2024年3月21日(木)

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

2024年3月21日(木) 13:00 ~ 15:10 H937(9号館 [3階] 937)

[H937-4pm] 02. 理論化学・情報化学・計算化学

座長：堤 拓朗、満田 祐樹

日本語
13:00 ~ 13:20
[H937-4pm-01]

Nudged Elastic Band法を改良するために剛性の力を加えたNudged Elastic Stiffness Band法の開発

○満田 祐樹[1,2]、麻田 俊雄[1,2] (1. 大公大・理、2. 大公大・RIMED)

日本語
13:20 ~ 13:40
[H937-4pm-02]

Post-Sabatierを目指した電極触媒理論の開拓：活性と安定性の両立に向けて

○大岡 英史[1]、中村 龍平[1,2] (1. 理研CSRS、2. 東工大ELSI)

日本語
13:40 ~ 14:00
[H937-4pm-03]

様々なSiアルコキシドを前駆体原料として用いたゾル-ゲル低反射膜特性の機械学習による外挿予測

○倉上 拓真[1]、白木 康一[1]、松田 瑞穂[1] (1. 日本板硝子株式会社)

日本語
14:10 ~ 14:30
[H937-4pm-04]

Heterogeneous metric learning に基づく結晶構造予測

○草場 穫[1]、劉 暢[1]、吉田 亮[1,2,3] (1. 統計数理研究所、2. 総合研究大学院大学、3. 物質・材料研究機構)

日本語
14:30 ~ 14:50
[H937-4pm-05]

汎用ニューラルネットワークポテンシャルと生成モデルを用いた高活性合金触媒の原子配置探索

○久間 馨[1]、石川 敦之[2]、スーサンメニェス アスペラ[1]、古山 通久[1] (1. 信州大学、2. 東京工業大学)

英語
14:50 ~ 15:10
[H937-4pm-06]

Can LLMs be Lab Assistants?

○Gergely Juhasz[1] (1. Tokyo Institute of Technology)

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21日(木) 11:00 ~ 11:40 A1441(14号館 [4階] 1441)

[A1441-4am] 04. 物理化学—物性

座長：佐々木 陽一、竹清 貴浩

日本語

11:00 ~ 11:20

[A1441-4am-01]

高分子界面近傍における水素結合特性と赤外振動バンドの全原子解析

○石井 良樹[1]、鳥居 肇[2]、池本 夕佳[3]、鷲津 仁志[4] (1. 北里大学、2. 静岡大学、3. JASRI、4. 兵庫県立大学)

英語

11:20 ~ 11:40

[A1441-4am-02]

アルキル鎖長が脂肪族カルボン酸分子の金属酸化物表面への吸着挙動に与える影響について。

○雷 文瑾[1]、細見 拓郎[1]、劉 江洋[1]、田中 航[1]、高橋 綱己[1]、柳田 剛[1,2] (1. 東大院工、2. 九大先導研)

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21日(木) 13:00 ~ 14:00 A1444(14号館 [4階] 1444)

[A1444-4pm] 07. 無機化学

座長：細見 拓郎、中室 貴幸

英語

13:00 ~ 13:20

[A1444-4pm-01]

原子分解能電顕による炭酸化反応における多段階反応機構解析

○花澤 美幸[1]、Xin Li[1]、中室 貴幸[1]、中村 栄一[1] (1. 東京大学)

日本語

13:20 ~ 13:40

[A1444-4pm-02]

放射光X線を用いた$Ca_2(Mn,Ti)O_4$黒色遮熱顔料の局所構造解析

○岡 亮平[1]、早川 知克[1] (1. 名古屋工業大学)

英語

13:40 ~ 14:00

[A1444-4pm-03]

完全気相で成長過程を追跡可能な有機・無機原子層堆積システム

○松尾 秀明[1]、細見 拓郎[1]、Jiangyang Liu[1]、田中 航[1]、高橋 綱己[1]、柳田 剛[1,2] (1. 東大院工、2. 九大先導研)

アカデミックプログラム［Ｂ講演］ | 08. 触媒：口頭Ｂ講演

2024年3月21日(木) 9:00 ~ 11:30 A1457(14号館 [5階] 1457)

[A1457-4am] 08. 触媒

座長：森 浩亮、谷田部 孝文

日本語
9:00 ~ 9:20
[A1457-4am-01]

密度汎関数理論計算を用いた白金(111)によるメラミン吸着機構の解明

〇多田 幸平[1]、山崎 眞一[1]、朝日 将史[1]、五百蔵 勉[1] (1. 国立研究開発法人　産業技術総合研究所)

英語
9:20 ~ 9:40
[A1457-4am-02]

異種金属添加による非還元性酸化物上における水素スピルオーバーの発現とその拡散経路

〇俊 和希[1]、森 浩亮[1]、木俵 拓海[1]、山下 弘巳[1] (1. 阪大院工)

英語
9:40 ~ 10:00
[A1457-4am-03]

CeO_2のLewis酸塩基点および酸化還元特性の協働触媒作用による1,2-ジケトンの形式的脱カルボニル反応

〇松山 剛大[1]、谷田部 孝文[1]、山口 和也[1] (1. 東京大学)

日本語
10:10 ~ 10:30
[A1457-4am-04]

酸化銅サブナノ粒子の酸化触媒機能

〇田辺 真[1]、園部 量崇[2]、山元 公寿[2] (1. 福島県医大、2. 東工大化生研)

英語
10:30 ~ 10:50
[A1457-4am-05]

アンモ酸化活性を有するCu, Ruを添加したセリア系複合酸化物触媒の低温レドックス特性に伴う構造変化

〇Chaoqi CHEN[1]、邨次 智[1]、唯 美津木[1,2] (1. 名古屋大学、2. 名大物国セ)

日本語
10:50 ~ 11:10
[A1457-4am-06]

Ru-Ce系触媒のNH_3合成活性に影響を与える因子の解明

〇後藤 能宏[1]、菊川 将嗣[1]、山崎 清[1]、佐藤 彰倫[2]、眞中 雄一[3]、難波 哲哉[3]、松本 秀行[4]、大川原 真一[4] (1. 株式会社豊田中央研究所、2. トヨタ自動車株式会社、3. 産業技術総合研究所、4. 東京工業大学)

英語
11:10 ~ 11:30
[A1457-4am-07]

サイズ制御したCuFe、CuRu合金ナノ粒子の調製と電解窒素還元反応への応用

〇張 凱朝[1]、佐々木 岳彦[1] (1. 東京大学大学院理学系研究科)

アカデミックプログラム［Ｂ講演］｜08. 触媒：口頭Ｂ講演

2024年3月21日(木) 13:00 ~ 15:30 A1458(14号館 [5階] 1458)

[A1458-4pm] 08. 触媒

座長：高田 剛、鈴木 肇

英語

13:00 ~ 13:20

[A1458-4pm-01]

サルバナイト型の黒色金属硫化物光カソードを利用したグリーン合成ガスを生成するための光電気化学セルの開発

○永塚 健悟[1]、山口 友一[1,2]、工藤 昭彦[1,2] (1. 東理大理、2. 東理大総研カーボンバリュー)

英語

13:20 ~ 13:40

[A1458-4pm-02]

Ru(II)-Re(I)二核錯体とC_3N_4 の複合型CO_2還元光触媒におけるOs(II)錯体光増感剤の添加効果

○田中 寿弥[1]、玉置 悠祐[2]、前田 和彦[1]、石谷 治[1,3] (1. 東京工業大学、2. 産業技術総合研究所、3. 広島大院先進理工)

日本語

13:40 ~ 14:00

[A1458-4pm-03]

半導体表面への位置選択的なCO_2還元反応活性点の設計を指向した、光還元重合によるハイブリッド光触媒の開発

○榊原 教貴[1]、Ewan McQueen[2]、Sebastian Sprick[2]、石谷 治[1,3] (1. 東工大、2. ストラスクライド大、3. 広島大)

日本語

14:10 ~ 14:30

[A1458-4pm-04]

電解合成した熱非平衡金属間化合物によるCO_2電解還元

○幸林 竜也[1]、吉川 聡一[1]、渡辺 剛[2]、本間 徹生[2]、山添 誠司[1] (1. 東京都立大学、2. JASRI)

日本語

14:30 ~ 14:50

[A1458-4pm-05]

1 A/cm^{2}を超える電流密度でのCO_2電解還元反応

○神谷 和秀[1]、井上 明哲[1]、Tengyi Liu[1]、原田 隆史[1]、中西 周次[1] (1. 大阪大学)

英語

14:50 ~ 15:10

[A1458-4pm-06]

Cu/M表面合金ナノキューブ(M=Pd,Pt,Ir,Ru)の合成と電気化学的CO_2還元特性の系統的制御

○小林 浩和[1]、引野 幸枝[1]、山内 美穂[1,2,3,4] (1. 九大K-NETs、2. 九大先導研、3. 九大I2CNER、4. 東北大AIMR)

英語

15:10 ~ 15:30

[A1458-4pm-07]

金属3Dプリンティング及び選択的電気化学的溶解で設計されたCO2メタン化のためのNi磁気触媒反応器

○金 孝鎭[1]、森 浩亮[1]、中野 貴由 貴由 [1]、山下 弘巳[1] (1. 大阪大学)

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21日(木) 13:00 ~ 15:40 F1231(12号館 [3階] 1231)

[F1231-4pm] 09. 錯体化学・有機金属化学

座長：谷藤 一樹、福井 智也

日本語
13:00 ~ 13:20
[F1231-4pm-01]
N_2型の電子配置を有する$Pd_2Au_{17}(PR_3)_{10}Cl_7$クラスターの合成

○齋藤 亮平[1]、水畑 吉行[1]、磯﨑 勝弘[1]、中村 正治[1] (1. 京都大学)

英語
13:20 ~ 13:40
[F1231-4pm-02]
リン酸水素イオンがオキシドあるいはヒドロキシド二重架橋コアに架橋したルテニウム二核錯体の性質

○三澤 智世[1]、長尾 宏隆[1] (1. 上智大理工)

日本語
13:40 ~ 14:00
[F1231-4pm-03]
α-シクロデキストリン（CDX）に糸通しした1,12-ジアミノドデカン（don）の両末端に異なるコバルト(III)錯体をもつロタキサンの合成

○荻野 博[1]、猪俣 慎二[2]、笠井 香代子[3] (1. 東北大学、2. 福島大学、3. 宮城教育大学)

英語
14:00 ~ 14:20
[F1231-4pm-04]
NHC/ピリジル混合系配位子を用いた第10族遷移金属錯体の合成と反応性

○岡村 将也[1]、小花 咲季[1]、今泉 公太[1]、北原 美彩[1]、鈴木 伶奈[1]、引地 史郎[1] (1. 神奈川大)

日本語
14:20 ~ 14:40
[F1231-4pm-05]
ホウ素置換シリルリチウムの合成，反応および構造

小和田 雄太[1]、○河内 敦[2] (1. 法政大学大学院理工学研究科応用化学専攻、2. 法政大学生命科学部環境応用化学科)

英語
14:40 ~ 15:00
[F1231-4pm-06]
求核的アルミニウムと求電子的アルミニウムの反応によるAl-Al結合の構築

○山梨 遼太朗[1]、水谷 奏太[1]、山下 誠[1] (1. 名古屋大学大学院)

英語
15:00 ~ 15:20
[F1231-4pm-07]
大環状分子を配座固定できる拡張中空錯体の固相テンプレート合成

○飯塚 健太[1]、竹澤 浩気[1]、藤田 誠[1,2] (1. 東大、2. 分子研)

英語
15:20 ~ 15:40

[F1231-4pm-08]

アズレン誘導体を配位子とした金属錯体の合成とその構造解析

○岩品 達矢[1]、山本 一樹[1]、郡司 天博[1] (1. 東京理科大学)

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21日(木) 13:00 ~ 15:10 F1232(12号館 [3階] 1232)

[F1232-4pm] 09. 錯体化学・有機金属化学

座長：浦 康之、中島 裕美子

英語

13:00 ~ 13:20

[F1232-4pm-01]

Ruレドックス光増感部の還元力がRu(II)-Re(I)超分子光触媒のCO_2還元光触媒能に及ぼす影響

○鴨川 径[1]、石谷 治[1,2] (1. 東工大理、2. 広島大院先進理工)

英語

13:20 ~ 13:40

[F1232-4pm-02]

Electrocatalytic Reduction of Low Concentration CO_2 to CO Using Phenol and a Re(I) complex

○Siby Mathew[1], Osamu Ishitani [1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

英語

13:40 ~ 14:00

[F1232-4pm-03]

トリオルガノヒドロシランからのシリレン発生を利用したイリジウム触媒分子間シリレントランスファー反応

○宋 ユンハオ[1]、杉野目 道紀[1] (1. 京都大学)

英語

14:10 ~ 14:30

[F1232-4pm-04]

三配位ホウ素ルイス酸部位を有する弱配位アニオンによるイリジウム触媒反応の選択性制御

○萬代 遼[1]、岩﨑 孝紀[1]、野崎 京子[1] (1. 東大)

英語

14:30 ~ 14:50

[F1232-4pm-05]

Electrochemical Homogeneous CO_2 Reduction Catalyzed by N-Heterocyclic Carbene Stabilized Au-Nanoclusters

○Samuel Jacob[1], Joey DeJesus[1], Masakazu Nambo[1,2], Cathleen Crudden[1,3,4] (1. Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya, Aichi, Japan, 2. Department of Chemistry, Graduate School of Science, Nagoya University; Furo, Chikusa, Nagoya, Aichi, Japan, 3. Department of Chemistry, Queen’s University, Chernoff Hall, Kingston Ontario, Canada, 4. Carbon to Metal Coating Institute, Queen’s University, Kingston, Ontario, K7L 3N6, Canada)

英語

14:50 ~ 15:10

[F1232-4pm-06]

超分子反応場を有する金ナノクラスターの触媒的アルキン変換反応への応用

○井芹 建太[1]、磯﨑 勝弘[1]、中村 正治[1] (1. 京都大学)

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21日(木) 13:00 ~ 15:10 F1233(12号館 [3階] 1233)

[F1233-4pm] 09. 錯体化学・有機金属化学

座長：榎本 真哉、志賀 拓也

英語

13:00 ~ 13:20

[F1233-4pm-01]

二酸化炭素に応答する多孔性磁石：電荷移動型層状配位格子における常磁性相から反強磁性相の創出

○高坂 亘[1,2]、張 俊[3]、刘　新[1,2]、甘水 君佳[4]、北河 康隆[4] (1. 東北大金研、2. 東北大院理、3. 武漢大、4. 阪大院基礎工)

英語

13:20 ~ 13:40

[F1233-4pm-02]

Photoinduced magnetization in organometallic and organic compounds

○Verner Saeaesk[1] (1. Kyushu Universtiy)

英語

13:40 ~ 14:00

[F1233-4pm-03]

Thermal and Light-induced Switching Effects Based on Fe(II)-Hg(II) Spin-crossover Networks

○Guanping Li[1], Olaf Stefanczyk[1], Kunal Kumar[1], Koji Nakabayashi[1], Kenta Imoto[1], Guillaume Chastanet[2], Shin-ichi Ohkoshi[1] (1. Department of Chemistry, School of Science, University of Tokyo, 2. Université de Bordeaux, ICMCB)

英語

14:10 ~ 14:30

[F1233-4pm-04]

水素結合型スピンクロスオーバー錯体を用いたプロトン伝導性超分子構造体の開発

○小林 文也[1]、田所 誠[1] (1. 東理大理)

日本語

14:30 ~ 14:50

[F1233-4pm-05]

1,2-ジチオシュウ酸配位子が架橋する2次元鉄混合原子価錯体における積層構造と磁気挙動の相関

○金友 拓哉[1]、澤柳 佑希[1]、遠藤 翼[1]、岡澤 厚[2]、榎本 真哉[1] (1. 東理大、2. 早大)

英語

14:50 ~ 15:10

[F1233-4pm-06]

S=1/2銅(II)置換Keggin型スルホタングステン酸のスピン-格子緩和挙動

○石崎 聡晴[1]、尾関 智二[1] (1. 日大)

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21日(木) 13:00 ~ 15:10 F1234(12号館 [3階] 1234)

[F1234-4pm] 09. 錯体化学・有機金属化学

座長：松岡 亮太、川守田 創一郎

英語

13:00 ~ 13:20

[F1234-4pm-01]

フェニルアゾメチンデンドリマーへの貴金属-卑金属の混合集積

○飯塚 忠寿[1]、森合 達也[1]、塚本 孝政[2]、葛目 陽義[3]、今岡 享稔[1]、山元 公寿[1] (1. 東工大化生研、2. 東大生研、3. 山梨大学クリーンエネルギー研究センター)

英語

13:20 ~ 13:40

[F1234-4pm-02]

共焦点レーザー顕微鏡を用いたレニウム(Ⅰ)錯体分子性結晶のベイポクロミック相転移及び微動の観察

○馬 驍[1]、榎本 恭子[1]、石井 和之[1]、松田 雄貴[2]、阿部 正明[2] (1. 東大生研、2. 兵庫県立大院理)

英語

13:40 ~ 14:00

[F1234-4pm-03]

柔軟な発光性錯体ネットワーク結晶の創製と構造ダイナミクス観測

○松田 雄貴[1]、中村 瞭汰[1]、小澤 芳樹[1]、田原 圭志朗[1]、小野 利和[2]、吉成 信人[3]、今野 巧[3]、杉本 邦久[4]、小林 慎太郎[5]、河口 彰吾[5]、阿部 正明[1] (1. 兵庫県立大院理、2. 九大院工、3. 阪大院理、4. 近畿大理工、5. SPring-8/JASRI)

日本語

14:10 ~ 14:30

[F1234-4pm-04]

温度および圧力効果に基づく一次元d^8金属錯体の金属間距離と集積発光の詳細検討

○吉田 将己[1]、三谷 開[1]、瀬川 海斗[1]、江口 大地[1]、玉井 尚登[1]、加藤 昌子[1] (1. 関学大)

日本語

14:30 ~ 14:50

[F1234-4pm-05]

塩基性水溶液中で二酸化炭素によって誘起されるN^C^N型白金(II)錯体の自己集合

○服部 伸吾[1]、三田 博之[1]、篠﨑 一英[1] (1. 横浜市立大学)

英語

14:50 ~ 15:10

[F1234-4pm-06]

Au(I)錯体を基盤とした配位高分子の結晶サイズに依存した二重発光特性

○芳野 遼[1]、江原 巧[2]、宮田 潔志[2]、恩田 健[2]、宮坂 等[1] (1. 東北大金研、2. 九大院理)

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21日(木) 9:30 ~ 11:30 E1111(11号館 [1階] 1111)

[E1111-4am] 10. 有機化学―有機金属化合物

座長：小西 彬仁、上野 雅晴

英語

9:30 ~ 9:50

[E1111-4am-01]

芳香族基質の選択的活性化を指向したカゴ型ホウ素錯体の合成：π-ポケットへの複素環導入による効果

〇筒井 裕哉[1]、小西 彬仁[1,2]、安田 誠[1,2] (1. 阪大院工、2. ICS-OTRI)

英語

9:50 ~ 10:10

[E1111-4am-02]

アミノ酸の還元的アルキル化を志向した、トリアリールボランライブラリーの構築および機械学習を用いた触媒構造最適化

〇久田 悠靖[1]、鷲尾 隆[2]、滝澤 忍[3]、生越 専介[1]、星本 陽一[1,4] (1. 大阪大学大学院工学研究科、2. 大阪大学産業科学研究所、産業科学AIセンター、3. 大阪大学産業科学研究所、4. 大阪大学大学院工学研究科附属フューチャーイノベーションセンター)

英語

10:10 ~ 10:30

[E1111-4am-03]

カリウム還元剤を用いたアルキンの*anti*二重ホウ素化

〇張 紫薇[1]、黒木 尭[1]、依光 英樹[1] (1. 京都大学)

英語

10:50 ~ 11:10

[E1111-4am-04]

シクロプロパノールを用いたシクロプロペンの立体選択的ヒドロキシアリル化：NHCによるエノール化亜鉛ホモエノラートの反応制御

〇築地 健人[1]、金本 和也[1]、松本 有正[2]、吉戒 直彦[1] (1. 東北大学、2. 奈良女子大学)

