

剛直なトリプチセン三座配位子を用いたヘテロ金属酸化物クラスターの精密合成

（東工大化生研 [1]・東工大物質理工 [2]）○福井 智也 [1,2]・伊藤 圭亮 [1,2]・嘉藤 幹也 [1,2]・福島 孝典 [1,2]

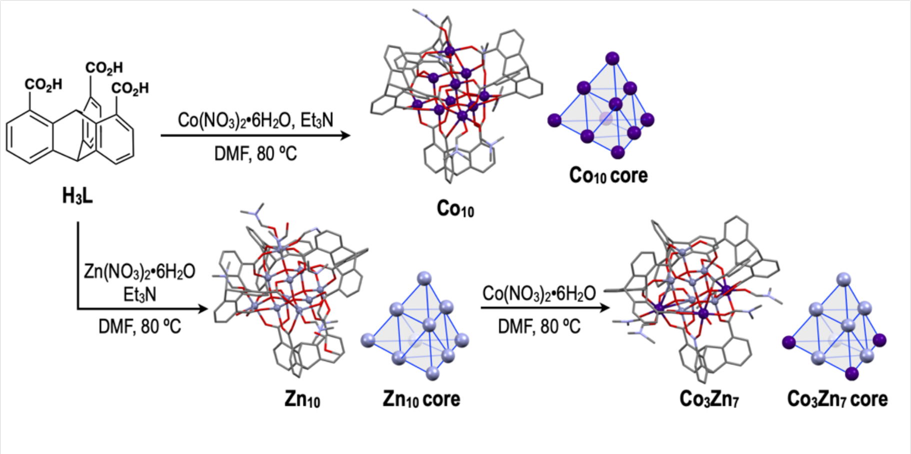
Precision Synthesis of Hetero-Multinuclear Metal-oxo Clusters Using Rigid Tridentate Triptycene Ligands

([1]*Lab. Chem. Life Sci.*, *Tokyo Tech.*, [2]*Sch. Mater. and Chem. Tech.*, *Tokyo Tech.*) ○Tomoya Fukui,[1,2] Keisuke Ito,[1,2] Mikya Kato,[1,2] Takanori Fukushima[1,2]

We have recently reported the selective construction of a decanuclear zinc-oxo cluster by the complexation of 1,8,13-tricarboxytriptycene with zinc acetate dihydrate1). In the present work, we investigated the synthesis of hetero-metal-oxo clusters through metal exchange reactions of the decanuclear zinc-oxo cluster with cobalt ions. When the zinc-oxo cluster was allowed to react with cobalt nitrate hexahydrate in solution, regioselective metal-ion substitution of zinc with cobalt took place, giving a new hetero-metal-oxo cluster, which retains the number and position of the metal ions from the original cluster. Here we report details of the metal-exchange reaction, as well as the characterization and properties of the resulting hetero-metal-oxo clusters.

Keywords : Polynuclear complexes; Multidentate ligands; Triptycene; Hetero-Multinuclear Metal-oxo cluster; Cobalt oxide

異種金属イオンを含むヘテロ金属酸化物クラスターにおいては、異種金属イオン間の相互作用や相乗効果に由来する機能の発現が期待されている。最近、我々は 1,8,13-トリカルボキシトリプチセンと酢酸亜鉛の錯形成により、四面体状 10 核亜鉛酸化物クラスターが選択的に形成されることを報告した 1)。今回、10 核亜鉛酸化物クラスターと硝酸コバルト六水和物を反応させると、位置選択的な金属イオンの置換が進行し、異種金属イオンの位置と数が定まったヘテロ金属酸化物クラスターが得られることを見いだした。本発表では、ヘテロ金属酸化物クラスターの合成と構造について発表する。



1) M. Kato, T. Fukui, H. Sato, Y. Shoji, T. Fukushima, *Inorg. Chem.* **2022**, *61*, 3649.

Synthesis of electrically conductive [Fe_4S_4]-based organometallic polymers

([1]*Graduate School of Science, Kyoto University*, [2]*Department of Chemistry and Biochemistry, University of Oregon*) ○Kentaro Kadota,[1] Carl K. Brozek[2]

Keywords: Electronic conduction; Coordination Polymers; N-heterocyclic carbene; Iron-sulfur clusters

Tailoring the molecular building units of hybrid organic-inorganic materials enables precise control over the electronic properties. Design of electrically conductive coordination materials, e.g. coordination polymers (CPs), has been limited to single-metal nodes. This is because the metal–oxo clusters present in the majority of CPs are not suitable for electrical conduction due to the localized electron orbitals. The development of metal-cluster nodes with charge-delocalized bonds would expand the structural and electrochemical tunability of conductive CPs. Whereas the cuboidal [Fe_4S_4] cluster is a ubiquitous cofactor for electron transport in biological systems, the limited electrically conductive materials employ the [Fe_4S_4] cluster as a building unit due to the lack of suitable bridging linkers.[1]

In this work, we employed ditopic *N*-heterocyclic carbene (NHC) linkers to bridge the [Fe_4S_4] clusters through charge-delocalized Fe–C bonds to enhance electronic communication between the clusters. [$Fe_4S_4Cl_2$(ditopic-NHC)] (**1**) was synthesized from the preformed discrete [Fe_4S_4] cluster and *in situ* formed NHC linkers (Figure 1). Linear sweep voltammetry of **1** exhibited a high electrical conductivity of 1 mS cm^{-1} at 25 °C under Ar, surpassing the conductivity of related analogues consisting of less charge-delocalized Fe–S bonds. We comprehensively studied the amorphous structure of **1** by total X-ray scattering and FT-IR and the bonding character by DFT calculations.[2]

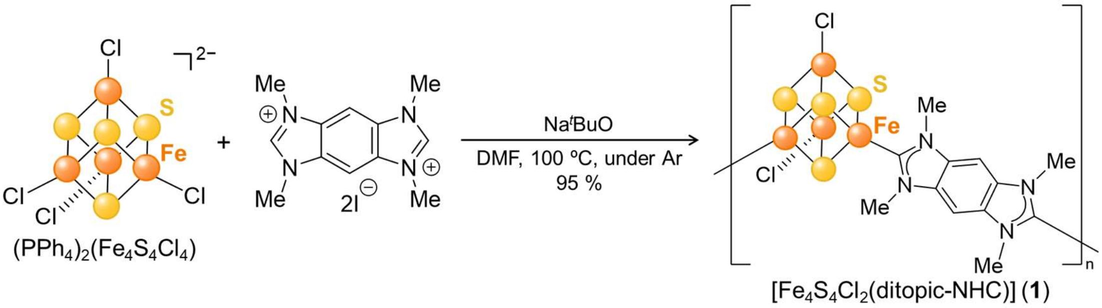


Figure 1. Schematic illustration of formation of **1** synthesized from the preformed [Fe_4S_4] cluster and *in situ* formed NHC linker.

1) N. E. Horwitz, J. Xie, A. S. Filatov, R. J. Papoular, W. E. Shepard, D. Z. Zee, M. P. Grahn, C. Gilder, J. S. Anderson, *J. Am. Chem. Soc.* **2019**, *141*, 3940. 2) K. Kadota, T. Chen, E. L. Gormley, C. H. Hendon, M. Dincă, C. K. Brozek, *Chem. Sci.* **2023**, *14*, 11410.

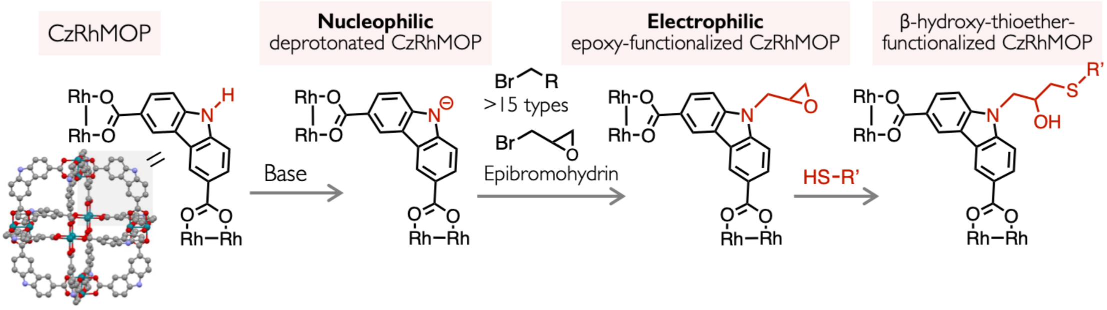
Covalent post-synthetic modification of the surface of metal–organic polyhedra

([1]*Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*) ○ Tomoki Tateishi,[1] Shun Tokuda,[1,2] Shuhei Furukawa[1,2]

Keywords: metal–organic polyhedra; post-synthetic modification

Metal–organic polyhedra (MOPs) are a class of molecules with an intrinsic void and are synthesized by connecting metal nodes with designed organic links.[1] In particular, MOPs based on Rh(II) paddlewheels (RhMOPs) are chemically robust because of the inertness of the coordination bonds at the equatorial sites. Thanks to the robustness, post-synthetic modification (PSM) of RhMOPs is available through coordination and covalent chemistry.[2,3] However, these studies aimed at applications only in the solid state such as amorphous solids or gels based on MOPs. Towards the application in solution particularly biological applications, the development of bioorthogonal reaction system is required. Here, we show a novel approach to modifying the surface of MOPs by sequential reactions.

We designed and synthesized an octahedral RhMOP with 9*H*-carbazole dicarboxylate, hereafter CzRhMOP.[4] CzRhMOP was dissolved in the DMA solution with NaH and further reacted with alkyl bromides, yielding the *N*-functionalized CzRhMOP. This result suggests that CzRhMOP is stable in the basic solution as a deprotonated form and becomes nucleophilic for substitution reactions with alkyl bromides. By changing the type of alkyl bromides, over 15 different *N*-functionalized CzRhMOPs were synthesized. The reaction of the deprotonated CzRhMOP with epibromohydrin produced epoxy-functionalized CzRhMOP. The epoxy group, a highly electrophilic functional group, allowed us to implement the sequential reaction with nucleophilic thiol molecules to produce β-hydroxy-thioether-functionalized CzRhMOPs. This study shows that covalent PSM can be used to realize the umpolung (polarity inversion) on the MOP surface, from the nucleophile to the electrophile. This capability to tune the properties of the MOP surface through covalent PSM will give a new application opportunity in bioconjugation chemistry.



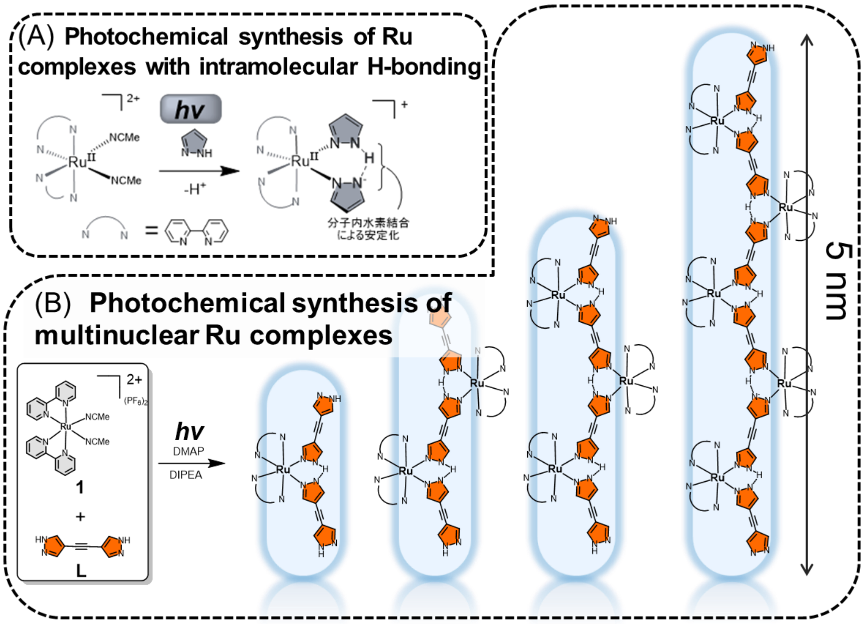
[1] T. Tateishi, *et al. Coord. Chem. Rev.* **2022**, *467*, 214612. [2] A. Carne-Sanchez, *et al. J. Am. Chem. Soc.* **2019**, *141*, 4094. [3] A. Carne-Sanchez, *et al. Adv. Funct. Mater.* **2023**, 2312166. [4] T. Tateishi, *et al. in preparation.*

Photosubstitution: A New Strategy for the Synthesis of Multinuclear Metal Complexes

(*Department of Applied Chemistry, Osaka Institute of Technology*)
○Masanari Hirahara, Takuma Honda, Takumi Hirake

Keywords: Ruthenium; Photosubstitution; Multinuclear Complexes; Photochemistry; Hydrogen Bonding

Photosubstitution of ruthenium complexes have been reported since 1970s and extensively studied for their numerous applications.[1] We reported that intramolecular hydrogen bonding is a key factor controlling the photosubstitution reaction.[2] The ruthenium pyrazole-pyrazolate complex with intramolecular hydrogen bonding displayed unprecedentedly high photostability under visible light irradiation. From this finding, we recently reported photochemical synthesis of ruthenium complex bearing pyrazole and pyrazolate ligands.[3] The photochemically labile pyrazole ligand displayed stepwise photosubstitution reactions as shown in Figure 1A. In this study, we report the photochemical synthesis of multinuclear ruthenium complexes by using pyrazole-based bridging ligands (Figure 1B). Mono-, di-, tri-, and tetranuclear ruthenium complexes have been successfully synthesized and isolated. ESI spectra of the mono-, di-, tri- and tetranuclear complexes displayed peaks at 729.3, 649.9. 623.7, 610.6 m/z respectively.



1. S. Bonnet, *J. Am. Chem. Soc.*, 2023, **145**, 23397-23415.
2. M. Hirahara, H. Nakano, K. Uchida, R. Yamamoto and Y. Umemura, *Inorg. Chem.*, 2020, **59**, 11273-11286.
3. M. Hirahara and Y. Umemura, *Inorg. Chem.*, 2021, **60**, 13193-13199.

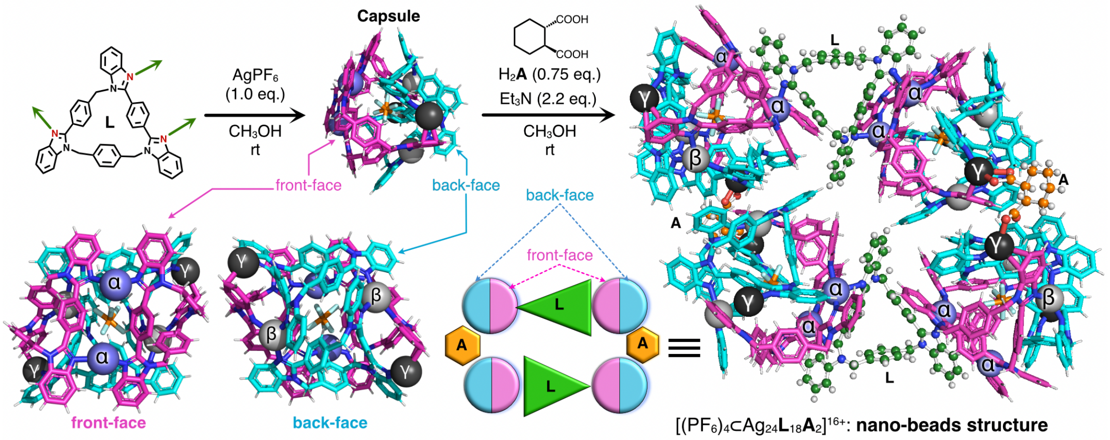
Hierarchical self-assembly of a multinuclear silver(I) nano-beads structure consisting of low-symmetric silver(I) capsule complexes

([1]*Graduate School of Science, The University of Tokyo*) ○Yoshihiko YAMADA,[1] Shohei TASHIRO,[1] Mitsuhiko SHIONOYA[1]

Keywords: Capsule; Supramolecular complex; Ag(I) ion; Multinuclear complex; Hierarchical self-assembly

Inspired by the hierarchical self-assembly of biomolecules, the construction of hierarchical assemblies of supramolecular complexes consisting of organic ligands and metal ions has attracted much interest. However, it remains difficult to construct discrete hierarchical structures with low symmetry, such as those found in biomolecules. We have previously reported that a capsule complex was formed when benzimidazole[3]arene (**L**)[1], a macrocyclic ligand with three nitrogen coordination sites arranged asymmetrically on the ring periphery, was reacted with $AgBF_4$ in an organic solvent. Three types of Ag(I) ion sites with different coordination geometries exist on the capsule surface. Therefore, the capsule has a bifacial structure consisting of a front-face with two Ag^{α} (two Ag–N coordinates) and a back face with two Ag^{β} (three Ag–N coordinates) and Ag^{γ} (an Ag–N coordinate with Ag–π). Here we report that four capsules self-assemble hierarchically to form a multinuclear nano-beads complex through circular cross-linking by two types of ligands coordinated to Ag(I) ions on the capsule surface.

Chiral (1*S*,2*S*)-1,2-cyclohexanedicarboxylic acid ($H_2\mathbf{A}$) and triethylamine were added to a methanol solution of the capsule consisting of **L** and $AgPF_6$ to obtain colorless block crystals. Single-crystal X-ray diffraction measurements showed that the product is an asymmetric tetracosanuclear silver(I) nano-beads complex $[(PF_6)_4\subset Ag_{24}\mathbf{L}_{18}\mathbf{A}_2]^{16+}$ with two free **L**s and two carboxylates **A** linking four capsule complexes in a circular shape. In this hierarchical structure, ligands **L** and **A** coordinated to Ag^{α} and Ag^{γ} on the capsule surface, respectively, due to the presence of Ag(I) with different coordination geometries.



1) S. Tashiro, T. Umeki, R. Kubota, M. Shionoya, *Chem. Sci.* **2018**, *9*, 7614–7619.

Phase controls of cyanido-based luminescent organic-inorganic hybrids

(*Graduate School of Science, Kyushu University*) ○Yuudai Iwai, Ryo Ohtani, Masaaki Ohba

Keywords: *Organic-inorganic hybrid, amorphous, cyanide*

Organic-inorganic hybrids (OIHs) are a class of materials that demonstrate high functionality based on metal ions and flexible organic moiety. In addition to the crystalline phase, amorphous states such as glass of OIHs have been recently explored for deriving hidden properties that cannot be realized in crystal phase. In this study, we synthesized new OIHs, $(C_1)_2[MN(CN)_4]$ (**C_1M**; C_1 = 3-methylpyridinium, M = Re, Mn), and investigated their phase transition behavior by means of thermal treatment and ball-milling.

C_1M were synthesized by thermal treatment of hydrated precursor obtained with the metathesis method from $(PPh_4)_2[MN(CN)_4]$ and $(C_1)[Ntf_2]$ (Ntf_2 = bis(trifluoromethyl sulfonyl)imide). Both compounds crystalized in $P2_1/c$ (Fig. 1). $[MN(CN)_4]$ units formed one-dimensional zigzag chains bridged with cyanidos along c-axis. **C_1Re** underwent its glass formation by ball-milling. The glassy samples recrystallized by hydration and/or heating. Uniquely, we found two distinct amorphous states of **C_1Re** with different magnitudes of entropy change in the glass-crystal transition by changing ball-milling time (Fig. 2). On the other hand, **C_1Mn** underwent its melting at 436.5 K, confirmed by TG-DTA and DSC measurements.

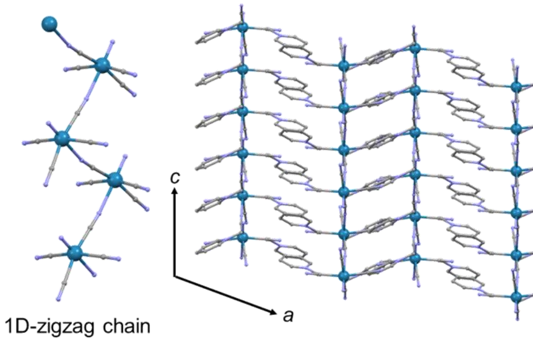


Fig. 1 Crystal structure of **C_1M**

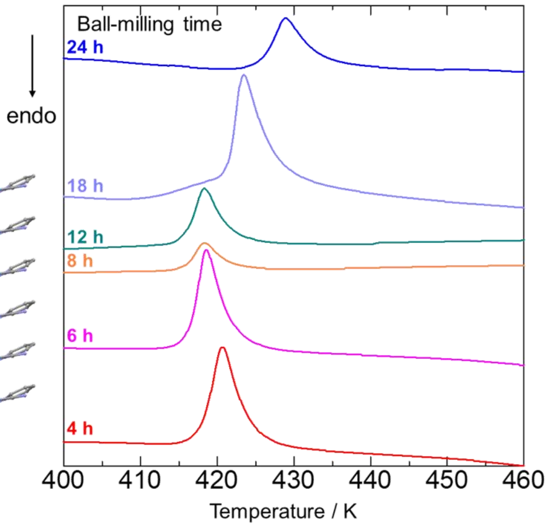


Fig. 2 DSC curves displaying crystallization of glassy **C_1Re**

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18日(月) 13:00 ~ 15:30 F1232(12号館 [3階] 1232)

[F1232-1pm] 09. 錯体化学・有機金属化学

座長：伊東 忍、桑田 繁樹

日本語
13:00 ~ 13:20
[F1232-1pm-01]
プロトン共役電子移動を指向したピリジン部位を有するコバルトセン誘導体の合成と反応性

〇大塚 滉喜[1]、荒芝 和也[1]、西林 仁昭[1] (1. 東京大学大学院工学系研究科)

日本語
13:20 ~ 13:40
[F1232-1pm-02]
Co錯体触媒を用いたカチオン添加による高効率CO_2電解還元反応

〇佐藤 俊介[1]、関澤 佳太[1]、白井 聡一[1]、坂本 直柔[1]、森川 健志[1] (1. 豊田中央研究所)

日本語
13:40 ~ 14:00
[F1232-1pm-03]
アルカリ光水素生成反応を高速駆動するCo-NHC錯体触媒の電子状態制御

〇河村 佳央理[1]、山内 幸正[1]、酒井 健[1] (1. 九大)

英語
14:00 ~ 14:20
[F1232-1pm-04]
コバルト二核錯体$(Co_2L_2)(NO_3)_2$(HL=3,5-bis(2′-pyridyl)pyrazole)の合成とその電気化学二酸化炭素還元特性

〇潘 雲逸[1]、堂ノ下 将希[2]、山内 美穂[1,2,3,4,5] (1. 九大院理、2. 九大先導研、3. 九大I2CNER、4. 九大K-NETs、5. 東北大AIMR)

14:20 ~ 14:30
休憩

英語
14:30 ~ 14:50
[F1232-1pm-05]
Co-NHC錯体触媒による水からの電気化学的水素生成に対する触媒回転頻度の精査

〇管 昌権[1]、山内 幸正[1]、酒井 健[1] (1. 九大)

日本語
14:50 ~ 15:10
[F1232-1pm-06]
Coポルフィリン触媒修飾TiO_2カソードとポリピリジルルテニウム光増感剤修飾TIO_2フォトアノードを用いた光電気化学的CO_2還元反応

〇合屋 祐輝[1]、Yan Xin[1]、酒井 健[1]、小澤 弘宜[1] (1. 九大)

日本語
15:10 ~ 15:30

[F1232-1pm-07]

アニオン添加で加速する二酸化炭素還元光触媒反応

○木原 咲穂[1]、下地 浩希[2]、前田 大光[3]、森本 樹[1] (1. 東京工科大学大学院、2. 東京工科大学、3. 立命館大学)

プロトン共役電子移動を指向したピリジン部位を有するコバルトセン誘導体の合成と反応性

（東大院工）○大塚 滉喜・荒芝 和也・西林 仁昭

Preparation and Reactivity of Cobaltocene Derivatives Bearing Pyridine Group toward Proton-Coupled Electron Transfer

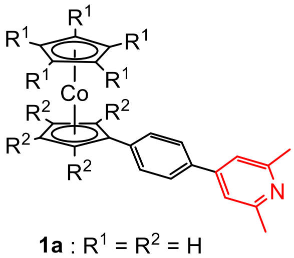
(*School of Engineering, The University of Tokyo*) ○Hiroki Otsuka, Kazuya Arashiba, Yoshiaki Nishibayashi

In the catalytic ammonia synthesis with transition metal complexes, it is revealed that proton-coupled electron transfer (PCET) plays a key role to promote the ammonia production. We previously reported highly efficient reaction systems using the combination of SmI_2 and H_2O as a PCET reagent.[1] In this context, we have designed and prepared novel cobaltocene derivatives bearing a pyridine group as new PCET reagents (**1**). The stoichiometric reaction of molybdenum-nitride complex with an excess amount of protonated **1b**, generated *in situ* from **1b** at -78 °C for 3 minutes, afforded ammonia in 70% yield. This result indicates that the protonated **1b** may work as a PCET reagent.

Keywords : Metallocene; Reduction Reaction; Proton-coupled Electron Transfer (PCET); Electrochemistry; Nitrogen Fixation

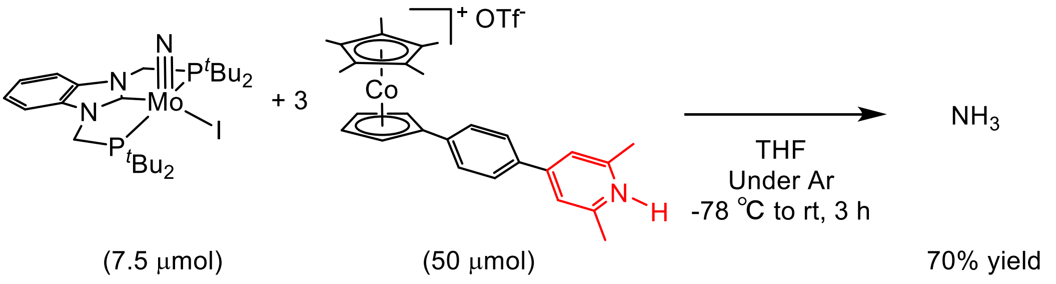
遷移金属錯体を利用した触媒的アンモニア生成反応において、プロトン共役電子移動 (PCET) が触媒反応を進行させる鍵反応の一つであることが明らかになっている。当研究室でもヨウ化サマリウム (SmI_2) と水との組み合わせが極めて有効であることを報告してきた[1]。

これらの研究背景を踏まえ、還元的 PCET 反応を促進する新たな試薬の開発を指向し、分子内にプロトン伝達部としてピリジン部位を導入した一連の新規コバルトセン誘導体 **1** の設計と合成を行った (Fig. 1)。モリブデン－ニトリド錯体からの化学量論的なアンモニア生成反応に適用したところ、期待通りに PCET 試薬として機能することが明らかとなった (Scheme 1)。講演ではこれらの誘導体の物性および反応性について詳細に報告する。



1a : $R^1 = R^2 = H$
1b : $R^1 = Me, R^2 = H$
1c : $R^1 = R^2 = Me$

Fig. 1 New PCET reagent **1**.



Scheme 1 Stoichiometric reaction of molybdenum-nitride complex with an excess amount of protonated **1b**.

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1) (a) Y. Ashida *et al.*, *Nature* **2019**, *568*, 536. (b) Y. Ashida *et al.*, *Nat. Synth.*, **2023**, *2*, 635.

この成果は、NEDO の委託業務 (JPNP21020) の結果に基づくものです。

日本化学会 第104春季年会 (2024)

Co 錯体触媒を用いたカチオン添加による高効率 CO_2 電解還元反応

（豊田中研）○佐藤　俊介・関澤　佳太・白井 聡一・坂本 直柔・森川　健志

Enhanced performance of molecular electrocatalysts for CO_2 reduction by cations

(Toyota Central R&D Labs., Inc.）○Shunsuke Sato, Keita Sekizawa, Soichi Shirai, Naonari Sakamoto, Takeshi Morikawa

Electrocatalytic carbon dioxide (CO_2) reduction using water is the key to artificial photosynthesis systems designed to produce fuels. Molecular metal complex catalysts for CO_2 reduction have been researched by a lot of researchers because they have a high selectivity for CO_2 reduction reactions. However, because of the low durability for CO_2 reduction, new catalysts need to be developed. In this presentation, we will talk about new metal complex catalysts for CO_2 reduction using a flow cell with cations effects.

Keywords：CO_2 reduction, electrocatalyst, metal complex catalysts, electrolysis,

電気化学的な CO_2 還元反応は、ガス拡散電極を用いることで 1A/cm^2 以上の電流密度が実現されるなど、ここ数年で飛躍的に性能が向上している。その一方で、大電流密度を実現するために高い電圧を用いており、その結果、電気エネルギーから化学エネルギーへと変換される効率が極めて低い問題がある。電解システムに用いられる触媒は Au や Ag などの貴金属がメインであり、錯体触媒の報告例は少ない。その理由として、錯体触媒は溶液に浸漬する H 型セルでは安定にも関わらず、ガス拡散電極で用いると数時間で失活するなど耐久性が乏しく[1]、触媒性能が金属に及ばないためである。我々は、普通には触媒として駆動しない Mn 錯体を、カーボンとアルカリ金属カチオンの効果で、水溶液中においても CO_2 還元触媒として駆動させることに成功している[2]。この効果は、他の錯体触媒においても有効であることを示しており、CO_2 還元反応の本質的な部分に関わる効果と考察している。ここで、ガス拡散電極における触媒周辺の反応環境に着目すると、触媒周辺にアルカリ金属カチオンが存在しない状態となっている。そこで、ガス拡散電極のカーボン層にアルカリ金属カチオンを導入し、CO_2 還元性能の向上できないか検討を行った。

発表では、カチオン添加による高効率・高耐久性を示す CO_2 電解還元反応[3]について報告する。

[1] S. Ren et al., *Science* **2019,** 365, 367.
[2] S. Sato et al., *ACS Catal.* **2018,** 8, 4452.
[3] S. Sato et al., *Sci. Adv.* **2023,** 9, eadh9986.

アルカリ光水素生成反応を高速駆動する Co-NHC 錯体触媒の電子状態制御

（九大 [1]）○河村佳央理 [1]、山内幸正 [1]、酒井 健 [1]

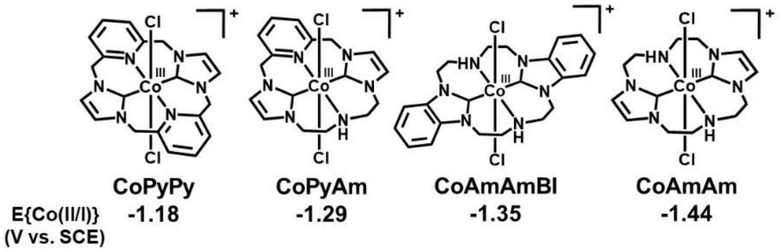
Controlling the Electronic State of Co-NHC Catalysts Accelerating Photochemical Hydrogen Evolution from Alkaline Water

([1]Kyushu Univ.) ○Kaori Kawamura[1], Kosei Yamauchi[1], Ken Sakai[1]

We have previously reported that the N-heterocyclic carbene cobalt complexes **CoPyPy**[1,2] and **CoPyAm** serve as excellent molecular catalysts in photochemical hydrogen evolution from neutral and alkaline water. In this study, we evaluate the H_2-evolving activity of new cobalt complexes, **CoAmAm** and **CoAmAmBI**, as molecular catalysts in alkaline aqueous media.

Keywords: Alkaline hydrogen evolution reaction, Co-NHC complexes, Molecular catalyst

当研究室では以前、N-ヘテロ環状カルベン（NHC）配位子を有するコバルト錯体 **CoPyPy**[1,2] および **CoPyAm** がアルカリ性条件下で水からの優れた水素生成触媒特性並びに耐久性を示すことを明らかにした。本研究では、電子状態制御に基づく Co-NHC 錯体触媒の高活性化を志向した。具体的には、鍵中間種として目される Co(I)種の反応性を向上させることを目的とし、**CoPyPy** の二つのピリジン部位をアミン部位に置き換えた **CoAmAm**、及びその NHC 誘導体 **CoAmAmBI** を合成し、アルカリ水からの光水素生成触媒機能について評価した。



CV 測定より、**CoAmAm** と **CoAmAmBI** は、**CoPyPy** や **CoPyAm** と比較しより負側に Co(II/I)に基づく酸化還元電位を示した。次に、$[Ru(bpy)_3]^{2+}$/アスコルビン酸イオン光反応系を用いた水素定量実験の結果、**CoPyAm** が最も優れた触媒特性を示した。また、**CoAmAmBI** では **CoAmAm** と比較して光水素生成の初期速度が大きくなったが、しだいに光水素生成の速度は下がり、6 時間後の水素生成量では **CoAmAm** のほうが大きくなった（Figure 1）。発表では、これらの構造活性相関について考察し議論する。

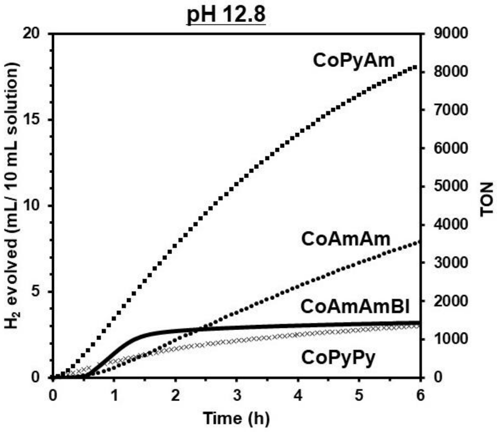


Figure 1. Photochemical H_2 evolution from alkaline water (pH = 12.8, 0.3 M ascorbate, 0.5 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, 0.01 mM catalyst, under Ar. Irradiated by 300 W Xe lamp (λ > 400 nm).

1. K. Kawano, K. Yamauchi, and K. Sakai, *Chem. Commun.*, **50**, 9872-9875 (2014).
2. K. Yatsuzuka, K. Yamauchi, K. Kawano, H. Ozawa, and K. Sakai, *Sustainable Energy Fuels*, **5**, 740-749 (2021).

Synthesis of a cobalt dinuclear complex $(Co_2L_2)(NO_3)_2$(HL=3,5-bis(2'-pyridyl)pyrazole) and its catalytic property for electrochemical CO_2 reduction

([1]*Graduate School of Science, Kyushu University*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University,* [3]*International Institute for Carbon-Neutral Energy Research, Kyushu University,* [4]*Research Center for Negative Emissions Technologies, Kyushu University,* [5]*Advanced Institute for Materials Research, Tohoku University*) ○ Yunyi Pan,[1] Masaki Donoshita,[2] Miho Yamauchi,[1,2,3,4,5]

Keywords: Electrochemical CO_2 Reduction; Dinuclear Complex

Electrochemical CO_2 reduction (ECO_2R) is a promising method for the production of value-added compounds by using renewable electricity. Metal-complex catalysts are intriguing because of their well-defined local structures and the structural designability that can be achieved through ligand modifications. Mononuclear complexes such as metal phthalocyanines and metal porphyrins have been primarily studied as a catalyst for ECO_2R,[1,2] and there is growing interest in multinuclear complexes for their potentially unique catalytic properties. In this study, we focus on a dinuclear cobalt complex $[Co_2(bpypz)_2](NO_3)_2$ (Hbpypz=3,5-bis(2'-pyridyl)pyrazole), referred to as $\mathbf{Co_{di}}$ (**Fig.1b** inset), and present the synthesis and characterization of $\mathbf{Co_{di}}$. The catalytic performances of $\mathbf{Co_{di}}$ were studied and compared with those of the well-known mononuclear complex, cobalt tetraphenylporphyrin ($\mathbf{Co_{mono}}$; **Fig. 1a** inset).

$\mathbf{Co_{di}}$ was synthesized by mixing $Co(NO_3)_2 \cdot 6H_2O$ and Hbpypz in methanol. Single-crystal X-ray diffraction revealed the molecular structure of $\mathbf{Co_{di}}$ with a square-planar coordination structure similar to that of $\mathbf{Co_{mono}}$. Cyclic voltammograms (**Fig. 1**) were recorded under Ar/CO_2 atmospheres using DMF solutions containing 0.1 M tetrabutylammonium perchlorate, revealing a more positive onset potential for ECO_2R of $\mathbf{Co_{di}}$ compared with that of $\mathbf{Co_{mono}}$. Controlled potential electrolysis at −1.95 V (Fc/Fc^+) with $\mathbf{Co_{di}}$ yielded CO as a reaction product, in contrast to the production of H_2 with $\mathbf{Co_{mono}}$.

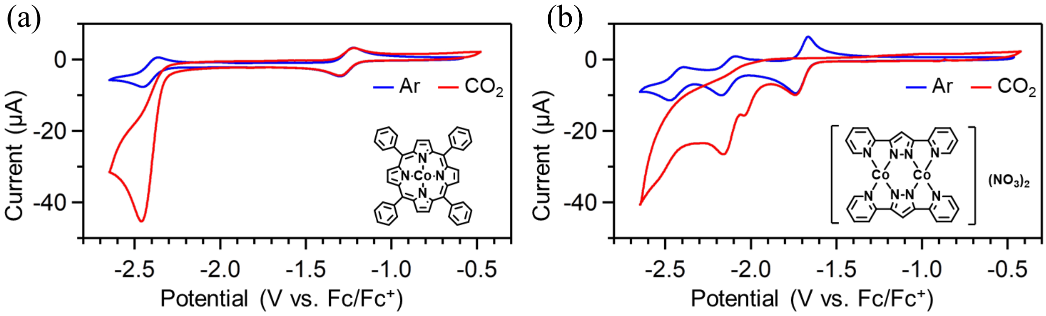


Fig. 1 Cyclic voltammograms of (a) $\mathbf{Co_{mono}}$ and (b) $\mathbf{Co_{di}}$ recorded under Ar (blue) and CO_2 (red) atmospheres. Insets show molecular structures of (a) $\mathbf{Co_{mono}}$ and (b) $\mathbf{Co_{di}}$.

1) N. Latiff *et al.*, *Carbon*, **2020**, *168*, 245. 2) K. Kosugi *et al.*, *Chem. Commun.*, **2022**, *58*, 29750.

Assessing the Actual Turnover Frequency of a Co-NHC Catalyst for Electrochemical Hydrogen Evolution from Water

([1]*Kyushu Univ.*) ○Masanori Kan,[1] Kosei Yamauchi,[1] Ken Sakai[1]

Keywords: Hydrogen evolution reaction (HER); Molecular catalyst; Electrochemistry; Turnover frequency (TOF); Catalytic Tafel plot

Our laboratory previously reported that an N-heterocyclic carbene cobalt complex, **Co-NHC1**, promotes photochemical hydrogen evolution from water with low driving force.[1,2] In this study, electrochemical studies were carried out to accurately assess the turnover frequency (TOF) of the hydrogen evolution reaction (HER) catalyzed by **Co-NHC1**.

When a linear sweep voltammogram (LSV) for the phosphate buffer solution (pH 7) of **Co-NHC1** was scanned to cathodic domain, a large catalytic current derived from HER was observed. To confirm whether the catalytic reaction proceeds under the homogeneous conditions or not, so-called rinse test was carried out using glassy carbon (GC) working electrode. As a result, a minor increase of current compared to the blank measurement was observed. It was also found that dipping GC electrode into **Co-NHC1** solution leads to the almost consistent LSV profile even for the blank solution with that for the rinse test. Therefore, it was concluded that the increase of current in the rinse test derives from dip-coated effect of **Co-NHC1** on GC electrode. To determine the actual TOF of HER under the homogeneous solution conditions, further electrochemical evaluation was conducted to eliminate the dip-coated effect on GC surface. Consequently, the TOF was determined to be 22,000,000 s^{-1}. By developing the catalytic Tafel plots (**Figure 1**), the catalytic activity of **Co-NHC1** was compared with other homogeneous electrocatalysts of HER. Importantly, **Co-NHC1** shows the most excellent activity among H_2-evolving catalysts, when considering both the TOF (y axis) and the overpotential (x axis).

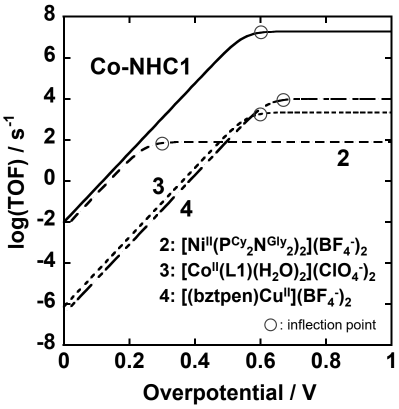
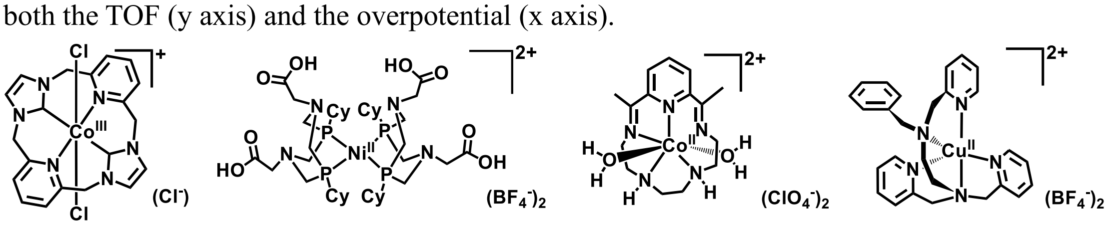


Figure 1. Catalytic Tafel plots of homogeneous electrocatalysts for H_2 evolution in aqueous media.



Co-NHC1 **$[Ni^{II}(P^{Cy}_2N^{Gly}_2)_2](BF_4^-)_2$** **$[Co^{II}(L1)(H_2O)_2](ClO_4^-)_2$** **$[(bztpen)Cu^{II}](BF_4^-)_2$**

Figure 2. Homogeneous electrocatalysts of HER evaluated in aqueous media.

1) K. Kawano, K. Yamauchi, K. Sakai, *Chem. Commun*. **2014**, *50*, 9872. 2) K. Yatsuzuka, K. Yamauchi, K. Kawano, H. Ozawa, K. Sakai, *Sustainable Energy Fuels* **2021**, *5*, 740.

光増感剤を修飾した TiO_2 フォトアノードおよび Co ポルフィリン触媒を修飾した TiO_2 カソードを用いた光電気化学的 CO_2 還元反応

（九大 [1]）〇合屋 祐輝 [1]・Yan Xin[1]・酒井 健 [1]・小澤 弘宜 [1]

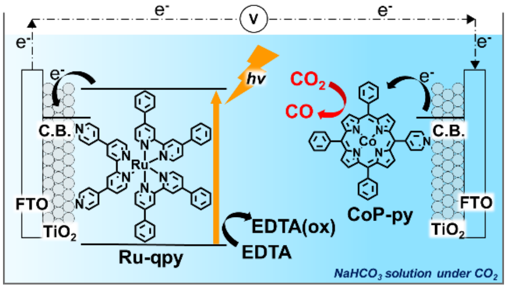
Photoelectrochemical CO_2 Reduction Using a Photosensitizer-Modified TiO_2 Photoanode and a Co-Porphyrin-Catalyst-Modified TiO_2 Cathode

([1]*Kyushu Univ.*) 〇Yuki Goya,[1] Xin Yan,[1] Ken Sakai[1], Hironobu Ozawa[1]

Recently, we have reported that CO_2-to-CO conversion with a relatively higher selectivity proceeds even in aqueous media by using the TiO_2 electrode modified with a Co porphyrin molecular catalyst having a pyridyl anchor (i.e., FTO/TiO_2/CoP-py cathode). In this study, in order to achieve CO_2-to-CO conversion coupled with water oxidation, the molecular-based photoelectrochemical cell consisting of the FTO/TiO_2/CoP-py cathode and the TiO_2 photoanode modified with a polypyridyl ruthenium photosensitizer (i.e., FTO/TiO_2/Ru-qpy photoanode) has been developed, and the photoelectrocatalytic performance for CO_2-to-CO conversion in aqueous media has been evaluated in the presence of the sacrificial electron donor. The detailed results of the photoelectrochemical measurements will be discussed.

Keywords : CO_2 Reduction; Photoelectrochemical Cell; Co Porphyrin; TiO_2; Photosensitizer

最近我々は、ピリジルアンカーを有する Co ポルフィリン触媒(CoP-py)を修飾した TiO_2 電極(FTO/TiO_2/CoP-py カソード)を用いることによって、水溶液中においても比較的高選択に CO_2 を CO に還元できることを報告した[1]。本研究では、水を電子源とする光電気化学的な CO_2 還元反応の達成に向け、FTO/TiO_2/CoP-py カソード、およびポリピリジルルテニウム光増感剤(Ru-qpy)を修飾した TiO_2 光電極(FTO/TiO_2/Ru-qpy フォトアノード)[2]からなる分子性光電気化学セル(下図)において、犠牲還元剤(EDTA)の存在下における光電気化学的 CO_2 還元反応について検討を行った。CO_2 を飽和させた $NaHCO_3$ 水溶液(pH 6.5)を電解液として用い、フォトアノードのみに疑似太陽光($\lambda > 410$ nm)を照射して LSV 測定を行ったところ、-0.3 V vs. cathode 付近からアノード電流が観測され、1.0 V 付近で最大(約 2.4 mA/cm^2)となった。本測定中において、カソード表面から気泡の発生が確認されたことから、光電気化学的 CO_2 還元反応が進行したと期待される。講演では、より詳細な検討結果を報告する予定である。



[1] H. Ozawa, R. Kikunaga, H. Suzuki, R. Abe, K. Sakai, *Sustain. Energy Fuels*, 2023, 7, 1627.
[2] K. Morita, K. Sakai, H. Ozawa, *ACS Appl. Energy Mater.,* **2019**, *2*, 987.

アニオン添加で加速する二酸化炭素還元光触媒反応

（東京工科大院工 [1]・東京工科大工 [2]・立命館大生命科学 [3]）○木原 咲穂 [1]・下地 浩希 [2]・前田 大光 [3]・森本 樹 [1]

Anion-Accelerated Photocatalytic Reduction of Carbon Dioxide

([1]*Graduate School of Engineering, Tokyo University of Technology* [2] *School of Engineering, Tokyo University of Technology,* [3]*College of Life Sciences, Ritsumeikan University*) ○Sakiho Kihara[1], Hiroki Shimoji[2], Hiromitsu Maeda[3], Tatsuki Morimoto[1]

Photocatalytic carbon dioxide reduction using sunlight is attracting much interest as a fundamental technology for solving global warming and energy problems. However, previous complexes adopted as photosensitizers for photocatalytic CO_2 reduction usually contain rare metals. We focused on dipyrrolyldiketone boron complexes[1)], which can absorb visible light and also exhibit anion-bindng ability, and investigated a CO_2 reduction photocatalytic reaction system in combination with a rhenium complex. As a result, the turnover number of the CO_2 reduction to CO reached about 340 in 9 hours. Moreover, CO formation rate was found to be highly affected by the existence of anion species.

Keywords : CO_2 reduction, Photocatalyst, Boron complex, Anion binding

太陽光を利用した光触媒的二酸化炭素(CO_2)還元は、地球温暖化やエネルギー問題を解決する基盤技術として注目されている。しかし、光エネルギーを用いた CO_2 還元反応には、従来希少な金属を含む錯体が光増感剤として主に用いられてきた。本研究では、その代替となる入手容易な錯体として、可視光に応答し、かつ、アニオン補足能も示すジピロリルジケトンホウ素錯体 [1)]に注目し、レニウム錯体と組み合わせた新たな CO_2 還元光触媒反応系を検討した。このホウ素錯体は、500 nm 付近の可視光をよく吸収し、また、その一電子還元種は CO_2 還元触媒に電子を渡すのに十分な還元力を示すことがわかった。そこで、500 nm の単色光を用いて CO_2 還元光触媒反応を行ったところ CO が生成し、9 時間で約 340 の触媒回転数を示した(図)。さらに、特定のアニオンを共存させることで、CO の生成速度が大きく向上することも見出した。

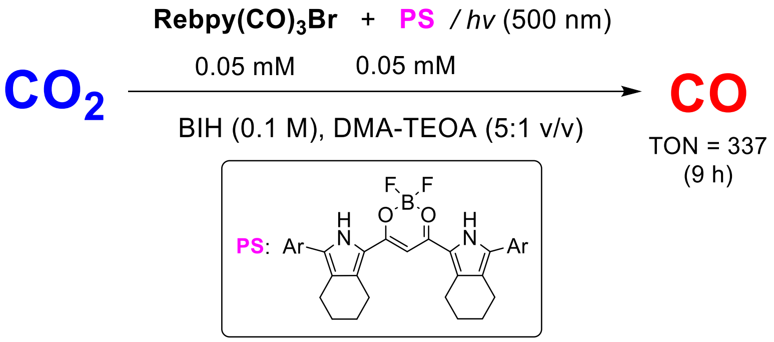


図 ジピロリルジケトンホウ素錯体とレニウム錯体を用いた CO_2 還元光触媒反応

1) Maeda, H.; Terasaki, M.; Haketa, Y.; Mihashi, Y.; Kusunose, Y. *Org. Biomol. Chem.* **2008**, *6*, 433-436.

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18日(月) 13:00 ~ 15:30 F1233(12号館 [3階] 1233)

[F1233-1pm] 09. 錯体化学・有機金属化学

座長：高橋 仁徳、長尾 祐樹

英語

13:00 ~ 13:20

[F1233-1pm-01]

光誘起多段階イオン伝導度スイッチング材料の構築と機構解明

○青木 健太郎[1]、長尾 祐樹[1] (1. 北陸先端科学技術大学院大学)

日本語

13:20 ~ 13:40

[F1233-1pm-02]

レドックスフロー電池正極液用のターピリジン鉄錯体の溶解度向上

○岡澤 厚[1]、角地 貴行[1]、赤堀 圭祐[1]、川合 航右[1]、大久保 將史[1] (1. 早稲田大学)

英語

13:40 ~ 14:00

[F1233-1pm-03]

デヒドロベンゾアヌレンをビルディングブロックとする導電性金属有機構造体の構築

○大久保 円造[1]、相澤 直矢[1]、中山 健一[1]、鈴木 充朗[1] (1. 阪大)

日本語

14:00 ~ 14:20

[F1233-1pm-04]

パドルホイール型錯体を用いたd-π複合電子系単分子素子の設計指針に関する理論研究

○甘水 君佳[1]、西田 光博[1]、岸 亮平[1,2,3,4]、北河 康隆[1,2,3,4,5] (1. 阪大院基礎工、2. 阪大QIQB、3. 阪大RCSEC、4. 阪大ICS-OTRI、5. 阪大SRN-OTRI)

14:20 ~ 14:30

休憩

英語

14:30 ~ 14:50

[F1233-1pm-05]

Stable Neutral Iridium & Rhodium-Radical Species with an N-confused Tetrapyrrane That Exhibits Near-infrared Absorption

○ANINDA GHOSH[1], Ken-ichi Sugiura[1], Masatoshi Ishida[1] (1. TOKYO METROPOLITAN UNIVERSITY)

英語

14:50 ~ 15:10

[F1233-1pm-06]

単純なプロトンワイヤーで連結された金属ジチオレン錯体とカリックスアレーンの水素結合共結晶の電子構造と物性

○林 幹大[1] (1. 長崎大学)

英語

15:10 ~ 15:30

[F1233-1pm-07]

一次元πスタッキングを有する有機無機ハイブリッド結晶の創製と機能

○増田 峻也[1]、楠本 壮太郎[1]、小出 芳弘[1] (1. 神奈川大学)

Construction of a Light-induced Multi-step Ion Conductivity Switching Material and Elucidation of Its Mechanism

([1]*Japan Advanced Institute of Science and Technology*) ○Kentaro Aoki,[1] Yuki Nagao[1]

Keywords: Ion Conductor; Conductivity Switching; Photoisomerization; Proton

Ion conductivity switching materials have attracted great attention toward the application in memory or sensors. Previous reports introduced one stimulus-responsive unit to investigate ion conductivity switching, however, the on·off ratios of the ion conductivity were far from electron conductivity switching material, transistor (> 10^6 on·off ratio).1) In this research, we aimed at high on·off ratio of ion conductivity by concerted effect of two light-responsive units, (i) azo group for conduction path formation and (ii) *o*-nitrobenzaldehyde group for carrier injection via pK_a change.2) Moreover, we revealed the multi-step ion conductivity switching properties using the two light-responsive units.

A novel metal complex (**1** in **Figure**) composed of Fe^{III} ions and ligand containing (i) azo and (ii) *o*-nitrobenzaldehyde groups was synthesized, and the structure before the light irradiation was determined by the single-crystal X-ray structural analysis at 100 K. From solid-state ultraviolet-visible spectroscopy, it was clarified that azo and *o*-nitrobenzaldehyde groups of **1** were isomerized at 470 nm and 340 nm, respectively. From ion conductivity of **1** at 298 K and 95% relative humidity, we found that on·off ratio of ion conductivity when isomerizing azo or *o*-nitrobenzaldehyde group was low, 2.5 (**1A phase**) and 1.1×10^2 (**1B phase**), respectively). In contrast, a high proton conductivity (5.5×10^{-3} S/cm) with 1.0×10^5 on·off ratio was achieved by isomerizing the two light-responsible units simultaneously, due to the concerted effect (**1C phase**). Moreover, by exploring further phase transition of **1**, we unveiled an intermediate phase (**1D phase**) where the on·off ratio of ion conductivity was 5.7×10^2, and its irreversible phase transition to **1C phase** at high light power.

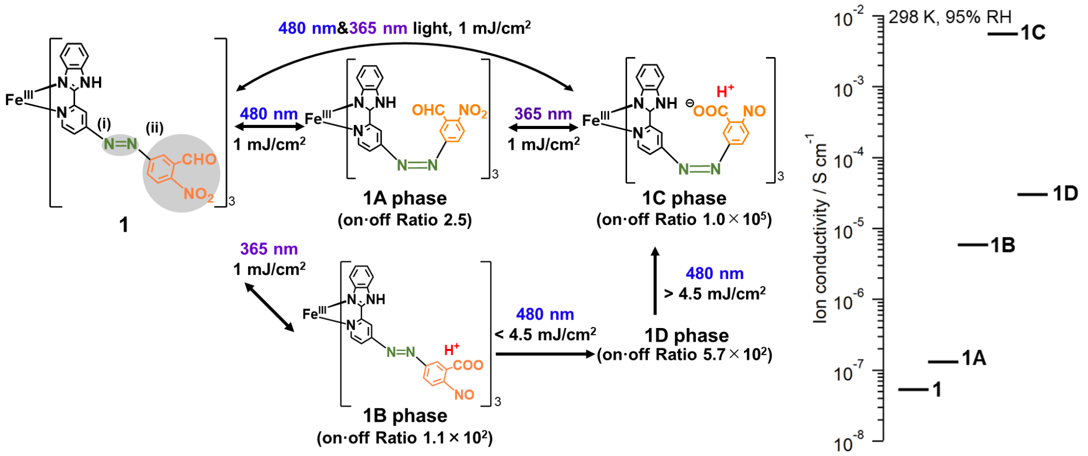


Figure. Summary of light-induced ion conductivity switching behavior of **1**.

1) F. Xiang *et al.*, *J. Am. Chem. Soc. Au*, **2022**, *2*, 1043. 2) C. Choi *et al.*, *J. Phys. Chem. A*, **2001**, *105*, 12.

レドックスフロー電池正極液用のターピリジン鉄錯体の溶解度向上

（早大先進理工）○岡澤 厚・角地貴行・赤堀圭祐・川合航右・大久保將史

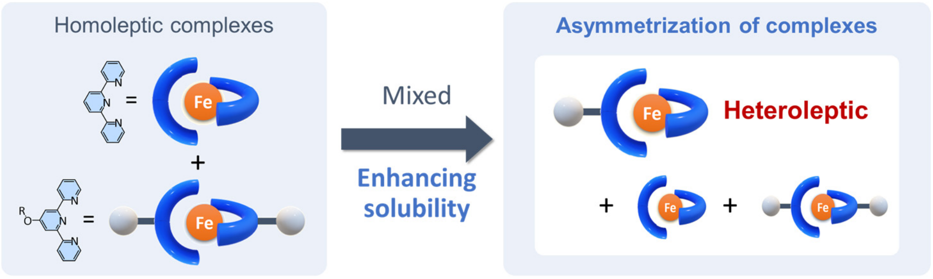
Improving the Solubility of Terpyridine Iron Complexes for Redox Flow Battery Catholytes

(*School of Advanced Science and Engineering, Waseda University*) ○Atsushi Okazawa, Takayuki Kakuchi, Keisuke Akahori, Kosuke Kawai, Masashi Okubo

Redox flow batteries (RFBs) are promising candidates for stationary grid-scale energy storage devices load-leveling intermittent power from the renewables. Although vanadium RFBs have been commercialized, the use of vanadium causes severe difficulties such as high cost and low abundance. To replace vanadium in the current RFBs, terpyridine iron complexes that have higher redox potential of approximately 1 V (vs. SHE) are promising catholyte active materials. However, terpyridine iron complexes generally possess low solubility (~0.16 M) in nonaqueous media. In this study, we successfully improved their solubility by asymmetrization: a new heteroleptic complex was produced by mixing of the parent terpyridine and the substituted one with an iron source. The maximum concentration of active materials increased from 0.16 M to 0.49 M, which provides a theoretical volumetric capacity of catholytes three times larger than those of the single-component ones. Further solubility improvement was achieved using complexes substituted with poly(ethylene glycol)-type chains.

Keywords : Terpyridine; Iron Complex; Solubility; Diverse Ion Effect; Redox Flow Battery

レドックスフロー電池 (RFBs) は再生可能エネルギー由来の間欠性電力を負荷平準化する、大規模定置型蓄電デバイスの有力候補である。既にバナジウム RFB が商用化されているが、高コストかつ希少なバナジウムを使用している、という問題を抱えている。そこで、我々は非水系 RFB の正極液活物質として、1 V（vs. SHE）程度の高電圧を示す安価なターピリジン鉄錯体に着目した。しかし、ターピリジン鉄錯体はアセトニトリルに対する溶解度が低く、RFB のエネルギー密度も低いという課題があった。そこで、我々は無置換ターピリジンと置換誘導体との混合からヘテロレプティック錯体を生成させ、分子非対称化による鉄錯体の溶解度向上に成功した。具体的には、溶解度が 0.16 M から 0.49 M へと増加したことで、理論体積容量を単一成分と比べて三倍程度に改善できた。また、ポリエチレングリコール系側鎖を配位子に置換させた錯体では、さらなる溶解度の向上に成功した。



Construction of Conductive Metal–Organic Frameworks with Dehydrobenzoannulenes

(*Graduate School of Engineering, Osaka University*) ○Enzo Ohkubo, Naoya Aizawa, Ken-ichi Nakayama, Mitsuharu Suzuki

Keywords: Metal–Organic Frameworks; Dehydrobenzoannulenes; Porous Materials; Two-Dimensional Polymers

Two-dimensional metal–organic frameworks (2D MOFs) are crystalline, porous polymers often associated with decent conductivity, being promising for a variety of applications including electrocatalysis and chemiresistive sensing. However, development of 2D MOFs has been considerably hampered by limited structural diversity and pore size.[1]

In this work, we attempted to synthesize dehydrobenzoannulene-based 2D MOFs aiming improved guest capacity and diffusivity by enlarging the pore size as compared to the prototypical triphenylene-based systems. Reactions of hexaamino derivatives of dehydrobenzo[12]annulene (HA[12]) or dehydrobenzo[18]annulene (HA[18]) with a nickel salt led to porous crystalline compounds (Ni-HA[12] and Ni-HA[18], respectively; Fig. 1). Especially, Ni-HA[18] showed an excellent BET surface area of 1720 m² g⁻¹, exceeding the previously reported maximum value for 2D MOFs.[2] The presentation will delve into the synthesis, structure, and electronic properties of the two newly developed compounds.

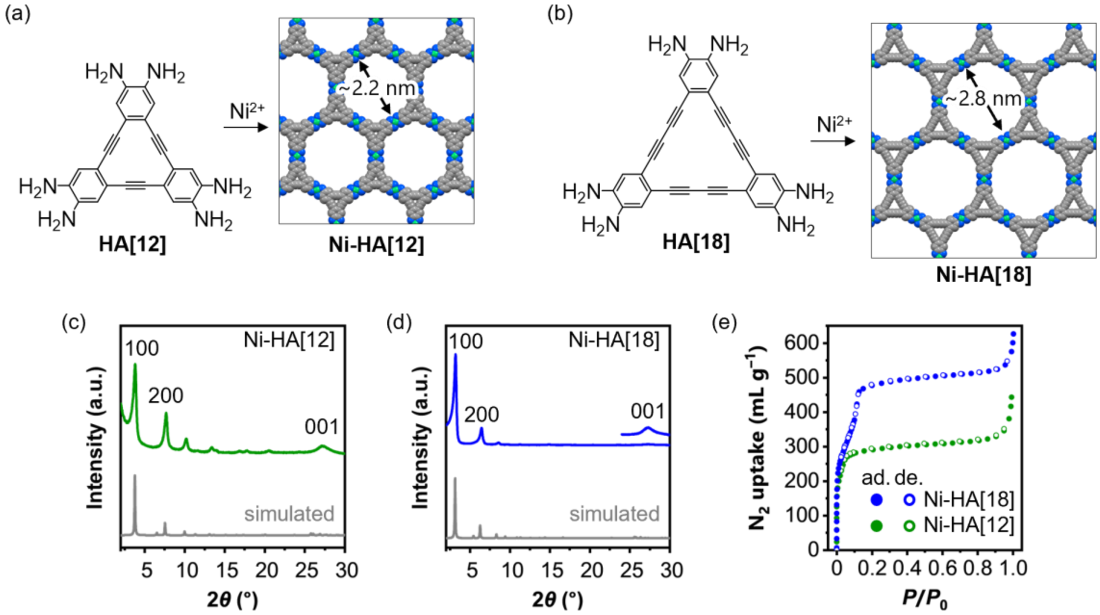


Fig. 1 (a, b) Expected structures of Ni-HA[12] and Ni-HA[18]. (c, d) PXRD profiles of Ni-HA[12] and Ni-HA[18] compared with the corresponding simulated patterns of the expected eclipsed stacking models. (e) N_2 sorption isotherms of Ni-HA[12] and Ni-HA[18].

(1) Xie, S. L. et al. *Chem. Rev.* **2020**, *120*, 8536. (2) Dou, J.-H. et al. *Nat. Mater.* **2021**, *20*, 222.

パドルホイール型錯体を用いたd-π複合電子系単分子素子の設計指針に関する理論研究

(阪大院基礎工 [1]・阪大 QIQB[2]・阪大 RCSEC[3]・阪大 ICS-OTRI[4]・阪大 SRN-OTRI[5])
○甘水 君佳 [1]・西田 光博 [1]・岸 亮平 [1,2,3,4]・北河 康隆 [1,2,3,4,5]

Theoretical study on a design guideline for single-molecule components based on paddle-wheel type d-π conjugated compounds

([1]*Graduate School of Engineering Science, Osaka Univ.*, [2]*QIQB, Osaka Univ.*, [3]*RCSEC, Osaka Univ.*, [4]*ICS-OTRI, Osaka Univ.*, [5]*SRN-OTRI, Osaka Univ.*) ○Naoka Amamizu,[1] Mitsuhiro Nishida,[1] Ryohei Kishi,[1,2,3,4] Yasutaka Kitagawa,[1,2,3,4,5]

In recent years, molecular electronics, which aims to use functional single-molecules as the electronic components, has attracted much attention in the field of nanomaterials. The d-π conjugated compounds often show not only the high electron conductivity with a widely delocalized π orbitals but also various functionalities that mainly originate from the localized d-orbitals on the metal ions. In this study, we investigated the difference in the electron conductivity between anti-ferromagnetic and ferromagnetic states on paddlewheel-type binuclear complexes, in detail, by the quantum chemical calculations and elastic scattering Green's function method. In addition, the effect of the electron donating/withdrawing substituents on both electronic structures and the conductivities is also examined to obtain design guidelines for the molecular transistors.

Keywords : Molecular Electronics; d-π Conjugated Compound; Quantum Chemical Calculation; Density Functional Theory

近年、1 つの分子に電子素子の機能をもたせた単分子素子と呼ばれる機能性分子が新たなナノ材料として注目を集めている [1)]。金属錯体のような d-π複合電子系化合物は、有機配位子の非局在化したπ軌道による高い伝導性と、金属イオンの d 軌道に由来する局在スピンによる高い機能性から単分子素子の候補分子として注目されている。特に、当研究グループでは外部磁場による金属錯体のスピン状態変化を利用した単分子トランジスタの可能性を示唆している [2)]。

本研究では、パドルホイール型錯体(Figure 1a)をモデル分子として、置換基や金属イオンなどの部分構造と単分子電気伝導性の関係を密度汎関数理論法によって調べ、d-π複合電子系単分子素子の設計指針を提案することを目的とした。また、金属イオンのスピン状態を反強磁性(AFM)状態から強磁性(FM)状態に変化させた場合(Figure 1b)の伝導性変化から、スイッチング性能の検討も行なった。詳しい結果は当日報告する。

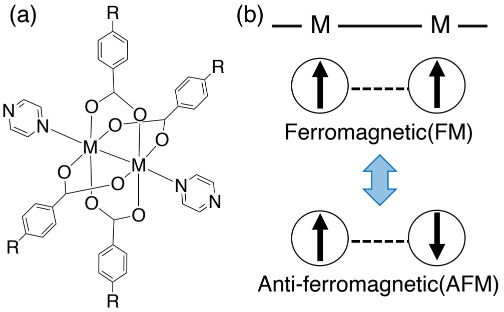


Figure 1. (a)Structure of the model complex, (b)Illustration of spin states of metal ions.

1) D. Xiang, X. Wang, C. Jia, T. Lee, X. Guo, *Chem. Rev.* **2016**, *116*, 4318.
2) Y. Kitagawa et. al., *Molecules* **2019**, *24*, 1956.

Stable Neutral Iridium- and Rhodium-Radical Species with a N-confused Tetrapyrrane showing Near-infrared-II Absorption

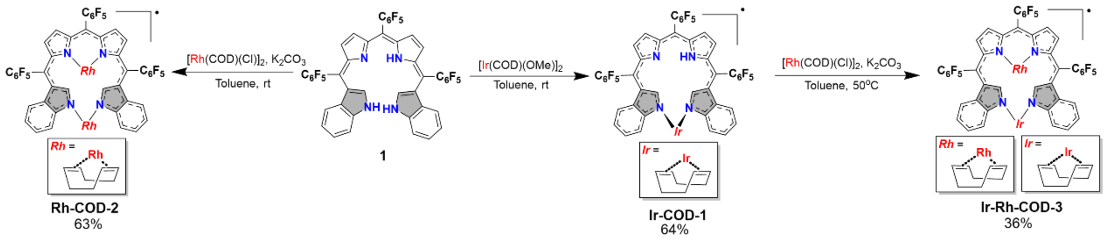
(*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University*)

○ **Aninda Ghosh, Ken-ichi Sugiura and Masatoshi Ishida**

Keywords: Structural Properties, Iridium, Rhodium, Stable Radical, NIR-II absorption

Abstract: The pursuit of persistent and stable radicaloid species in materials science has intensified due to their unique physicochemical properties and potential applications in diverse devices [1]. Overcoming challenges related to the inherent instability of open-shell radicals, recent advancements involve porphyrins and porphyrinoids, which shows thermodynamic and kinetic stabilization mechanisms, exhibit intriguing magnetic and optoelectronic properties. We recently designed a unique metal coordination ligand— an open-chain tetrapyrrane derivative (**1**) embedded with two N-confused pyrrole moieties. The NNCC core facilitates the formation of a distinctive closed-shell organocopper(III) species[2]. Using an unconventional approach, we incorporated a metal atom into an N-confused open porphyrin system, generating a redox non-innocent radical species with the pseudo-porphyrinoid structure, employing iridium(I) and rhodium(I) cyclooctadiene (cod) synthons in this work.

Ligand **1** underwent the Ir(COD)- complexation at the outer indole nitrogen sites, yielding the complex (**Ir-COD-1**) in 64% yield. Using a Rh(COD)Cl dimer a bis-Rh complex (**Rh-COD-2**) with the additional Rh coordination at the inner dipyrrin core was formed. Similarly, the further metalation of **Ir-COD-1** with the Rh(COD)Cl fragment afforded the hetero-metalated species (**Ir-Rh-COD-3**). The structures were elucidated by X-ray crystallographic analysis. Notably, the macrocyclic metallaporphyrinoid exhibited organic radical features as inferred from the distinct EPR spectroscopy. The DFT based spin population analysis revealed effective electron delocalization over the tetrapyrrane ligand and electrochemical analysis also indicated two oxidation waves and one reversible reduction wave, with extremely narrow HOMO-LUMO gaps of 0.36 V (**Ir-COD-1**), 0.48 V (**Rh-COD-2**) and 0.47 V (**Ir-Rh-COD-3**). These stable Ir and Rh-radical complexes exhibited second NIR absorption up to 1400 nm, which would be utilized for potential NIR-based imaging applications.