日本語

11:10 ~ 11:30

[E1111-4am-05]

亜鉛/フッ素カルベノイド： 調製、安定性、構造および求核的モノフルオロアルキル化反応への応用

〇宮本 公平[1]、川口 瑛美子[1]、森崎 一宏[1]、佐藤 美洋[1] (1. 北大院薬)

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21日(木) 9:30 ~ 11:30 E1112(11号館 [1階] 1112)

[E1112-4am] 10. 有機化学—有機金属化合物

座長：栗山 翔吾、藤田 健一

日本語
9:30 ~ 9:50
[E1112-4am-01]

アニオン性PCP型ピンサー配位子を有する鉄錯体を触媒としたエーテル類のC(sp^3)–H結合ホウ素化反応

〇栗山 翔吾[1]、坂田 健[2]、西林 仁昭[1] (1. 東京大学大学院工学系研究科、2. 東邦大学薬学部)

英語
9:50 ~ 10:10
[E1112-4am-02]

鉄錯体を光触媒とする易酸化性の官能基を有するカルボン酸の脱炭酸－官能基化反応

〇玉木 颯太[1]、草本 哲郎[1]、劒 隼人[1] (1. 阪大院基礎工)

英語
10:10 ~ 10:30
[E1112-4am-03]

エンインの環化反応を経る鉄触媒を用いた芳香族ケトンのC–H官能基化反応

〇北澤 瑶一[1]、河内 卓彌[1]、垣内 史敏[1] (1. 慶大理工)

日本語
10:50 ~ 11:10
[E1112-4am-04]

Hoveyda-Grubbs型触媒のオレフィンメタセシス活性に対する配位子上のカルコゲン元素の効果

〇衣川 翼[1]、廣田 俊[1]、松尾 貴史[1] (1. 奈良先端大・物質創成)

英語
11:10 ~ 11:30
[E1112-4am-05]

ルテナビシクロボロヒドリド錯体(RUCY®-BH)を用いた塩基無添加条件下でのケトンの不斉水素化反応およびアリルアルコールの不斉ヒドロアミノ化反応

〇石坂 智洋[1]、中山 裕治[1]、峠 太一郎[1]、結城 大和[1]、松村 和彦[1]、百合野 大雅[2,3]、大熊 毅[2,3] (1. 高砂香料工業株式会社、2. 北大院工、3. 北大フロンティア化学教育研究センター)

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21日(木) 13:00 ~ 14:20 E1122(11号館 [2階] 1122)

[E1122-4pm] 12. 有機化学—有機結晶・超分子化学

座長：井手 雄紀、湯浅 順平

英語
13:00 ~ 13:20
[E1122-4pm-01]

ロタキサン構造を介してメソゲンコアとフレキシブルテールとを一体化させたイオン性液晶の設計

〇鷲野 豪介[1]、西村 涼[2]、宍戸 厚[1] (1. 東工化生研、2. 東工大物質)

英語
13:20 ~ 13:40
[E1122-4pm-02]

二次元COFの積層構造変形による蛍光スイッチング

〇葉 思遠[1]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工)

英語
13:40 ~ 14:00
[E1122-4pm-03]

高出力する光駆動結晶の機械学習による材料設計と条件最適化

〇石崎 一輝[1]、朝日 透[1]、谷口 卓也[1] (1. 早稲田大学)

日本語
14:00 ~ 14:20
[E1122-4pm-04]

偏光照射下における光駆動自励振動結晶の挙動の反応速度論に基づいた数理モデルからの解析

〇景山 義之[1]、松浦 真紀子[1] (1. 北大)

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

2024年3月21日(木) 13:00 ~ 15:10 E1123(11号館 [2階] 1123)

[E1123-4pm] 12. 有機化学—有機結晶・超分子化学

座長：土戸 良高、木村 真也

日本語
13:00 ~ 13:20
[E1123-4pm-01]

超分子ゲルにより時空間的に制御されたフォトクロミック反応

○永井 邑樹^{1}、藤﨑 壮太^{1}、岡安 祥徳^{1}、小林 洋一^{1,2} (1. 立命館大学、2. JSTさきがけ)

日本語
13:20 ~ 13:40
[E1123-4pm-02]

アルキル化ジフェニルアントラセン液体の物性に及ぼすアトロプ異性体の効果

Xiao Zheng^{1,2}、名倉 和彦^{1}、松下 能孝^{1}、○中西 尚志^{1,2} (1. 物質・材料研究機構、2. 北海道大学)

英語
13:40 ~ 14:00
[E1123-4pm-03]

Chirality-controlling supramolecular assemblies of acidic and basic pillar[5]arenes

○Dehui Tuo^{1,2}, Shixin Fa^{3}, Seigo Tanaka ^{2}, Kenichi Kato^{2}, Tomoki Ogoshi^{2,1} (1. WPI-NanoLSI, Kanazawa Univ., 2. Grad.Sch.Eng., Kyoto Univ., 3. Northwestern Polytechnical Univ.)

英語
14:10 ~ 14:30
[E1123-4pm-04]

固液界面におけるC_{3h}対称性コアを持つ分子の自己識別を利用した階層的なホモキラル分子集合体の構築

○前田 松祐^{1}、Steven De Feyter^{2}、田原 一邦^{3} (1. 明大院理工、2. ルーバン大化、3. 明大理工)

日本語
14:30 ~ 14:50
[E1123-4pm-05]

温度に依存して左右にねじれた立体配座が変換する1:1ホスト-ゲストシステムの解析

○鈴木 望^{1}、田浦 大輔^{2}、古田 裕亮^{2} (1. 神大、2. 名城大)

英語
14:50 ~ 15:10
[E1123-4pm-06]

イソオキサゾール骨格を側鎖にもつ白金錯体集合体の攪拌により誘導されるキロプティカル応答

○吉田 真也^{1,2}、平尾 岳大^{1}、灰野 岳晴^{1,2} (1. 広島大院先進理工、2. 広島大WPI-SKCM²)

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21日(木) 13:00 ~ 14:50 🏛 E1131(11号館 [3階] 1131)

[E1131-4pm] 12. 有機化学―有機結晶・超分子化学

座長：林 正太郎、燒山 佑美

英語
13:00 ~ 13:20
[E1131-4pm-01]

Triptycene Frameworks for Orientational Control over Electroactive Subunits in STM Break-Junction

〇Colin John Martin[1], Tomoya Fukui[1], Ryosuke Takehara[1], Shintaro Fujii[2], Takanori Fukushima[1] (1. CLS, Tokyo Tech., 2. School of Science, Tokyo Tech.)

日本語
13:20 ~ 13:40
[E1131-4pm-02]

アルキル鎖長に依存した高移動度N字型有機半導体分子の結晶多形・相転移挙動の実測とシミュレーション

〇三谷 真人[1]、Craig Yu[2]、沢辺 千鶴[2]、三津井 親彦[2]、關 拓和[3]、篠崎 雄大[3]、渡辺 豪[3]、橋爪 大輔[4]、熊谷 翔平[1]、竹谷 純一[2]、岡本 敏宏[1] (1. 東京工業大学、2. 東京大学、3. 北里大学、4. 理化学研究所)

英語
13:50 ~ 14:10
[E1131-4pm-03]

ハロゲンおよびエチニルを置換したカルド型芳香族ニトロキシド誘導体の固体磁気特性

〇瀧井 優臣[1]、三浦 洋平[1]、吉岡 直樹[1] (1. 慶應義塾大学)

日本語
14:10 ~ 14:30
[E1131-4pm-04]

凝集誘起増強発光性を示すフマロニトリル系分子から成る低次元単結晶レーザー

〇松尾 匠[1]、林 正太郎[1] (1. 高知工科大学)

日本語
14:30 ~ 14:50
[E1131-4pm-05]

ねじり天秤分子モデルを用いた芳香環–フラーレン間の非共有結合性相互作用の定量評価

〇山田 道夫[1]、佐原 弘起[1]、栗原 幸代[1]、小泉 政彰[1]、辻 香澄[1]、成田 陽奈[1]、前田 優[1]、鈴木 光明[2] (1. 東京学芸大学、2. 城西大学)

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

2024年3月21日(木) 13:00 ~ 14:00 E1132(11号館 [3階] 1132)

[E1132-4pm] 13. 有機化学—反応機構・光化学・電気化学

座長：臼井 聡、高橋 明

日本語

13:00 ~ 13:20

[E1132-4pm-01]

フッ素置換アクリジニウムをフォトレドックス触媒としたベンゼンの空気酸化反応

○赤尾 祐介[1,2]、大野 祥平[2]、板橋 勇輝[3]、淺原 時泰[1]、小泉 靖明[1]、田井 国憲[1]、近藤 一見[1]、長瀬 剛[1]、井上 豪[2]、大久保 敬[3,4] (1. 大塚製薬（株）、2. 阪大院薬、3. 阪大先導的学際研、4. 阪大高等共創研)

英語

13:20 ~ 13:40

[E1132-4pm-02]

Mechanisms and the Role of Lewis Acids in Transition Metal Catalysts for C-O, C-F, and H-H Activation

○Panida Surawatanawong[1] (1. Mahidol University, Faculty of Science)

日本語

13:40 ~ 14:00

[E1132-4pm-03]

ラジカルジホスフィン化による歪んだ小分子からのリン配位子合成

○美多 剛[1,2]、Chandu G. Krishnan[1,2]、髙野 秀明[1,2]、勝山 瞳[1,2]、林 裕樹[1,2]、神名 航[3]、前田 理[1,2,3] (1. 北大WPI-ICReDD、2. JST-ERATO、3. 北大院理)

アカデミックプログラム［Ｂ講演］｜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21日(木) 13:00 ~ 14:20 E1141(11号館 [4階] 1141)

[E1141-4pm] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：隅田 有人、土肥 寿文

日本語

13:00 ~ 13:20

[E1141-4pm-01]

酵素反応を利用した光学活性なデルタラクトン類の合成と香気評価

○川崎 正志[1]、岡田 卓哉[2]、田中 康雄[3]、豊岡 尚樹[2] (1. 富山県立大学、2. 富山大学、3. 大洋香料株式会社)

英語

13:20 ~ 13:40

[E1141-4pm-02]

水素結合供与触媒による、α位ヘテロ原子置換アミノニトリルの不斉合成

○小山田 悠介[1]、藤井 未来[1]、中村 修一[1] (1. 名古屋工業大学)

英語

13:40 ~ 14:00

[E1141-4pm-03]

重金属応答性新規C4N4蛍光プローブの創製

○公平 実希[1,2]、Harald Gröger[2]、熊谷 直哉[1,3] (1. 慶大院薬、2. Bielefeld University、3. 微化研)

英語

14:00 ~ 14:20

[E1141-4pm-04]

自己集合環状3量体分子[HyAl-Py]$_3$の合成と機能開発

○鶴岡 航太朗[1]、熊谷 直哉[1,2] (1. 慶應義塾大学大学院、2. 微生物科学研究所)

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21日(木) 13:00 ~ 14:50 E1142(11号館 [4階] 1142)

[E1142-4pm] 15. 有機化学―脂肪族・脂環式化合物，新反応技術

座長：齋藤 由樹、浅野 圭佑

英語
13:00 ~ 13:20
[E1142-4pm-01]
テトラコナゾールの連結・連続フロー合成
○笹谷 将洋[1]、石谷 暖郎[1]、小林 修[1] (1. 東京大学)

英語
13:20 ~ 13:40
[E1142-4pm-02]
ビーズミル法を用いたポリエチレンテレフタレートの触媒的低温解重合反応
○川瀬 智也[1]、石谷 暖郎[1]、小林 修[1] (1. 東大)

英語
13:40 ~ 14:00
[E1142-4pm-03]
ジアザベンゾアセナフテン光酸化還元触媒によるエステルの多電子還元
○服部 修佑[1,2]、奥村 慎太郎[1,2]、魚住 泰広[1,2] (1. 分子研、2. 総研大)

英語
14:10 ~ 14:30
[E1142-4pm-04]
トランスシクロオクテンを利用した触媒的臭素化におけるBr_2捕捉剤の開発
○村田 竜一[1]、下道 謙太[1]、平松 将嗣[1]、松原 誠二郎[1]、浦口 大輔[2]、浅野 圭佑[2] (1. 京大院工、2. 北大触媒研)

英語
14:30 ~ 14:50
[E1142-4pm-05]
光酸化還元/コバルト協働触媒によるアルケンの分岐選択的ヒドロハロゲン化反応
○渋谷 将太郎[1]、長尾 一哲[1]、大宮 寛久[1] (1. 京大化研)

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21日(木) 13:00 ~ 14:20 E1143(11号館 [4階] 1143)

[E1143-4pm] 15. 有機化学—脂肪族・脂環式化合物，新反応技術

座長：村田 貴嗣、波多野 学

日本語
13:00 ~ 13:20
[E1143-4pm-01]

ジボロン酸無水物触媒によるアミン水溶液を用いた脱水縮合アミド化反応の開発

〇岩澤 太陽[1]、高橋 那央也[2]、嶋田 修之[1] (1. 日本大、2. 北里大)

日本語
13:20 ~ 13:40
[E1143-4pm-02]

N-トリフルオロメタンスルホニルイミダゾールを用いる高化学選択的トリフリル化反応

〇平田 翼[1]、波多野 学[1]、新田 純基[2]、山﨑 貴子[2]、富田 廉[2]、秋山 勝宏[2] (1. 神戸薬科大学、2. セントラル硝子株式会社)

日本語
13:40 ~ 14:00
[E1143-4pm-03]

Weinrebアミド型Horner–Wadsworth–Emmons（HWE）試薬を用いたHWE反応の実験的機構解析研究

村田 貴嗣[1]、〇筒井 久澄[1]、椎名 勇[1] (1. 東京理科大学)

日本語
14:00 ~ 14:20
[E1143-4pm-04]

第三級脂肪族アミンのγ位選択的な官能基化[2]

〇榊原 陽太[1]、濱脇 康佑[1]、平手 和希[1]、千葉 将真[1]、寺田 昂祐[1]、木之下 拓海[1]、村上 慧[1] (1. 関西学院大学)

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

2024年3月21日(木) 13:00 ~ 15:40 H935(9号館 [3階] 935)

[H935-4pm] 16. 天然物化学・ケミカルバイオロジー

座長：高橋 大介、佐々木 要

日本語
13:00 ~ 13:20
[H935-4pm-01]

アルドール反応を用いたN末端アミノ酸の化学修飾

○花屋 賢悟[1]、和田 雄貴[2]、河野 正規[2]、田口 和明[1]、松元 一明[1]、東林 修平[1]、須貝 威[1] (1. 慶應義塾大学、2. 東京工業大学)

英語
13:20 ~ 13:40
[H935-4pm-02]

α-ヒドラジノ酸含有大環状ペプチドのin vitroセレクションと薬剤候補の探索

○松本 聡美[1]、加藤 敬行[1]、菅 裕明[1] (1. 東京大学)

英語
13:50 ~ 14:10
[H935-4pm-03]

分子内水素結合により加速される2,5-ジケトピペラジン形成反応を用いたタグ付きチオエステル合成

○中津 幸輝[1]、林 剛介[1]、村上 裕[1,2] (1. 名大院工、2. 名大ナノライフ)

日本語
14:10 ~ 14:30
[H935-4pm-04]

光応答性RNA結合低分子を用いたUGGAAリピートRNAの相分離体形成の光誘導とメカニズム解析

○藤原 侑亮[1,2]、柴田 知範[1,2]、堂野 主税[1,2]、中谷 和彦[1,2] (1. 大阪大学　産業科学研究所、2. JST, CREST)

英語
14:40 ~ 15:00
[H935-4pm-05]

脂質ナノ粒子化セルフアジュバンティングがんワクチンの調製と機能評価

○伊藤 啓太[1]、真鍋 良幸[1,2]、大島 志乃[3]、亀谷 美恵[3]、真栄城 正寿[4]、渡慶次 学[4]、深瀬 浩一[1,2] (1. 阪大院理、2. フォアフロント研究センター、3. 東海大医、4. 北大院工)

英語
15:00 ~ 15:20
[H935-4pm-06]

酢酸菌由来リポ多糖部分構造の化学合成および機能評価

○山浦 遼生[1]、下山 敦史[1]、深瀬 浩一[1] (1. 大阪大学大学院)

英語
15:20 ~ 15:40
[H935-4pm-07]

4分枝シアリル*N*-グリカンの化学合成

○矢野 君晟[1]、真鍋 良幸[1,2]、深瀬 浩一[1,2] (1. 阪大院理、2. 阪大院理FRC)

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21日(木) 9:00 ~ 11:30 H931(9号館 [3階] 931)

[H931-4am] 17. 生体機能関連化学・バイオテクノロジー

座長：岡村 秀紀、石渡 明弘

日本語
9:00 ~ 9:20
[H931-4am-01]

毛髪トリートメント効果を有する有機酸とアミンの新規化合物合成

○片山 耕太郎[1]、宮本 紘幸[1]、望月 佑次[2]、新 菜摘[2]、山崎 祥子[3]、堀田 弘樹[1,4]、辻野 義雄[4] (1. 神戸大学大学院海事科学研究科、2. ロート製薬株式会社、3. 奈良教育大学、4. 神戸大学大学院科学技術イノベーション研究科)

日本語
9:20 ~ 9:40
[H931-4am-02]

神経分化の誘導および蛍光特性を有するチエノピリジン誘導体

○園田 健登[1]、浅尾 和弥[1,2]、川口 真一[1,2]、川添 嘉徳[1,2] (1. 佐大農、2. 佐大院先進)

日本語
9:40 ~ 10:00
[H931-4am-03]

金触媒反応を引き金とする超分子ハイドロゲル形成

○山本 智也[1,2]、中村 亜希子[2]、向峯 あかり[2]、田中 克典[2,3] (1. 大阪大学・大学院工学研究科、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室、3. 東京工業大学・物質理工学院・応用化学系)

英語
10:00 ~ 10:20
[H931-4am-04]

NIR Fluorescence analysis of the trypsin enzyme using unsymmetrical squaraine dye-peptide conjugate.