[1] Wilcox, D. A, et al., *Annu. Rev. Chem. Biomol. Eng.* **2018**, *9,* 83−103

[2] Basumatary, B, et al, *Angew. Chem. Int. Ed.***, 2020***, 132.37*, 16031-16035

Electronic Structure and Physical Properties of Hydrogen-Bonded Cocrystals with Simple Proton Wires Connecting Metal-Dithiolene Complexes and Calix[4]arenes

(*Faculty of Education, Nagasaki University*) ○Mikihiro Hayashi

Keywords: Hydrogen Bonded Crystal; Dithiolene Complex; Calix[4]resorcinarene; Redox;

[Introduction] Hydrogen bond (H-bond) is an important non-covalent force to construct crystalline molecular assemblies, and potentially offers proton movements accompanied by electronic-structure perturbations of the paired molecules. These features of H-bond have motivated researchers to produce functional materials, where associations between H-bond and electronic states lead to unique chromic or magnetic/conductive behaviors.[1] As design strategies of H-bond in such assemblies, many attentions have focused on pK_a matching of paired components to increase degrees of freedom in proton displacements. Whereas, there are a few attempts to introduce multi-centered H-bond, repeating units of proton wires, into the assemblies, although proton wires flexibly allow proton displacements within the pairs to undergo redox or energy-transfer reactions in nature assembly systems.[2] This presentation aims to provide a rational approach to give assemblies with three-centered H-bond and to show characteristic properties arising from the simple proton-wire structure.

[Result and Discussion] Assembly of metal dithiolate with pyrazine scaffold (containing d^8 ions, Cu^{III} or Ni^{II}) and calix[4]resorcinarene (CR) gave 1:1 cocrystals stabilized by a three-centered O–H···O–H···N type H-bonds (Fig.1a). Both cocrystals showed broad absorption bands around 2500 cm^{-1}. Note, Cu^{III}–CR system showed weak ESR signals assigned to Cu^{II} and organic-radical species, that disappeared by thermal annealing (TA) (Fig.1b). Results of TG-DTA, PXRD, and spectroscopic measurements indicated the TA causes a structural transition accompanied by crystal-solvent releases and H-bond deformations. A plausible mechanism to generate ESR-active species in the H-bonded crystal of Cu^{III}–CR system will be discussed based on Pourbaix diagrams of metal dithiolate[3] and CR.

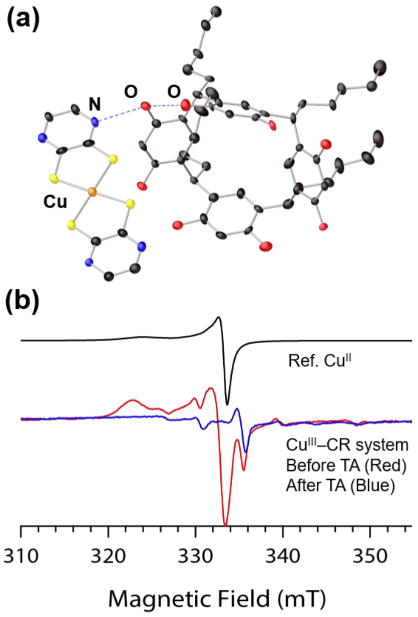


Fig.1 A three-centered H-bond (dotted line) in crystal structure (a) and ESR signals (b) of Cu^{III}–CR system.

1) a) T. Murata, *et al.*, *Angew. Chem.*, *Int. Ed.* **2004**, *43*, 6343. b) H. Mori, *et al.*, *Chem. Commun.* **2022**, *58*, 5668. 2) A. R. Offenbacher, *et al.*, *J. Phys. Chem. B* **2020**, *124*, 345. 3) M. Hayashi, *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 11686.

Syntheses and Properties of Organic-Inorganic Metal Halide Hybrid Crystals with One-Dimensional π-stacking

(*Graduate School of Engineering, Kanagawa University*)
○ Shunya Masuda, Sotaro Kusumoto, Yoshihiro Koide

Keywords: Organic-inorganic metal halide hybrids; Mechanochromism; Elastic deformation

In recent years, flexible crystals have received much attention for the applications of flexible devices[1]. Most studies have focused on the use of neutral organic molecules[2] or metal complexes[3], but flexible crystals with ionic materials is unexplored due to the presence of strong electrostatic interactions in the crystal, resulting in brittle properties.

Organic-inorganic metal halide hybrid (OIMHs), composed of organic cations and metal halide anions, are a well-studied class of functional ionic materials due to their diverse properties such as semiconductors and multiferroics[4].

Naphthalene diimide derivative (NDI), known as a highly planar and electron acceptor, is used to develop the soft framework OIMHs. There were two types of crystals that were produced dark brown crystal of **1** and pale yellow crystal **1w** depending on the concentration of HCl solution, which **1w** contains water molecules in the framework and the other is not (Fig. 1a). **1w** exhibited elastic flexibility (Fig. 1b) and mechnochromism (Fig. 1c) due to the presence of slip-stacked 1D π---π interactions of the NDI cations in the crystals. In particular, **1** exhibited near infrared (NIR) induced photothermal conversion due to the production of stable organic radical in the NDI moiety (Fig. 1d). Summery, we prepared multi-stimulus soft OIMHs hybrids exhibiting exceptional crystal flexibility and mechanochromic properties and photothermal conversion by developing OIMHs with 1D π---π stacking of NDI cations.

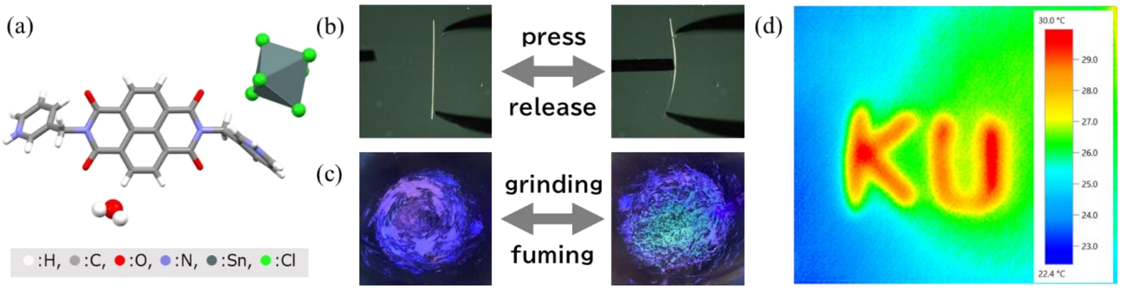


Fig. 1 (a) Crystal structure of Tin(IV) halides OIMHs **1w**. (b) Elastic bending and (c) Mechanochromism of **1w**. (d) Photothermal conversion induced by near infrared (NIR) light (λ_{ex}= 880 nm).

1) S. Ghosh, and C. M. Reddy., *Angew. Chem. Int. Ed.,* **2012***, 51*, 10319 –10323. 2) A. J. Thompson, J. K. Clegg et al., *Chem. Soc. Rev*., **2021**, *50*, 11725–11740. 3) S. Kusumoto, S. Hayami et al., *Coordination Chemistry Reviews*., **2023**, *475*, 214890. 4) M. Li, and Z. Xia, *Chem. Soc. Rev*., **2021**, *50*, 2626-2662.

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18日(月) 13:00 ~ 15:30 🏛 F1234(12号館 [3階] 1234)

[F1234-1pm] 09. 錯体化学・有機金属化学

座長：太田 俊、南保 正和

🏷 日本語

13:00 ~ 13:20

[F1234-1pm-01]

ホスフィン配位子の修飾に利用される嵩高い置換アリール基の立体的/電子的パラメータの定量化

○政岡 翔[1]、脇岡 正幸[2]、大木 靖弘[3]、小笠原 正道[1] (1. 徳島大学、2. 相模中央研究所、3. 京都大学)

🏷 日本語

13:20 ~ 13:40

[F1234-1pm-02]

ゲルマベンゼニルゲルミレン–ルイス塩基錯体の反応性

○西野 龍平[1]、時任 宣博[1]、山田 容子[1]、水畑 吉行[1] (1. 京大化研)

🏷 日本語

13:40 ~ 14:00

[F1234-1pm-03]

2位に2価ゲルマニウムを有する1,2,3-トリゲルマビシクロ[1.1.0]ブタンの合成とその骨格変換

○内田 大地[1]、水畑 吉行[1]、時任 宣博[1]、山田 容子[1]、行本 万里子[2] (1. 京大化研、2. 富山大)

🏷 英語

14:00 ~ 14:20

[F1234-1pm-04]

Synthesis, characterization, and reactivity of a novel di(μ-hydrido) dirhodium(II) complex bearing a reduced macrocyclic PDI ligand

○Liping YAN[1], Yuma MORIMOTO[1], Makoto YAMASHITA[1] (1. Nagoya University)

14:20 ~ 14:30

休憩

🏷 英語

14:30 ~ 14:50

[F1234-1pm-05]

^{1}H-NMRスペクトル上での環電流効果に着目した*tert*-Butylcalix[4]thiacrown-5－水銀(Ⅱ)錯体の結合能の評価と結合サイトの特定

○瀧本 竜哉[1]、橋本 悠[1]、井上 元[1]、高橋 弘樹[2]、津江 広人[2]、日置 和人[1]、佐々木 秀明[1]、袁 德其[1] (1. 神院大、2. 京大院)

🏷 日本語

14:50 ~ 15:10

[F1234-1pm-06]

配位子保護金ナノクラスターにおける位置選択的な配位子脱離反応

○鈴木 航[1]、髙畑 遼[2,3]、寺西 利治[2,3]、梅山 有和[1] (1. 兵庫県大院工、2. 京大化研、3. 京大院理)

🏷 英語

15:10 ~ 15:30

[F1234-1pm-07]

Sterically Demanding N-Heterocyclic Carbene Results in Selective Formation and Isolation of an Au_8Pt Nanocluster

〇Joseph Felix DeJesus[1], Yoshitaka Aramaki[2], Samuel I. Jacob[1], Quan Manh Phung[1,4], Takashi Ooi[1,2], Masakazu Nambo[1,4], Cathleen M. Crudden[1,3] (1. Institute of Transformative Bio-Molecules, 2. Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, 3. Department of Chemistry, Queen's University, 4. Department of Chemistry, Graduate School of Science, Nagoya University)

ホスフィン配位子の修飾に利用されている嵩高い置換アリール基の立体的/電子的パラメータの定量化

（徳島大学[1]・相模中央研究所[2]・京都大学[3]）○政岡　翔[1]・脇岡　正幸[2]・大木　靖弘[3]・小笠原正道[1]

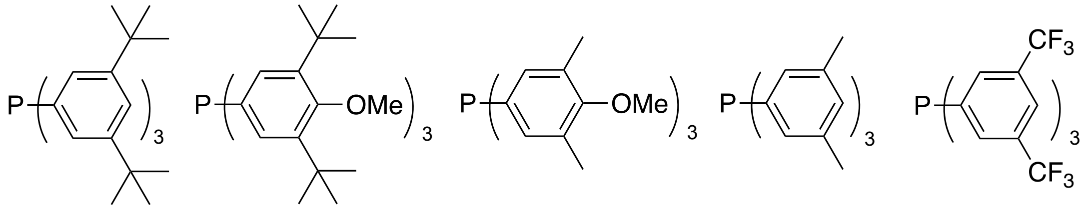
Estimating Effective Steric and Electronic Impacts of Bulky Aryl Groups in Organophosphines

([1]*Tokushima University*, [2]*Sagami Chemical Research Institute*, [3]*Kyoto University)* ○ Kakeru Masaoka,[1] Masayuki Wakioka,[2] Yasuhiro Ohki,[3] Masamichi Ogasawara.[1]

Tertiary phosphines are important ancillary ligands in homogeneous catalysis, and the reactivity and the properties of metal catalysts can be controlled by proper choices of these ligands. Diarylphosphino moieties are common motifs in phosphine ligands and appropriate modifications of the aryl substituents realize the fine-tunings of the phosphine ligands as well as their metal catalysts. In this study, the steric and the electronic parameters of the five representative "decorated' aryl groups were quantified by measuring the TEP values, the cone angles, and the %V_{bur} values of the respective PAr$_3$ compounds.

Keywords : organometallic complex; phosphine ligand; aryl substituent; electronic parameter; steric parameter

三級ホスフィン類は均一系遷移金属触媒の補助配位子として多方面に利用されており、これらを適宜選択することにより、金属触媒の反応性・選択性を制御することができる。ジアリールホスフィノ基をもつホスフィン配位子は多数知られており、リン上のアリール基を適切に修飾することでホスフィン配位子の特性を変調し、それらが配位した金属触媒の特性の微調整も可能となる。本研究では、ホスフィン配位子類の改良に利用される代表的な５つの嵩高いアリール基（下図参照）の単座トリアリールホスフィンを合成し、それらのトリカルボニルニッケル錯体の IR 測定、クロロ金錯体の X 線結晶構造解析をおこなった。それらの測定結果をもとに、それぞれの TEP (Tolman Electronic Parameter) 値[1]、ホスフィン円錐角 (Tolman Cone Angle)[2]、%V_{bur} (Percent Buried Volume)[3] を算出し、５つの嵩高いアリール基の立体的／電子的パラメータを定量化した。



[1] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.
[2] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.
[3] Nolan, S. P., Clavier, H. *Chem. Commun.* **2010**, *46*, 841.

ゲルマベンゼニルゲルミレン–ルイス塩基錯体の反応性

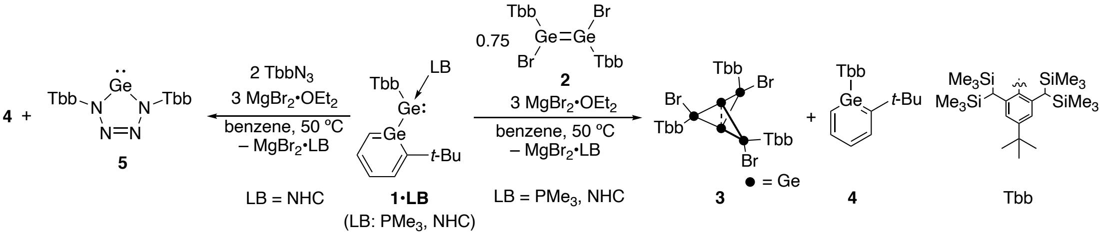
（京大化研）○西野 龍平、時任 宣博、山田 容子、水畑 吉行
Reactivities of Germabenzenylgermylene Lewis-base Complexes (*Institute for Chemical Research, Kyoto University*) ○Ryohei Nishino, Norihiro Tokitoh, Hiroko Yamada, Yoshiyuki Mizuhata

We have reported a single Ge atom transfer reaction using a germabenzenyl anion and a dibromodigermene. In this reaction, germabenzenylgermylene **1** plays a key role, and it is possible to isolate as Lewis-base complexes **1**･**LB**. We report here the reactivities of **1**･**LB**. Although the heating of **1**･**LB** lead to the Ge atom transfer to other chemical species, the reaction was inhibited by Lewis-bases formed simultaneously. On the other hand, the addition of $MgBr_2$•OEt_2 as a Lewis-base scavenger was effective to promote the transfer reaction.

Keywords : Germanium, Single Atom Transfer Reaction, Germylene, NHC, Cluster Compound

近年、ケイ素やゲルマニウムを主骨格とするクラスター化合物、とりわけ置換基を持たない“naked vertex”を持つかご状化合物（不飽和クラスター）に注目が集まっている。しかし高周期 14 族元素では、炭素のような多彩な骨格形成反応は開発されておらず､特に naked vertex の形成に関して多くの課題が残されている。一方ごく最近、高周期 14 族元素の単原子輸送反応 1)が報告されるようになり、新たな不飽和クラスター化合物合成への展開が期待されている。

すでに我々は､フェニルアニオンのゲルマニウム類縁体であるゲルマベンゼニルアニオンとジブロモジゲルメンを用いた Ge 原子輸送反応を報告している 2)。この反応では初期中間体としてゲルマベンゼニルゲルミレン **1** が生成する。**1** は Lewis 塩基錯体 **1**･**LB** (LB = PMe_3 or NHC;–NHC = $Im^{iPr2Me2}$)として単離可能であったため、**1**･**LB** の反応性、特にそれらを用いた Ge 原子輸送試反応ついて検討した。**1**･**LB** は、加熱によって Ge 原子輸送反応を起こすものの、同時に生成するルイス塩基によりその反応が阻害されることがわかった。そこで、ルイス塩基捕捉剤として $MgBr_2$･OEt_2 を共存させたところ、反応の効率が大幅に向上した。ジブロモジゲルメン **2** との反応ではプロペラン骨格を持つ **3** が、かさ高いアジドとの反応では GeN_4 五員環化合物 **5** が生成した。



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2位に2価ゲルマニウムを有する1,2,3-トリゲルマビシクロ[1.1.0]ブタンの合成とその骨格変換

（京大化研[1]・富山大都市デ[2]）○内田 大地[1]・水畑 吉行[1]・時任 宣博[1]・山田 容子[1]・行本 万里子[2]

Synthesis of 1,2,3-Trigermabicyclo[1.1.0]butane with a Divalent Germanium at the 2-Position and Its Skeletal Transformation

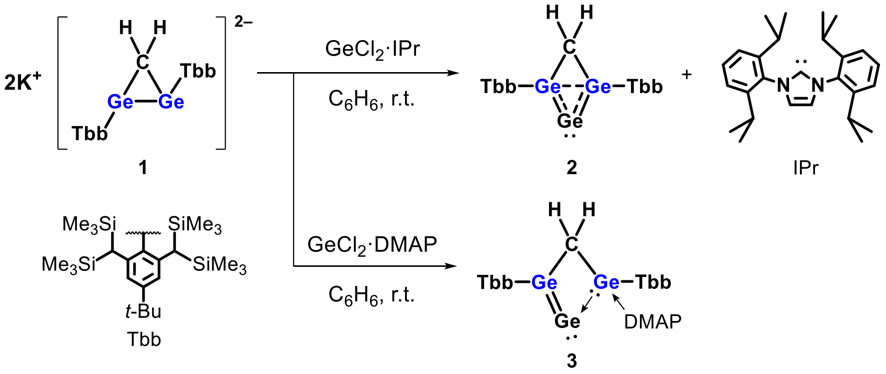
([1]*Institute for Chemical Research, Kyoto University*, [2]*School of Sustainable Design, University of Toyama*) ○Daichi Uchida,[1] Yoshiyuki Mizuhata,[1] Norihiro Tokitoh,[1] Hiroko Yamada,[1] Mariko Yukimoto[2]

Bicyclo[1.1.0]butane is a kind of bicyclic compounds in which two cyclopropane rings share a carbon-carbon bond. As for the heavier group 14 element analogues of bicyclo[1.1.0]butanes, they often exhibit properties as bond-stretch isomers and undergo skeletal transformation to valence isomers. In this study, we synthesized 1,2,3-trigermabicyclo[1.1.0]butane **2** having a divalent germanium at the 2-position by the reaction of dianion **1** with $GeCl_2$·IPr. In addition, it was confirmed that the reaction of **1** with $GeCl_2$·DMAP did not give **2**-type product but resulted in the skeletal conversion to the corresponding ylidene form **3**.

Keywords : Bicyclo[1.1.0]butane; X-Ray Crystallographic Structural Analysis; Germanium; Highly Reactive Species

ビシクロ[1.1.0]ブタンは、2 つのシクロプロパン環が炭素—炭素結合を共有する二環式化合物の 1 つである。ビシクロ[1.1.0]ブタンの高周期元素類縁体においては、2 つの橋頭位の原子を繋ぐ単結合の長さが異なる”*bond-stretch isomer*”や、熱による原子価異性体への骨格変換が知られている 1)。

本研究では、かさ高いアリール置換基である Tbb 基を導入したジアニオン **1** と $GeCl_2$·IPr との反応により、2 位に 2 価ゲルマニウムを有する 1,2,3-トリゲルマビシクロ[1.1.0]ブタン **2** の合成を行った。**2** はX線結晶構造解析により構造を決定した。また、**1** と $GeCl_2$·DMAP との反応においては、DMAP が 1 位のゲルマニウムに配位することにより、イリデン型の寄与が大きい DMAP 錯体 **3** が生成することが明らかとなった。**2** と **3** の構造的特徴およびその性質について併せて報告する。



1) V. Ya. Lee, O. A. Gapurenko, *Chem. Asian J.* **2023**, *18*, e202300903.

Synthesis, characterization, and reactivity of a novel di(μ-hydrido) dirhodium(II) complex bearing a reduced macrocyclic PDI ligand

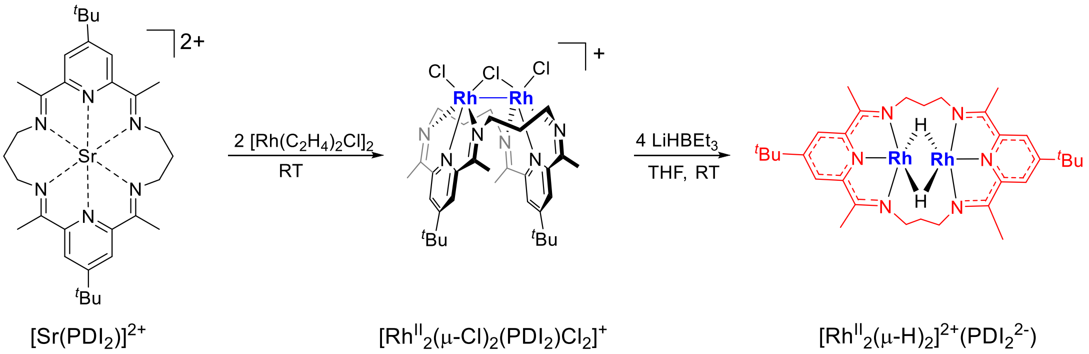
([1]*Graduate of Engineering, Nagoya University*) ○Liping YAN,[1] Yuma Morimoto,[1] Makoto Yamashita[1]

Keywords: Dirhodium Complex, Macrocyclic Ligand, Hydride, Redox Active Ligand

Dinuclear metal complexes, promising in versatile catalytic applications, derive their functions from the coordination environments of each metal centers as well as the arrangement of the metal centers. However, the impact of the distance and relative position of the metal centers on the redox properties and cooperativity in chemical reactions remains a challenging aspect, posing hurdles for the efficient design of dinuclear metal catalysts. Catalytic ability of mononuclear metal complexes with pyridinediimine (PDI) ligand, a NNN pincer-type ligand, have been extensively explored, owing to the redox behavior, the high designability, and the robustness of the ligands. We herein report synthesis and characterization of a novel dirhodium system supported by a macrocyclic ligand (PDI_2) consisting of two PDI moieties and a propylene linker (PDI_2), and investigated their catalytic activity in hydrogenation.

A strontium complex having PDI_2 was treated with $[Rh(C_2H_4)_2Cl]_2$ to give a dinuclear rhodium(II) complex $[Rh^{II}_2(\mu\text{-}Cl)_2(PDI_2)Cl_2]^+$ in 72% yield (**Scheme 1**). Further treatment of this complex with $LiHBEt_3$ (4 equiv.) in THF quantitatively yielded a dirhodium(II) dihydride complex $[Rh^{II}_2(\mu\text{-}H)_2]^{2+}(PDI_2^{2-})$, which was characterized by ^1H NMR spectrum exhibiting a hydride signal (triplet, 2H, –9.8 ppm) and single crystal X-ray diffraction analysis. The Rh–Rh distance was elongated from 2.5804(6) Å to 2.8286(8) Å upon hydride reduction of the complex with a change in ligand folding structure, indicating the decrease of the Rh–Rh interaction. The PDI moieties were determined to have a reduced state based on the numerical analysis of change in bond-lengths and a characteristic absorption band in the UV-vis spectrum (620 nm, 1600 M^{-1} cm^{-1}). The electronic structure of $[Rh^{II}_2(\mu\text{-}H)_2]^{2+}(PDI_2^{2-})$ was further elucidated with density functional theory (DFT) calculations. In this talk, the catalytic activity of $[Rh^{II}_2(\mu\text{-}H)_2]^{2+}(PDI_2^{2-})$ in hydrogenation reactions will also be discussed.

Scheme 1. Synthesis of $[Rh^{II}_2(\mu\text{-}H)_2]^{2+}(PDI_2^{2-})$



Assessment of Binding Affinity and Identification of Binding Sites of Complexes of *tert*-Butylcalix[4]thiacrown-5 with Mercury(II) Compounds with a Focus on Ring Current Effects in ^{1}H-NMR Spectra

([1]*Faculty of Pharmaceutical Sciences, Kobe Gakuin University*, [2]*Graduate School of Human and Environmental Studies, Kyoto University*) ○Tatsuya Takimoto[1], Yuu Hashimoto[1], Gen Inoue[1], Hiroki Takahashi[2], Hirohito Tsue[2], Kazuhito Hioki[1], Hideaki Sasaki[1], Deqi Yuan[1]

Keywords: *tert*-Butylcalix[4]thiacrown-5; Mercury(II) Complexes with Calix[4]thiacrown; NMR Titration; Ring Current Effect; Computational Simulation

We are currently engaged in the development of adsorbents to capture harmful organic mercury compounds in the human body and have previously reported on the potential of *tert*-butylcalix[4]thiacrown-5 (**CS4SC5**) as an adsorbent. Presently, we are working on the development of evaluation methods to conveniently assess its encapsulation ability. In this study, based on the changes in ^{1}H-NMR spectra chemical shifts induced by the ring current effects of the aromatic ring within the compound, we were able to conveniently identify the encapsulation ability and binding sites of **CS4SC5** for organic mercury compound models.

We investigated the affinity of the crown moiety of **CS4SC5** to inorganic compounds, NaI, KF, CsF, $CaCl_2$, $HgCl_2$, and $HgBr_2$, and organic mercury models, $Hg(CH_3COO)_2$ and $Hg(Pic)_2$ using ^{1}H-NMR technique. Only in the presence of the mercury(II) compounds, the change of spectra was observed; the signals of two ^{1}H nuclei of the crown moiety of **CS4SC5** shifted downfield. This phenomenon exhibited that the thiacrown moiety traps the mercury(II) compounds with high selectivity. Furthermore, it was found that the changes in the conformation of the calix[4]arene moiety were observed depending on the strength of **CS4SC5** binding with the mercury(II) compounds. The degree of transition of protons of *tert*-butyl groups and phenyl rings allowed the calculation of binding constants that were also discovered. While focusing on the degree of transition of these protons, the binding constants of **CS4SC5** with the mercury(II) compounds, including $HgCl_2$, $HgBr_2$, and $Hg(CH_3COO)_2$, were estimated using ^{1}H-NMR titration. **CS4SC5** showed the highest affinity to $Hg(CH_3COO)_2$ among the three compounds, with a binding constant of $7.5x10^4$ M^{-1}. That is, **CS4SC5** has a much higher affinity to $Hg(CH_3COO)_2$ than to the inorganic compounds. To investigate **CS4SC5** of the higher affinity for the organic mercury models, a method for a convenient comparison of binding affinities was proposed using the ring current effect and semiempirical simulation, SCIGRESS. Finally, the binding sites was also estimated using it.

配位子保護金クラスターの位置選択的な配位子脱離反応

（兵庫県大院工 [1]、京大化研 [2]、京大院理 [3]）○鈴木 航 [1]・高畑 遼 [2,3]・寺西 利治 [2,3]・梅山 有和 [1]

Regioselective ligand elimination reactions on gold nanoclusters

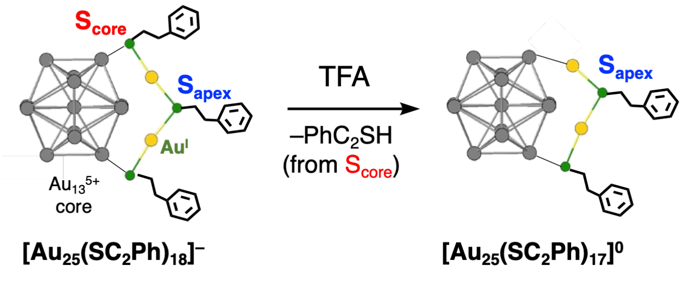
([1]*Graduate School of Engineering, University of Hyogo*, [2]*Institute for Chemical Research, Kyoto University*, [3]*Graduate School of Science, Kyoto University*) ○Wataru Suzuki[1], Ryo Takahata[2,3], Toshiharu Teranishi[2,3], Tomokazu Umeyama[1]

Elimination of organic ligands from ligand-protected gold nanoclusters is one of the simplest methods to improve their catalytic reactivities by generating exposed metal-core as active sites. In this work, we found the regioselective ligand elimination reaction of thiolate-protected Au_{25} cluster ($[Au_{25}(SR)_{18}]^q$, q = –1, 0, +1) through the protonation of a thiolate ligand by strong Brønsted acid. It has been revealed that the reactivities of ligand removal could be controlled by the oxidation states of $[Au_{25}(SR)_{18}]^q$ or solvent polarity. The formed ligand-eliminated species, $[Au_{25}(SR)_{17}]^0$, was too unstable to be isolated, suggesting the high reactivity of core-exposed metal nanoclusters.

Keywords : Ligand-protected gold nanocluster, Protonation, Regioselectivity, Oxidation state

金属ナノ材料の表面に存在する有機配位子の脱離は、材料の触媒反応活性を向上させるための最もシンプルかつ汎用的な方法である[1)]。しかしながら、脱離させる配位子数や脱離位置を精密に制御可能な手法は未だ知られていない。本研究では、フェニルエタンチオラート保護金 25 量体$[Au_{25}(SC_2Ph)_{18}]^-$に対するブレンステッド酸の添加により、位置選択的に配位子脱離反応が進行することを見出した。

$[Au_{25}(SC_2Ph)_{18}]^-$のトルエン溶液に対してトリフルオロ酢酸（TFA）を過剰量添加したところ、チオラート配位子($^-SC_2Ph$)がプロトン化されたフェニルエタンチオール(PhC_2SH)の生成が ^1H NMR 測定より確認された。生成した PhC_2SH を定量したところ、一つの$[Au_{25}(SC_2Ph)_{18}]^-$に対し PhC_2SH が 1 分子生成することが明らかとなり、選択的な配位子脱離体($[Au_{25}(SC_2Ph)_{17}]^0$)の生成が示唆された。加えて、$[Au_{25}(SC_2Ph)_{18}]^-$の 1 電子酸化体($[Au_{25}(SC_2Ph)_{18}]^0$)との配位子脱離反応性の比較や理論計算による推定等から、Scheme 1 に示したように$[Au_{25}(SC_2Ph)_{18}]^-$中の 2 種類のチオラート配位子(S_{core}, S_{apex})のうち、Au_{13} コアに直接結合した S_{core} 配位子が位置選択的に脱離していることが示唆された。



Scheme 1. $[Au_{25}(SC_2Ph)_{18}]^-$の位置選択的な配位子脱離反応
(配位子は一部省略)

1) J. S. Yoo, D. Lee and co-workers, *Angew. Chem. Int. Ed.* **2021**, *60,* 14563.

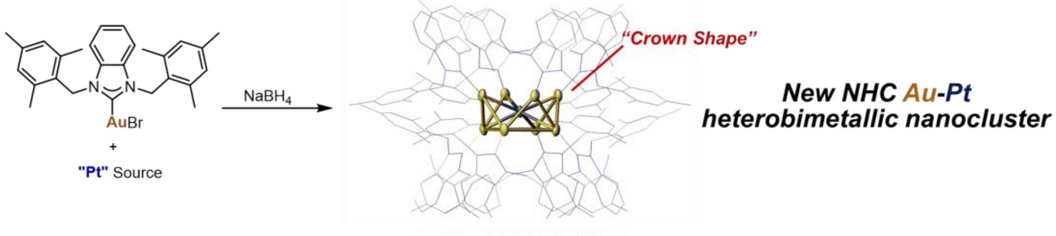
Sterically Demanding *N*-Heterocyclic Carbene Results in Selective Formation and Isolation of Au_8Pt Nanocluster

(*[1]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, [2]Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, [3]Department of Chemistry, Graduate School of Science, Nagoya University, [4]Department of Chemistry, Queen's University*) ○Joseph F. DeJesus,[1] Yoshitaka Aramaki,[2] Samuel I. Jacob,[1] Quan Manh Phung,[1,3] Takashi Ooi,[1,2] Masakazu Nambo,[1,3] Cathleen M. Crudden[1,4]

Keywords: gold, platinum, NHC, nanocluster

Utilization of *N*-heterocyclic carbenes (NHCs) as a ligand platform for nanomaterials has received increased attention in recent years, due to generally enhanced thermal and oxidative conferred by the NHCs over phosphine and thiolate ligands. Our group[1-3] and others[4-6] have recently utilized Au-NHC complexes to synthesize atomically precise nanoclusters (NCs) that possess enhanced thermal stability and greatly enhanced photophysical properties. However, beyond gold, there are very few examples of heterometallic Au NHC clusters.[7,8] No examples of Au-Pt heterobimetallic NHC clusters exist, which may possess desirable catalytic properties.

This presentation details the synthesis and characterization of an NHC adorned Au-Pt NHC cluster through the straightforward reduction of the corresponding NHC-AuBr complex with $NaBH_4$ in presence of a Pt source, resulting in a crown shaped $[Au_8Pt(NHC)_8](Br)_2$ cluster. This route was viable with a variety of Pt sources, as well as with both electron-rich and electron-poor NHC ligands. High selectivity for the desired cluster allowed for isolation without chromatography. This cluster was fully characterized by multinuclear NMR, ESI-MS and UV-Vis spectroscopies. Additionally, three NHC clusters were unambiguously characterized by SCXRD analysis, confirming the crown shaped core and chemical composition. The clusters were examined electrochemically to yield preliminary information regarding reactivity. Moreover, due to high selectivity towards productive cluster formation, it was possible to monitor cluster formation through in-situ ESI-MS experiments.



$[Au_8Pt(NHC)_8]^{2+}$

1) Narouz, M. R. *et al. JACS*, **2019**, *141*, 14997. 2) Lummis, P. A. *et al. JACS Au*. **2022**, *2*, 875. 3) Yi, H. *et. al. Chem. Sci.* **2021**, *12*, 10436. 4) Shen, M. R. *et. al. JACS,* **2022**, *144*, 10844. 5) Hirano K., *et. al. J. Phys. Chem. C*, **2021**, *125*, 9930. 6) Luo, P. *et. al. Adv. Opt. Mater.* **2021**, *9*, 2001936. 7) Shen, H. *et. al. Chem. Sci.* **2022**, *8*, 2380. 8) Lei, Z. *et. al. Nat. Comm.* **2022**, *13*, 4288.

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18日(月) 13:00 ~ 15:40 E1111(11号館 [1階] 1111)

[E1111-1pm] 10. 有機化学—有機金属化合物

座長：高橋 講平、兒玉 拓也

英語

13:00 ~ 13:20

[E1111-1pm-01]

Pd触媒によるブロモアレーンの脱芳香族的二官能基化と不斉反応への展開

〇加藤 弘基[1]、山口 滋[2]、武藤 慶[1]、山口 潤一郎[1] (1. 早稲田大学、2. 理研CSRS)

英語

13:20 ~ 13:40

[E1111-1pm-02]

Nickel-Catalyzed C(sp^3)−O Hydrogenolysis via a Remote Concerted Oxidative Addition and its Application to Degradation of a Bisphenol A-Based Epoxy Resin

〇Yumeng Liao[1], Kohei Takahashi[1], Kyoko Nozaki[1] (1. The University of Tokyo)

英語

13:40 ~ 14:00

[E1111-1pm-03]

触媒的炭素ー水素結合活性化による含七員環ナノカーボンの合成

〇山田 圭悟[1]、Iain Stepek[1]、松岡 和[1]、伊藤 英人[1]、伊丹 健一郎[1] (1. 名大)

14:00 ~ 14:20

休憩

英語

14:20 ~ 14:40

[E1111-1pm-04]

パラジウムフィッシャー型カルベン中間体を経るアシルシランとイミンと一酸化炭素との反応による触媒的β—ラクタム合成

〇稲垣 徹哉[1]、兒玉 拓也[1,2]、鳶巣 守[1,2] (1. 阪大院工、2. ICS-OTRI)

英語

14:40 ~ 15:00

[E1111-1pm-05]

Nickel-Catalyzed Cross-Coupling of Allyl Ethers with Organoboron Reagents: A Remarkable Effect of Pyrimidine

〇Thakun Chen[1], Takanori Iwasaki[1], Kyoko Nozaki[1] (1. The University of Tokyo)

英語

15:00 ~ 15:20

[E1111-1pm-06]

配向基を導入したポリエーテルエーテルケトン誘導体の合成とニッケル触媒による炭素–酸素結合切断を経るモノマーへの制御分解

〇小川 敏史[1]、徐 于懿[1]、宇山 浩[1]、鳶巣 守[1,2] (1. 阪大院工、2. ICS-OTRI)

英語

15:20 ~ 15:40

[E1111-1pm-07]

Enantiospecific Cross-coupling of Cyclic Alkyl Sulfones

〇Roberto Nolla Saltiel[1,2], Zachary T. Ariki[2], Stefanie Schiele[2], Jana Alpin[2], Yasuyo Tahara[1], Masakazu Nambo[1,4], Cathleen M. Crudden[2,1,3] (1. Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya, Aichi 464-8601, Japan., 2. Department of Chemistry, Queen's University, Chernoff Hall, Kingston Ontario, Canada., 3. Carbon to Metal Coating Institute, Queen's University, Kingston, Ontario, K7L 3N6, Canada., 4. Department of Chemistry, Graduate School of Science, Nagoya University; Furo, Chikusa, Nagoya, Aichi, 464-8601, Japan.)

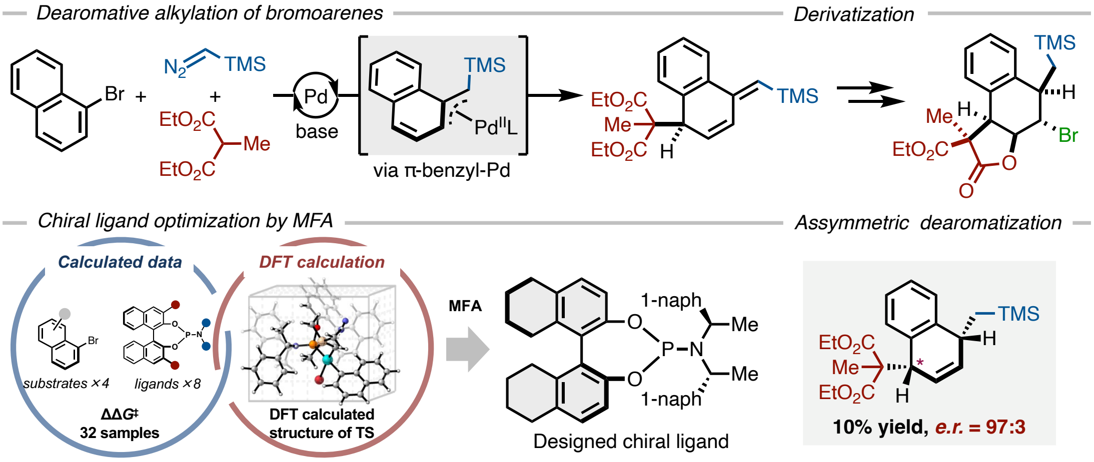
Pd-Catalyzed Dearomative Difunctionalization of Bromoarenes and Its Enantioselective Approach

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*RIKEN CSRS*, [3]*Institute for Advanced Study, Waseda University*) ○ Hiroki Kato,[1] Shigeru Yamaguchi,[2] Kei Muto,[3] Junichiro Yamaguchi[1]

Keywords: Dearomative Functionalization; π-Benzyl Palladium; Asymmetric Catalyst; Molecular Field Analysis; Alicyclic Compound

Dearomative functionalization is a powerful method to construct structurally complex alicyclic frameworks from simple and abundant aromatic molecules. Although many dearomative functionalizations have been reported so far, the reaction of electron-neutral arenes such as benzenes and naphthalenes are a still challenging issue due to their high aromatic stability.[1]

In this work, we developed a Pd-catalyzed dearomative alkylation of bromoarenes with diazo compounds and malonate.[2] This reaction is thought to proceed via the generation of a Pd-carbene followed by a π-benzyl-Pd intermediate. Various arenes ranging from benzenoids to heteroarenes were applicable to this reaction. The utility of this reaction was demonstrated by the diastereoselective derivatization of product, resulting in a formation of densely functionalized alicyclic compounds. Furthermore, in the pursuit of achieving asymmetric version of this reaction, we endeavored to design a chiral ligand using a data-driven approach, specifically employing molecular field analysis (MFA).[3] This approach facilitated the efficient identification of a chiral ligand that exhibited notable enantioselectivity (up to *e.r.* = 97:3), albeit with modest yields.



1) Wertjes, W. C.; Southgate, E. H.; Sarlah, D. *Chem. Soc. Rev.* **2018**, *47*, 7996–8017.
2) Kato, H.; Musha, I.; Komatsuda, M.; Muto, K.; Yamaguchi, J. *Chem. Sci.* **2020**, *11*, 8779–8784.
3) Yamaguchi, S. *Org. Biomol. Chem.* **2022**, *20*, 6057–6071.

Nickel-Catalyzed C(sp^3)–O Hydrogenolysis via a Remote-Concerted Oxidative Addition and its Application to Degradation of a Bisphenol A-Based Epoxy Resin

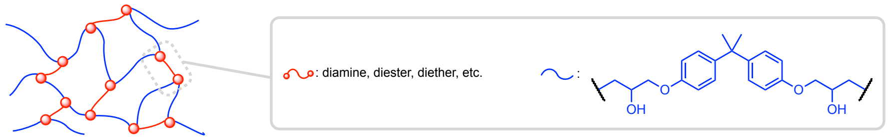
([1]*Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo*) ○Yumeng Liao,[1] Kohei Takahashi,[1] Kyoko Nozaki[1]

Keywords: C–O Hydrogenolysis, Remote Oxidative Addition, Epoxy Resin.

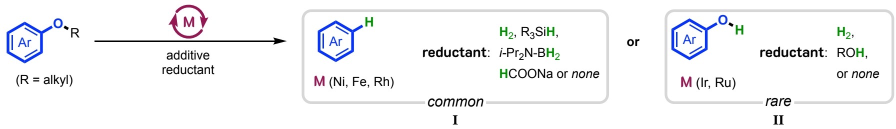
Ethereal C–O bond is a fundamental connection in plastic materials as the building block including bisphenol A (BPA)-based epoxy resins (Figure 1a).[1] The selective and reductive cleavage of ethereal C(sp^3)–O bonds to C–H and O–H bonds is attractive since it allows the direct recovery of BPA as an appealing recycling approach for gaining valuable chemical feedstocks from discarded plastic wastes. Over a decade, transition metal-catalyzed reductive cleavage of ethereal C–O bonds has been extensively developed with Ni, Fe, or Rh targeted C(sp^2)–O bonds and Ir or Ru targeted C(sp^3)–O bonds, especially Ru contributed to the hydrogenolysis of C(sp^3)–O bonds in lignin-related polymers and epoxy resin (Figure 1a&b).[2,3]

Here, we report a nickel-catalyzed transfer hydrogenolysis of β-hydroxyalkyl aryl ethers to afford arenols selectively. Mechanistic investigation revealed that the hydroxy group acts as the hydrogen donor to generate α-aryloxy ketone, which undergoes a concerted-remote oxidative addition of the C(sp^3)–O bond as suggested by DFT calculation. Successful application of this method was demonstrated by the degradation of a diamine-cured BPA-based epoxy resin, where BPA was directly recovered from the resin (Figure 1c).

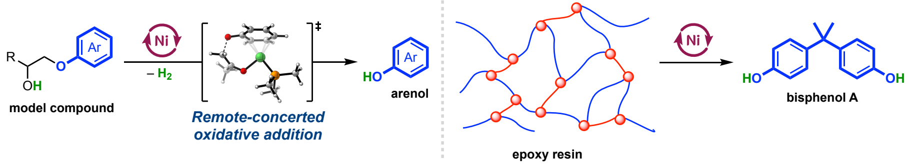
(a) General structure of BPA-based epoxy resin



(b) Transition metal-catalyzed reductive cleavage of ethereal C−O bond



(c) This work



✓ excellent C(sp^3)–O selectivity ✓ additive-free transfer hydrogenolysis ✓ computational and crystallographic study

1) B. Ellis, *Introduction to the chemistry, synthesis, manufacture and characterization of epoxy resins,* **1993**, 37. 2) J. M. Nichols *et al. J. Am. Chem. Soc.* **2010**, *132*, 12554. 3) A. Ahrens *et al. Nature* **2023**, *617*, 730.

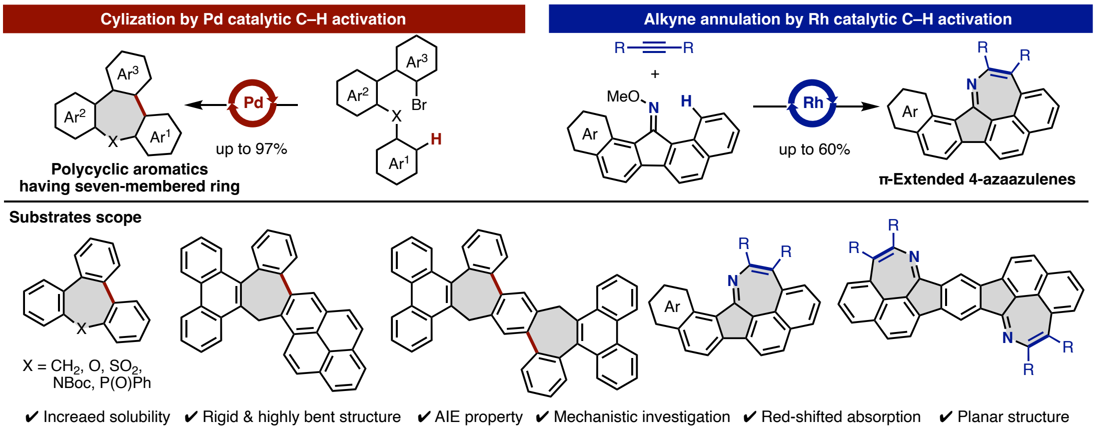
Synthesis of Heptagon-Containing Nanocarbons by Catalytic C–H Activation

([1]*Graduate School of Science, Nagoya University*) ○Keigo E. Yamada,[1] Iain A. Stepek,[1] Wataru Matsuoka,[1] Hideto Ito,[1] Kenichiro Itami[1]

Keywords: Transition Metal Catalyst; π-Extension; Nanocarbon; Polycyclic Aromatic Hydrocarbon; Seven-Membered Ring

The precise incorporation of seven-membered rings and azulene units in nanocarbon materials often leads to appealing topological, optoelectronic, aromatic and magnetic properties. Thorough investigations into the huge potential of heptagon-embedded molecular nanocarbons in materials science have been limited by difficulties encountered in their synthesis.[1]

Herein, we report on general and efficient novel methods for synthesis of heptagon-containing nanocarbons by Pd- and Rh-catalyzed intra- and intermolecular cross-coupling reactions involving a catalytic C–H bond activation. In the Pd-catalyzed seven-membered ring construction method, a wide range of heptagon-containing polycyclic (hetero)arenes were obtained from bromoarenes in good yields.[2] In the Rh-catalyzed seven-membered ring construction method, we achieved to synthesize π-extended 4-aza-azulenes by alkyne annulation using benzofluorenone methyl oxime derivatives. With the obtained heptagonal nanocarbons by both methods, we thoroughly investigated on structural and physicochemical properties by X-ray diffraction analyses, measurements of absorption and emission and DFT calculations, and elucidated unique properties such as increased solubility, aggregation-induced emission, red-shifted absorption, bent and planar structures, aromaticity and so on. Furthermore, we also demonstrated the mechanistic study on Pd-catalyzed seven-membered ring formation by DFT calculations.



[1] Chaolumen, I. A. Stepek, K. E. Yamada, H. Ito, K. Itami, *Angew. Chem., Int. Ed.* **2021**, *60*, 23508-23532.

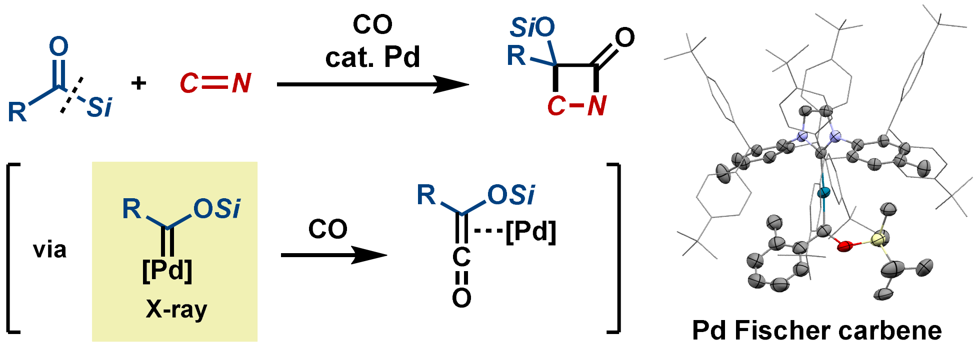
[2] K. E. Yamada, I. A. Stepek, W. Matsuoka, H. Ito, K. Itami, *Angew. Chem., Int. Ed.* **2023**, *62*, e202311770.

Catalytic Synthesis of β-Lactams by the Reaction of Acylsilanes, Imines and Carbon Monoxide via a Palladium Fischer Carbene Intermediate

([1]*Graduate School of Engineering, Osaka University*, [2]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University*) ○Tetsuya Inagaki,[1] Takuya Kodama,[1,2] Mamoru Tobisu[1,2]

Keywords: Palladium Catalysis; Acylsilanes; Imines; β-Lactam; Fischer Carbene Complex

Fischer carbene complexes are characterized by the presence of a π-donating group (mainly an alkoxy group) on the carbene carbon. Although these complexes are recognized as powerful reagents for organic synthesis, catalytic reactions that involve Fischer carbene complexes have been limited.[1] We recently reported that Fischer carbenes can be generated in situ from acylsilanes by palladium catalysis, which is successfully applied to siloxycyclopropanation of alkenes.[2] Among the most useful reactions using Fischer carbene complexes is the synthesis of β-lactams via photo-induced reaction of chromium-carbenes with imines.[3] We report herein on the development of the catalytic variant of the β-lactam synthesis by using our palladium-catalyzed protocol.[4] A key palladium-siloxycarbene intermediate complex is isolated and successfully characterized by X-ray crystallography.



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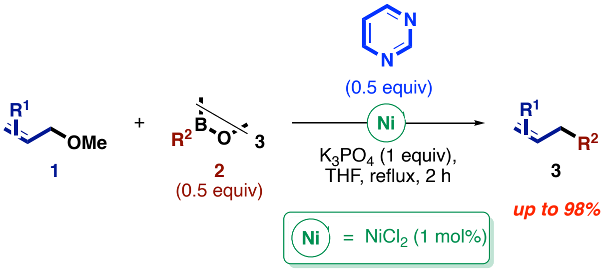
Nickel-Catalyzed Cross-Coupling of Allyl Ethers with Organoboron Reagents: A Remarkable Effect of Pyrimidine

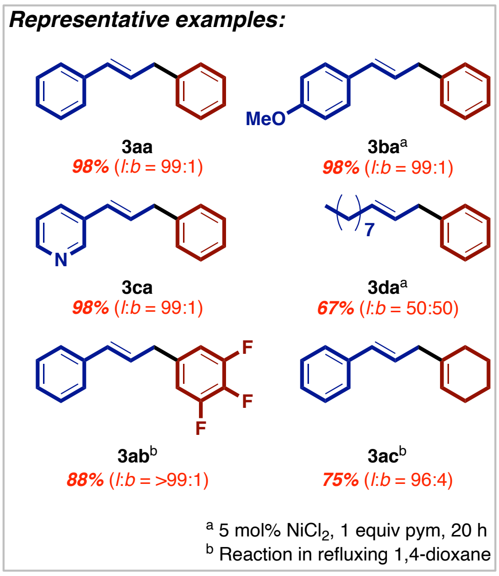
(*Graduate School of Engineering, The University of Tokyo*) ○Thakun Chen, Takanori Iwasaki, Kyoko Nozaki

Keywords: Allylic Substitution; Cross-Coupling; Ether; Nickel; Pyrimidine

Transformations at the allylic position are ubiquitous in organic synthesis, typically proceeding under transition metal catalysis. Although the environmental benignity and relatively low toxicity of allyl ethers make them alluring feedstocks for allylic substitution, they still face limited use due to the poor leaving ability of alkoxy groups. While the coupling of allyl ethers has been reported with highly reactive organometallic nucleophiles, Suzuki–Miyaura-type coupling with an organoboron compound remains attractive due to its greater functional group tolerance and more facile accessibility. Indeed, there exist two reports of such a transformation, though one which is catalyzed by nickel suffers from low activity,[1] while the other under palladium catalysis is uneconomical.[2] Herein, we developed an efficient nickel-catalyzed protocol for the cross-coupling of allyl ethers utilizing cheaply-available reagents; in particular, a remarkable accelerative effect of pyrimidine was observed.

We discovered that the addition of catalytic amounts of pyrimidine and $NiCl_2$ to a mixture of an allyl methyl ether (**1**), a boroxine (**2**), and K_3PO_4 as base regioselectively provided the linear coupling product (**3**) in excellent yields. While the present catalytic system could be applied to a wide variety of aromatic allyl ethers, aliphatic ethers suffered from lowered yields and regioselectivity. Aryl and vinyl boroxines coupled with allylic ethers to yield $C(sp^3)–C(sp^2)$ coupling products in good to excellent yields. Under the same reaction conditions, allyl alkyl and silyl ethers, and even allyl alcohols and fluorides, were applicable in the cross-coupling reaction to varying degrees.





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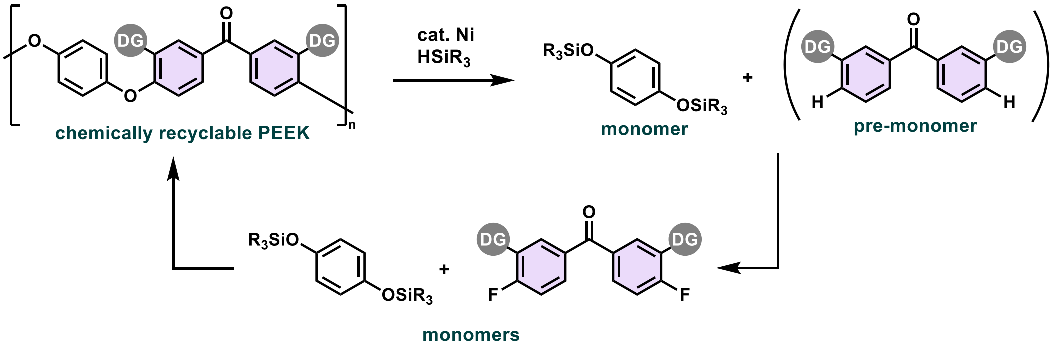
Synthesis and Controlled Depolymerization of Poly(ether ether ketone) Bearing a Directing Group

([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka University*)
○Satoshi Ogawa,[1] Yu-I Hsu,[1,2] Hiroshi Uyama,[1] Mamoru Tobisu[1, 2]

Keywords: Poly(ether ether ketone); Nickel Catalyst; C–O Activation; Chemical Recycling

In recent years, development of functional polymers that can be depolymerized into monomers is becoming increasingly important for establishing sustainable society. Despite the importance, chemically depolymerizable polymers are primarily limited to those containing hydrolyzable groups in their backbone (e.g., polyesters, polycarbonates, and polyamides).[1] Therefore, depolymerization of functional polymers that do not contain hydrolyzable groups in the main chain poses a principal challenge. Herein, we report on the synthesis of a poly(ether ether ketone)[2] bearing a directing group, which is designed for chemical recycling. Controlled depolymerization of this polymer can be achieved by nickel-catalyzed cleavage of C–O bonds in the polymer backbone.



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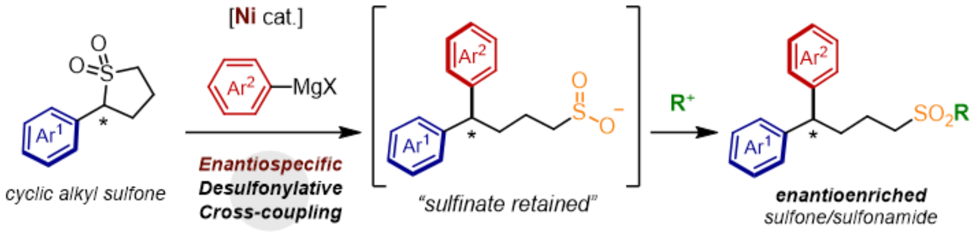
Enantiospecific Cross-coupling of Cyclic Alkyl Sulfones

(*[1]Department of Chemistry, Queen's University, [2]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, [3]Carbon to Metal Coating Institute, Queen's University, [4]Department of Chemistry, Graduate School of Science, Nagoya University.*)
○ Roberto Nolla-Saltiel,[1,2] Zachary T. Ariki,[1] Stefanie Schiele,[1] Jana Alpin,[1] Yasuyo Tahara,[2] Masakazu Nambo[2,4] and Cathleen M. Crudden[1,2,3]

Keywords: Sulfones; Stereochemistry; Nickel catalysis; Cross-coupling; Carbon–sulfonyl bond activation

Methods to form carbon-carbon bonds efficiently and with control of stereochemistry are critical for the construction of complex molecules. Cross-coupling reactions are among the most efficient and widely used reactions for this effect, with reactions enabling the retention or installation of chirality as recent additions to this powerful toolbox. Sulfones are robust, accessible organic electrophiles that have many attractive features as cross-coupling partners.[1] Our groups have demonstrated the versatility of sulfones as both directing groups and electrophiles in metal-catalyzed cross-coupling reactions.[2]

Despite significant progress in desulfonylative cross-couplings, one major limitation remains: enantioselective or enantiospecific cross-coupling of sulfones have yet to be demonstrated. Considering the importance of chiral molecules in materials science and medicinal chemistry, this is an area that must be addressed. More importantly, the ability of sulfones to increase the acidity of α-protons brings into question whether stereospecific cross-couplings would even be possible. We will present our work pertaining to the enantiospecific cross-coupling of cyclic sulfones and Grignard reagents.[3] Up to 99% chirality transfer is observed despite the strong basicity of the Grignard components. In situ monitoring reveals that the cross-coupling is kinetically viable with competing deprotonation, resulting in a highly enantioselective transformation.



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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18日(月) 13:00 ~ 15:40 E1112(11号館 [1階] 1112)

[E1112-1pm] 10. 有機化学—有機金属化合物

座長：伊藤 繁和、山本 武司

日本語

13:00 ~ 13:20

[E1112-1pm-01]

動的らせん高分子骨格を有するキラリティ可変ホスホロアミダイト配位子の開発

〇松本 祐輔[1]、藤江 峻也[1]、山本 武司[1]、杉野目 道紀[1] (1. 京都大学)

英語

13:20 ~ 13:40

[E1112-1pm-02]

銅触媒を用いた1-トリフルオロメチルチオアルケンのヒドロホウ素化およびヒドロアリル化

〇小島 有貴[1]、平野 康次[1] (1. 阪大院工)

英語

13:40 ~ 14:00

[E1112-1pm-03]

高い酸化力を有する銅光酸化還元触媒によるスチレンの逆マルコフニコフ型水和反応

〇奥 直樹[1]、福家 啓仁[2]、山崎 賢[2]、松井 康哲[3]、池田 浩[3]、三浦 智也[2] (1. 京大院工、2. 岡山大院環境生命自然、3. 阪公大院工)

14:00 ~ 14:20

休憩

英語

14:20 ~ 14:40

[E1112-1pm-04]

電子不足CpIr(III)触媒を利用した位置選択的なC-H官能基化の研究

〇平田 裕己[1,3]、木邨 俊介[2]、東田 皓介[3]、吉野 達彦[1]、松永 茂樹[3,1] (1. 北大院薬、2. 京大理、3. 京大院理)

英語

14:40 ~ 15:00

[E1112-1pm-05]

Rh/ルイス酸性金属協働触媒による$C(sp^3)$–O 結合の還元的シリル化反応

〇関 凜[1]、城戸 春香[1]、黄 嘉名[2]、井元 郁[2]、三浦 大樹[2]、中尾 佳亮[1] (1. 京都大学　、2. 東京都立大学)

英語

15:00 ~ 15:20

[E1112-1pm-06]

Rh触媒を用いた[2+2+2]環化付加反応による含フッ素四置換不斉炭素の構築

〇濱田 慎太郎[1]、小宮 由信[1]、鈴木 俊介[1]、野上 純太郎[1]、佐藤 悠[1]、永島 佑貴[1]、田中 健[1] (1. 東工大物質理工)

英語

15:20 ~ 15:40

[E1112-1pm-07]

ロジウム錯体触媒存在下、*N*-メトキシベンズアミドと *in situ* で発生したヨードニウムイリドとの連続反応によるイソクマリンおよびイソキノロン誘導体の化学選択的合成法の開発

○金 東映[1]、三浦 理紗子[1]、木村 祐[1]、近藤 輝幸[1] (1. 京大)

動的らせん高分子骨格を有する
キラリティ可変ホスホロアミダイト配位子の開発

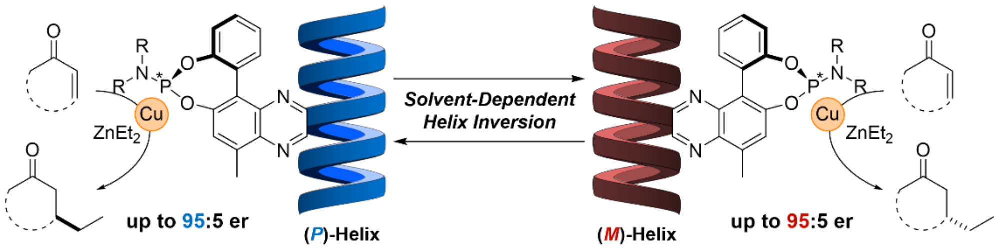
（京大院工）○松本 祐輔・藤江 峻也・山本 武司・杉野目 道紀

Chirality-Switchable Phosphoramidite Ligands Attached to Helical Poly(quinoxaline-2,3-diyl)s (*Graduate School of Engineering, Kyoto University*) ○Yusuke Matsumoto, Takaya Fujie, Takeshi Yamamoto, Michinori Suginome

Chiral phosphoramidite is one of the most privileged classes of ligand in asymmetric catalysis.[1] We previously reported chirality-switchable monophosphine and bipyridine ligands attached to dynamic helical poly(quinoxaline-2,3-diyl)s (PQXs), whose helicity can be controlled by solvents.[2] In this work, PQX-based chiral phosphoramidite ligands **PQXpham** were synthesized by post-polymerization functionalization of PQXs bearing diol units. The **PQXpham** served as chirality-switchable ligands in copper-catalyzed asymmetric conjugate addition reaction.

Keywords: Polyquinoxaline; Polymer Ligands; Post-polymerization Functionalization; Copper Catalysis; Asymmetric Conjugate Addition Reaction

キラルなジオールとアミンから合成されるホスホロアミダイトは、不斉遷移金属触媒反応において最も有効なキラル配位子の一つであり、新たな分子設計に基づいた高機能化が期待される[1]。当研究室では、キラル側鎖を有するポリ（キノキサリン-2,3-ジイル）（PQX）の溶媒による主鎖らせん不斉制御を報告しており、PQX に単座ホスフィンやビピリジン部位を導入することで立体選択性をスイッチングできるキラルらせん高分子配位子を開発している[2]。今回我々は、ジオール部位を導入した PQX の重合後修飾を行うことで、様々なアミノ基が置換したホスホロアミダイト部位を有するキラルらせん高分子配位子 (**PQXpham**)を新たに開発した。右巻きの(*P*)-**PQXpham** を配位子として用いて銅触媒による不斉共役付加反応を行ったところ、最高で 99% 収率、95:5 er の立体選択性で生成物が得られた。また、溶媒によるらせん反転によって調製した左巻きの(*M*)-**PQXpham** を用いると立体選択性が逆転し、もう一方の鏡像体が得られた。**PQXpham** の配位部位構造を模した低分子モデル配位子では、リン原子上の不斉中心は立体選択性にほとんど影響を与えなかったことから、高分子主鎖のキラルらせん構造が反応の立体選択性に大きく寄与することが示された。



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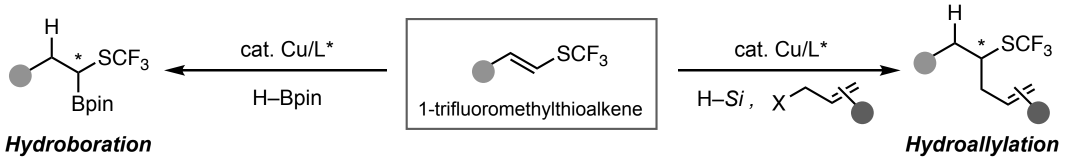
Copper-Catalyzed Hydroboration and Hydroallylation of 1-Trifluoromethylthioalkenes

(*Graduate School of Engineering, Osaka University*) ○Yuki Kojima, Koji Hirano

Keywords: Copper Catalysts; Hydroboration; Hydroallylation; Organofluorine Compounds; Trifluoromethylthio Group

Since their enhanced lipophilicity, metabolic stability, and bioavailability, organofluorine derivatives are an important class of compounds in medicinal chemistry. In particular, trifluoromethylthio (SCF_3) group has received significant attention in the design and synthesis of pharmaceuticals and agrochemicals because of its strong electron-withdrawing nature and high lipophilicity.[1] Although various methods for the synthesis of SCF_3-containing compounds have been reported,[2] it is still difficult to obtain optically active SCF_3 derivatives with high enantiopurity. Therefore, the development of efficient synthetic methods for chiral SCF_3 molecules is highly desired.

Herein, we report a copper-catalyzed regio- and enantioselective hydroboration of 1-trifluoromethylthioalkenes with pinacolborane (H–Bpin). 1-Trifluoromethylthioalkenes can be easily prepared from the corresponding alkenyl halides according to the literature methods.[3] Using the 1-trifluoromethylthioalkene as a starting platform, the in-situ generated copper hydride species undergoes the regio- and enantioselective insertion to form an optically active α-SCF_3 alkylcopper intermediate. Subsequent σ-bond metathesis with H–Bpin provides the boron-substituted SCF_3 compound in an enantioenriched form. Moreover, the copper hydride-based strategy can also be expanded to the three-component coupling reaction of 1-trifluoromethylthioalkenes, hydrosilanes, and allylic electrophiles. Also in this reaction, the judicious choice of chiral ligand induces the high regio- and enantioselectivity. These approaches can provide the chiral SCF_3 compounds, which are difficult to prepare by other means.



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高い酸化力を有する銅光酸化還元触媒によるスチレンの逆マルコフニコフ型水和反応

（京大院工[1]・岡山大院環境生命自然[2]・阪公大院工[3]）○奥 直樹[1]・福家 啓仁[2]・山崎 賢[2]・松井 康哲[3]・池田 浩[3]・三浦 智也[2]

Copper Photoredox Catalyst Exhibiting Strong Oxidizing Ability for *anti*-Markovnikov Hydration of Styrenes

([1]*Graduate School of Engineering, Kyoto University*, [2]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*, [3]*Graduate School of Engineering, Osaka Metropolitan University*) ○Naoki Oku,[1] Keito Fuke,[2] Ken Yamazaki,[2] Yasunori Matsui,[3] Hiroshi Ikeda,[3] Tomoya Miura[2]

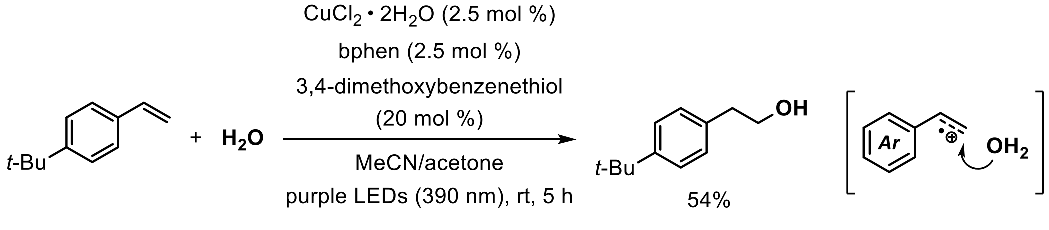
Photoredox catalysts have regained the spotlight in organic synthesis. Photoexcited catalysts act as either single-electron oxidants or reductants, generating radical ions from various organic molecules. In terms of availability and cost, the development of photoredox catalysts using abundant first-row transition metals is highly required. Here, we report a copper photoredox catalyst exhibiting strong oxidizing ability and its application to *anti*-Markovnikov hydration of styrenes.

A mixture of 4-*tert*-butylstyrene, $CuCl_2 \cdot 2H_2O$ (2.5 mol %), bathophenanthroline (bphen; 2.5 mol %), and 3,4-dimethoxybenzenethiol (20 mol %) in MeCN/acetone/H_2O (5:5:1, 4.5 mL) was irradiated with purple LEDs (390 nm) at ambient temperature. After 5 hours, the primary alcohol was formed in 60% NMR yield. Purification by preparative thin-layer chromatography gave the product in 54% isolated yield. Single-electron oxidation of styrenes proceeds by the photoexcited copper catalyst. The generated radical cations undergo a direct addition of H_2O in an *anti*-Markovnikov manner to furnish the desired alcohols.

Keywords : Copper; Photoredox Catalysis; Radicals; Hydration; anti-Markovnikov Addition

可視光酸化還元触媒は、その光励起状態が一電子酸化剤あるいは還元剤として働くことで、簡便にさまざまなラジカルイオンを発生できることが知られている。そのため入手コストの観点から、安価で入手容易な第一遷移金属を用いた光酸化還元触媒の開発は重要な研究課題である。我々は新たに開発した銅可視光酸化還元触媒を用いるスチレン類の逆マルコフニコフ型水和反応を見出したので報告する。

銅触媒およびチオール触媒の存在下、4-*tert*-ブチルスチレンをアセトニトリル/アセトン/水溶媒中、室温で可視光（390 nm）を照射しながら撹拌すると、目的の 1 級アルコールが収率 54%で得られた。本反応は光励起された銅触媒によるスチレンの一電子酸化で生じたラジカルカチオン種に対し、水が逆マルコフニコフ選択的に付加することで進行すると考えている。

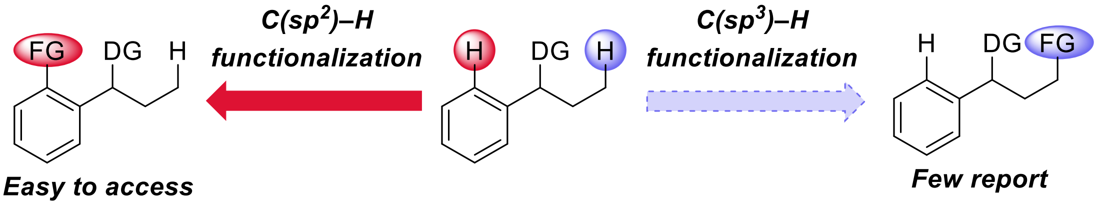


Site-selective C–H functionalization catalyzed by electron-deficient CpIr(III) catalyst

([1]*Grad. Sch. Pharm. Sci. Hokkaido Univ.*, [2]*Fac. Sci., Kyoto Univ.*, [3]*Grad. Sch. Sci. Kyoto Univ.*)
○ Yuki Hirata[1,3], Shunsuke Kimura[2], Kosuke Higashida[3], Tatsuhiko Yoshino[1], Shigeki Matsunaga[1,3]

Keywords: C–H activation, iridium catalyst

Direct C–H functionalization of inert C–H bond is known as a convenient tool that enable step- and atom-economical synthesis of various organic molecules. Group 9 transition metals (Co, Rh, Ir) bearing cyclopentadienyl ligands (Cp) show high reactivity to C–H functionalization. The mechanism of CpM(III) catalyzed C–H activation is generally proposed to proceed via concerted-metallation deprotonation (CMD), which is a concerted mechanism for hydrogen to be abstracted as a proton by a weak base such as a carboxylate. Generally, C(sp^2)–H bond cleavage step is supposed to proceed more easily than C(sp^3)–H bond due to various factor, mainly difference of Bond Dissociation Energy (BDE) and acidity of C–H bond. Therefore, C(sp^3)-H functionalization is fewer than C(sp^2)-H functionalization. In addition, when a substrate that has both C(sp^2) and C(sp^3)–H bond on accessible sites for C–H activation is used, the product from C(sp^2)–H activation or the mixture of C(sp^2) and C(sp^3)–H functionalized product or both was obtained due to C(sp^2)–H functionalization prior to C(sp^3)–H. Thus, site-selective C(sp^3)–H functionalization has been challenging, and the achievement of selective C(sp^3)–H functionalization is highly demanded towards flexible modification of molecules. Recently, several site-selective C(sp^3)–H functionalization was reported. Yu's group achieved selective C(sp^3)–H iodination by chelation-control in 2017.1) In 2018, Xu's group enabled to control its selectivity by the number of atoms in metallacycle.2) However, these reports depended on the structure of a substrate, and flexible and switchable C(sp^3)–H functionalization of compounds that have both C(sp^2) and C(sp^3)–H bond, has not been achieved by high-valent metal catalysis. Here in, we demonstrate flexible and switchable C(sp^3)–H functionalization catalyzed by electron-deficient CpIr(III) catalyst. Substrate scope as well as synthetic application will be explained in this presentation.



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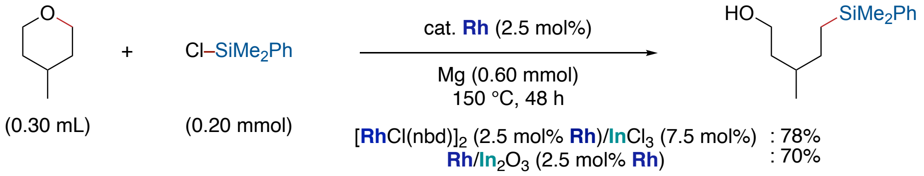
Reductive C(sp^3)–O Silylation by Cooperative Rhodium/Lewis Acidic Metal Catalysis

(*[1]Department of Material Chemistry, Graduate School of Engineering, Kyoto University, [2]Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Science, Tokyo Metropolitan University)* ○Rin Seki,[1] Haruka Kido,[1] Kana Ko,[2] Kaoru Imoto,[2] Hiroki Miura,[2] Yoshiaki Nakao[1]

Keywords: C(sp^3)–O bond, silylation, rhodium, Lewis acids, Cooperative catalysis

Alcohol and ethers represent ubiquitous structural motifs in both feedstock and fine chemicals. Abundant biopolymers such as cellulose and lignin, characterized by their primary skeletons composed of multiple C–O bonds, are anticipated as sources for organic compounds. Furthermore, the industrial synthetic process for alcohols and ethers has been established. C–O bond transformations directly edit the main skeleton of these molecules and allow access to a wide range of molecules from simple feedstock. However, the formidable chemical stability of alcohols and ethers, arising from the diminished leaving group ability of alkoxides and hydroxides, makes this difficult. Conventional transformations of alcohols and ethers have heavily relied on conversion to more facile leaving groups, such as sulfonates and phosphates, and the direct conversion of C–OR (R = alkyl, H) bonds has proven to be intricate. Recently, the Dong group[1] and the Miura and Shishido group[2,3] have reported the C(sp^3)–O bond functionalization of alkyl ethers. As elucidated above, this type of transformation has garnered substantial attention recently.

We have found that reductive C(sp^3)–O silylation catalyzed cooperatively by rhodium and Lewis acidic metals in the presence of magnesium powder. For instance, the reaction of 4-methyltetrahydropyrane (0.30 mL) with chlorodimethylphenylsilane (0.20 mmol) in the presence of $[RhCl(nbd)]_2$ (2.5 mol%), $InCl_3$ (7.5 mol%), and magnesium powder (0.60 mmol) afforded the ring-opened and C(sp^3)–O silylated product in 78% yield. We also found that rhodium nanoparticles supported on indium oxide catalyzed the same type of transformation. Experiments have suggested that the reaction is catalyzed by nanoparticles containing multi-metallic species in both conditions. We will present the results focusing on chemo-selectivity and the reaction mechanism.



1) H. Lyu, I. Kevlishvili, X. Yu, P. Liu, G. Dong *Science* **2021**, *372*, 175. 2) H. Miura, M. Doi, Y. Yasui, Y. Masaki, H. Nishio, T. Shishido *J. Am. Chem. Soc.* **2023**, *145*, 4613. 3) H. Miura, Y. Yasui, Y. Masaki, M. Doi, T. Shishido *ACS Catal.* **2023**, *13*, 6787.

Enantioselective construction of tetrasubstituted fluorine stereocenters by Rh-catalyzed [2+2+2] cycloaddition reaction

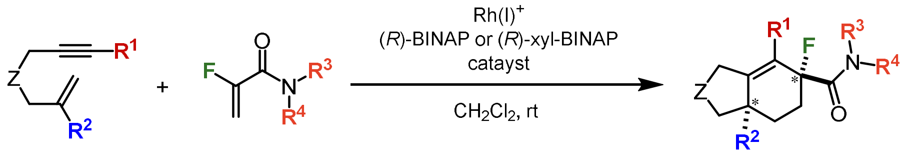
([1]*Department of Chemical Science and Engineering, Tokyo Institute of Technology*)
○Shintaro Hamada,[1] Yoshinobu Komiya,[1] Shunsuke Suzuki,[1] Juntaro Nogami,[1] Yu Sato,[1] Yuki Nagashima,[1] Ken Tanaka[1]

Keywords: *cycloaddition, C-H activation, Rhodium, fluorine*

The asymmetric construction of tetrasubstituted fluorine stereocenter is one of the most synthetically challenging areas. Although asymmetric C–F bond formation using fluorination reagents and asymmetric C–C bond formation of fluorinated compounds by nucleophilic or coupling reactions have been developed, asymmetric cycloaddition reactions of fluoroalkenes have been limited in only three reports [1].

On the other hand, our group has reported that acrylamide derivatives, which have higher coordination ability than enones and acrylates, are excellent substrates for addition reactions catalyzed by cationic Rh(I) complexes. We have established the enantioselective [2+2+2] cycloaddition reaction with acrylamides and 1,6-enynes proceeded smoothly to give chiral cyclohexene derivatives in high yields and high ee's [2].

In this presentation, we report an efficient method for constructing chiral fluorinated cyclohexene derivatives by the Rh(I)-catalyzed [2+2+2] cycloaddition reaction with fluoroacrylamides and 1,6-enynes. Detailed investigations revealed that C–H activation of acrylamides proceeds as a side reaction, and substituents and ligands control these cycloaddition and C–H activation reactions.



1

2
(1.2 equiv)

3
up to 84% yield, >99% ee

✓Enantioselective construction of tetrasubstituted fluorine stereocenter
✓High yields and high ee's
✓Substituents and Ligand controlled reaction mechanism

References:

[1] (a) Shibatomi, K.; Futatsugi, K.; Kobayashi, F.; Iwasa, S.; Yamamoto, H. *J. Am. Chem. Soc.* **2010**, *132*, 5625. (b)Hatano, M.; Mizuno, T.; Izumiseki, A.; Usami, R.; Asai, T.; Akakura, M.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 12189. (c) Kalita, S. J.; Cheng, F.; Fan, Q.-H.; Shibata, N.; Huang, Y.-Y. *J. Org. Chem.* **2021**, *86*, 8695.

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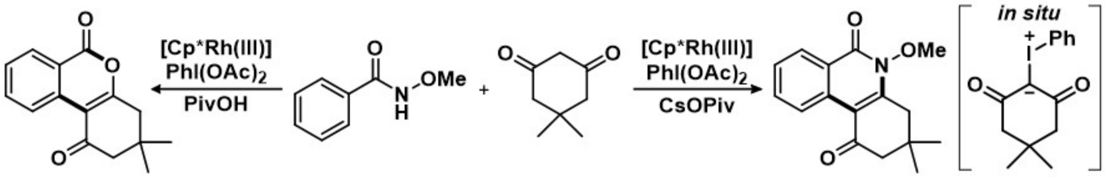
Chemodivergent Synthesis of Isocoumarins and Isoquinolones by Rhodium-catalyzed Consecutive Reaction of *N*-Methoxybenzamide with *in situ* Generated Iodonium Ylides

(*Graduate School of Engineering, Kyoto University*) ○Dongyoung Kim, Risako Miura, Yu Kimura, Teruyuki Kondo

Keywords: Rhodium; C-H activation; Heterocyclization; Isocoumarin; Isoquinolone

Over the past decade, transition metal-catalyzed direct C-H bond activation, insertion, and annulation reactions using diverse carbene precursors such as diazo compounds, sulfoxonium ylides, iodonium ylides, and others have been developed for the synthesis of various heterocyclic compounds.[1] However, almost all reactions required the preparation of carbene precursors from 1,3-dicarbonyl compounds in advance. In addition, attempts to use only 1,3-dicarbonyl compounds for catalytic construction of diverse heterocyclic scaffolds have been failed. In 2020, Li and co-workers first reported that Rh-catalyzed coupling reaction of benzoic acids with 1,3-dicarbonyl compounds gave isocoumarins, selectively, in which the generated iodonium ylides would give a carbene species.[2] Thus, the development of environmentally benign and atom-efficient catalytic synthesis of heterocyclic compounds using *in situ* generated carbene species from simple 1,3-dicarbonyl compounds is highly demanded.[3]

In a continuation of our study on catalytic synthesis of several *N*-heterocyclic compounds via C(sp^2)-H bond activation, we succeeded in developing novel Rh-catalyzed consecutive reaction, which consists of catalytic cleavage of C(sp^2)-H bond of *N*-methoxybenzamide to give a five-membered rhodacyclic intermediate, and insertion of *in situ* generated carbene species by only mixing 1,3-diketones with (diacetoxyiodo)benzene, followed by two-kinds of distinct intramolecular cyclization, enabled chemodivergent synthesis of isocoumarins and isoquinolones in one-pot. The two-kinds of distinct intramolecular cyclization pathways could be controlled, completely, by appropriate use of either Lewis acids (for isoquinolones) or carboxylic acids (for isocoumarins) in the presence of the same [Cp*$RhCl_2$]$_2$ catalyst.



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2) Y. Jiang, P. Li, J. Zhao, B. Liu, X. Li, *Org. Lett.* **2020**, *22*, 7475.

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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18日(月) 15:55 ~ 17:15 E1121(11号館 [2階] 1121)

[E1121-1vn] 11. 有機化学—構造有機化学

座長：猪熊 泰英、福井 識人

日本語

15:55 ~ 16:15

[E1121-1vn-01]

環状BODIPYの超酸耐性

○稲葉 佑哉[1]、米田 友貴[1]、井手 雄紀[2]、猪熊 泰英[1,2] (1. 北大院工、2. 北大WPI-ICReDD)

日本語

16:15 ~ 16:35

[E1121-1vn-02]

シクロパラフェニレンと共役した環状カルベニウムイオンの合成とメビウス芳香族性

○茅原 栄一[1]、鳥越 優河[1]、山子 茂[1] (1. 京大化研)

英語

16:35 ~ 16:55

[E1121-1vn-03]

カテナン形成を鍵とするシクロパラフェニレンの非共有結合修飾

○石橋 弥泰[1]、Manuel Rondelli[1]、周戸 大季[1]、前川 健久[2]、伊藤 英人[1]、水上 輝市[3]、君塚 信夫[3]、八木 亜樹子[1,4]、伊丹 健一郎[1,2,4] (1. 名古屋大学、2. 中央研究院化学研究所、3. 九州大学、4. トランスフォーマティブ生命分子研究所)

日本語

16:55 ~ 17:15

[E1121-1vn-04]

架橋部位に窒素原子を導入したPillar[6]areneの合成と電荷移動型発光特性

○大谷 俊介[1]、中口 風斗[1]、加藤 研一[1]、生越 友樹[1,2] (1. 京都大学大学院工学研究科、2. 金沢大WPI-NanoLSI)

環状 BODIPY の超酸耐性

（北大院工 [1]・北大 WPI-ICReDD[2]）○稲葉佑哉 [1]・米田友貴 [1]・井手雄紀 [2]・猪熊泰英 [1,2]

Super-acid Resistance of Macrocyclic BODIPYs

([1]*Grad. Sch. Eng., Hokkaido Univ.* [2]*WPI-ICReDD, Hokkaido Univ.*) ○Yuya Inaba,[1] Tomoki Yoneda,[1] Yuki Ide,[2] Yasuhide Inokuma[1,2]

Boron-dipyrromethenes (BODIPYs) are widely used as a fluorescence probe due to its high quantum yield and narrow Stokes shift. However, BODIPYs often cause deboronation and lose their fluorescence under acidic conditions, which limits their use. Recently, we reported the synthesis of calix[3]pyrrole and the acid-stability of its boron complex.[1] Detailed analysis revealed that boron complex of calix[3]pyrrole exists as an adduct with acid by protonation at pyrrole under acidic conditions. In this work, we applied this protonation behavior to a new cyclic BODIPY **1**, which showed super-acid resistance and applicability for staining acidic materials.

Keywords : BODIPY; Tripyrrolic Macrocycle; Boron Complex; Acid Resistance; Calix[3]pyrrole

BODIPY (boron dipyrromethene) は高い蛍光量子収率と小さなストークスシフトに特徴付けられる蛍光を示すことから、蛍光プローブとして広く利用されている。一方で BODIPY は酸性条件では脱ホウ素化を起こしてその蛍光特性を損失してしまうために、その利用が制限されることもある。最近我々は calix[3]pyrrole の合成を報告し、そのホウ素錯体は高い酸耐性を示すことを見出した [1]。詳細な検討を行った結果、calix[3]pyrrole のホウ素錯体は酸の共存下でピロールのプロトン化により酸との付加体を形成し、安定に存在していることがわかった。本研究では、calix[3]pyrrole のホウ素錯体に見られたプロトン化挙動と酸耐性を参考に非共役型のピロールを含んだ構造の環状 BODIPY **1** を合成し、その酸耐性を検討した。

環状 BODIPY **1** はトリピラン **2** にホウ素を導入し、得られたホウ素錯体 **3** を閉環することによって合成した（Figure 1a）。**1** は TFA や $MeSO_3H$ といった強酸中でも安定であったことに加え、ピロール部位のプロトン化によって蛍光のスイッチングを示した（Figure 1b）。さらに **1** は HF 水溶液のような腐食性の酸中でも耐性を示した他、超酸として知られる FSO_3H や CF_3SO_3H に対しても耐性を示し、脱ホウ素化を起こさなかった。環状 BODIPY **1** は従来の BODIPY が耐えられない強酸性条件にも耐えられるため、強酸性材料の染色に用いることも可能な色素となった。

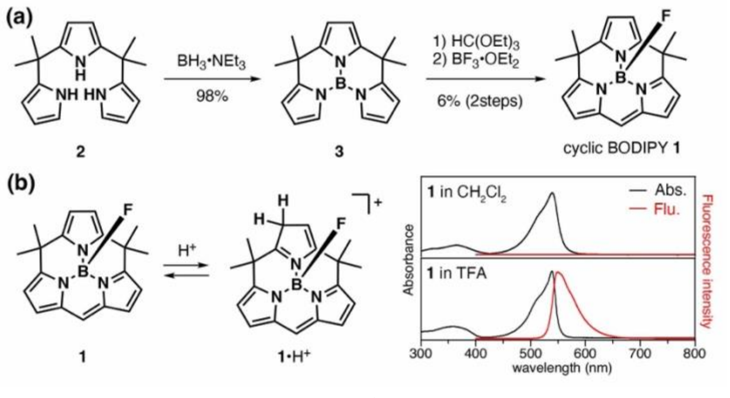

Figure 1. (a) 環状 BODIPY **1** の合成および (b) 酸による **1** のプロトン化と吸収および蛍光スペクトルの変化 ($\lambda_{ex} = 360$ nm)

1) Y. Inaba, Y. Nomata, Y. Ide, J. Pirillo, Y. Hijikata, T. Yoneda, A. Osuka, J. L. Sessler, Y. Inokuma, *J. Am. Chem. Soc.* **2021**, *143*, 12355–12360.

シクロパラフェニレンと共役した環状カルベニウムイオンの合成とメビウス芳香族性

（京大化研）○茅原栄一・鳥越優河・山子茂

Synthesis of Cyclic Carbenium Ion Conjugated with [N]Cycloparaphenylene and Its Möbius aromaticity (*Institute for Chemical Research, Kyoto Univ.*) ○Eiichi Kayahara, Yuga Torigoe, and Shigeru Yamago

We report here the synthesis of cyclic carbenium ion **1** conjugated with [*N*]cycloparaphenylene ([*N*]CPP) with Möbius topology. **1a-d** [*N* = 6-8, and 10, R = Mes, X = $B(C_6F_5)_4$] were synthesized by the addition of a Grignard reagent to CPP ketone **2**, followed by an acid-mediated dihydroxylation reaction. Absorption spectra of **1** showed remarkable bathochromic shifts relative to that of triphenylmethyl (trityl) cation, suggesting the cationic charge is delocalized to the CPP site in **1**. The ^{1}H NMR measurement revealed that the protons of the paraphenylene units for **1a** were upfield-shifted as compared to those of trityl cation due to the diatropic ring current derived from Möbius aromaticity. Structural analysis by the theoretical calculations and the NICS and ACID analyses revealed that **1** has Möbius aromaticity.

Keywords：*Carbenium Ion; Cycloparaphenylens; Möbius aromaticity; Topology; Cyclic Conjugation*

メビウス芳香族分子は、トポロジーに由来する芳香族性の反転が起こることから興味深いが、これを示す化合物は極めて限られている。[1] 我々は最近、アルケン等の通常の平面π共役ユニットを、面内π軌道を持つ[*N*]シクロパラフェニレン（[*N*]CPP）に挿入することで、メビウス構造を持つπ共役分子が得られることを明らかにした。[2] 本研究では、カルベニウムイオンの平面性に着目し、これを[*N*]CPP に挿入した環状カルベニウムイオン **1**（*N* = 6-8, 10）の合成に成功したので報告する（Figure 1)。さらに、**1** のメビウス芳香族性についても併せて報告する。

1a-d は、CPP ケトン **2**[3] に Grignard 試薬を付加させたのち、生成物 **3** の水酸基を酸脱離することで得られた。例えば、**1a** では、吸収スペクトルにおいて、近赤外領域まで広がるブロードな吸収を示し、トリフェニルメチルカチオン[4]の吸収に比べ大きく長波長シフトしていた。これは、電荷が CPP 部位まで非局在化していることを示している。さらに、^{1}H NMR では、**1a** のパラフェニレン水素が 6-7 ppm 付近に高磁場シフトしていた。これは、メビウス芳香族性による遮蔽効果のためと考えられる。また、DFT 計算よるパラフェニレンユニットの結合交替の変化や、NICS や ACID 計算からも **1a** のメビウス芳香族性が支持された。本発表では、**1** におけるメビウス芳香族性の環サイズ依存性も報告する。

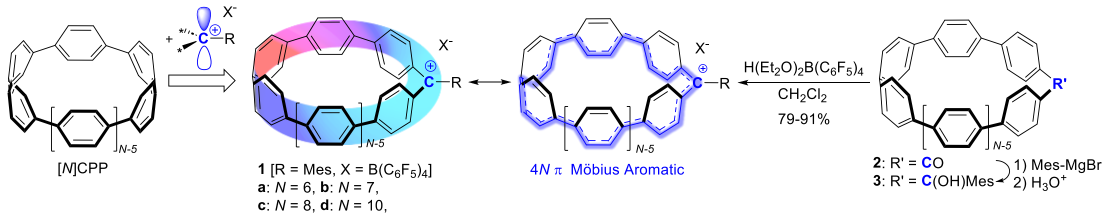

Figure 1. Synthesis and Möbius aromaticity of **1**.

References

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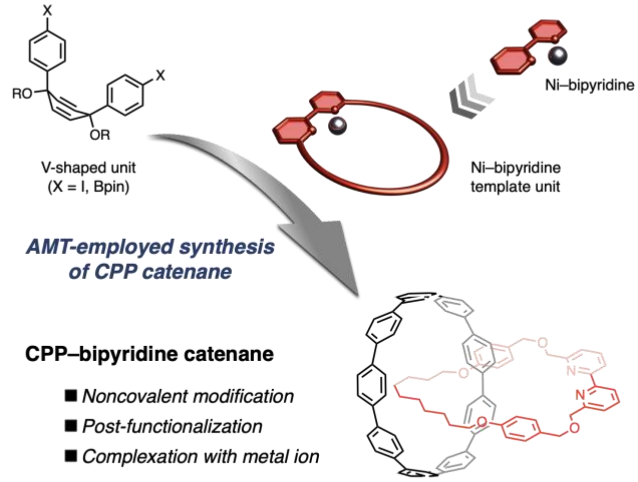
Noncovalent modification of cycloparaphenylene by catenane formation

([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Chemistry, Academia Sinica*, [3]*Department of Applied Chemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), Kyushu University*, [4]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*)
○Hisayasu Ishibashi,[1] Manuel Rondelli,[1] Hiroki Shudo,[1] Maekawa Takehisa,[2] Hideto Ito,[1] Kiichi Mizukami,[3] Nobuo Kimizuka,[3] Akiko Yagi,[1,4] Kenichiro Itami[1,2,4]

Keywords: Cycloparaphenylene; Bipyridine; Catenane

Cycloparaphenylenes (CPPs), in which benzene rings are cyclically linked at the *para* position, have unique electronic properties. Therefore, diverse modifications of CPPs are necessary for its wide application. However, most CPP modifications require early-stage functionalization and the direct modification of CPPs is very limited. Herein, we report the synthesis of a catenane consisting of [9]CPP and a 2,2´-bipyridine macrocycle as a new CPP analogue.[1] The [9]CPP–bipyridine catenane provides a reliable synthetic scaffold, enabling diverse and concise post-functionalization. In accordance with the active metal template (AMT) strategy,[2] [9]CPP–bipyridine catenane was successfully synthesized through Ni-mediated aryl–aryl coupling. Catalytic C–H borylation/cross-coupling and silver(I)-coordination at bipyridine macrocycle moiety, which are effective post-functionalization methods, were also demonstrated with the [9]CPP–bipyridine catenane. Single-crystal X-ray structural analysis revealed that the silver(I)-coordinated [9]CPP–bipyridine catenane forms a tridentated complex with an Ag ion inside the CPP ring. This interaction significantly enhances the phosphorescence lifetime through improved intermolecular interactions.



1) Ishibashi, H.; Rondelli, M.; Shudo, H.; Maekawa, T.; Ito, H.; Mizukami, K.; Kimizuka, N.; Yagi, A.; Itami, K. *Angew. Chem., Int. Ed.* **2023**, e202310613. 2) Crowley, J. D.; Goldup, S. M.; Lee, A.-L.; Leigh, D. A.; McBurney, R. T. *Chem. Soc. Rev.* **2009**, *38*, 1530.

架橋部位に窒素原子を導入した Pillar[6]arene の合成と電荷移動型発光特性

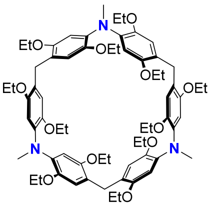
（京大院工 [1]・金沢大 WPI-NanoLSI[2]）○大谷 俊介 [1]・中口 風斗 [1]・加藤 研一 [1]・生越 友樹 [1,2]

Synthesis and Charge Transfer Emission Properties of Pillar[6]arene Derivatives Containing Nitrogen Atoms in Bridging Moieties

([1]*Graduate School of Engineering, Kyoto University,* [2]*WPI-Nano Life Science Institute, Kanazawa University*)
○Shunsuke Ohtani,[1] Kazeto Nakaguchi,[1] Kenichi Kato,[1] Tomoki Ogoshi[1,2]

Organic molecules with luminescence in the solid states can be utilized for low-cost and practical chemo-sensors. Pillar[6]arene (**P6**) is a macrocyclic compound linked by methylene bridges at the para positions of 1,4-dialkoxybenzene rings. Owing to the internal and external space of the cavity, **P6** can capture guest molecules in the solid state.[1] However, the photoluminescence (PL) lies in the ultraviolet region and the PL quantum efficiency is significantly reduced in the solid-state from that in the solution state. In this work, we synthesized a pillar[*n*]arene derivative containing nitrogen atoms in the bridging moieties (**P6NMe**, Figure 1) and it showed charge transfer (CT) emission due to the introduction of nitrogen atoms, leading to the solid-state emission (Figure 2). Owing to the solid-state emission, **P6NMe** displayed a sensing ability to detect nitrobenzene (NB) vapor by PL quenching.

Keywords : Macrocyclic Molecule; Charge Transfer Emission; Solid-State Emission



P6NMe

Figure 1. Chemical structure of **P6NMe**.

Pillar[6]arene (**P6**) は、6 枚のベンゼン環がメチレン基により架橋された環状分子である [1)]。固体状態における **P6** は、環内部の空孔や環同士の空隙にゲスト分子を取り込むことができる。そのため、固体発光性の付与により、ゲスト分子の取り込みに応答した発光特性変化が期待できる。一方で、**P6** の固体発光は紫外域に位置しており、さらに濃度消光と呼ばれる現象により溶液状態に比べて著しく低下する。本研究では、架橋部位に窒素原子を導入した Pillar[6]arene (**P6NMe**, Figure 1) が可視領域で固体発光性を示すことが分かった（Figure 2）。これは窒素架橋部位が電子ドナーとして働くことで分子内電荷移動（CT）発光へと変化し、自己吸収が抑制されたことに起因する。また長波長領域に新たな発光ピークが観測され、固体状態に由来した発光種の存在が示唆された。さらに、この発光ピークは、ニトロベンゼン（NB）蒸気の曝露により消失することが分かった。これは NB との分子間 CT 錯体の形成に起因しており、蛍光センサーとしての利用が期待できる。

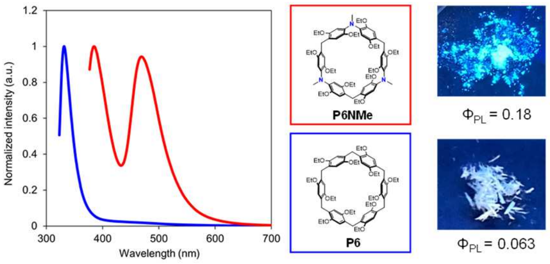


Figure 2. PL spectra of **P6NMe** and **P6** in the solid states and picture images obtained under UV irradiation (λ_{ex} = 365 nm).

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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18日(月) 13:00 ~ 15:10 E1123(11号館 [2階] 1123)

[E1123-1pm] 12. 有機化学—有機結晶・超分子化学

座長：関谷 亮、山内 光陽

英語
13:00 ~ 13:20
[E1123-1pm-01]
キラルなレゾルシンアレーンカプセルを用いた第二級アルコールの速度論的光学分割

〇原田 健太郎[1]、関谷 亮[1]、灰野 岳晴[1,2] (1. 広島大学、2. 持続可能性に寄与するキラルノット超物質拠点)

日本語
13:20 ~ 13:40
[E1123-1pm-02]
芳香環ミセル：多孔性高分子の内包による水溶性多空間ホストの構築

〇青山 慎治[1]、Lorenzo Catti、吉沢 道人 (1. 東工大・化生研)

日本語
13:40 ~ 14:00
[E1123-1pm-03]
ジスルフィドステープルの酸化還元を駆動力としたα-ヘリカルペプチドの可逆的な静的/動的らせん変換

〇逢坂 直樹[1]、Mark J MacLachlan[1,2]、秋根 茂久[1,3] (1. 金沢大 NanoLSI、2. ブリティッシュコロンビア大、3. 金沢大院自然)

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30
[E1123-1pm-04]
多座配位子内の二面角変化による自己集合性金属錯体のコントロール

〇阿部 司[1]、平岡 秀一[1] (1. 東京大学)

英語
14:30 ~ 14:50
[E1123-1pm-05]
Donor-Appended Pyrazinacenes - Switching Absorption and Fluoresence from Visible to Near Infrared Region Through a Simple REDOX Process.

〇Gary James Richards[1], Keita Aoki[1], Kou Kanehisa[1], Kazushi Nakada[1], Ryo Nakamura[1], Jonathan P. Hill[2], Akiko Hori[1] (1. Shibaura Institute of Technology, 2. National Institute of Materials Science)

日本語
14:50 ~ 15:10
[E1123-1pm-06]
前駆体法を利用した水素結合性ベンゾポルフィリン集合体の基板上形成と薄膜トランジスタへの展開

○上野 創[1]、山内 光陽[1]、松尾 恭平[1]、水畑 吉行[1]、山田 容子[1] (1. 京大化研)

キラルなレゾルシンアレーンカプセルを用いた第二級アルコールの速度論的光学分割

（広大院先進理工 [1]・WPI-SKCM[2 2]）原田 健太郎 [1]・○関谷 亮 [1]・灰野 岳晴 [1,2]

Kinetic Resolution of Secondary Alcohols Using a Chiral Resorcinarene-based Capsule

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*, [2]*International Institute for Sustainability with Knotted Chiral Matter / WPI-SKCM*[2]) ○Kentaro Harada,[1] Ryo Sekiya,[1] Takeharu Haino[1,2]

Our group has reported that two resorcinarene-based cavitands were self-assembled with copper cations to form D_4 symmetric metal-coordination capsule. When a chiral template was encapsulated, a diastereomerically enriched host-guest complex was obtained with >90%*de*, followed by a chiral empty capsule with >90%*ee*. The host guest complex of the enantiomerically enriched capsule and an achiral acylation catalyst provided a chiral reaction environment, resulting in the kinetic resolution of racemic mixture of secondary alcohols.

Keywords : Host-Guest Chemistry; Molecular Recognition; Chiral Induction; Kinetic Resolution

当研究室では, 四つのビピリジン骨格を有するレゾルシンアレーンキャビタンドが一価の銅イオン存在下で自己集合し，D_4対称性の超分子カプセル**1**を形成することを報告している(Fig. 1a)。**1**のらせん性に由来する*P*と*M*のエナンチオマーはアセトニトリルを含むクロロホルムやTHFの混合溶媒中で相互変換する。先行研究で，キラルな水素結合三量体$(AcOH)_2$·(2*R*, 3*R*)-**G1**の包接により，**1**の軸性キラリティーが片側に偏った後，三量体を再沈澱により除去することでキラルカプセル(*P*)-**1**が得られることを報告した(Fig. 1b)。(*P*)-**1**にアルコールのアシル化を促進するDMAP触媒**G2a-c**を包接させれば，反応基質はカプセルの配位結合に起因するキラル環境付近で反応する。よって，カプセルの不斉が反応生成物に影響を及ぼし，アルコールアシル化の速度論的光学分割が起こるのではないかと考えた。当日詳細を報告する。

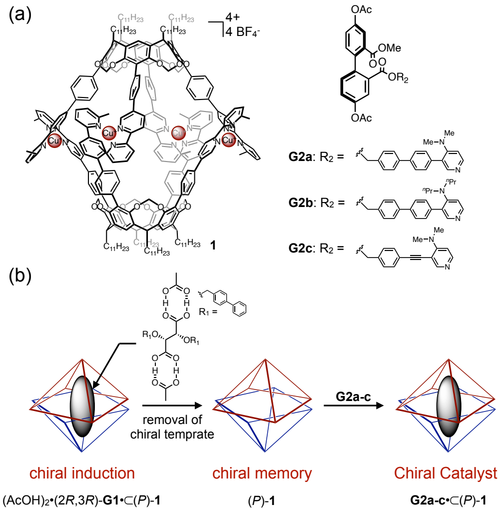
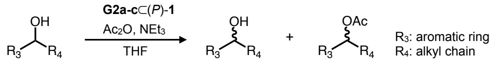


Fig. 1 (a) Molecular structures of capsule 1 and catalytic guest G2a-c (b) Preparation of a supramolecular catalyst.

Table 1. Kinetic Resolution of Alcohols catalyzed by host-guest complex **G2a-c**⊂(*P*)-**1**



entry	Guest	alcohol	R_3	R_4	temp. / °C	Time / h	Conv. / %	*ee*% of alcohol	*ee*% of ester	*s* value	chirality of alcohol
1	**G2a**	**2a**	1-naphthyl	Me	0	4	54	6.2	5.0	1.2	*R*
2	**G2a**	**2a**	1-naphthyl	Me	-40	20	49	13	14	1.4	*R*
3	**G2a**	**2a**	1-naphthyl	Me	-80	72	43	23	31	2.3	*R*
4	**G2c**	**2a**	1-naphthyl	Me	-80	102	13	0.7	5.5	1.1	*R*
5	**G2b**	**2a**	1-naphthyl	Me	-80	120	35	7.5	16	1.4	*R*
6	**G2a**	**2b**	Ph	Me	-80	72	35	2.0	3.5	1.1	*S*
7	**G2a**	**2c**	9-anthracene	Me	-80	12	49	23	24	2.0	*R*
8	**G2a**	**2d**	4-formyl-1-naphthyl	Et	-80	48	51	28	27	2.3	*R*
9	**G2a**	**2e**	4-methoxy-1-naphthyl	Me	-80	100	44	21	29	2.1	*R*
10	**G2a**	**2f**	1-naphthyl	Et	-80	100	52	35	34	2.6	*R*
11	**G2a**	**2g**	1-naphthyl	iPr	-80	100	43	15	21	1.7	*R*

芳香環ミセル：多孔性高分子の内包による水溶性多空間ホストの構築

（東工大 化生研）○青山慎治・Lorenzo Catti・吉沢道人

Preparation of Aqueous Multicavity Hosts from Porous Polymers and Aromatic Micelles

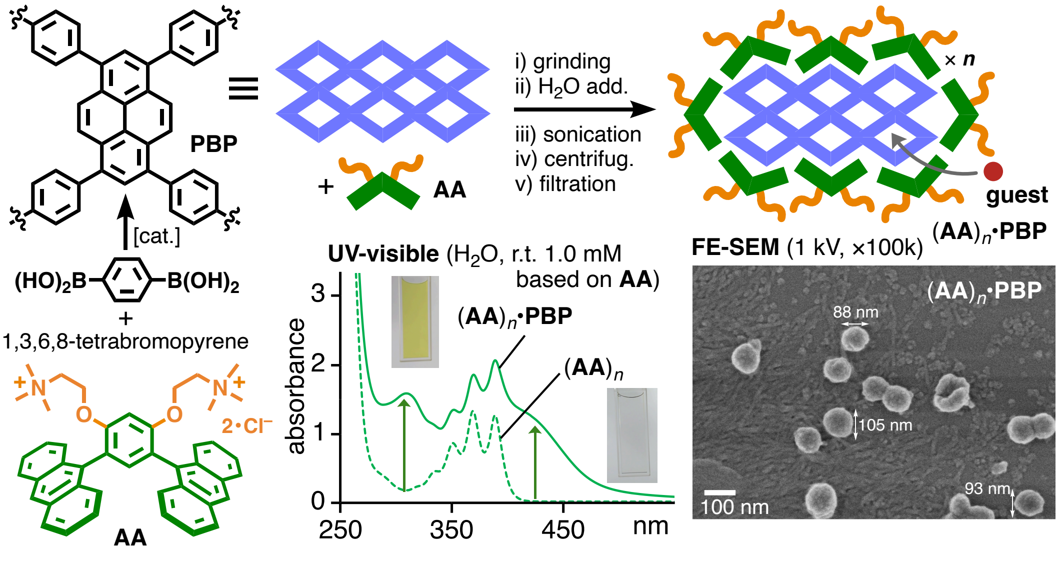
(*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Shinji Aoyama, Lorenzo Catti, Michito Yoshizawa

Here we report the successful preparation of aqueous multicavity hosts via the encapsulation of insoluble porous polymers by aromatic micelles. Through a facile grinding and sonication protocol, a conjugated porous polymer composed of pyrene and benzene frameworks was encircled by bent aromatic amphiphiles in water under ambient conditions. Combination of DLS, AFM, and SEM analyses revealed the formation of spheroidal products with dimensions of 100-250 nm. Importantly, the obtained multi-cavity hosts displayed unusual uptake functions in water.

Keywords: Aromatic micelle, Porous polymer, Water-solubilization, Encapsulation

多くのホスト化合物は１つの空間を有し、種々のゲスト分子を捕捉できる。一方、多数（４つ以上）の空間を有する可溶性ホスト化合物はほとんど例がない。今回、芳香環ミセルにより不溶性の多孔性高分子を内包することで、新規な水溶性多空間ホストを構築したので報告する。

２つの芳香環パネルを持つＶ型両親媒性分子 **AA** とペリレン-ベンゼン骨格から成る共役多孔性高分子 **PBP** を、グラインディング-超音波照射することで、内包体 $(\mathrm{AA})_n$·PBP の黄色水溶液を得た（下図上）。この溶液の UV-visible 測定より **PBP** に特徴的な吸収帯を観測することで水溶化を達成した。DLS、AFM および SEM 測定から、得られた多空間ホストは 100-250 nm サイズの扁球構造を形成していることが明らかとなった（下図下）。さらに、この多空間ホストはトルエンや有機色素分子を取り込むことが可能であった。



ジスルフィドステープルの酸化還元を駆動力としたα-ヘリカルペプチドの可逆的な静的/動的らせん変換

（金沢大 NanoLSI[1]・ブリティッシュコロンビア大[2,3]・金沢大院自然[3]）○逢坂 直樹[1]・Mark J. MacLachlan[1,2]・秋根 茂久[1,3]

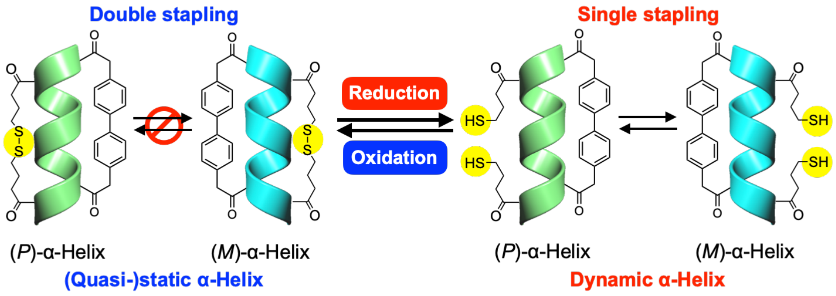
Reversible Transformation Between Quasi-Static and Dynamic α-Helical Peptides Driven by a Redox Reaction of a Disulfide Staple

([1]*Kanazawa Univ. NanoLSI,* [2]*The Univ. of British Columbia,* [3]*Kanazawa Univ. Grad. Sch. of Nat. Sci. & Tech.*) ○Naoki Ousaka[1], Mark J. MacLachlan[1,2], Shigehisa Akine[1,3]

We have successfully demonstrated a redox-driven reversible transformation between quasi-static and dynamic stapled α-helical peptides composed mainly of strongly helicogenic achiral amino acid residues. A key to this system is that a doubly stapled quasi-static α-helical peptide containing one disulfide staple can be reversibly transformed into a singly stapled dynamic α-helical peptide bearing two thiol side chains by the redox reaction of the disulfide bond.

Keywords : Helical Structure; α-Helix; Chirality; Helix Inversion; Redox

1951 年に α-ヘリックス構造が発見されて以来、非生物学的な骨格からなる多種多様な人工らせん分子・高分子・超分子が合成されてきた1)。これらのらせんは、主に、右巻きと左巻きのらせんが相互交換する“動的”ならせんとほとんど相互交換しない“静的”ならせんに分類される。最近、我々は、らせん形成性の高いアキラルなアミノ酸からなるペプチド鎖に剛直なビフェニル誘導体で一重または二重のステープリング（分子内架橋）を施すことで、動的ならびに静的な α-ヘリカルペプチドの構築に成功した2)。本研究では、アキラルペプチド鎖の側鎖間を剛直なビフェニル誘導体ならびにジスルフィド結合を有するアルキル鎖で二重にステープル化するとともに C 末端に光学活性なアミノ酸残基を導入した新規な α-ヘリカルペプチドを合成し、ステープル部位のジスルフィド結合の酸化還元を駆動力とすることで、らせん反転速度が著しく異なる擬静的と動的ならせん間の可逆的な変換が可能かどうか検討を行った。その結果、ジスルフィド結合の可逆的な酸化還元により、らせん反転速度が約 10^3 倍変化することがわかった。



1) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116*, 13752.
2) N. Ousaka, M. J. MacLachlan, S. Akine, *Nat. Commun.* **2023**, *14*, 6834.

Control of self-assembled metal-organic cages by dihedral angle change in multitopic ligands

(*Graduate School of Arts and Sciences, The University of Tokyo*)
○Tsukasa Abe, Shuichi Hiraoka

Keywords: Molecular Self-assembly; Kinetic Control; Thermodynamic Control; Dihedral Angle Change

Molecular self-assembly of a giant discrete entity composed of many components is challenging because of the large entropic cost by increasing the number of components. The elaborate design of multitopic ligands such as precisely tuning the bent angle[1] or introducing the twist[2] can solve this problem. In both cases, a general design principle is that assembled structures composed of fewer building blocks are enthalpically destabilized due to their structural distortion, which can be relieved by the formation of a large self-assembly.

In this study, we show several types of metal-organic assemblies based on dihedral angle control in multitopic ligands although they have the same coordination directions. The self-assembly of the tritopic ligand with a triazine core (**1**) and *cis*-protected Pd^{2+} ions (***Pd***) was reported to afford the $[\boldsymbol{Pd}_6\mathbf{1}_4]^{12+}$ truncated tetrahedron.[3] It was found that the tritopic ligand **2** with a benzene ring provided larger structures, $[\boldsymbol{Pd}_9\mathbf{2}_6]^{18+}$ and $[\boldsymbol{Pd}_{12}\mathbf{2}_8]^{24+}$, as kinetic and thermodynamic products, respectively. The difference between **1** and **2** is the dihedral angle (φ) between 4-pyridyl groups and the central ring, which altered the assembled structures, indicating that increase in the dihedral angle in the multitopic ligand prefers larger assemblies. We also discuss the general principle to provide large assemblies based on remote geometric communication among multitopic ligands through coordination bonds.

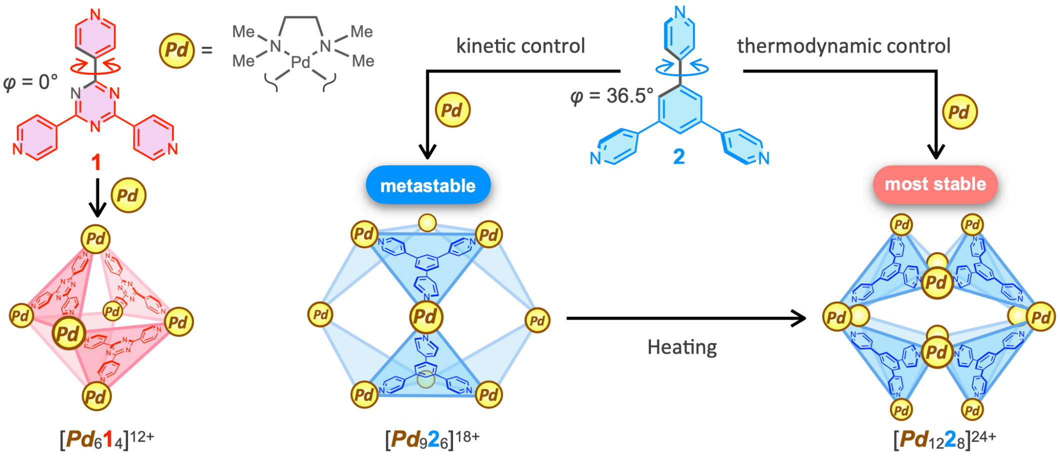


Figure Self-assembled structures from tritopic ligand **1** or **2** and ***Pd***.

1) M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem. Int. Ed.* **2004**, *43*, 5621. 2) J. A. Davies, T. K. Ronson, J. R. Nitschke, *Chem* **2022**, *8*, 1099. 3) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469.

Donor-Appended Pyrazinacenes - Switching Absorption and Fluoresence from Visible to Near Infrared Region Through a Simple REDOX Process.

Gary J. Richards[1], Keita Aoki[1], Kou Kanehisa[1], Kazushi Nakada[1], Ryo Nakamura[1], Jonathan P. Hill[2] and Akiko Hori[1]

(1. College of Engineering, Department of Applied Chemistry, Shibaura Institute of Technology, 2. National Institute of Materials Science)

Pyrazinacenes[1] are analogues of classic acenes with apical CH groups replaced with nitrogen atoms. These stable compounds are currently being investigated for a variety of applications based on their photophysical and electronic propeties.[2,3] Here we describe REDOX active octaazatetracenes and decaazapentacenes appended with electron rich triphenylamine (TPA) or phenanthrene units. For TPA appended molecules a large shift in absorption from 586 nm in the reduced form to 1050 nm when oxidized is observed in chloroform solution. In the reduced state, these compounds show fluorescence in the visible region with high fluorescence quantum yields and in non-polar solvents, fluorescence in the NIR region up to 1020 nm is observed. In this presentation, we will discuss the photophysical properties of these compounds including absorption and fluorescence as well as the REDOX dependence of these properties.

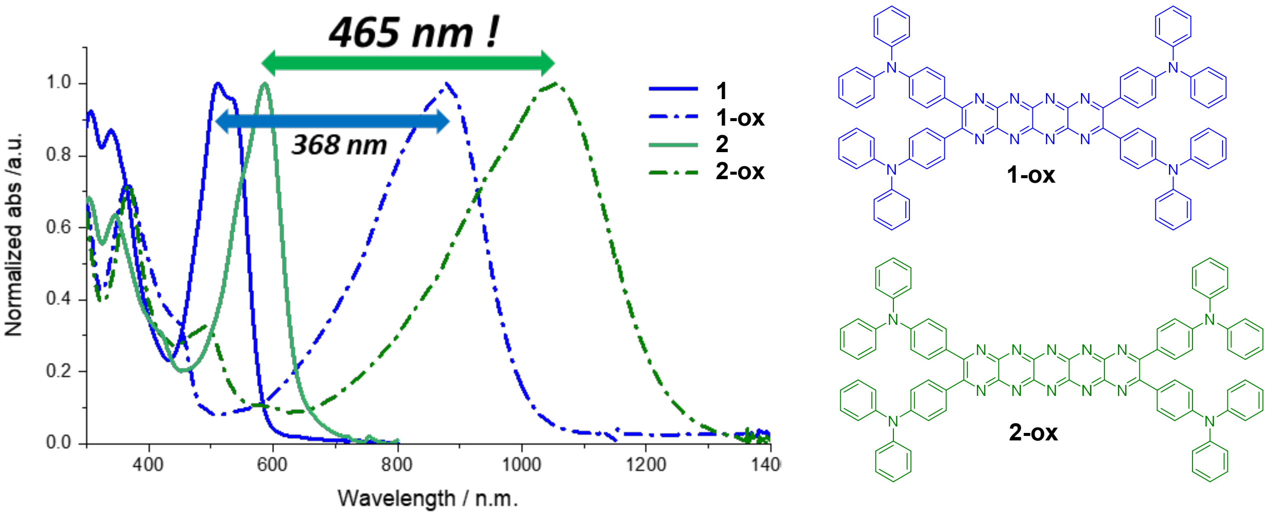


Figure 1. Large bathochromic shift in absorption (left) through a simple oxidation of a single dihydropyrazine ring to the fully oxidized species shown on the right.

1) a) G. J. Richards, J. P. Hill, Acc. Chem. Res. 2021, 54, 16, 3228-3240. b) G. J. Richards, J. P. Hill, N. K. Subbaiyan, F. D'Souza, P. A. Karr, M. R. J. Elsegood, S. J. Teat, T. Mori, K. Ariga, J. Org. Chem. 2009, 74, 8914-8923.
2) G. J. Richards, A. Cador, S. Yamada, A. Middleton, W. A. Webre, J. Labuta, P. A. Karr, K. Ariga, F. D'Souza, S. Kahlal, J.-F. Halet, J. P. Hill, J. Am. Chem. Soc. 2019, 141, 50, 19570- 19574.
3) G. J. Richards, S. Ishihara, J. Labuta, D. Miklík, T. Mori, S. Yamada, K. Ariga, J. P. Hill, J. Mater. Chem. C. 2016, 4, 11514-11523.

前駆体法を利用した水素結合性ベンゾポルフィリン集合体の基板上形成と薄膜トランジスタへの展開

（京大化研[1]）〇上野 創[1]・山内 光陽[1]・松尾 恭平[1]・水畑 吉行[1]・山田 容子[1]

Formation of Hydrogen-Bonded Benzoporphyrin Assemblies on Substrates Using Precursor Approach and Their Application to Thin Film Transistor

([1]*Institute for Chemical Research, Kyoto University*) ○So Ueno,[1] Mitsuaki Yamauchi,[1] Kyohei Matsuo,[1] Yoshiyuki Mizuhata,[1] Hiroko Yamada[1]

In organic semiconductor materials, controlling the packing structure of organic molecules is important, enabling the improvement of the mobility of thin-film transistor. Previously, our group has successfully fabricated organic thin-film transistors via the thermal conversion of highly soluble tetrabicycloporphyrin (**CP**) precursor to poorly soluble tetrabenzoporphyrin (**BP**) on the substrate. Herein, we synthesized a thermal precursor **CP1** with two amide groups and two phenyl groups that are introduced to realize the 2D packing structure of **BP** suitable for charge-carrier transport, and evaluated the packing structure and transistor properties of the **BP1** thin-film fabricated by thermal conversion. UV-vis absorption spectral analysis indicated the thermal conversion of **CP1** to **BP1** in the thin-film. The absorption bands of the **BP1** thin-film were red-shifted on comparison to those of the monomeric **BP1**, suggesting the slipped stacking of **BP1**. Moreover, the thin-film transistor of **BP1** exhibited hole mobility of 0.03 $cm^2 V^{-1} s^{-1}$.

Keywords: *Organic Semiconductor; Precursor Approach; Benzoporphyrin; Thin Film Transistor; Hydrogen Bond*

有機半導体材料の高性能化のためには、電荷輸送に適した有機分子のパッキング構造の構築が重要である。当研究室はこれまで、溶解性の高いテトラビシクロポルフィリン(**CP**)前駆体を成膜した後、基板上で難溶性のテトラベンゾポルフィリン(**BP**)に熱変換させることで、薄膜トランジスタの作製に成功している[1)]。本研究では、より電荷輸送に適した **BP** の 2 次元パッキング構造の構築のためにフェニル基、パッキング構造安定化のためにアミド基を導入した熱前駆体 **CP1** を合成した。**CP1** を成膜後、基板上での熱変換により **BP1** 薄膜へと変換し、パッキング構造、トランジスタ特性を評価した。吸収スペクトル測定より、**CP1** 薄膜から **BP1** 薄膜への熱変換が進行したことを確認した。モノマー溶液と比較して、薄膜の吸収帯が長波長シフトしたことにより、**BP1** が薄膜中でずれたスタッキング構造を形成していることを明らかにした。薄膜トランジスタ特性を評価したところ、0.03 $cm^2 V^{-1} s^{-1}$ のホール移動度が得られため、その薄膜構造と合わせて報告する。

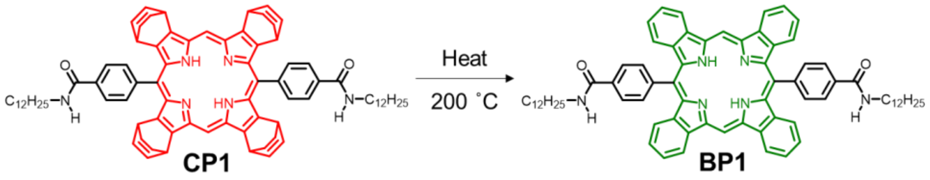


Fig. 1 Molecular structures of **CP1** and **BP1**.

1) P. B. Shea, L. R. Pattison, M. Kawano, C. Chen, J. Chen, P. Petroff, D. C. Martin, H. Yamada, N. Ono, J. Kanicki, *Synth. Met.* **2007**, *157*, 190–197.

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18日(月) 13:00 ~ 15:30 E1131(11号館 [3階] 1131)

[E1131-1pm] 12. 有機化学—有機結晶・超分子化学

座長：阿南 静佳、桶谷 龍成

日本語
13:00 ~ 13:20
[E1131-1pm-01]
低対称トリカルボン酸による水素結合性はしご型多孔質構造体の構築

〇田中 那樹[1]、鈴木 悠斗[1]、桶谷 龍成[1]、久木 一朗[1] (1. 阪大院基礎工)

日本語
13:20 ~ 13:40
[E1131-1pm-02]
水素結合性固溶体フレームワークの構築と成分比に依存した構造転移挙動

〇橋本 泰利[1]、桶谷 龍成[1]、久木 一朗[1]、間下 以大[2] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院情報科学研究科)

日本語
13:40 ~ 14:00
[E1131-1pm-03]
トリス(フェニルイソオキサゾリル)ベンゼンの分子結晶中に現れる多孔性と選択的分子吸着

〇小野 雄大[1]、平尾 岳大[1]、灰野 岳晴[1,2] (1. 広島大、2. 広島大 WPI-SKCM²)

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30
[E1131-1pm-04]
Development of Catenane-based Supramolecular Mechanophores

〇Fazil Thuluvanchery Salim[2], Nobuyuki Tamaoki[2], Yoshimitsu Sagara[1] (1. Tokyo Institute of Technology, 2. Hokkaido University)

英語
14:30 ~ 14:50
[E1131-1pm-05]
sp^2-およびsp^3-ナノカーボン分子を複合した結晶性分子ピーポッド

〇寺崎 成哉[1]、小谷 祐希[1]、勝野 亮祐[1]、福永 隼也[1]、松野 太輔[1]、磯部 寛之[1] (1. 東京大学)

英語
14:50 ~ 15:10
[E1131-1pm-06]
o-カルボラン誘導体におけるπ積層構造に基づく多刺激応答特性

〇油原 和公[1]、田中 一生[1] (1. 京大院工)

日本語
15:10 ~ 15:30
[E1131-1pm-07]

ジアリール置換した縮環ブタジエン類の固体発光および結晶構造

○長岡 朋希[1]、南 春彦[1]、曽 思悦[1]、松井 康哲[1]、大垣 拓也[1]、池田 浩[1] (1. 阪公大)

低対称トリカルボン酸による水素結合性はしご型多孔質構造体の構築

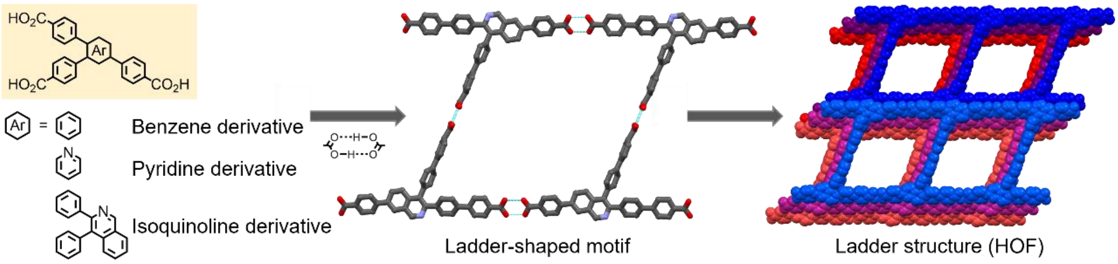
（阪大院基礎工）○田中 那樹・鈴木 悠斗・桶谷 龍成・久木 一朗

Construction of hydrogen-bonded, ladder-shaped, porous structures using a low-symmetric isoquinoline derivate. (*Graduate School of Engineering Science, Osaka University*) ○Namiki Tanaka, Yuto Suzuki, Ryusei Oketani, Ichiro Hisaki

Hydrogen-bonded organic frameworks (HOFs), in which molecules are assembled into porous structures by reversible hydrogen bond, can be easily obtained by recrystallization of highly crystalline structures, and HOFs with a wide variety of structures using various molecules have been reported extensively in recent years. In general, it is well known that molecules with high symmetry, such as those with three rotational axes, give HOFs more easily than those with low symmetry.[1] On the other hand, in our laboratory, we have found that benzene derivatives with low symmetry, which have four carboxy groups, form more anisotropic ladder-like networks.[2] In this study, we synthesized three-armed benzene, pyridine, and isoquinoline derivatives with lower symmetry (**8**, **9**, **5**) to construct HOFs. The resulting HOFs have a ladder-shaped framework with rhombic vacancies. In this presentation, we report on the crystal structures, thermal analysis results and porosity evaluations.

Keywords : Hydrogen bond; Supramolecular chemistry; Hydrogen-bonded organic framework; Low-symmetry π-conjugated molecules; Aromatic heterocyclic compounds

可逆的な水素結合によって分子を多孔質構造へと集積させた有機フレームワーク(HOF)は、結晶性の高い構造体を再結晶により簡便に得ることができるため、様々な分子を用いた多様な構造をもつ HOF が近年盛んに報告されている。一般に、3 回軸をもつような高対称性分子は、より対称性の低い分子よりも容易に HOF を与えることがよく知られている [1]。一方当研究室では、4 つのカルボキシ基を周辺にもつ低対称性のベンゼン誘導体を用いることでより異方的なはしご型ネットワークを形成することを見出した [2]。本研究では、さらに対称性を低くした 3 本の腕をもつベンゼン、ピリジン、イソキノリンそれぞれの誘導体 (**8**, **9**, **5**)を用いて HOF の構築を行った。得られた HOF は菱形の空孔をもつはしご型フレームワークを有していた。本発表では、結晶構造と併せて熱的評価、多孔性の評価を報告する。



1) B. Chen *et al. Chem. Soc. Rev.* **2019**, *48*, 1362.

2) Hisaki, I. *et al.*, *Angew Chem. Int. Ed.* **2015**, *54*, 3008.

水素結合性固溶体フレームワークの構築と成分比に依存した構造転移挙動

(阪大院基礎工 [1]・情報科学 [2]) ○橋本 泰利 [1]・桶谷 龍成 [1]・間下 以大 [2]・久木 一朗 [1]

Construction of non-stoichiometric hydrogen-bonded framework and its structural transformation behavior depending on the component ratios.

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Information Science and Technology, Osaka University*) ○Taito Hashimoto[1], Ryusei Oketani[1], Tomohiro Mashita[2], Ichiro Hisaki[1]

Solid solution frameworks constructed from multi components make it possible to tune material properties. In this study, we demonstrated that hydrogen-bonded solid solution frameworks composed of two tetracarboxylic acids with hydropyrene (**CP-Hp**) or pyrene (**CP-Py**) core undergo the structural transformation depending on the composition ratios. The HOFs obtained from cocrystallization of these two compounds undergo structural transformations from Form-1 to Form-2 with the release of guest molecules by single crystal X-ray diffraction analysis (Figure 1a, 1b). This structural change resulted in the stepwise cracking of the single crystal (Figure 1c), and it was revealed that the time taken for the entire crystal to crack varies depending on the composition ratios (Figure 1d). These results indicate that the speed of the structural transformation is tunable by modulating the composition ratios in single crystals.

Keywords : Hydrogen-bonded organic framework; Structural transformation; Solid solution

複数の成分から構築された固溶体フレームワークは、成分比による物性変調が可能である。本研究では、カルボキシフェニル基をもつヘキサヒドロピレン誘導体 (**CP-Hp**) およびピレン誘導体 (**CP-Py**) を用いて構築した水素結合性固溶体フレームワーク (固溶体 HOF) の構造転移速度を、単結晶中の組成比によって変調できることを実証した。**CP-Py** と **CP-Hp** の共結晶化により得られた固溶体 HOF は、ゲスト分子の自然放出によって Form-1 から Form-2 へと構造転移することを単結晶 X 線構造解析により明らかにした (Figure 1a, 1b)。また、構造転移によって単結晶が端から段階的に割れることが分かった (Figure 1c)。「種々の固溶体単結晶の長さ」に対する「結晶全体が割れるのに要した時間」のプロットによって、フレームワークの転移速度が組成比に依存して変化することが明らかになった (Figure 1d)。

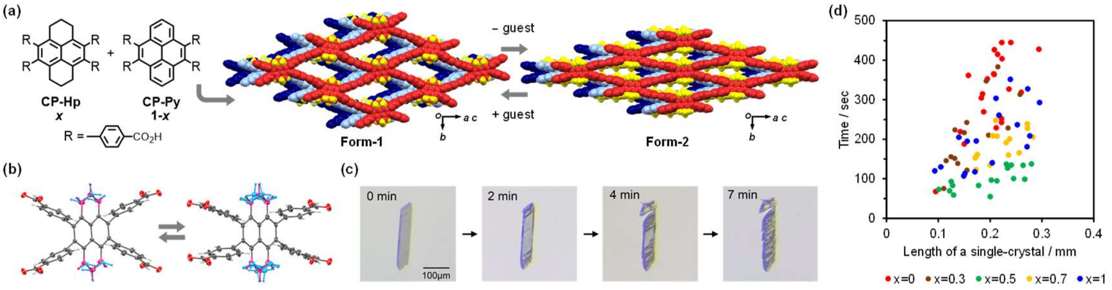


Figure 1. (a) Structural transformation behavior of solid solution HOF (b) Disorder structures of core moieties (c) Cracking behavior of the single crystal (d) Relationship between the time taken for the entire single crystals to crack and its length. x is the mixing ratio of **CP-Hp** in initial solution.

1) T. Hashimoto *et al*., *Angew. Chem. Int. Ed.* **2023**, *62*, e202215836.

日本化学会 第104春季年会 (2024)

トリス(フェニルイソオキサゾリル)ベンゼンの分子結晶中に現れる多孔性と選択的分子吸着

(広島大院先進理工[1]・広島大 WPI-SKCM[22]) ○小野 雄大[1]・平尾 岳大[1]・灰野 岳晴[1,2]

Latent Porosity and Selective Molecular Adsorption in a Molecular Crystal of Tris(phenylisoxazolyl)benzene ([1]Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, [2]International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM2), Hiroshima University) ○Yudai Ono,[1] Takehiro Hirao,[1] Takeharu Haino[1,2]

Porous organic compounds have a great potential of adsorption and separation for molecular mixtures. Our group has reported tris(phenylisoxazolyl)benzene derivatives formed stacked structures via its dipole-dipole and π-π stacking interactions in organic solvents. In this study, we designed and synthesized tris(phenylisoxazolyl)benzene **1** for crystallography. The single crystal X-ray diffraction analysis provide insight into the crystal structure of **1**. In the crystal structure, molecules **1** stacked in a columnar fashion and created the channel-like spaces for solvent encapsulation. Furthermore, the adsorption experiment using *cis-*/*tran*s-decalin mixture revealed that **1** showed *cis*-selective-adsorption behavior. Here, we introduce detailed crystal structures and adsorption behavior of **1**.

Keywords : Organic Crystal; X-Ray Diffraction Analysis; Porosity; Adsorption

空孔をもつ有機化合物は，吸着や分離などへの応用が期待され，盛んに研究が行われてきた。当研究室では，平面分子のトリス(フェニルイソオキサゾリル)ベンゼンがπ-π スタッキングや双極子-双極子相互作用を駆動力として溶液中で自己集合し，積層型の超分子構造体を形成することを報告している[1]。本研究では，結晶性のよいトリス(フェニルイソオキサゾリル)ベンゼン **1** を設計・合成した(Figure 1a)。クロロホルムを結晶化溶媒として作製した $CHCl_3$@**1** の単結晶について X 線構造解析を行った結果，**1** は結晶中で積層し，積層構造間に溶媒分子を包接可能な空間を形成していることがわかった(Figure 1b)。さらに，シス-トランスデカリン混合物を用いた吸着実験は，**1** の積層構造間の空間にシスデカリンを選択的に吸着できることを明らかにした(Figure 1c)。本発表では，**1** の結晶構造と選択的分子吸着について発表する。

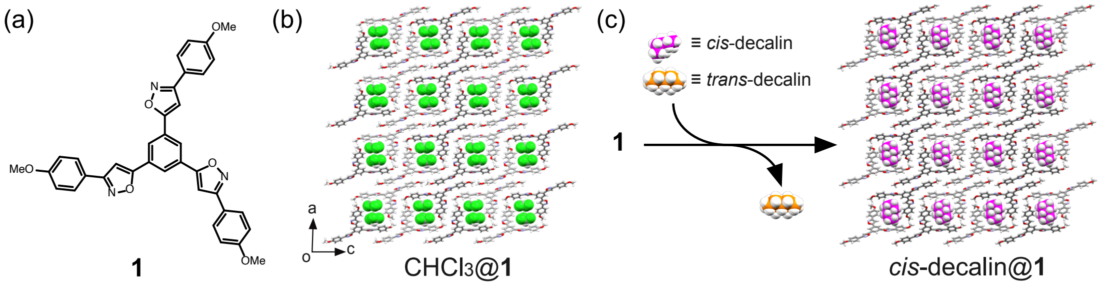


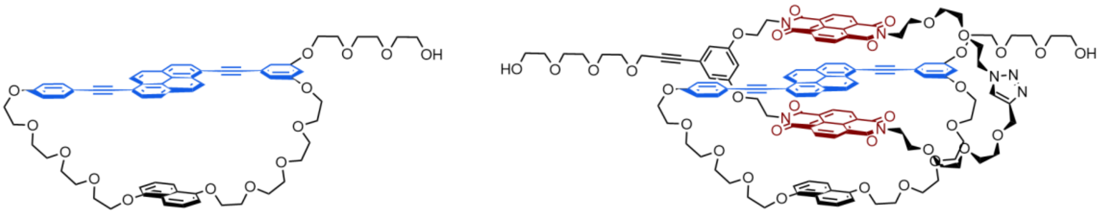
Figure 1. (a) Molecular structure of **1**. (b) Single crystal structure of $CHCl_3$@**1** generated from the $CHCl_3$ solution. (c) Schematic representation of selective adsorption of **1** against *cis-*/*trans*-decallin mixture.