○PRIYANKA Priyanka[1,2], Shekhar Gupta[1], Tamaki Kato[1] (1. Kyushu Institute of Technology,Japan, 2. Kyushu Institute of Technology, Japan)

英語
10:30 ~ 10:50
[H931-4am-05]

Near Infrared Fluorescent Detection of Protease Activity using Peptide-Bound Squaraine Dye

○Shekhar Gupta[1], Priyanka Balyan [1], Sai Kiran Mavileti[1], Shyam Sudhir Pandey[1], Tamaki Kato[1] (1. Kyushu Institute of Technology)

英語
10:50 ~ 11:10
[H931-4am-06]

がん代謝物との[3+2]付加環化反応を利用したRI内用療法

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

英語
11:10 ~ 11:30
[H931-4am-07]

RNA標的創薬を指向した新規RNA結合分子探索システムの開発

○長澤 瞭佑[1,2]、鬼塚 和光[1,2]、岩田 遼平[1,2]、小松 馨[3,4]、宮下 映見[3,4]、壇辻 さやか[4]、村瀬 裕貴[1,2]、小澤 眞美子[1]、齊藤 博英[3]、永次 史[1,2] (1. 東北大多元研、2. 東北大院理、3. 京大CiRA、4. xFOREST Therapeutics)

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21日(木) 9:00 ~ 11:30 H936(9号館 [3階] 936)

[H936-4am] 17. 生体機能関連化学・バイオテクノロジー

座長：細野 暢彦、川上 了史

英語
9:00 ~ 9:20
[H936-4am-01]

内部表面にピレンを化学修飾したタンパク質ナノケージTIP60の物性評価

○山下 舞佳[1]、宮本 憲二[1]、川上 了史[1] (1. 慶應義塾大学)

英語
9:20 ~ 9:40
[H936-4am-02]

オキシダーゼ模倣触媒作用のためのフェリチンケージ内でのヒスチジンクラスターの構築

○Tian Jiaxin[1]、Maity Basudev[1]、Pan Tiezheng[1]、Abe Satoshi[1]、Ueno Takafumi[1] (1. 東京工業大学)

英語
9:40 ~ 10:00
[H936-4am-03]

ナノ細孔への選択的吸着による変性タンパク質の除去

○武富 大空[1]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工)

英語
10:00 ~ 10:20
[H936-4am-04]

Tau由来ペプチドを融合した光応答性4量体タンパク質による微小管構造の光操作

○渡 宗英[1]、稲葉 央[1]、岩崎 崇[2]、角五 彰[3]、松浦 和則[1] (1. 鳥取大院工、2. 鳥取大院農、3. 京大院理)

日本語
10:30 ~ 10:50
[H936-4am-05]

蛍光タンパク質修飾人工ウイルス殻の細胞内自己集合

○坂本 健太郎[1]、山本 優香[1]、稲葉 央[1]、松浦 和則[1] (1. 鳥大院工)

日本語
10:50 ~ 11:10
[H936-4am-06]

SARS-CoV-2由来スパイクタンパク質を搭載したエンベロープウイルスレプリカの構築

○古川 寛人[1]、中村 圭祐[2]、稲葉 央[1]、佐々木 善浩[2]、秋吉 一成[2]、松浦 和則[1] (1. 鳥取大院工、2. 京大院工)

英語
11:10 ~ 11:30
[H936-4am-07]

Accurate Prediction of Protein pK_a by Geometric Deep Learning

○Shijie Xu[1], Akira Onoda[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido 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21日(木) 13:00 ~ 15:30 H931(9号館 [3階] 931)

[H931-4pm] 17. 生体機能関連化学・バイオテクノロジー

座長：森廣 邦彦、神谷 由紀子

英語
13:00 ~ 13:20
[H931-4pm-01]

FRETを応用した抗miRNA核酸の作用機序解析法の開発

〇朱 紅宇[1]、神谷 由紀子[1,2]、浅沼 浩之[1] (1. 名古屋大学、2. 神戸薬科大学)

日本語
13:20 ~ 13:40
[H931-4pm-02]

非環状型人工核酸からなる抗miR-21核酸の開発

〇神谷 由紀子[1,2]、佐藤 史経[2]、浅沼 浩之[2] (1. 神薬大、2. 名大)

英語
13:40 ~ 14:00
[H931-4pm-03]

アゾベンゼン塩基含有DNAアプタマーによる受容体活性の可逆的光制御

〇若野 将大[1]、村山 恵司[2]、植木 亮介、浅沼 浩之[2]、山東 信介[1] (1. 東京大学大学院工学系研究科、2. 名古屋大学大学院工学系研究科)

英語
14:10 ~ 14:30
[H931-4pm-04]

メチル化DNAが鎖置換能を持つDNAポリメラーゼに与える影響

〇富澤 美月[1]、渡邊 貴和子[1]、塚越 かおり[1]、池袋 一典[1] (1. 東京農工大学)

英語
14:30 ~ 14:50
[H931-4pm-05]

Vinyl-quinazolione derivatives-based RNA alkylation and the single-nucleotide resolution analysis by next generation sequencing

〇Yutong Chen[1,2], Kazumitsu Onizuka[1,2], Kaoru Richard Komatsu[3], Emi Miyashita[3,4], Kaho Maeta[3], Hirohide Saito[4], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku University, 2. Department of Chemistry, Graduate school of Science, Tohoku University, 3. xFOREST Therapeutics, 4. CiRA, Kyoto University)

英語
14:50 ~ 15:10
[H931-4pm-06]

弱酸性微小環境応答性人工核酸塩基を用いたがん選択的DNAアプタマーの開発

〇陳 鈺媛[1]、森廣 邦彦[1]、根本 祐衣[1]、市村 晃人[1]、植木 亮介[1]、山東 信介[1]、岡本 晃充[1] (1. 東京大学)

日本語
15:10 ~ 15:30
[H931-4pm-07]

フッ素官能基修飾核酸における修飾基の数とリンカー構造が細胞取り込みおよびsiRNAノックダウン機能に与える影響

〇高津 正子[1]、森廣 邦彦[1]、太田 有羽[1,2]、相川 光介[1]、岡添 隆[1,2]、岡本 晃充[1] (1. 東京大学、2. AGC株式会社)

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21日(木) 13:00 ~ 15:30 H932(9号館 [3階] 932)

[H932-4pm] 17. 生体機能関連化学・バイオテクノロジー

座長：中田 栄司、堂浦 智裕

日本語

13:00 ~ 13:20

[H932-4pm-01]

アデノシンA_{2A}受容体サブタイプ選択的な光応答性リガンドの開発およびその構造基盤

○鈴木 啓文[1]、堂浦 智裕[1]、荒谷 剛史[2]、浅田 秀基[2]、岩田 想[2]、清中 茂樹[1] (1. 名古屋大学、2. 京都大学)

日本語

13:20 ~ 13:40

[H932-4pm-02]

新規イメージングプローブによるシナプス可塑性時のAMPA受容体の精密動態解析

○曽我 恭平[1]、柴田 晃大[1]、Hansel Adriel[2]、藤原 孝彰[2]、南後 恵理子[2,3]、清中 茂樹[1] (1. 名古屋大学大学院・工、2. 東北大学・多元研、3. 理研 SPring-8)

日本語

13:40 ~ 14:00

[H932-4pm-03]

BODIPY類を骨格とする赤色および深赤色蛍光性分子による細胞および組織内脂質滴の可視化

○吉原 利忠[1]、宇田 梨紗[1]、飯島 鈴七[1]、嶋貫 真由子[1]、塩崎 秀一[1] (1. 群馬大)

日本語

14:00 ~ 14:20

[H932-4pm-04]

細胞内酸化還元ホメオスタシスを制御し得る低分子アロステリックジスルフィド/ジセレニド試薬

○三神 瑠美[1]、金村 進吾[2]、奥村 正樹[3]、荒井 堅太[1] (1. 東海大、2. 関学大、3. 東北大)

英語

14:30 ~ 14:50

[H932-4pm-05]

蛍光や生物発光を利用した生細胞内RNA動態の可視化解析

○吉村 英哲[1]、江口 正敏[1]、上田 善文[1]、小澤 岳昌[1] (1. 国立大学法人東京大学)

日本語

14:50 ~ 15:10

[H932-4pm-06]

組織内チオール代謝物イメージング及び組成解析を実現するTLC蛍光ラベル化剤の開発

○西原 達哉[1]、鈴木 我空[1]、西田 光輝[1]、塚目 莉加[1]、田邉 一仁[1] (1. 青山学院大学)

日本語

15:10 ~ 15:30

[H932-4pm-07]

新規ミスマッチ認識分子の創生とその特性

○武井 史恵[1]、山田 直生[1]、比留間 寿美代[1] (1. 防衛医科大学校)

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21日(木) 13:00 ~ 14:50 H936(9号館 [3階] 936)

[H936-4pm] 17. 生体機能関連化学・バイオテクノロジー

座長：田村 朋則、野中 洋

英語

13:00 ~ 13:20

[H936-4pm-01]

化学合成タンパク質のハイスループット合成を志向した、Diketopiperazineチオエステルペプチドの固相合成法開発

○中嶋 雄哉[1]、中津 幸輝[1]、林 剛介[1]、村上 裕[1,2] (1. 名大院工、2. 名大ナノライフ)

英語

13:20 ~ 13:40

[H936-4pm-02]

4量化する抗体軽鎖の会合挙動と3Dドメインスワッピング構造の解明

○酒井 隆裕[1]、山口 将平[1]、真島 剛史[1]、小林 直也[1]、段 練[2]、藤木 涼[2]、Kowit Hengphasatporn[2]、重田 育照[2]、緒方 英明[3]、一二三 恵美[4]、宇田 泰三[5]、廣田 俊[1] (1. 奈良先端大・先端科技、2. 筑波大・計算科学研究センター、3. 兵庫県大・院理、4. 大分大・研究マネジメント機構、5. 九州先端研・ナノテク)

英語

13:40 ~ 14:00

[H936-4pm-03]

ミセル形成チオール化合物による高濃度でのタンパク質フォールディング促進

○喜多村 真衣[1]、村岡 貴博[1,2] (1. 東京農工大学、2. 神奈川県立産業技術総合研究所)

日本語

14:10 ~ 14:30

[H936-4pm-04]

構造変化を干渉する分子ストッパーによるAMPA受容体のケモジェネティック制御

○三浦 裕太[1]、小島 憲人[1,2]、宮下 治[3]、堤 尚孝[4]、浜地 格[2]、山下 敦子[4]、清中 茂樹[1] (1. 名大、2. 京大、3. 理研、4. 岡大)

日本語

14:30 ~ 14:50

[H936-4pm-05]

N-acyl-N-aryl sulfonamide(ArNASA)反応基: タンパク質の化学修飾と不可逆阻害

○河野 正晴[1]、村川 駿介[1]、杉原 大[2]、田村 朋則[1]、浜地 格[1,3] (1. 京都大学大学院、2. 京都大学、3. JST ERATO)

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21日(木) 9:00 ~ 11:30 D342(3号館 [4階] 342)

[D342-4am] 18. 高分子

座長：樋口 昌芳、福元 博基

日本語
9:00 ~ 9:20
[D342-4am-01]

有機アルミニウム触媒による不飽和炭化水素モノマーの重合・共重合

〇木村 なな子[1]、竹内 大介[1] (1. 弘前大学)

英語
9:20 ~ 9:40
[D342-4am-02]

Substituent effects of ether-functionalized propylenes on scandium-catalyzed copolymerization with ethylene

〇Mingjun Chi[1,2], Hao Wang[2], Masayoshi Nishiura[2], Lin Huang[2], Haoran Zhang[2], Zhaomin Hou[1,2] (1. Saitama University, 2. RIKEN)

英語
9:40 ~ 10:00
[D342-4am-03]

耐アルカリ特性に優れたトリアリールスルホニウム塩を含む高分子材料の開発と応用

〇今井 智大[1]、一二三 遼祐[1]、稲木 信介[1]、冨田 育義[1] (1. 東京工業大学)

英語
10:00 ~ 10:20
[D342-4am-04]

Synthesis of functional polyesters containing cleavable linkages and AIE luminogen via Passerini-type multicomponent polymerizations

〇Chih-Feng HUANG[1], Li-Chieh CHOU[1], Yi-Shen HUANG[1] (1. National Chung Hsing University)

英語
10:30 ~ 10:50
[D342-4am-05]

過酸化水素を酸化剤として用いたベンゼンからヒドロキノン重合体の一段階合成

〇杉本 秀樹[1]、宮田 憲伸[1]、中野 晟志[2]、東村 秀之[2]、伊東 忍 (1. 大阪大学、2. 岡山理科大学)

英語
10:50 ~ 11:10
[D342-4am-06]

A New Synthetic Approach of Metallosupramolecular Polymer and its Electrochromic Application

〇Satya Ranjan Jena[1], Masayoshi HIGUCHI[1], Chih-Wei Hu[1] (1. National Institute for Materials Science)

日本語
11:10 ~ 11:30
[D342-4am-07]

主鎖骨格に含フッ素ベンゾジチオフェンを用いたπ共役高分子の開発および光学特性評価

〇奥崎 秀俊[1]、佐藤 世良[1]、吾郷 友宏[2]、久保田 敏夫[1]、福元 博基[1] (1. 茨城大学大学院理工学研究科、2. 兵庫県立大学大学院理学研究科)

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21日(木) 13:00 ~ 15:10 D341(3号館 [4階] 341)

[D341-4pm] 18. 高分子

座長：松岡 慶太郎、西村 達也

日本語
13:00 ~ 13:20
[D341-4pm-01]

水溶性ナイロンの系統的評価に基づくLCST型温度応答性の理解

○菅野 明梨[1]、松岡 慶太郎[1,2]、佐田 和己[1,2] (1. 北大院総化、2. 北大院理)

英語
13:20 ~ 13:40
[D341-4pm-02]

精密ラジカル重合法による液晶高分子修飾ZnOナノロッドの合成と配向挙動

○中野 果穂[1]、久保 祥一[1]、宍戸 厚[1] (1. 東工大化生研)

英語
13:40 ~ 14:00
[D341-4pm-03]

Mechano-responsive supramolecular hydrogel driven by stretch induced phase separation

○Sooyeon Noh[1], Akihide Sugawara[1], Yoshinori Takashima[1], Hiroshi Uyama[1] (1. Osaka Univ.)

日本語
14:10 ~ 14:30
[D341-4pm-04]

次世代イメージングツールへの応用を指向した撥水性ナノ薄膜の大量調製法の確立と機能評価

○内田 頼[1]、平塚 達也[2]、青木 拓斗[3]、岡村 陽介[1,3,4] (1. 東海大学院工、2. 東海大学工、3. 東海大院総理工、4. 東海大マイクロ・ナノ研)

日本語
14:30 ~ 14:50
[D341-4pm-05]

カーボン複合可動性架橋材料を用いた応力-ひずみセンシング

○以倉 崚平[1,2]、梶本 晃太[1]、朴 峻秀[1,2]、高島 義徳[1,2,3] (1. 阪大院理、2. 阪大FRC、3. 阪大OTRI)

日本語
14:50 ~ 15:10
[D341-4pm-06]

両親媒性ジブロックポリペプチドとDawson型ポリオキソメタレートとの複合化による三角形ナノプレート構造とその触媒活性の評価

宮本 翔唯[1]、○黒岩 敬太[1] (1. 崇城大学)

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

2024年3月21日(木) 13:00 ~ 15:10 A1442(14号館 [4階] 1442)

[A1442-4pm] 19. コロイド・界面化学

座長：亀山 達矢、神戸 徹也

英語
13:00 ~ 13:20
[A1442-4pm-01]

機械学習を用いた多元素合金ナノ粒子における高活性水素発生反応触媒の探索

○丸田 悠斗[1]、草田 康平[1,2]、Seo Okkyun[5]、坂田 修身[5]、河口 彰吾[5]、久保田 佳基[6]、金子 弘昌[7]、鳥山 誉亮[3]、山本 知一[3]、村上 恭和[3,4]、北川 宏[1] (1. 京大院理、2. 京大白眉センター、3. 九大URC、4. 九大院工、5. 高輝度光科学研究センター、6. 阪公大院理、7. 明大院理工)

英語
13:20 ~ 13:40
[A1442-4pm-02]

Machine learning guided development of size and shape controlled inorganic nanoparticles

○Quan ZOU[1], Kiyoshi Kanie[1,2] (1. International Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai, Miyagi 980- 8577, Japan, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan)

英語
13:40 ~ 14:00
[A1442-4pm-03]

多元系合金ナノ粒子触媒によるCO_2水素化反応における元素–電子構造–生成物選択性相関

○中村 雅史[1]、Dongshuang Wu[1]、向吉 恵[1]、草田 康平[1,2]、鳥山 誉亮[3]、山本 知一[3]、村上 恭和[3,4]、河口 彰吾[5]、伊奈 稔哲[5]、久保田 佳基[6]、北川 宏[1] (1. 京大院理、2. 京大白眉セ、3. 九大URC、4. 九大院工、5. JASRI/SPring-8、6. 阪公大院理)

日本語
14:10 ~ 14:30
[A1442-4pm-04]

Au-Fe_3O_4ヤヌスナノ粒子の液液界面における自己組織化によるベシクル形成

○谷地 赳拓[1,2]、三友 秀之[2,4]、蟹江 澄志[3,4]、居城 邦治[2] (1. 日本学術振興会、2. 北大電子研、3. 東北大SRIS、4. 東北大多元研)

英語
14:30 ~ 14:50
[A1442-4pm-05]

Highly ordered $L1_0$-type Pt-*M*-Zn Nanoparticles for Electrocatalysts

○Wu Tian[1], Ryota Sato[2], Yoshiharu Uchimoto[3], Toshiharu Teranishi[1,2] (1. Grad. Sch. of Sci., Kyoto Univ., 2. Inst. for Chem. Res., Kyoto Univ., 3. Grad. Sch. of Human and Environ. Stud., Kyoto Univ.)

英語
14:50 ~ 15:10
[A1442-4pm-06]

三次元銀ナノ粒子超格子の合成と構造特異的機能

○ZHU LINGKAI[1]、猿山 雅亮[2]、寺西 利治[1,2] (1. 京都大学　理学研究科、2. 京都大学 化学研究所)

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

2024年3月21日(木) 9:00 ~ 11:30 A1455(14号館 [5階] 1455)

[A1455-4am] 21. エネルギーとその関連化学，地球・宇宙化学

座長：前田 和彦、鳥本 司

日本語
9:00 ~ 9:20
[A1455-4am-01]

膜蒸留と気液交換を融合したHTOのH_2Oからの効率的分離

○三好 弘一[1]、藤原 正浩[2] (1. 徳島大学、2. 大阪大学)

英語
9:20 ~ 9:40
[A1455-4am-02]

Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

○Susmita Roy[1], Masayoshi Higuchi Higuchi[1], Sanjoy Mandal[1] (1. National Institute for Materials Science (NIMS), 1 -1 Namiki)

英語
9:40 ~ 10:00
[A1455-4am-03]

有機薄膜太陽電池材料における自発的対称性の破れによる電荷分離

○在間 嵩朗[1,2]、大田 航[1,2]、春田 直毅[1,2]、 上島 基之[3]、大北 英生[2]、佐藤 徹[1,2] (1. 京大福井セ、2. 京大院工、3.（株）MOLFEX)

英語
10:00 ~ 10:20
[A1455-4am-04]

Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

○Wentao Zhang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)

英語
10:30 ~ 10:50
[A1455-4am-05]

層状ペロブスカイト酸フッ化物$Pb_3Fe_2O_5F_2$を電極触媒とした水の酸化反応

○水落 隆介[1]、菅原 勇貴[1]、山口 猛央[1]、前田 和彦[1] (1. 東京工業大学)

日本語
10:50 ~ 11:10
[A1455-4am-06]

CO_2と水からギ酸を生成する電気化学リアクタの長期耐久性向上

○加藤 直彦[1]、河合 泰明[1]、野尻 菜摘[1]、塩澤 真人[1]、菊澤 良弘[1]、鈴木 伸明[1]、小坂 悟[1]、濱口 豪[1]、竹田 康彦[1] (1. 株式会社　豊田中央研究所)

日本語
11:10 ~ 11:30
[A1455-4am-07]

光触媒型膜-電極接合体へのプロトン伝導性配位高分子の適用

○竝木 裕司[1,2]、田部 博康[1]、堀毛 悟史[1] (1. 京大、2. ポーラ化成工業)

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

2024年3月21日(木) 13:00 ~ 15:10 H937(9号館 [3階] 937)

[H937-4pm] 02. 理論化学・情報化学・計算化学

座長：堤 拓朗、満田 祐樹

日本語
13:00 ~ 13:20
[H937-4pm-01]
Nudged Elastic Band法を改良するために剛性の力を加えたNudged Elastic Stiffness Band法の開発

〇満田 祐樹[1,2]、麻田 俊雄[1,2] (1. 大公大・理、2. 大公大・RIMED)

日本語
13:20 ~ 13:40
[H937-4pm-02]
Post-Sabatierを目指した電極触媒理論の開拓：活性と安定性の両立に向けて

〇大岡 英史[1]、中村 龍平[1,2] (1. 理研CSRS、2. 東工大ELSI)

日本語
13:40 ~ 14:00
[H937-4pm-03]
様々なSiアルコキシドを前駆体原料として用いたゾル-ゲル低反射膜特性の機械学習による外挿予測

〇倉上 拓真[1]、白木 康一[1]、松田 瑞穂[1] (1. 日本板硝子株式会社)

14:00 ~ 14:10
休憩

日本語
14:10 ~ 14:30
[H937-4pm-04]
Heterogeneous metric learning に基づく結晶構造予測

〇草場 穫[1]、劉 暢[1]、吉田 亮[1,2,3] (1. 統計数理研究所、2. 総合研究大学院大学、3. 物質・材料研究機構)

日本語
14:30 ~ 14:50
[H937-4pm-05]
汎用ニューラルネットワークポテンシャルと生成モデルを用いた高活性合金触媒の原子配置探索

〇久間 馨[1]、石川 敦之[2]、スーサンメニェス アスペラ[1]、古山 通久[1] (1. 信州大学、2. 東京工業大学)

英語
14:50 ~ 15:10
[H937-4pm-06]
Can LLMs be Lab Assistants?

〇Gergely Juhasz[1] (1. Tokyo Institute of Technology)

Nudged Elastic Band 法を改良するために剛性の力を加えた Nudged Elastic Stiffness Band 法の開発

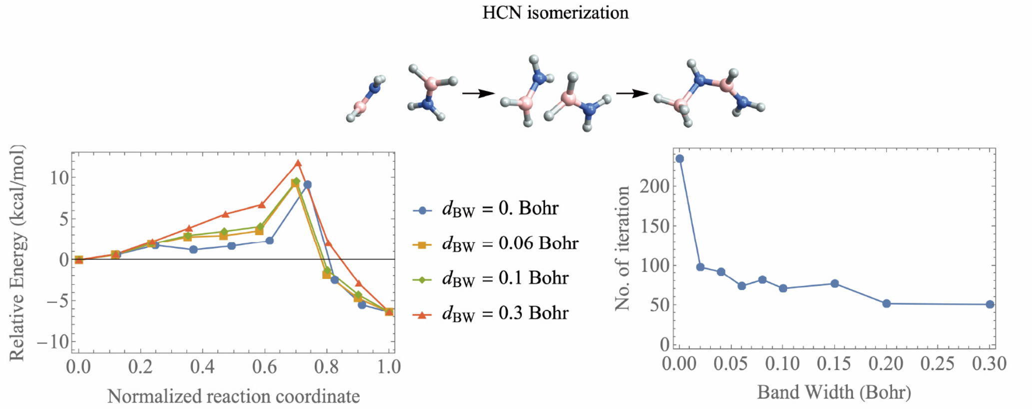
(阪公大院理[1]・阪公大 RIMED[2]) ○満田 祐樹[1,2]・麻田 俊雄[1,2]

Development of a Nudged Elastic Stiffness Band Method by Adding Stiffness Force to Improve the Nudged Elastic Band Method ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*RIMED, Osaka Metropolitan University*) ○Yuki Mitsuta,[1,2] Toshio Asada[1,2]

The nudged elastic band (NEB) method1) has been used to calculate reaction paths using a single band of intermediate structures from a reactant to a product. However, the NEB method has the "kinks" problem, which is caused by the free bending of the bands. Thus, we proposed the nudged elastic stiffness band (NESB) method2). In this method, we applied the beam theory and added stiffness force by extending the single to double band. This additional force allowed us to prevent excessive bending of the bands. We also calculated the NESB combined with the Energy Weighted Climbing Image NEB (EW-CI-NEB)3), and discussed the convergence of the calculations.

Keywords : Optimization; Chemical Reaction Path; Nudged Elastic Band; Quantum Chemistry

Nudged Elastic Band (NEB)法 1)は化学反応や固体の構造変化などの反応経路を計算する代表的な手法の 1 つである。しかしながら、系によっては経路が大きく曲がることで計算が収束しなくなる kink 問題が起こり、最適化計算が収束しない場合がある。そこで我々は、新しく Nudged Elastic Stiffness Band (NESB)法 2)を開発した。この方法では梁理論を応用することで剛性の力を計算し、経路の曲がりを補正する。梁の幅であるバンド幅 d_{BW} をコントロールすることで適切な最適化を設定し、収束性を上げることが可能となった。また、NEB 法には様々な改良手法があり、それらと NESB を組み合わせることによって収束性を上げることができる。そこで、鞍点を発見するための手法である Energy Weighted Climbing Image NEB (EW-CI-NEB)3)と組み合わせた EW-CI-NESB を行い、収束性の向上を確認した。



1) G. Mills *et al.*, *Phys. Rev. Lett.*, **1944**, *72*, 1124–1127; G. Mills *et. al.*, *Surf. Sci.*, **1995**, *324*, 305–337; H. Jónsson *et al., Class. Quantum Dyn. Condens. Phase Simulations,* **1998**.
2) Y. Mitsuta, and T. Asada. *J. Comp. Chem.*, **2023**, *44*, 1884-1897.
3) V. Ásgeirsson et al., J. Chem. Theory Comput., **2021**, *17*, 4929-4945

Post-Sabatier を目指した電極触媒理論の開拓：活性と安定性の両立に向けて

(理研 CSRS[1]・東工大 ELSI[2]) ○大岡英史 [1]・中村龍平 [1,2]

Towards a Post-Sabatier Theory of Electrocatalysis: Realizing Activity and Stability

([1]RIKEN CSRS, [2]Tokyo Inst. Tech. ELSI) ○Hideshi Ooka,[1] Ryuhei Nakamura[1,2]

Active and stable electrocatalysts are necessary to realize clean energy technology such as fuel cells or water electrolyzers. So far, the binding energy between the catalyst and the substrate has been used as a key descriptor to develop new catalysts. The Sabatier principle, which states that catalytic activity will be maximized at an intermediate binding energy, has been central to this approach. However, while the Sabatier principle provides a theoretical framework to understand catalytic activity, a similar framework for stability is lacking.

In this presentation, we will present our ongoing efforts to realize a theory which quantifies catalytic lifetime. Based on this theory, we will highlight the challenges towards realizing a catalyst which is both active and stable. Finally, we will present our ongoing efforts to verify the theory based on experimental measurements of the oxygen evolution reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) on manganese oxide.

Keywords：Electrocatalysis, Microkinetics, Applied Mathematics

水素製造や燃料電池など、今後のクリーンエネルギー技術を実現するには、高い活性と安定性を両立した電極触媒が不可欠である。これまで、触媒と反応基質の吸着エネルギーに着目した触媒開発が行われてきた。特に、適度な強さの吸着エネルギーにおいて活性が最大化される、と主張する Sabatier 則は、中心的な役割を果たしてきた。しかし、活性に関する理論的な枠組みは Sabatier 則を中心に確立されてきた一方で、触媒の寿命を定量的に議論する理論はまだ構築されていない。

そこで本発表では、触媒寿命の定式化に向けて行った数理的な検討について発表する。そして、触媒寿命を記述する数式から想定される、活性と安定性の両立に必要な条件について考察を行う。また、酸化マンガン上の酸素発生反応 ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$)をモデル系とした実験検証についても報告する。

様々な Si アルコキシドを前駆体原料として用いたゾル-ゲル低反射膜特性の機械学習による外挿予測

（日本板硝子株式会社 [1]）○倉上 拓真 [1]・白木 康一 [1]・松田 瑞穂 [1]

Extrapolation Prediction of Properties of Sol-Gel Anti-Reflection Coating with Various Silicon Alkoxides as Precursors by Machine Learning

([1]*NIPPON SHEET GLASS CO., LTD.*) ○ Takuma Kurakami[1], Koichi Shiraki[1], Mizuho Matsuda[1]

Sol-gel method is a process that can produce organic-inorganic hybrid materials with functionality and formability. The properties of sol-gel materials depend on many factors, for example, what kind of organic group modified precursors to use. In this study, we built machine learning models to predict sol-gel coating properties from precursors and synthesis conditions, and evaluated extrapolated prediction accuracy by predicting the properties of the coatings which contain silicon alkoxides as precursors not included in training data. The data of coating properties for training and evaluation was obtained by measuring optical property and various durability of the coatings with 8 types of silicon alkoxides as precursors. The use of molecular descriptors as explanatory variables allows the model to make extrapolated predictions, and the evaluation results confirmed good prediction accuracy.

Keywords : Sol-Gel; Machine Learning; Molecular Descriptor; Fingerprint; Materials Informatics

ゾル-ゲル法は液相合成、低温合成という特徴から、機能性・成形性に富んだ有機-無機ハイブリッド材料を作製可能な手法である。ゾル-ゲル法で得られる材料の特性を支配するパラメータは多岐にわたり、例えばどのような有機基を修飾した金属アルコキシドをゾル-ゲル前駆体原料として用いるのかによって得られる材料の特性は大きく異なる。そこで本研究ではゾル-ゲル前駆体原料および合成条件からゾル-ゲル低反射膜の特性を予測する機械学習モデルを構築し、学習データに含まれないゾル-ゲル前駆体を原料とした膜特性の予測（外挿予測）精度の評価を行った。膜特性データの収集ために、8 種類の Si アルコキシドを原料としたゾル-ゲル低反射膜をガラス基板上に成膜し、光学特性と各種耐久性を評価した。分子記述子を説明変数に用いたモデルを構築し、良好な予測結果が得られた。

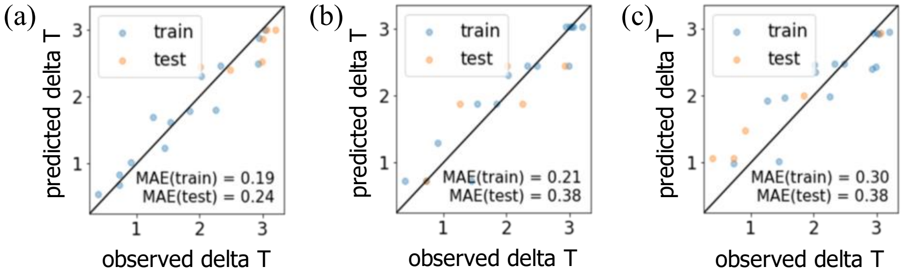


Fig. 1 Scatterplots between the observed and predicted delta Transmittance of (a) methyltriethoxysilane, (b) 3-glycidyloxypropyltriethoxysilane, and (c) phenyltriethoxysilane test data.

日本化学会 第104春季年会 (2024)

Heterogeneous metric learning に基づく結晶構造予測

(統計数理研究所 [1]・総合研究大学院大 [2]・物質・材料研究機構 [3])
○草場 穫 [1]・劉 暢 [1]・吉田 亮 [1,2,3]

Crystal structure prediction based on heterogeneous metric learning

([1] *The Institute of Statistical Mathematics*, [2] *SOKENDAI,* [3] *National Institute for Materials Science*)
○Minoru Kusaba,[1] Chang Liu,[1] Ryo Yoshida[1,2,3]

We propose a template-based crystal structure prediction method based on heterogeneous metric learning. In this method, a function is learned from the crystal structure database to determine whether a given chemical composition and crystal structure pair is a stable structure or not. The function is used to select a template structure that has a high stability evaluation value when paired with a composition for which the stable structure is unknown, and the crystal structure of the composition is predicted by element substitution of the selected template structure.

Keywords：Crystal structure prediction; Materials informatics; Machine learning

任意の化学組成によって形成されるエネルギー的に安定した結晶構造を予測することは、固体物理学における未解決問題である。安定した原子の結晶状態は、第一原理計算によって評価されるエネルギー曲面の最適化によって決定される。しかし、この最適化問題を解くことは計算コストが高く、大規模なシステムに適用することができない。一方、エネルギー曲面の最適化に基づかない高速な手法として、既知構造の元素置き換えによって予測を行うテンプレートベースの手法が提案されている。我々は、この手法群に分類される結晶構造予測手法を2022年に発表した1) が、以下三つの問題点が未解決であった；①準安定構造予測に対応していない ②構造から組成を探す逆向きの予測に対応していない ③データベースに無い構造を予測することができない。

そこで、本研究ではheterogeneous metric learningに基づいたテンプレートベースの新たな結晶構造予測手法の構築を目指す。本手法では、与えられた化学組成と結晶構造のペアが安定構造であるか否かを判別する関数を結晶構造データベースから学習し、その関数に基づいた結晶構造の提案によって構造予測を行う。この新しい方法論では、組成と構造を別々に扱っているため、上記三つの問題点を解決することができる。本研究では、組成と構造ともに我々が開発したカーネル平均埋め込みに基づく記述子生成手法2)によって固定長ベクトルに変換される。発表では、幾つかの heterogeneous metric learning のモデルによる、組成と構造ペアの安定性予測性能の比較と結晶構造予測結果を紹介する。

Acknowledgment: This work was supported by JSPS KAKENHI Grant Number 22K21292.

1) Kusaba, M., Liu, C., & Yoshida, R. (2022). Crystal structure prediction with machine learning-based element substitution. *Computational Materials Science*, *211*, 111496.
2) Kusaba, M., Hayashi, Y., Liu, C., Wakiuchi, A., & Yoshida, R. (2023). Representation of materials by kernel mean embedding. *Physical Review B*, *108*(13), 134107.

汎用ニューラルネットワークポテンシャルと生成モデルを用いた高活性合金触媒の原子配置探索

（信州大[1]・東工大[2]）○久間 馨[1]，石川 敦之[2], Aspera Susan Menez[1]，古山 通久[1]

Exploration of alloy catalyst with highly reactive atomic configuration using a universal neural network potential and a generative model

([1]*Center for Research Initiative for Supra-Materials, Shinshu University*, [2]*Department of Transdisciplinary Science and Engineering, Tokyo Institute of Technology*) ○Kaoru Hisama[1], Atsushi Ishikawa[2], Susan Menez Aspera[1], Michihisa Koyama[1]

It is important for alloy catalyst design to reveal highly reactive atomic configurations. Therefore, we developed a fast calculation method for finding highly reactive surfaces, by generating candidates of atomic configurations with high activity using a generative adversarial networks (GAN) and evaluating the reaction energy [1], accelerated by a universal neural network potential, PFP [2]. By iterating between the generation and evaluation process, we explored atomic configurations that maximize the reactivity for ammonia synthesis of an alloy catalyst composed of Pd, Rh, and Ru elements. As a result, alloy surface structures with higher turn-over frequencies (TOF) than the monometal Ru are successfully identified [Fig. 1].

Keywords : Heterogeneous catalyst, Neural Network Potential, Generative adversarial networks, Density functional theory

合金触媒表面において，どのような元素配置や構造が高活性となるのかは触媒設計上重要である．本研究では，機械学習を用いた効率的な配置探索を行うことで，活性の高い合金配置とそのメカニズムの解明を図る．敵対的生成ネットワーク(GAN)で触媒活性の高い原子配置を模倣した構造を生成し，反応エネルギーから活性評価を繰り返し行う手法 [1]に汎用ニューラルネットワークポテンシャル PFP [2]を組み合わせることで，高活性な触媒表面を高速に自動探索する手法を開発した．アンモニア合成反応に対する Pd, Rh, Ru の三元素を組み合わせた触媒について探索を行ったところ，Fig. 1 に示すように，2 元系・3 元系合金において単体では最も活性が高い Ru を上回る触媒回転頻度(TOF)を持つ配置が見出され，本手法の有効性が示唆された．

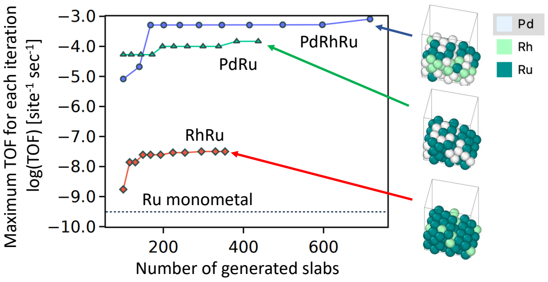


Figure 1 Maximum TOF for each alloy, as a function of the number of generated slab models.

[1] A. Ishikawa, Sci. Rep. 12, 11657 (2022). [2] S. Takamoto et al., Nat. Commun. 13, 2991 (2022).

謝辞 本研究は科研費 20H05623 の支援を受けた．また，本計算の一部は東北大学計算材料科学センターMASAMUNE-IMR を用いて行った

Can LLMs be Lab Assistants?

([1]*Graduate School of Science, Tokyo Institute of Technology*) ○Gergely Juhasz[1]

Keywords: Chemical Literature Review, Knowledge Extraction, Automation

Scientific research has traditionally relied heavily on knowledge of relevant scientific literature, individual expertise, and know-how in the given field. This approach makes research an intellectually rewarding adventure, but also limits what individual researchers or research laboratories can achieve. The recent breakthroughs in AI, specifically in the real-world applications of large language models (LLMs), raise hopes that clever use of these tools can augment human skills and multiply what can be achieved in a laboratory. Several reports suggest that LLMs may be able to autonomously perform quantum chemical calculations,[1] answer scientific questions by performing autonomous literature reviews,[2] or run experiments autonomously.[3]

Here, we present our ongoing experiments, focusing primarily on how accurately LLMs can analyze the content of research papers and suggest calculation methods to interpret experiments. We compared the abilities of some major LLMs, including GPT-3.5 and GPT-4.0, Gemini, and open-source models. We tested the suggested input files on Orca and Gaussian software, as they are widely available and popular computational tools. We have found that careful few-shot learning prompts can significantly improve the reliability of the suggested methods. However, detailed analysis of chemical structures remains the Achilles heel of these models.

Our study reveals the immense potential of LLMs in aiding chemical research, yet also points to the necessity of further development, especially in the detailed analysis of chemical structures, to fully harness their capabilities.

1) A. D. White, et al. *Digital Discovery*, **2023**, 2-2 368–76. 2) A. M. Bran, S. Cox, A. D. White, P. Schwaller. *arXiv*, **2023**. https://doi.org/10.48550/arXiv.2304.05376. 3) Boiko, Daniil A., R. MacKnight, B. Kline, G. Gomes. *Nature* **2023**, *624*, 570–78.

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21日(木) 11:00 ~ 11:40 A1441(14号館 [4階] 1441)

[A1441-4am] 04. 物理化学—物性

座長：佐々木 陽一、竹清 貴浩

日本語

11:00 ~ 11:20

[A1441-4am-01]

高分子界面近傍における水素結合特性と赤外振動バンドの全原子解析

○石井 良樹[1]、鳥居 肇[2]、池本 夕佳[3]、鷲津 仁志[4] (1. 北里大学、2. 静岡大学、3. JASRI、4. 兵庫県立大学)

英語

11:20 ~ 11:40

[A1441-4am-02]

アルキル鎖長が脂肪族カルボン酸分子の金属酸化物表面への吸着挙動に与える影響について。

○雷 文瑾[1]、細見 拓郎[1]、劉 江洋[1]、田中 航[1]、高橋 綱己[1]、柳田 剛[1,2] (1. 東大院工、2. 九大先導研)

高分子界面近傍における水素結合特性と赤外振動バンドの全原子解析

（北里大未来工 [1]・静岡大工 [2]・JASRI[3]・兵庫県大院情報 [4]）
○石井 良樹 [1]・鳥居 肇 [2]・池本 夕佳 [3]・鷲津 仁志 [4]

All-atomic Analyses on the Properties of Hydrogen Bonds and Infrared Vibrational Bands in the Vicinity of Polymer Interfaces

([1]*School of Frontier Engineering, Kitasato University*, [2]*Faculty of Engineering, Shizuoka University,* [3]*Spectroscopy Division, JASRI,* [4]*Graduate School of Information Science, University of Hyogo*)
○Yoshiki Ishii,[1] Hajime Torii,[2] Yuka Ikemoto,[3] Hitoshi Washizu[4]

Hydrogen-bonding network of water molecules in the vicinity of polymer interfaces is considered to have a key role to avoid the adsorption of biomolecules. To clarify hydrogen-bonding structures and their functions of water molecules around the polymer-water interface, experimental measurements of infrared spectroscopy and its theoretical analysis based on molecular dynamics simulation have been widely reported to investigate specific properties of the polymer interfaces. Here we recently developed a spatially-decomposed approach of the IR band analysis, which can be adopted to nanoscopic regions in the polymer-water interface. With this theoretical approach, the modulation of OH stretching vibrational mode occurs in the region of a several nanometer space in the vicinity of polymer-water interface.