Development of Catenane-based Supramolecular Mechanophores

([1]*Research Institute of Electronic Science, Hokkaido University*, [2]*Department of Material Science and Engineering, Tokyo Institute of Technology*) ○Fazil Thuluvanchery Salim,[1,2] Nobuyuki Tamaoki,[1] Yoshimitsu Sagara[2]

Keywords: Mechanophore; Catenane; Rotaxane; Supramolecular mechanophore

The mechanophores are molecular structures that show various responses when a mechanical force is applied.[1] Supramolecular mechanophores can be activated without covalent bond scission.[2] Several supramolecular mechanophores, including rotaxane, cyclophane, and loop-forming structures, have recently been developed to exhibit various activation behaviors.[2–4] Catenane, a promising molecular motif with mechanically interlocked architecture consisting of two or more interlocked macrocycles,[5] can be explored to expand the supramolecular mechanophores library. We developed a catenane-based supramolecular mechanophore **Cat**, which consists of one quencher ring and one photoluminescence ring **Lum**. The latter ring features a 1,6-bis(phenylethynyl)pyrene luminophore, while the former has two 1,4,5,8-naphthalene tetracarboxylic diimide (NpI) quenchers. In chloroform solutions, the fluorescence of **Cat** is almost completely quenched by the NpI groups. After covalently incorporated into polyurethane elastomer (**CatPU**), thin films of **CatPU** were prepared. When the **CatPU** films were stretched, reversible on/off fluorescence behavior was observed. The luminophore and two NpI groups are spatially separated, leading to the turn-on of photoluminescence. We also investigated the difference in activation behavior between **Cat** and a rotaxane-based supramolecular mechanophore that we had previously developed[6] after preparing a polyurethane elastomer featuring both mechanophores.



Lum **Cat**

Fig. 1. Molecular structures of photoluminescent cycle **Lum** and catenane-based supramolecular mechanophore **Cat**.

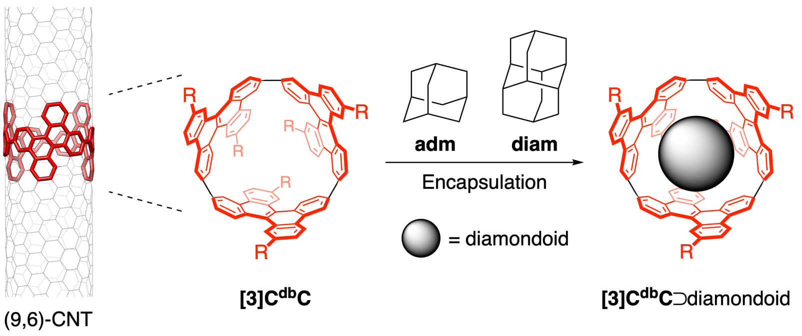
1) Y. Chen, G. Mellot, D. V. Luijk, C. Creton, R. P. Sijbesma, *Chem. Soc. Rev.* **2021**, *50*, 4100. 2) Y. Sagara, M. Karman, E. Verde-Sesto, K. Matsuo, Y. Kim, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2018**, *140*, 1584. 3) Y. Sagara, H. Traeger, J. Li, Y. Okado, S. Schrettl, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2021**, *143*, 5519. 4) H. Traeger, Y. Sagara, D. J. Kiebala, S. Schrettl, C. Weder, *Angew. Chem. Int. Ed.* **2021**, *60*, 16191. 5) Q. H. Guo, Y. Jiao, Y. Feng, J. F. Stoddart, *CCS Chem.* **2021**, *3*, 1542. 6) Y. Sagara, M. Karman, A. Seki, M. Pannipara, N. Tamaoki, C. Weder, *ACS Cent. Sci.* **2019**, *5*, 874.

Crystalline Molecular Peapod of sp^2- and sp^3-Nanocarbon Molecules

([1]*Department of Chemistry, The University of Tokyo*) ○Seiya Terasaki,[1] Yuki Kotani,[1] Ryosuke Katsuno,[1] Toshiya M. Fukunaga,[1] Taisuke Matsuno,[1] Koki Ikemoto,[1] Hiroyuki Isobe[1]

Keywords: Finite Carbon Nanotube Molecules, Supramolecular Chemistry, Solid-State NMR Analysis, Solid-State Motion

The internal hollow space of carbon nanotubes provides a unique nanometer-sized space to capture various molecular entities. The inner space circumfused by sp^2-carbon networks can also encapsulate diamondoid molecules to afford sp^2/sp^3-hybrid nanocarbon peapods that have recently emerged as unique nanostructures.[1] In this study, the sp^2/sp^3-hybrid peapods have been mimicked by adopting a cylindrical molecule, (9,6)-[3]cyclodibenzochrysenylene (**[3]C^{db}C**),[2] and the diamondoids, i.e., adamantane (**adm**) and diamantane (**diam**), to demonstrate the existence of rotational motions. The solid-state rotational frequency of **[3]C^{db}C$\supset$adm** is measured by NMR spectroscopy to record 1.06 THz that is, to the best of our knowledge, the largest value recorded for solid-state rotations of molecules. Theoretical calculations revealed that multivalent CH-π hydrogen bonds anchored the diamondoid guest on the π-wall of the cylindrical host. The weak hydrogen bonds are prone not only to cleave but also to regenerate at the interfaces, which give freedom to the guest for ultrafast isotropic rotations in the inertial regime.[3] The solid-state rotational motion was preserved with **[3]C^{db}C$\supset$diam** but was altered to biased, single-axis rotation due to a cylindrical molecular shape of the guest. Detailed studies on the dynamics revealed a severe entropic penalty for the single-axis motions.



1) Yao, M.; Stenmark, P.; Abou-Hamad, E.; Nitze, F.; Qin, J.; Goze-Bac, C.; Wågberg, T. *Carbon* **2011**, *49*, 1159-1166. 2) Kogashi, K.; Matsuno, T.; Sato, S.; Isobe H. *Angew. Chem. Int. Ed.* **2019**, 58, 7385-7389. 3) Matsuno, T.; Terasaki, S.; Kogashi, K.; Katsuno, R.; Isobe, H. *Nat. Commun.* **2021**, *12*, 5062.

Multi-Stimuli-Responsiveness Based on π-Stacking Structure of *o*-Carborane Derivatives

(*Graduate School of Engineering, Kyoto University*) ○Kazuhiro Yuhara, Kazuo Tanaka

Keywords: Carborane; Optical Property; Solid-state Luminescence; Thermochormism; Photosalient

o-Carborane is an icosahedral carbon and boron cluster. We have regarded the cluster as a "element-block" constructing crystalline stimuli-responsive materials.[1] Aryl-substituted o-carborane derivatives exhibit intramolecular charge transfer (ICT) emission as a single molecular process.[2] To improve functionality, in addition to ICT emission, we have explored a molecular design utilizing intermolecular interactions.[3,4] In this work, we synthesized *o*-carborane-substituted anthracene derivatives (**1,8-H**, **1-H** and **1,4-H**, Figure 1a) and investigated the relationship between crystal structure and stimuli-responsiveness.

Dependent on the recrystallization solvent, two polymorphs (**α** and **β**) were obtained from **1,8-H**. The crystal structure of **1,8-H(α)** was determined as π-stacking structure (Figure 1a). From photoluminescence (PL) measurement, non-unimodal spectrum and two-component decay (16 ns (11%), 53 ns (89%)) were obtained (Figure 1b). The shorter one at 650 nm and the longer one at 550 nm were assigned to typical ICT emission and novel excimer emission of anthracene, respectively. **1-H** also formed π-stacking structure in crystal and similar two component luminescence was observed. In contrast, for **1,8-H(β)** and **1,4-H**, such structure was not formed and only ICT emission was obtained.

Multi-stimuli-responsiveness was observed based on the π-stacking structure of **1,8-H(α)** and **1-H**. With heating crystals, ICT/excimer intensity ratio increased (Figure 1b). From variable temperature X-ray diffraction, this can be attributed to the elongation of π-π distance with volume expansion, which suppressed excimer emission. In addition, under UV light irradiation, crystal jumping (Photosalient effect) was observed. The product was characterized as dimer (**1,8-H$_{\textbf{dimer}}$** and **1-H$_{\textbf{dimer}}$**) formed by [4+4] cycloaddition (Figure 1c). Details of mechanism will be discussed in the presentation.

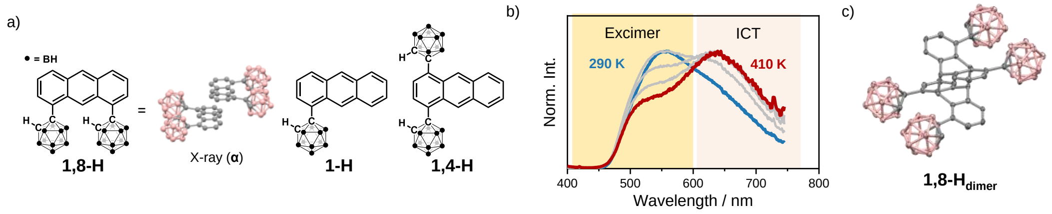


Figure 1. a) Molecular structures of **1,8-H**, **1-H** and **1,4-H**. b) Variable temperature PL spectra of **1,8-H(α)** (30 K steps). c) ORTEP drawing of **1,8-H**$_{\text{dimer}}$ (H atoms were omitted. Grey: C, Pink: B).

1) Tanaka, K. *et al. ACIE.* **2020**, 9841. 2) Chujo, Y. *et al. ACIE.* **2017**, 254. 3) Tanaka, K. *et al. Mater. Chem. Front.* **2022**, 1414. 4) Tanaka, K. *et al. Chem. Eur. J.* **2023**, e202301189.

ジアリール置換した縮環ブタジエン類の固体発光および結晶構造

（阪公大院工）○長岡 朋希・南 春彦・曽 思悦・松井 康哲・大垣 拓也・池田 浩

Solid-state Emission and Crystal Structure of Diaryl-substituted Fused-butadienes

(Grad. *Sch. of Eng., Osaka Metro. Univ.*) ○Tomoki Nagaoka, Haruhiko Minami, Si Yue Zeng, Yasunori Matsui, Takuya Ogaki, Hiroshi Ikeda

Bicycloocadienedione (BD, Fig. 1a) is a unique example of fused-butadines and possesses a 1,3-butadiene and two *α*,*β*-unsaturated ketone subunits in a two-cyclopentanes-fused framework. We previously reported the solid-state emission properties of a dianisyltetramethyl derivative of BD.[1] In this work, we newly synthesized a bis(dicyanomethylene) derivative of BD (DCBD-An, Fig. 1b) and investigated its solid-state emission properties.

Recrystallization of DCBD-An from CH_2Cl_2–CH_3OH provides two crystalline polymorphs, DCBD-An-*O* (orange crystal) and -*R* (red crystal), which exhibited photoluminescence at λ_{EM} = 615 (Φ_{EM} = 0.10) and 651 (0.03), respectively. Dihedral angles between the BD core and an anisyl group of DCBD-An-*O* and -*R* are 51.0 and 41.5°, respectively, indicating that observed longer λ_{EM} of DCBD-An-*R* is due to a large degree of π-conjugation.

In presentation, we will discuss the solid-state emission properties of some oxa-analogs of BD, diarylfurofurandiones (FD-Ph, -Tol, and -An, Fig. 1c).

Keywords: Organic Crystal; X-ray Crystallographic Analysis; Crystalline Polymorph; Conformation; Excimer

ビシクロオクタジエンジオン（BD, Fig. 1a）は縮環ブタジエン類のユニークな一例であり，2 つのシクロペンタノンが縮環した骨格に 1,3-ブタジエンと 2 つの*α*,*β*-不飽和ケトンを有する．当研究室では以前，BD のジアニシルテトラメチル誘導体の固体発光特性を報告した [1]．本研究ではあらたに BD のビス(ジシアノメチレン)誘導体（DCBD-An, Fig. 1b）を合成し，その固体発光特性を調査した．

DCBD-An は CH_2Cl_2–CH_3OH から再結晶すると 2 種類の結晶多形，DCBD-An-*O*（橙色）および-*R*（赤色）が得られ，それぞれ 615 (Φ_{EM} = 0.10) および 651 nm (0.03) に発光を示した．BD 骨格とアニシル基がなす二面角は DCBD-An-*O* および-*R* でそれぞれ 51.0 および 41.5°であったことから，DCBD-An-*R* は π 共役の程度がより大きく，したがってより長波長側に発光すると説明できる．

発表では BD の酸素類縁体ジアリールフロフランジオン（FD-Ph, -Tol, および-An, Fig. 1c）の固体発光特性についても議論する．

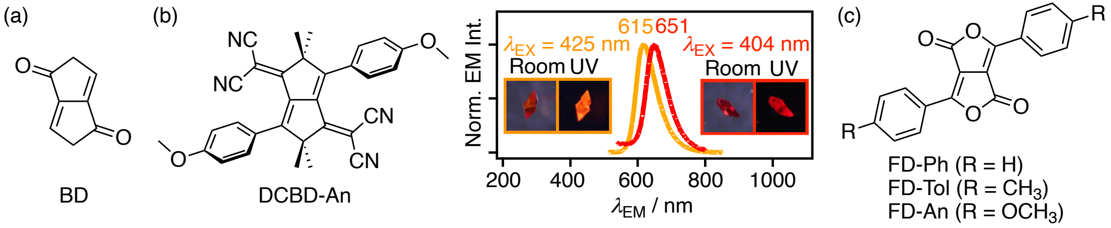


Fig. 1. (a) A chemical structure of BD. (b) A chemical structure of DCBD-An and emission spectra of DCBD-An-*O* (orange line) and -*R* (red line). (c) Chemical structures of FD-Ph, -Tol, and -An.

1) Nagaoka, T.; Matsui, Y.; Fuki, M.; Ogaki, T.; Ohta, E.; Kobori, Y.; Ikeda, H. *ACS Omega* **2022**, *7*, 40364.

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18日(月) 13:00 ~ 15:30 E1132(11号館 [3階] 1132)

[E1132-1pm] 13. 有機化学—反応機構・光化学・電気化学

座長：池田 浩、嶌越 恒

英語

13:00 ~ 13:20

[E1132-1pm-01]

電子供与/求引性の置換基導入に基づく羽ばたく分子の二重発光特性の制御

〇須賀 健介[1]、齊藤 尚平[1] (1. 京大)

英語

13:20 ~ 13:40

[E1132-1pm-02]

Substitution Effect on Photorelease Reaction of Alcohols from Photolabile Molecules Based on 1,4-Naphthoquinone and Its Mechanism

〇Beta Achromi Nurohmah[1], Motonori Washisaka[1], Tsumoru Morimoto[1], Tsuyoshi Kawai[1] (1. Nara Inst. Sci. Technol.)

英語

13:40 ~ 14:00

[E1132-1pm-03]

可視光からUVB光へのフォトン・アップコンバージョンに向けた新規発光体材料の開発

〇宇治 雅記[1]、Moghtader Julian[2]、Roy Bibhisan[3]、楊井 伸浩[1,4] (1. 九大院工、2. Johannes Gutenberg Univ. Mainz、3. H.N.B. Garhwal Univ.、4. JST CREST)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[E1132-1pm-04]

ラジカル連鎖機構によるスルホニル/ハロアレーンを用いる含ヘテロ原子脂肪族の光および電気化学的直接 α-アリール化反応

〇青木 航平[1]、室岡 茉里[1]、西田 智哉[1]、江島 渉[1]、池田 佑子[1]、繁田 愛美[1]、田中 勝大[1]、米倉 恭平[1]、白川 英二[1,2] (1. 関西学院大生命環境、2. JST CREST)

英語

14:30 ~ 14:50

[E1132-1pm-05]

CO_2を用いたアルケンの可視光駆動３成分アシルカルボキシ化反応

〇渡部 太登[1]、ロールウォンカモル プリナット[1]、小杉 健斗[1]、嵯峨 裕[1]、神戸 徹也[1]、近藤 美欧[2,1,3]、正岡 重行[1] (1. 阪大院工、2. 東工大院理、3. JSTさきがけ)

英語

14:50 ~ 15:10

[E1132-1pm-06]

光照射による電子操作を鍵とするアリール金属反応剤とハロゲン化アリール/アリールトリフラートの電子触媒クロスカップリング反応

〇太田 優輝[1]、向井 渓斗[1]、大倉 圭翔[1]、水澤 冴碩[1]、正木 脩[1]、米倉 恭平[1]、白川 英二[1,2] (1. 関西学院大生命環境、2. JST CREST)

🏷 日本語

15:10 ~ 15:30

[E1132-1pm-07]

光アップコンバージョン系におけるエネルギー捕集過程の過渡吸収スペクトル解析

〇松井 康哲[1]、高橋 拓海[1]、大垣 拓也[1]、池田 浩[1] (1. 阪公大)

Controlling dual emission properties of the flapping molecules by electronic tuning

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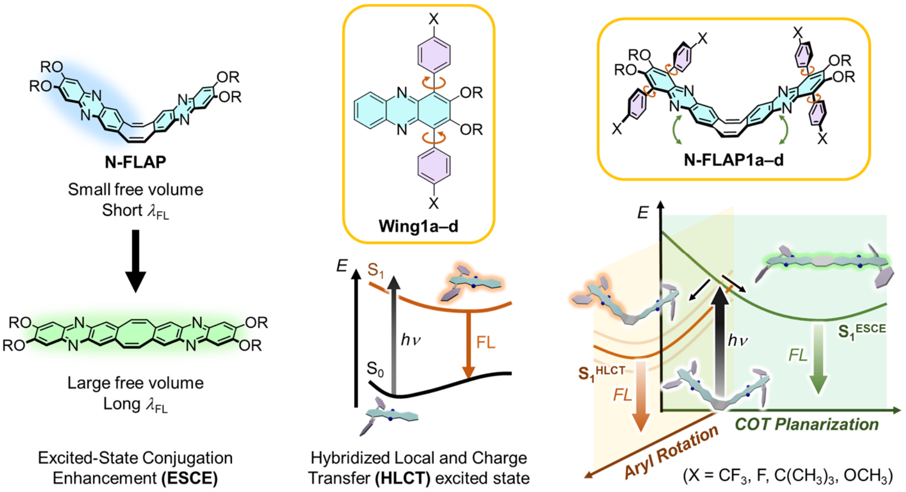
Keywords: Dual Emission; Fluorescence; Quantum Chemical Calculation; Excited State; Intersystem Crossing

Molecular designs for exhibiting dual emission have been widely explored,[1] in which fine tuning of the excited-state energy levels is required. Here we propose an unexplored dual emission mechanism that combines hybridized localized charge transfer (HLCT)[2] and excited-state conjugation enhancement (ESCE) motifs. We developed an HLCT framework by introducing various substituents into the phenazine skeleton. Modulation of the electron-donating/accepting character of the substituents tunes the excited state energy level of the HLCT state. The introduction of electron-donating substituents not only led to the red-shifted fluorescence wavelength, but also increased the fluorescence quantum yield. Quantum chemical calculations suggested an efficient intersystem crossing from the HLCT state to the triplet state in the phenazine derivatives. Incorporation of the phenazine derivative into a flapping molecule (N-FLAP)[3] allowed precise tuning of the dual fluorescence emitted from the HLCT and ESCE states. The energy balance was dependent on the nature of the substituents as well as the solvent polarity. Detailed investigations involving quantum chemical calculations and fluorescence lifetime measurements provided important insights into the deactivation pathways from the excited state. The combination of the HLCT and ESCE states extends the potential functions of dual emissive molecules.



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Substitution Effect on Photorelease Reaction of Alcohols from Photolabile Molecules Based on 1,4-Naphthoquinone and Its Mechanism

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Keywords: 1,4-Naphthoquinone, Photolabile Molecule, Photorelease reaction, Alcohol

Photolabile molecules are described as a type of compound that can release molecules under light irradiation. The general approach to the development of these compounds is by introducing a certain functional group that can be cleaved under light irradiation. Recently, our team has developed new photolabile molecules from commercially available 1,4-naphthoquinone (NQ) in a short-step reaction.[1] Our new photolabile molecules can release various functional compounds, such as alcohols, amines, carboxylic acids, phosphoric acids, and sulfonic acids, under 360 nm light irradiation. However, the reaction mechanism of this photoreaction has not been elucidated. Therefore, in this work, we attempt to elucidate the reaction mechanism of the photorelease reaction of alcohol particularly from the NQ-based photolabile molecules.

The NQ-based photolabile compounds **6-9** with different substituents were successfully synthesized (Fig 1) by attaching the carbonate group to the photolabile platform compound. These compounds can release pentanol along with dimer products that have fluorescence properties, allowing for further application in the bio-imaging field. Our study revealed that the presence of electron-donating and electron-withdrawing groups in the aryl part significantly affects the photorelease sensitivity (yield of pentanol and reaction time) in both polar and non-polar solvents. The DFT calculation showed that there is a charge transfer transition from the aryl group (HOMO) to the quinone ring (LUMO) that might affect the excited state energies in quinone (n-π* electronic configuration) which is sensitive to the polarity of the solvent.[1,2] A study of the presence of TEMPO, a radical scavenger compound, proposed the formation of radical species. Based on our findings, we proposed that the polar solvent might not act as a proton source but be involved in the charge transfer process. The DFT calculation was also performed to propose the mechanism of the photorelease reaction of pentanol.

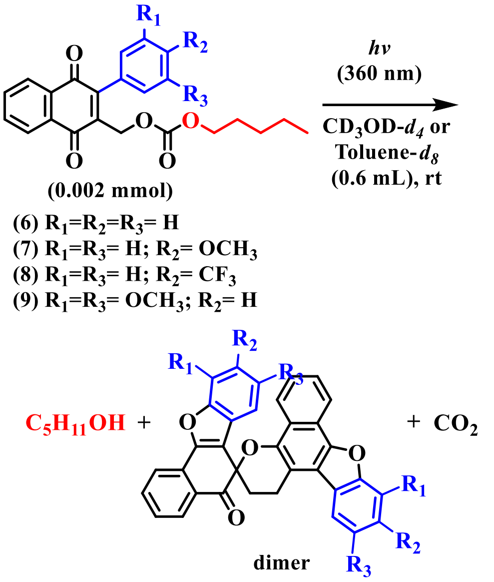

Fig 1. Photorelease reaction of NQ-based photolabile 6-9

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Development of New Emitters for Visible-to-UVB Photon Upconversion Systems

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Keywords: Photon Upconversion, Triplet-triplet Annihilation, UVB Light, Bond Activation

UVB energy (λ < 315 nm) plays a pivotal role in many photochemical applications.[1] However, Since UVB energy is almost non-existent in our living environment, a great deal of effort has been devoted to UVB generation by using inefficient artificial UVB light sources. As an alternative route for generating UVB energy, triplet-triplet annihilation-based photon upconversion (TTA-UC) from visible (λ > 400 nm) to UVB energy has attracted attention due to its ability to achieve relatively high UC efficiency at low excitation light intensity (Fig. 1a).

Recently, our group has reported the first example of TTA-UC from visible light to UVB energy.[2] However, the efficiency of UVB energy generation is low. In addition, the excitation light intensity required to obtain TTA-UC is relatively high compared to TTA-UC in the longer wavelength ranges. Here, we report on the development of new UVB emitters. We focused on furan derivatives that exhibit singlet energy levels near the UVB region (Fig. 1b). 4CzIPN was selected as the sensitizer. Under excitation by a 445 nm laser, the TTA-UC emissions were observed in the UV region. In this presentation, the TTA-UC performance of furan derivatives will be compared and the application to bond activation reactions will be discussed.

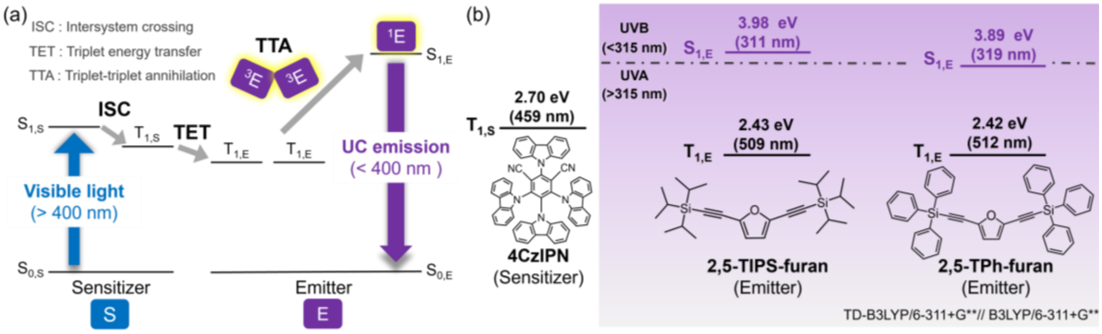

Fig. 1. (a) Energy diagram of visible-to-UVB TTA-UC. (b) Molecular structures and energy levels of singlet (S_1) and triplet (T_1) excited states of the sensitizer and emitters.

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Photo- and Electrochemical Direct α-Arylation of Heteroatom-Containing Aliphatic Compounds with Sulfonyl- or Haloarenes through Radical Chain Mechanism

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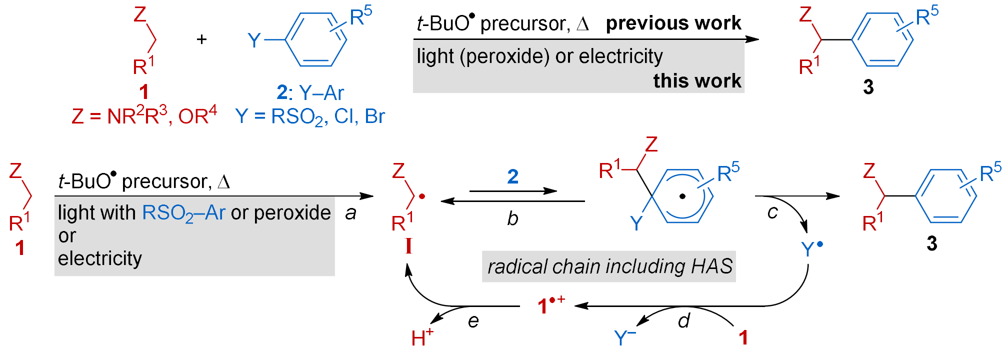
Keywords: Radical Mechanism; Carbon–Carbon Bond Formation; Homolytic Aromatic Substitution; Photoirradiation; Anodic Oxidation

We have already reported the direct α-arylation of heteroatom-containing aliphatic compounds (**1**: alkylamine, alkylamide, alcohol) with sulfonylarenes or aryl halides (**2**: Y–Ar) in the presence of a small amount of a t-BuO$^{\bullet}$ precursor under thermal conditions.[1] The reaction is initiated by thermal homolysis of a t-BuO$^{\bullet}$ precursor, requiring a high temperature, followed by abstraction of an α-hydrogen of **1** by t-BuO$^{\bullet}$ to generate a carbon radical (**I**) (step *a*). Then the reaction goes into a radical chain including a homolytic aromatic substitution (HAS) process consisting of addition of **I** to **2** (step *b*) and elimination of heteroatom radical Y$^{\bullet}$ (step *c*) to give an α-arylation product (**3**), where **I** is regenerated through single-electron oxidation of **1** by Y$^{\bullet}$ (step *d*) followed by deprotonation (step *e*). Here we report that light and electricity were found to induce generation of **I** (step *a*) and accelerate the radical chain to promote the direct α-arylation of alkylamines, alcohols and ethers with sulfonyl- or haloarenes.[2]

Light and electricity work in the α-arylation as follows. In the initiation step (step *a*), light excites RSO$_2$–Ar or peroxides to respectively induce homolysis of the S–Ar bond of RSO$_2$–Ar or the O–O bond of peroxides to generate Ar$^{\bullet}$ or an oxy radical, which abstracts an α-hydrogen from **1** to generate **I**. On the other hand, electricity oxidizes **1** into $\mathbf{1}^{\bullet+}$ to generate **I** through deprotonation. Furthermore, light and electricity were found to take effect also on the radical chain (steps *b*–*e*).



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2) For photo-induced α-arylation of alkylamines, see: K. Yonekura, K. Aoki, T. Nishida, Y. Ikeda, R. Oyama, S. Hatano, M. Abe, E. Shirakawa, *Chem. Eur. J.* **2023**, e202302658. For electrochemical α-arylation of alkylamines, see: K. Yonekura, M. Murooka, K. Aoki, E. Shirakawa, *Org. Lett.* **2023**, *25*, 6682.

Visible-light-driven Three-component Acylcarboxylation of Alkenes with CO_2

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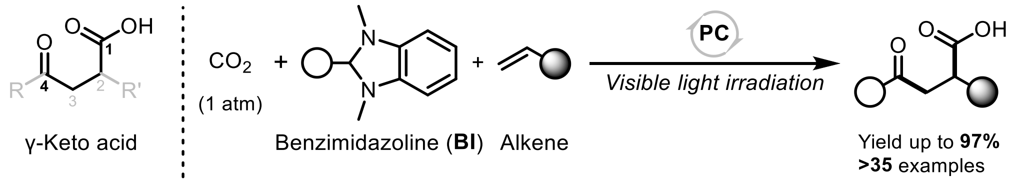
Shigeyuki Masaoka[1]

Keywords: Photocatalysis; γ-Keto acid; Alkene; CO_2

γ-Keto acids are one of the most important chemical motifs widely found in natural products and bioactive molecules.[1] However, their single-step synthesis is challenging because of the intrinsic mismatch of a 1,4-dicarbonyl skeleton[2] and the necessity of a carboxylic protecting group during synthesis. Recently, four examples of the single-step synthesis of γ-keto acids have been reported.[3] Despite their outstanding achievements, these methods have several drawbacks, specifically, the need for special equipment or harsh reaction conditions (with excess hazardous metal reagents or under UV light irradiation) and the use of restricted substrates such as α,β-unsaturated carbonyl compounds, which limit the substrate generality.

Herein, we report the single-step synthesis of γ-keto acids without ester formation using easily preparable starting materials under mild conditions. Our keys to success consist of three aspects; the use of (1) alkenes as abundant feedstocks that can overcome the narrow substrate generality, (2) benzimidazolines (**BI**s) as easily preparable acyl radical donors[4] and (3) CO_2 as an abundant C1 building block. Our photocatalytic system proceeds under mild conditions (visible-light irradiation and modest temperature), in high to excellent yields (up to 97%), with perfect regioselectivity (>20/1), and broad substrate generality (>35 examples). This is also the first example of photocatalytic three-component acylcarboxylation of alkenes. Moreover, sets of mechanistic studies supported our proposed mechanism. Collectively, this study offers a new avenue for providing a wide range of γ-keto acids in a single step from readily available feedstocks in an environmentally friendly manner.



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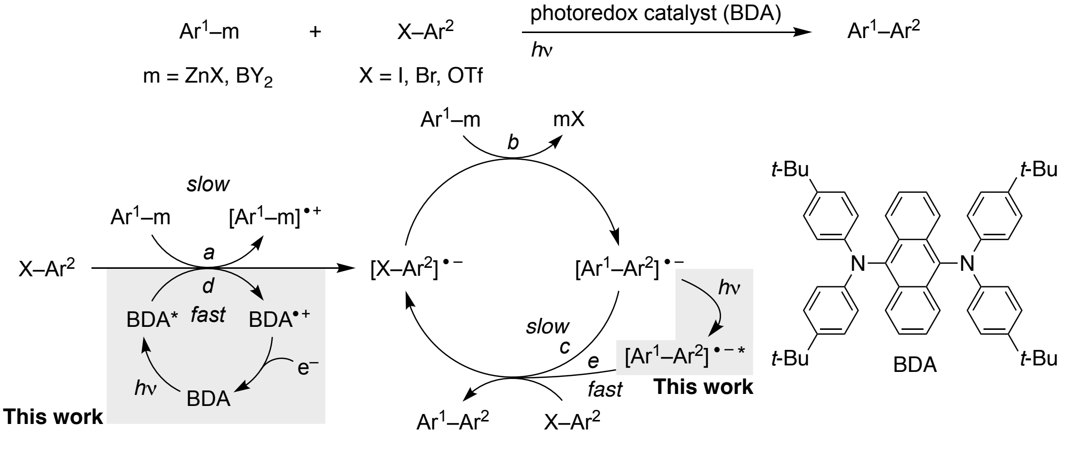
Electron-Catalyzed Cross-Coupling Reaction of Arylmetals with Aryl Halides/Triflates with Manipulation of an Electron by Photoirradiation

([1]*School of Biological and Environmental Sciences, Kwansei Gakuin University*, [2]*CREST, JST*) ○Yuki Ota,[1] Keito Mukai,[1] Keisho Okura,[1] Sahiro Mizusawa,[1] Shu Masaki,[1] Kyohei Yonekura,[1] Eiji Shirakawa[1,2]

Keywords: Radical Mechanism; Electron Catalysis; The Negishi Coupling; The Suzuki–Miyaura Coupling; Photoredox Catalysis

We have already reported the electron-catalyzed cross-coupling reaction of arylmetals with aryl halides.[1] The reaction is initiated by supply of the electron catalyst through single electron transfer (SET) from an arylmetal ($\text{Ar}^1\text{–m}$) toward an aryl halide (X–Ar^2) (step *a*). The resulting anion radical ($[\text{X–Ar}^2]^{\bullet-}$) undergoes carbon–carbon bond formation with $\text{Ar}^1\text{–m}$ to be converted to an anion radical of the coupling product ($[\text{Ar}^1\text{–Ar}^2]^{\bullet-}$) (step *b*), from which SET toward X–Ar^2 takes place to give the coupling product ($\text{Ar}^1\text{–Ar}^2$) and regenerate $[\text{X–Ar}^2]^{\bullet-}$ (step *c*). Here SET in step *a* is slow and thus a high temperature over 100 °C is required for the reaction to proceed. Here we report that the electron-catalyzed cross-coupling reaction of arylzinc/boron reagents with aryl halides/triflates was found to be accelerated by photoirradiation in the presence/absence of a photoredox catalyst (BDA).[2] The photoirradiation plays two roles: making BDA excited to work as an electron catalyst supplier (step *d*) and photoexciting $[\text{Ar}^1\text{–Ar}^2]^{\bullet-}$ to facilitate transfer of the electron catalyst toward X–Ar^2 (step *e*). By utilizing the both roles, the coupling of arylzinc/boron reagents with aryl halides proceeds at a low temperature. In addition, the coupling of arylzinc reagents with aryl halides/triflates is accelerated alone by photoirradiation in the absence of any photoredox catalyst, utilizing the effect of light in step *e*.



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光アップコンバージョン系におけるエネルギー捕集過程の過渡吸収スペクトル解析

(阪公大院工 ^{1}・阪公大 RIMED^{2})
◯松井 康哲 ^{1,2}・高橋 拓海 ^{1}・大垣 拓也 ^{1,2}・池田 浩 ^{1,2}

Transient Absorption Spectroscopic Analysis of Energy Harvesting Process in the Photon Upconversion System

(^{1}*Grad. Sch. of Eng., Osaka Metro. Univ.*, ^{2}*RIMED, Osaka Metro. Univ.*)
◯Yasunori Matsui,^{1,2} Takumi Takahashi,^{1} Takuya Ogaki,^{1,2} Hiroshi Ikeda^{1,2}

Photon upconversion (UC) is a molecular technology that converts a low-energy light to a higher-energy light by employing triplet energy transfer and triplet–triplet annihilation (TTA). To achieve an efficient TTA-UC in the solid-state, intermolecular energy-transfer (ET) process is quite important. In this study, we analyzed the ET behavior of triplet species in the polyurethane composite by using transient absorption spectroscopy.

Keywords : Transient Absorption; Energy Transfer; Triplet–Triplet Annihilation; Dexter Mechanism

光アップコンバージョン（PUC）とは，三重項エネルギー移動と三重項—三重項消滅（TTA）を利用して低エネルギー光子を高エネルギー光子に変換する技術である．固体中において高効率な PUC を実現するには，エネルギードナー（D）およびアクセプター（A）を効果的に分散させ，励起三重項エネルギーの捕集と高効率な TTA が必要である．本研究では，ポリマー媒体において高効率な PUC を達成するため，ポリウレタン（PU）樹脂に D として白金オクタエチルポルフィリン（PtOEP，Fig. 1），メディエータ（M）としてアントラセン（An），A の連結体としてダイアド DPA–Ad–DPA を添加し，三重項エネルギー捕集が期待できる複合体（Fig. 2）の調製と，PUC 過程における過渡吸収スペクトル解析を行った．

PtOEP，An，DPA の E_T の序列は，E_T(PtOEP) = 1.91 eV > E_T(An) = 1.83 eV > E_T(DPA) = 1.75 eV であり，実際に PU 複合体に 532 nm 光を照射すると，励起子が ^{3}PtOEP*から ^{3}An*を経由して ^{3}DPA*–Ad–DPA に捕集される挙動が観測された．発表では，DPA–Ad–DPA 以外の種々の連結体を添加した複合体の挙動の差についても述べる．

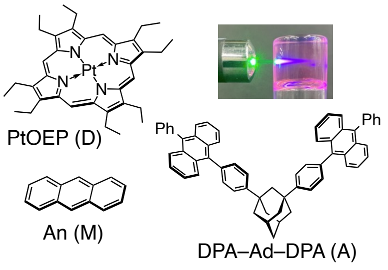

Fig. 1. Structures of PtOEP, An, and DPA–Ad–DPA, and a photograph of the PU composite.

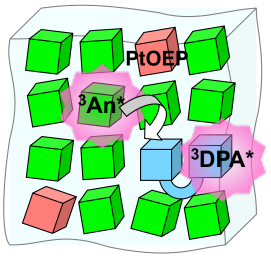

Fig. 2. A schematic representation of polymer composites containing PtOEP, An, and DPA–Ad–DPA.

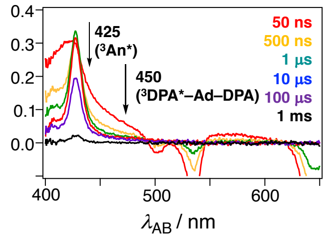

Fig. 3. Transient absorption spectra of the PU composite of PtOEP (50 μM), An (10 mM), and DPA–Ad–DPA (0.5 mM) (λ_{EX} = 532 nm).

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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18日(月) 15:55 ~ 17:15 E1123(11号館 [2階] 1123)

[E1123-1vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：佐藤 隆章、中 建介

英語

15:55 ~ 16:15

[E1123-1vn-01]

ワンポット3成分反応による硫黄官能基の合成

○齋藤 文登[1]、David Austrup[1]、Simon Euteneuer[1]、Marc Fimm[1] (1. ルートヴィヒ・マクシミリアン大学ミュンヘン)

英語

16:15 ~ 16:35

[E1123-1vn-02]

光励起を利用したニトロアレーン還元法の開発とニトロソDiels-Alder反応への応用

○岡村 俊孝[1]、金子 泰己[1]、伊藤 凛[1]、佐藤 隆章[1] (1. 慶應義塾大学)

英語

16:35 ~ 16:55

[E1123-1vn-03]

ホスファボラタトリプチセン骨格を有するホスホニウムベタインの観測とその反応

○内山 洋介[1]、山岸 正太郎[1]、安川 拓哉[1] (1. 北里大学)

日本語

16:55 ~ 17:15

[E1123-1vn-04]

アミノ(ホスフィニル)アレーンの一電子還元によるパイ拡張カルバゾールの化学選択的合成

○奥田 靖浩[1]、森 まつり[1]、今田 裕二[1]、松永 夏旺[1]、折田 明浩[1] (1. 岡山理大)

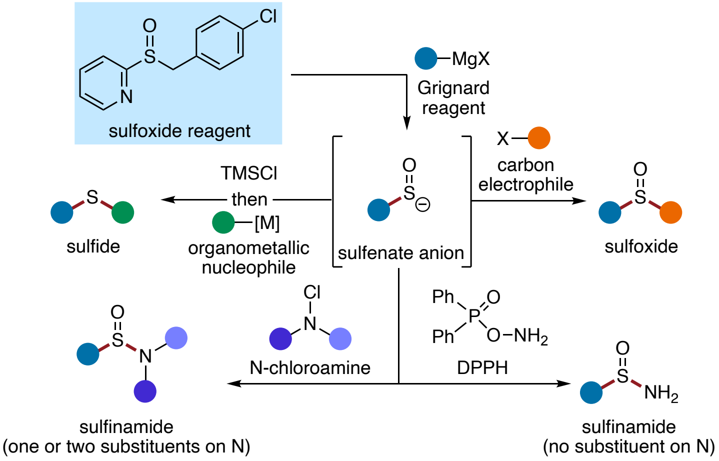
One-Pot, Three-Component Assembly of Sulfur Functionalities

([1]*Department of Chemistry, Ludwig Maximilian University Munich*) ○Fumito Saito,[1] David Austrup,[1] Simon Euteneuer,[1] Marc Fimm[1]

Keywords: Sulfoxides; Sulfinamides; Sulfinamidines; Sulfur Monoxide; One-Pot Synthesis

Sulfoxides and sulfinamides represent versatile sulfur(IV) functional groups that have found many applications as ligands in transition metal catalysis, chiral auxiliaries, and key intermediates to access sulfur(VI) motifs such as sulfoximines and sulfonimidamides. Synthetic methods to prepare sulfur functionalities, including sulfoxides and sulfinamides, typically rely on substrates bearing preinstalled sulfur functional groups, most commonly foul-smelling, oxidation-sensitive thiols. These canonical protocols, however, suffer from limited synthetic efficiency and substrate scope, as thiols and other substrates with a preformed C–S bond have limited availability. To rapidly assemble a large number of organosulfur products with different substitution patterns, a three-component coupling to install two substituents onto the central sulfur unit in a single operation would be an ideal approach.

I will present the application of a readily prepared, bench-stable sulfoxide reagent for one-pot, three-component syntheses of sulfoxides, sulfinamides, and sulfides.[1,2] Sulfenate anions (RSO^-), in situ generated from the sulfoxide reagent and Grignard reagents (RMgX), serve as diverging points to access these distinct product classes. I will also demonstrate a designed sulfinylhydrazine reagent as another effective "S=O" unit donor for one-pot synthesis of sulfoxides and sulfinamides.[3] Finally, I will discuss our recent findings on the first enantioselective synthesis of sulfinamidines.



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Photoinduced Reduction of Nitroarene and Application to Nitroso Diels-Alder Reaction

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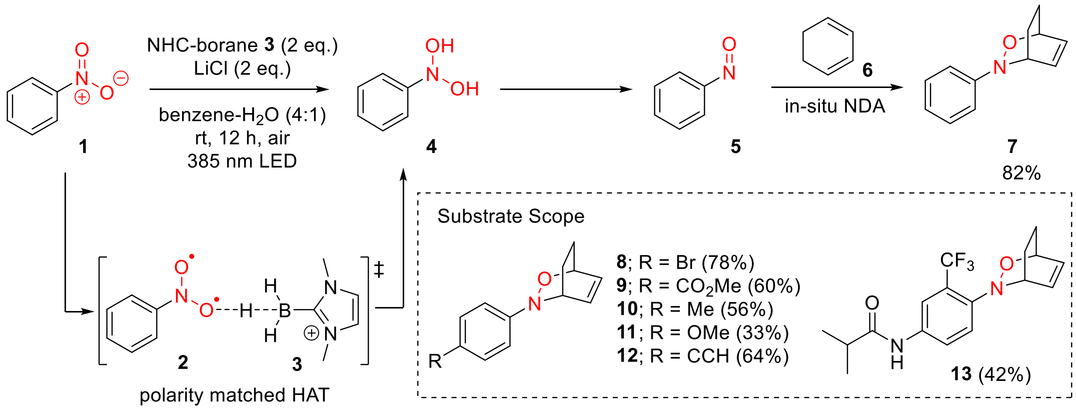
Keywords: Nitroarenes; Nitrogen-containing Aromatic Compounds; Photoexcitation; NHC-borane; Hydrogen Atom Transfer; Nitroso Diels-Alder Reaction

The rapid synthesis of nitrogen-containing aromatic compounds is high importance to the chemistry community. These compounds can be readily obtained from nitroarenes, which are cost-effective starting materials. However, the development of strategies for direct C-N bond formation in nitroarenes, bypassing fully reduced anilines, remains an underexplored area. This is notable considering the numerous applications of these aromatic amines in the pharmaceutical and materials industries. Herein, we report a photochemical strategy for the conversion of nitroarenes into nitrosoarenes via hydrogen atom transfer and application to nitroso Diels-Alder reaction.[1]

Upon photoirradiation and intersystem crossing, nitroarene **1** would populate its triplet state **2** featuring biradical character.[2] We hypothesized that efficient hydrogen atom transfer (HAT) with NHC-borane **3**[3] would provide access to nitrosoarene **5**, which is applied to nitroso Diels-Alder reaction and other reactions. Based on this plan, we selected nitrobenzene (**1**) as a starting material, cyclohexadiene (**6**) as a diene source. A brief survey of reaction conditions, the desired product **7** was yielded in 82% when NHC-borane and LiCl were used under blue LED irradiation (385 nm). Substituted nitroarenes featuring electron donating and electron withdrawing groups were found to be suitable for nitroso precursors and allowed for significant conversion to the corresponding 3,6-dihydro-1,2-oxazines in moderate-to-good yields (**8**–**12**). The late-stage functionalization of flutamide was also achieved to give **13** in moderate yield, further highlighted the utility of our developed reaction.

Scheme. Overview of Photoinduced Nitroarene Reduction and Application to Nitroso Diels-Alder Reaction



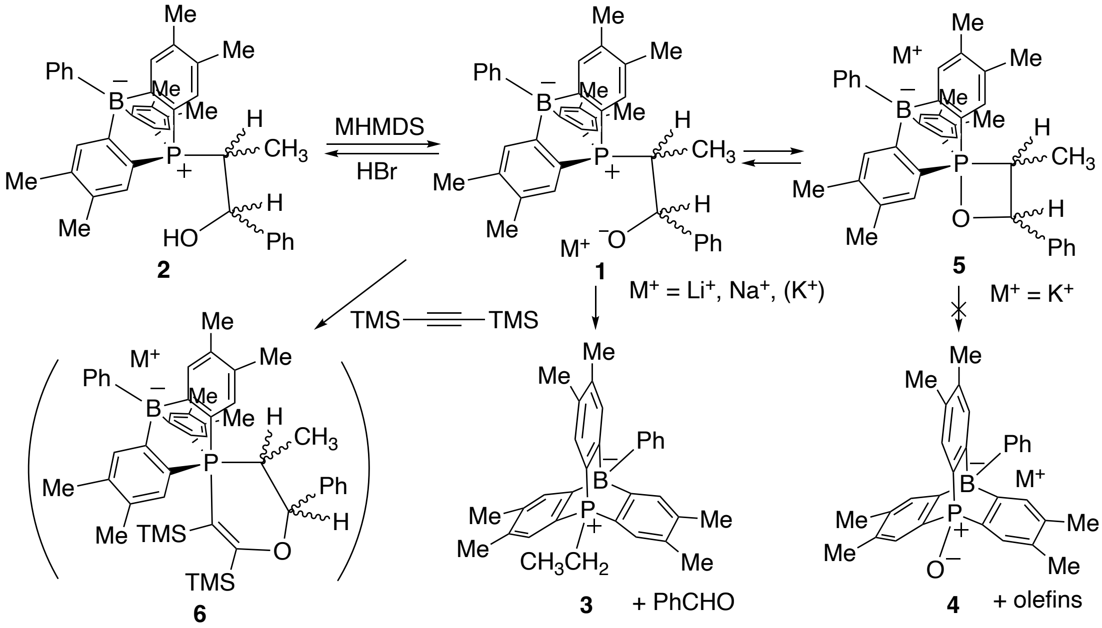
1) S. Carosso and M. J. Miller, *Org. Bionol. Chem.* **2014**, *12*, 7445. 2) R. Hurley and C. Testa, *J. Am. Chem. Soc.* **1966**, *88*, 4330. 3) T. Taniguchi, *Chem. Soc. Rev.* **2021**, *50*, 8995.

Observation and Reactivities of Phosphonium Betaines Containing a Phosphaboratatriptycene Skeleton

([1]*School of Science, Kitasato University*) ○Yosuke Uchiyama,[1] Shotaro Yamagishi,[1] Takuya Yasukawa[1]

Keywords: Wittig reaction; Reactive Intermediate; Phosphonium betaine; Deprotonation; 1,2-Oxaphosphetane

To investigate the role of phosphonium betaines in the Wittig reaction, their generation and reactivities were studied by means of the deprotonations of *β*-hydroxyethylphosphonium salts containing a phosphaboratatriptycene skeleton using MHMDS (M = Li, Na, and K) and the dipolar cycloaddition reactions, respectively. The phosphonium betaines **1-Li** were thermodynamically stable and converted to *β*-hydroxyalkylphosphonium salts **2** by the addition of HBr in MeOH, whereas the phosphonium betaines **1-Na** were unstable at 0 °C, providing the corresponding ethylphosphonium salt **3** and PhCHO. On the other hand, 1,2-oxaphosphetanes **5** were observed upon using KHMDS by $^{31}P\{^{1}H\}$ NMR spectroscopy and gave also **3** and PhCHO instead of the corresponding olefin and phosphine oxide **4**. The deprotonations of *β*-hydroxyalkylphosphonium salts **3** with NaHMDS and KHMDS followed by the addition of bis(trimethylsilyl)acetylene seemed to provide cycloadducts **6** *via* **1**, which were stable at 25 °C and showed phosphorus-31 signals at around –50.8 ppm in the lower field than that of **5**, respectively. We will report the calculated results and reactivities of the phosphonium betaines **1** in this presentation.



1) Y. Uchiyama, S. Yamagishi, T. Yasukawa, *J. Org. Chem.*, **2022**, *87(23)*, 15899. 2) Y. Uchiyama, S. Yamagishi, T. Yasukawa, *Phosphorus Sulfur Silicon Relat. Elem.*, **2022**, *197(5-6)*, 457.

日本化学会 第104春季年会 (2024)

アミノ(ホスフィニル)アレーンの一電子還元によるパイ拡張カルバゾールの化学選択的合成

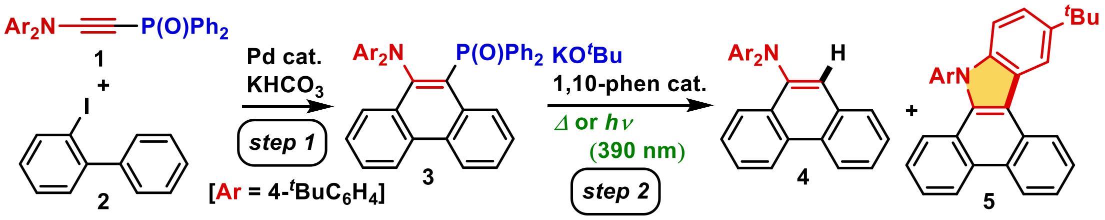
（岡山理大工）○奥田 靖浩・森 まつり・今田 裕二・松永 夏旺・折田 明浩
Chemoselective Synthesis of π-Expanded Carbazoles via Single-Electron Reduction-Promoted Dephosphinylative Cyclization of Amino(phosphinyl)arenes (*Faculty of Engineering, Okayama University of Science*) ○Yasuhiro Okuda, Matsuri Mori, Yuji Imada, Natsuo Matsunaga, Akihiro Orita

Carbazoles are widely employed as superior electronic and optical materials, for example *spiro*-OMe-TAD as a hole transporting material and 4CzIPN as an OLED with thermally activated delayed fluorescence (TADF) properties. Recently, we synthesized amino(phosphinyl) phenanthrene **3** via a palladium-catalyzed direct [4+2] benzannulation of phosphinyl ($Ph_2P(O)$) ynamine **1** and 2-iodobiphenyl (**2**) (Scheme 1, *step 1*). We present herein a chemodivergent dephosphinylation of **3** with KO^{t}Bu/1,10-phen under thermal and photochemical conditions (*step 2*). When the annulation product **3** was treated with KO^{t}Bu/1,10-phen in 1,4-dioxane solvent at 100 °C, aminophenanthrene **4** was obtained. On the other hand, the dephosphinylative cyclization product **5** was predominantly formed under 390 nm LED irradiation conditions. In this presentation, we also discuss a theoretically analyzed single-electron reduction mechanism.

Keywords : Phosphinyl Group; Photocyclization; Carbazole; Anion Radical; Chemoselective

カルバゾール誘導体は spiro-OMe-TAD が正孔輸送材料，4CzIPN が TADF 特性を有する有機 EL 材料として利用されるなど，エレクトロニクス・光学材料として優れた特性を発現する。最近，我々はパラジウム触媒を用いてホスフィニル基 ($P(O)Ph_2$) を置換したイナミン **1** と 2-ヨードビフェニル (**2**) の [4+2] 環化を行い，アミノ (ホスフィニル) フェナントレン **3** を合成した (Scheme 1, *step 1*)。本発表では，**3** に KO^{t}Bu と触媒量の 1,10-フェナントロリンを加えて脱ホスフィニル化したところ，熱的条件と光照射条件では化学選択性が転換したので，この内容について述べる (*step* 2)。

二置換フェナントレン **3** に KO^{t}Bu と触媒量の 1,10-フェナントロリンを加え，1,4-ジオキサン溶液中，100 °C に加熱するとヒドロ化体 **4** が得られた。一方，紫色 LED を照射した際には脱ホスフィニル化と同時に分子内環化が進行してパイ拡張カルバゾール **5** が化学選択的に得られた。これらの反応は一電子還元で発生したフェナントレニドを経て進行すると予想している。本発表では詳細なメカニズムについて説明する。



Scheme 1. イナミン **1** の直截環化に続く異なる型の化学選択的な脱ホスフィニル化

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18日(月) 15:55 ~ 17:15 E1141(11号館 [4階] 1141)

[E1141-1vn] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：盛田 大輝、武藤 慶

英語

15:55 ~ 16:15

[E1141-1vn-01]

Non-electronic activation on anthracene ring by steric repulsion between substituents

○Annisa Indah Reza[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

英語

16:15 ~ 16:35

[E1141-1vn-02]

鉄触媒による自己酸化イミンのアザ環化π拡張反応

○張 岩[1]、福間 翔太[1]、尚 睿[1]、中村 栄一[1] (1. 東京大学)

英語

16:35 ~ 16:55

[E1141-1vn-03]

ベンザインと窒素置換アルキンの新奇な分子内環化付加反応の開発

○田渡 司[1]、坂上 峻哉[1]、伊藤 琢磨[2]、原渕 祐[3,4]、前田 理[3,4,5]、高須 清誠[1]、瀧川 紘[1] (1. 京大院薬、2. 北大院総化、3. 北大WPI-ICReDD、4. JST-ERATO、5. 北大院理)

日本語

16:55 ~ 17:15

[E1141-1vn-04]

シクロドデシプチセンの合成

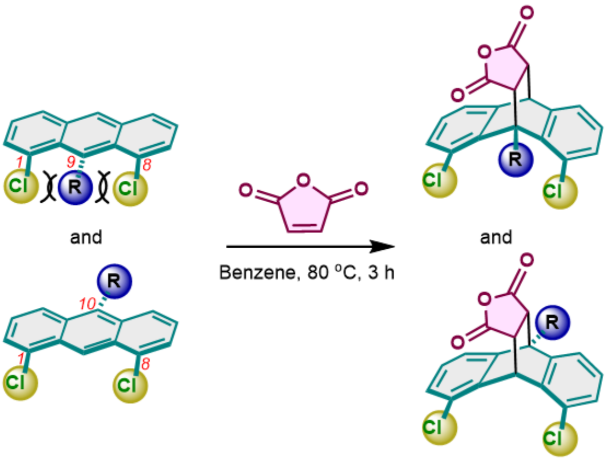
○兵頭 瑞樹[1]、岩田 隆幸[2]、新藤 充[2] (1. 九大院総理工、2. 九大先導研)

Non-Electronic Activation on Anthracene Ring by Steric Repulsion between Substituents

([1]*Graduate School of Engineering Science, Kochi University of Technology,* [2]*Research Center for Molecular Design, Kochi University of Technology*) ○Annisa Indah Reza,[1] Kento Iwai,[1,2] Nagatoshi Nishiwaki[1,2]

Keywords: Non-electronic activation; Steric repulsion; Ring distortion; Anthracene; Diels-Alder reaction

In our previous work, aromatic distortion of 1-methylquinolinium salts[1] and 1,8-dimethyl- and 1,8-diidonaphthalenes[2,3] was achieved using an intense steric repulsion between the *peri*-substituents. The reactivity was found to be higher as the substituent was bulkier. Herein, we extensively explored this non-electronic activation into another aromatic system using 1,8-dichloroantracene, where its 9- and 10-positions are separately substituted with methoxy and alkyl groups. The anthracene framework was distorted, especially in the vertical direction, compared to its 10-substituted counterparts, and the distortion was significant as the bulkiness of the substituent was larger. Thus, the distortion of the anthracene ring is due to the steric repulsion with chloro groups at the *peri*-positions. The Diels-Alder reactions with maleic anhydride were conducted to evaluate the distorted anthracenes' activation. Generally, the product yields became higher as the substituent was bulkier. Moreover, anthracene possessing an isopropyl group was more highly activated than derivative with a strongly electron-donating methoxy group, indicating the anthracene framework was activated non-electronically rather than influenced electronically.



R	Yield/%	Recovery/%
OMe	75	18
Me	79	15
Et	75	20
^{n}Pr	80	12
^{i}Pr	91	5

R	Yield/%	Recovery/%
OMe	53	36
Me	50	35
Et	63	20
^{n}Pr	58	30
^{i}Pr	75	12

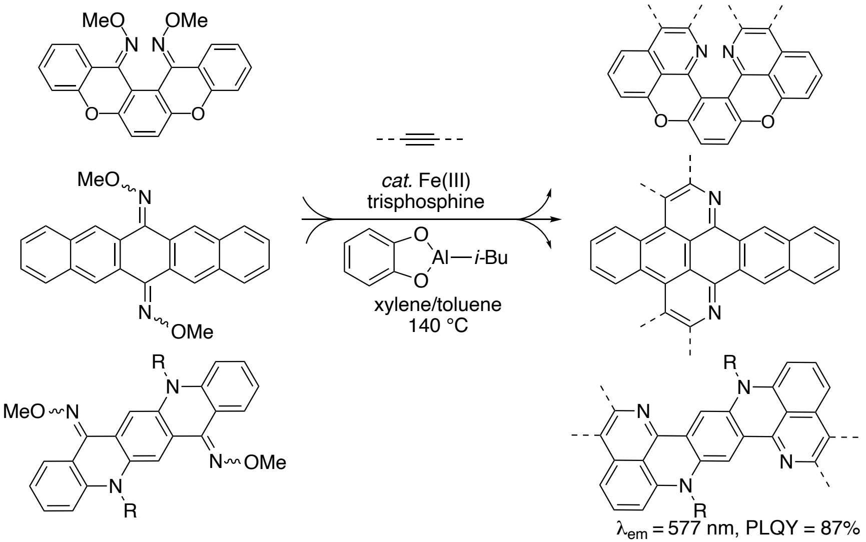
1) *Bull. Chem. Soc. Jpn.* **2020**, *93*, 50–58. 2) *Molecules* **2023**, *28*, 5343. 3) *J. Org. Chem.* **2023**, *88*, 9409–9412.

Iron-Catalyzed Aza-Annulative π-Extension using a Self-Oxidation Auxiliary

(*Graduate School of Science, The University of Tokyo*) ○Yan Zhang, Shota Fukuma, Rui Shang, Eiichi Nakamura

Keywords: Aza-Annulative π-Extension, Iron Catalysis, C−H Activation, Narrow-Band Emissive Molecules

Aza-annulative π-extension (**AAPE**) reactions[1] offer a potent pathway to create novel donor-acceptor conjugated materials by integrating an imine moiety into the conjugated system, serving as an electron-accepting unit[2]. However, the affinity of late-transition metals for conjugated π-systems, coupled with their elevated cost, has posed significant challenges, restricting efficient **AAPE** reactions on straightforward C–H substrates for developing conjugated new materials. In this study, we unveil an iron-catalyzed C–H activation methodology[3], facilitating **AAPE** with diverse internal alkynes and employing oxime ether as both a self-oxidizing auxiliary[4] and nitrogen source, derived seamlessly from accessible carbonyl compounds. The **AAPE** reaction was enabled by using trisphosphine as a ligand, and isobutyl aluminum(III) catecholate as a base.[5] By using the reaction, we discovered an aza-oxa[5]helicene from dixanthone as a potential circularly polarized luminescence material and two narrow-band-emissive molecules from easily accessible pentacene-6,13-dione and quinacridone, which emit blue and yellow light with high color purity and high fluorescence quantum yield. These findings emphasize the potential of iron-catalyzed C–H activation in expanding the range of donor-acceptor-type conjugated materials for organic electronics.



λ_{em} = 577 nm, PLQY = 87%
FWHM = 25 nm

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2. Patel, D. G.; Feng, F.; Ohnishi, Y.-y.; Abboud, K. A.; Hirata, S.; Schanze, K. S.; Reynolds, J. R. *J. Am. Chem. Soc.* **2012**, *134* (5), 2599-2612.
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5. Shang, R.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2016**, *138*, 10132−10135.

ベンザインと窒素置換アルキンの新奇な分子内環化付加反応の開発

（京大院薬 [1]・北大院総化 [2]・北大 WPI-ICReDD[3]・JST-ERATO[4]・北大院理 [5]）○田渡 司 [1]・坂上 峻哉 [1]・伊藤 琢磨 [2]・原渕 祐 [3,4]・前田 理 [3,4,5]・高須 清誠 [1]・瀧川 紘 [1]

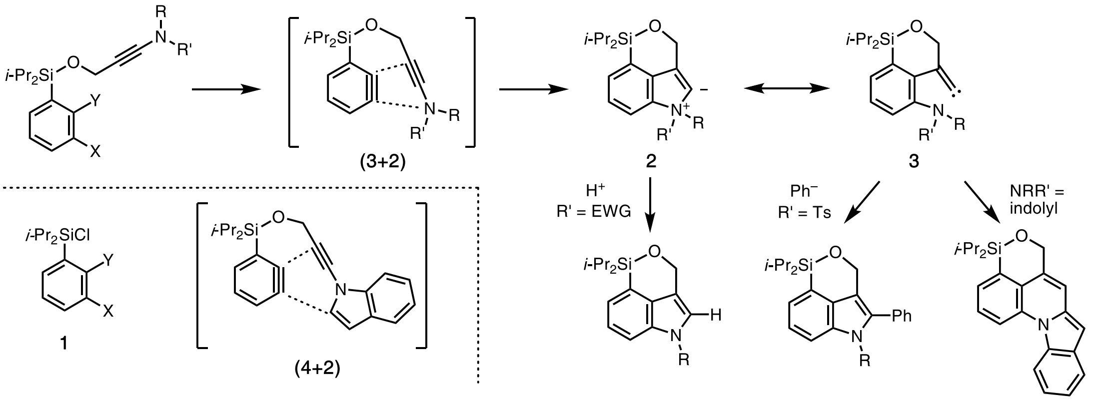
Novel Intramolecular Cycloadditions of Benzyne with Nitrogen-substituted Alkynes

([1]*Graduate School of Pharmaceutical Sciences, Kyoto University*, [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [3]*WPI-ICReDD*, [4]*JST-ERATO*, [5]*Faculty of Science, Hokkaido University*) ○Tsukasa Tawatari,[1] Takaya Sakaue,[1] Takuma Ito,[2] Yu Harabuchi,[3,4] Satoshi Maeda,[3,4,5] Kiyosei Takasu,[1] Hiroshi Takikawa[1]

Herein, we report novel cycloaddition reactions of benzyne with nitrogen-substituted alkynes, using our originally-developed benzyne precursor **1**.[1,2] Our findings include intramolecular (3+2) cycloadditions of ynamides and *N*-alkynylindoles as three-atom components.[3] A notable feature is that indolium ylide intermediate **2**, whose resonance structure is vinylidene **3**, displays an ambivalent character with both nucleophilic and electrophilic properties, which facilitates the construction of various nitrogen-containing aromatic compounds. A further significant finding is the unprecedented (4+2) cycloadditions observed when employing *N*-alkynylindoles. In this presentation, the details of these reactions including substrate scope and mechanistic study by DFT calculations will be discussed.

Keywords : Benzyne; Ynamide; N-alkynylindole; Intramolecular reaction; Heteroaromatic

今回、我々は、ベンザインと窒素置換アルキンとの新奇な分子内環化付加反応を見出したので報告する。すなわち、独自に開発したベンザイン前駆体 **1**[1,2] を活用し、イナミドおよび *N*-アルキニルインドールとの分子内反応を検討した結果、窒素置換アルキンを三原子成分とする新奇な(3+2)環化付加反応が進行することが分かった[3]。また、環化付加反応の後に生じる中間体は、イリド **2** とその共鳴構造であるカルベン **3** の両方に相当する反応性を示し、多様な含窒素芳香族化合物の合成に展開できることを明らかにした。さらに、*N*-アルキニルインドールとの反応では、前例のない(4+2)環化付加反応が進行することも判明した。本講演では、基質一般性や DFT 計算による反応機構解析など、この反応の詳細について発表する。



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2) T. Tawatari, K. Takasu, H. Takikawa, *Chem. Commun.* **2021**, *57*, 11863.
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シクロドデシプチセンの合成

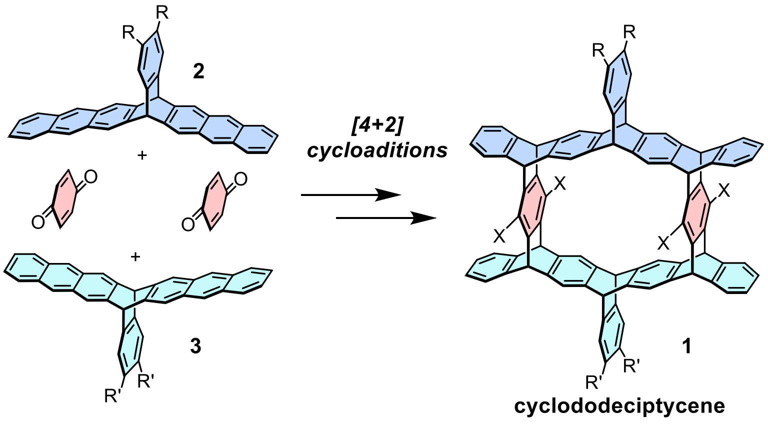
（九大総理工[1]・九大先導研[2]）○兵頭 瑞樹[1]・岩田 隆幸[2]・新藤 充[2]
Synthesis of cyclododeciptycene ([1]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University,* [2]*Institute for Materials Chemistry and Engineering, Kyushu University*)
○Mizuki Hyodo,[1] Takayuki Iwata,[2] Shindo Mitsuru[2]

Cyclododeciptycene **1** is a macrocyclic compound consisting of six triptycene units, which was proposed by Hart. Although Hua synthesized its quinone derivative, and Itami and Segawa reported synthesis of its regioisomer, synthesis of compound **1** has not yet been achieved. In this study, based on our previous findings,[3,4] we constructed the cyclic structure through stepwise [4+2] cycloaddition reactions between the quinone unit and the anthracene unit. we have successfully synthesized cyclododeciptycene **1** for the first time by reducing the quinone.

Keywords : Cyclic Iptycenes; Macrocyclic compounds; Cycloaddition; Triptycenes

シクロドデシプチセン**1**は、6つのトリプチセンユニットからなる大環状イプチセンである。1986年にHartらによりその構造が提唱された後、Huaらによるキノン体の合成[1]や伊丹、瀬川らによる異性体の合成[2]が報告されたが、**1**の合成は未だ達成されていない。我々は、これまでに活性アントラセンを用いた新規トリプチセン合成法を開発し[3]、これを基盤として、「ambidentアントラセン」を用いた鎖状イプチセンの系統的合成の開発に成功した[4]。本研究では、これらの知見をもとに、シクロドデシプチセン**1**の合成について検討した。

トリプチセンを原料にアントラセン構造を2つもつトリプチセン**2**および**3**を合成した。これらに対して、キノンユニットを段階的に反応させることで、4度の[4+2]環化付加反応を行い、環状構造を構築した。最後に、キノン部位の還元を経て、シクロドデシプチセン**1**の初の合成に成功した。



(1) H. Hua, *et al.*, *J. Am. Chem. Soc.* **2010**, *132,* 17635. (2) Y. Segawa, K, Itami, *et al.*, *Chem. Sci.* **2020,** *11,* 6775. (3) T. Iwata, M. Hyodo, T. Fukami, Y. Shiota, K. Yoshizawa, M. Shindo*, Chem. Eur. J,* **2020**, *26,* 8506. (4) T. Iwata, M. Hyodo, R. Kawano, M. Shindo*, Chem. Eur. J.* **2023**, e20230368.