Keywords : Polymer; Hydrogen Bonds; Interface; Molecular Dynamics; Infrared Bands

高分子界面における水分子集団の水素結合は，生体分子の吸着を阻害する特性をもつことが提案され [1)]，その高分子-水界面における水素結合構造と機能を解明する観点から，赤外分光スペクトルの実験測定と分子シミュレーションに基づく理論解析が進められてきた [2-4)]。そこで我々は近年，高分子界面の分子動力学（MD）シミュレーションから得られた構造情報から，任意の局所空間に存在する水分子の OH 伸縮振動モードに由来する赤外（IR）スペクトルを解析可能な空間分割 IR バンド解析法を開発した [5)]。この手法では，水分子の水素原子にかかる静電場と OH 伸縮振動シフトの第一原理計算に基づく関係式 [6)]を基にしていることから，IR バンドのサンプリングをエネルギー座標や界面からの空間座標で分割させることが可能となる。本研究ではその空間分割法を応用して，生体適合性の優れた高分子 poly(2-methoxyethyl acrylate) (PMEA)の界面で生じる水分子の OH 伸縮振動モードを解析することで，界面近傍の数 nm 領域で IR ピークの増減が生じていることを見出した。

1) M. Tanaka, S. Kobayashi, D. Murakami, F. Aratsu, A. Kashiwazaki, T. Hoshiba, K. Fukushima, *Bull. Chem. Soc. Japan* **2019**, *92*, 2043.
2) M. Tanaka, T. Hayashi, S. Morita, *Polym. J.* **2013**, *45*, 701.
3) N. Yasoshima, T. Ishiyama, M. Gemmei-Ide, N. Matubayasi, *J. Phys. Chem. B* **2021**, *125*, 12095.
4) Y. Ikemoto, Y. Harada, M. Tanaka, S. Nishimura, D. Murakami, N. Kurahashi, T. Moriwaki, K. Yamazoe, H. Washizu, Y. Ishii, H. Torii, *J. Phys. Chem. B* **2022**, *126*, 4143.
5) Y. Ishii, H. Torii, Y. Ikemoto, H. Washizu et al., *in preparation*, **2024**.
6) H. Torii, R. Ukawa, *J. Phys. Chem. B* **2021**, *125*, 1468.

The Influence of Alkyl Chain Length on Carboxylic Acid Molecule Adsorption onto Various Metal Oxide Surfaces

([1.] School of Engineering, The Univ. of Tokyo, [2.] IMCE, Kyushu Univ.) ○Wenjin Lei[1], Takuro Hosomi[1], Jianyang Liu[1], Wataru Tanaka[1], Tsunaki Takahashi[1], Takeshi Yanagida[1,2]

Keywords: Molecular Adsorption; Metal Oxide; VOC

The recent developments in internet-of-things have led to a growing interest in molecular sensors. However, discriminating aliphatic compounds with similar skeletons is considered one of the most challenging issues in that field. This is because these skeletons have poor interactions and reactivities with metal oxides (MOx), the most common chemical sensor materials. [1,2] This study aimed to examine the discrimination of aliphatic compounds from mixtures by utilizing various MOx species.

We first investigated the molecular adsorption behavior of various MOx surfaces by exposing them to a mixture gas of aliphatic carboxylic acids (C3-C9). As shown in **Figure 2**, the certain metal oxides exhibited unexpected selectivity toward the molecule with specific carbon chain lengths. Further investigation with molecular dynamics simulation suggested that the stronger interaction between the alkyl chain and MOx surface could deny the functional group access to the surface. These results indicated that the strength of those interactions plays a crucial role in their adsorption behaviors and may affect the molecular selectivity of the MOx surface.

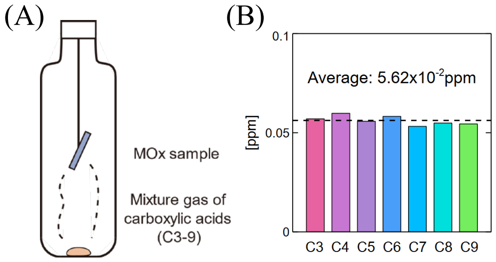


Fig 1. (A) Illustration of exposing MOx sample to the mixture gas. (B) Concentrations of C3-C9 carboxylic acids in the mixture gas.

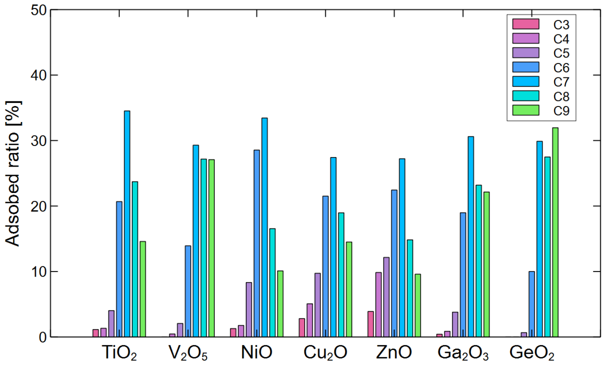


Fig 2. Relative ratios of carboxylic acids desorbed from each MOx surface after exposing the sample to the mixture gas.

1) A. Dey, *Mater. Sci. Eng. B* **2018,** 229, 206. 2) 1. R. A. Potyrailo, *Chem. Rev.* **2016**, 116, 11877.

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21日(木) 13:00 ~ 14:00 A1444(14号館 [4階] 1444)

[A1444-4pm] 07. 無機化学

座長：細見 拓郎、中室 貴幸

英語

13:00 ~ 13:20

[A1444-4pm-01]

原子分解能電顕による炭酸化反応における多段階反応機構解析

〇花澤 美幸[1]、Xin Li[1]、中室 貴幸[1]、中村 栄一[1] (1. 東京大学)

日本語

13:20 ~ 13:40

[A1444-4pm-02]

放射光X線を用いた$Ca_2(Mn,Ti)O_4$黒色遮熱顔料の局所構造解析

〇岡 亮平[1]、早川 知克[1] (1. 名古屋工業大学)

英語

13:40 ~ 14:00

[A1444-4pm-03]

完全気相で成長過程を追跡可能な有機・無機原子層堆積システム

〇松尾 秀明[1]、細見 拓郎[1]、Jiangyang Liu[1]、田中 航[1]、高橋 綱己[1]、柳田 剛[1,2] (1. 東大院工、2. 九大先導研)

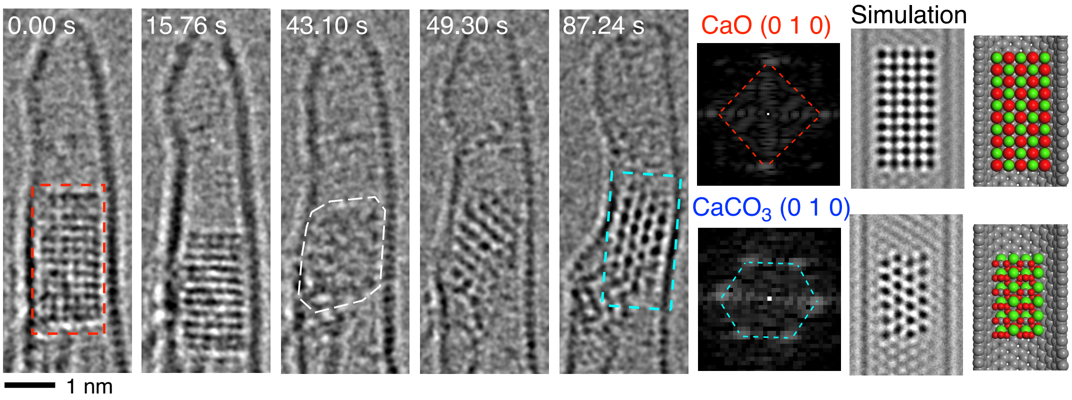
Multi-step Mechanism of Carbonation Reaction Analysed by Atomic-resolution Electron Microscopy

(*Department of Chemistry, The University of Tokyo*)
○Miyuki Hanazawa, Xin Li, Takayuki Nakamuro, Eiichi Nakamura

Keywords: Intermolecular Reaction; In-situ Observation; Transmission Electron Microscopy; Calcium Carbonate; Atomic-resolution

Calcium carbonate ($CaCO_3$) plays an important role in biology and materials engineering.[1] In recent years, the application of biomineralization, which is typical of $CaCO_3$-based biomaterials, has attracted attention in the development of new materials, and an understanding of the formation mechanism is required to control their structures and properties. However, the dynamic behavior at the atomic level is not well understood due to difficulties in experimental observation of the process with high spatial and temporal resolutions. Based on this background, here we demonstrate in-situ observation of a $CaCO_3$ formation process through an intermolecular reaction of calcium oxide (CaO) and carbon dioxide (CO_2) inside a conical-shaped carbon nanotube (CNT) by single-molecule atomic-resolution time-resolved electron microscopy (SMART-EM).[2]

Under SMART-EM observation, a CaO nanocrystal was detected at the initial state (0.00 s, red dashed line). The crystal structure began to fluctuate and decreased in size layer-by-layer from the surface by CO_2 supply to the CaO crystal (15.76 s). At a certain size, the entire cluster transformed into an amorphous structure (43.10 s, white dashed line), and a periodic structure different from the initial one was formed (49.30 s). The structural analysis revealed that the nanocrystal obtained by the gas-solid reaction was reasonably matched to the bulk crystal of aragonite structure, which is a metastable polymorph of $CaCO_3$ at ambient conditions (87.24 s, blue dashed line).[3] In the presentation, detailed analyses of local structures transiently formed on the surface and reaction mechanism will be discussed.



1) T. Akiyama *et al.*, *Phys. Rev. B*, **2011**, *84*, 085428. 2) T. Nakamuro *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 1763. 3) S. Sovova *et al.*, *J. Mater. Chem. B*, **2021**, *9*, 8308.

放射光 X 線を用いた $Ca_2(Mn,Ti)O_4$ 黒色遮熱顔料の局所構造解析

（名工大院工）○岡 亮平・早川 知克

Local structure analysis of near-infrared reflective black $Ca_2(Mn.Ti)O_4$ pigments using synchrotron radiation X-ray

(*Graduate School of Engineering, Nagoya Institute of Technology*)
○Ryohei Oka, Tomokatsu Hayakawa

Local structures of NIR-reflective black $Ca_2(Mn,Ti)O_4$ pigments were analyzed by using X-ray synchrotron radiation. A comparison of the atomic distances estimated from the Rietveld analysis and radial distribution function (RDF) revealed that there were large differences between the M–M distances (M = Mn, Ti). Therefore, XANES simulations were carried out to obtain models of the local structure. The experimental and theoretical data indicate that the Mn atoms were configured in a zigzagging arrangement, and the distortion of the MnO_6 octahedra increased with the increase in the degree of Ti^{4+} doping.

Keywords : Inorganic pigments; NIR-reflective properties; Synchrotron radiation X-ray; Local structures; First-principles calculations

近年，熱を吸収しない（遮熱）顔料の要求が高まっており，特に黒色の遮熱顔料の開発が望まれている．これまでに Ti を固溶させた $Ca_2(Mn,Ti)O_4$ が黒色遮熱顔料として高い性能を有することを明らかにした[1]．また，結晶格子内に，ある一定の相関距離をもつ Ti–Ti 配列が存在することを報告した[2]．しかしながら，Ti の固溶状態や価数変化などについては未解明な部分があり，$Ca_2(Mn,Ti)O_4$ がもつ特性をより理解するためには，構成元素の価数や局所構造，電子状態などの情報が不可欠である．そこで本研究では，放射光 X 線を用いた粉末 X 線回折（XRD）及び X 線吸収微細構造分光（XAFS）測定により，平均および局所構造を解析するとともに，第一原理計算により XANES スペクトルのシミュレーションを行った[3]．

XANES スペクトルより，Mn^{4+}及び Ti^{4+}の割合を見積もった結果，いずれの試料においてもそれぞれ約 82%及び約 95%で，Mn 及び Ti の価数は 4+が支配的であり，これらの価数は Ti の固溶によって変化しないことがわかった．また，Mn-XANES スペクトルにおいて 2 つの pre-edge ピークが観測され，Ti^{4+}の固溶によりピーク位置・強度が変化していたことから，MnO_6 八面体の対称性が変化していると考えられる．Rietveld 及び RDF 解析より M–O, M–Ca, M–M（M = Mn,Ti）原子間距離を算出したところ，M–M 間では両者に大きな差があることがわかった．以上の結果を踏まえ，**Figure 1** に示すような構造モデルを構築し XANES シミュレーションを行った．その結果，Mn^{4+}を a 軸方向に沿ってジグザグ配列させた局所構造モデルにおいて，実測スペクトルの変化をよく再現し，Ti^{4+}固溶により Mn^{4+}の c 軸方向への変位すなわち MnO_6 八面体の歪みが大きくなることがわかった．

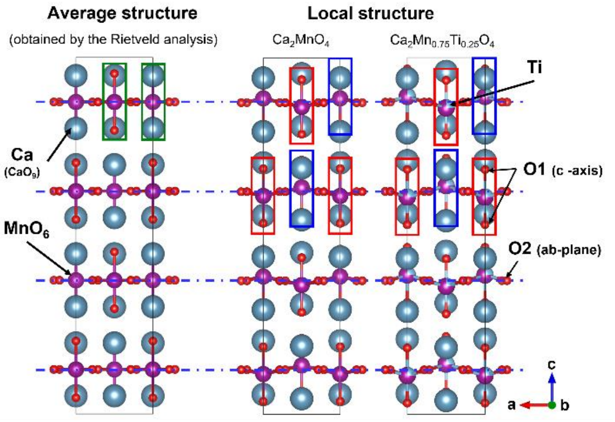


Figure 1 Average and local structure models of $Ca_2(Mn,Ti)O_4$. The green/red/blue frames indicate O–Mn/Ti–O bond unit in the c-axis direction.

1) R. Oka, T. Masui, *RSC Adv.* **2016**, *6*, 90952. 2) R. Oka, T. Hayakawa, *Inorg. Chem.* **2022**, *61*, 6500. 3) R. Oka, T. Hayakawa, *Inorg. Chem.* **2023**, *62*, 14647.

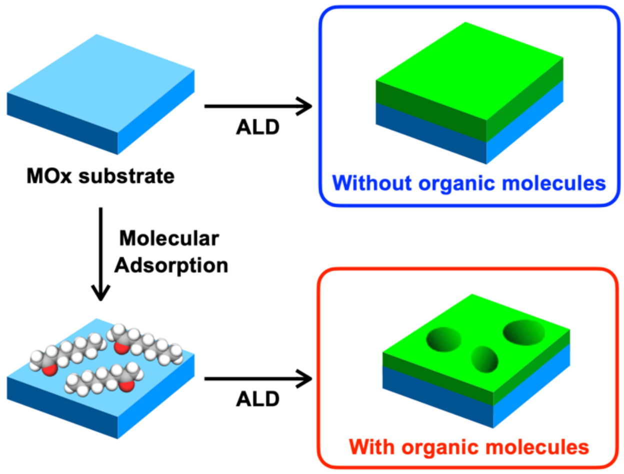
Growth-Traceable Fully Vapor-Phase Organic-Inorganic Atomic Layer Deposition System

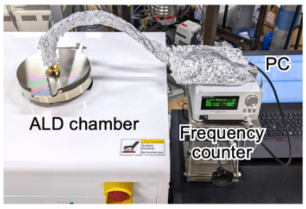
([1]*Graduate School of Engineering, University of Tokyo*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Hideaki Matsuo,[1] Takuro Hosomi,[1] Jiangyang Liu,[1] Wataru Tanaka,[1] Tsunaki Takahashi,[1] Takeshi Yanagida[1,2]

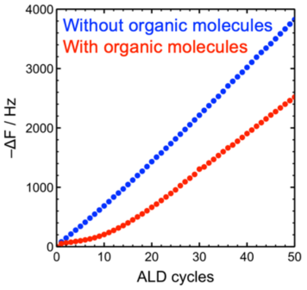
Keywords: Atomic Layer Deposition; Quartz Crystal Microbalance

Various methods have been developed to create nanoscale structures by growing metal oxide structures in the presence of organic molecules. Thin-film deposition of inorganic materials on organic molecules dispersed on a surface has attracted particular attention in recent years, as it is considered possible to design inorganic thin-film structures that reflect the structural features of the organic molecules.[1–3] Although monomolecular dispersion of organic molecules is essential for this method, conventional solution phase adsorption cannot avoid aggregation between molecules. In addition, the state of both organic and inorganic materials during growth is in the almost black box.

In this research, we designed a device that not only deposits metal oxides but also adsorbs target organic molecules in the gas phase using atomic layer deposition (ALD), a thin film formation method that can be controlled at the atomic layer level. In addition, by introducing quartz crystal microbalance (QCM) method and tracking mass changes on the substrate surface in real time, we were able to track the adsorption process of organic molecules and the subsequent deposition process of metal oxides. As a result, it was confirmed that there were differences in the deposition behavior of metal oxides depending on whether or not organic molecules were adsorbed, so the physical properties of both were also evaluated.







1) C. P. Canlas *et al.*, *Nature Chem.* **2012**, *4*, 1030–1036. 2) P. Ruff *et al.*, *Microporous Mesoporous Mater.* **2016**, *235*, 160–169. 3) N. Sobel and C. Hess, *Angew. Chem. Int. Ed.* **2015**, *54*, 15014–15021.

アカデミックプログラム［Ｂ講演］ | 08. 触媒：口頭Ｂ講演

2024年3月21日(木) 9:00 ~ 11:30 A1457(14号館 [5階] 1457)

[A1457-4am] 08. 触媒

座長：森 浩亮、谷田部 孝文

日本語

9:00 ~ 9:20

[A1457-4am-01]

密度汎関数理論計算を用いた白金(111)によるメラミン吸着機構の解明

〇多田 幸平[1]、山崎 眞一[1]、朝日 将史[1]、五百蔵 勉[1] (1. 国立研究開発法人　産業技術総合研究所)

英語

9:20 ~ 9:40

[A1457-4am-02]

異種金属添加による非還元性酸化物上における水素スピルオーバーの発現とその拡散経路

〇俊 和希[1]、森 浩亮[1]、木俵 拓海[1]、山下 弘巳[1] (1. 阪大院工)

英語

9:40 ~ 10:00

[A1457-4am-03]

CeO$_2$のLewis酸塩基点および酸化還元特性の協働触媒作用による1,2-ジケトンの形式的脱カルボニル反応

〇松山 剛大[1]、谷田部 孝文[1]、山口 和也[1] (1. 東京大学)

10:00 ~ 10:10

休憩

日本語

10:10 ~ 10:30

[A1457-4am-04]

酸化銅サブナノ粒子の酸化触媒機能

〇田辺 真[1]、園部 量崇[2]、山元 公寿[2] (1. 福島県医大、2. 東工大化生研)

英語

10:30 ~ 10:50

[A1457-4am-05]

アンモ酸化活性を有するCu, Ruを添加したセリア系複合酸化物触媒の低温レドックス特性に伴う構造変化

〇Chaoqi CHEN[1]、邨次 智[1]、唯 美津木[1,2] (1. 名古屋大学、2. 名大物国セ)

日本語

10:50 ~ 11:10

[A1457-4am-06]

Ru-Ce系触媒のNH$_3$合成活性に影響を与える因子の解明

〇後藤 能宏[1]、菊川 将嗣[1]、山崎 清[1]、佐藤 彰倫[2]、眞中 雄一[3]、難波 哲哉[3]、松本 秀行[4]、大川原 真一[4] (1. 株式会社豊田中央研究所、2. トヨタ自動車株式会社、3. 産業技術総合研究所、4. 東京工業大学)

英語

11:10 ~ 11:30

[A1457-4am-07]

サイズ制御したCuFe、CuRu合金ナノ粒子の調製と電解窒素還元反応への応用

○張 凱朝[1]、佐々木 岳彦[1] (1. 東京大学大学院理学系研究科)

本講演の予稿原稿は、当日の発表内容と異なることが判明したため、講演発表後に差し替えを行いました（2024年10月8日）。

なお差し替え前の原稿は、次の通りです。
「表面場を用いた開殻分子のジラジカル性変調に関する理論検討　〇多田 幸平¹、川上 貴資²、日沼 洋陽¹ (1.産総研、2.大阪大理)」

密度汎関数理論計算を用いた白金(111)によるメラミン吸着機構の解明

（産総研 [1]）〇多田　幸平 [1]・山崎　眞一 [1]・朝日　将史 [1]・五百蔵　勉 [1]

Elucidation of the mechanism of melamine adsorption on Pt(111) surface via density functional theory calculations

([1]*AIST*) 〇Kohei Tada,[1] Shin-ichi Yamazaki,[1] Masafumi Asahi,[1] Tsutomu Ioroi[1]

Improving the oxygen reduction reaction activity (ORR activity) of Pt catalysts in polymer electrolyte fuel cells (PEFCs) is important to reduce the amount of Pt used. It has been found that the ORR activity is improved by adsorption of molecules such as melamine and tetraazaporphyrins on the Pt surface. However, in the enhancement of ORR activity using such molecules, over-adsorption of the molecules by the Pt surface significantly reduces the ORR activity. Therefore, it is important to adjust the amount of adsorbed molecules, but it is unclear how the molecules with the ORR activity enhancing effect are adsorbed on the Pt surface. We then performed density functional theory (DFT) calculations using more than 10,000 adsorption models and elucidated the adsorption mechanism of melamine/Pt (111).

Keywords： PEFC; ORR activity; Pt catalyst; Melamine; DFT calculation

固体高分子形燃料電池（PEFC）における白金触媒の酸素還元反応活性（ORR 活性）の向上は、白金使用量を減らすうえで重要である。メラミンやテトラアザポルフィリンといった分子を白金表面へ吸着させることで ORR 活性が向上することが見出された [1,2]。一方で、このような分子を用いた ORR 活性向上においては、触媒である白金表面による分子の過剰吸着が ORR 活性を著しく低下させる。そのため、吸着量や溶液中の分子濃度の調整が重要となるが、ORR 活性向上効果を持つ分子が白金表面にどのように吸着されるかはわかっていなかった。

我々は１万構造を超える吸着モデルに対して密度汎関数理論計算（DFT 計算）を実行し、メラミン/白金(111)の吸着メカニズムを解明した [3]。メラミンは 2 つの N で白金に配位する形で傾いて吸着され、吸着構造の安定性は共鳴構造によって説明された。この結果は、「トリアジン環に対して、電子供与性の置換基が複数ついた分子」に ORR 活性向上効果があり、「置換基の電子供与性の強弱で吸着力を制御可能」であることを示すものである。実際に、アミノ基をより電子供与性の低い置換基にすることで ORR 活性向上効果が得られる濃度範囲が拡張した [4]。

1) S. Yamazaki, M. Asahi, T. Ioroi, *Electrochim. Acta*, **2019**, *297*, 725
2) M. Asahi, S. Yamazaki, N. Taguchi, T. Ioroi, *J. Electrochem. Soc.*, **2019**, *166*, F498
3) K. Tada, S. Yamazaki, M. Asahi, T. Ioroi, *Phys. Chem. Chem. Phys.*, **2023**, *25*, 23047
4) S. Yamazaki, M. Asahi, N. Taguchi, T. Ioroi, *Electrochimica Acta*, **2023**, *472*, 143417

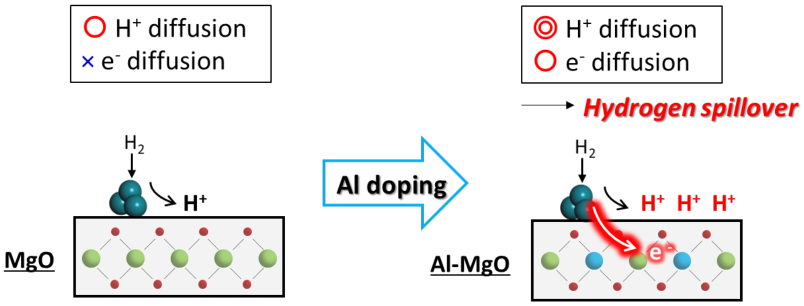
Hydrogen Spillover on a Non-reducible Metal Oxide by a Heteroatom Doping and its Diffusion Pathways

([1]*Graduate School of Engineering, Osaka University*)
○Kazuki Shun,[1] Kohsuke Mori,[1] Takumi Kidawara,[1] Hiromi Yamashita[1]

Keywords: Hydrogen Spillover; Non-reducible Metal Oxide; Heteroatom Doping

The hydrogen spillover, a concomitant diffusion of proton (H^+) and electron (e^-), is a phenomenon enabling the solidification of gaseous H_2 into dynamic and reactive hydrogen species and expected to be a new hydrogen handling technology.[1] It is known that its occurrence requires the redox of cations and therefore is limited to on reducible metal oxides composed of rare elements, which prevents the development of technologies using hydrogen spillover.[2] Based on this consideration, non-reducible metal oxides, such as MgO and Al_2O_3, are suitable platforms because their components are only ubiquitous elements. However, only H^+ can diffuse over such metal oxides because their metal cations prohibit the conduction of e^- due to low reducibility, which significantly decreases migration distance and reactivity of spilled hydrogen.[3] Stated differently, the creation of materials with such ubiquitous elements that displays superior hydrogen spillover ability will provide a new way of handing hydrogen.

In the present work, we firstly report that Al doped MgO (Al-MgO) composed of only ubiquitous elements exhibits excellent hydrogen spillover performance. Al-MgO stored a 0.29 wt% of H^+, which was more than 3.1 times higher than not only MgO but also a number of typical reducible metal oxides composed of rare elements. Surprisingly, Al-MgO allowed concurrent H^+ and e^- diffusion as hydrogen spillover on reducible metal oxides even though Mg^{2+} and Al^{3+} are both originally irreducible. The diffusion pathways of H^+ and e^- evolved within Al-MgO were comprehensively studied by the systematic characterizations, thermodynamical analysis, and theorical calculations. Furthermore, hydrogen spillover on Al-MgO significantly accelerated the catalysis of Ni during CO_2 hydrogenation reaction.



1) K. Shun, K. Mori, S. Masuda, N. Hashimoto, Y. Hinuma, H. Kobayashi, H. Yamashita, *Chem. Sci.* **2022**, 13, 8137. 2) R. Prins, *Chem. Rev.* **2012**, 112, 2714. 3) W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, J. Bokhoven, *Nature*, **2017**, 541, 68.

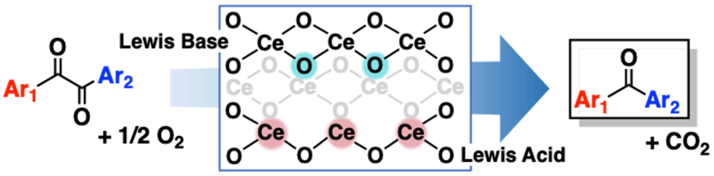
Formal 1,2-Diketone Decarbonylation Enabled by Synergistic Catalysis of Lewis Acid-Base Sites and Redox Properties in CeO_2

([1]*School of Engineering, The University of Tokyo*) ○Takehiro Matsuyama,[1] Takafumi Yatabe,[1] Kazuya Yamaguchi[1]

Keywords: Ceria; Formal Decarbonylation; 1,2-Diketones; Heterogeneous Catalysts; Synergistic Catalysis

Diaryl ketone is an essential moiety widely seen in various chemistry fields.[1)] In recent years, diaryl ketone synthesis via 1,2-diketones has attracted much attention because 1,2-diketones can be synthesized from various starting materials including ketones, aldehydes, alkynes, and alkenes. However, there are some problems in reported diaryl ketone synthesis via 1,2-diketones; decarbonylation of 1,2-diketones via oxidative addition have difficulty in selectivity control due to double-decarbonylation to afford biaryls,[2)] and formal decarbonylation via benzilic acid rearrangement, which enables highly selective molecular transformations, required stoichiometric amounts of bases and anilines.[3)]

In this study, we have developed CeO_2-catalyzed formal decarbonylation of different diaryl 1,2-diketones to afford diaryl ketones with no additives by using O_2 as the terminal oxidant. A series of control experiments combined with catalyst characterization revealed that the present formal decarbonylation was achieved by the synergistic catalysis of CeO_2: Lewis acid–base pairs synergistically catalyzed efficient benzilic acid rearrangement followed by aerobic oxidative decarboxylation via redox of CeO_2. This system exhibited wide substrate scope and was applicable to the decarbonylation of *ortho*-substituted and halogenated 1,2-diketones, which could not be performed using our previous decarbonylation via oxidative addition.[2)] The catalyst proved to function as a heterogeneous catalyst and could be reused several times. In this presentation, we will discuss the synergistic catalysis of CeO_2 for the formal 1,2-diketone decarbonylation in detail based on the thorough catalyst characterization and control experiments.



✓ formal diaryl 1,2-diketone decarbonylation catalyzed by CeO_2
✓ synergistic Lewis acid–base and redox properties

1) M. L. N. Rao, B. S. Ramakrishna, *Eur. J. Org. Chem*. **2017**, *2017*, 5080. 2) T. Matsuyama, T. Yatabe, T. Yabe, K. Yamaguchi, *ACS Catal.* **2022**, *12*, 13600. 3) a) A. Maji, S. Rana, Akanksha, D. Maiti, *Angew. Chem. Int. Ed*. **2014**, *53*, 2428. b) X. Wang, R.-X. Chen, Z.-F. Wei, C.-Y. Zhang, H.-Y. Tu, A.-D. Zhang, *J. Org. Chem.* **2016**, *81*, 238. c) X. Li, W. Huang, D. Liang, L. Yuan, Y. Ma, L. Gu, *Tetrahedron* **2015**, *71*, 1045. d) L. Gu, H. Zhang, *RSC Adv*. **2015**, *5*, 690.

酸化銅サブナノ粒子の酸化触媒機能

(福島県医大[1]・東工大化生研[2]) ○田辺 真[1]・園部 量崇[2]・山元 公寿[2]
Subnanometer Copper Nanoparticles for Oxidative Catalysis ([1]*Fukushima Medical University,* [2]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○ Makoto Tanabe,[1] Kazutaka Sonobe,[2] Kimihisa Yamamoto[2]

Subnanoparticles (SNPs) with sizes of ~1 nm are attractive for enhancing the catalytic performance of transition metals and their oxides. Copper-based SNPs particularly have been focused on activating hydrocarbons at low temperatures. However, the electronic states and the geometric structures of copper oxide SNPs are still a subject of debate in terms of their redox properties during oxidation reactions for hydrocarbons. Herein, *in situ* X-ray absorption fine structure (XAFS) measurements of Cu$_{28}$O$_x$ SNPs, which were prepared using a dendritic phenylazomethine template, during temperature-programmed reduction (TPR) with H_2 achieved lowering of the temperature reported thus far for the Cu(II)→Cu(I) reduction reaction because of Cu–O bond elongation in the ultrasmall copper oxide particles. Methane activation was also achieved by Cu$_{28}$O$_x$ SNPs under mild conditions. These results highlight the mineralized local structures in the copper oxide SNPs induce the generation of active oxygen species by their atomic configurations.

Keywords: Nanoparticles, Copper, H_2 reduction, Methane activation, Dendrimer

約1 nmサイズのサブナノ粒子は、ナノ粒子とは異なる幾何構造や電子状態を示すため、それらを活かした触媒反応が注目されている。近年では、元素代替の概念から貴金属より安価な銅を用いた触媒開発が注目されている。しかしながら、サブナノ粒子の反応性が向上する構造的要因は議論されている。本研究では、XAFS法を用いて酸化銅サブナノ粒子 Cu$_{28}$O$_x$ の構造解析をおこない、その知見を基に酸素分子を酸化剤とするメタン酸化反応を検討した。既報に応じて、フェニルアゾメチンデンドリマーDPA を鋳型とし、原子数が規定された不均一系触媒 Cu$_{28}$O$_x$/SiO$_2$ を合成した[1]。Cu$_{28}$O$_x$/SiO$_2$ の H_2 TPR における ***in situ*** XAFS 測定結果、Cu(II)→Cu(I)への還元温度の低下が観察された (図1左)[2]。Cu$_{28}$O$_x$/SiO$_2$ に対して CH_4 と O_2 の混合ガス雰囲気下 (1.8 MPa)、110 °C で MeOH と HCO_2H を生成する低温メタン酸化が達成された (図1右)[3]。

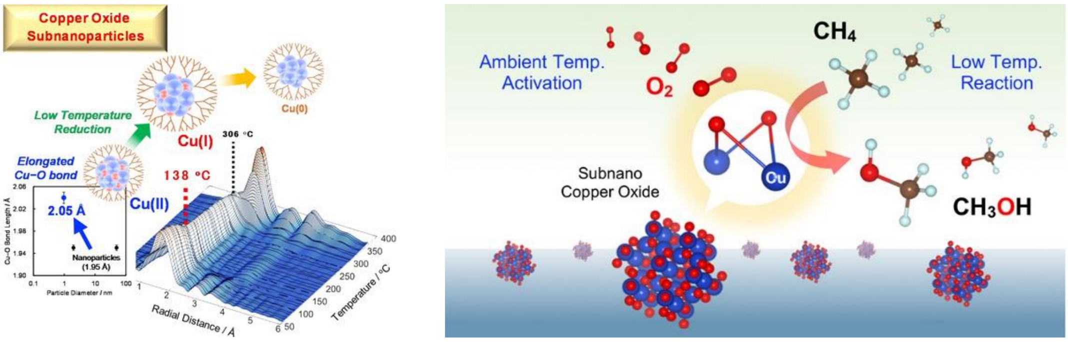


図1 Cu$_{28}$O$_x$/SiO$_2$ による水素還元反応(左)およびメタン酸化反応(右)の概念図

1) Sonobe, K.; Tanabe, M.; Yamamoto, K. *ACS Nano* **2020**, *14*, 1804. 2) Sonobe, K.; Tanabe, M.; Imaoka, T.; Chun, W.-J.; Yamamoto, K. *Chem. Eur. J.* **2021**, *27*, 8452. 3) Sonobe, K.; Tanabe, M.; Imaoka, T.; Chun, W.-J.; Ida, Y.; Kuzume, A.; Yamamoto, K. *ACS Appl. Nano Mater.* **2023**, *in press.*

Structural Characterization during the Low Temperature Redox Reaction of Copper and Ruthenium Incorporated Ceria for Ammoxidation

([1]*Graduate School of Science, Nagoya University*, [2]*Research Center for Materials Science (RCMS), Nagoya University*) ○Chaoqi Chen,[1] Satoshi Muratsugu,[1] Mizuki Tada[1,2]

Keywords: Mixed metal ceria; Redox property; Ammoxidation; Copper, Ruthenium

We reported mixed metal ceria with the incorporation of Cu and the trace amount of Ru (denoted as $Cu_{0.18}Ru_{0.05}CeO_z$) with remarkable redox property and catalytic performances toward the ammoxidation of benzyl alcohol.[1] The structural characterization of $Cu_{0.18}Ru_{0.05}CeO_z$ was fully investigated during the redox process and the catalysis to clarify the structural changes in each metal species in the mixed oxide catalyst.

$Cu_{0.18}Ru_{0.05}CeO_z$ was prepared by a hydrothermal method, and its structure was characterized by XRD, TEM, XAFS and XPS; the Cu^{2+} oxide and Ru^{n+} ($4 < n < 6$) oxide nanodomains were found to be finely dispersed over the bulk ceria. $Cu_{0.18}Ru_{0.05}CeO_z$ showed remarkable redox performance below 523 K (**Figure 1(A)**) with 2.38 mmol g^{-1} H_2 consumption. Ru *K*-edge, Cu *K*-edge and Ce L_{III}-edge XANES during H_2 TPR clearly showed that all the metal species were reduced; Ru species was initially reduced and after that both Cu and Ce species were subsequently reduced (**Figure 1(B,C,D)**). In addition, the Ru *K*-edge and Cu *K*-edge EXAFS of $Cu_{0.18}Ru_{0.05}CeO_z$ after the reduction with H_2 newly showed Ru-Ru and Cu-Cu bonds, respectively, indicating the formation of both Ru and Cu nanoclusters on the reduced ceria surface. When reduced $Cu_{0.18}Ru_{0.05}CeO_z$ was reacted with O_2, the average oxidation states of all metal species were almost recovered to the original values, and Ru-O and Cu-O bonds regenerated after the oxidation with O_2. It is to be noted that the reduction temperature of $Cu_{0.18}Ru_{0.05}CeO_z$ was slightly decreased from the 2nd redox cycles, and it became steady up to 4th redox cycle below 523 K. The onset temperature of the oxidation state changes in the XANES spectra was also decreased. The detailed relationship between the catalyst structure and the redox and catalytic ammoxidation performances of $Cu_{0.18}Ru_{0.05}CeO_z$ after H_2 reduction and O_2 oxidation will also be discussed.

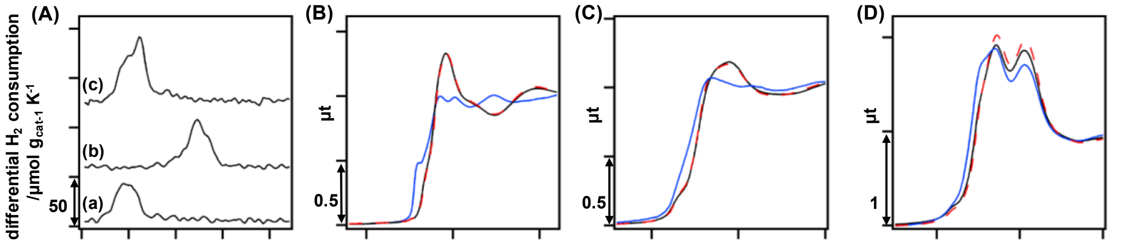


Figure 1. (A) The redox performances of (a) $Ru_{0.04}CeO_z$ (b)$Cu_{0.18}CeO_z$ and (c) $Cu_{0.18}Ru_{0.05}CeO_z$ below 523 K. XANES spectra of (B) Cu *K*-edge (C) Ru *K*-edge and (D) Ce L_{III}-edge. Black line: as-prepared $Cu_{0.18}Ru_{0.05}CeO_z$, blue line: after temperature programmed reduction with H_2, red dash line: after temperature programmed oxidation with O_2.

[1] Chen, C. et al. The 102nd CSJ Annual Meeting, **2022**, B304-1am-02.

Ru-Ce 系触媒の NH_3 合成活性に影響を与える因子の解明

（豊田中研[1]・トヨタ自動車[2]・産総研[3]・東工大[4]）○後藤 能宏[1]・菊川 将嗣[1]・山崎 清[1]・佐藤 彰倫[2]・眞中 雄一[3]・難波 哲哉[3]・松本 秀行[4]・大川原 真一[4]

Analysis of factors affecting the NH_3 synthesis activity of Ru-Ce based catalysts

([1] *Toyota Central R&D Labs., Inc.*, [2] *Toyota Motor Corporation*, [3] *Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology*, [4] *Chemical Science and Engineering, Tokyo Institute of Technology*) ○Yoshihiro Goto,[1] Masashi Kikugawa,[1] Kiyoshi Yamazaki,[1] Akinori Sato,[2] Yuichi Manaka,[3] Tetsuya Nanba,[3] Hideyuki Matsumoto,[4] Shinichi Ookawara[4]

Ammonia (NH_3) has recently attracted attention owing to its applicability as a H_2 carrier or fuel; thus, the development of both catalysts and reaction systems that allow the synthesis of NH_3 under mild conditions is desired. Although Ru-Ce catalysts[1)] are reported to show high NH_3 synthesis activity at lower pressure, the factors affecting their activity require further discussion (Fig. 1). We present here the investigation of Ru/$Ce_{1-x}Pr_xO_\delta$[2)], Ru/$Ce_{0.5}La_{0.5-x}A_xO_\delta$ (A = Ti, Si)[3)], and Ru/BO_x/CeO_2 (B = Si, Zr, Mg) catalysts. The valence of Ru and the pore volumes of the support oxides dominantly affected the NH_3 synthesis activity. Moreover, controlling H/N ratios in feed gases was effective in suppressing hydrogen poisoning that inhibits the activity of Ru catalysts.