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

2024年3月18日(月) 13:00 ~ 15:40 E1142(11号館 [4階] 1142)

[E1142-1pm] 15. 有機化学—脂肪族・脂環式化合物，新反応技術

座長：荒巻 吉孝、太田 英介

英語

13:00 ~ 13:20

[E1142-1pm-01]

gem-ジフルオロシクロプロパン誘導体の双方向性均等開裂の制御によるレジオ分岐型[3+2]環化付加反応

○内田 裕貴[1]、Tobias Schirmer[1]、Julian Kürschner[2]、田浦 悠也[1]、荒巻 吉孝[1]、大井 貴史[1] (1. 名大院工・ITbM、2. ミュンスター大)

英語

13:20 ~ 13:40

[E1142-1pm-02]

アニオン性8π系電子環状反応による7員環β-ケトエステル誘導体の合成

○加藤 蘭丸[1]、斎藤 優輝[1]、谷野 圭持[2] (1. 北大院総化、2. 北大院理)

13:40 ~ 13:50

休憩

英語

13:50 ~ 14:10

[E1142-1pm-03]

ヘテロ芳香族エステルを用いたケトンとエステルの結合交換反応

○中原 輝[1]、一色 遼大[1]、山口 潤一郎[1] (1. 早稲田大学)

英語

14:10 ~ 14:30

[E1142-1pm-04]

亜鉛触媒を用いた亜リン酸ジエステル合成

○松永 晃[1]、齋藤 由樹[1]、小林 修[1] (1. 東京大学)

英語

14:30 ~ 14:50

[E1142-1pm-05]

Catalytic phosphonylation of alcohols with bis(2,2,2-trifluoroethyl) phosphite for the synthesis of phosphite diesters

○Dario Mrdovic[1], Yuki Saito[1], Shu Kobayashi[1] (1. The University of Tokyo)

14:50 ~ 15:00

休憩

日本語

15:00 ~ 15:20

[E1142-1pm-06]

金ナノ粒子触媒を用いたカルボニル化合物の直接シリルエノールエーテル化

○町田 陸[1]、浅尾 直樹[1] (1. 信州大院総理工)

日本語
15:20 ~ 15:40
[E1142-1pm-07]

活性メチレンおよびメチン化合物の不活性アルケンによる光アルキル化反応

○山下 恭弘[1]、小林 修[1] (1. 東京大学)

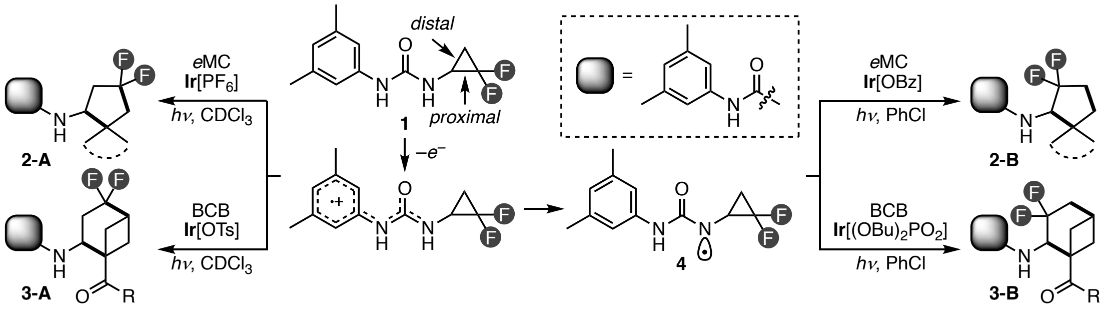
Regio-divergent [3+2] Cycloaddition of *gem*-Difluorocyclopropane Derivatives Based on the Control of Bidirectional Bond Cleavage

([1]*Graduate School of Engineering and Institute of Transformative Bio-Moleclues (ITbM), Nagoya University*, [2]*Universität Münster*) ○Yuki Uchida,[1] Tobias E. Schirmer,[1] Julian C. G. Kürschner,[2] Yuya Taura,[1] Yoshitaka Aramaki,[1] Takashi Ooi[1]

Keywords: Regio-divergent synthesis; Radical cycloaddition reaction; Fluorine compounds, Photoredox catalysis

As aliphatic fluorine compounds play an important role in pharmaceutical and biofunctional chemistry, their regio-divergent synthesis provides a powerful method for rapidly expanding the chemical library.[1] Cyclopropane derivatives featuring the activated bonds that can be easily cleaved would serve as C3 units suitable for addressing the regioselectivity issue. Here, we report the regio-divergent synthesis of aliphatic fluorine compounds, which relies on the control of bidirectional bond cleavage of *gem*-difluorocyclopropane. Based on our previous experience of utilizing an urea group as an anion-binding and redox-active amine equivalent,[2] we hypothesized that the difference in the interactions between a difluorocyclopropyl urea and a counter anion of a cationic iridium photoredox catalyst would lead to control the direction of the bond cleavage of difluorocyclopropane, thereby enabling the regio-divergent synthesis.

To substantiate our hypothesis, urea **1** was treated with *exo*-methylene cyclic compounds (*e*MC) in the presence of [Ir(dF(CF_3)ppy)(dtbbpy)][PF_6] (**Ir**[PF_6]) under blue LED irradiation in $CDCl_3$, which afforded **2-A** as a major product, while the use of **Ir**[OBz] as a catalyst in chlorobenzene led to the formation of **2-B** as a major product. This strategy was also applicable to the reactions with bicyclobutanes (BCB), affording **3-A** and **3-B**, respectively. Importantly, the urea group was readily transformed into a free amino group. DFT calculations revealed the origin of the effect exerted by the counter anion of the iridium cation on the selectivity. With less basic counter anions such as PF_6 and OTs, the C–C bond cleavage proceeds from a radical cation intermediate, which prefers the proximal C–C bond cleavage to give terminal CF_2 radical. Meanwhile, basic OBz or $(OBu)_2PO_2$ deprotonates radical cation intermediate to generate neutral radical **4**, which prefers the distal C–C bond cleavage to give terminal CH_2 radical.



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アニオン性 8π 系電子環状反応による 7 員環 β-ケトエステル誘導体の合成

（北大院総化[1]・北大院理[2]）○加藤 蘭丸[1]・斎藤 優輝[1]・谷野 圭持[2]

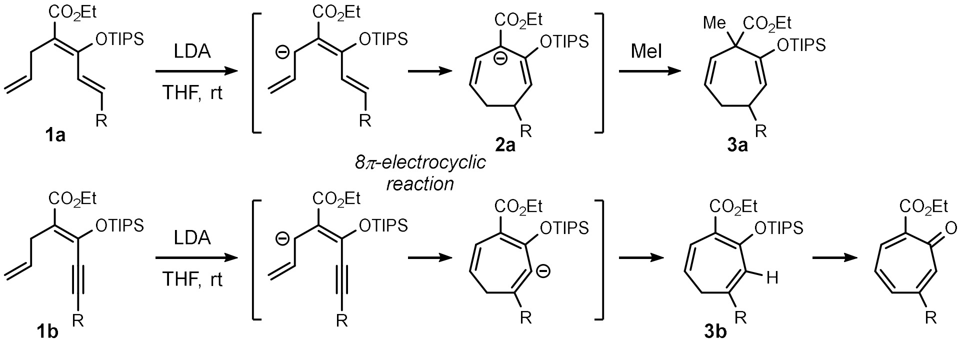
Synthesis of Seven-Membered Cyclic *β*-Ketoester Derivatives by Anionic 8*π*-Electrocyclic Reaction

([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Faculty of Science, Hokkaido University*) ○Ranmaru Kato,[1] Hiroki Saito,[1] Keiji Tanino[2]

We recently reported the 8*π*-electrocyclic reactions of triene derivatives under basic conditions, giving rise to seven-membered carbocycles.[1)] Under the influence of LDA, substrate **1a** underwent deprotonation at the bis-allylic position followed by the anionic electrocyclic reaction to form carbanion **2a** which was treated with methyl iodide to afford seven-membered cyclic diene **3a** as the single regioisomer of double bonds. The utility of the highly functionalized cyclization product led us to explore the scope and limitation of the electrocyclic reactions. Dienyne **1b** afforded seven-membered cyclic triene **3b** after protonation of the anion species under the same conditions. It was also revealed that **3b** could be the useful synthetic precursor of substituted tropones after oxidation.

Keywords: Electrocyclic Reaction, π-Conjugate System, Carbanion, Seven-Membered Carbocycle, β-Ketoester

8*π* 系共役アニオンの電子環状反応による炭素 7 員環形成は古くから知られているが、実用的な合成手法とは見なされていなかった。これに対して我々は、適切な電子求引基を導入したトリエン基質を用いることで、天然物合成にも応用可能な炭素 7 員環構築法を開発した[1)]。すなわち、トリエン **1a** に LDA を作用させると、ビスアリル位での脱プロトン化と続くアニオン性電子環状反応により 7 員環アニオン **2a** を生じ、このものは one-pot でのメチル化を経て 7 員環ジエン **3a** を二重結合に関する単一の位置異性体として与えた。今回我々は、本反応基質の適用範囲の拡張を目指して検討を行った。その過程で、ジエニン **1b** を同様の反応条件に付すことで、炭素 7 員環トリエン **3b** が得られることを見出した。さらにこの **3b** は、酸化により多置換トロポンの有用な合成前駆体となることも明らかとなった。



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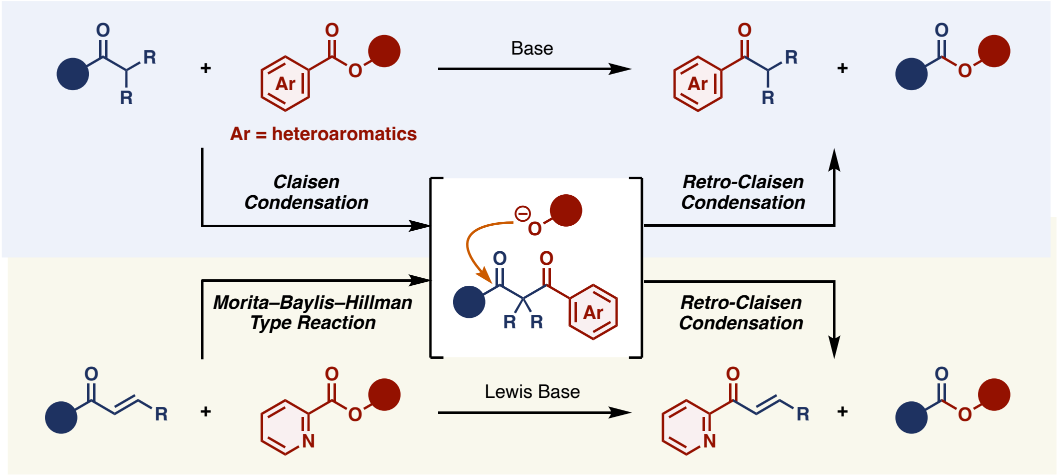
Bond Exchange Reaction between Ketones and Esters using Heteroaromatic Esters

(Graduate School of Advanced Science and Engineering, Waseda University)
○Hikaru Nakahara, Ryota Isshiki, Junichiro Yamaguchi

Keywords: Claisen Condensation; Retro-Claisen Condensation; Morita–Baylis–Hillman Reaction; Lewis Base; Bond Exchange Reaction

Bond exchange reactions between distinct functional groups offer a means to modify two organic molecules with high atom efficiency. Recently, various methods involving transition-metal catalysts have been reported for the replacement of substituents in two aromatics.[1] Additional example of bond exchange reactions without transition-metal catalysts include a Claisen and retro-Claisen condensation sequence between ketones and esters.[2] However, this approach is limited to the exchange between α-2° ketones and alkyl perfluorocarboxylate such as methyl trifluoroacetate. Herein, we have developed a concise method for the exchange between diverse ketones and heteroaromatic esters. This method is also applicable not only to α-2° ketones but also to methyl ketones and α-3° ketones. It can facilitate the ring-open macrocyclic ketones and strained cyclic ketones. Using Lewis bases, exchange reactions of unsaturated ketones were also achieved *via* a Morita–Baylis–Hillman type reaction and retro-Claisen reaction sequence. This methodology not only provides a novel synthetic route for heteroaromatic compounds frequently found in pharmaceuticals and natural products, but also convert ketones to esters without oxidants.



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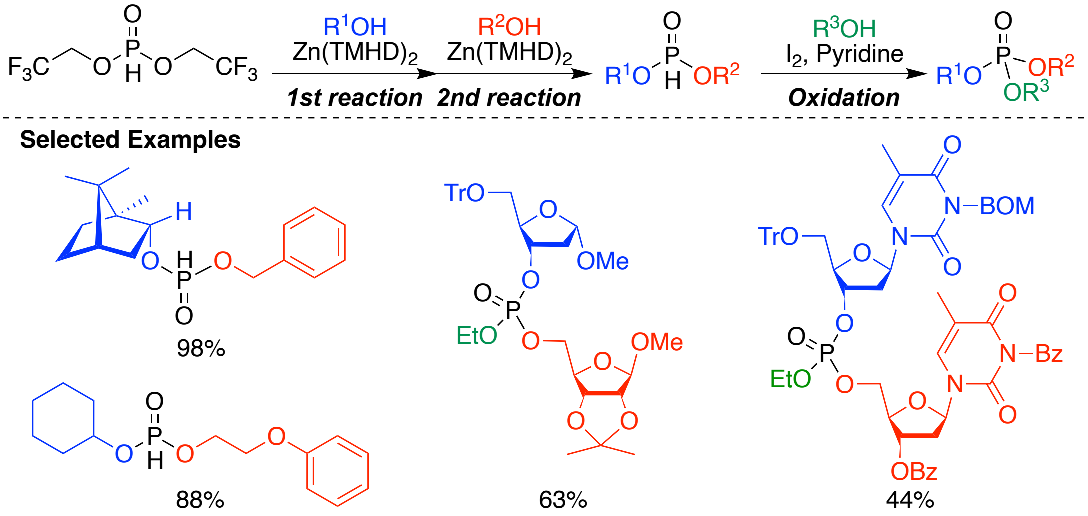
One-pot Catalytic Reactions of Phosphite Diesters toward the Synthesis of Oligonucleotides

(School of Science, The University of Tokyo) ○Akira MATSUNAGA, Yuki SAITO, Shū KOBAYASHI

Keywords: One-pot Synthesis; Phosphite Diester; Zinc Catalyst; Transesterification; Oligonucleotide

Organophosphates play vital roles in various fields, ranging from biology to material science. In particular, oligonucleotide therapeutics have gained a significant attention as promising novel therapeutic modalities due to their high specificity and potential application in treating incurable diseases. Solid-phase phosphoramidite reactions have commonly been the method of choice for oligonucleotide synthesis, offering high reliability.[1] However, this method suffers from requiring excessive amounts of activating reagents. To address this limitation, our laboratory previously reported a zinc-catalyzed synthesis of phosphite diesters under mild conditions.[2] Despite making significant progress, this approach still possess several limitations; for example, a need for the addition of molecular sieves and a reduction in selectivity for the second phosphonylation step. In this study, we discovered that changing the leaving group from a methoxy group to a 2,2,2-trifluoroethoxy group enabled the desired reaction to proceed with excellent reactivity and selectivity in the absence of molecular sieves. This approach enabled synthesis of asymmetric phosphite diesters in a one-pot manner by using various simple alcohols as nucleophiles. Furthermore, by carefully controlling solvent and temperature, this method proved successful with substrates such as carbohydrates and nucleosides, which possess sterically hindered structures and multiple Lewis basic functional groups. Finally, the obtained phosphite diesters could be readily converted to stable phosphate triesters via oxidative conversion.



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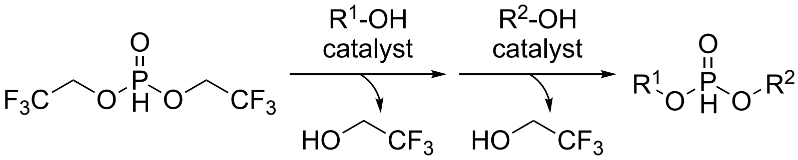
Catalytic Phosphonylation of Alcohols with Bis(2,2,2-trifluoroethyl) Phosphite for the Synthesis of Phosphite Diesters

(School of Science, The University of Tokyo) ○Dario MRDOVIĆ, Yuki SAITO, Shū KOBAYASHI

Keywords: Hafnium catalyst; Organocatalyst; Phosphonylation; Phosphite diesters; Bis(2,2,2-trifluoroethyl) phosphite

Phosphite diesters, a class of organophosphorus compounds, find diverse applications. They serve as key intermediates in the synthesis of organophosphonates, -phosphoramidates and -phosphates, which have garnered attention for their biological activities and medicinal chemistry relevance. Efficient synthesis of phosphite diesters is crucial for advancing the synthesis of P(V) compounds and expanding the scope of phosphorus chemistry. While traditional methods like phosphoramidite and H-phosphonate approaches are well-established, they suffer from drawbacks like excess substrate/reagent usage and dependence on additives. Catalytic and additive-free phosphorylation methods using P(V) reagents often require harsh conditions or are limited to monoesters. Therefore, development of a catalytic approach for additive-free synthesis of organophosphite diesters under mild conditions with minimal waste is a more sustainable alternative. Our group previously reported the use of dimethyl phosphite as a phosphonylating reagent to form phosphite diesters with various alcohols using a Zn catalyst.[1] Expanding this convenient approach using Zn(II) catalysis to a one-pot synthesis of phosphite diesters utilizing bis(2,2,2-trifluoroethyl) phosphite as the P(III) reagent revealed selectivity issues for challenging substrates. This led us to investigate the metal effect in Lewis acid catalysts, revealing that four metals, Zn(II), Hf(IV), Zr(IV) and Al(III), efficiently catalyzed the phosphonylation of various alcohols and diols. Notably, Hf(IV) and Zr(IV) displayed superior selectivity compared to Zn(II). Further exploration into organocatalysts identified several Lewis base catalysts, particularly imidazole-type ones, with remarkable activity in promoting alcohol phosphonylation.



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金ナノ粒子触媒を用いたカルボニル化合物の直接シリルエノールエーテル化

（信州大院総理工）○町田 陸・浅尾 直樹

Gold nanoparticle-catalyzed direct synthesis of silyl enol ethers from carbonyl compounds

(*Graduate School of Science and Technology, Shinshu University*) ○Riku Machida, Naoki Asao

Silyl enol ethers are key nucleophilic synthons in various organic reactions. Silylation of enolate ions is a most common synthetic method, but it needs a stoichiometric amount of bases for the formation of enolate ions from ketones. Some alternative base-free approaches have been reported with homogeneous catalysts so far, but only a few with heterogeneous ones. Here we report a new synthestic method of silyl enol ethers from ketones or aldehydes with disilanes by use of gold nanoparticles under neutral conditions.

A catalytic amount of titanium oxide supported gold nanoparticles (Au/TiO_2) was added to a solution of cyclohexanone and hexamethyldisilane in 1,4-dioxane under an inert gas. The resulting mixture was heated at 80 degrees for 2 hours to give a desired product in 80 % yield. This method was applicable to various ketones or aldehydes and the corresponding products were obtained in moderate to good yields. The reaction is stopped by the addition of TEMPO, suggesting that a radical intermediate would be involved.

Keywords：gold nanoparticles; heterogeneous catalyst; neutral conditions; silyl enol ether

シリルエノールエーテルは、重要な求核性シントンとして様々な有機合成反応に利用されている。その合成方法は、エノラートイオンのシリル化反応が最も一般的であるが、ケトンからエノラートイオンを生成するために化学量論量の塩基が必要となる。これまでに均一系遷移金属触媒を用いた塩基不要の合成法がいくつか開発されてきたが、不均一系触媒を用いた例は少ない。今回我々は、金ナノ粒子触媒を用いることにより、ケトンやアルデヒドとジシランを用いた中性条件下で進行する新しい合成法を見出したので報告する。

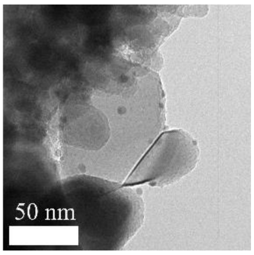
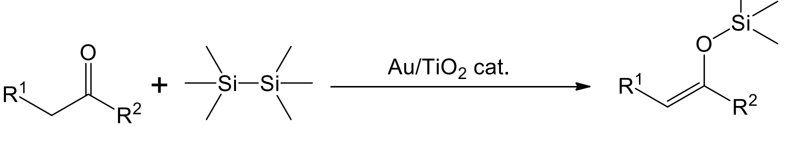


Fig. TEM image of Au/TiO_2

シクロヘキサノンとヘキサメチルジシランの 1,4-ジオキサン溶液に、酸化チタン担持金ナノ粒子（Au/TiO_2）を触媒量加え、不活性ガス雰囲気下で 2 時間 80 ℃で攪拌したところ反応が進行し、シリルエノールエーテルが 80 %の収率で得られた。本手法は、様々なアルデヒドやケトンにも適用可能であり、対応する生成物が中程度から良好な収率で得られた。本反応の機構解明のため、TEMPO を加えたところ反応が停止したことから、本反応はラジカル中間体の関与が示唆された。



活性メチレンおよびメチン化合物の不活性アルケンによる光アルキル化反応

(東大院理) ○山下恭弘・小林 修

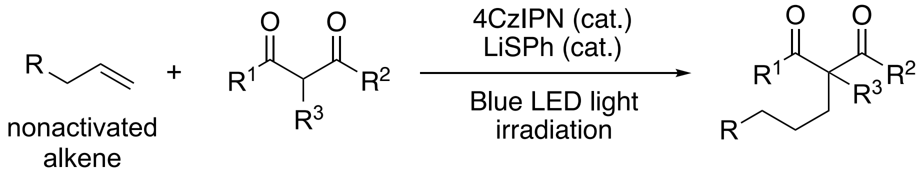
Development of Photoinduced Alkylation Reactions of Active Methylene and Methine Compounds with Nonactivated Alkenes

(School of Science, The Univ. of Tokyo) ○Yasuhiro YAMASHITA・Shū KOBAYASHI

α-Alkylation reactions of carbonyl compounds are a fundamental methodology in organic synthesis. While traditional alkylation methods based on nucleophilic substitution of alkyl halides are less atom-economical, the addition reactions of alkenes offer a more sustainable approach. However, utilizing nonactivated alkenes like 1-decene has been historically challenging due to their limited reactivity. Recently, we have reported the development of a photoinduced α-alkylation strategy for active methylene and methine compounds with nonactivated alkenes.1) This reaction employs an organophotocatalyst such as 4CzIPN and lithium thiophenoxide (LiSPh) under blue LED light irradiation. Under mild reaction conditions and with low catalyst loading, the desired products are obtained in high yields with a slight excess of active methylene/methine compound relative to the alkene. In this presentation, we will report our recent findings on this novel alkylation reactions of active methylene and methine compounds with nonactivated alkenes.

Keywords: Nonactivated Alkene; Photocatalyst; Active methylene compound; Alkylation; Visible light

カルボニル化合物α位でのアルキル化反応は、これまで求電子剤としてハロゲン化アルキル等を用いる求核置換反応によって主に行われている。一方で、アルケンに対する求核付加反応によるアルキル化は、高い原子効率を実現できるが、電子求引基(EWG)を持たないアルケンは反応性が低く、特に 1-デセン等の不活性アルケンを用いた反応は非常に困難であった。最近、演者らは、不活性アルケンによる活性メチレン化合物等のアルキル化反応を、有機光触媒である 4CzIPN とリチウムチオフェノキシド触媒を用いることにより、青色光照射下で実現することに成功した 1)。この反応は、温和な条件下、アルケンに対して少過剰量の活性メチレン化合物の使用で高収率にて進行することや、用いる触媒量が少なくて良いこと等の特徴を有し、実用性の面からも理想的なアルキル化反応の一つであると言える。本講演では、この反応に関する研究の最新の成果について報告する。



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

2024年3月18日(月) 13:00 ~ 15:40　E1143(11号館 [4階] 1143)

[E1143-1pm] 15. 有機化学―脂肪族・脂環式化合物，新反応技術

座長：安藤 吉勇、美多 剛

日本語
13:00 ~ 13:20

[E1143-1pm-01]
新規ビタミンD誘導体の合成と活性

○伊部 公太[1]、掘田 稜二[1]、中田 春樹、大上 真由、岡本 専太郎[1] (1. 神奈川大)

英語
13:20 ~ 13:40

[E1143-1pm-02]
グリーンものづくり：ファインバブル法によるフェアリー化合物の合成

○Arun Kumar Manna[1]、佐藤 浩平[1]、鳴海 哲夫[1]、間瀬 暢之[1] (1. 静大院)

日本語
13:40 ~ 14:00

[E1143-1pm-03]
H/D同位体性キラル分子の速度論的分割

○内田 竜也[1,2]、中川 雄太[1]、渡 直樹[1] (1. 九大、2. 科学技術振興機構)

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30

[E1143-1pm-04]
Nickel-Iridium Dual Catalyzed Buchwald-Hartwig-Type Amination Reaction of Aryl Chlorides under Microwave and Visible Light Dual Irradiation

○Abhijit Sen[1], Bukhanko Valerii[1], Heeyoel Baek[1], Aya Ohno[1], Atsuya Muranaka[1], Yoichi M. A. Yamada[1] (1. RIKEN, Center for Sustainable Resource Science)

日本語
14:30 ~ 14:50

[E1143-1pm-05]
量子化学計算に基づくアミンと二酸化炭素からのアルケンの触媒的アミノカルボキシル化：気液フローシステムへの展開

○神名 航[1]、原渕 祐[2,3]、林 裕樹[2,3]、髙野 秀明[2,3]、小塚 智貴[4]、櫻井 大斗[4]、間瀬 暢之[4]、前田 理[2,3,5]、美多 剛[2,3] (1. 北大院総化、2. 北大WPI-ICReDD、3. JST-ERATO、4. 静岡大工、5. 北大院理)

14:50 ~ 15:00
休憩

日本語
15:00 ~ 15:20

[E1143-1pm-06]
独自に合成した多孔性塩基性樹脂による連続フローHenry反応

〇降矢 裕一[1]、石谷 暖郎[1]、小林 修[1] (1. 東京大学)

🏷 日本語

15:20 ~ 15:40

[E1143-1pm-07]

安定化高分子パラジウム触媒を用いた連続フロー式鈴木-宮浦反応の開発

〇Zhang Zhenzhong[1]、大野 綾[1]、山田 陽一[1] (1. 理化学研究所)

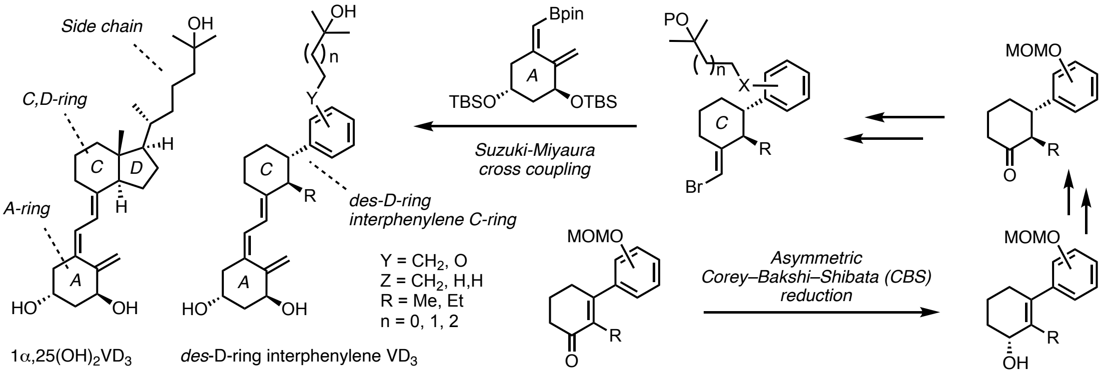
Design, synthesis, and properties of novel vitamin D_3 derivatives

([1]*Department of Frontier Bioscience, Kanagawa University*) ○Kouta Ibe,[1] Ryoji Hotta,[1] Haruki Nakada,[1] Mayu Ohgami,[1] Sentaro Okamoto[1]

Keywords: *des*-D-ring interphenylene vitamin D derivatives; *des*-D-ring interphenylene C-ring unit; A-ring unit; vitamin D receptor

1α,25-dihydroxyvitamin D_3 discovered as a main hormone of calcium and phosphate metabolism, that have a wide range of biological functions including the cell proliferation-differentiation, apoptosis, and the immune systems.[1] However, the therapeutic application of the 1α,25-dihydroxyvitamin D_3 have been limited due to its serious side effects hypercalcemia and hyperphosphatemia. Therefore, the development of more efficient, safer, and topically treatable vitamin D_3 analogues remains an unmet needs. Most of the vitamin D_3 analogues are modified in the side chain and/or A-ring counterparts, only a few having structural modified C,D-ring analogues have been developed. Nevertheless, biological studies on these analogues have been suggested that modified C,D-ring can reduce the calcemic side effects.[2]

Accordingly, we report the design and synthesis of novel C,D-ring modified 1α,25-dihydroxyvitamin D_3 derivatives as a *des*-D-ring interphenylene vitamin D_3, which lack the D-ring and have an interphenylene structure attached to the C-ring. Synthesis of the *des*-D-ring interphenylene C-ring units were carried out using a modified Corey-Bakshi-Shibata (CBS) reduction for key reactions. And its derivatives are then constructed via the Suzuki–Miyaura coupling reaction with the corresponding A-ring unit, and the evaluated on their VDR binding affinity and a reporter-gene assay.[3]



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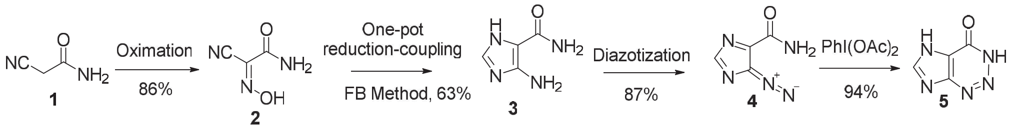
Green Manufacturing: Synthesis of Fairy Chemicals Using Fine Bubble Strategy

(*Graduate School of Science and Technology*, *Shizuoka University)*
○Arun Kumar Manna, Kohei Sato, Tetsuo Narumi, Nobuyuki Mase

Keywords: Green Manufacturing; Fairy Chemicals; Fine Bubble Organic Synthesis; Plant Growth Regulator; Hypervalent Iodine

2-Azahypoxanthine (AHX), 2-aza-8-oxohypoxanthine (AOH), and 1H-imidazole-4-carboxamide (ICA), collectively referred to as fairy chemicals (FCs), which are known for their plant growth-regulating properties. Kawagishi *et al.* have confirmed that these compounds can increase seed production in crops such as rice, wheat, and tomato by over 30-40%.[1] However, large-scale synthesis of these FCs remains underdeveloped due to the absence of efficient chemical synthetic pathways.

In the context of green process developments, we have demonstrated efficient gas-mediated reactions using fine bubbles (FB, <100 μm), which enhance gas concentration in the solution even under ambient pressure because of the long resident time, large surface area, and self-pressurization.[2,3] For AHX synthesis, commercially available 2-cyanoacetamide (**1**) was used as the starting material. Oxime **2** was synthesized using $NaNO_2$ and acetic acid in 86% yield. Compound **3** was obtained through a one-pot reductive coupling reaction employing FB-H_2 as a green reactant, Pt/C as a catalyst, and formamidine acetate as a coupling partner. We explored four distinct FB technologies, with the highest yield of 63% achieved using a multi-stacking element (MSE) FB generator under atmospheric H_2 pressure. Although compound **3** formation depends on various factors, the formed microbubbles (MB, 1-100 μm) concentration plays a major role in the reaction. The big MB covers the catalyst's active site and reduces the catalytic activity.[4] The resulting compound **3** was subjected to diazotization, affording diazene **4** intermediate stable in a solid state at room temperature.[5] After optimization of the subsequent intramolecular cyclization, we found PhI(OAc)$_2$ was effective as a catalyst (0.5 mol%),[6] facilitating the intramolecular cyclization in water within 15 minutes and precipitating the desired product in 94% yield.



1) H. Kawagishi, *Proc. Jpn. Acad. Ser. B Phys. Biol. Sci.* **2019**, *95*, 29–38; 2) M. Takahashi, *J. Phys. Chem. B.* **2005**,*109,* 21858-21864; 3) W. B. Zimmerman *et al.*, *Ind. Eng. Chem. Res.* **2012**, *51*, 1864–1877; 4) N. Mase *et al., Bull. Chem. Soc. Jpn.,* **2023***, 96,* 752–758; 5) T. Kan *et al.*, *Org. Biomol. Chem.* **2014**, *12*, 3813–3815; 6) J. Liu *et al.*, *RSC Adv.* **2015**, *5*, 25485–25488.

H/D 同位体性キラル分子の速度論的分割

（九大 I2CNER・九大基幹・JST PREST[1]・九大院理[2]）[1]○内田 竜也[1]・中川 雄太[2]・渡 直樹[2]

Optical resolution of H/D isotopic chiral molecule

([1]*International Institute for Carbon Neutral Energy Research, Kyushu University, Faculty of Arts and Science, Kyushu University, JST PREST*, [2]*Graduate School of Science, Kyushu University*) ○ Tatsuya Uchida,[1] Yuta Nakagawa,[2] Naoki Watari[2]

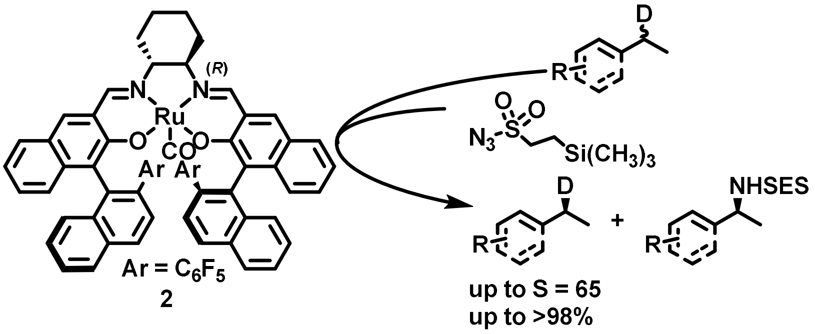
The direct recognition and resolution of H/D isotopic chirality remain challenges in chemistry because there is no difference in size and bond length between each isotopomer. Therefore, isotopic chirality is considered a cryptochiral compound. However, there is a significant difference in the bond dissociation energy between C–H and C–D bonds. Therefore, it was considered that enantiomerically pure H/D isotopic chiral compounds could be obtained through kinetic resolution by using highly enantioselecive C-H functionalization that exhibits a large kinetic isotope effect.

Based on the consideration, we conducted the asymmetric amidation of H/D isotopic racemic compounds bearing stereogenic center as a reactive site, such as benzylic and allylic positions. We found that almost enantiomerically pure H/D isotopic chiral molecule could be obtained via Ru(CO)-salen **2**-catalyzed asymmetric C–H amidation.

Keywords : H/D isotopic chirality; C–H amidation; Asymmetric C–H functionalization; Kinetic Resolution; Ruthenium

水素（H）および重水素（D）のように同位体元素によって構築される同位体性立体中心は、同位体間に大きさや結合長にほとんど差がなく、構造的には単純なメチレンのように振舞うゆえに、H および D からなる立体中心のみで構成される同位体性キラル分子は、現在も分離困難である。しかし、C–H 結合と C–D 結合間には、明確なエネルギー差があり、このエネルギー差をエナンチオマー間で反応速度差に反映させることができれば、H/D 同位体性キラル分子は、速度論的に分割することができ、その光学純度をほぼ純粋なレベルまで向上させることが可能と考えられた。

実際に、高エナンチオ選択的かつ大きな重水素効果を示すルテニウム-サレン錯体を用いた不斉 C–H アミノ化を用いることで、H/D 同位体性キラル分子の速度論的分割に成功し、その不斉収率をほぼ純粋なレベルまで向上させることに成功した。

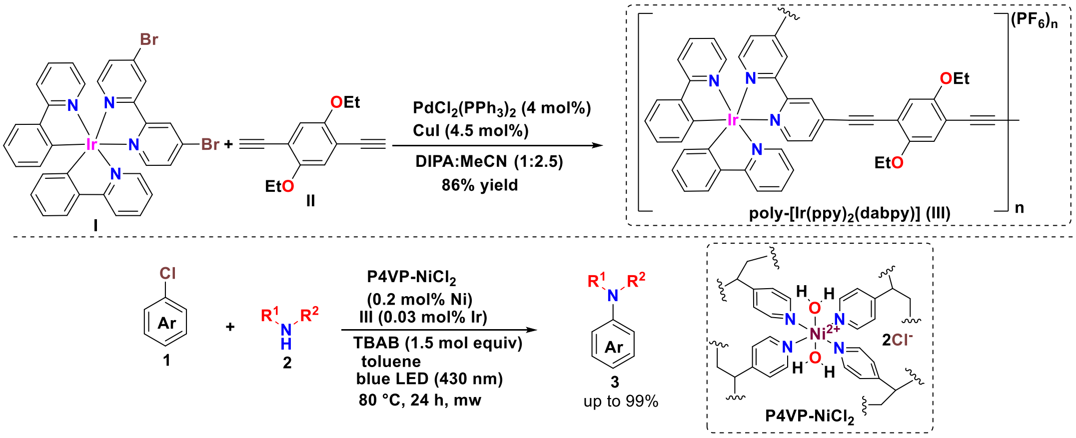


Nickel-Iridium Dual-Catalyzed Buchwald-Hartwig Type Amination Reaction of Aryl Chlorides under Microwave and Visible Light Dual Irradiation

([1]*RIKEN CSRS*) ○Abhijit Sen,[1] Valerii Bukhanko,[1] Heeyoel Baek,[1] Aya Ohno,[1] Atsuya Muranaka,[1] Yoichi, M. A. Yamada[1]

Keywords: Amination; Microwave; Photocatalysis; Heterogeneous catalysis; Nickel catalysis

Nickel-iridium dual-catalyzed Buchwald-Hartwig type C–N bond-forming amination is one of the most important research topics in modern chemistry. Despite being a useful reaction, it is still limited to the reaction of aryl iodides, bromides, and electron-deficient aryl chlorides mainly.[1] This time, we developed a nickel-iridium dual-catalyzed amination of aryl chlorides, independent of the electronic or steric nature.[2] For this purpose, we developed a novel, stable, and reusable polymeric iridium photocatalyst, poly-[Ir(ppy)$_2$(dabpy)] **III**, via the Sonogashira coupling of **I** with **II**. The C–N bond-forming Buchwald-Hartwig type amination of aryl chlorides **1** with amines **2** proceeded with 0.2 mol% of P4VP-NiCl$_2$ and 0.03 mol% of **III**, affording the corresponding amination products in up to 99% yield. Aliphatic (primary, secondary, cyclic, and acyclic) and aromatic amines were tolerable in the reaction. Both nickel and iridium catalysts were recovered and reused 4 times without significant loss of catalytic activity. Microwave and visible light irradiation were essential for this reaction. Multiple biologically active molecules were synthesized, including anti-malaria, anti-HIV, anti-cancer, anti-virus, and anti-bacterial compounds. Complete substrate scope and mechanistic studies will be discussed.



1) E. B. Corcoran, M. T. Pirnot, S. Lin, S. D. Dreher, D. A. DiRocco, I. W. Davies, S. L. Buchwald, D. W. C. MacMillan, *Science* **2016**, *353*, 279–283.

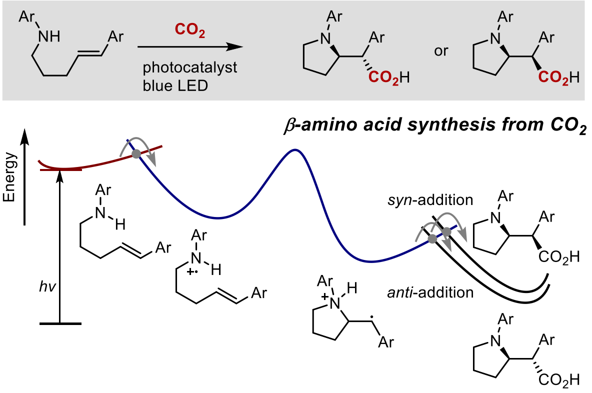
2) A. Sen, V. Bukhanko, H. Baek, A. Ohno, A. Muranaka, Y. M. A. Yamada, *ACS Catal.* **2023**, *13*, 12665–12672.

Catalytic Aminocarboxylation of Alkenes from Amines and CO_2: Application to Gas-Liquid Flow System

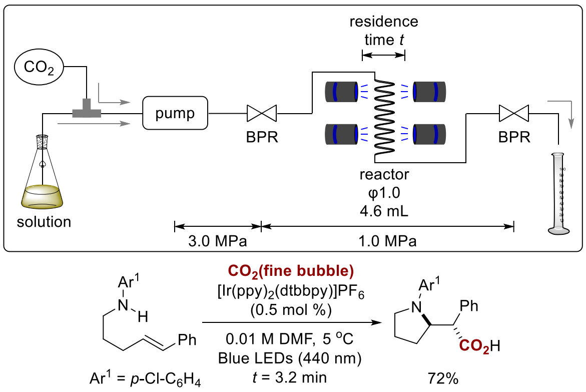
(*[1]Grad. School of Chem. Sci. and Eng, Hokkaido Univ., [2]WPI-ICReDD, Hokkaido Univ., [3]JST-ERATO, [4]Fac. of Eng., Shizuoka Univ., [5]Fac. of Sci, Hokkaido Univ.*)
○Wataru Kanna[1], Yu Harabuchi[2,3], Hayashi Hiroki[2,3], Hideaki Takano[2,3], Tomoki Kozuka[4], Hiroto Sakurai[4], Nobuyuki Mase[4], Satoshi Maeda[2,3,5], Tsuyoshi Mita[2,3]

Keywords: *Flow System; β-amino acid; carboxylation; amine; quantum chemical calculations*

β-Amino acids play a crucial role in the design of biologically active compounds, including pharmaceuticals. On the other hand, carbon dioxide (CO_2) stands out as an attractive C1 source in organic synthesis due to its abundant, cost-effective, non-toxic, and renewable nature. In this study, we have developed a synthetic method of β-amino acids via aminocarboxylation of alkenes with aminium radical and CO_2 in the presence of a photoredox catalyst, based on the artificial force induced reaction (AFIR) method.[1] A comprehensive understanding of the reaction mechanism has been achieved through a novel computational method developed within our research group.[2]



Furthermore, we have successfully adapted this synthetic strategy to a gas-liquid flow system. Prior to photoirradiation, the solution of the substrate amino alkane (Ar^1 = *p*-Cl-C_6H_4) and the photocatalyst $[Ir(ppy)_2(dtbbpy)]PF_6$ in DMF was circulated in the reactor without LED irradiation, thereby maximizing CO_2 concentration. Upon initiating the reaction with blue LED lamps, optimal conditions resulted in the production of the target β-amino acid in 72% yield with a residence time *t* of 3.2 min.



1) Maeda, S.; Harabuchi, Y. *WIREs Comput. Mol. Sci.* **2021**, *11*, e1538.
2) Harabuchi, Y.; Hayashi, H.; Takano, H.; Mita, T.; Maeda, S. *Angew. Chem. Int. Ed.*, **2023**, *62*, e202211936.

独自に合成した多孔性塩基性樹脂による連続フローHenry 反応

(*東大院理*[1]・*東大院理GSC社会連携講座*[2]) ○降矢裕一[1]・石谷暖郎[2]・小林修[1,2]

Continuous-flow Henry Reactions Using House-made Porous Basic Resins

(School of Science[1] and GSC Social Cooperation Laboratory[2], The Univ. of Tokyo)
○Yuichi FURIYA,[1] Haruro ISHITANI,[2] Shū KOBAYASHI[1,2]

To understand the influence of factors in synthesis of resins on basic catalytic activity of quaternary ammonium hydroxide resins for continuous-flow Henry reactions, we synthesized resins with varying porogen, crosslinker, and functional copolymer ratios. The optimal catalyst, QA-8-105(100), demonstrated higher catalytic ability and turnover number (TON) than commercially available strong basic resins. In order to maximize the production efficiency of the current catalytic flow reaction, a multi-step continuous SV deviation was performed semi-automatically using a HPLC gradient liquid delivery system, and the reaction conditions were efficiently evaluated. The TON reached when the yield decreased by about 10% from the initial yield was 33 for 0.2 M and 53 for 0.9 M. When the flow reaction was performed under an appropriate back pressure, the above TON value reached 70.

Keywords: *Heterogeneous Catalyst, Continuous-flow Reaction, Heterogeneous Base Catalyst, Henry Reaction*

連続フロー条件下で高活性を示す塩基性樹脂を創出するために、多孔化剤、架橋剤、官能基モノマー添加量を系統的に変えた樹脂を合成し、フローヘンリー反応をモデル系として評価した。触媒合成時の上記諸要因を最適化することで得られた新規塩基性樹脂QA-8-105(100)は、フローヘンリー反応において市販の塩基性樹脂A26と同等の官能基量を有し、官能基あたりの触媒作用および触媒リアクターとしての耐久性はA26を大きく上回った。一方、上記の評価は一定供給量に対する収率を基準としているが、連続フロー条件下での不均一系触媒評価には時間生産量やTONを基軸とした評価が重要である。本反応系でのそれらの最大化を目指し、スループットアップ条件に対する触媒性能の評価を行った。実験では、HPLCグラジエントシステムを利用して濃度および送液速度を調整し、時間あたりの供給物質量を8段階で連続的に変化させた。収率変化は、送液条件変更と連動させたオンラインHPLCで効率よく解析した。その結果、高濃度溶液でも十分に高い変換収率が得られることが明らかとなった。次いで、反応器内の触媒活性点量を増やすことで、高生産量と耐久性が両立できる条件を決定することができた。

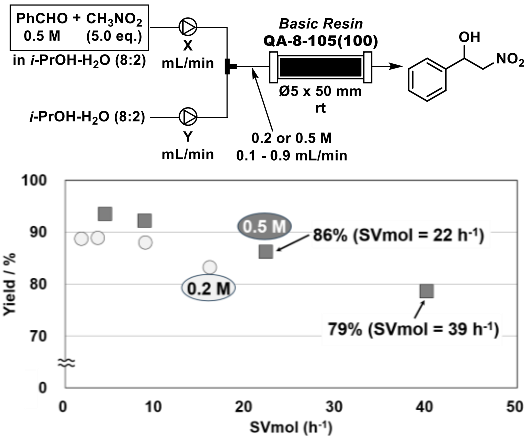


Figure. SVmol-based Evaluation of QA-8-105(100).

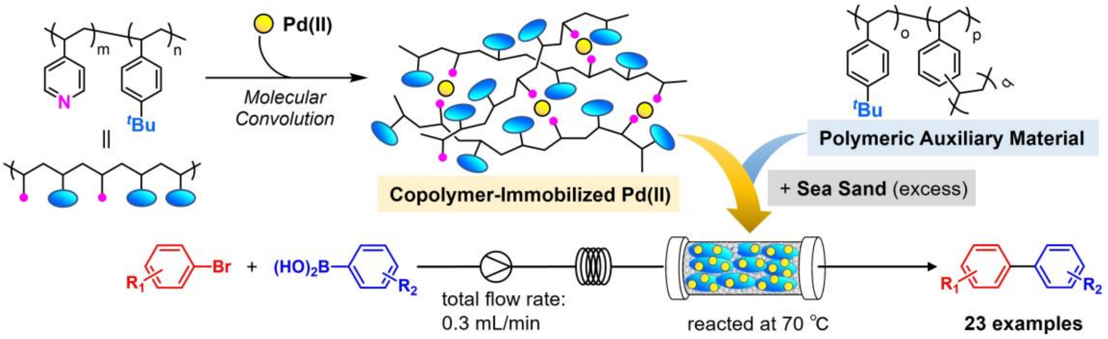
Development of Highly Dispersed and Stabilized Polymeric Pd Catalysts for Continuous Flow Suzuki-Miyaura Coupling

([1]*RIKEN Center for Sustainable Resource Science*, [2]*Department of Life Science Faculty of Life & Environmental Sciences, Teikyo University of Science*) ○Zhenzhong Zhang,[1] Aya Ohno,[1] Hikaru Takaya,[2] Yoichi M. A. Yamada[1]

Keywords: Continuous Flow; Suzuki-Miyaura Coupling; Heterogeneous Palladium Catalysts; Biaryls; XAFS analysis

We developed highly dispersed and stabilized polymeric Pd catalysts for continuous flow Suzuki-Miyaura coupling.[1] A series of copolymers were prepared by polymerizing 4-vinylpyridine with 4-*tert*-butylstyrene, and then Pd(II) species were immobilized via our convolution methodology. In the composite, pyridine units work as the coordination sites for Pd which are sterically separated by bulky *tert*-butyl groups on the polymer chain. This copolymeric Pd catalyst was initially packed with sea sand in a column reactor for the coupling of 4-bromotoluene with phenylboronic acid under continuous flow conditions to optimize the monomer ratio. In addition, cross-linked poly(4-*tert*-butylstyrene) was prepared as a polymeric auxiliary material to disperse further and stabilize the catalyst in the column reactor.

Using this novel catalytic system, a solution of aryl bromides and arylboronic acids in THF/EtOH (5:1, v:v) with an aqueous K_3PO_4 solution flowed over the catalyst at 70 °C with 12–15 min of the residence time. The designed copolymer structure and the cross-linked polymeric auxiliary material effectively dispersed and stabilized the Pd species, enabling the continuous synthesis of a broad spectrum of biaryl products. Liquid-crystalline materials and organic electroluminescent compounds were readily synthesized by the flow system. Furthermore, this catalytic system facilitated a continuous flow process in water as a sole solvent. Two pharmaceutical compounds, felbinac and fenbufen, were synthesized with turnover frequencies of up to 238 h^{-1}. The stability of the catalyst was confirmed through long-term testing in the synthesis of fenbufen in water for 67 h. Subsequently, X-ray absorption spectroscopy studies of the recovered catalyst revealed that almost no Pd aggregation occurred during the reaction.



1) Z. Zhang, A. Ohno, H. Takaya, Y. M. A. Yamada, *Chem. Eur. J.* **2023**, 29, e202300494.

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18日(月) 9:00 ~ 11:30 H932(9号館 [3階] 932)

[H932-1am] 17. 生体機能関連化学・バイオテクノロジー

座長：永次 史、和田 健彦

日本語
9:00 ~ 9:20
[H932-1am-01]
Ru錯体を利用した部位特異的DNA光架橋法の開発

○樫田 啓[1]、東 秀憲[1]、五月女 光[2]、宮坂 博[2]、浅沼 浩之[1] (1. 名大院工、2. 阪大院基礎工)

日本語
9:20 ~ 9:40
[H932-1am-02]
光応答性核酸塩基を導入したXNA三重鎖によるナノ構造体形成

○村山 恵司[1]、平野 桂人[1]、浅沼 浩之[1] (1. 名大)

日本語
9:40 ~ 10:00
[H932-1am-03]
光酸化によるDNA中のAbasic site生成反応の解析

○山野 雄平[1]、鬼塚 和光[1,2]、アルタン オーカン[1]、佐々木 まどか[1,2]、アーメド アブデルハーディ[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
[H932-1am-04]
核酸化学のNew Data Science (1): 細胞内の核酸構造安定性を予測できる新規の最近接塩基対パラメータの開発

○杉本 直己[1,2]、ゴッシュ サトパティ[1]、ディパニタ バナジー[1]、大山 達也[1]、遠藤 玉樹[1]、高橋 俊太郎[1]、建石 寿枝[1] (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))

英語
10:30 ~ 10:50
[H932-1am-05]
核酸化学のNew Data Science (2): 最近接塩基対パラメータとAIを用いたリボザイムの機能予測

○高橋 俊太郎[1]、Saptarshi Ghosh[1]、建石 寿枝[1]、福永 津嵩[3]、浜田 道昭[3]、杉本 直己[1,2] (1. 甲南大FIBER、2. 甲南大FIRST、3. 早稲田大)

英語
10:50 ~ 11:10
[H932-1am-06]
核酸化学のNew Data Science (3): 最近接塩基対パラメータ、擬似細胞システム、AIを用いたRNAの構造安定性予測

〇Dipanwita Banerjee[1]、建石 寿枝[1]、高橋 俊太郎[1]、福永 津嵩[2]、浜田 道昭[3,4]、杉本 直己[1,5] (1. 甲南大学　先端生命工学研究所（FIBER)、2. 早稲田大学高等研究所、3. 早稲田大学 理工学術院、4. 産総研・早大 生体システムビッグデータ解析オープンイノベーションラボラトリ、5. 甲南大学　フロンティアサイエンス研究科)

英語

11:10 ~ 11:30

[H932-1am-07]

Staple核酸の合理的な設計を志向した化学的パラメーターの算出

〇木田 朋輝[1]、勝田 陽介[1]、北村 裕介[1]、井原 敏博[1] (1. 熊大院)

日本化学会 第104春季年会 (2024)

Ru 錯体を利用した部位特異的 DNA 光架橋法の開発

(名大院工[1]・阪大院基礎工[2]) ○樫田 啓[1]・東 秀憲[1]・五月女 光[2]・宮坂 博[2]・浅沼 浩之[1]

Development of a site-selective photocrosslinking method using Ru complex

([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Engineering Science, Osaka University*) ○Hiromu Kashida,[1] Hidenori Azuma[1], Hikaru Sotome,[2] Hiroshi Miyasaka,[2] Hiroyuki Asanuma[1]

Photocrosslinking of DNA duplex has been widely used to stabilize DNA duplexes and nanostructures. However, it was difficult to achieve orthogonal photocrosslinking due to spectral overlaps. We herein report a method for site-selective photo-crosslinking of a DNA duplex. A stilbene pair was introduced into a DNA duplex and a ruthenium complex was conjugated with a triplex-forming oligonucleotide. We demonstrated that [2+2] photocycloaddition of the stilbene pair occurred upon irradiating with visible light when the ruthenium complex was in close proximity. Quantum chemical calculation indicated that ruthenium complex catalyzed the photocycloaddition via triplet-triplet energy transfer.

Keywords : DNA; Photocrosslinking; Ruthenium; Stilbene; Triplet-triplet energy transfer

DNA の光架橋は DNA 二重鎖やナノ構造体の安定化などのために幅広く利用されている。当研究室ではこれまでにスチルベン誘導体の[2+2]光環化付加反応を利用した DNA 光架橋法を報告している。しかしながら、従来の手法では励起波長にオーバーラップがあるために、複数部位における光架橋を制御することは困難であった。

そこで、本研究では Ru 錯体を利用した部位特異的 DNA 光架橋法の開発を目指した。具体的には、スチルベンペアを DNA 二重鎖に導入し、$\mathrm{Ru(bpy)_3}$ 錯体を三重鎖形成核酸に導入した（Fig.1）。Ru 錯体非存在下では可視光を照射しても反応しないのに対し、Ru 錯体存在下ではスチルベンの[2+2]光環付加反応が進行することがわかった。量子化学計算の結果、Ru 錯体からの三重項—三重項エネルギー移動によって反応が進行していることが示唆された。また、Ru 錯体から離れた位置にスチルベンペアを導入したところ、反応が進行しないことがわかった。以上のことから、Ru 錯体を利用した部位特異的光架橋法の開発に成功した。

1) H. Kashida, T. Doi, T. Sakakibara, T. Hayashi, H. Asanuma, *J. Am. Chem. Soc.* **2013**, *135*, 7960-7966.

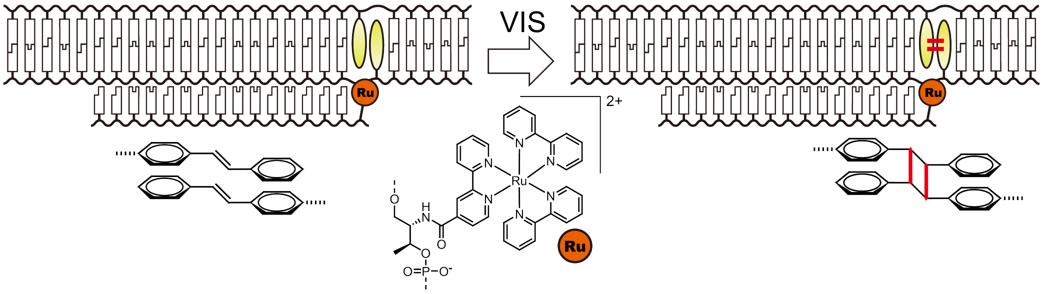


Fig. 1. Illustration of our photocrosslinking system.

光応答性核酸塩基を導入したXNA三重鎖によるナノ構造体形成

（名大院工）○村山 恵司・平野 桂人・浅沼 浩之

Nanostructure based on XNA triplex containing photoresponsive nucleobase

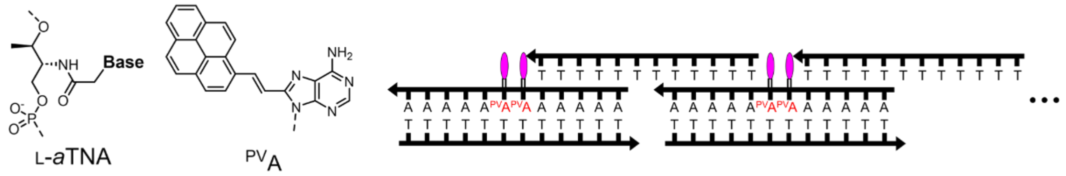
([1]*Graduate School of Engineering, Nagoya University*) ○Keiji Murayama, Keito Hirano, Hiroyuki Asanuma

Xeno nucleic acids (XNAs), synthetic analogues of DNA and RNA, impart new functions and high nuclease resistance in biological applications. SNA and L-*a*TNA, acyclic XNAs developed in our group, can form stable homo- and hetero-duplexes and triplexes[1-3)]. We also achieved photo-control of formation of SNA/RNA duplex by incorporation of 8-pyrenylvinyl adenine (^{PV}A) residues[4)]. In this study, we synthesized L-*a*TNA-poly A sequence carrying two ^{PV}A residues. We revealed that the ^{PV}A-modified L-*a*TNA-poly A and L-*a*TNA-poly T formed triplex-based linear polymer. The size of the nanostructure can be controlled via photoirradiation inducing photo-cycloaddition and cycloreversion between two ^{PV}A residues. This new photo-control system promises application to construction of functional nanomachines and nanoarchitectures.

Keywords : XNA; Photoregulation; Triplex; Nanostructure

二重鎖形成能と高い分解酵素耐性を持つ骨格改変型人工核酸XNAは、様々な生物学的応用が期待される。我々が開発した非環状型XNAであるSNA及びL-*a*TNAは、安定な二重鎖・三重鎖を形成するだけでなく、DNAやRNAとも二重鎖形成することを明らかにしている[1-3)]。更にSNAに光応答性の修飾核酸塩基8-Pyrenylvinyl adenine (^{PV}A)を2残基導入することで、鎖内の^{PV}A同士の光架橋・開裂を介したSNA/RNA二重鎖の解離・形成の光制御に成功している[4)]。

本研究では、poly A鎖中央に^{PV}Aを2残基導入したL-*a*TNA配列を合成し、二重鎖・三重鎖形成能を評価した。その結果、^{PV}A導入L-*a*TNA-poly A鎖はL-*a*TNA-poly T鎖と安定な二重鎖形成することが確認され、更にpoly T鎖が^{PV}Aを避けるように三重鎖形成することで、二重鎖が架橋された長鎖の超分子ナノ構造体が形成されることを明らかにした。また、この構造体に448 nmの光照射を行った結果、鎖内で^{PV}A間の架橋反応が進行し、構造体が不安定化し分子サイズが低下することが示唆された。この光照射産物に対し340 nmの光照射を行うと逆反応が観測され、可逆的な光制御が可能であることが確認された。



1) H. Kashida *et al.*, *Angew. Chem. Int. Ed.*, **2011**, *50*, 1285-1288. 2) K. Murayama *et al., Chem. Commun.*, **2015**, *51*, 6500-6503. 3) K. Murayama, H. Asanuma, *ChemBioChem*, **2021**, *22*, 2507-2515. 4) K. Murayama et al., *J. Am. Chem. Soc.*, **2019**, *141*, 9485-9489.

光酸化による DNA 中の Abasic site 生成反応の解析

（東北大多元研 [1]・東北大院理 [2]）○山野 雄平 [1]・鬼塚 和光 [1,2]・アルタン オーカン [1]・
佐々木 まどか [1,2]・アーメド アブデルハーディ [1]・永次 史 [1,2]

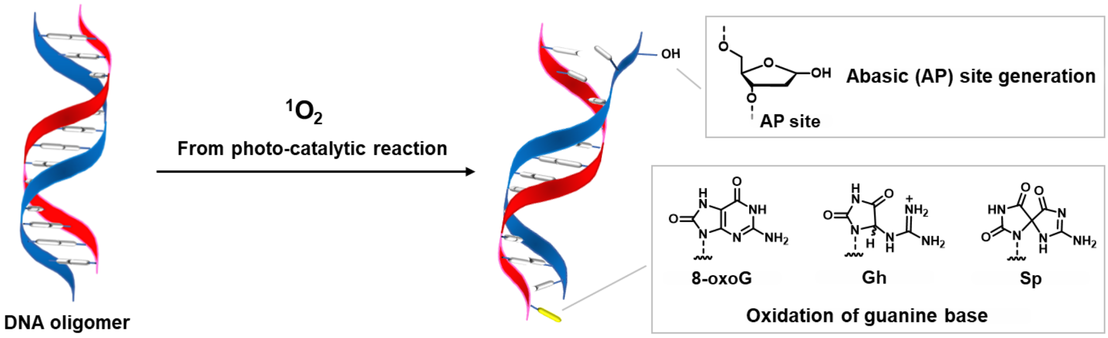
Analysis of abasic site generation reaction in DNA by photo-oxidation ([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku Univ.*, [2]*Graduate School of Science, Tohoku Univ.*) ○Yuuhei Yamano[1], Kazumitsu Onizuka[1, 2], Altan Okan[1], Madoka Sasaki[1, 2], Ahmed Abdelhady[1], Fumi Nagatsugi[1, 2]

Guanine is converted to various oxidized products including 8-oxoguanine (8-oxoG) under oxidative reaction conditions.[1] This guanine oxidation product passes through the abasic (AP) site during the repair process and the producing mechanism of AP site is being actively studied. In this study, we irradiated various DNA oligomers with light in the presence of a photocatalyst that generates singlet oxygen and analyzed the products by MALDI-TOF-MS measurements. As a result, we found that the guanine residues were directly converted to AP site by photo-oxidation without any enzymatic reactions (Fig). Furthermore, it was also suggested that the generation ratio of this AP site has sequence and structure dependence. In this presentation, we will report the reactions investigated for AP site generation and the assumed reaction mechanism.

Keywords : Nucleic acid, Photo reaction, Photo catalyst, Oxidation, Abasic site

グアニンは酸化反応条件下で 8-オキソグアニン（8-oxoG）をはじめとする様々な酸化体へと変換され、細胞のがん化や細胞死に繋がる可能性があることが知られている [1]。これらのグアニン酸化体は修復過程で Abasic （AP）サイトを経由することが知られており、その生成機構の詳細なメカニズムについて研究が進められている。

我々は、様々な DNA オリゴマーに対し一重項酸素を生成する光触媒存在下で光を照射後、MALDI-TOF-MS で解析を行った。その結果、グアニン残基が光酸化反応により非酵素的に AP サイトに変換されることを見出した（図）。また、この光触媒反応に基づく AP サイトの生成率には配列・構造依存性があることも示唆された。本発表では、この AP サイト生成反応の想定反応機構についても紹介する予定である。



1) G. Pratviel, B. Meunier, *Chem. Eur. J.* **2006**, *12*, 6018–6030.

New Data Science in Nucleic Acids Chemistry (1): Development of new nearest neighbor parameters that can predict nucleic acids structure in cells

([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*) ○Naoki Sugimoto,[1,2] Ghosh Saptarshi,[1] Banerjee Dipanwita,[1] Tatsuya Ohyama,[1] Tamaki Endoh,[1] Shuntaro Takahashi,[1] Hisae Tateishi-Karimata[1]

Keywords: Duplex; Watson-Crick base pairs; Intracellular conditions; Nearest-neighbor (NN) model; Stability prediction

The most successful prediction method for nucleic acids duplex stability is based on the nearest-neighbor (NN) model, which assumes that the free energy change ($\Delta G°$) for the duplex formation comprises the sum of the $\Delta G°$ values of adjacent NN base pairs and helix initiation.[1] Similarly, the relevant thermodynamic parameters, such as changes in enthalpy ($\Delta H°$) and entropy ($\Delta S°$), can be also predicted from the base sequence. Based on this model, parameters for predicting the thermodynamics of RNA/RNA duplex, DNA/DNA duplex, and RNA/DNA hybrid duplex formations were developed. However, these methods have a critical limitation for their application in cells, because the classical NN parameters for RNA duplex formation, for instance, were determined under conditions of 1 M NaCl, whereas the intracellular environment contains much lower and various cation concentrations. Therefore, prediction parameters applicable for various cation conditions are required. Furthermore, intracellular environments remain populated with highly concentrated molecules termed 'molecular crowding'. Such molecular crowding in cell significantly affects nucleic acid structure, stability, and function. Here, new NN parameters for Watson-Crick base pairing and helix initiation factors have been developed to predict duplex stability with high accuracy, even in solutions containing accurate intracellular cation composition.[2] Moreover, our newly derived parameters can be used to estimate the efficiency of transcription, genome editing, and silencing techniques in cells. This supports the broad applicability of our parameters in the elucidation of cellular mechanisms of gene expression and the development of nucleic acid-based therapeutics targeting different cells.

1) a) N. Sugimoto, ed., "Handbook of Chemical Biology of Nucleic Acids", *SPRINGER NATURE,* 2023, Vols 1, 2, and 3. b) "Chemistry and Biology of Non-Canonical Nucleic Acids", *WILEY,* **2021**, 1-276.

2) a) Our Group, *J. Am. Chem. Soc.,* **2023**, *145,* 23503. b) *Nucleic Acids Res.* **2023**, *51*, 4101. c) *Chem. Commun.* **2023**, *59*, 872. d) *Chem. Commun.* **2023**, *59*, 4891. e) *Sci. Adv.* **2022**, *8*, eadc9785. f) *J. Am. Chem. Soc.* **2022**, *144*, 5956. g) *Chem. Commun*. **2022,** *58*, 5952. h) *J. Am. Chem. Soc.* **2021**, *143*, 16458. i) *Nucleic Acids Res.* **2021**, *49*, 7839. j) *Nucleic Acids Res.* **2021**, *49*, 8449. k) *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 14194. l) *Ncleic Acids Res.* **2020**, *48*, 3975.

New Data Science in Nucleic Acids Chemistry (2): Functional prediction of ribozymes using nearest neighbor parameters and AI

([1]*FIBER, Konan Univ.,* [2]*Waseda Univ.* [3]*FIRST, Konan Univ.*)
○Shuntaro Takahashi,[1] Saptarshi Ghosh,[1] Hisae Tateishi-Karimata,[1] Tsukasa Fukunaga,[2] Michiaki Hamada,[2] Naoki Sugimoto[1,3]

Keywords: Nearest neighbor (NN) model, Duplex, Stability prediction, AI, Functional prediction

Nucleic acids (DNA and RNA) dynamically fold and unfold to exert their functions in cells. These folding and unfolding behaviors are also basis for various technical applications. To understand the biological mechanism of nucleic acid function and design active materials using nucleic acids, the prediction method for each function from the sequence information of DNA and RNA is required. As these functions based on base pairing such as Watson-Crick base pairs, the stability of forming base pairing is fundamental information to establish the functional prediction of DNA and RNA. Nearest neighbor (NN) model is the most successful method to predict the Gibbs free energy (ΔG°_{37}) of the formation of duplexes such as DNA/DNA, RNA/RNA, and RNA/DNA.[1-3] Thus, the NN model can be used as a dataset to predict the nucleic acids function based on the duplex stability, although such functional prediction has been not developed yet.