Keywords ：Ammonia synthesis; Ru catalyst; Ceria; H/N ratio control; Hydrogen carrier

アンモニア(NH_3)は農業用肥料や化成品の合成に必須な原料であり、工業的には Fe 系触媒を用いたハーバーボッシュ法により高圧下(20–30 MPa)で合成される。近年は水素キャリアや燃料としての利用に注目が集まっており、より低圧で NH_3 を合成できる触媒の開発と触媒の特性を活かした反応システムの構築の両方が望まれる。

低圧(10 MPa 以下)で高い NH_3 合成活性を示しかつ安定性の高い触媒として、Ce 系酸化物に Ru を担持した Ru-Ce 触媒[1)]が報告されているが、その活性に寄与する要因は不明な部分が多い(Fig. 1)。本研究では、Ru-Ce 触媒として開発した Ru/$Ce_{1-x}Pr_xO_\delta$[2)]、Ru/$Ce_{0.5}La_{0.5-x}A_xO_\delta$ (A = Ti, Si)[3)]、および Ru/BO_x/CeO_2 (B = Si, Zr, Mg)の状態解析から、NH_3 合成活性には Ce 還元状態よりも Ru 還元状態および担体の細孔構造が大きく寄与することが分かった。また反応ガス中の H/N 比制御により、Ru 触媒に固有な水素被毒という活性低下現象を抑制でき、NH_3 合成活性を向上できた。これらの観点から開発した触媒と反応システムにより、我々は低圧での NH_3 合成（8 MPa, 1 kg day^{-1}）をデモプラントで実証した。当日の発表では、検討触媒の in-situ 状態解析、並びに反応条件が NH_3 合成活性に与える影響を中心に、Ru-Ce 触媒の性質について報告する。

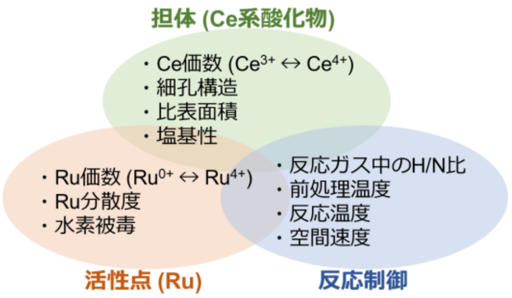


Fig. 1 Ru-Ce 触媒の NH_3 合成活性に影響を与える因子

1) Y. Ogura, et al., *Chem. Sci.*, **2018**, *9*, 2230; 2) M. Kikugawa, et al., *J. Catal.*, **2022**, *413*, 934.
3) Y. Goto, et al. *Chem. Commun.*, 2022, *58*, 3210.

Size-controlled synthesis of CuFe, CuRu alloy nanoparticle catalysts for electrochemical nitrogen reduction reaction

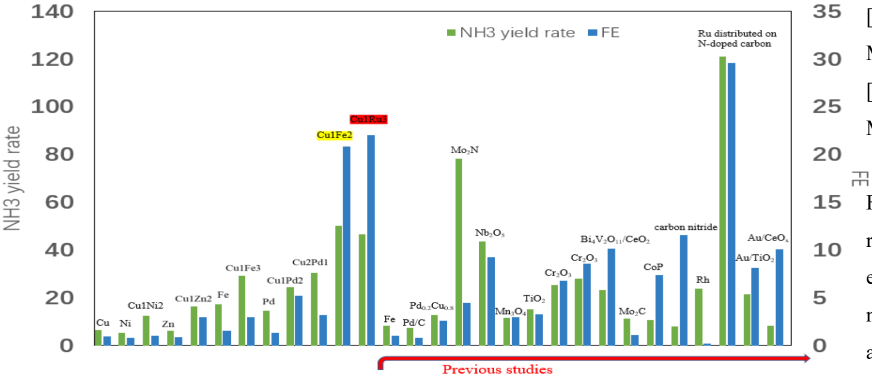
([1]*Graduate School of Science, The University of Tokyo*) ○Kaichao Zhang[1], Takehiko Sasaki[1]

Keywords: alloy nanoparticle, ammonia synthesis, N_2RR, Faradaic efficiency

To enhance catalytic activity and selectivity and investigate the effect of nanoparticle size on catalytic performance, in this study, CuFe, CuRu alloy nanoparticles were synthesized and used for electrochemical nitrogen reduction reaction. As to synthesis of alloy nanoparticles, a typical precursor solution was prepared by mixing metal chlorides in deionized water. Surfactant CTAB was added at different concentrations to control nanoparticle size. PH of the solution was adjusted with NaOH. Then, $N_2H_4 \cdot H_2O$ was added slowly with stirring. The obtained solution was transferred into Teflon autoclave and heated. After cooling down to room temperature, the solid product was filtered, washed and dried to yield a powder. Synthesized catalyst and Nafion solution were dispersed in a solution containing ethanol and water. After forming a homogeneous ink through sonicating, catalyst ink was loaded onto a carbon paper and dried under ambient condition.

A three-electrode configuration (working electrode: prepared catalyst electrode; counter electrode: Pt wire; reference electrode: Ag/AgCl) was used in an H-type electrochemical cell. Each compartment was filled with 0.1 M Na_2SO_4 aqueous solution. N_2 gas was bubbled into the chamber before and during the measurement. LSV (linear sweep voltammetry), CA (Chronoamperometry) and CV (cyclic voltammetry) were tested. After reduction, working electrode-side electrolyte was collected for the indophenol blue method with UV-Vis measurements for determination of produced ammonia. Catalysts were characterized with EXAFS, XRD and TEM.

Compared with previous studies, as shown in Fig.1, Cu_1Fe_2 achieved the Faradaic efficiency (20.81%) and the ammonia yield rate (50.18 μg mg^{-1}cat. h^{-1}), which is better than the previous study (2.94% and 29.13 μg mg^{-1}cat. h^{-1}). [1] With Cu_1Ru_3, the Faradaic efficiency (22.06%) and the ammonia yield rate (46.52 μg mg^{-1}cat. h^{-1}) were obtained, which are also superior to the previous study. [2] It was also discovered that the smaller alloy nanoparticles exhibited better catalytic performances.



[1] X. Wang et al., Adv. Mater., 2020, 32, 2004382.
[2] C. Kim et al., Adv. Mater., 2022, 34, 2205270.

Fig1. Ammonia formation rate and Faradaic efficiency for synthesized nanoalloy catalysts in this and previous research

アカデミックプログラム［Ｂ講演］｜08. 触媒：口頭Ｂ講演

2024年3月21日(木) 13:00 ~ 15:30 A1458(14号館 [5階] 1458)

[A1458-4pm] 08. 触媒

座長：高田 剛、鈴木 肇

英語
13:00 ~ 13:20
[A1458-4pm-01]
サルバナイト型の黒色金属硫化物光カソードを利用したグリーン合成ガスを生成するための光電気化学セルの開発

○永塚 健悟[1]、山口 友一[1,2]、工藤 昭彦[1,2] (1. 東理大理、2. 東理大総研カーボンバリュー)

英語
13:20 ~ 13:40
[A1458-4pm-02]
Ru(II)-Re(I)二核錯体とC_3N_4 の複合型CO_2還元光触媒におけるOs(II)錯体光増感剤の添加効果

○田中 寿弥[1]、玉置 悠祐[2]、前田 和彦[1]、石谷 治[1,3] (1. 東京工業大学、2. 産業技術総合研究所、3. 広島大院先進理工)

日本語
13:40 ~ 14:00
[A1458-4pm-03]
半導体表面への位置選択的なCO_2還元反応活性点の設計を指向した、光還元重合によるハイブリッド光触媒の開発

○榊原 教貴[1]、Ewan McQueen[2]、Sebastian Sprick[2]、石谷 治[1,3] (1. 東工大、2. ストラスクライド大、3. 広島大)

14:00 ~ 14:10
休憩

日本語
14:10 ~ 14:30
[A1458-4pm-04]
電解合成した熱非平衡金属間化合物によるCO_2電解還元

○幸林 竜也[1]、吉川 聡一[1]、渡辺 剛[2]、本間 徹生[2]、山添 誠司[1] (1. 東京都立大学、2. JASRI)

日本語
14:30 ~ 14:50
[A1458-4pm-05]
1 A/cm^{2}を超える電流密度でのCO_2電解還元反応

○神谷 和秀[1]、井上 明哲[1]、Tengyi Liu[1]、原田 隆史[1]、中西 周次[1] (1. 大阪大学)

英語
14:50 ~ 15:10
[A1458-4pm-06]
Cu/M表面合金ナノキューブ(M=Pd,Pt,Ir,Ru)の合成と電気化学的CO_2還元特性の系統的制御

○小林 浩和[1]、引野 幸枝[1]、山内 美穂[1,2,3,4] (1. 九大K-NETs、2. 九大先導研、3. 九大I2CNER、4. 東北大AIMR)

英語

15:10 ~ 15:30

[A1458-4pm-07]

金属3Dプリンティング及び選択的電気化学的溶解で設計されたCO2メタン化のためのNi磁気触媒反応器

○金 孝鎭[1]、森 浩亮[1]、中野 貴由 貴由 [1]、山下 弘巳[1] (1. 大阪大学)

Development of a Photoelectrochemical Cell Utilizing a Sulvanite-type Black Metal Sulfide Photocathode for CO_2 Reduction to Produce a Green Syngas

([1]*Faculty of Science, Tokyo University of Science*, [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Kengo Nagatsuka,[1] Yuichi Yamaguchi,[1,2] Akihiko Kudo[1,2]

Keywords: Metal Sulfide; Photocathode; CO_2 Reduction; Water as an Electron Donor; Whole Range of Visible Light

Photoelectrochemical solar CO_2 reduction in water is a worthwhile CCU technology because this reaction produces a mixture of H_2 and CO gases, so called "green syngas." We have reported a variety of visible light-driven Cu(I)-containing metal sulfide photocathodes which directly reduce CO_2 to form CO.[1] Additionally, we have reported that a powder-based Cu_3VS_4 photocathode with a sulvanite structure was active for solar hydrogen production.[2] This material is a Cu(I)-containing black metal sulfide which can utilize the whole range of visible light. Therefore, the photocathode is expected to be also active for CO_2 reduction. In the present study, we demonstrated photoelectrochemical CO_2 reduction under visible light and simulated sunlight using a Cu_3VS_4 black photocathode to form a green syngas.

A powder-based Cu_3VS_4 photocathode was fabricated by a particle transfer method deposited with an Au layer[1, 3], and an Au cocatalyst was loaded on the photocathode. Fisrt, photoelectrochemical CO_2 reduction under visible light irradiation using the black photocathode was carried out. As a result, a green syngas evolved, giving almost 100% of total faraday efficiency (Fig. 1). During the reaction, 24% of a selectivity was obtained for CO formation from an aqueous $KHCO_3$ solution without any organic solvents. Notably, it was revealed by an action spectrum that the black metal sulfide photocathode utilized visible light up to 820 nm. Furthermore, solar CO_2 reduction utilizing a photoelectrochemical cell consisting of the Cu_3VS_4 photocathode and a $BiVO_4$:Mo photoanode was successfully achieved under simulated sunlight irradiation at 1.0 V. This reaction proceeded even without a pH adjustment at ambient conditions. The ratio of reacted electrons to holes was unity, indicating that the CO_2 reduction reaction proceeded using water as an electron donor.

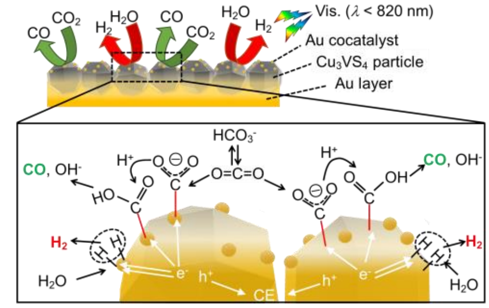


Fig. 1 Schematic illustration of photoelectrochemical CO_2 reduction using a powder-based Cu_3VS_4 photocathode.

1) S. Yoshino, T. Takayama, Y. Yamaguchi, A. Iwase, A. Kudo, *Acc. Chem. Res.* **2022**, *55*, 966. 2) H. Fukai, K. Nagatsuka, Y. Yamaguchi, A. Iwase, A. Kudo, *ECS J. Solid State Sci. Technol.* **2022**, *11*, 063002. 3) T. Minegishi, N. Nishimura. J. Kubota, K. Domen, *Chem. Sci.* **2013**, *4*, 1120.

Addition effect of Os(II) complex photosensitizers on hybrid CO_2 reduction photocatalysts of Ru(II)-Re(I) and C_3N_4

([1] *School of Science, Tokyo Institute of Technology*, [2] *National Institute of Advanced Industrial Science and Technology,* [3] *Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Toshiya Tanaka,[1] Yusuke Tamaki,[2] Kazuhiko Maeda,[1] Osamu Ishitani[1, 3]

Keywords: hybrid photocatalyst, CO_2 reduction, Os(II) complex photosensitizer

The supramolecular photocatalyst (**RuRe** of Figure 1) consisting of photosensitizer of Ru tris-diimine complex and $[Re(CO)_3(dmb)(L)]^{n+}$ of CO_2 reduction catalyst can reduce CO_2 to CO with high selectively (dmb = dimethylbipyridine). The hybrid photocatalyst of **RuRe**/TiO_2/C_3N_4 which constructed with this supramolecular photocatalyst and semiconductor of TiO_2/C_3N_4 with strong photo-oxidative power can reduce CO_2 by triethanolamine (TEOA) as a reductant.[1] However, this hybrid photocatalyst had a problem of low durability.

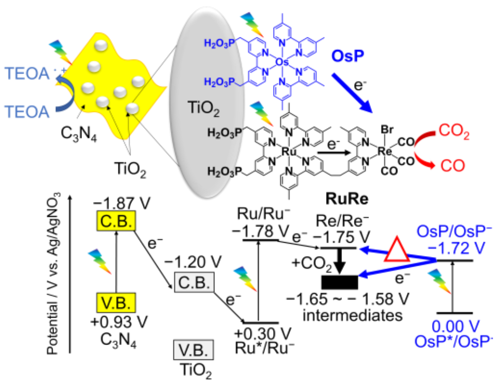


Figure 1 the structure of **OsP**+**RuRe**/TiO_2/C_3N_4 and predicted photo-electron transfer.

Therefore, in this study, we developed a new system that Os(II) complex photosensitizers (**OsP**), which absorb longer wavelength photons than Ru(II) photosensitizers, additionally introduced around **RuRe** in **RuRe**/TiO_2/C_3N_4 (Figure 1). It is reported that Re(I) catalyst becomes intermediates by reaction with CO_2 after receiving an electron.[2] Therefore, the **OsP** can supply the second electron to these intermediates. The durability of photocatalytic reaction in **OsP+RuRe**/TiO_2/C_3N_4 was improved, compared with that of **RuRe**/TiO_2/C_3N_4 (Figure 2), and the turnover number (TON) of evolved CO was increased from 120±26 to 223±30 after irradiating 48 h (TON was calculated based on adsorbed **RuRe**). The addition effects of irradiation of longer wavelength will be also reported in this presentation.

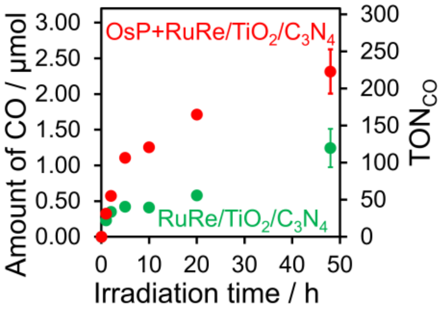


Figure 2 Time course of CO formation during the photocatalytic reduction under CO_2 in **RuRe**/TiO_2/C_3N_4 and **OsP+RuRe**/TiO_2/C_3N_4.

1) M. Shizuno, K. Kato, S. Nishioka, T. Kanazawa, D. Saito, S. Nozawa, A. Yamakata, O. Ishitani, K. Maeda, *ACS Appl. Energy Mater*. **2022**, *5*, 9479. 2) M. Takahashi, T. Asatani, T. Morimoto, Y. Kamakura, K. Fujii, M. Yashima, N. Hosokawa, Y. Tamaki, O. Ishitani, *Chem. Sci.* **2023**, *14*, 691.

半導体表面への位置選択的な CO_2 還元反応活性点の設計を指向した、光還元重合によるハイブリッド光触媒の開発

（東工大理 [1]・ストラスクライド大 [2]・広島大院先進理工 [3]）○榊原 教貴 [1]・Ewan McQueen[2]・Sebastian Sprick[2]・石谷 治 [1, 3]

Hybrid photocatalyst prepared via photo-reductive polymerization for site-selective introduction of CO_2 reduction active sites onto a semiconductor

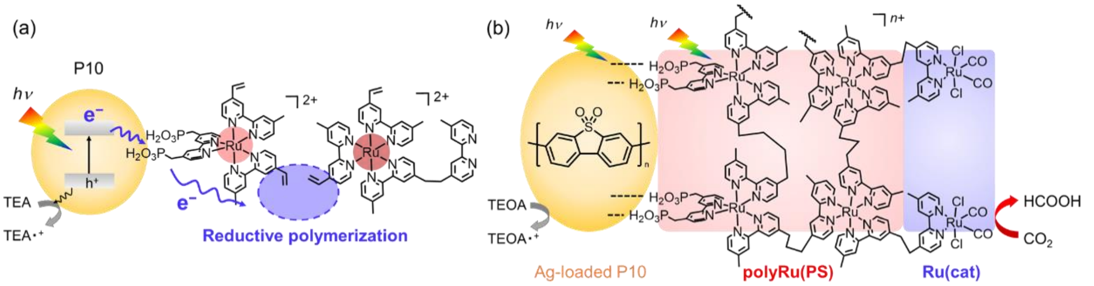
([1]*Tokyo Tech.*, [2]*Univ. of Strathclyde*, [3]*Hiroshima Univ.*) ○Noritaka Sakakibara,[1] Ewan McQueen,[2] Sebastian Sprick,[2] Osamu Ishitani[1, 3]

In the development of highly efficient hybrid photocatalysts for CO_2 reduction, separation of active sites for CO_2 reduction and oxidation of reductant is of paramount importance. In this study, we have developed a new methodology to prepare hybrid photocatalyst. Ru(II) photosensitizing polymer was formed onto the semiconductor surface via photo-reductive polymerization, and then Ru(II) catalysts were coordinated onto the Ru(II) photosensitizing polymer. When poly(dibenzo[*b*,*d*]thiophene sulfone) was used as a semiconductor, the hybrid photocatalyst reduced CO_2 to formate almost quantitatively under visible light irradiation with maintaining high selectivity (> 85%) for CO_2 reduction.

Keywords：*Conjugated polymer; Supramolecular photocatalyst; CO_2 reduction*

半導体と超分子光触媒からなるハイブリッド光触媒は、可視光を有効利用し CO_2 を有用資源へと変換する高性能なシステムの構築に向けて大変有望である [1]。本研究では、CO_2 還元反応活性点と、対をなす酸化反応活性点の分離を目的として、光増感錯体の光還元重合を用いた、新たなハイブリッド光触媒作製法を開発した。

共役ポリマー半導体であるポリジベンゾ[*b,d*]チオフェンスルホン（P10）を還元剤共存下で光励起し、Ru(II)光増感錯体のビニル基を還元的にラジカル重合することで、P10 表面に Ru(II)光増感ポリマー層（**polyRu(PS)**）を形成した（図 a）。その後、ポリマー層へ Ru(II)触媒（**Ru(cat)**）を配位させることでハイブリッド光触媒を得た。CO_2 で飽和させた *N,N'*-ジメチルアセトアミド／トリエタノールアミン（TEOA）中にハイブリッド光触媒を懸濁させ、可視光（$\lambda = 460$ nm）を照射したところ、ギ酸と少量の CO、および副生成物の H_2 を生成した（図 b）。光照射 144 時間にて、高い CO_2 還元反応の選択率（> 85%）を維持しながら、系中に存在する CO_2 がほぼすべて還元された。



1) H. Kumagai, Y. Tamaki, O. Ishitani, *Acc. Chem. Res.* **2022**, *55*, 978-990.