In this study, we focused on the nuclease reaction of DNAzyme and ribozyme (here mainly used RNA-cleaving 10-23 DNAzyme). These enzymatic reactions were based on the ΔG°_{37} of the formation of duplex with a target strand as well as the secondary structure of the enzyme strand. As the enzymatic activity depends on Mg^{2+} concentrations and molecular crowding conditions, we improved the NN model to segmentate the thermodynamic parameters of each NN base pair into those affected by cation and cosolulte concentrations. As a result, we could extend the NN model available in different Mg^{2+} concentrations and various molecular crowding conditions with different water activity, dielectric constants, and excluded volume effect. By using the updated NN parameters and enzymatic activity in different Mg^{2+} concentrations and various molecular crowding as a database, we characterized the relationship between the sequence information and enzymatic activity with AI techniques. Our results suggest that NN parameters supported to efficiently and accurately predict the enzymatic reaction, which highlights the advantage of NN parameters for predicting the functions of nucleic acids from the sequence information.

1) D. Banerjee, H. Tateishi-Karimata, T. Ohyama, S. Ghosh, T. Endoh, S. Takahashi, and N. Sugimoto. *Nucleic Acids Res.,* **2020,** *48*, 12042. 2) S. Ghosh, S. Takahashi, T. Ohyama, T. Endoh, H. Tateishi-Karimata, and N. Sugimoto. *Proc. Natl. Acad. Sci. U. S. A.,* **2020,** *117*, 14194. 3) S. Ghosh, S. Takahashi, D. Banerjee, T. Ohyama, T. Endoh, H. Tateishi-Karimata and N. Sugimoto. *Nucleic Acids Res.*, **2023,** *51*, 4101

New Data Science in Nucleic Acids Chemistry (3): Stability prediction of RNA structures using nearest neighbor parameters, pseudo-cellular systems, and AI

(^1^*Frontier Institute for Biomolecular Engineering Research (FIBER) Konan University,* [2]*Waseda Institute for Advanced Study, Waseda University,* [3]*Department of Electrical Engineering and Bioscience, Graduate School of Advanced Science and Engineering, Waseda University,* [4]*Computational Bio Big-Data Open Innovation Laboratory, AIST-Waseda University* [5]*Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University*)
Banerjee Dipanwita,[1] ○Hisae Tateishi-Karimata,[1] Shuntaro Takahashi,[1] Tsukasa Fukunaga ,[2] Michiaki Hamada,[3,4] Naoki Sugimoto,[1,2]

Keywords: RNA/RNA duplex; Molecular crowding; Stability prediction; Nearest neighbor parameters; AI

The stability of RNA structures in cells is important for predicting RNA functions. Intracellular crowded environments affect significantly structure and stability of nucleic acids.[1] In order to predict the RNA structures, we have developed nearest neighbor parameters for RNA/RNA duplexes consisting with Watson-Crick base pairs.[2] However, it is essential to accurately predict the stability of not only Watson-Crick base pairs, but also Non-Watson-Crick base pairs base pairs. Here, we evaluated the thermodynamic parameters of duplexes with single mismatched and fully matched base pairs in dilute and crowded conditions (Figure 1). Mismatched duplexes were destabilized with the increasing order of pyrimidine•pyrimidine < purine•pyrimidine < purine•purine under the crowding condition, with the exception of A•G mismatch. We proposed a method for predicting individual contribution of the 12 mismatches to the stability of RNA that provided a basis for an increasingly accurate prediction of intracellular RNA secondary structure. In the presentation we will discuss the results of using pseudo-cellular systems and AI to predict RNA structure in the intracellular environments.

1) D. Banerjee, H. Tateishi-Karimata, M. Toplishek, T. Ohyama, S. Ghosh, S. Takahashi, M. Trajkovski, J. Plavec, N. Sugimoto, *J. Am. Chem. Soc*. **2023**, *145*, 23503.
2) S. Ghosh, S. Takahashi, D. Banerjee, T. Ohyama, T. Endoh, H. Tateishi-Karimata, N. Sugimoto, *Nucleic Acids Res*. **2023**, *51*, 4101.

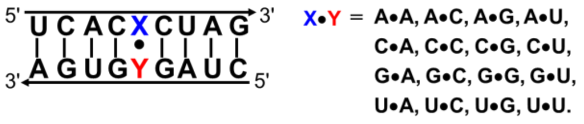


Figure 1. Schematic representation of RNA duplexes formed by 5′ -rUCACXCUAG-3′ and 5′ -rCUAGYGUGA-3′ sed in this study. “X” and “Y” denote positions of base pairs and mismatches shown on the right.

Chemical parameter derivation for strategic Staple Oligomer design

([1] *Faculty of Advance Science and Technology, Kumamoto University*) ○Tomoki Kida,[1] Yousuke Katsuda,[1] Yusuke Kitamura,[1] Toshihiro Ihara,[1]

Keywords: *RNA G-quadruplex; Staple oligomer; Inhibition translation; Chemical parameter; Nucleic acids*

Our research group has developed a technique called "RNA hacking," utilizing short-chain nucleic acids named "Staple oligomers" to artificially induce the formation of RNA G-quadruplexes (RGq) on target mRNA.1) This approach involves the ability of Staple oligomers to bring guanine repeat sequences into proximity. Unlike traditional nucleic acid therapeutics, this method operates independently of enzyme reactions, allowing for the complete conversion of Staple oligomer constituents to L-aTNA without compromising their therapeutic efficacy. Furthermore, our studies have demonstrated significant therapeutic effects in a mouse model of cardiac hypertrophy (**Fig. 1(a)**).

While our previous research has predominantly followed a top-down approach, it is essential to possess thermodynamic insights and kinetic understanding of the binding between Staple oligomers and target mRNA, as well as the subsequent formation of RNA G-quadruplexes (RGq), to pursue the effective design of Staple oligomers.

To address this, we have employed target nucleic acids assuming an infinite length of loop bases to evaluate the T_m (melting temperature) values associated with reactions involving Staple oligomers. We aim to provide explanations based on thermodynamic understanding for the results obtained through the top-down approach (**Fig. 1(b)**).

In this presentation, we intend to introduce results showcasing the formation of RGq induced by Staple oligomer binding, which occurs at a notably slow rate, and the maintenance of RGq formation even when Staple oligomers are dissociated from the target.

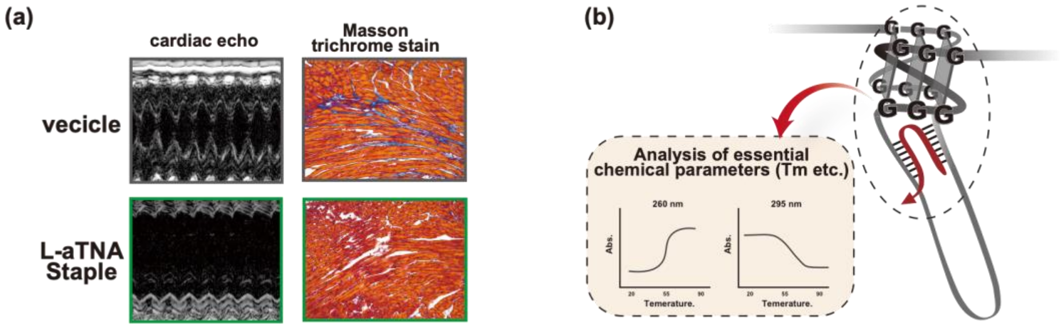


Fig. 1 (a) The therapeutic effect of L-aTNA Staple in vivo. Successful suppression of cardiac hypertrophy as evidenced by echocardiography and Masson's trichrome staining images. (b) Conceptual diagram for the calculation of chemical parameters.

1) Y. Katsuda, T. Kamura, T. Kida, T. Saeki, Y. Itsuki, Y. Kato, T. Nakamura, M. Nishida, Y. Kitamura, T. Ihara, M. Hagihara, S. Sato, *bioRxiv,* doi: https://doi.org/10.1101/2023.04.18.537290

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18日(月) 9:00 ~ 11:30 H936(9号館 [3階] 936)

[H936-1am] 17. 生体機能関連化学・バイオテクノロジー

座長：安部 聡、藤枝 伸宇

英語

9:00 ~ 9:20

[H936-1am-01]

ミオグロビンを利用した人工金属酵素の新規触媒機能拡張：アルドキシム脱水反応によるニトリル合成

○阿部 美笛[1]、加藤 俊介[1]、林 高史[1] (1. 大阪大学大学院)

英語

9:20 ~ 9:40

[H936-1am-02]

野生型シトクロムP450BM3発現大腸菌によるプロパンからプロパノールへの生体変換

○須貝 友紀[1]、唐澤 昌之[1]、児玉 侑朔[1]、米村 開[1]、有安 真也[1]、愛場 雄一郎[1]、荘司 長三[1] (1. 名古屋大学)

英語

9:40 ~ 10:00

[H936-1am-03]

細胞内結晶化タンパク質ケージの結晶・溶液構造の解析

○田中 潤子[1]、安部 聡[1]、金丸 周司[1]、横山 武司[2]、鉄錚 潘 [1]、永間 美咲[1]、上野 隆史[1] (1. 東工大、2. 東北大)

10:00 ~ 10:10

休憩

日本語

10:10 ~ 10:30

[H936-1am-04]

緑膿菌のヘム獲得機構の制御を志向したペプチド修飾ヘム

○松井 弘季[1]、愛場 雄一郎[1]、渡邉 菜々花[1]、有安 真也[1]、荘司 長三[1] (1. 名古屋大学)

英語

10:30 ~ 10:50

[H936-1am-05]

Redox Tuning of Myoglobin by Cofactor Replacement to Enhance Cyclopropanation Reactivity

○Yoshiyuki Kagawa[1], Koji Oohora[1], Tomoki Himiyama[2], Akihiro Suzuki[3], Takashi Hayashi[1] (1. Osaka University, 2. AIST, 3. NIT Ibaraki College)

日本語

10:50 ~ 11:10

[H936-1am-06]

人工非ヘム銅タンパク質が触媒する立体選択的ヘテロDiels-Alder反応

○松本 隆聖[1]、吉岡 紗穂[2]、森田 能次[1]、藤枝 伸宇[1,2] (1. 大阪公大院農、2. 大阪府大院生命)

英語

11:10 ~ 11:30

[H936-1am-07]

トリスルフィド架橋フェレドキシン二量体の構築とその生成機構

○真島 剛史[1]、田中 萌奈実[1]、Nur Afiqah binti Azmi[1]、山中 優[1]、緒方 英明[2]、廣田 俊[1] (1. 奈良先端大、2. 兵庫県立大)

Expansion of New Catalytic Functions of Artificial Metalloenzyme Utilizing Myoglobin: Nitrile Synthesis via Aldoxime Dehydration Reaction

(*Graduate School of Engineering, Osaka University*) ○Miteki Abe, Shunsuke Kato, Takashi Hayashi

Keywords: Biocatalyst; Artificial Metalloenzyme; Nitrile Synthesis; Myoglobin; Aldoxime Dehydratase

Industrial processes for nitrile synthesis typically require harsh conditions (high temperature and strong basicity) and the use of specialized reagents, thereby posing environmental concerns from a green chemistry perspective. In this study, we focus on the design and application of an artificial metalloenzyme to achieve highly efficient nitrile synthesis under mild conditions (Figure 1). The artificial metalloenzyme (rMb-FePc) was constructed by replacing heme *b*, a cofactor of myoglobin (Mb), with iron porphycene (FePc). This substitution facilitates the reaction through a robust back donation from the iron atom.[1] rMb-FePc exhibited significant catalytic activity toward the dehydration of aldoximes, yielding nitriles. The total turnover number reached up to 5.0×10^3 under mild conditions (30 ℃, pH 7.0). Furthermore, rMb-FePc had versatile activity in converting various aldoximes and their derivatives into nitriles. Notably, less reactive *O*-alkyl aldoximes underwent dealcoholization reaction, which exceeded the activity of natural aldoxime dehydratase. Additionally, the introduction of an amino acid residue with a hydroxyl group into the active site significantly enhanced the initial rate of rMb-FePc catalyzed dehydration by more than 24-fold.

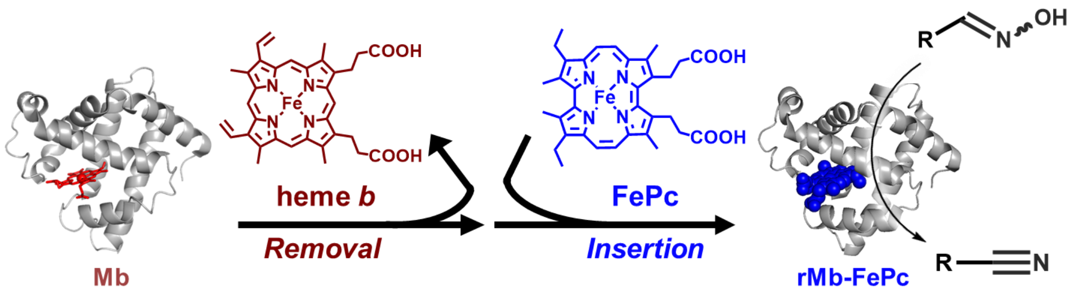


Figure 1. Construction of rMb-FePc catalyzing aldoxime dehydration.

1) T. Hayashi *et al.*, *Acc. Chem. Res.*, **2019**, *52*, 945–954.

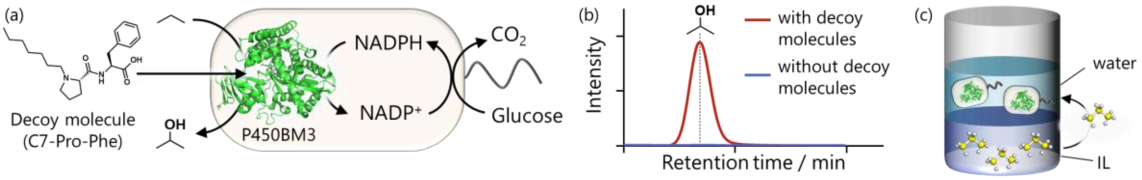
Biotransformation of Propane to Propanol by E. coli Expressing Wild-type Cytochrome P450BM3

([1]*Graduate School of Science, Nagoya University*) ○Yuki Sugai,[1] Masayuki Karasawa,[1] Yusaku Kodama,[1] Kai Yonemura, [1] Shinya Ariyasu,[1] Yuichiro Aiba,[1] Osami Shoji[1]

Keywords: P450 Enzymes; Biotransformation; Ionic liquid; High-throughput screening

Gaseous alkanes are expected to be used as starting materials in industrial chemistry by introducing functional groups such as hydroxyl groups. To hydroxylate gaseous alkanes directly under mild conditions, our research group has focused on cytochrome P450BM3 (P450BM3). P450BM3 is a heme enzyme which catalyzes hydroxylation of long-chain fatty acids at an extremely high rate, thus it has been intensively studied for application in catalyzing the oxidation of non-native substrates. While many researchers attempt to achieve non-natural reactions by P450BM3 mutants, we have succeeded in altering the substrate specificity of wild-type P450BM3 by employing synthesized dummy substrates named decoy molecules. Decoy molecules bind to P450BM3 in the same manner as native substrates and activate the enzyme. Since decoy molecules are shorter than native substrates, non-native substrates such as propane and methane can be taken into the reaction space and hydroxylated.[1,2] However, the reaction requires a stoichiometric amount of expensive cofactor, NADPH, as electron donors. To overcome this problem, we conceived of employing whole-cell catalysis and succeeded in the biotransformation of benzene by E. coli overexpressing P450BM3.[3]

In this research, we adapted the whole-cell catalysis to hydroxylation of propane (Fig. a) and searched for decoy molecules suitable for the reaction. First, P450BM3-expressing E. coli is incubated in an atmosphere of propane and the formation of 2-propanol was observed by the addition of some decoy molecules (Fig. b). Then, we screened decoy molecules suitable for this reaction to improve the activity. Because it is practically difficult to maintain a high concentration of propane dissolved in water during microplate-based screening, we have developed an aqueous/ionic liquid biphasic system in which ionic liquid can store large amounts of propane and work as a propane pool (Fig. c).



1) K. Yonemura, S. Ariyasu, J. K. Stanfield, K. Suzuki, H. Onoda, C. Kasai, H. Sugimoto, Y. Aiba, Y. Watanabe, O. Shoji, *ACS Catal.*, **2020**, *10*, 9136. 2) S. Ariyasu, K. Yonemura, C. Kasai, Y. Aiba, H. Onoda, Y. Shisaka, H. Sugimoto, T. Tosha, M. Kubo, T. Kamachi, K. Yoshizawa, O. Shoji, *ACS Catal.*, **2023**, *13*, 8613. 3) M. Karasawa, J. K. Stanfield, S. Yanagisawa, O. Shoji, Y. Watanabe, *Angew. Chem. Int. Ed.*, **2018**, *57*, 12264.

Structure analysis of crystal and solution state of in-cell crystallized protein cage

([1]*Graduate School of Life-Science and Technology, Tokyo Institute of Technology,* [2]*Graduate School of Life Science, Tohoku University*) ○Junko Tanaka[1], Satoshi Abe[1], Shuji Kanamaru[1], Takeshi Yokoyama[2], Tiezheng Pan[1], Misaki Nagama[1], Takafumi Ueno [1]

Keywords: *Protein cage; Protein crystal; In-cell protein crystal; X-ray crystallography; Cryo-EM*

Protein cages, which form highly symmetric and robust nanostructures with inner cavities, utilize their structural properties to perform various functions. Crystals of protein cages are expected to be used as solid materials that utilize the inside and outside of the cage. Recently, protein cage crystals with various functions have been artificially synthesized by molecular design. However, it is necessary to consider crystallization conditions for synthesizing designed protein cage crystals, and simple crystallization methods are needed.

Recently, “In-cell protein crystals,” spontaneously formed in living cells, have attracted attention as a rapid crystallization.[1] We focused on crystalline inclusion protein B (CipB), formed in *P. luminescens* and *E.coli* with unknown structure.[2] We found that CipB was composed of a protein cage by analyzing proteins eluted from CipB crystals purified from *E. coli.* The solubilized CipB cages were re-crystallized. The crystal structure was determined by X-ray crystallography.[3] The CipB cage is composed of 24-mer consisting of six tetramers. Cryo-EM analysis was performed to characterize the cage structure in solution. The cage structures of CipB in crystalline and solution states were compared. In this presentation, we report the details of the CipB structures by X-ray and cryo-EM. The unique structural features of the CipB cage are expected to be applied to developing solid-state materials using in vivo crystals of protein cages (Fig1).

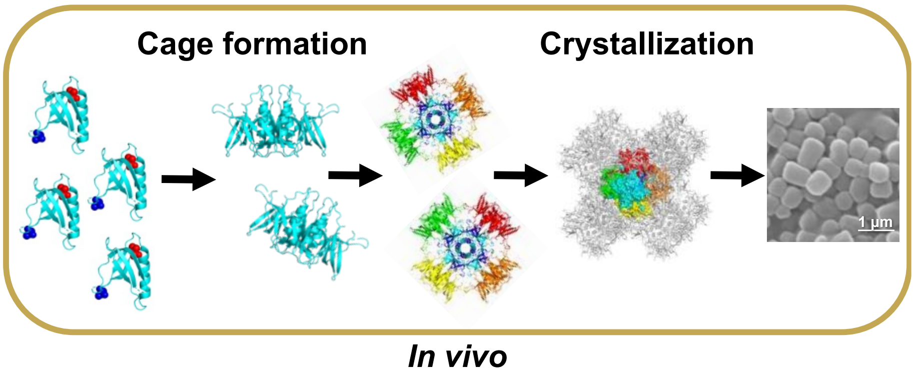


Figure1. The schematic image of CipB crystallization *in vivo*.

1) M. Kojima, *et al., Biomater. Sci.*, **2022**, 10, 354-367, 2) Y. Wang, *et al., ACS Synth. Biol.*, **2017**, 6, 826-836, 3) S. Abe, J. Tanaka *et al.,* 103rd CSJ Annual Meeting. **2023**

緑膿菌のヘム獲得機構の制御を志向したペプチド修飾ヘム

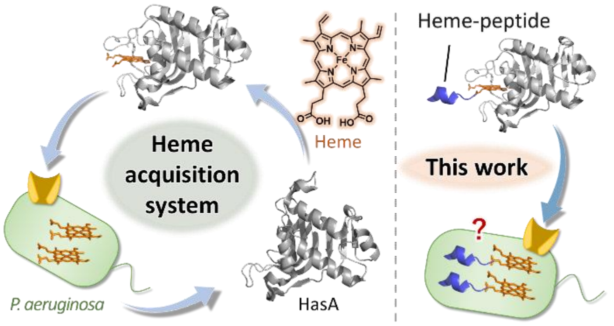
（名大院理）○松井 弘季・愛場 雄一郎・渡邉 菜々花・有安 真也・荘司 長三

Peptide-modified heme to control the heme acquisition system of *Pseudomonas aeruginosa*

(*Graduate School of Science, Nagoya University*)
○Hiroki Matsui, Yuichiro Aiba, Nanaka Watanabe, Shinya Ariyasu, Osami Shoji

Pseudomonas aeruginosa (*P. aeruginosa*) is a pathogen that causes opportunistic infections. The emergence of multidrug-resistant strains of *P. aeruginosa* has become a problem, and it is desirable to develop an antibiotic-free sterilization method. In an iron-deficient environment, *P. aeruginosa* secretes HasA protein to acquire heme from its host. It has been shown that HasA can be reconstituted with artificial metal complexes that are structurally different from heme, such as iron phthalocyanine1). Furthermore, the reconstituted HasAs exhibit the growth inhibitory effect on *P. aeruginosa*, and the potency depends on the structure of the metal complex2). Although we have examined the growth inhibitory effects depending on the structures of metal complexes described above, the studies on modifying heme have been limited. In this study, the effects of chemical modifications on the heme acquisition system were investigated by modifying peptides to the carboxy groups of the heme, a natural target of HasA. Heme modified with a single peptide chain was found to be delivered into *P. aeruginosa* by complexing with HasA and used as an iron source.

Keywords : Pseudomonas aeruginosa; Heme; Peptide; Protein; Metal Complex



緑膿菌は日和見感染症を引き起こす病原菌であり､抗生物質に対して耐性を獲得した多剤耐性緑膿菌の出現が世界的な問題となっている。そのため､抗生物質によらない殺菌手法の開発が望まれており､当研究室では緑膿菌のヘム獲得機構に着目して研究を行ってきた。鉄欠乏状態の緑膿菌は､ヘム獲得タンパク質 HasA を分泌し、宿主から奪い取ったヘムを鉄源として利用することで増殖する。さらに、鉄フタロシアニンなどのヘムと構造の異なる人工金属錯体とも HasA は複合化可能であり､その複合体は緑膿菌の増殖抑制能を示した 1)。また、その増殖抑制効果は、錯体の構造により異なることも明らかにした 2)。しかし、これまでの検討では錯体構造のみに焦点を当てており、ヘム自体の改変については検討が限定的であった。そこで本研究では、天然の標的であるヘムに対し、カルボキシ基を介してペプチドを修飾することで、ヘム獲得機構における化学修飾の影響について検討した。その結果、一方のカルボキシ基のみにペプチドを修飾したヘムは、HasA と複合化されることで緑膿菌内まで送達され、鉄源として利用されることを明らかにした。

1) C. Shirataki *et al.*, *Angew. Chem. Int. Ed.*, **2014**, *53*, 2862-2866

2) H. Uehara *et al.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 15279-15283

Redox Tuning of Myoglobin by Cofactor Replacement to Enhance Cyclopropanation Reactivity

(¹*Graduate School of Engineering, Osaka University*, ²*National Institute of Advanced Industrial Science and Technology,* ³*National Institute of Technology, Ibaraki College*)
○Yoshiyuki Kagawa,¹ Koji Oohora,¹ Tomoki Himiyama,² Akihiro Suzuki,³ Takashi Hayashi¹

Keywords: Porphyrin; Artificial Metalloenzyme; Myoglobin; Cyclopropanation; Redox Potential

Engineered hemoproteins are known to be promising catalysts for alkene cyclopropanation. However, most of them have little activity towards aliphatic alkenes due to the low reactivity of carbene species, an active intermediate. Recently, several studies have suggested that the more positive the redox potential of iron porphyrin cofactors in hemoproteins, the higher the reactivity of the cyclopropanation reactions.[1] In this context, we hypothesized that studies using myoglobins reconstituted with synthetic cofactors possessing various redox potentials would reveal a correlation between redox potential and cyclopropanation reactivity. Here, iron porphyrins with two or one trifluoromethyl groups at the peripheral sites (FePor(CF_3)$_2$ and FePorCF$_3$, respectively), native heme and iron porphycene (FePc) were used as cofactors, and the range of Fe(II)/Fe(III) redox potentials of the four myoglobins exceeds 340 mV (Fig. 1). It was found that myoglobin with more positive redox potential shows higher reactivity toward inert alkenes. In particular, myoglobin reconstituted with FePor(CF_3)$_2$ (rMb(FePor(CF_3)$_2$)) exhibits a 165-fold higher turnover number for 1-octene cyclopropanation compared to native myoglobin. Mechanistic studies indicate that rMb(FePor(CF_3)$_2$) generates an active species with a radical character. In contrast, myoglobin reconstituted with FePc provides a detectable iron–carbene species[2] with an electrophilic character. This work highlights the significance of redox-focused design of the iron porphyrinoid cofactor in hemoproteins to enhance cyclopropanation reactivity.

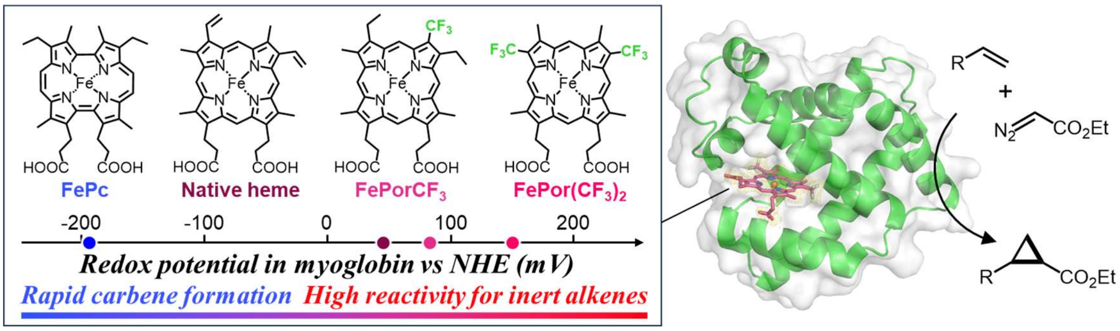


Fig. 1. Alkene cyclopropanation by redox diverse myoglobins containing modified cofactors.

1) a) D. Hilvert, *et al., Angew. Chem. Int. Ed.* **2021**, *60*, 15063–15068. b) R. Fasan, *et al., ACS Catal.* **2019**, *9*, 9683–9697. 2) T. Hayashi, *et al. J. Am. Chem. Soc.* **2017**, *139*, 17265–17268.

人工非ヘム銅タンパク質が触媒する立体選択的ヘテロ Diels-Alder 反応

（大阪公大院農 [1]・大阪府大院生命 [2]）○松本 隆聖 [1]・吉岡 紗穂 [2]・森田 能次 [1]・藤枝 伸宇 [1,2]

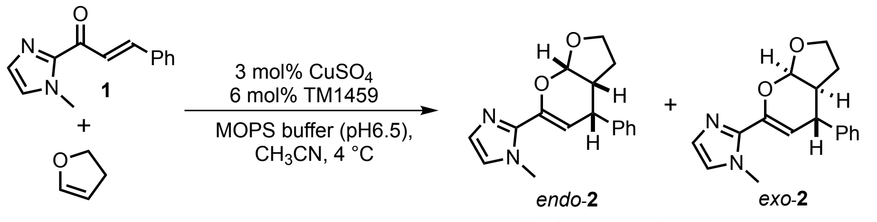
Stereoselective Inverse Electron-Demand Hetero-Diels-Alder Reactions catalyzed by non-heme copper proteins ([1]*Graduate School of Agriculture, Osaka Metropolitan University*, [2]*Graduate School of Life and Environmental Sciences, Osaka Prefecture University*)
○Ryusei Matsumoto[1], Saho Yoshioka[2], Yoshitsugu Morita[1], Nobutaka Fujieda[1,2]

Lately, artificial metalloenzymes have garnered enormous interest as emerging biohybrid catalysts, the integration of chemical catalysis and biocatalysis. TM1459 from *Thermotoga maritima* has highly thermal stability and contains a metal binding site consisting of 4-histidine residues. By using this protein as metal-ligands, we have recently developed the artificial non-heme metalloenzymes. In this study, we attempted to construct enzymes with high stereoselectivity by mutating four histidines at this metal binding site. We screened thus obtained mini-library of mutants for the inverse electron-demand hetero-Diels-Alder reaction, and showed high stereoselectivity when several mutants were used.

Keywords : Artificial Metalloenzymes, Macromolecular Ligands, Stereodivergent reaction

近年、遷移金属錯体の反応性や立体選択性を向上させたハイブリッド触媒である人工金属酵素 [1] が注目を集めている。一方で、当研究室では超好熱菌由来の TM1459 タンパク質を金属配位子として用いたより簡便な人工非ヘム金属酵素の創製手法を報告してきた [2]。本研究では、これらタンパク質配位子を立体選択的ヘテロディールズアルダー反応に用いた結果について報告する。

第一配位圏にあるヒスチジンのうち 1 つあるいは 2 つをアラニンに変異させたライブラリーをα, β-不飽和アシルイミダゾール誘導体 (**1**)とジヒドロフランを用いたディールスアルダー反応においてスクリーニングを行なった。野生型ではほとんどエナンチオ選択性が見られなかったが、H52A 変異体を用いた場合には反応が進行した。さらに、第一配位圏や第二配位圏に位置するアミノ酸残基もアラニンに変異させることでキャビティを拡大し、より基質のアクセスを促進するような変異体を作製した結果、生成物を収率 89 %、エナンチオ過剰率 94 %で合成することに成功した。本発表では変異体の設計や基質結合の詳細について議論する。



1) Ward, T. R. *et al.*, *ACS Cent. Sci.* **2019**, 5, 7, 1120. 2) (a) Fujieda, N.; Itoh, S. *et al.*, *J. Am. Chem. Soc.*, **2017**, 139, 5149. (b) Fujieda, N.; Itoh, S. *et al.*, *Angew. Chem. Int. Ed.*, **2020**, 59, 7717. (c) Matsumoto, R.; Fujieda, N. *et al.*, *Chem. Sci.*, **2023**, 14, 3932.

Construction of a trisulfide ferredoxin dimer and its formation mechanism

([1]*Graduate School of Science and Technology, NAIST*, [2]*Graduate School of Science, University of Hyogo*) ○Tsuyoshi Mashima[1], Monami Tanaka[1], Nur Afiqah binti Azmi[1], Masaru Yamanaka[1], Hideaki Ogata[2], Shun Hirota[1]

Keywords: *Ferredoxin*; *Iron-sulfur cluster*; *Persulfide*; *Protein oligomerization*; *Trisulfide bond*

Ferredoxin is an electron transfer protein containing an iron-sulfur cluster. On the other hand, persulfide (RS-S$^-$) is gaining attention as a signaling molecule and a regulator of enzyme activities in living organisms.[1] In this study, we found that oxidized *Thermotoga maritima* ferredoxin dimerizes by incubation in the presence of guanidine hydrochloride under basic conditions, where monomers are connected via a trisulfide bond (Fig. 1). Ferredoxin was expressed in *E. coli* and purified with ion-exchange and size exclusion chromatography (SEC). Purified ferredoxin was incubated for 3 days under optimized dimerization conditions, and the obtained dimer was purified with SEC. After further purification of the dimer with anion-exchange chromatography, it was crystalized and the three-dimensional structure was determined by X-ray crystallography. In the dimer structure, the [4Fe4S] cluster in the monomer was converted to a [4Fe3S] cluster. Cys13, which coordinates to the iron atom of the iron-sulfur cluster in the monomer, dissociated from the iron atom and formed an intermolecular bond in the dimer with a sulfur atom bridged between two Cys13 sulfur atoms. The properties of the iron-sulfur clusters of the monomer and dimer obtained after incubation were investigated by EPR and mass spectrometry measurements. To identify the active species of the dimerization, maleimide, methyl methanethiosulfonate, and glutathione were added to the reaction solution to quench the reaction. After confirming effective quenching of these compounds using SEC, the composition of the iron-sulfur cluster of the quenched monomer was investigated by mass spectrometry. Based on these results, we will discuss the dimerization mechanism.

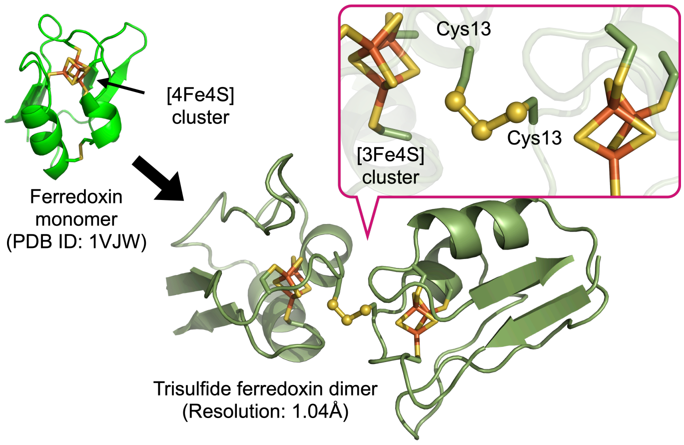


Figure 1. Schematic representation of the trisulfide ferredoxin dimer formation.

1) K. R. Olson, *Biochemical Pharmacology*, **2018**, *149*, 77.

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18日(月) 13:00 ~ 15:30 H931(9号館 [3階] 931)

[H931-1pm] 17. 生体機能関連化学・バイオテクノロジー

座長：Arivazhagan Rajendran、遠藤 玉樹

英語
13:00 ~ 13:20
[H931-1pm-01]

アルギニンに富んだペプチドとグアニン四重らせん構造によって誘起される液液相分離を制御する因子の検討

○シル シュミット[1]、鶴田 充生[1]、川内 敬子[1]、三好 大輔[1] (1. 甲南大学)

英語
13:20 ~ 13:40
[H931-1pm-02]

核酸のグアニン四重らせん構造標的分子を用いたテロメア長—TERRA発現量相関の制御

○橋本 佳樹[1]、川内 敬子[1]、三好 大輔[1] (1. 甲南大学)

英語
13:40 ~ 14:00
[H931-1pm-03]

グアニン四重らせん構造のトポロジー依存的な液液相分離

○鶴田 充生[1]、取井 猛流[1]、川内 敬子[1]、杉本 直己[1]、三好 大輔[1] (1. 甲南大学)

14:00 ~ 14:10

休憩

日本語
14:10 ~ 14:30
[H931-1pm-04]

リン酸骨格およびダイナミクスに着目したミスマッチDNA-低分子複合体のNMR解析

○櫻林 修平[1,2]、古板 恭子[1]、山田 剛史[2]、藤原 敏道[1]、中谷 和彦[2]、児嶋 長次郎[1,3] (1. 阪大蛋白研、2. 阪大産研、3. 横国大)

英語
14:30 ~ 14:50
[H931-1pm-05]

Chemical ligation of staple nicks in DNA origami

○Arivazhagan Rajendran[1], Kirankumar Krishnamurthy[1], Eiji Nakata[1], Takashi Morii[1] (1. Kyoto University)

英語
14:50 ~ 15:10
[H931-1pm-06]

核酸化学のNew Data Science (8): ハイスピード共焦点イメージングを利用した生細胞内での核酸構造変化の解析

○遠藤 玉樹[1]、建石 寿枝[1]、筒井 啓太[2]、深谷 陽子[2]、築地 真也[2]、杉本 直己[1,3] (1. 甲南大 FIBER、2. 名工大院工、3. 甲南大 FIRST)

英語

15:10 ~ 15:30

[H931-1pm-07]

New Data Science in Nucleic Acids Chemistry (9): Conformational transition of nucleic acids with virus genome sequences inside cell-like nanoconfinements

〇Sunipa Sarkar[1], Hisae Tateishi-Karimata [1], Kazunori Matsuura[2,3], Tamaki Endoh[1], Naoki Sugimoto[1,4] (1. Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, 2. Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 3. Centre for Research on Green Sustainable Chemistry, Tottori University, 4. Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University)

Arginine-Rich Peptides and G-Quadruplex: A Systematic Study on Factors Influencing Their Liquid-Liquid Phase Separation

([1]*Frontiers of Innovative Research in Science and Technology FIRST, Konan University, Japan*)
○Sumit Shil,[1] Mitsuki Tsuruta,[1] Keiko Kawauchi,[1] Daisuke Miyoshi[1]

Keywords: *G-Quadruplexes; Arginine Rich Proteins; Liquid-Liquid Phase Separation; Structure-function Relationships; Liquid Droplets*

G-Quadruplex (G4) is a secondary structure formed by guanine-rich sequences in DNA and RNA[1]. G4 nucleic acids have recently received attention because of their distinctive structural features and probable functions in cellular regulation[1]. Recently, it has been discovered that certain G4 structures are suitable for inducing LLPS, leading to the formation of membrane-less compartments within test tubes and cells[2]. Moreover, it was discovered that certain peptides can induce LLPS of G4 nucleic acids[2] (Fig.1). We previously reported that the RGG motif, in which Arg and Gly are enriched, derived from FMRP strongly and selectively underwent LLPS with G4 forming RNAs[3]. However, it is still not clear which factors of peptide sequences and G4 structures are important for the G4 LLPS. Understanding the interaction between G4 nucleic acid structure and sequence composition of peptides is critical for the mechanisms that drive LLPS.

Here, we investigated the effects of the different G4 nucleic acid structures and diverse peptide sequences on the G4 LLPS. Here, we systematically designed oligonucleotide forming G4s with different structural topologies, as well as diverse peptides derived from proteins, whose functions are related to LLPS and nucleic acid binding. Using CD spectroscopy, turbidity, and microscopy investigations, we find out that Arg, specifically a specific quantity of Arg is essential for undergoing the G4 LLPS to form liquid droplets. On the other hand, the parallel G4 nucleic acid structure is the most capable structure of inducing LLPS compared to the other G4 structures.

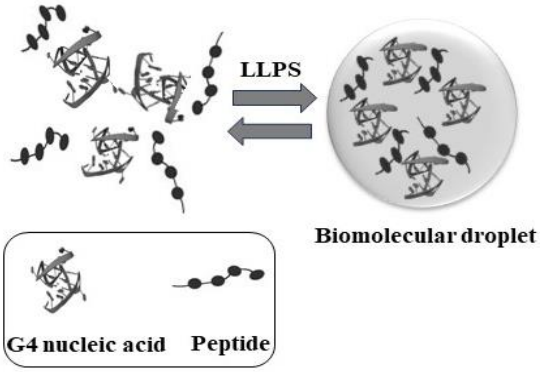


Fig.1. LLPS of G4 nucleic acid and peptide

1) Yang D., *et al.*, *Method Mol Biol.* **2019**, *2035*, 1. 2) Xu. Liu, *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 11036. 3) Tsuruta, M., *et al.*, *Chem. Commun.*, **2022**, *58*, 12931.

核酸のグアニン四重らせん構造標的分子を用いたテロメア長—TERRA 発現量相関の制御

（甲南大 FIRST）○橋本佳樹・川内敬子・三好大輔

Regulating telomere length-TERRA expression relationship with G-quadruplex-targeting molecules

(*Frontiers of Innovative Research in Science and Technology, Konan University*) ○Yoshiki Hashimoto, Keiko Kawauchi, Daisuke Miyoshi

Telomere and Telomeric repeat-containing RNA (TERRA) are related in cancer proliferation and malignancy. TERRA expression inhibits cancer malignancy and is down-regulated by telomere elongation[1, 2]. Telomeres contain G-quadruplex (G4) forming sequences. Telomere G4 formation can shorten telomere length. One of the promising strategies for inhibition of telomere elongation is G4 targeting molecule (G4 ligand). Inhibition in telomere elongation by G4 ligand has been reported[3]. Structure-selectivity is necessary for intracellular G4 targeting. Although a wide variety of G4 ligands have been developed, so far, only a few structure-selective G4 ligands have been reported. Therefore, the G4 ligand which can shorten telomere length and promote TERRA expression has not been reported yet. Here, we attempted to obtain some G4 ligands which can alter telomere length-TERRA expression by used of TD assay[4] Factors in G4 ligand affecting the telomere length-TERRA expression will be discussed.

Keywords : Telomere; TERRA; G-Quadruplex; G4 Ligand; Cancer

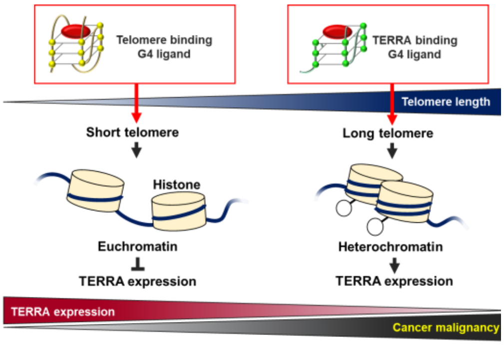


Fig. Effects of structure-selective G4 ligands on telomere length and TERRA expression.

テロメアとその転写産物であるTERRA はがん細胞の増殖や悪性化に関与している 1)。テロメア伸長を阻害することは TERRA の発現を誘導できることが示唆されている 2)。テロメアはグアニン四重らせん構造（G4）形成配列であり、テロメア G4 はテロメアの伸長を阻害できる。そのため、テロメアを標的とした G4 リガンドはテロメアの伸長阻害に有用であると考えられている。このような G4 リガンドを用いた細胞内 G4 ターゲティングでは G4 リガンドの構造選択性が重要である 3)。しかしながら、構造選択的 G4 リガンドの報告例は少なく、テロメア長を短縮し、TERRA 発現を亢進できる G4 リガンドは報告されていない。そこで本研究では独自のスクリーニングシステム 4)を用いて構造選択的 G4 リガンドを取得し、構造選択的 G4 リガンドのテロメア長と TERRA 発現量の相関に及ぼす効果を検討した。その結果、G4 リガンドの DNA/RNA 選択性がテロメア長—TERRA 発現量制御に重要であることが示唆された。

1) K. Hirashima, *et al.*, *Nucleic Acids Res.*, **2015**, 43, 2022-2032.
2) N. Arnoult, *et al.*, *Nat. Struct. Mol. Biol.*, **2012**, 19, 948-956.
3) H. Yaku, *et al., J. Phys. Chem. B*, **2014**, 118, 2605-2614.
4) Y. Hashimoto, *et al., Chem. Commun.*, **2023**, 59, 4891-4894.

グアニン四重らせん構造のトポロジー依存的な液液相分離

（甲南大 FIRST[1]・甲南大 FIBER[2]）○鶴田充生[1]・川内敬子[1]・杉本直己[1,2]・三好大輔[1]

Effect of G-quadruplex topology on liquid-liquid phase separation with cationic peptide

([1]*Graduate school of faculty of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University,* [2]*Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University*) ○Mitsuki Tsuruta, Keiko Kawauchi, Naoki Sugimoto, Daisuke Miyoshi

Biomolecular droplets formed via liquid-liquid phase separation (LLPS) is now attracting attention as a novel biological phenomenon. The biomolecular droplets inside cells regulate various cellular functions such as transcription, RNA processing, and translation. Although proteins and domains which bind to specific G4 topology are reported to undergo LLPS, it is unknown that proteins (domains) undergo LLPS with specific G4 topology (Fig. 1). Here, we investigated effects of G4 topology on LLPS with Arg-rich peptides. It was showed that a parallel type G4 is favorable to undergoes LLPS. Furthermore, we found that loop regions in G4s is an important factor for undergoing LLPS.

Keywords : Liquid-Liquid Phase Separation; DNA; G-quadruplex; Topology; Peptide

生体分子の液液相分離によって誘起される液滴は、転写や翻訳をはじめとする様々な細胞内反応を制御する[1]。細胞内の一部の液滴では、核酸の非標準的な二次構造であるグアニン四重鎖（G4）が局在することから、G4 が液滴形成に重要であると考えられている。G4 には、三種類のトポロジーが存在し、それぞれに選択的な結合するタンパク質も報告されている。これらのタンパク質のトポロジー選択的な結合により、より精密な液滴形成制御方法を構築できる可能性がある（Fig. 1）。そこで本研究は、G4 と LLPS を誘起することが知られているカチオン性ペプチドをモデルとして使用し、LLPS に対する G4 のトポロジーの影響を検討した[2]。その結果、パラレル型 G4 は他の G4 トポロジーと比較して、より LLPS を誘起しやすいことが明らかとなった。さらに、G4 のループ領域が LLPS において重要でることも明らかとなった。

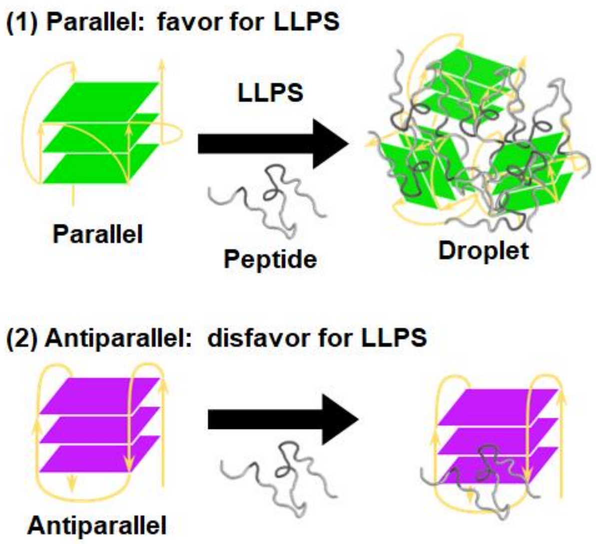


Fig. 1 Schematics of parallel and antiparallel G4 as a component that favor for LLPS (1) and disfavor for LLPS (2), respectively.

1) R. L. Kan *et al., Trends. Genet.* **2022**, *38*, 182.
2) M. Tsuruta *et al*., *Chem. Commun*. **2022**, *58*, 12931.

リン酸骨格およびダイナミクスに着目したミスマッチ DNA-低分子複合体の NMR 解析

(阪大蛋白研[1]・阪大産研[2]・横国大[3]) ○櫻林 修平[1,2]、古板 恭子[1]、山田 剛史[2]、藤原 敏道[1]、中谷 和彦[2]、児嶋 長次郎[1,3]

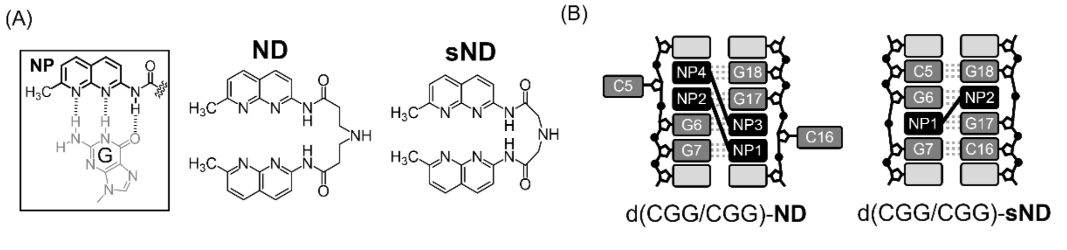
NMR analysis of the mismatched DNA-small molecule complex — phosphate backbone and dynamics

([1]*Institute for Protein Research*, *Osaka University*, [2]*SANKEN, Osaka University*, [3]*Yokohama National University*) ○Shuhei Sakurabayashi[1,2], Kyoko Furuita[1], Noriaki Sugiura[2], Takeshi Yamada[2], Toshimichi Fujiwara[1], Kazuhiko Nakatani[2], Chojiro Kojima[1,3]

Small molecules that recognize specific structures in DNA have potential applications as tools in chemical biology. To date, two molecules, **ND** and **sND**, have been developed as G-G mismatch recognition molecules (Fig. 1A、ref.1). Although these molecules have similar chemical structures, their binding modes with DNA are revealed to be significantly different (Fig. 1B). In this study, we conducted quantitative kinetic analysis of conformational transitions based on ^{1}H-^{1}H and ^{31}P-^{31}P EXSY spectra. Also, phosphate backbone of DNA was analyzed based on the chemical shifts and J-coupling of ^{31}P based on ^{31}P-NMR spectra. Then we considered the reason why this conformation difference is caused.

Keywords : NMR, mismatch, dynamics, isotope labeling, ^{31}P

DNA 中の特異構造を認識する低分子は、ケミカルバイオロジーのツールとしての応用が期待できる。これまでに G-G ミスマッチ認識分子として **ND** および **sND** という 2 種の分子が開発されている（Fig.1A, ref.1）。これらの分子は、類似した化学構造を有しているが、DNA との結合様式が大きく異なることをこれまでに明らかにしている（Fig.1B）。本研究では、^{1}H-^{1}H および ^{31}P-^{31}P EXSY スペクトルによる、コンホメーションの移行の定量的な速度論的解析と、^{31}P-NMR のケミカルシフトおよび ^{1}H との J カップリングを基にしたリン酸骨格のコンホメーションの解析を行い、結合様式に違いが生じる原因を考察した。



(A) Chemical structure of **ND** and **sND**. (B) Binding mode of **ND** and **sND** to the d(CGG/CGG) triad revealed by NMR.

(ref. 1) K. Nakatani, S. Sando, H. Kumasawa, J. Kikuchi and I. Saito, *J. Am. Chem. Soc.*, 2001, **123**, 12650–12657

Chemical Ligation of Staple Nicks in DNA Origami

([1]*Institute of Advanced Energy, Kyoto University*) ○Arivazhagan Rajendran,[1] Kirankumar Krishnamurthy,[1] Eiji Nakata,[1] Takashi Morii[1]

Keywords: DNA Origami; DNA Nanotechnology; Chemical Ligation; DNA Origami Stability; Atomic Force Microscopy

The DNA origami field has seen enormous growth during the past one and a half decades, and various nano- and micro-meter scale structures have been synthesized with sub-nanometer addressability.[1] Despite the proof-of-concept demonstrations of the applications,[2] the real-life utilization of the origami materials is limited due to their insufficient stability. There have been limited efforts to stabilize the origami against thermal, mechanical, chemical, and biological modifications/environments. We have recently performed a detailed characterization of the enzymatic ligation of 2D DNA origami to establish the optimized process.[3] Under the optimum conditions, up to 10 staples ligation with a maximum ligation efficiency of ~55% was achieved. This, in turn, resulted in the increase in thermal stability of the origami from as low as 5°C to as high as 20°C, depending on the structure. Besides our initial demonstration, due to the tightly packed anti-parallelly oriented arrangement of multiple duplexes in the origami and the difficulties in the accessibility of the nicks by ligase, enzymatic ligation was only partly successful. Therefore, it is necessary to develop methods to enhance the ligation efficiency, particularly for 3D origami structures.

Here, we demonstrate enzyme-free chemical ligation of 2D and 3D origami.[4,5] This method results in the native phosphate backbone ligation. The reaction conditions are optimized to attain the maximum possible ligation efficiency. This method achieved near quantitative ligation of the nicks in 2D and 3D origami. Though enzymatic ligation requires overnight even for the partial ligation, the pure chemical ligation reaction was completed within 5 min. In addition, only the chemical ligation method worked efficiently for the nick ligation in 3D origami. Compared to non-ligated origami, chemical ligation improved the stabilities against thermal treatments, during electrophoretic mobility of origami, and against nucleases and cell lysate in a structure-dependent manner. Overall, this ligation method is straightforward, requires no tedious process, and is superior in terms of cost, reaction time, efficiency, and stabilization of 2D and 3D origami.

1) P. W. K. Rothemund, *Nature*, **2006,** *440*, 297-302. 2) A. Rajendran, E. Nakata, S. Nakano, and T. Morii, *ChemBioChem*, **2017,** *18*, 696-716. 3) A. Rajendran, K. Krishnamurthy, A. Giridasappa, E. Nakata, and T. Morii, *Nucleic Acids Res.*, **2021,** *49*, 7884-7900. 4) O. A. Fedorova, M. B. Gottikh, T. S. Oretskaya, and Z. A. Shabarova, *Nucleosides and Nucleotides*, **1996**, *15*, 1137-1147. 5) K. Krishnamurthy, A. Rajendran, E. Nakata, and T. Morii, *Small Methods*, **2023,** 2300999, In press.

New Data Science in Nucleic Acids Chemistry (8): Real-time monitoring of nucleic acids conformational change in living cells using high-speed confocal imaging system

([1]*Frontier Institute for Biomolecular Engineering Research (FIBER) Konan University,* [2]*Graduate School of Engineering, Nagoya Institute of Technology,* [3]*Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University*) ○Tamaki Endoh,[1] Hisae Tateishi-Karimata,[1] Keita Tsutsui,[2] Yoko Fukaya,[2] Shinya Tsukiji,[2] Naoki Sugimoto[1,3]

Keywords: Nucleic acid structure; Dynamics; Confocal; Imaging; Quadruplex

The dynamic behaviors of the nucleic acid structures, which are influenced by the intracellular multimolecular crowding environment, impact protein expressions. For example, since the folding rate of G-quadruplexes are generally slower than that of secondary structures, nascent RNAs have potential to form kinetically preferred hairpin-like structures during transcription that the region transitions to the thermodynamically more stable G-quadruplex after the transcription.[1] The conformational transition rate of the nascent mRNA from the kinetically formed hairpin to the G-quadruplex potentially affects an efficiency of protein translation.[2] In this context, the quantitative analysis of the structure dynamics of nucleic acids in cells is important to make insight to the dynamic regulation of biological reactions by the nucleic acids. In this study, we have performed real-time monitoring of nucleic acids conformational changes from secondary structure to maturely exclusive G-quadruplex structure in living cells. Oligonucleotide probes, which were labeled with two fluorophores for FRET imaging and trimethoprim (TMP), were injected into cells expressing *E. coli* dihydrofolate reductase (eDHFR) in cytosol or nucleus. Interaction between TMP and eDHFR localized the oligonucleotide probes at cytosol and nucleus and enabled analysis of different conformational dynamics of the nucleic acids depending on the cellular compartment by high-speed FRET imaging using multibeam scanning confocal imaging using Nipkow disks (Figure 1).

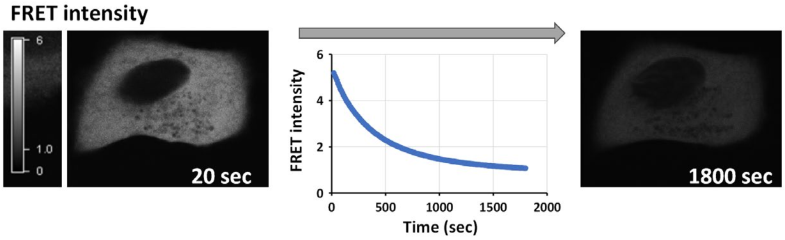


Figure 1. Change of FRET signal after injection of oligonucleotide probe localized to cytosol. FRET images after subtraction of background signal are shown.

1) T. Endoh, A. B. Rode, S. Takahashi, Y. Kataoka, M. Kuwahara, N. Sugimoto, *Anal. Chem.*, **2016**, *88*, 1984; A. B. Rode, T. Endoh, N. Sugimoto, *Angew. Chem. Int. Ed.*, **2016**,*55*, 14315
2) T. Endoh, H. Tateishi-Karimata, N. Sugimoto, *Handbook of Chemical Biology of Nucleic Acids*, Springer, Singapore, **2023**, https://doi.org/10.1007/978-981-16-1313-5_40-1

New Data Science in Nucleic Acids Chemistry (9): Conformational Transition of Nucleic Acids with Virus Genome Sequences inside Cell-like Nanoconfinements

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Keywords: Virus capsid; Nanoconfinement; G-quadruplex-hairpin equilibrium; Reverse transcription; Therapeutics

All living cells possess double-stranded DNAs as their genetic material, while viruses exhibit genomes with either DNA or RNA. To protect the fragile nucleic acids, the virus envelops its genetic material with a protein shell known as the capsid (Figure 1a). The size of the nucleocapsid varies significantly depending on the viruses, and this variation can impact the behavior of the viral genome.[1] Moreover, after infecting a host cell, the virus releases the nucleic acids into the cellular environment, emphasizing the impact of the cellular environment on nucleic acids.[2] Conformational equilibria between G-quadruplexes (G4s) and hairpins (Hps) are critical for the functional regulation of nucleic acids.[3] However, a little is known about the relationship between nucleocapsid size and the G4-Hp equilibrium of the viral genome.

In this study, we mimicked the variation of nucleocapsid size using nanoconfinement and investigated the RNA G4-Hp equilibrium inside the confinement. We chose reverse micelle (RM) as it allowed us to change the size of the confinement by adjusting the extent of water loading. We selected the sequences from RNA viruses (Human immunodeficiency virus, Hepatitis C virus, and SARS-Cov-2) with the possibility of folding into G4 and Hp structures in the presence of K^+ ion. The Circular Dichroism (CD) and Forster resonance energy transfer (FRET) results revealed that nanoconfinement size influenced G4-Hp equilibrium of virus RNAs, probably favoring G4 at lower sizes and Hp at higher sizes (Figure 1b). Furthermore, we also found the effect of the cellular environments on the G4-Hp equilibrium of the virus genes.

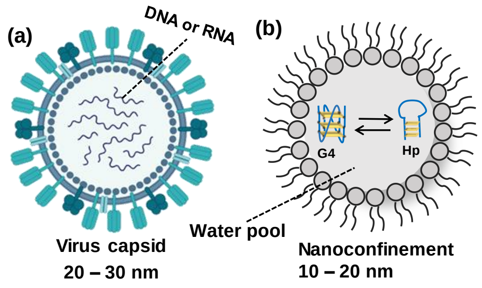


Figure 1. (a) Schematic representation of virus capsid which contains nucleic acids inside the capsid. (b) The equilibrium between G4 and Hp inside nanoconfinement.

1) H. Furukawa, H. Inaba, F. Inoue, Y. Sasaki, K. Akiyoshi, K. Matsuura, *Chem. Comm.* **2020**, *56*, 7092. 2) D. Banerjee, H. Tateishi-Karimata, M. Toplishek, T. Ohyama, S. Ghosh, S. Takahashi, M. Trajkovski, J. Plavec, N. Sugimoto, *J. Am. Chem. Soc.*, **2023,** *145*, 23503. 3) A. B. Rode, T. Endoh, N. Sugimoto, *Angew. Chem. Int. Ed.* **2016,** *55*, 14315.

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18日(月) 13:00 ~ 15:30 H934(9号館 [3階] 934)

[H934-1pm] 17. 生体機能関連化学・バイオテクノロジー

座長：山村 昌平、小澤 岳昌

日本語
13:00 ~ 13:20
[H934-1pm-01]
細胞膜固定化材料の作製と生体材料としての特性解析

○岡本 行広[1,2]、Xuehui Rui[1]、渡邊 望美[1]、馬越 大[1] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院基礎工学研究科未来ラボ)

日本語
13:20 ~ 13:40
[H934-1pm-02]
脂質複合化 DNA ブラシに吸着した金ナノ粒子の溶媒による集合変化

○与那嶺 雄介[1]、石 雅麗[2]、三友 秀之[1]、居城 邦治[1] (1. 北大電子研、2. 北大院生命)

英語
13:40 ~ 14:00
[H934-1pm-03]
ペプチドナノファイバーを基盤とした光応答性人工細胞骨格の創製

○梁 応冰[1]、稲葉 央[1]、松浦 和則[1] (1. 鳥取大学大学院)

英語
14:00 ~ 14:20
[H934-1pm-04]
Surface coating of an algal cell with elongated DNA strands to control the loading and releasing of cationic materials.

○YINGQI MU[1], Yuseke Yonamine[2], Hideyuki Mitomo[2], Kuniharu Ijiro[2] (1. Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University (RIES, Hokkaido Univ.))

14:20 ~ 14:30
休憩

日本語
14:30 ~ 14:50
[H934-1pm-05]
遺伝子変異がん細胞の検出のためのペプチド核酸プローブと1細胞マイクロアレイチップ技術の開発

○重藤 元[1]、北松 瑞生[2]、大槻 高史[3]、飯塚 明[4]、秋山 靖人[4]、山村 昌平[1] (1. 産総研、2. 近畿大、3. 岡山大、4. 静岡がんセンター)

英語
14:50 ~ 15:10
[H934-1pm-06]
概日時計同調時におけるNADPHオキシダーゼの役割を解明するための発光プローブの開発

○河村 玄気[1]、田丸 輝也[2]、小澤 岳昌[1] (1. 東京大学、2. 東邦大学)

英語

15:10 ~ 15:30

[H934-1pm-07]

光制御と数理モデルを用いたAktアイソフォーム活性化の時間的ダイナミクスと下流シグナル伝達の定量的解析

○関根 由佳[1]、河村 玄気[1]、小澤 岳昌[1] (1. 東大院理・化学)

細胞膜固定化材料の作製とその同定

(阪大院基礎工[1]・阪大院基礎工未来ラボ[2])
○岡本 行広[1,2]・Xuehui Rui[1]・渡邊 望美[1]・馬越 大[1]

Preparation and Characterization of Cell Membrane Coated Materials

([1]*Graduated School of Engineering Science, Osaka University,* [2]*Graduated School of Engineering Science, the Multidisciplinary Research Laboratory System at Osaka University*)
○Yukihiro Okamoto[1,2], Xuehui Rui[1], Nozomi Watanabe[1], Hiroshi Umakosh[1]

We can find various and tremendous cell species in our body and in nature, and these cells possess specific molecules and show superior functions. Thus, cell membrane coated materials can be expected as superior materials mimicking the cell ability. In drug delivery system (DDS), the escape from immune system is one of the most required matters, and DDS carriers must be equipped with this ability. In this paper, we attempted to prepare cell membrane coated DDS carriers to attain this demand. At first, the confirmation of cell membrane coated lipid nanoparticles was conducted by cryo-TEM, and subsequently the property analysis of the nanoparticles was performed by DLS, zeta potential, SDS PAGE *etc*. Finally, the performance as DDS carriers was evaluated by toxicity assay, drug release assay, uptake ratio by tumor cells and macrophage cells *etc*. These data successfully demonstrated that cell membrane coating is effective approach for superior DDS carriers.

Keywords : cell membrane coating; membrane property analysis; drug delivery system material

我々の体内，自然界には多種多様な細胞が存在しており，優れた機能を呈している．この優れた機能を模倣する手法の一つとして，細胞膜の利用が考えられる．DDS において免疫系からの回避は重要な事項の一つであり，自己の体内に存在する細胞から細胞膜を回収し，DDS キャリアに固定化することで，従来の DDS キャリア材料に免疫系からの回避という特性を付与できると考えられる．

今回採用した脂質ナノ粒子は，粒径を 50 nm～400 nm 前後に調製可能であり，疎水性/親水性薬物を含有できるため，DDS 材料として期待されている．これをコア材料とし，この表層を細胞膜で修飾したナノ粒子を作製した．その後，DDS キャリアとしての特性を評価した．

Cryo-TEM や SAXS 解析から細胞膜を固定化した脂質ナノ粒子の形成を確認した．続いて，粒子径，ゼータ電位，細胞膜固定化後の膜タンパク質の評価を DLS, zeta 電位測定，SDS-PAGE により実施し，膜タンパク質分子を損なうことなく，200 nm 前後のナノ粒子の形成を確認した．最後に，DDS キャリアとしての性能評価を実施した．調製したナノ粒子の取り込み量をマクロファージと腫瘍細胞で比較した結果，マクロファージ細胞での取り込む量の低下が確認された．このため，調製したナノ粒子は免疫系を回避し，多くのナノ粒子が腫瘍細胞に取り込まれることが期待できる．

以上の結果より，細胞膜を固定化した脂質ナノ粒子は DDS キャリアとして有望な材料であると考えられる．

脂質複合化 DNA ブラシに吸着した金ナノ粒子の溶媒による集合変化

(北大電子研[1]・北大院生命[2]) ○与那嶺 雄介[1]・石 雅麗[2]・三友 秀之[1]・居城 邦治[1]

Assembly of Gold Nanoparticles Absorbed into a DNA-Lipid Complex Brush Responding to Solvent Environments

([1]*Research Institute for Electronic Science, Hokkaido University*, [2]*Graduate School of Life Science, Hokkaido University*) ○Yusuke Yonamine,[1] Yali Shi,[2] Hideyuki Mitomo,[1] Kuniharu Ijiro[2]

A complex of positively charged lipid membranes and nucleic acids forms dynamic and diverse structures due to the fluidity of the long alkyl chains of the lipids. Previously, we fabricated a DNA brush of a defined length on a substrate at high density.[1] In this study, we developed a DNA -lipid complex brush via modifying cationic lipids with ionic bonds, adsorbed gold nanoparticles (AuNP) through hydrophobic interactions, and investigated the behavior when the solvent environment was changed (Fig. 1). As a result, hydrophobic AuNPs bound to a double-stranded DNA-lipid complex brush showed peak shift of the extinction spectrum to longer wavelengths when the solution was changed from organic solvent to water. This result suggested that long alkyl groups of the DNA-lipid complex aggregated with each other in a polar solvent and the distance of AuNPs became closer, causing plasmon coupling.

Keywords：DNA-Lipid complex; Gold nanoparticle; Polymer brushes

正電荷を持つ脂質膜と核酸は静電的相互作用によって結合し、その複合体は脂質の長鎖アルキル基の流動性によって動的で多様な構造を形成する。我々はこれまでに、規定した長さのDNAを基板上に高密度に固定したDNAブラシを作製してきた[1]。本研究では、これにイオン結合でカチオン性脂質を修飾した、脂質複合化DNAブラシを作製し、金ナノ粒子（AuNP）を疎水性相互作用により吸着させ、溶媒環境を変化させた際の挙動を調査した（Fig. 1）。その結果、疎水性AuNPは二本鎖の脂質複合化DNAブラシに結合し、溶液を有機溶媒から水に変えたところ、消光スペクトルのピーク位置が長波長側にシフトした。極性溶媒下ではアルキル基同士が凝集し、それに伴いAuNPが近接し、プラズモンカップリングが起こったと考えられる。この変化は可逆的であった。

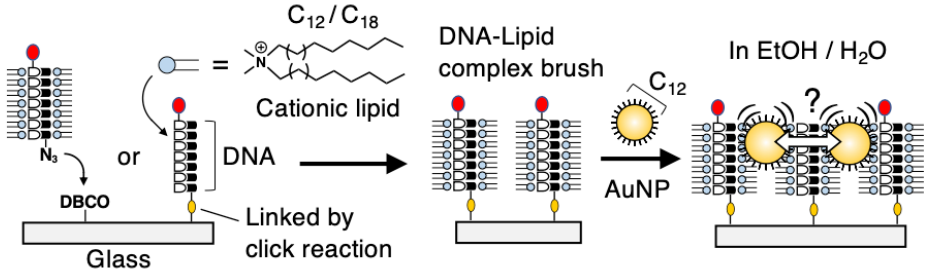


Figure 1. A DNA-Lipid complex brush was formed on a glass substrate and gold nanoparticles were absorbed into the brush through hydrophobic interaction. Assemble behavior was investigated when solvent environment was changed.

1) S. Nakamura *et al., ACS Omega,* **2017,** *2,* 2208.

Creation of Photoresponsive Artificial Cytoskeleton based on Peptide Nanofibers

(*Graduate School of Engineering, Tottori University*) ○Yingbing Liang, Hiroshi Inaba, Kazunori Matsuura

Keywords: Cytoskeleton; Liposome; Peptide Nanofiber; Assembly/Disassembly; Photoresponse

Polymerization and depolymerization of cytoskeleton structures such as microtubules and actin filaments in eukaryotic cells impact cell deformation and migration. Recently, it has reported that the assembly and disassembly of nanofibers composed of actin inside giant unilamellar vesicles (GUVs) can affect their morphology.[1] However, there are no studies on spatiotemporal control of GUV deformation using cytoskeleton-like self-assembled nanofibers. In this study, we developed photoresponsive spiropyran/merocyanine (SP/MC)-modified peptide nanofibers to create an artificial cytoskeleton that can induce a morphological change in GUVs (Fig. 1A).[2]

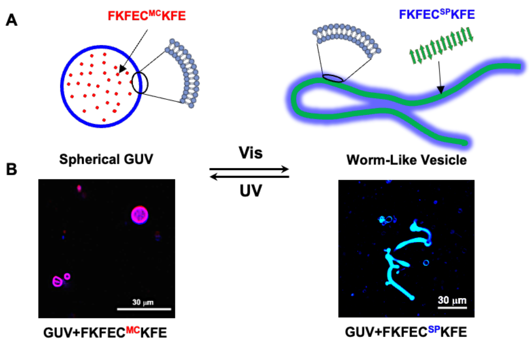


Fig. 1 Schematic diagram (A) and CLSM images (B) of the reversible morphologic changes of GUVs encapsulated FKFEC$^{SP/MC}$KFE .

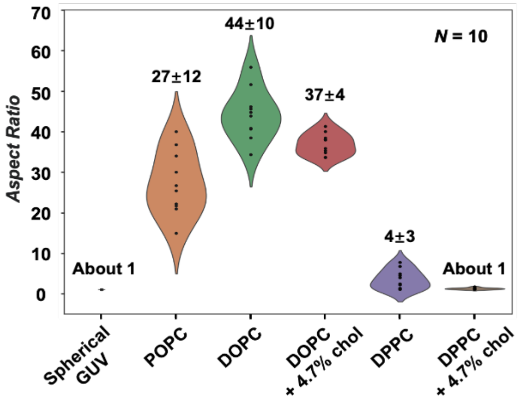


Fig. 2 The effect of membrane fluidity on the aspect ratio of GUVs induced by photoisomerization of SP/MC-peptide.

We synthesized an SP/MC-modified *β*-sheet peptide (FKFEC$^{SP/MC}$KFE) with reversible structural conversion by photo-irradiation. The SP-peptide formed β-sheet nanofibers, whereas the photoisomerization to the MC-peptide almost completely dissociated the nanofibers. Spherical GUVs encapsulating the MC-peptide dramatically and reversibly changed into worm-like vesicles by the photoisomerization to the SP-modified peptide (Fig. 1B). In addition, we investigated how membrane fluidity affects the GUV deformation induced by photoisomerization of SP/MC-peptide (Fig. 2). GUV conprising of flexible DOPC with two double bonds in their structure deformed more drastically than GUV conprising of mono-unsaturated POPC. The addition of cholesterol decreased the membrane fluidity, but the deformation remained drastic. In contrast, GUV conprising of rigid DPPC with a saturated fatty acid chain underwent minimal morphological changes.

[1] C. Li, X. Zhang, B. Yang, F. Wei, Y. Ren, W. Mu, X. Han, *Adv. Mater.*, **34**, 2204039 (2022)
[2] Y. Liang, S. Ogawa, H. Inaba, K. Matsuura, *Front. Mol. Biosci.*, **10**, 1137885 (2023)

Surface Coating of an Algal Cell with Elongated DNA Strands to Control the Loading and Releasing of Cationic Materials

([1]*Graduate School of Life Science, Hokkaido University,* [2]*Research Institute for Electronic Science, Hokkaido University*) ○Yingqi Mu[1], Yusuke Yonamine[2], Hideyuki Mitomo[2], Kuniharu Ijiro[2]

Keywords: Cell Engineering, DNA Polymerase, Algae Cell, Functional Materials

【Introduction】Cell engineering has been utilized to alter cellular functions. However, it is still challenging to significantly enhance them by gene manipulation. Conversely, modifying natural cells with artificial materials can strikingly extend cellular functions. To produce the “functionalized cell”, it is supportive to form a polymer layer on the cell surface that mediates adhesion between cells and functional materials in physiological conditions. DNA is a suitable polymer as it is biocompatible and can be extended even under cell culture conditions with enzymatic reactions. Furthermore, negatively charged phosphate groups of DNA can function as a scaffold for loading cationic materials. In this study, as a model cell for functionalization, a unicellular alga, Chlamydomonas reinhardtii (CR), was modified with a DNA primer. The immobilized DNA primers were then elongated with a DNA polymerase to cover the CR cells with long DNA chains. A cationic gold nanoparticle was loaded onto the DNA layer through electrostatic interaction and released via degradation with an endonuclease to demonstrate endowment and deprivation of the function.

【Results and Discussion】

A DNA primer (X-motif) was conjugated with an oligopeptide of 4-hydroxyproline (HYP_{10}) that binds tightly to the CR cell wall[1] and immobilizes onto CR cell surface. By adding a DNA polymerase, Klenow fragment exo (-) (KF^-),[2] long double-stranded DNA chains with repeating sequences were elongated via slippage mechanisum[2] to form a thick DNA layer on the cell surface (Figure 1). A gold nanorod (GNR) coated with a cationic ligand (11-MTAB) was further modified onto the surface of the elongated DNA-coated cells through electrostatic interaction. Moreover, the release of modified GNRs was demonstrated by adding an endonuclease, DNase I, which degrades double- and single-stranded DNA (Figure 2).

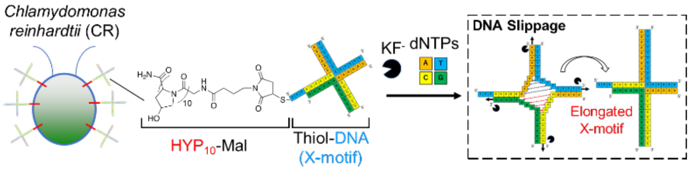


Figure 1. Elongation of DNA primers (X-motif) immobilized on CR cell surface with a DNA polymerase (KF-).

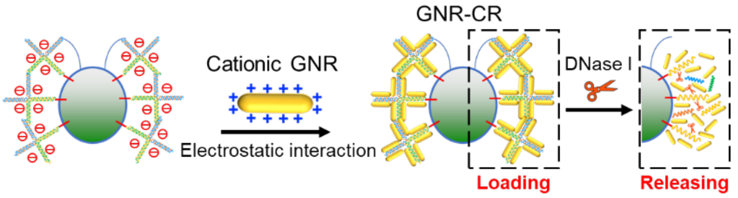


Figure 2. Cationic GNRs were loaded on CR cell surface through electrostatic interaction and released with an endonuclease (DNase I).

1) D. B Weibel *et al.*, *PNAS*, **2005,** *102*, 11963-11967.

2) A. B. Kotlyar *et al.*, *Nucleic Acids Res.*, **2005,** *33*, 525–535.

遺伝子変異がん細胞の検出のためのペプチド核酸プローブと 1 細胞マイクロアレイチップ技術の開発

（産総研・健康医工学 [1]・近畿大・応用化学 [2]・岡大院・統合科学 [3]・静岡がんセンター・免疫治療研究部 [4]） 重藤 元 [1]・北松 瑞生 [2]・大槻 高史 [3]・飯塚 明 [4]・秋山 靖人 [4]・山村 昌平 [1]

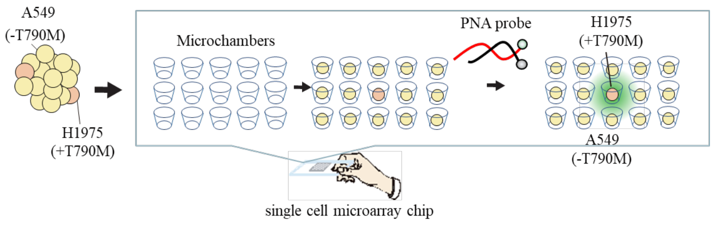
Development of the analyzing method for single nucleotide-mutated single-cancer cells using Peptide Nucleic acid Probes and Single-Cell Microarray

([1] *Health & Medical Res. Inst., AIST*, [2] *Dep. of App. Chem., Kindai Univ.*, [3] *Grad. Sch. of ISEHS, Okayama Univ.*, [4] *Immunotherapy Div., Shizuoka Cancer Cent. Res. Inst.*) ○Hajime Shigeto,[1] Mizuki Kitamatsu,[2] Takashi Ohtsuki,[3] Akira Iizuka, [4] Yasuto Akiyama,[4] Shohei Yamamura[1]

The gene mutations such as T790M in EGFR provides to cell proliferation and acquisition against anticancer drug resistance. In this study, we developed a novel system to detect the cancer cells harboring T790M mutation by combining technology of peptide nucleic acid probes and cell microarray chip. The developed method enables the easily and sensitively detection a small number of target cells from a various number of non-mutated cells.

Keywords : PNA probe; Single Cell Microarray Chip; SNP; EGFR; Lung cancer

がん細胞は発生過程において多様な遺伝子変異を獲得する。Epidermal Growth Factor Receptor (EGFR)における exon19 E746-A750 の欠損や L858R、T790M の非同義置換変異を獲得することはがん細胞の増殖促進、抗がん剤耐性能の獲得をもたらす。我々はこれまで抗がん剤耐性細胞の新たな診断方法の開発を目的とし EGFR mRNA 中の 3 つの遺伝子変異をそれぞれ検出するためのペプチド核酸 (Peptide Nucleic Acid, PNA) を使用した PNA プローブを開発してきた。また数百万個～数千万個の細胞から 1 個の標的を検出する集積型の細胞マイクロアレイチップの開発に成功している。本研究では非変異がん細胞中から、T790M に変異を有する EGFR mRNA を発現する単一がん細胞を検出・分離するシステムを開発した。T790M に変異を有する肺がん細胞株 NCI-H1975 と変異を持たない肺がん細胞株 A549 を混合したサンプルを、1 細胞マイクロアレイチップにより単一細胞に分離した。その後 T790M 変異を特異的に検出する PNA プローブを用いてチップ上で染色を行った。NCI-H1975 細胞を A549 にスパイクし解析を行ったところ 10%以下の NCI-H1975 細胞を定量検出することが可能であった。これらの結果から我々の開発するシステムは多様な細胞が含まれるがん組織中の少数の抗がん剤耐性細胞を簡易、高感度に検出可能であることが示された。



(1) Yamamura., et al., *sensors*, 17, 2410 (2017)
(2) Shigeto H., et al., *Analyst*, 144, 4613-4621 (2019)
(3) Shigeto H., et. al., *Micromachines*, 11, 628 (2020)

Development of bioluminescent probes to analyze the role of NADPH oxidase 1 in circadian clock synchronization

([1]*Graduate School of Science, The University of Tokyo,* [2]*School of Medicine, Toho University*) ○Genki Kawamura,[1] Teruya Tamaru,[2] Takeaki Ozawa[1]

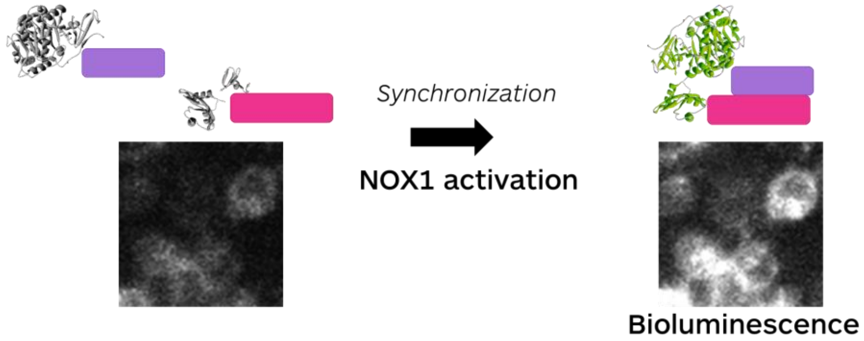
Keywords: Split-luciferase, Bioluminescence imaging, Circadian clock, NADPH oxidase

Cellular circadian clocks adjust their circadian phases to external cues through a process called synchronization. We have previously demonstrated that clocks synchronize to cellular stressors such as reactive oxygen species (ROS) and ultraviolet radiation (UV).[1,2] However, the role of physiological ROS signaling in this synchronization process remains elusive.

In this study, we investigated the role of NADPH oxidase (NOX), a primary source of intracellular ROS, in clock synchronization. NOX is an enzyme family that catalyzes the production of cellular $O_2^{\cdot-}$ and H_2O_2, believed to play a unique role in cellular ROS signaling.[3] We observed that the administration of low levels of H_2O_2 enhances clock oscillation. Moreover, we found that genetical knock-down of a NOX family member, NOX1, disrupted clock synchronization. We found that synchronization stimulation increased cellular H_2O_2 levels, while NOX1 suppression decreased them, suggesting that ROS produced by NOX1 mediates cellular synchronization.

To track NOX1 activity in real-time, we developed a split-luciferase complementation probe that detects temporal changes in NOX1 activity. We found that NOX1 activity increased upon synchronization stimulation concomitantly with cellular ROS level increase. Moreover, we discovered that NOX1 activity oscillates in a circadian manner, suggesting that the circadian clock system regulates NOX1 activity.

In conclusion, we propose a model where the circadian clock controls NOX1 activity, which generates ROS signals that, in turn, maintain the circadian clock synchronization.



References: 1) Kawamura, G. et al, *Commun. Biol.* **2018**, 1 (1), 204. 2) Tamaru, T. et al, *PLOS ONE* **2013**, 8 (12), 1–16. 3) Sies, H.; Jones, D. *Nat Rev Mol Cell Biol* **2020**, 21 (7), 363–383.

Quantitative analysis of Akt isoforms' temporal dynamics and downstream signaling with optogenetics and a mathematical model

([1]*School of Science, The University of Tokyo*) ○Yuka Sekine,[1] Genki Kawamura,[1] Takeaki Ozawa[1]

Keywords: Optogenetics, mathematical model, Akt isoform, temporal dynamics, cell morphology change

Ser/Thr kinase Akt plays pivotal roles in cellular signal transduction pathways. There are three isoforms of Akt; Akt1, Akt2, and Akt3, that shows several different functions. It is suggested that each Akt isoform has its specific temporal dynamics and selectively regulates its downstream signaling and subsequent cellular responses.

To individually examine each Akt isoform's phosphorylation dynamics, we utilized optogenetics approach. We applied a principle of photoactivatable Akt (PA-Akt)[1], which activates Akt by using CRY2/CIBN photo-dimerization, to all the Akt isoforms. We measured the CRY2-Akt isoforms' temporal phosphorylation patterns of light illuminated PA-Akt isoform expressing cells. As a result, we found that each CRY2-Akt isoform has its specific temporal properties. To numerically analyze the measured Akt isoforms' temporal dynamics, we employed mathematical models to estimate isoform-specific kinetic parameters. Moreover, we examined roles of each Akt isoform's dynamics on downstream signaling regulation and found that cell protrusion and retraction occur upon each Akt isoform's photo-activation. From these results, we aim to quantitatively clarify the Akt isoforms' temporal activation kinetics and how each isoform regulates cell morphology change.

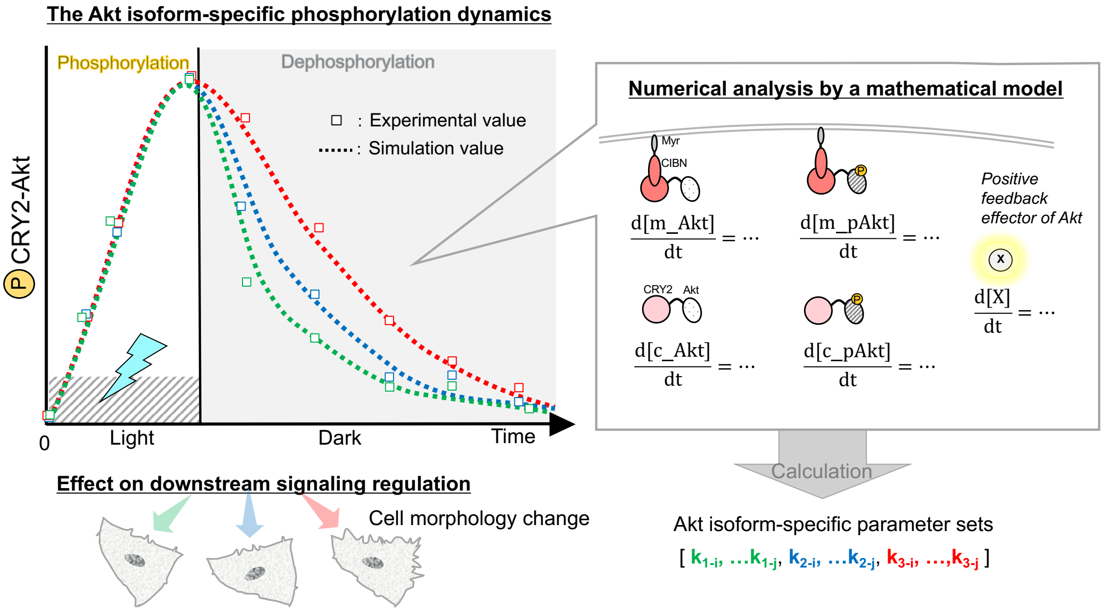


Figure 1 Quantitative analysis of the Akt isoform-specific signaling

1) Katsura Y et al. *Sci. Rep.* **2015**, 5, 14589.

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18日(月) 15:55 ~ 16:55 H936(9号館 [3階] 936)

[H936-1vn] 17. 生体機能関連化学・バイオテクノロジー

座長：大嶋 孝志、李 秀栄

英語

15:55 ~ 16:15

[H936-1vn-01]

原子間力顕微鏡によるpH応答性リボン状タンパク質の構造とダイナミクスの解析

○Xin Li[1]、Thuc Toan PHAM[1]、菊池 幸祐[1]、伊達 弘貴[1]、鱒村 颯太[1]、上野 隆史[1] (1. 東京工業大学生命理工学院)

日本語

16:15 ~ 16:35

[H936-1vn-02]

ペプチド阻害剤設計における動的構造の影響

○李 秀栄[1]、水口 賢司[1,2]、本多 優作[3]、高橋 大輔[3,4]、矢崎 亮[3]、大嶋 孝志[3] (1. 医薬基盤・健康・栄養研究所、2. 大阪大学蛋白質研究所、3. 九州大学大学院薬学研究院、4. 崇城大学薬学部)

日本語

16:35 ~ 16:55

[H936-1vn-03]

ヒト型抗体(T99wt)を抗体酵素に変換したときの立体構造変化の静的及び動的解析

○宇田 泰三[1,6]、加藤 龍一[2]、重田　育照[3]、廣田 俊[4,5]、一二三　恵美[6] (1. 九州先端研、2. 高エネルギー加速器研究機構、3. 筑波大学、4. 奈良先端科学技術大学院大学、5. CREST、6. 大分大学)

Structure and dynamics of pH-responsive ribbon-like protein analyzed by atomic force microscopy

([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Xin Li,[1] Thuc Toan Pham,[1] Kosuke Kikuchi,[1] Koki Date,[1] Souta Masumura,[1] Takafumi Ueno[1]

Keywords: Protein Assembly; Ribbon-like Protein; pH-responsiveness; Atomic Force Microscope; Force Curve

Proteins form hierarchical structures equipped with unique functions through self-assembly. Type 51 Refractile body (R-bodies) is a ribbon-like protein assembly and punctures cell membranes by its pH-responsive extension.[1,2] R-bodies possess 400-nanometers-wide coil-like morphologies at neutral pH and turn into 20-micrometers-long spiral-like morphologies at acidic pH (Figure 1a, b). This transformation is reversible and happens in less than one second. These features inspire us to use R-bodies as mechanochemical actuators, however, the structural and mechanical properties of R-bodies remain largely unclear.

In this study, we aimed to characterize R-bodies using an atomic force microscope (AFM) to quantify their structural and mechanical properties. We directly observed the spiral morphology in solution on mica and measured their size and stiffness. We also established the methodology to prepare fragmented R-body sheets (Figure 1c), which allowed us to investigate the precise thickness and curling of sheets by AFM. Furthermore, the synthesized R-body mutants, exhibited different properties compared to the wild-type, providing the underlying structural and mechanical insights of R-bodies.

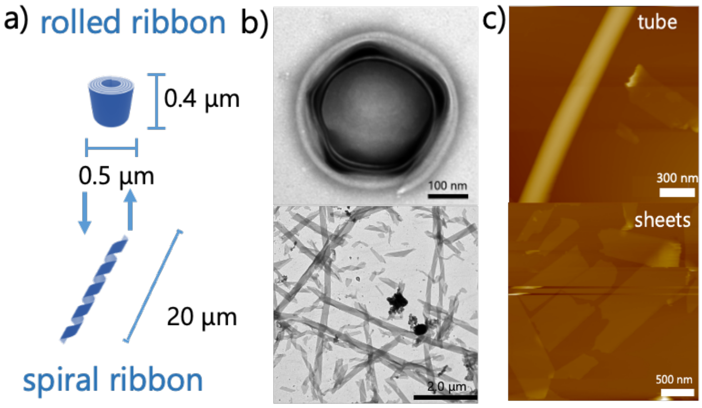


Figure 1. R-body coil and spiral morphologies. a) Schematic map, b) TEM and c) AFM.

1) Pond, F. R, *Microbiol. Rev.* **1989**, 53, 25–67.
2) Polka, J. K., *ACS Synth. Biol.* **2016**, 5, 303–311.

日本化学会 第104春季年会 (2024)

Impact of dynamical structure on peptide inhibitor design

([1] *Artificial Intelligence Center for Health and Biomedical Research, National Institutes of Biomedical Innovation, Health, and Nutrition*, [2] *Institute for Protein Research, Osaka University,* [3] *Graduate School of Pharmaceutical Sciences, Kyushu University,* [4] *Faculty of Pharmaceutical Sciences, Sojo University*) ○ Suyong Re,[1] Kenji Mizuguchi,[1,2] Yusaku Honda,[3] Daisuke Takahashi,[3,4] Ryo Yazaki, [3] Takashi Ohshima [3]

Keywords: *Protein-Protein Interaction, Peptide Inhibitor, Unnatural Amino Acids, Molecular Dynamics Simulation*

Protein-protein interactions (PPIs) are essential for many biological functions and are therefore important targets for drug design. Medium-sized peptides have the potential to inhibit specific PPIs, which is difficult with small molecules. A major problem is how to suppress and stabilize the inherent conformational flexibility of peptides. This problem can be solved by introducing unnatural amino acids into the peptide.[1] Not only do unnatural amino acids stabilize the conformation of the peptide, but they also have additional benefits, such as improving peptidase resistance. While this approach is promising, it remains elusive how and to what extent the peptide dynamics are controlled by the inserted unnatural amino acids.

Here, we analyzed the conformational properties of peptide inhibitors targeting SARS-CoV-2 spike protein using both public[2] and in-house data. To this end, features representing the dynamical conformation of the peptide were obtained from molecular dynamics simulations. Comparison with available experimental data showed that these features (distance between peptide ends, residue fluctuations, and side chain orientation) correlated with the activity of the designed peptides, indicating that nonnatural amino acids indeed help stabilize the conformation. It appears that better correlation with experimental data can be obtained by accounting for changes in conformational dynamics upon binding to the target. These results emphasize the importance of considering dynamic conformation when designing peptide inhibitors. Further details will be discussed in the presentation.

1) T. Tsuji, K. Hashiguchi, M. Yoshida, T. Ikeda, Y. Koga, Y. Honda, T. Tanaka, S. Re, K. Mizuguchi, D. Takahashi1, R. Yazaki, and T. Ohshima. *Nat. Synth.* **2022**, 1: 304-312.
2) P. Karoyan, V. Vieillard, L. Gómez-Morales, E. Odile, A. Guihot, C-E. Luyt, A. Denis, P. Grondin, and O. Lequin. *Commun. Biol.* **2021**, 4: 197.

日本化学会 第104春季年会 (2024)

ヒト型抗体(T99wt)を抗体酵素に変換したときの立体構造変化の静的及び動的解析

(九州先端研[1]・高エネ機構[2]・筑波大計算科学[3]・奈良先端大[4]・JST-CREST[5]・大分大全学研究機構[6]）○宇田泰三[1,6]・加藤龍一[2]・重田育照[3]・廣田　俊[4,5]　・一二三恵美[6]

Static and dynamic analysis of structural changes between T99wt antibody and the catalytic antibody T99-Pro95(-) converted from T99wt.

([1]*Nanotech. Lab., ISIT,* [2]*High Energy Accel. Res. Org.,* [3]*Center Com. Sci., Tsukuba Univ.,*[4]*Div. Mat. Sci., NAIST,* ,[5]*JST-CREST,*[6]*Inst. Res. Mgmt., Oita Univ.)* ○Taizo Uda,[1,6] Ryuichi Kato,[2] Yasuteru Shigeta,[3] Shun Hirota,[4,5] Emi Hifumi[6]

Pro95 in the CDR-3 of the antibody light chain is highly conserved. When the Pro is deleted, the antibody acquires antigen-degrading activity. The T99-Pro95(-) mutant, which deletes Pro95 in the human-type antibody light chain T99wt, was converted to a catalytic antibody that degraded Amyloid-beta. In this study, static (X-ray crystallography) and molecular dynamics simulations analyses (MD) of the structural changes associated with this conversion were carried out. From the analysis, it was clarified that the distances between Asp1(O)-His93(H) in the structure of T99-Pro95(-) were shortened, while it was not observed in T99wt.

Keywords: Catalytic antibody, Steric conformation, X-ray analysis, Molecular dynamics

【目的】抗体の軽鎖 CDR-3 に存在する Pro95 は高度に保存されている。この Pro95 を欠失させると抗体軽鎖は抗原分解機能を持つように変換される 1)。僅か一残基の変異がこうした性質を獲得することは、免疫学的、生化学的および構造学的観点から興味深い。本研究では、ヒト型抗体軽鎖 T99 野生型(T99wt)と、これを Pro95(-)変異型（抗体酵素）に変換したときの X-線結晶構造解析（静的解析）と分子動力学シミュレーション解析(MD)を行い、両者の解析から抗体酵素の構造と機能の関連性を検討した。

【実験手法】サンプルの結晶化は 0.1 M Sodium cacodylate, 36% PEG2000MME、Beam line は BL-5A/PF KEK や BL32XU/SPring-8 で実行した。MD 計算には Amber22 を用い NPT アンサンブルのもと 300ns 実行し、解析には最後の 50ns のデータを使用した。

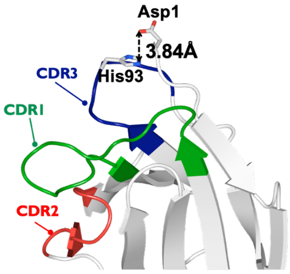


**Fig.1 Structure of T99-P95(-)
(X-ray crystallography)**

【結果と考察】ヒト型抗体軽鎖 T99wt および抗体酵素に変換された T99-Pro95(-)の結晶構造は、それぞれ、2.6 および 2.0 Å の解像度で解析できた。その結果、触媒三つ組残基 (Asp1, Ser27a, His93)の中で Asp1(O)-His93(H)間の距離が Pro95 を欠失させると 5.72 Å短縮され、Asp の CO^-と His の $N\text{-}H^+$とが強い相互作用を持つようなり、活性サイトが形成すると考えられた (Fig. 1)。一方、MD を用いて T99wt および T99- Pro95(-)の動的解析を行った結果では、His93 残基と Asp1 残基の立体構造は大きく揺らぎ、Pro95(-)の場合のみ上述した触媒三ツ組残基がかなり近接する時間帯の存在する事が分かった。この最近接構造（動的）と X-線結晶構造（静的）解析の結果とが類似していた。また、MD で観られた大きな揺らぎは、抗原を Induced fit し、抗体酵素との親和性を高めると推測されるばかりでなく、抗体酵素の特徴である multi-cleaving sites 説を裏付ける事にも繋がると考えられた。1) Hifumi et al., *Science Adv.,* **6**(13), eaay6441(2020).

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18日(月) 13:00 ~ 14:40 D341(3号館 [4階] 341)

[D341-1pm] 18. 高分子

座長：稲木 信介、相見 順子

日本語

13:00 ~ 13:20

[D341-1pm-01]

共有結合性有機構造体の電極表面への間接電解合成とその応用

○佐藤 宏亮[1]、白倉 智基[1]、稲木 信介[1] (1. 東京工業大学)

日本語

13:20 ~ 13:40

[D341-1pm-02]

電荷蓄積高分子を用いて溶液プロセスで作製する有機トランジスタメモリ

○相見 順子[1] (1. 物質・材料研究機構)

英語

13:40 ~ 14:00

[D341-1pm-03]

Tailoring Electrochromic Properties through Ru-Carbon Covalent Bonds: Design and Synthesis of Metallosupramolecular Polymers

○BANCHHANIDHI PRUSTI[1], Takasi Sato[1], Ritsuko Nagahata[2], Masayoshi Higuchi[1] (1. National Institute for Materials Science, 2. National Institute of Advanced Industrial Science and Technology)

英語

14:00 ~ 14:20

[D341-1pm-04]

Image Data Analysis of Electrochromic Display Devices for Improvement of the Durability

○Shifa Sarkar[1,2], Masayoshi Higuchi[1,2] (1. National Institute for Materials Science, 2. Osaka University)

英語

14:20 ~ 14:40

[D341-1pm-05]

大気安定性の高いn型化学ドーピングによる高分子半導体ダイオードの電子注入特性向上

○山下 侑[1,2]、刑部 永祥[2]、田嶋 陽子[2]、Stephen Barlow[3]、Seth Marder[3]、渡邉 峻一郎[2]、竹谷 純一[1,2] (1. 物材機構、2. 東大、3. コロラド大ボルダー校)

共有結合性有機構造体の電極表面への間接電解合成とその応用

（東工大物質理工 [1]）　○佐藤宏亮 [1]・白倉智基 [1]・稲木信介 [1]
Indirect Electrochemical Synthesis of Covalent Organic Frameworks on Electrode Surface and Its Application ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*)
○Kosuke Sato[1], Tomoki Shirokura[1], Shinsuke Inagi[1]

Covalent organic framework (COF) is known as a functional polymer material with stability and porosity. In our previous work, we have reported an indirect electrolytic method to form imine-base COFs by using electrochemically generated acid (EGA). However, the practical application of the resultant COF film was unexplored. In this study, we attempted to control the morphology of the COF thin films by controlling the amount of EGA. Under the coexistence of monomers, the COF film was synthesized by electrochemical oxidation of diphenylhydrazine, a precursor of EGA, in the DMF electrolyte (Fig. 1a). The thickness of the film was controllable within a range of 1 to 10 μm, depending on the conditions. Furthermore, under low EGA source concentration conditions, we effectively controlled the coating thickness of the COFs on carbon nanotubes, achieving a range between 6 and 32 nm. (Fig. 1b). We applied the EGA-assisted synthesis method to various carbon materials and evaluated them as electrocatalysts related to water spiriting reaction. *Keywords : Covalent Organic Frameworks; Electrochemical Synthesis; Composite Materials; Thin Film; Electrocatalyst*

共有結合性有機構造体(COF)は、分子構造に基づく機能と安定性・多孔性とを両立した材料であり、合成法に依存して形態や特性が左右される。COF の合成法として、当研究室では電解発生酸(EGA)でイミン結合を形成させる間接電解法を報告している [1]。しかし、本手法は COF 粒子凝集体を得るに留まっており、COF の機能を活かした応用は達成されていない。本研究では、EGA 発生量すなわち COF 生成の駆動力を電解条件によりコントロールすることで、COF の形態制御とその応用を検討した。

モノマーの共存下、EGA 源であるジフェニルヒドラジンを DMF 中で電解酸化することで COF の合成を行った(Fig. 1a)。EGA 源濃度 20 mM のとき、膜厚は電解条件に依存し 1–10 μm の範囲で変化した。EGA 源濃度 2 mM の条件下、電解時間を 10–90 sec の間で変化させると、多層カーボンナノチューブ上に形成される COF 層の厚さを 6–32 nm の範囲で制御可能であった(Fig. 1b)。種々のカーボンに本手法を適用し得られた複合体を、電極触媒として評価しその形状と電極触媒活性について考察した。

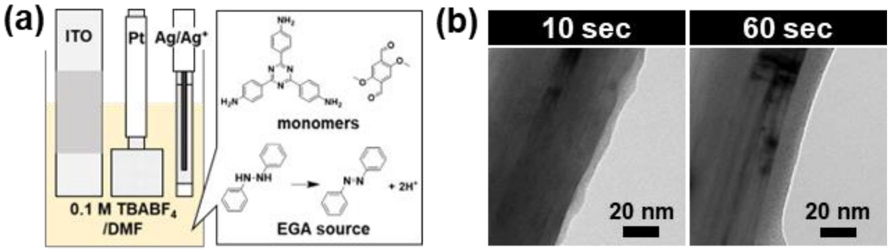


Fig. 1 (a) Electrochemical cell setup in this work (b)TEM images of the COF/carbon nanotube

1) S. Inagi, *et al. Angew. Chem. Int. Ed.*, **2023**, *62*, e202307343.

電荷蓄積高分子を用いて溶液プロセスで作成する有機トランジスタメモリ

（物質・材料研究機構 [1]）○相見順子 [1]

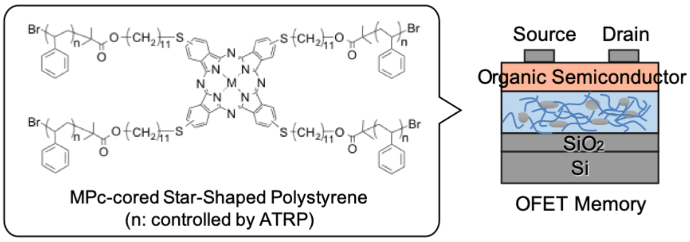
Solution-processable OFET memory devices based on star-shaped polymers with a phthalocyanine core

([1]*National Institute for Materials Science* (NIMS)) ○Junko Aimi[1]

Non-volatile organic filed-effect transistor (OFET) memory is an emerging and promising technology for possible use in wearable data storage. We have developed charge-trapping materials for the organic memory based on a metallophthalocyanine (MPc)-cored star-shaped polystyrene (MSP). The MPc cores form self-assembled nano-sized aggregates dispersed in and isolated by the surrounding polystyrene arms, permitting them to store or release hole charges in a manner similar to a nano-floating gate. In this study, we prepared OFET memory devices by a one-pot solution process via polymer-matrix assisted phase separation of MSP and a soluble organic semiconductor.

Keywords : OFET Memory Device; Star polymer; Phthalocyanine, Phase Separation

多様化する市場ニーズに伴い、有機材料を用いる有機不揮発性メモリが近年注目されている。我々は、金属フタロシアニンをコアに持つスターポリマー（MSP）を有機トランジスタメモリの記録層（ナノフローティングゲート）材料に用いて、高性能有機フラッシュメモリを開発した。このスターポリマーは、電荷蓄積部位である金属フタロシアニンコアが絶縁体のポリスチレンに囲まれた構造を持ち、有機トランジスタ素子中で有機半導体との電荷の授受により安定な電荷蓄積材料として機能する [1)]。ポリスチレン鎖を精密重合することで、ナノフローティングゲート構造を調節することができ、最終的なデバイス性能を向上させることができる [2)]。また、可溶性有機半導体とスターポリマーの相分離を利用することで、基板上に有機半導体・メモリ層を一度に成膜することが可能である [3)]。本研究では、成膜条件の検討により、有機半導体の真空蒸着プロセスを必要とせずに OFET メモリを作製するプロセス技術を開発した。



MPc-cored Star-Shaped Polystyrene
(n: controlled by ATRP)

1) J. Aimi, C. T. Lo, H. C. Wu, C. F. Huang, T. Nakanishi, M. Takeuchi, W. C. Chen, *Adv. Electron. Mater.*, **2016**, *2*, 1500300. 2) J. Aimi, P. H. Wang, C. C. Shih, C. F. Huang, T. Nakanishi, M. Takeuchi, H. Y. Hsueh, W. C. Chen, *J. Mater. Chem. C.* **2018**, 6, 2724. 3) J. Aimi, T. Yasuda, C. F. Huang, M. Yoshio, W. C. Chen, *Mater. Adv.*, **2022**, 3, 3128.

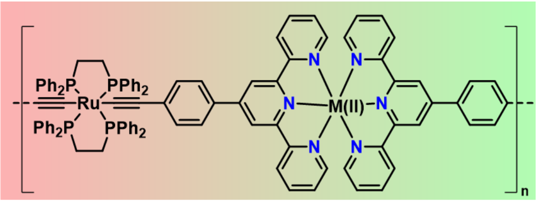
Tailoring Electrochromic Properties through Ru-Carbon Covalent Bonds: Design and Synthesis of Metallosupramolecular Polymers

([1]*National Institute for Materials Science*, [2]*National Institute of Advanced Industrial Science and Technology*) ○ Banchhanidhi Prusti,[1] Takasi Sato,[1] Ritsuko Nagahata,[2] Masayoshi Higuchi[1]

Keywords: Metallosupramolecular Polymer; Electrochromism; Near-Infrared Absorption; Device Fabrication; Ru-Based Polymer

Electrochromism refers to the phenomenon of color alteration when an electrical voltage is applied. Its application is extensive, finding relevance in practical, real-world scenarios.[1-3] The incorporation of metal species into the organic framework introduces color to these systems. Consequently, the control of the metal-to-ligand charge transfer phenomenon can be achieved through the application of an external potential. Metallosupramolecular polymers (MSPs), belonging to the category of amorphous materials, exhibit rapid color changes, robust durability, and facile fabrication. Therefore, there is a need to explore these materials for various applications. Recently, there has been a notable focus on investigating near-infrared (NIR) electrochromism, particularly due to its promising applications in the development of smart windows designed for heat-shading.

Our research group has been dedicated to the development of metallosupramolecular polymers (MSPs). This report outlines the synthesis of a series of organometallic-bonded MSPs, namely **PolyRuRu**, **PolyRuFe**, and **PolyRuZn**. Characterization was carried out using ^{1}H NMR, revealing an average molecular weight on the order of 10^4. Among these polymers, **PolyRuZn** demonstrated NIR absorption (1100 nm) under the influence of voltage, attributed to intervalence charge transfer, whereas **PolyRuFe** and **PolyRuRu** did not exhibit NIR switching. Notably, **PolyRuZn** exhibited outstanding features, including a high contrast ratio ($\Delta T > 60\%$), impressive color efficiency ($\eta = 333$ cm^2/C), and a rapid response rate (within 3 seconds) in the NIR spectrum. Consequently, a device incorporating PolyRuZn was crafted for UV-vis and NIR absorption studies.



❑ Organometallic-Bonded MSPs ❑ UV-Vis to NIR Switching

1) Y. Wang, R. Shen, S. Wang, Y. -M. Zhang, S. X. -A. Zhang, *Adv. Mater.* **2021**, *34*, 2104413. 2) X. Liu, J. Wu, Z. Tang, J. Wu, Z.. Huang, X. Yin, J. Du, X. Lin, W. Lin, G. Yi, *ACS Appl. Mater. Interfaces.* **2022**, *14*, 33829. 3) a) G. Cai, J. Wang, P. S. Lee, *Acc. Chem. Res.* **2016**, *49*, 1469.

Image Data Analysis of Electrochromic Display Devices for Improvement of the Durability

([1]*Graduate School of Information Science and Technology*, *Osaka University*, [2]*National Institute for Materials Science*) ○Shifa Sarkar,[1,2] Masayoshi Higuchi[1,2]

Keywords: Electrochromic Devices; Metallo-Supramolecular Polymer; Degradation Analysis; Image Data; Durability

Electrochromic devices (ECDs) are cutting-edge technologies for their applications ranging from smart windows to electronic paper that change optical properties in response to an applied voltage. Among the various electrochromic (EC) materials, metallo-supramolecular polymers (MSPs), specifically Fe(II)-based MSP (polyFe), have received much attention for their unique properties. However, the long-term performance and stability of these devices are critical factors for practical applications. These devices might degrade over time, which would decrease their effectiveness and functionality. It becomes essential to conduct a detailed analysis of the degradation patterns in electrochromic devices to address this problem. This work employs the Python OpenCV library to perform advanced grayscale image processing techniques for the degradation analysis of polyFe-based ECDs.

Here, a solid-state polyFe-based ECD was fabricated by a spray coating method. Then chronoamperometric technique was used to understand the EC properties of the device for each cycle by taking movies and images. The device changed its color from purple to colorless at a low voltage of 1.0V. For the 1st cycle, the images showed a colorless state of the device but in the case 1000th cycle, the device was not able to show a completely bleached state. Besides during the cyclic test, for image data analysis, movies were taken to record the degradation performance phenomenon of the device. Python OpenCV was used to extract images from movies which were then cropped and converted into grayscale images from where pixel values were extracted. By using the pixel values time vs. contrast graphs were plotted for 1st to every 100th cycle till the 1000th cycle. The time vs. contrast graph for the 1st cycle exhibited a sharp change of purple color to a colorless state in the device; on the other hand, the graph for the 1000th cycle didn't show a sharp color change which indicates, the performance of the device becomes slower as the cycle number increases.

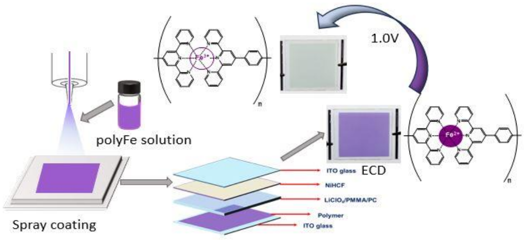


Fig.1: Fabrication and EC properties of a polyFe-based ECD

1) Monk, P. M. S.; ECM and Devices; John Wiley & Sons, **2015**. 2) Gustavsen, A; Sol. Energy Mater. Sol. Cells, **2010**, *94*, 105.

Highly air-stable n-type chemical doping improving electron injection properties in polymeric semiconductor diodes

([1]NIMS, [2]The Univ. of Tokyo, [3]CU-Boulder) ○Yu Yamashita[1,2], Nobutaka Osakabe[2], Akiko Tajima[2], Stephen Barlow[3], Seth R. Marder[3], Shun Watanabe[2], Jun Takeya[1,2]

Keywords: organic semiconductor, chemical doping, diode

Chemical doping using redox reactions has been used to control the electronic properties of organic semiconductors[1]. Redox reactions between effective n-type dopants and organic semiconductors introduce electrons and cationic dopants into the semiconductors. However, owing to the reactivity and diffusivity of dopant molecules, a doping process that is stable and selective to certain parts of devices has been challenging. Recently, we reported novel doping processes that achieve moderately ambient-stable n-type doping[2,3]. The dimer of metal complexes $(RuCp^*Mes)_2$ shown in Fig. a is a strong reducing agent that forms a cationic monomer through dimer cleavage and redox reactions. The use of this dopant dramatically improves the stability of n-type doping compared with the conventionally employed cobaltocene, where the former can maintain a stable 18-electron cationic state[2].

We have developed a method to selectively introduce this stable dopant material at the electrode/semiconductor interface in diodes, which improve injection characteristics and enable GHz operation of the fabricated diodes. In this method (Fig. a), the Au electrode was treated with $(RuCp^*Mes)_2$ to introduce electrons and dopant cations on the electrode surface, which dramatically shifts the work function to 3.7 eV (Fig. b). Following this process, a polymer semiconductor thin film and a top electrode were fabricated. The selective introduction of dopant cations at the electrode/semiconductor interface without diffusion was evident from electrical conduction measurements of the diode and X-ray photoelectron spectroscopy. The mechanisms for the adsorption of dopant molecules through redox reactions and the suppression of their diffusion will be discussed in this talk.

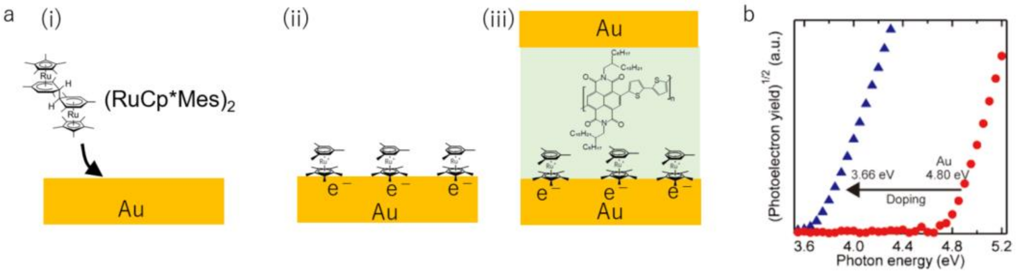


Figure a. The processes and materials to fabricate diodes. (b) Photoelectron yield spectroscopy of Au electrode before (red) and after (blue) the treatment with $(RuCp^*Mes)_2$.

(1) Y. Yamashita, J. Takeya, S. Watanabe et al., Nature 572, 634 (2019). (2) Y. Yamashita, S. R. Marder, J. Takeya et al., J. Mater. Chem. C, 9 4105 (2021). (3) Y. Yamashita, S. R. Marder, S. Watanabe *et al.*, preprint DOI: 10.21203/rs.3.rs-3484432/v1.

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18日(月) 15:55 ~ 16:55 D342(3号館 [4階] 342)

[D342-1vn] 18. 高分子

座長：細野 暢彦、飯田 拡基

日本語

15:55 ~ 16:15

[D342-1vn-01]

多孔性金属錯体を用いたポリアルキルチオフェンの頭尾結合の識別と分離

○高島 優[1]、澤山 拓[2]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工、2. 東大院新領域)

英語

16:15 ~ 16:35

[D342-1vn-02]

ダブルネットワーク化と無機染色によるハイドロゲル中の荷電ポリマーネットワークの実空間可視化

○野口 真司[1]、木山 竜二[1]、吉田 匡宏[1]、樫村 尚宏[1]、忠永 清治[1]、龔 剣萍[1]、野々山 貴行[1] (1. 北海道大学)

日本語

16:35 ~ 16:55

[D342-1vn-03]

超分子架橋による有機-無機高分子の複合化

山下 尚樹[1]、○山岡 賢司[1]、以倉 崚平[1]、高島 義徳[1] (1. 大阪大学)

多孔性金属錯体を用いたポリアルキルチオフェンの頭尾結合の識別と分離

（東大院工 [1]・東大院新領域 [2]）○高島 優 [1]・澤山 拓 [2]・細野暢彦 [1]・植村卓史 [1]

Recognition and Separation of Head-to-Tail Polyalkylthiophenes by Metal–Organic Frameworks

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Frontier Sciences, The University of Tokyo*) ○Yu Takashima,[1] Taku Sawayama,[2] Nobuhiko Hosono,[1] Takashi Uemura[1]

Poly(3-hexylthiophene) (P3HT) is a widely studied semiconductive polymer in the field of organic electronics. The electron conductivity of P3HT is known to be significantly influenced by the regioregularity (RR) of the main chain, making regioselective polymerization techniques crucial for achieving high-performance P3HT. However, conventional polymerization approaches face challenges related to catalyst design and technical complexity.[1,2] In this study, we developed a structure recognition and separation technique using nano-sized pores of metal-organic frameworks (MOFs) to give a new approach to obtain regioregular P3HT. We discovered that certain MOFs recognized regio-isomers of P3HT oligomers (dimer and tetramer) upon adsorption into the nanopores. Based on this finding, we successfully developed a column chromatography method using the MOFs as the stationary phase. This approach allows for RR-based separation of P3HT, enabling the extraction of highly regioregular P3HT from crude materials with lower RR.

Poly(3-hexylthiophene) (P3HT)は、有機エレクトロニクス分野において広く研究が行われている代表的な有機半導体高分子である。P3HT の導電性を向上させるためには高い頭尾結合割合（Regioregularity, RR）の実現が不可欠であるが、従来の合成方法では触媒設計や技術的煩雑さといった課題が残されていた[1,2]。そこで本研究では、高いRRのP3HTを得る全く新しいアプローチとして、多孔性金属錯体（MOF）が持つナノサイズの細孔を利用した精密な構造認識技術を開発した（Figure 1）。

数種のMOFを用いたオリゴチオフェン（二量体および四量体）の分離実験により、適切な細孔径の選択により結合位置異性を識別可能であることを発見した。また、MOFの細孔内にP3HTを直接導入する実験を試みたところ、RRが高いP3HTが選択的に吸着されることを見出した。さらに、同MOFを充填剤とした分取用カラムを作成し液体クロマトグラフィーを用いて分離することで、P3HTの粗重合生成物からRRが高いP3HTを選択的に抽出することに成功した。

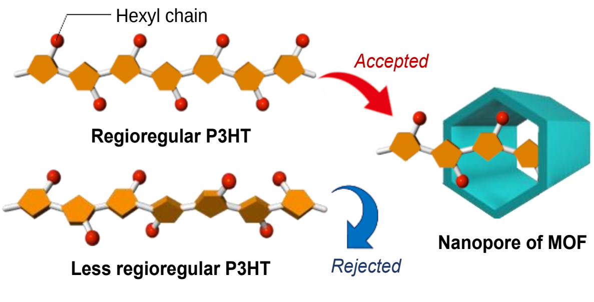


Figure 1. Schematic diagram of the regioselective adsorption of P3HT in the nanopores MOFs.

1) Y. Kim, et al., *Nat. Mater.* **2006**, *5*, 197-203.
2) P. Kohn, et al., *J. Am. Chem. Soc.* **2012**, 134, 4790-4805.

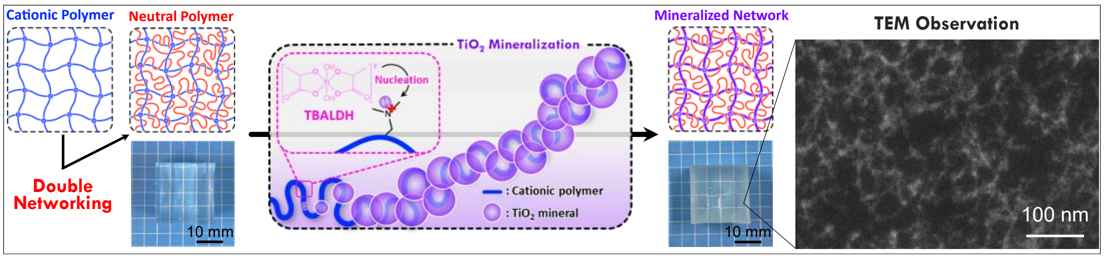
Real-Space Visualization of Charged Polymer Network of Hydrogel by Double Network Strategy and Mineral Staining

([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Graduate School of Life Science, Hokkaido University*, [3]*Faculty of Advanced Life Science, Hokkaido University*, [4]*Faculty of Engineering, Hokkaido University,* [5]*ICReDD, Hokkaido University*)
○ Shinji Noguchi,[1] Maradhana Agung Marsudi,[2] Ryuji Kiyama,[3] Naohiro Kashimura,[2] Masahiro Yoshida,[2] Kiyoharu Tadanaga,[4] Jian Ping Gong,[3,5] Takayuki Nonoyama[3]

Keywords: Mineral staining; Transmission Electron Microscopy; Hydrogels; Nanostructure

Hydrogels consist of three-dimensional polymer networks and water, and the network structure affects their physical properties. Synthetic hydrogels inevitably possess a hierarchical inhomogeneous network structure, and specific properties, such as fracture and subsequent crack propagation, strongly depend on the "local" structure. Thus, the local structure is essential for predicting such a phenomenon, and ideal techniques for analysis are required. Among the methods for structural analyses of hydrogels, the real-space imaging of a polymer network of hydrogel on a nanometer scale is one of the optimal ones; however, it is highly challenging. A well-known technique to enhance the electron density is electron staining with heavy element compounds such as uranyl acetate1) and phosphotungstic acid.2) However, synthetic polymer strands are thin, flexible, and susceptible to aggregation during staining or resinification. Then, the structural information at the mesh size scale is lost during sample preparation.

In this study, we propose a direct observation technique for cationic polymer networks using transmission electron microscopy (TEM). By combining the double network strategy and a TiO_2 mineral staining technique, we overcame the polymer aggregation and the low electron density of the polymer. An objective cationic network was incorporated into a neutral skeleton network to suppress shrinkage during subsequent staining. Titania mineralization using titanium bis (ammonium lactate) dihydroxide along the cationic polymer strands provided sufficient electron density for the objective polymer network for TEM observation.3) This observation technique enables the visualization of local structures in real space and is complementary to scattering methods for soft matter structure analysis.



Scheme 1. Strategy of the present study.

1) J. G. Stempak, R. T. Ward, *The Journal of Cell Biology* **1964**, *22*, 697–701. 2) W. F. Sheridan, R. J. Barnett, *J Ultrastruct Res* **1969**, *27*, 216–229. 3) S. Noguchi, M.A. Marsudi, R. Kiyama, N. Kashimura, M. Yoshida, K. Tadanaga, J. Gong, T. Nonoyama, *submitted*.

超分子架橋による有機-無機高分子の複合化

（阪大院理）山下尚樹・○山岡賢司・以倉崚平・高島義徳

Organic-Inorganic Polymer Composites by Supramolecular Cross-linking Design (*Graduate School of Science, Osaka University*) Naoki Yamashita, ○Kenji Yamaoka, Ryohei Ikura, Yoshinori Takashima

Organic–inorganic materials have been widely utilized in various fields as multifunctional materials. Poly(dimethyl siloxane) (PDMS), a typical inorganic polymer, is blended with organic polymers for multifunctionality, but is immiscible with most polymers. We incorporated organic‐inorganic hybrid elastomers (PDMS-γCD-AAl⊃P(EA-HEMA) (*x*)) with movable and reversible crosslinks (**Fig. 1a**). Poly ethyl acrylate-r-hydroxy ethyl methacrylate (P(EA-HEMA)) penetrated the cavity of triacetylated γ-cyclodextrin (γCD), which was introduced into the side chains of PDMS-γCD-AAl. Allyl alcohol groups (AAl) of PDMS-γCD-AAl and HEMA in P(EA-HEMA) form hydrogen bonds between the polymers as reversible cross-links. *x* is molar ratio of HEMA in P(EA-HEMA). Introducing movable cross-links improved the compatibility of organic and inorganic polymers. The synergy of movable and reversible cross-links improved the toughness values (**Fig. 1b**). The design of PDMS-γCD-AAl⊃P(EA-HEMA) (*x*) incorporated cooperatively movable and reversible crosslinks to achieve high compatibility and mechanical properties[1].

Keywords : Movable cross-link, Hydrogen bond, Polymer blend, Mechanical properties, Structural analysis

有機高分子と無機高分子の複合化は、それぞれの特長を併せ持つ機能性材料を作製できるが、代表的な無機高分子であるポリジメチルシロキサン(PDMS)は、有機高分子と非相溶であるため、相分離し材料機能が失われる。本研究ではシクロデキストリン(CD)の空孔に高分子主鎖が貫通した可動性架橋と水素結合由来の可逆性架橋を PDMS とアクリレート系高分子(P(EA-HEMA) (*x*))間に導入し、混和性と靭性の向上に成功した [1]。

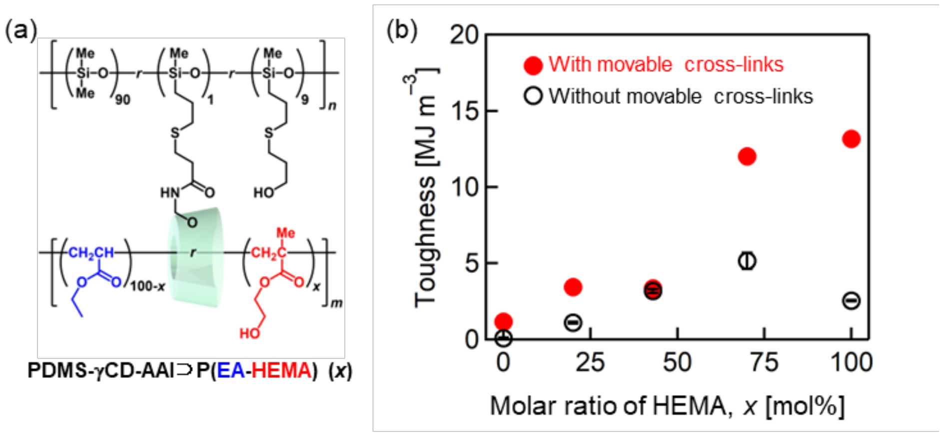


Figure 1. (a) Chemical structure and **(b)** toughness of PDMS-γCD-AAl⊃P(EA-HEMA) (*x*).

Ref. 1) N. Yamashita, K. Yamaoka, R. Ikura, Y. Takashima, et al., *Soft Matter* **2023**, *19*, 9074-9081.

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18日(月) 9:00 ~ 11:30 C443(4号館 [4階] 443)

[C443-1am] 20. 材料化学—基礎と応用

座長：加藤 雄一、小林 浩和

英語

9:00 ~ 9:20

[C443-1am-01]

In situ structure characterization of graphene-valve mediated carbons

○Wang Shuwen[1]、Fernando Vallejos-Burgos[2]、Furuse Ayumi [1]、Marco-Lozar Juan P. [3]、Otsuka Hayato[1]、Nagae Miu[1]、Kawamata Yuma[1]、Kanoh Hirofumi[4]、Urita Koki[5]、Notohara Hiroo[5]、Moriguchi Isamu[5]、Tanaka Hideki[1]、Silvestre-Albero Joaquín[6]、Hayashi Takuya[7]、Kaneko Katsumi[1] (1. 信州大学先鋭材料研究所、2. Morgan Advanced Materials, State College, USA. 、3. G2MTech, Alicante, Spain.、4. 千葉大学理学部、5. 長崎大学工学部、6. Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, Spain.、7. 信州大学水環境・土木工学科)

日本語

9:20 ~ 9:40

[C443-1am-02]

カーボンナノチューブ用分散剤フラビンの10-N位-直鎖アルキル側鎖長が昇華性に与える影響

○加藤 雄一[1]、杉野 卓司[1]、物部 浩達[1] (1. 国立研究開発法人産業技術総合研究所)

英語

9:40 ~ 10:00

[C443-1am-03]

層状複水酸化物を触媒前駆体として用いたカーボンナノチューブの合成に関する研究

○千田 知香[1]、横山 渓[2]、熊谷 陸駆[2]、會澤 純雄[1]、桑 静[1]、平原 英俊[1]、木村 寛恵[2]、二葉 ドン[3] (1. 岩手大学、2. 一関高専、3. 産総研)

日本語

10:00 ~ 10:20

[C443-1am-04]

高速充放電可能な電気二重層キャパシタのカーボンナノチューブ電極作製に向けたシンプルな”ブレンド”アプローチ

○清水 太陽[1]、小橋 和文[1]、中島 秀朗[1]、室賀 駿[1]、山田 健郎[1]、岡崎 俊也[1]、小久保 研[1]、畠 賢治[1] (1. 国立研究開発法人産業技術総合研究所)

10:20 ~ 10:30

休憩

英語

10:30 ~ 10:50

[C443-1am-05]

テンプレート反応による無機ナノチューブの単層合成と構造多様性

○中西 勇介[1]、古澤 慎平[1]、佐藤 雄太[2]、加藤 俊顕[3]、宮田 耕充[1] (1. 都立大、2. 産総研、3. 東北大)

英語

10:50 ~ 11:10

[C443-1am-06]

超音波処理による無機炭素源からカーボンナノオニオンの室温合成

〇ヨウ ロンウェン[1]、長谷部 靖[2]、内田 正哉[3] (1. 埼玉工業大学 工学研究科　情報システム専攻、2. 埼玉工業大学　生命環境化学科、3. 埼玉工業大学　先端科学研究所)

🏷 日本語

11:10 ~ 11:30

[C443-1am-07]

バイポーラ電気化学反応による黒鉛からの化学修飾グラフェン合成

金野 裕太[1]、下豊留 慧[1]、〇沖本 治哉[1] (1. 山形大学)

In situ structure characterization of graphene-valve mediated carbons

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Keywords: in situ characterization; molecular dynamics; methane storage

In the current study, we developed a methane storage method at ambient conditions by using a graphene-valve-mediated porous carbon. The graphene valve at the pore entrance installed by a CVD method is stable enough to keep a large amount of methane under ambient conditions and can be opened by using low-temperature waste heat at 473 K for encapsulation and release of methane. To understand this pore opening/closing mechanism with temperature variation, a series of in situ structural characterizations were performed, including in situ transmission electron microscope (TEM), Raman spectroscopy, X-ray Diffraction (XRD) and molecular dynamic (MD) simulations.

The direct observation of the pore opening/closing was achieved by in situ TEM. The gaps with distinct edges could be opened on the graphene assembly at 473 K and closed by lowering the temperature to 298 K. The D and G bands of the Raman spectra for the graphene valve showed a marked downshift with increasing temperature, being indicative of significant phonon anharmonicity induced by the enhanced motion of carbon atoms.[1] The d_{002}-spacing of the graphene valve increased with the temperature more than twice that observed in graphite[2] according to in situ synchrotron XRD. The more marked increase of d_{002}-spacing in the graphene valve than graphite indicates partial exfoliation of the stacked graphene layers. The MD simulations were performed with a weak graphene valve with single-atomic array interaction, and a strong graphene valve with multi-atomic array interaction. Heating at 448 K opened the weak graphene valve, while the opening temperature for the strong graphene valve was 673 K.

The ambient methane storage method has several advantages. For example, the containers for ambient pressure methane storage do not require a cylindrical thick-walled storage vessel and can be designed into a flexible shape to achieve maximum space utilization. Moreover, methane storage at ambient conditions minimizes the safety hazards caused by high pressure. The approach introduced in this article offers new paths for a safe, efficient, cost-effective methane storage method and paves a new way to design energy and environmental processes requiring controllable accessibility.

1) H.-N., Liu, *Carbon* **2019** *152*, 451. 2) K. Akikubo, *Carbon* **2020** 169, 307.

カーボンナノチューブ用分散剤フラビンの 10-N 位-直鎖アルキル側鎖長が昇華性に与える影響

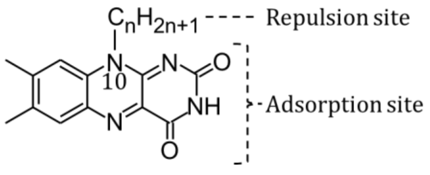
（産総研 [1]）○加藤 雄一 [1]、杉野 卓司 [1]、物部 浩達 [1]

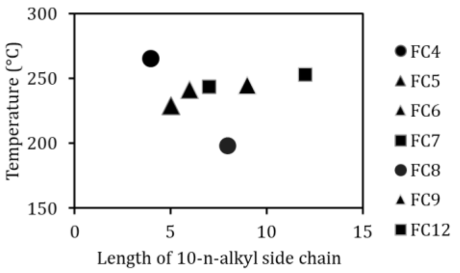
Effect of the Length of 10-*n*-Alkyl Side Chains of Flavin on Sublimation ([1]*Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology*) ○ Yuichi Kato[1], Takushi Sugino[1], Hirosato Monobe[1]

Dispersion of single-walled carbon nanotubes (SWNTs) in liquids with surfactants is an important strategy for the effective utilization of the unique electronic properties of SWNTs. However, strongly adsorbed surfactants are difficult to remove, and residual surfactants interfere with the desired functions of SWNTs. The aim of this study is to find the best sublimable surfactant among 10-n-alkyl-substituted flavins (n=4–9,12) in order to disperse SWNTs and separate semiconductive SWNTs. Thermogravimetric analyses under vacuum indicated that the 10-octyl-alkyl side chain of flavin (FC8) sublimated at a lower temperature than the other flavins, with a saturation vapor pressure of 0.1 Pa at 200 °C. This allowed FC8 to sublimate without the competing thermal reaction.[1]

Keywords： *Sublimation; Surfactant; Flavin; Thermogravimetry; Carbon nanotube*

単層カーボンナノチューブ（SWNT）には金属性と半導体性を示すものがあり、分散剤を用いて液中に分散させることは、その電気特性の異なる SWNT を分離するために必要である。しかしながら強く吸着した分散剤の残留が課題であり、除去する必要がある。直鎖ドデシルを 10-N 位に有するフラビン誘導体は半導体性カーボンナノチューブを選択的に分散させることができ、また昇華性も有する。しかし昇華温度（飽和蒸気圧が 0.1 Pa に達する温度）は 250℃と高く、熱変性と競合する問題があった（FC12）。そこで、側鎖のアルキル鎖長と昇華性および単層カーボンナノチューブ分散性について調べた。オクチル基を側鎖に有するフラビン（FC8）は昇華温度が 200℃と低く、また半導体性カーボンナノチューブを選択的に分散させることが分かった。





1) The temperature at which the saturation vapor pressure of 10-*n*-alkyl-substituted flavins becomes 0.1 Pa has been reported. Y. Kato, T. Sugino, *Bull. Chem. Soc. Jpn,* **2023**, Advanced publication.

Study on the synthesis of carbon nanotubes using layered double hydroxides as catalyst precursors

([1]*Iwate Univ.*, [2]*NIT, Ichinoseki College*, [3]*AIST*) ○Chika Chida[1], Kei Yokoyama[2], Riku Kumagai[2], Sumio Aisawa[1], Jing Sang[1], Hidetoshi Hirahara[1], Hiroe Kimura[2], Don Futaba[3]

Keywords: layered double hydroxide, carbon nanotube, catalyst, chemical vapor deposition

Layered double hydroxides (LDH) are a type of inorganic nanomaterial with a layered structure in which the basal layer contains trivalent metal ions homogeneously distributed for divalent metal hydroxides, and the interlayer spacing is occupied by anions and water molecules. Carbon nanotubes (CNT) are a unique nanocarbon material characterized by a tubular structure of a single or multiple graphene sheets, which exhibit excellent electrical and thermal conductivities. One method of synthesizing CNTs, the water-assisted chemical vapor deposition (CVD) method, uses a small amount of water supply to the feed gas as a catalyst activator to produce high-quality CNTs for large volume production. Typically, the catalyst substrate consists of Si wafers with catalysts, commonly consisting of Fe, Co, and Ni supported on metal oxides, such as Al_2O_3 and MgO. LDH, which is composed of two or more types of metal ions, can be used as this catalyst precursor. Therefore, in this study, we synthesized LDH with different combinations of metal ions and demonstrated the use of the metal ions as catalysts by the synthesis of CNTs by the water-assisted CVD method.

LDH was synthesized by hydrothermal method. The metal compositions of LDHs were Ni-Al, Mg-Al, Co-Al, and Co-Mg-Al. The synthesized LDH powder was dispersed in water and drop-cast onto Si substrates to fabricate a LDH film (LDH-Si). The CNTs were synthesized in a CVD reactor at a process temperature of 750°C. Following a reduction process in a N_2-H_2 ambient, CNT was initiated by the introduction of ethylene gas as the carbon feedstock. Characterization was performed using XRD, FT-IR, AAS, SEM-EDS, TEM, XPS, and Raman spectroscopy.

Our results showed that CNTs could be synthesized using Ni-Al and Co-Al LDH. The Mg-Al LDH without transition metals could not synthesize CNTs. Using LDH as a catalyst precursor, the CNT yield per LDH catalyst was found to be as high as 4.5 g/g-LDH in the Co-Al LDH, compared to 0.76 g/g-LDH in the Ni-Al LDH, indicating that Co was effective for CNT synthesis. The synthesized CNTs were multi-walled CNTs containing a large amount of carbonaceous impurities attributed to the excessive Co content. Therefore, to synthesize single-walled (SW) and well-crystallized CNTs, we synthesized the Co-Mg-Al LDH with lower Co content to serve as the catalyst. Using this material, CNTs with a diameter of less than 4 nm were produced by controlling the ethylene gas supply during CNT synthesis. The G/D-ratio, a measure of CNT crystallinity, was 9.7, and the presence of radial breathing modes (RBM) indicated the growth of SWCNTs. These results demonstrate LDH as an effective catalyst precursor for CNT and SWCNT synthesis.

高速充放電可能な電気二重層キャパシタのカーボンナノチューブ電極作製に向けたシンプルな“ブレンド”アプローチ

（産総研）○清水　太陽・小橋　和文・中島　秀朗・室賀　駿・山田　健郎・岡崎　俊也・小久保　研・畠　賢治

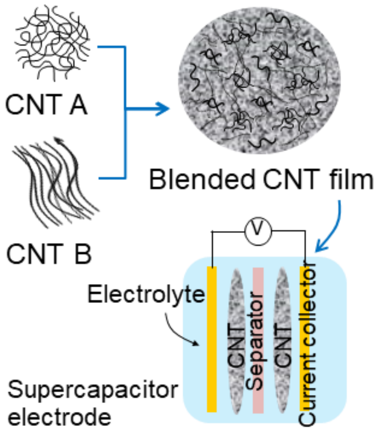
A Simple “Blending” Approach toward the Fabrication of Carbon Nanotube Electrodes for Electric Double Layer Capacitors Enabling High Charge-Discharge Rates

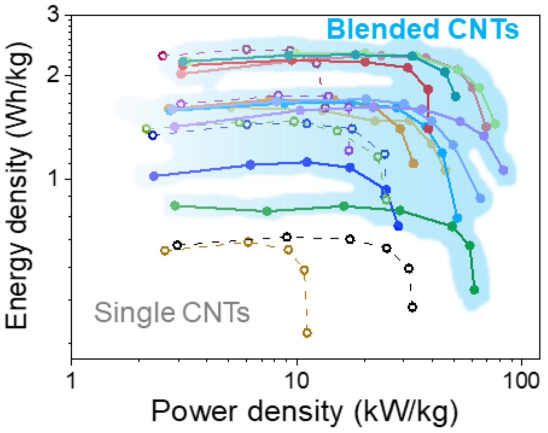
(*AIST*) ○Taiyo Shimizu, Kazufumi Kobashi, Hideaki Nakajima, Shun Muroga, Takeo Yamada, Toshiya Okazaki, Ken Kokubo, Kenji Hata

Electrode materials for high-performance electric double layer capacitors require high electrical conductivity and designed pore characteristics. Carbon nanotubes (CNTs) are an excellent candidate due to their high electrical conductivity and high surface area, whereas the control of the pore structure formed by assembled CNTs still remains challenging. Here, we demonstrate the potential of a simple “blending” approach (i.e., mixing with diverse kinds of CNTs) toward the fabrication of CNT electrodes with desired pore structure. Obtained blended-CNT electrodes showed improved electrochemical performance such as higher power densities than single-type-CNT electrodes, suggesting the practicality of our blending approach.

Keywords：carbon nanotube; electric double layer capacitor; pore structure

高性能な電気二重層キャパシタの実現には、電極材料における優れた導電性と制御された細孔特性の両立が必要である。カーボンナノチューブは高い電気伝導性を有する一方で、細孔特性の制御が難しい。我々は、異なる特徴をもつCNT種同士を“ブレンド”するという、シンプルな手法によって細孔特性を制御することを試みた[1]。CNT分散液の混合、濾過によってブレンドCNT膜を作製し、水系電解液を用いる電気二重層キャパシタの電極材料に利用した。結果として、ブレンドCNTを用いた場合にはほとんどの系でパワー密度が向上するなどの優れた特性を示しており、これはブレンドによる細孔特性の変化、特に細孔容積の増加が寄与していると考えられる。





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1) T. Shimizu, K. Kobashi, H. Nakajima, S. Muroga, T. Yamada, T. Okazaki, K. Hata, *ACS Appl. Energy Mater.* **2021**, 4, 9712.

Structural diversity of single-walled transition metal dichalcogenide nanotubes grown via template reaction

([1]*Department of Physics, Tokyo Metropolitan University*, [2]*Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology,* [3]*Department of Electronic Engineering, Tohoku University*) ○ Yusuke Nakanishi,[1] Shinpei Furusawa,[1] Yuta Sato,[2] Toshiaki Kato,[3] Yasumitsu Miyata[1]

Keywords: Inorganic nanotube; Transition metal dichalcogenide; Template; Transmission electron microscopy; Janus structures

A wealth of discoveries in the chemistry and physics of carbon nanotubes (CNTs) has sparked significant interest in inorganic nanotubes, particularly for transition metal dichalcogenides (TMDs). Single-walled TMD nanotubes (SW-TMDNTs) — seamless cylinders of rolled-up TMD sheets — are one-dimensional (1D) materials that can exhibit tunable electronic properties depending on both their chirality and composition (Fig. 1).[1] However, much less has been explored about their geometrical structures and chemical variations due to their instability under ambient conditions.

Here we report the structural diversity of SW-TMDNTs templated by boron-nitride nanotubes (BNNTs).[2] We have developed the facile preparation of well-dispersed BNNT networks via surfactant dispersion and the coaxial synthesis of TMDNTs using BNNTs as templates.[3] The outer surfaces and inner cavities of BNNTs promote and stabilize the coaxial growth of SW-TMDNTs with various diameters, including few-nm-wide species. The chiral indices (n, m) of individual SW-MoS_2NTs were assigned by high-resolution transmission electron microscopy (TEM), and statistical analyses revealed a broad chirality distribution ranging from zigzag to armchair configurations. Furthermore, this methodology can be applied to the synthesis of various TMDNTs such as selenides and alloyed $Mo_{1-x}W_xS_2$. Comprehensive microscopic and spectroscopic analyses also suggest the formation of Janus $MoS_{2(1-x)}Se_{2x}$. The BNNT-templated reaction provides a universal platform to characterize the chirality-dependent properties of 1D nanotubes with various electronic structures.

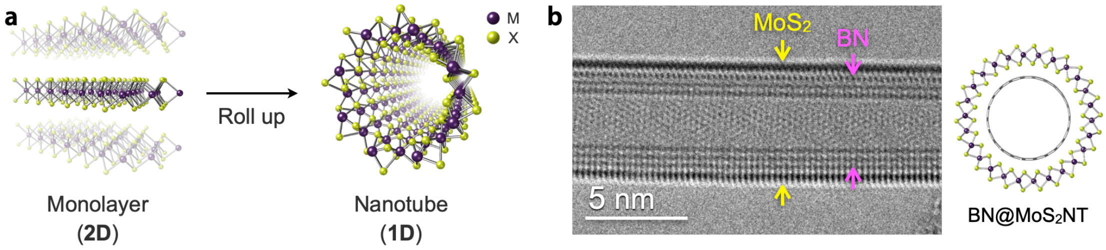


Fig. 1 (a) Schematic of rolling up 2D TMD sheets into the corresponding 1D nanotubes. (b) High-resolution TEM and the corresponding cross-sectional images of MoS_2NTs coaxially grown on BNNTs

1) J. L. Musfeldt et al., *Phys. Today* **2020**, *73*, 42. 2) Y. Nakanishi et al., *Adv. Mater.* **2023**, *35*, 2306631. 3) S. Furusawa, Y. Nakanishi, et al., *ACS Nano* **2022**, *16*, 16636.

Room-Temperature Synthesis of Carbon Nano-Onions through Sonication of Inorganic Carbon Sources

([1]. Department of Information Systems, Graduate School of Engineering Saitama Institute of Technology, [2]. Department of Life Science and Greene Chemistry, Saitama Institute of Technology, [3]. Advanced Science Research Laboratory, Saitama Institute of Technology)
○Jung Wen Yeh[1], Yasushi Hasebe[2], Masaya Uchida[3]

Keywords: carbon nano onions, inorganic carbon source, sonication

Carbon nano-onions (CNOs) are carbonaceous nanostructures composed of multiple concentric shells. Due to their unique structure, CNOs exhibit exceptional mechanical strength, and excellent electrical and thermal conductivity leading to a wide range of applications such as batteries and biosensors.[1] This study presents the synthesis of CNOs through sonication in room temperature water from three different inorganic carbon sources: (1) SiC, (2) B_4C, and (3) $CaCO_3$. Sonication induces and accelerates chemical reactions caused by acoustic cavitation. After sonication for several hours, the resulting mixture was centrifuged twice to separate CNOs from carbon sources.[2] The synthesized samples were characterized using different analytical techniques, including transmission electron microscopy (TEM) and Raman spectrometry. In figure 1, TEM images showed CNOs with diameters of approximately 20–30 nm in all three cases. Fourier-transform infrared spectroscopy (FTIR) and scanning transmission electron microscopy–electron energy loss spectroscopy (STEM-EELS) indicated the presence of oxygen-containing functional groups on the CNOs. Raman spectroscopy suggested the defects of the CNOs. In our TEM observations, we also observed graphene nanosheets, graphite hollow polyhedrons, carbon nanotubes, and carbon nanohorns though few in number. The presented method contributes to advancing the research of carbon nanomaterial synthesis with a facile and environmentally friendly approach.

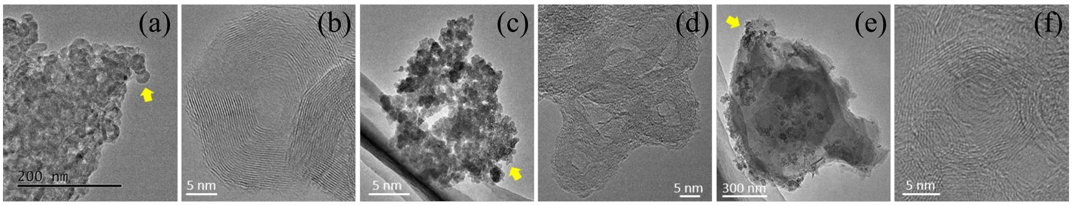


Fig1. TEM images of onion-like structures through sonication synthesis from (a) SiC, (c) B_4C and (e) $CaCO_3$. (b), (d) and (f) magnified HRTEM image of the observed region.

1) G. Yushin et al., Carbon Nanomaterials, **2006**, 239–282. 2) S. Wang et al., J. AM. CHEM. SOC., **2009**, *131*, 16832–16837.

日本化学会 第104春季年会 (2024)

バイポーラ電気化学反応による黒鉛からの化学修飾グラフェン合成

（山形大院有機 [1]・山形大工 [2]）金野 裕太 [1]・下豊留 慧 [2]・○沖本 治哉 [1]

Preparation of modified graphene from graphite powder via bipolar electrochemistry

([1]*Graduate School of Organic Materials Science, Yamagata University*, [2]*Faculty of Engineering, Yamagata University*) Yuta Konno,[1] Kei Shimotoyodome,[2] ○Haruya Okimoto,[1]

Chemically modified graphene is a material in which the surface of graphene is functionalized by chemical modification. The general method has been to use the Hummers oxidation to form graphene oxide and then functionally modify it, but a synthesis method that does not use an oxidizing agent is desired. In this research, we established a one-pot chemically modified graphene technique by combining graphite with bipolar electrochemical oxidation and modification, and succeeded in producing nitrogen-modified graphene with a modification amount of 15.7% and an oxidation degree of 7.9%.

Keywords：Graphene, Bipolar electrochemistry

グラフェン表面に官能基を持つ化学修飾グラフェンは、樹脂との複合化やキャパシタや燃料電池触媒などへの応用など多岐にわたる。その合成法は酸化グラフェンを経由する場合が多く、黒鉛を酸化グラフェン化した後に様々な官能基を修飾するが、酸化反応はグラフェンの導電性を低下させるとともに、非常に環境負荷の強い薬品を利用する。本研究では、酸化を抑制しつつ化学修飾グラフェンを黒鉛から得る方法として、バイポーラ電気化学反応を利用した化学修飾グラフェンの 1 段階合成法について報告する。白金板間に静置した黒鉛を反応溶液(図 1)に浸し、白金板間に 35V を 12 時間印加した。その後、黒鉛剥離物を回収し、DMF に分散させ、XPS、AFM を用いて構造評価及び表面修飾量の評価を行なった。図２に示すように剥離物の窒素含有量は白金板間の電圧に依存した。最終的に、窒素含有量 15.7%、酸化量 7.9%、膜厚 2～5 nm の窒素修飾グラフェンの合成に成功した。

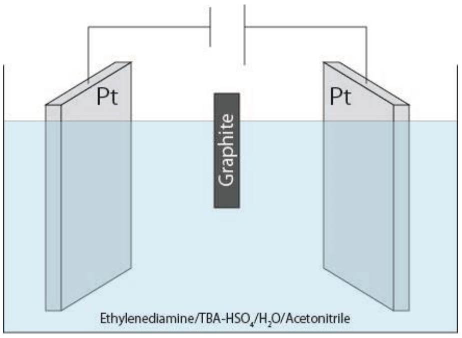


図 1 バイポーラ電気化学剥離装置図

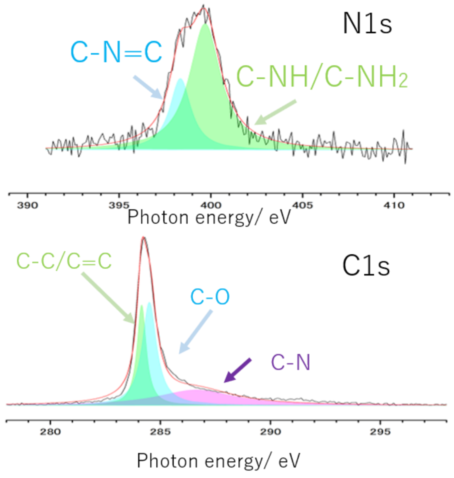


図 2 剥離修飾グラフェンの XPS スペクトル

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18日(月) 13:00 ~ 15:10 C442(4号館 [4階] 442)

[C442-1pm] 20. 材料化学—基礎と応用

座長：山内 美穂、田代 啓悟

日本語

13:00 ~ 13:20

[C442-1pm-01]

超分子ゲルを用いたTiO_2ナノ結晶のフォトドーピング制御

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

英語

13:20 ~ 13:40

[C442-1pm-02]

優れたプロトン伝導性を持つ蔗糖由来の酸化層炭素

○Liu Xinyao[1] (1. 熊本大学)

日本語

13:40 ~ 14:00

[C442-1pm-03]

アルキル基修飾POSSの耐原子状酸素特性

○行松 和輝[1,2]、横山 創一[2]、後藤 亜希[1]、丸山 幹人[2]、木本 雄吾[1]、家 裕隆[2] (1. 宇宙航空研究開発機構、2. 阪大産研)

14:00 ~ 14:10

休憩

日本語

14:10 ~ 14:30

[C442-1pm-04]

細孔サイズが制御されたCeO_2の細孔内担持ルテニウム触媒によるアンモニア合成

○滝本 皓也[1]、田代 啓悟[1]、里川 重夫[1] (1. 成蹊大学)

日本語

14:30 ~ 14:50

[C442-1pm-05]

極性勾配反応場を利用したスピロピランの光誘起型CO_2捕捉能制御

○田代 啓悟[1]、大鳥 誠生[1]、里川 重夫[1] (1. 成蹊大学)

英語

14:50 ~ 15:10

[C442-1pm-06]

Nacre-Inspired Graphene Oxide Bulk Materials Produced by Multiscale Interface Crosslinking

○Xuke Tang[1], Ke Chen[2], Binbin Jia[2], Cezhou Chao[2], Yan Wei[3], Junyu Hou[2], Leiting Dong[2], Xuliang Deng[3], Ting-Hui Xiao[1,6], Keisuke Goda[1,4,5], Lin Guo[2] (1. The Univ. of Tokyo, 2. Beihang Univ., 3. Peking Univ., 4. Wuhan Univ., 5. Univ. of California, 6. Zhenzhou Univ.)

超分子ゲルを用いた TiO_2 ナノ結晶のフォトドーピング制御

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

Photodoping of Titanium Dioxide Nanocrystals Controlled by Supramolecular Gel

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

Photodoping, where electrons are accumulated in the conduction band of semiconductor nanocrystals upon photoirradiation, is useful for photochromism and light energy storage. However, deoxygenated conditions have been necessary for photodoping because the accumulated electrons react with oxygen rapidly. In this study, we successfully achieved broadband coloration of TiO_2 nanocrystals based on photodoping[1)] stable under air atmosphere using a supramolecular gel. We also succeeded in on-demand decoloration upon the sol-gel transition induced by photothermal conversion using near-infrared light.

Keywords : Photochromism; Sol-gel Transition; Semiconductor Nanocrystals; Photothermal Conversion; Plasmon Resonance

光照射と正孔捕捉剤によって半導体ナノ結晶の伝導帯に電子が蓄積される現象はフォトドーピングとよばれ、フォトクロミズムや光エネルギー貯蔵において有用である。しかし、蓄積された電子は酸素と速やかに反応するため、一般に脱酸素条件が必要であり、応用に制限があった。本研究では、超分子ゲルを用いることにより、酸化チタンナノ結晶 (TiO_2 NCs) へのフォトドーピング[1)]を任意に制御することを試みた (Fig. 1a)。

TiO_2 NCs を含む空気飽和ゲルに対して紫外光(365 nm)を照射すると、伝導帯の自由電子に帰属される広帯域な吸収帯が生じて着色した (Fig. 1b, 青)。さらにこの状態のゲルに対して近赤外光(975 nm)レーザーを照射したところ、光熱変換によりゾル化し、気相から酸素が供給されることにより着色は消失した (Fig. 1b, 橙)。これらの結果から、超分子ゲルが TiO_2 NCs の空気下におけるフォトドーピングによる着色と、近赤外光によるゾル化に基づくオンデマンドな退色に有効であることが明らかになった。

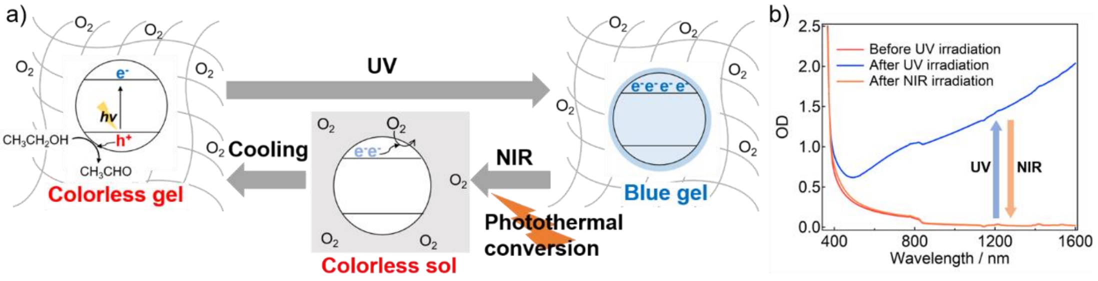


Figure 1. (a) Photodoping-based photochromism of TiO_2 NCs controlled in supramolecular gel. (b) Absorption spectra of TiO_2 NCs in a toluene gel before and after ultraviolet (UV, 365 nm) light irradiation and after the near-infrared (NIR, 975 nm) light-induced sol-gel transition.

1) M. Hirsimäki et.al., *Chem. Matter.*, **2018**, *30*, 8968.

Sucrose-derived oxidized layer carbon with excellent proton conductivity properties

([1]*Graduate School of Science, Kumamoto University*) ○Xinyao Liu,[1] Md. Saidul Islam,[1] Shinya Hayami[1]

Keywords: Graphene; proton conductivity; iron oxide; amorphous carbon; sucrose

Herin, we investigate sucrose-derived oxidized layer carbon and its distinctive proton conductivity properties, offering a promising pathway for advancing energy storage technologies. The research involves synthesizing and characterizing carbon layers derived from sucrose, undergoing oxidation processes to uncover their proton transport capabilities. The maintenance of a layered structure was confirmed through SEM images. The experimental results provide compelling evidence of enhanced proton conductivity, elucidating the material's potential applications in fuel cells and other proton-exchange membrane devices. These findings contribute valuable insights to developing sustainable and efficient energy storage systems, paving the way for future innovations.

The research shows that High-quality layer carbon can be synthesized through a simple pathway by using sucrose and $FeCl_3$. During the process of synthesizing samples $FeCl_3$ plays a crucial role in the formation of high-quality layer carbon, as it serves as both a template and a catalyst during the formation process.[1] The improvement in quantity and quality of the product was confirmed by the amount of $FeCl_3$. Furthermore, hummer's oxidation can effectively improve the quality of products. The Raman spectroscopy results indicate that the relative intensities of the G-band (IG), D-band (ID), provide evidence for studying the characteristics of the materials. High quality have a low D-band/G-band ratio. The sample treated by the Hummer oxidation has more functional groups, making it easier to disperse in water and other solvents, which can be helpful in improving proton conductivity.

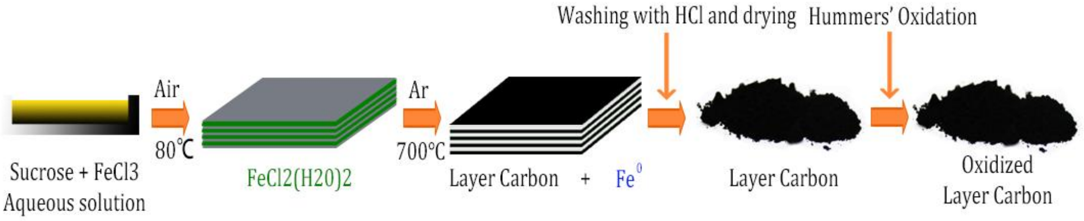


Fig.1 Preparation of layer carbon using a mixture of sucrose and $FeCl_3$

1) Binbin Zhang, *Chem. Sci.* **2014**, 5, 4656

アルキル基修飾 POSS の耐原子状酸素特性

（宇宙航空研究開発機構[1]・阪大産研[2]）○行松 和輝[1,2]・横山 創一[2]・後藤 亜希[1]・
丸山 幹人[2]・木本 雄吾[1]・家 裕隆[2]

Evaluation of Atomic Oxygen Resistance of alkyl-POSS film

([1]*Japan Aerospace Exploration Agency*, [2]*Sanken, Osaka University*) ○Kazuki Yukumatsu,[1,2] Soichi Yokoyama,[2] Aki Goto,[1] Mikito Maruyama, [2] Yugo Kimoto,[1] Yutaka Ie[2]

Polymeric materials used for the outermost layers of spacecraft are eroded by collisions with atomic oxygen (AO), which exists at low Earth orbit. Polyhedral oligomeric silsesquioxane (POSS), an organic-inorganic hybrid molecule, is known to have high AO resistance because of the formation of an inorganic silica layer by reactions with AO. However, silsesquioxane coating on polyimide surface resulted in the formation of physical defects by AO exposure[1,2]. Therefore, it is required to understand the relationship between POSS chemical structure and physical defect under AO exposure.

This study aims to clarify the molecular structures of POSS with high AO resistance and coating properties to polyimide. POSS bearing alkyl groups with different chain lengths (random-POSS) and octyl-substituted POSS were synthesized. Their changes in mass, surface morphology, and silica thickness were investigated after AO exposure (maximum 6×10^{20} atoms/cm^2, JAXA facility). The mass losses and formed silica thicknesses were almost the same regardless of the modified alkyl groups. The random-POSS could be coated on polyimide films by a simple spin-coating method, and its AO resistance will also be reported.

Keywords : Atomic Oxygen; Silsesquioxane; Alkyl-POSS

宇宙機最外層に用いられる高分子材料は、地球周回低軌道に存在する原子状酸素 (AO) と相対速度 8 km/s で衝突し、浸食される。有機無機ハイブリッド材料であるかご型シルセスキオキサン (POSS) は、AO との反応で無機シリカ層が形成されるため、耐 AO 性が高いことが知られている。ポリイミドへの塗布が可能なシルセスキオキサン材料は[1)]、AO との反応で物理的欠損が生じることが明らかとなっており[2)]、AO 照射下での POSS の分子構造と物理的欠損発現の相関解明が必要である。

本研究では、高い耐 AO 性とポリイミドへの塗布性を併せ持つ POSS 分子構造の理解を目的とした。異なる長さを持つアルキル基をランダムに導入した POSS (ランダム POSS) 、および、オクチル基のみで構成される POSS を合成し、AO 照射に伴う質量損失と表面形状変化、シリカ層の形成厚さを調べた。AO を照射した結果（最大 6×10^{20} atoms/cm^2、JAXA 設備）、導入したアルキル鎖長に関わらず、質量損失やシリカ形成厚さは同程度であった。また、ランダム POSS はスピンコートでのポリイミドフィルムへの塗布が可能であり、その耐 AO 性を評価した結果も報告する。

謝辞: 本研究は JSPS 科研費 (JP21K04494)の助成を受けたものである。

1) Y. Kimoto, et al., *J. Spacecraft Rockets,* **2016**, 53 (6), 1028–1034.
2) A. Goto, et al., *CEAS Space J.*, **2021**, 13 (3), 415–432.

細孔径が制御された CeO_2 の細孔内担持ルテニウム触媒によるアンモニア合成

（成蹊大院理工）○滝本 皓也・田代 啓悟・里川 重夫

Ammonia synthesis over ruthenium catalyst deposited in size-controlled mesopores of CeO_2 substrate (*Graduate School of Science and Technology, Seikei University*) ○Koya Takimoto, Keigo Tashiro , Shigeo Satokawa

Catalytic synthesis of ammonia as a hydrogen carrier under mild conditions, i.e. ambient pressure, is strongly desired and ruthenium (Ru) is one of the most useful candidates to accomplish this. In the present study, Ru catalyst deposited on the internal surface of well-pore-size-controlled ceria was synthesized by using hexadecylamine (HDA). The molar ratio of HDA to Ce (R_{HDA}) drastically affected pore sizes of the resulting CeO_2 and the condition of R_{HDA} = 0.50 afforded CeO_2 possessing 2–4 nm of diameter of mesopores with narrow distribution. The ammonia synthesis ability of Ru catalyst on pore-size-controlled CeO_2, especially smaller pore size and narrower distribution of them, was higher than that on bare CeO_2, suggesting pore with smaller size could enhance dispersion and Ru catalyst.

Keywords : Pore-size modulation; Cerium Oxide; Ammonia synthesis

アンモニアは有用な水素キャリアであり、温和な条件で窒素と水素からアンモニアを合成するために、低圧でもアンモニア合成活性を示すルテニウム（Ru）担持触媒が注目されている。当研究室では、多孔質な酸化セリウム（CeO_2）の細孔内にRuを担持させた触媒が高いアンモニア合成活性を示すことを見出した1)。本研究では、ヘキサデシルアミン（HDA）を用いて細孔サイズ制御が制御された。Fig. 1に示すようにHDAを使用せずに合成したCeO_2は10 nmオーダーの細孔径が最も多かったのに対して、Ce元素に対するHDAモル比（R_{HDA}）が0.50の時に最もピーク幅が狭くなった。それぞれのR_{HDA}で合成したCeO_2担体にセシウムイオン（Cs^+）をプロモーターとして導入し、その上にRuを担持させた触媒（Ru/Cs-CeO_2）を用いて400 ℃、大気圧下でアンモニア合成活性を評価したところ、細孔径が小さく、細孔分布が狭い触媒が高いアンモニア合成活性を示した。Ru粒子の分散性が高まりシンタリングが抑制されたためであると示唆された。

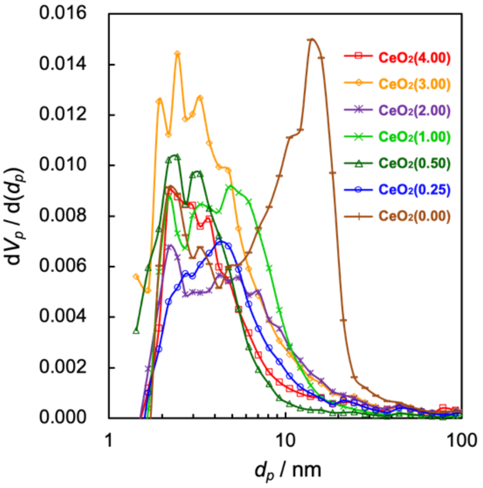


Fig. 1 Pore size distributions of prepared $CeO_2(R_{HDA})$ estimated by BJH analysis of N_2 adsorption/desorption isotherms. Here, R_{HDA} indicates the molar ratio of HDA to Ce atom; R_{HDA} = 0.00, 0.25, 0.50, 1.00, 2.00, 3.00, and 4.00.

1) M. Osozawa, S. Satokawa et al., *Int. J. Hydrog. Energy* **2022**, *47*, 2433.

日本化学会 第104春季年会 (2024)

極性勾配反応場を利用したスピロピランの光誘起型 CO_2 捕捉能制御

（成蹊大理工）○田代 啓悟・大鳥 誠生・里川 重夫

Modulation of CO_2 capture ability of spiropyran in polar gradient reaction field

(*Faculty of Science and Technology, Seikei University*) ○Keigo Tashiro, Masaki Otori, Shigeo Satokawa

Photo-triggered CO_2 concentration system using photochromic molecules is one of the most useful processes on the realization of carbon neutrality. In this system, azobenzene and diarylethene derivatives were widely used, while spiropyran which was one of the most famous photochromic molecules has not been utilized because spiropyran (SP) and isomerized merocyanine (MC) could not coexist under one polar environment due to large change of polarity upon the photoisomerization. Regarding this, we succeeded in a modulation of the CO_2 capture/release using SP/MC in the contentiously polar-gradient field constructed by surfactant self-assembly and montmorillonite clay mineral. Experimental and computational approaches demonstrated that the spiropyran could capture CO_2 via not only physical interaction but also electronic interaction, while photo-isomerized merocyanine was in a CO_2 release mode. We believed that the novel supramolecular approach for the development of CO_2 concentration system largely contributes environmental chemistry.

Keywords : *CO_2 capture; Spiropyran; Polar-gradient field; Photoisomerization; Clay mineral*

近年、フォトクロミック分子を用いた光駆動型二酸化炭素（CO_2）吸脱着制御が新たな CO_2 濃縮手法として注目されている。これまでアゾベンゼンやジアリールエテンを用いた光駆動型 CO_2 吸脱着制御がいくつも報告されているが、同じく有名なフォトクロミック分子であるスピロピラン（SP）は本系に全く利用されてこなかった。これは、SP が無極性であるのに対し、光異性化したメロシアニン（MC）が双性イオンに由来する極性構造をもつため、1 つの極性環境では両分子が同時に存在できないことが原因であった。

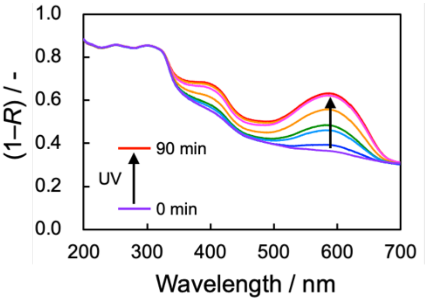


Figure 1 Absorption spectra on the photoisomerization from SP to MC under UV light irradiation in the polar-gradient field constructed by CTAB and montmorillonite.

本研究では、モンモリロナイトの層間にカチオン性界面活性剤である臭化セチルトリメチルアンモニウム（CTAB）を導入することで極性勾配場を構築し、SP/MC 系での CO_2 吸脱着能のスイッチングに成功した[1]。SP はヘキサンのような均一な無極性溶媒では紫外線照射下でも一切 MC へ異性化しなかったが、極性勾配場中では動的に MC へ異性化を起こすことがわかった（**Figure 1**）。この材料を用いて CO_2 の吸着等温線を測定したところ、SP は CO_2 を捕捉するのに対し、MC は CO_2 を全く捕捉しないことが実証された。また、DFT 計算の結果、SP は静電相互作用だけでなく、電子的な強い相互作用も介して CO_2 を捕捉していることが明らかになった。

1) K. Tashiro, M. Otori, S. Satokawa, *Chem. Commun.* **2023**, *59*, 4304.

Nacre-Inspired Graphene Oxide Bulk Materials Produced by Multiscale Interface Crosslinking

([1]*The University of Tokyo*, [2]*Beihang University*, [3]*Peking University*, [4]*Zhenzhou University*, [5]*Wuhan University*, [6]*University of California*) ○ Xuke Tang[1], Ke Chen[2], Binbin Jia[2], Cezhou Chao[2], Yan Wei[3], Junyu Hou[2], Leiting Dong[2], Xuliang Deng[3], Yasutaka Kitahama[1], Ting-Hui Xiao[1,4], Keisuke Goda[1,5,6], Lin Guo[2]

Keywords: Graphene Oxide; Composite Material; Nacre-Inspired; Interface Interaction; Mechanical Property

Graphene oxide (GO) and reduced GO have strong mechanical, electrical, and chemical properties, allowing for their wide applications in various fields[1]. For the application of flexural GO-based composites in three-dimensional (3D) bulk materials, it is imperative to overcome the challenges posed by the high flexibility and weak interlayer interactions of GO nanosheets. Natural structures with impressive mechanical properties often inspire the design of artificial materials to break through their mechanical limitations. A well-known example is the natural nacre, known for its orderly 3D "brick-and-mortar" (BM) structure, boosting a rapid expansion of research on artificial nacre[2]. However, some valuable structural features of the natural nacre still have not been considered in producing nacre-like 3D bulk materials. These features, notably the multiscale interface crosslinking and the distinct amorphous/crystalline heterophase structure, are crucial for maximizing the strength and toughness of nacre.

Here, inspired by the multiscale interface crosslinking and amorphous/crystalline features within natural nacre, we present a centimeter-sized GO-based bulk material consisting of building blocks of GO and amorphous/crystalline leaf-like MnO_2 hexagon (A/C-LMH) nanosheets adhered together with polymer-based crosslinkers[3]. These building blocks are stacked and hot-pressed with crosslinking between the layers to form a GO/MnO_2-based layered (GML) bulk material (Figure 1). The resultant GML bulk material exhibits a higher flexural strength (231.2 MPa) than nearly all GO-based bulk composites reported to date[3]. These results offer valuable insights for designing structural materials and expanding the use of high-performance GO-based materials in aerospace, biomedicine, and electronics.

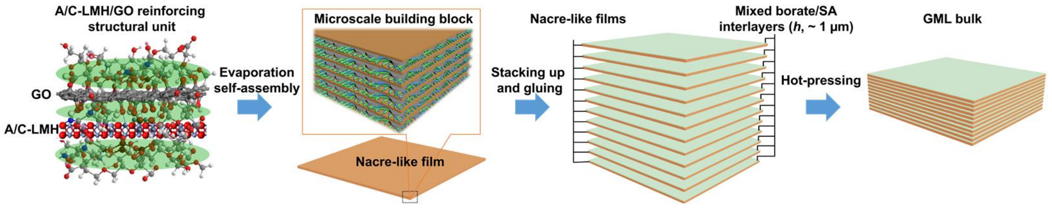


Figure 1. Schematic illustration of the design and assembly of the GML bulk material.

1) G. Xin, T. Yao, H. Sun, et al. *Science* **2015**, *349*, 1083–1087. 2) U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, et al. *Nat. Mater.* **2015**, *14*, 23–36. 3) K. Chen, X. Tang, B. Jia, et al. *Nat. Mater.* **2022**, *21*, 1121–1129.

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18日(月) 13:00 ~ 15:30 A1455(14号館 [5階] 1455)

[A1455-1pm] 22. 資源利用化学・環境・グリーンケミストリー

座長：吉川 聡一、大嶋 孝志

英語
13:00 ~ 13:20
[A1455-1pm-01]
ホルモース反応ネットワークの構造理解を通した反応選択性の制御
〇西島 弘晃[1]、近谷 元大[1]、石原 菜々子[1]、藤本 泰成[1]、田畑 裕[1]、長谷 陽子[1,2]、中西 周次[1] (1. 阪大院基礎工、2. (株）豊田中央研究所)

英語
13:20 ~ 13:40
[A1455-1pm-02]
Multicomponent Adsorption Equilibria Modeling of Phenol and Ciprofloxacin on Differently Prepared Polyethylene Terephthalate Microplastics
〇Christian Ebere Enyoh[1], Qingyue Wang[1] (1. Graduate School of Science and Engineering, Saitama University, Japan)

英語
13:40 ~ 14:00
[A1455-1pm-03]
ジアミンを二酸化炭素吸収材とする高効率Direct Air Capture
〇曹 芙蓉[1]、吉川 聡一[1]、山添 誠司[1] (1. 東京都立大学)

日本語
14:00 ~ 14:20
[A1455-1pm-04]
ジアミンのCO_2吸脱着特性評価
〇八木原 陸矢[1]、吉川 聡一[1]、山添 誠司[1] (1. 東京都立大学)

14:20 ~ 14:30
休憩

日本語
14:30 ~ 14:50
[A1455-1pm-05]
プルシアンブルー類似体を用いた水蒸気を含むガスおよび水中からのメタノール吸着
〇首藤 雄大[1]、川本 徹[1]、高橋 顕[1] (1. 産業技術総合研究所)

日本語
14:50 ~ 15:10
[A1455-1pm-06]
作業環境測定での活性炭・シリカゲル捕集剤と有機溶剤抽出効率
〇安彦 泰進[1] (1. 独立行政法人 労働者健康安全機構)

日本語
15:10 ~ 15:30

[A1455-1pm-07]

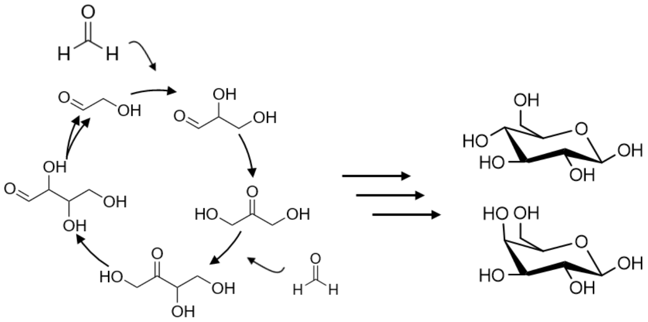
ヘテロジトピックレセプターを用いた塩化リチウムの選択的固-液抽出

◯三室 翼[1]、平澤 学[2,1]、近藤 慎一[1] (1. 山形大理、2. レゾナック)

Controlling Reaction Selectivity through Understanding of the Formose Reaction Network

(1. Osaka Univ., 2. Toyota Central R&D Labs., Inc.) ○Hiroaki Nishijima[1], Genta Chikatani[1], Nanako Ishihara[1], Taisei Fujimoto[1], Hiro Tabata[1], Yoko Hase[1,2], Shuji Nakanishi[1]

Keywords: Formose reaction, Chemical Reaction Networks, Sugar, Autocatalytic Reaction, Artificial Photosynthesis



With global warming emerging as an urgent issue, the development of technologies to support the carbon cycle is becoming increasingly critical. In this context, the formose reaction, which allows for the non-enzymatic synthesis of sugars from formaldehyde (HCHO) — itself can be reductively formed from CO_2 — has attracted significant interest[1]. In the formose reaction, sugars are produced through a combination of three types of reactions: the aldol reaction, the retro-aldol reaction, and the Lobry de Bruyn–van Ekenstein transformation[2]. Although the parasitic Cannizzaro reaction that converts sugars into sugar alcohols lowers the yield of sugar production in the formose reaction, we have recently succeeded in developing an WO_4^{2-} catalyst that allows to suppress the Cannizzaro reaction[3]. Nevertheless, the efficiency of producing linear sugars, like glucose and fructose, remains low when employing this catalyst. The next challenge is to enhance the production selectivity of such linear sugars that are easily metabolized by living organisms. In this study, we propose a cascade-type reaction using two types of catalysts as one strategy to enhance the production efficiency of converting HCHO to metabolizable sugars. The design of such reaction systems can only be achieved through a comprehensive structural understanding of the complex networks involved in the formose reaction. More specifically, in the first stage, we employ a WO_4^{2-} catalyst to efficiently convert HCHO into C3 and C4 compounds, key reaction intermediates. Subsequently, in the second stage, NaOH catalyst was used to facilitate the production of sugars from these C3 and C4 compounds. In this cascade reaction system employing two different catalysts, it has been confirmed that products such as galactose, which are not obtainable using either WO_4^{2-} or NaOH catalysts alone, are produced.

1) J.B. García Martínez et al., *J.CO_2 Util.* **2021,** 53, 101726

2) A. M. Butlerow, *Compt. Rendus Acad. Sci.* **1861**, 53, 145 –147

3) H. Tabata, G. Chikatani, et.al., *Chem. Sci.* **2023**, 14, 13475-13484.

Modeling of Multicomponent Adsorption Equilibria of Phenol and Ciprofloxacin on Differently Prepared Polyethylene Terephthalate Microplastics

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Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama City, Saitama 338-8570, Japan.
Correspondence: cenyoh@gmail.com, ORCID ID: 0000-0003-4132-8988 (C.E.E); seiyo@mail.saitama-u.ac.jp, ORCID ID: 0000-0002-7673-2836(Q.W.)

Abstract

Multicomponent systems are representative of the most common real situations as many industrial discharges contain a mixture of several pollutants [1]. This study explores the concurrent adsorption of phenol (PHE) and ciprofloxacin (CIP) onto distinct polyethylene terephthalate microplastics (PET MPs)—pristine (Pr-PET), acid-modified (Mod-PET), and thermal-oxidatively aged (Ag-PET)—in a multicomponent solution. Employing the Extended-Langmuir (EL), Extended-Freundlich isotherm (EF), and a newly developed Artificial Neural Network (ANN) model, equilibrium adsorption capacities were predicted. Model parameters were estimated using the SOLVER error minimization technique in Microsoft Excel. The EL isotherm exhibited superior fitting for Pr-PET MPs and Ag-PET MPs, while EF excelled for Mod-PET MPs. Monolayer adsorption capacities for both PHE and CIP surpassed those of single-component adsorption. The developed ANN featured 3 hidden layers for Pr-PET MPs and Ag-PET MPs, and 5 hidden layers for Mod-PET MPs **(Figure 1)**, employing a hyperbolic tangent (Tanh) activation function. These models showcased impressive performance metrics, including R^2 (0.989-0.999), low Root Mean Square Error (RMSE) (0.001 – 0.413), and Average Absolute Error (AAE) (0.009 – 0.327) values. P-factor values below 1 indicated synergistic interactions in the binary system **(Figure 2)**. Selectivity ratio (S_R) values ranged from 0.136 for Pr-PET MPs to 0.256 for Ag-PET MPs for PHE, and from 3.902 for Ag-PET MPs to 7.361 for Pr-PET MPs for CIP. This disparity suggests PET MPs exhibit higher selectivity toward CIP than PHE. The study underscores the efficacy of developed PET MPs for binary adsorption of PHE and CIP in aqueous solutions.

Keywords: Artificial neural network, Machine learning, PPCPs, Separation, Selective adsorption, Synergistic interaction, Water treatment

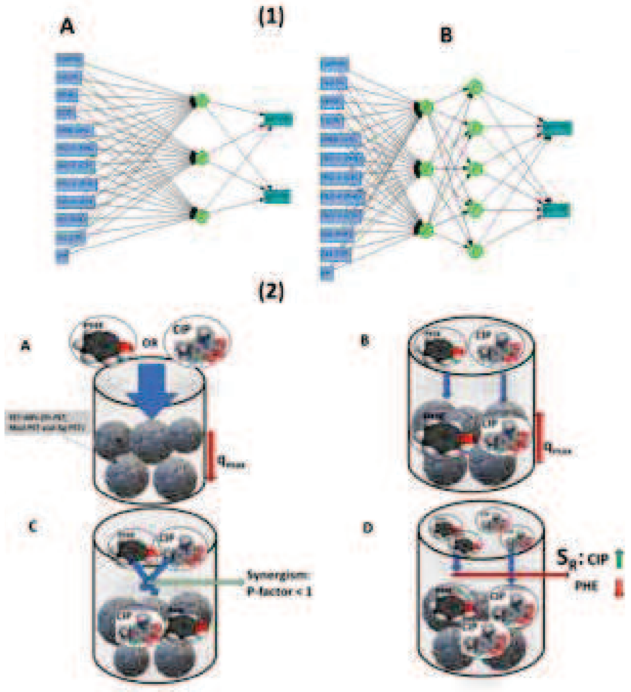


Figure (1). The developed ANN and (2) The graphical representation of the interactive effect of PHE and CIP in binary adsorption system to PET MPs adsorbent.

[1] Enyoh, C. E., & Isiuku, B. O. (2021). *Current Research in Green and Sustainable Chemistry*, 4, 100094. doi:10.1016/j.crgsc.2021.100094

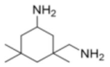
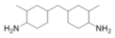
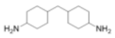
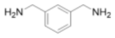
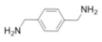
An efficient system for direct air capture utilizes diamine as sorbent.

(*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University*) ○Furong Cao, Soichi Kikkawa, Seiji Yamazoe

Key Words: Carbon Dioxide; Direct Air Capture; Diamine; Phase Separation

The liquid–solid phase separation phenomenon exhibited a high removal efficiency for low concentration CO_2, which has potential for direct air capture (DAC).[1] In this work, a series of aqueous diamine solutions was screened for capturing 400 ppm CO_2. All amine loaded more than1 equilibrium CO_2, and white solid precipitates appeared in this system at the begging stage of CO_2 absorption (**Table 1**). In particular, isophorone diamine (IPDA) maintained >90% CO_2 removal from 400 ppm CO_2 for 726 min (T_{90} value), and the durability was highest among tested amines, and IPDA showed >99% CO_2 removal even under a 500 mL min^{-1}, in which the contact rate between CO_2 and IPDA aqueous solution and the CO_2 absorption rate reached 13,760 h^{-1} and 540 μmol h^{-1} mol_{IPDA}^{-1}, respectively (Figure 1). The CO_2 was captured in aqueous IPDA solution that 90% of the captured CO_2 could be recycled. The precipitate from IPDA was analyzed by ^{13}C NMR (164.85 and 161.23 ppm) and FT-IR (absorption bands at 1600-1660 cm^{-1}), revealing the structure of products as (isophorondiamine)carbamic acid and bicarbonate (HCO_3^-/CO_3^{2-}). Therefore, this work provides a foundation for establishing a solid–liquid phase change system for a highly efficient and environmentally friendly DAC system using aqueous solvent.

Table1. CO_2 adsorption properties of various diamines in aqueous solution for 400 ppm CO_2-N_2.

Entry	Amine	T_{90}/min	CO_2/mmol
1		726	1.03
2		65	1.09
3		27	1.26
4		2	1.07
5		441	1.28

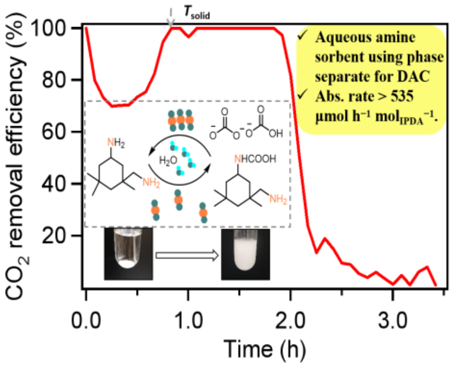


Figure 1. CO_2 removal efficiency over IPDA under 500 mL/min gas flow rates of 400 ppm CO_2. IPDA: 1 mmol; H_2O: 2 mL; (S_{abs} = 1.06).

1) (a) P. Luis *et. al.*, *Desalination* **2016**, *380*, 93−99. (b) X. Jin *et. al.*, *Sep. Purif. Technol.* **2022**, *298*, 120630. (c) S. Kikkawa *et. al.*, *ACS Environ. Au* **2022**, *2*, 354−362. (d) F. Inagaki *et. al.*, *J. Am. Chem. Soc.* **2017**, *139*, 4639−4642.

ジアミンの CO_2 吸脱着特性評価

（都立大院理）○八木原 陸矢・吉川 聡一・山添 誠司

Evaluation of CO_2 Absorption-Desorption Properties of Diamines

(*Tokyo Metropolitan University*) ○Rikuya Yagihara, Soichi Kikkawa, Seiji Yamazoe

Global warming and climate change are closely related to the rising concentration of CO_2 in the atmosphere. A large-scale CO_2 transport system is essential for CCUS technologies that enable to substantial reductions in carbon emissions. In typical, CO_2 is compressed into liquefied CO_2 or supercritical fluid and transported to consumption places by ship or pipeline[1]. However, these systems cost high energy to maintain the states and have safety issues[2].

Our group recently reported highly efficient CO_2 capture system accompanied with a liquid–solid phase change by using a DMSO solution of diamine with cyclohexyl group as a sorbent[3]. The carbamic acid was formed by capturing a molar of CO_2 per diamine molecule, and solid carbamic acid was precipitated simultaneously. Thus, highly efficient CO_2 absorption was achieved due to the low concentration of CO_2-absorbed diamine in the liquid phase. In this study, focusing on the chemical transport of CO_2, we investigate the CO_2 absorption capacity of various diamines and a DMSO solution of diamine can absorb 2 equimolar CO_2 to diamine under flowing certain concentration of CO_2 gas. Furthermore, the 1 equimolar CO_2 could be released under ambient temperature, and the captured CO_2 was perfectly released at 60 ℃. These results suggest the potential of a safer chemical transport system of CO_2 than existing systems using high pressure of CO_2.

Keywords：Carbon dioxide, Diamine, Carbamic acid, Chemical transportation, CCUS

大気中の CO_2 濃度は気候変動や地球温暖化と密接に関係しており，世界的に炭素排出量の削減が求められている．実質的な炭素排出を抑制する CCUS 技術において，CO_2 の大規模輸送技術は必要不可欠である．CO_2 は液化，または超臨界状態まで圧縮され，パイプラインや船舶で輸送される[1]．しかし，大容量の圧縮 CO_2 を扱うため，温度圧力の管理やタンクの設計開発，安全性などに課題が残る[2]．

我々は，CO_2 運搬技術としてアミンによる化学的輸送が有望と考えている．近年，シクロヘキシル環を有するジアミンを用いた固液相変化による低濃度 CO_2 の高効率吸収システムを報告した[3]．1 分子のジアミンが等量の CO_2 を吸収すると，カルバミン酸が固体として析出する．生成系の濃度が保たれることで平衡制約を回避し，低濃度 CO_2 の高効率吸収が可能となる．本研究では，CO_2 の化学的輸送を志向し，種々のジアミンの CO_2 吸収能を評価した．その結果，あるジアミンの DMSO 溶液が，2 等量の CO_2 をジカルバミン酸として吸収することを見出した．このうち 1 等量は室温で放出され，60℃ですべての CO_2 が放出された．これらの結果は，本システムが従来の高圧輸送システムと比べ安全な CO_2 の化学的輸送になる可能性を示している．

1) F. Neele *et al.*, *Energy Procedia,* ***2017***, 114, 6824.
2) 田中ら，*マリンエンジニアリング*, **2023**, 58, 29.
3) S. Kikkawa *et al.*, *ACS Environ. Au*, **2022**, 2, 4, 354.

プルシアンブルー類似体を用いた水蒸気を含むガスおよび水中からのメタノール吸着

（産総研）〇首藤 雄大・川本 徹・髙橋 顕

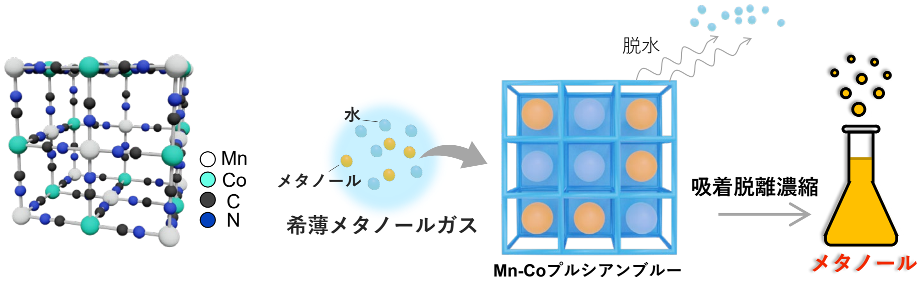
The Purification of Methanol using Prussian blue analogues capturing trace methanol gas

(National Institute of Advanced Industrial Science and Technology) 〇Yuta Shudo, Tohru Kawamoto, Akira Takahashi

Conventional methanol recovery processes are highly energy-intensive; processes using selective adsorbents that consume low energy are preferable. However, conventional adsorbents have low methanol selectivity under humid conditions. This study develops a selective methanol adsorbent, manganese hexacyanocobaltate (MnHCC), a Prussian blue analogue, that enables the efficient removal and reuse of methanol. MnHCC adsorbs 4.8 mmol-methanol/g-adsorbent at 25 degrees in a humid gas containing 5000 ppmv of methanol, which is five times higher than the adsorption capacity of activated carbon (0.86 mmol/g). Although MnHCC exhibits the simultaneous adsorption of methanol and water, it has a higher adsorption enthalpy for methanol than that for water. Thus, pure methanol (95%) was recovered via thermal desorption after dehydration.

Keywords : Adsorption; Methanol; Prussian blue; Porous materials.

本研究では水蒸気を含むガスからメタノールを選択的に濃縮できる吸着材を開発した。排ガス中のメタノールは大気放出される前にエネルギーを余分に加えて燃焼無害化処理している。そこで本研究ではメタノールを選択的に脱離させる Mn-Co プルシアンブルー類似体を開発することで希薄なメタノールガスから 95wt%の高濃度なメタノール液を回収することに成功した。このプロセスに必要なエネルギーを計算したところ、既存のメタノール製造プロセスよりも低いエネルギーでメタノールを資源化できることが明らかとなった。また最近では水中のメタノールを吸着できる Mn-Fe プルシアンブルー類似体を開発した。Mn-Fe プルシアンブルー類似体は 1000mg-MeOH/L のメタノール水から 0.36mg-MeOH/L 吸着することができ、こちらも活性炭と比較して 3 倍程度高い吸着量を示した。



図：Mn-Co プルシアンブルーの構造とメタノール濃縮プロセス

1) Recovery of Pure Methanol from Humid Gas Using Mn–Co Prussian Blue Analogue. Y. Shudo, S. Numano, T. Kawamoto, and A. Takahashi*, *ACS Appl. Mater. Interfaces,* **2023**, *15*, 11977–11982.

作業環境測定での活性炭・シリカゲル捕集剤と有機溶剤抽出効率

（独立行政法人労働者健康安全機構 労働安全衛生総合研究所）○安彦 泰進

Dependence of Extraction Efficiency of Activated Carbon and Silica Gel Sampling Agents for Work Environment Measurement on the Concentration of Organic Solvents

（*Work Environment Research Group*, *National Institute of Occupational Safety and Health*, *Japan Organization of Occupational Health and Safety*）○Hironobu Abiko

Activated carbon and silica gel are commonly used as sampling agents of organic solvent vapor in work environment measurement established by the Industrial Safety and Health Act in Japan. In the measurement, extraction efficiency of organic solvent from the agents is particularly important for accuracy of determination especially in the low concentration region of the vapor. In this study, we have measured the efficiencies of the agents using several types of organic solvent to investigate their concentration dependence. Clarification of the concentration dependence is necessary in examining of effective measurement methods using the agents in combination.

Keywords : *Activated Carbon*; *Extraction Efficiency*; *Organic Solvent Vapor*; *Silica Gel*; *Work Environment Measurement*

労働安全衛生法に基づく作業環境中の有機溶剤蒸気（有機ガス）濃度の測定方法には、活性炭などの捕集剤が充填された捕集管と吸引ポンプにより一定時間の濃縮捕集を行った後、各種の有機溶媒で対象の有機溶剤成分を捕集剤から抽出して測定を行う固体捕集法がある[1-3]。上記の濃度測定においては、近年は従来よりもさらに低濃度の領域の精確な測定にも関心が持たれているが、現在の主要な捕集剤である活性炭は有機溶剤の種類や濃度によっては抽出効率（脱着率）が好ましくなく、測定精度に影響を生じることが指摘されている。一方、シリカゲルは疎水性の活性炭を補う捕集剤とされるが、双方の適切な使い分けの詳細は未だ不明である。そこで本研究は双方での各種有機溶剤の脱着率の比較を進め、これらの併用による効果的な測定方法の検討を目的とする。当日の発表では、固体捕集法や各捕集剤の概要について示すと共に、幾つかの有機溶剤について活性炭捕集剤とシリカゲル捕集剤での抽出効率の濃度依存性を比較した結果（Fig.1）からの考察を報告する。

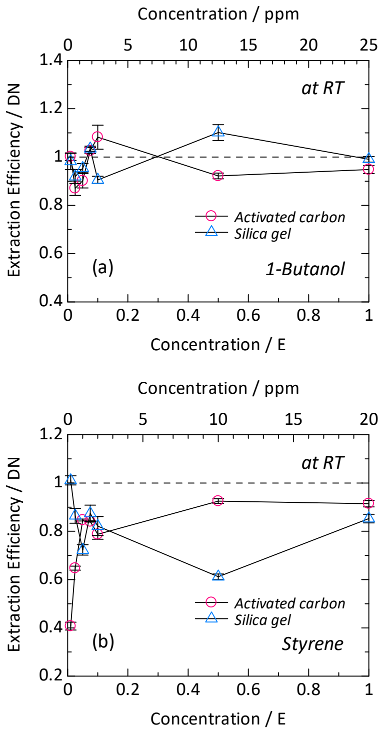


Fig.1 Examples of comparison of extraction efficiencies of organic solvent components determined by the direct addition method [3] between the petroleum-based activated carbon specimen (40 mg) and the silica gel specimen (70 mg). E= the control concentration as defined by the Industrial Safety and Health Act in Japan. DN= dimensionless number. RT= room temperature.

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1）公益社団法人日本作業環境測定協会編. 作業環境測定ガイドブック 5［有機溶剤（特別有機溶剤を含む)］― 物質別各論 初版（2019）.
2）安彦泰進. 産業衛生学雑誌 **62** (2020) 192−197.
3）H. Abiko. *SN Applied Sciences* **3** (2021) Article number 206.

ヘテロジトピックレセプターを用いた塩化リチウムの選択的固-液抽出

(山形大理[1]・レゾナック[2]) ○三室 翼[1]・平澤 学[1,2]・近藤 慎一[1]

Selective Solid-Liquid Extraction of Lithium Chloride with Heteroditopic Receptors

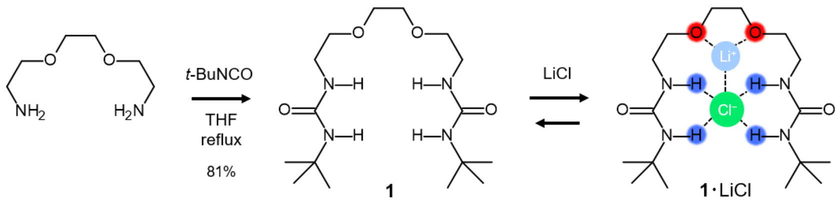
([1]*Faculty of Science, Yamagata University*, [2]*Resonac Corporation*) ○ Tsubasa Mimuro,[1] Manabu Hirasawa,[1,2] Shin-ichi Kondo[1]

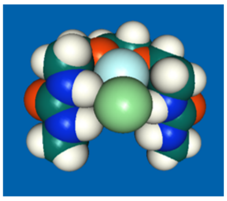
As the demand for lithium has increased over the years,1) extraction from seawater and used batteries has attracted attention. In addition, heteroditopic receptors are expected to be effective in the extraction of certain salts.2) However, there are still no reported examples of practical use of the receptor due to the inadequate capability. We report the development of a highly selective extraction method for lithium chloride by solid-liquid extraction at high concentration by using heteroditopic receptors with high solubility. Receptor **1** recognizes a cation at the ether site and an anion at the urea site, and the cavity size was found to be well match with LiCl. Solid-liquid extraction with **1** showed more than 70% recovery of LiCl even when K^+ and Na^+ were present 10 and 100 times higher, respectively. Li salt was also recovered from Uyuni lake salt and bitterness. The new recovery method also allows the use of industrial organic solvents and the reuse of receptors, and we have developed a more practical method for the recovery of LiCl.

Keywords : solid-liquid extraction, molecular recognition chemistry, host-guest chemistry, lithium salt

近年、リチウムの需要が逼迫する中、より効果的な生産法をもとめ、海水や廃電池からの抽出が注目されている1)。また、イオン対認識が可能なヘテロジトピックレセプターは、特定の塩の抽出が期待されている2)。しかし、レセプターの選択性や抽出能が十分でないため、実用的な報告例は未だ存在しない。本研究では、合成が簡便で溶解度の高いヘテロジトピックレセプターを用いることで、高濃度な固液抽出による塩化リチウムの高選択的な抽出手法を開発したことを報告する。

ヘテロジトピックなレセプター**1** は、エーテル部位でカチオンを、尿素部位でアニオンを認識し、分子の形成する空隙のサイズから、LiCl への選択性が高いことが分かっている。実際の固液抽出では、K^+が 10 倍、Na^+が 100 倍競合する条件においても LiCl の回収率が 7 割以上を示し、天然のサンプルであるウユニ塩湖の塩や日本近海で得られた苦汁などからも Li 塩を回収することができた。また、新たな回収手法は、工業的な有機溶媒の使用やレセプターの再利用が可能であり、より実用的な LiCl の回収手法を開発した。





B3LYP/6-31+G(d) in MeCN (PCM)

1) S. Mohr, G. Mudd, D. Giurco, *Minerals*, **2012**, *2*, 65.

2) J. Mahoney, A. Beatty, B. Smith, *Inorg. Chem.*, **2004**, *43*, 7617.

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18日(月) 15:55 ~ 16:55 A1454(14号館 [5階] 1454)

[A1454-1vn] 22. 資源利用化学・環境・グリーンケミストリー

座長：磯崎 勝弘、川口 真一

日本語

15:55 ~ 16:15

[A1454-1vn-01]

資源循環を目指した塩化リンフリーなリン酸エステルの製造とリン含有バイオマスの活用

○浅尾 和弥[1]、森 康貴[2]、松本 星奏[3]、早川 康之[4]、佐々木 猛[4]、平田 直也[4]、川口 真一[1,2,3] (1. 佐賀大学 農学部附属アグリ創生教育研究センター、2. 佐賀大学大学院 先進健康科学研究科、3. 佐賀大学農学部 生物資源科学科、4. 日本コンクリート工業株式会社)

日本語

16:15 ~ 16:35

[A1454-1vn-02]

エチレンジアミンによるPET繊維へのアミノ基の導入とメイラード反応による着色

○大江 猛[1]、吉村 由利香[1] (1. 大阪技術研)

日本語

16:35 ~ 16:55

[A1454-1vn-03]

再生樹脂添加用アルデヒド捕捉剤の開発

○須藤 幸徳[1]、木佐貫 紗也佳[1]、鈴木 孝生[1] (1. 東ソー株式会社)

資源循環を目指した塩化リンフリーなリン酸エステルの製造とリン含有バイオマスの活用

(佐大農附属アグリ創生教育センター[1]・佐大院先進[2]・佐賀大農[3]・日本コンクリート工業株式会社[4]) ○浅尾 和弥[1]・森 康貴[2]・松本 星奏[3]・早川 康之[4]・佐々木 猛[4]・平田 直也[4]・川口 真一[1,2,3]

Phosphorus chloride-free phosphate esterification aimed to the phosphorus recycling and biomass utilization ([1]Center for Education and Research in Agricultural Innovation, Faculty of Agriculture, Saga University, [2]Graduate School of Advanced Health Sciences, Saga University, [3]Faculty of Agriculture, Saga University, [4]NIPPON CONCRETE INDUSTRIES CO., LTD.) ○Kazuya Asao[1], Koki Mori[2], Seika Matsumoto[3], Yasuyuki Hayakawa[4], Takeshi Sasaki[4], Naoya Hirata[4], Shin-ichi Kawaguchi[1,2,3]

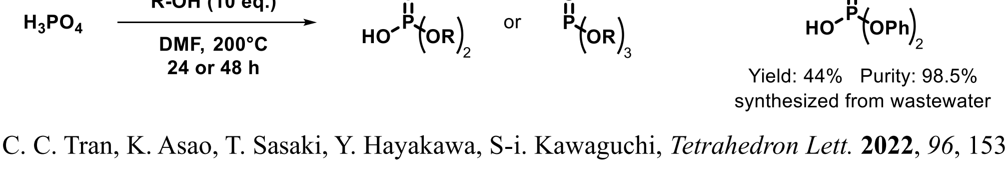
Phosphorus is a limited natural resource. Although large amounts of wastes containing phosphoric acid are discharged in the chemical and food industries, the reuse or recycling of them haven't been researched much before. In this work, we examined the conversion of these wastes into phosphate esters through a halogen-free phosphoric acid esterification. Although phosphate esters are easily synthesized from phosphorus chloride, the condensation of phosphoric acid and alcohols progresses hard due to its solubility and acidity. We present here a synthesis of phosphate triesters using phosphoric acid and some alcohols in addition to our previous report[1] regarding the synthesis of diaryl phosphates using phosphoric acid.

Furthermore, we are discussing the large-scale production (5 L scale) of phosphate esters using industrial wastewater and phytic acid (inositol hexakisphosphate) as the phosphorus source, as well as using phosphoric acid.

Keywords: Phosphate Esters; Phosphoric acid; Organophosphorus; Phytic acid; Phosphorus Recycling

リンは有限資源であるにもかかわらず、化学工業や食品工業分野では、リン酸としてリンを含む廃棄物が大量に排出されている。一方、これらに含まれるリン酸の再利用や有価物への変換に関する研究はあまり進んでいない。本研究ではリン酸を出発原料としたハロゲンフリーなリン酸エステル化反応により、廃リンのリン酸エステルとしての回収と再利用を検討した。リン酸エステルは一般的に塩化リンから製造される一方で、リン酸を原料としたリン酸エステル化反応は、リン酸の溶解性や酸性度の影響から縮合反応が進行しにくく、その反応に関する報告も限られている。本グループは以前の報告[1]であるリン酸と芳香族アルコールを用いたリン酸ジエステルの合成に加え、一部のアルコールにおいてはリン酸トリエステルの合成にも成功した。

本発表では、これらの反応を利用したリン酸エステルの大スケール試作（5 L）並びに、工業プロセス廃水やバイオマス由来原料としてフィチン酸（イノシトール六リン酸）を原料としたリン酸エステルの試作製造について報告する。



1. C. C. Tran, K. Asao, T. Sasaki, Y. Hayakawa, S-i. Kawaguchi, *Tetrahedron Lett.* **2022**, *96*, 153726.

エチレンジアミンによる PET 繊維へのアミノ基の導入とメイラード反応による着色

（大阪技術研）○大江 猛・吉村 由利香

Introduction of amino groups into PET fibers by ethylenediamine and their coloration by Maillard reaction (*Osaka Research Institute of Industrial Science and Technology*) ○Takeru Ohe, Yurika Yoshimura

Our laboratory has investigated the use of the Maillard reaction, a food coloring reaction, as an alternative to usual dyeing methods using synthetic dyes. In this study, we report that by pretreating PET fibers, which cannot be colored by the Maillard reaction, with ethylenediamine, we were able to color these PET fibers brown in the same way as protein fibers such as wool. However, the reaction between ethylenediamine and PET fibers involves cleavage of their ester bonds, which is the main chain of the polymer, and mechanical strength of the fibers decreases with the reaction. Therefore, we also investigated the reaction conditions to color the fibers darker while suppressing the decrease in their mechanical strength.

Keywords : PET Fiber; Ethylenediamine; Mechanical Strength; Maillard Reaction; Coloration

当研究室では、食品のメイラード反応を利用して、有害性が問題視されている合成染料の代替技術の開発に取り組んでいる。これまでに、メイラード反応に必要なアミノ基を有する羊毛、絹、ナイロンは着色できる一方で、衣料分野で広く利用されている綿やポリエステルの着色には適していない。最近の研究で、アミノ基を有するポリマーであるポリアリルアミンで前処理をすることによって綿を着色できることを確認した。ここでは、低分子であるエチレンジアミンでポリエステルを前処理した結果、キシロースなどの還元糖を用いてポリエステルを着色したので報告する。ただし、アミンとの反応では高分子の主鎖であるエステル結合の開裂が予測されるため、機械強度の低下の影響についても併せて検討した。

はじめに、エチレンジアミンおよびその水溶液中に PET 布を一定温度で含浸したところ、ジアミンによるアミノリシスによって布帛の機械強度は低下するものの、布帛表面にアミノ基が化学的に導入され、続くキシロースとの反応による布帛の着色が確認できた。次に、各温度における水溶液中のアミン濃度の影響について調べたところ、前処理の温度によってアミノリシスによる強度低下と着色の効果が一致しておらず（図 1）、検討した溶液の温度では 60℃の時に機械強度の低下を抑制しながら、効果的に PET 布を着色することが可能となった。

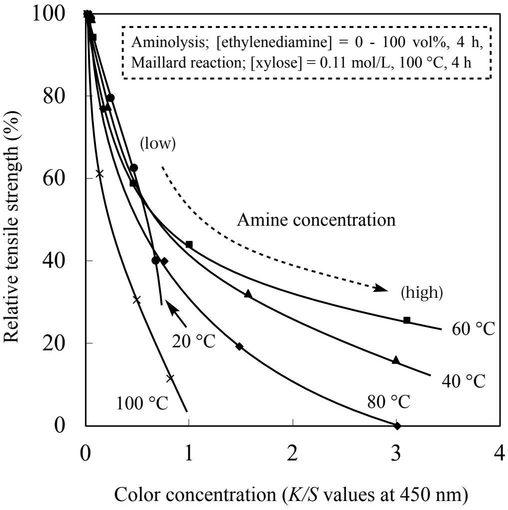


図 1 アミノリシス後の PET 布の引張強度とキシロースとの反応による着色濃度との関係

再生樹脂添加用アルデヒド捕捉剤の開発

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Novel Aldehyde Scavenger for Recycled Resins ([1]*Tosoh Corporation*) ○Yukinori Sudo,[1] Sayaka Kisanuki,[1] Takao Suzuki[1]

Material recycling of plastic waste is being conducted as part of efforts to reduce CO_2 emissions. On the other hand, the resulting recycled resins may have a problem of VOC emissions derived from impurities. To address this potent problem, we have developed AC103, an additive for resins.

AC103 is a silica gel-based agent modified with special organic functional groups and exhibits high capture performance for aldehydes. In fact, when AC103 was brought into contact with acetaldehyde (AA) gas, the capture rate was more than twice that of conventional scavenger (Figure 1). Furthermore, when PP or PE-based resins containing AC103 were heated at 65°C for 2 hours and the released VOCs were analyzed, AA emissions were reduced by more than 80% at blending rates of 0.1-0.3 wt% (Figure 2).

Keywords : Aldehyde Scavenger, Chemisorption, Resin Additive

近年、CO_2排出量削減に向けた取り組みの一環として、廃プラスチックのマテリアルリサイクルが行われている。一方、得られた再生樹脂は、不純物由来のVOCが問題となる場合がある。当社はこのような課題に対処すべく、樹脂添加剤AC103を開発した。

AC103は、シリカゲルを特殊な有機官能基で修飾した剤であり、アルデヒド類に対して高い捕捉性能を示す。実際に、AC103はアセトアルデヒド（AA）ガスに対し、従来品と比べ2倍以上の捕捉速度を示した（図1）。さらに、AC103を配合した樹脂試験片(PP系又はPE系)を65℃で2時間加熱し、放出されたVOCを分析したところ、配合率0.1−0.3wt%でAA放出量が80%以上低減した（図2）。

Figure 1. AA Capture Rate

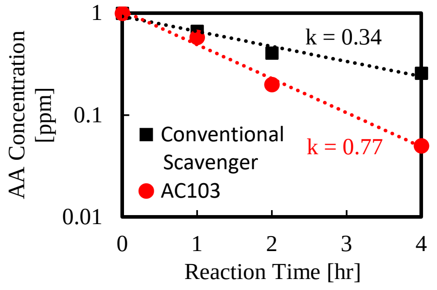

Figure 2. AA Emission from Resins