電解合成した熱非平衡金属間化合物による CO_2 電解還元

（都立大院理 [1]・JASRI[2]） ○幸林竜也 [1]・吉川聡一 [1]・渡辺剛 [2]・本間徹生 [2]・山添誠司 [1]

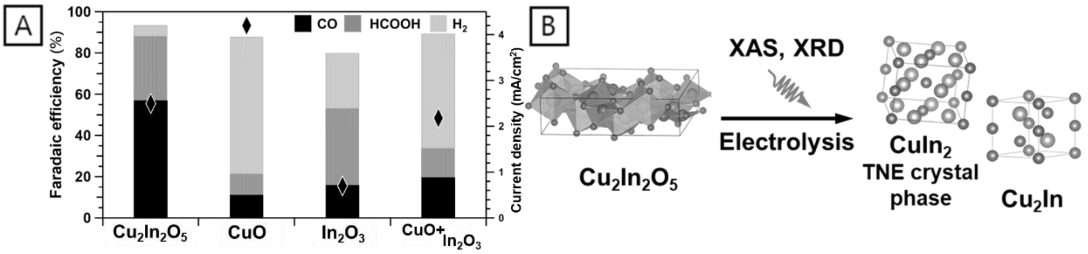
CO_2 electrochemical reduction over thermal non-equilibrium intermetallic compounds synthesized by electrolysis

([1]*Graduate School of Science, Tokyo Metropolitan University*, [2]*JASRI*) ○Tatsuya Koubayashi,[1] Soichi Kikkawa,[1] Tsuyoshi Watanabe,[2] Tetsuo Honma[2], Seiji Yamazoe[1]

Electrochemical conversion of CO_2 has attracted much attention from the viewpoint of effective utilization of carbon resources and surplus electricity. It is important to design an electrode that selectively reduces CO_2 while suppressing H_2 generation in aqueous solution. For example, it has been reported that Cu-based alloy electrode with the second metal species improved CO_2 reduction selectivity[1)]. In this study, we focused on Cu–In thermal non-equilibrium (TNE) intermetallic compound formed by electrochemical reduction of $Cu_2In_2O_5$, a Cu–In composite metal oxide, and applied to electroreduction of CO_2. The electrode after the reaction showed diffraction patterns of a TNE crystal phase, $CuIn_2$, with high crystallinity, and promoted highly selective CO_2 reduction with suppressing H_2 production. We caried out *in situ* observation of the structural change of electrode with XAS and XRD, and revealed that the preferential reduction of In species in $Cu_2In_2O_5$ was important to form the TNE phase $CuIn_2$.

Keywords : Electrochemical CO_2 reduction; intermetallic compound; thermal non-equilibrium crystal phase

CO_2 の電気化学変換は、炭素資源の有効利用と余剰電力の活用の観点から注目されている。水溶液中では H_2 生成を抑制しながら CO_2 を選択的に還元する電極設計が重要である。例えば、Cu 系電極と第二金属種との合金化により CO_2 還元選択性が向上することが報告されている [1)]。本研究では、Cu と In の複合金属酸化物 $Cu_2In_2O_5$ を電気化学的に還元して生成した Cu-In 非平衡金属間化合物に着目し、CO_2 電解還元特性を評価した。複合金属酸化物の還元により得られた電極は熱非平衡結晶相である $CuIn_2$ を高い結晶性で含んでおり、図のように H_2 生成を抑制し高選択的に CO_2 還元が進行した。還元に伴う電極構造の変化を X 線吸収分光と X 線回折の同時計測により *in situ* 観察したところ、複合金属酸化物中の In 種が優先的に還元されることが熱非平衡結晶相の $CuIn_2$ の生成に重要であることが示唆された。



図(A) 種々の酸化物電極の CO_2 電解活性. (B) 還元に伴う $Cu_2In_2O_5$ の構造変化.

1) S. Rasul *et al*, *Angew. Chem. Int. Ed.* **2015**, 54, 2146.

1 A/cm^2 を超える電流密度での CO_2 電解還元反応

（阪大院基礎工 [1]）○神谷和秀 [1]・井上明哲 [1]・Tengyi Liu[1]・原田隆史 [1]・中西周次 [1]

High-Rate CO_2 Reduction Reactions with a Current Density Exceeding 1 A/cm^2

([1]*Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University*) ○Kazuhide Kamiya,[1] Asato Inoue,[1] Tengyi Liu,[1] Takashi Harada,[1] Shuji Nakanishi[1]

Excessive emissions of carbon dioxide (CO_2) from the use of fossil fuels are becoming a serious obstacle to the sustainable development of society. Electrochemical CO_2 reduction (CO_2RR) into value-added products using solar electricity is a promising technology to close the carbon cycle and sequester anthropogenic CO_2 into chemical feedstocks[1)]. The practical implementation of CO_2RR requires a high current density, as the current density for CO_2RR is directly correlated to the capital cost of the electrodes and electrochemical cells. In the present work, we sophisticatedly fabricated a triple-phase interface composed of solid electrocatalysts, liquid electrolytes and gaseous CO_2 to achieve record current densities of over 1 A/cm^2 to produce multicarbon products (C_{2+}) and formic acid[2,3)].

Keywords：*CO_2 electrolysis; Multicarbon Products; High Current Density; A Triple-Phase Interface*

カーボンニュートラルの実現に向けて，再生可能エネルギー由来の電力を用いた CO_2 電解が大きな注目を集めている [1)]。特に近年、ガス拡散電極(GDE)を用いて基質 CO_2 をガス状のまま反応界面に供給することで、CO_2 電解を高電流化しようとする試みが活発になりつつある。これまでこのガス状 CO_2 電解の高活性化に向けては、触媒などの各構成要素を個別に設計・開発する研究が主流であった。

我々は分子スケールでの材料設計と、マクロスケールでの界面設計を組み合わせることで、材料のポテンシャルを最大限に発揮させるといった思想に基づき研究を行ってきた。その結果、最も標準的な触媒である金属銅ナノ粒子を用いて、その触媒層の厚みや多孔性を精密に制御することで、世界最高の電流密度で駆動する超高電流密度 CO_2 電解系（C2 以上の化合物の生成電流密度 $j_{C2+} = 1.7$ A/cm^2）の立ち上げに成功した [2)]。さらに、我々は金属ナノフォームとカーボンナノ粒子をハイブリッドすることで、親/疎水界面を厚み方向に増加させることで、反応面である三相界面の面積を大幅に増加させた。その結果、水素キャリアとして期待されるギ酸の生成電流密度を 1 A/cm^2 を超えるまでに増大させることに成功した [3)]。

1) CO_2 electrolysis in integrated artificial photosynthesis systems. K. Kamiya, K. Fujii, M. Sugiyama, S. Nakanishi *Chem. Lett.* **2021**, *50*, 166-179.
2) Ultra-high-rate CO_2 reduction reactions to multicarbon products with a current density of 1.7 A cm^{-2} in neutral electrolytes A. Inoue, T. Harada, S. Nakanishi, K. Kamiya *EES Catal.* **2023**, *1,* 9-16.
3) A tin oxide-coated copper foam hybridized with a gas diffusion electrode for efficient CO_2 reduction to formate with a current density exceeding 1 A cm^{-2} T. Liu, K. Ohashi, K. Nagita, T. Harada, S. Nakanishi, K. Kamiya *Small* **2022**, *18,* 2205323.

Systematic Control of Electrochemical CO_2 Reduction Reaction Performances on Cu Nanocube by Surface Alloying with M (M=Pd, Pt, Ir, Ru)

([1]*Research Center for Negative Emissions Technologies, Kyushu University*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*, [3]*International Institute for Carbon-Neutral Energy Research, Kyushu University*, [4]*Advanced Institute for Materials Research, Tohoku University*)
○Hirokazu Kobayashi,[1] Sachie Hikino,[1] Miho Yamauchi[1,2,3,4]

Keywords: Copper; Nanocubes; Electrochemistry; Carbon Dioxide Reduction

Converting carbon dioxide (CO_2) into valuable chemicals through an electrochemical process holds great promise for establishing a carbon-neutral cycle. Among monometallic catalysts, copper (Cu) has shown particular potential for the electrochemical reduction of CO_2 into C_2 chemicals including ethylene (C_2H_4) and ethanol (C_2H_5OH). The formation of C_2 products is believed to involve the dimerization of intermediate CO* species, which plays a crucial role in the process.1, 2) In order to control a selectivity for the production of C_2 chemicals, we have paid attention to alloying Cu nanocubes with a metal (such as Pd, Pt, Ru or Ir) that exhibits different CO adsorption properties compared to Cu, although H_2 evolution reaction (HER) facilely occurs on their metals.

We have synthesized Cu-M core-shell surface alloy nanocrystals (Cu-M NCs, M=Pd, Pt, Ru and Ir), where a shell part of Cu NCs is alloyed with M by a galvanic replacement reaction. To characterize the shape and structure of the synthesized nanocrystals, we conducted scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and powder X-ray diffraction (XRD) measurements. The electrochemical CO_2 reduction performance was investigated using a gas diffusion cell.

TEM images shown in Fig. 1 revealed that the synthesized Cu-M NCs have cubic shapes similar to Cu NCs. The STEM and energy-dispersive X-ray (EDX) mappings demonstrated that the M element (Pd, Pt, Ru or Ir) was uniformly distributed around the surface of Cu NCs, forming a core/shell surface alloy structure. From the results of CO_2 reduction performance of Cu-Pd NCs, the selectivity for C_2H_4 decreased with increasing Pd content, whereas the selectivity for H_2 increased. This suggests that the alloying with Pd promotes HER. Interestingly, Cu-Pt and Cu-Ir NCs exhibited high selectivity, approximately 40% and 70%, respectively, for the production of formic acid (HCOOH). Cu NCs exhibit low selectivity (< 5%) for HCOOH, and Pt or Ir predominantly produces H_2, indicating the emergence of novel catalytic properties of Cu-Pt and Cu-Ir nanoalloys, which are completely distinct from those in their monometallic counterparts.

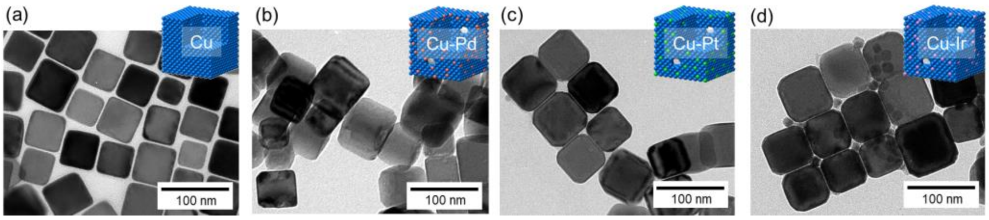


Fig. 1 TEM images of (a) Cu cubes, (b) Cu-Pd, (c) Cu-Pt and (d) Cu-Ir NCs.

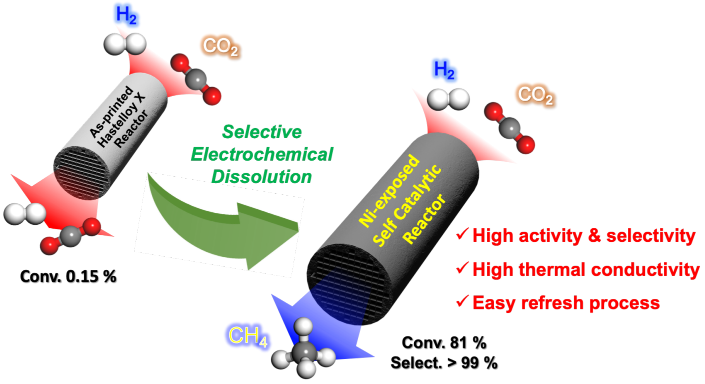
1) S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. Haasch, J. Gold, M. Yamauchi, P. Kenis, *J. Am. Chem. Soc.*, **2017**, *139*, 47.
2) M. Sun, A. Staykov, M. Yamauchi, *ACS Catal.*, **2022**, *12*, 14856.

Highly durable Ni-based self-catalytic reactor for CO_2 methanation designed by metal 3D printing combined and selective electrochemical dissolution

([1]*Division of Materials and Manufacturing Science, Osaka University*, [2]*Anisotropic Design & Additive Manufacturing Research Center, Osaka University*, [3]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University*) ○ Hyo-Jin Kim,[1] Kohsuke Mori,[1,2,3] Takayoshi Nakano,[1,2] Hiromi Yamashita,[1,3]

Keywords: CO_2 methanation, Metal 3D printing, Self-catalytic reactor, Selective electrochemical dissolution

CO_2 methanation ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is anticipated to play a pivotal role in future energy scenarios, owing to its high energy density and the accessibility of a well-established infrastructure. However, the commercial availability of catalysts is limited due to the intricacies involved in the catalyst development process. A recent breakthrough in addressing these challenges is the emergence of self-catalytic reactors (SCR). This innovative technology combines metal 3D printing with catalysis, integrating the functions of a catalyst and reactor into a single entity and simplifying the development process. Metal 3D printing technology has significantly facilitated the design of complex geometries for SCR, offering substantial benefits to catalytic performance.[1] In this study, we present the fabrication of a practical Ni self-catalytic reactor for CO_2 methanation using the selective laser melting (SLM) technique and electrochemical selective dissolution method.[2]



The as-printed Ni-SCR, treated at 50 $mV_{vsHg/HgO}$, exhibited the highest CO_2 conversion rate of 60% with > 99% CH_4 selectivity at 350 °C. This represents a 400-fold increase compared to the as-printed reactor. Analysis using SEM/EDS, XRD, and XPS indicated that the reactor surface treated at 50 $mV_{vsHg/HgO}$ transformed into β-$Ni(OH)_2$, characterized by a dark-green color, with a significant enrichment of nickel. Geometrically, an increase in the cell density of reactors was found to enhance the CO_2 conversion rate. The self-dissolution refresh process of the SCR proved to be a simple and effective method for regenerating active sites. This process resulted in overperformance, correlating with the number of refresh cycles undertaken.

1) Wei, Q, *Nat Commun* **11**, 1–8 (2020). 2) Kim, H. J., *Adv Funct Mater* **2303994**, 1–11 (2023).

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21日(木) 13:00 ~ 15:40 F1231(12号館 [3階] 1231)

[F1231-4pm] 09. 錯体化学・有機金属化学

座長：谷藤 一樹、福井 智也

日本語
13:00 ~ 13:20
[F1231-4pm-01]
N_2型の電子配置を有する$Pd_2Au_{17}(PR_3)_{10}Cl_7$クラスターの合成

○齋藤 亮平[1]、水畑 吉行[1]、磯﨑 勝弘[1]、中村 正治[1] (1. 京都大学)

英語
13:20 ~ 13:40
[F1231-4pm-02]
リン酸水素イオンがオキシドあるいはヒドロキシド二重架橋コアに架橋したルテニウム二核錯体の性質

○三澤 智世[1]、長尾 宏隆[1] (1. 上智大理工)

日本語
13:40 ~ 14:00
[F1231-4pm-03]
α-シクロデキストリン（CDX）に糸通しした1,12-ジアミノドデカン（don）の両末端に異なるコバルト(III)錯体をもつロタキサンの合成

○荻野 博[1]、猪俣 慎二[2]、笠井 香代子[3] (1. 東北大学、2. 福島大学、3. 宮城教育大学)

英語
14:00 ~ 14:20
[F1231-4pm-04]
NHC/ピリジル混合系配位子を用いた第10族遷移金属錯体の合成と反応性

○岡村 将也[1]、小花 咲季[1]、今泉 公太[1]、北原 美彩[1]、鈴木 伶奈[1]、引地 史郎[1] (1. 神奈川大)

日本語
14:20 ~ 14:40
[F1231-4pm-05]
ホウ素置換シリルリチウムの合成，反応および構造

小和田 雄太[1]、○河内 敦[2] (1. 法政大学大学院理工学研究科応用化学専攻、2. 法政大学生命科学部環境応用化学科)

英語
14:40 ~ 15:00
[F1231-4pm-06]
求核的アルミニウムと求電子的アルミニウムの反応によるAl-Al結合の構築

○山梨 遼太朗[1]、水谷 奏太[1]、山下 誠[1] (1. 名古屋大学大学院)

英語
15:00 ~ 15:20
[F1231-4pm-07]
大環状分子を配座固定できる拡張中空錯体の固相テンプレート合成

○飯塚 健太[1]、竹澤 浩気[1]、藤田 誠[1,2] (1. 東大、2. 分子研)

🏷 英語
15:20 ~ 15:40
[F1231-4pm-08]

アズレン誘導体を配位子とした金属錯体の合成とその構造解析

○岩品 達矢[1]、山本 一樹[1]、郡司 天博[1] (1. 東京理科大学)

日本化学会 第104春季年会 (2024)

N_2 型の電子配置を有する $Pd_2Au_{17}(PR_3)_{10}Cl_7$ クラスターの合成

（京大院工・京大化研）○齋藤　亮平 [1,2]・水畑　吉行 [2]・磯﨑　勝弘 [1,2]・中村　正治 [1,2]

Synthesis of a Phosphine-protected $Pd_2Au_{17}(PR_3)_{10}Cl_7$ Nanocluster with N_2-type Electron Configuration

([1]*Graduate School of Engineering, Kyoto University,* [2]*Institute for Chemical Research*, *Kyoto University*) ○ Ryohei Saito, Yoshiyuki Mizuhata, Katsuhiro Isozaki, Masaharu Nakamura

Metal nanoclusters often have an electronic structure resembling small molecules due to the formation of superatomic molecular orbitals originating from the linear combination of superatomic orbitals. In this study, we successfully synthesized novel $Pd_2Au_{17}(depp)_{10}Cl_7$ (depp = diethylphenylphosphine) by visible light irradiating to $PdAu_{12}(depp)_8Cl_4$. Single crystal X-ray diffraction revealed that this new cluster has a Pd_2Au_{17} core composed of two $PdAu_{12}$ units sharing an Au_5 facet. Density-functional theory (DFT) calculations reveal that superatomic orbitals of the two icosahedrons construct dinitrogen (N_2)-type superatomic molecular orbitals having the electron configuration of $(1\Sigma_s)^2(1\Sigma_s*)^2(1\Pi_{px,\,py})^4(1\Sigma_{pz})^2$.

Keywords : Gold Nanocluster; Superatom; Superatomic molecule; Electron Configuration

正二十面体形のM_{13}コアを有する金属ナノクラスターは，8つの価電子を1S, 1P超原子軌道に収容したNe型の閉殻電子配置を取る際に安定化される。さらにM_{13}超原子がそれぞれの頂点や面の金原子を共有したコア構造を有する金属ナノクラスターでは，複数のM_{13}コアの超原子軌道同士が線形結合し超原子分子軌道を形成し，結合性軌道に価電子を収容するために安定化すると考えられている。例として，2つのAu_{13}超原子が3つの金原子を面共有して結合したコア構造を持つ$Au_{38}(SR)_{24}$クラスターは安定であるが，これは F_2分子様の閉殻電子配置をとるためと考えられている[1]。しかしながら，このような小分子と類似した超原子分子軌道を有するクラスターの合成例は少なく，超原子軌道間の相互作用や，それにより発現する機能は未解明である。

今回我々は，中心にPdを有する正二十面体形の$PdAu_{12}(depp)_8Cl_4$ (depp = diethylphenylphosphine) を前駆体とし，可視光を照射することで，新規の組成と構造を有する$Pd_2Au_{17}(depp)_{10}Cl_7$の合成に成功した(Figure 1)。単結晶構造解析から，得られた新規クラスターは二つのMAu_{12}超原子が5つの金原子を面共有したコアを有することが明らかとなった。DFT計算からは，M_2Au_{17}クラスターは，2つのMAu_{12}超原子の超原子軌道が線型結合することで，10個の価電子が窒素分子と同様の電子配置 $(1\Sigma_s)^2(1\Sigma_s*)^2(1\Pi_{px,\,py})^4(1\Pi_{pz})^2$ をとることが示唆された。本発表では，クラスターの合成法や構造，計算により得られた結果の詳細について報告する。

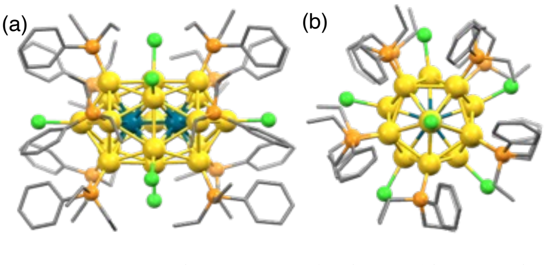


Figure 1. Crystal structure of $Pd_2Au_{17}(depp)_{10}Cl_7$: (a) front and (b) side view.

1. Jin, R. *et al. J. Am. Chem. Soc.* **2010,** *132*, 8280–8281.

Properties of Diruthenium Complexes Having a Hydrogenphosphato Ligand Bridged on the $\{Ru_2(\mu\text{-}O(H))_2\}$ Core

([1]*Fac. of Sci. and Tech., Sophia University*) ○Tomoyo Misawa-Suzuki,[1] Hirotaka Nagao[1]

Keywords: *Dinuclear Complex, Doubly Oxido-Bridge, Redox Behaviors, Spectroscopic Behaviors*

For the development of model compounds of natural metalloenzymes having diiron centers, we have been studying a series of diruthenium complexes having the doubly oxido-/hydroxido-bridged core, $\{Ru_2(\mu\text{-}O(H))_n\}$ ($n = 1, 2$).[1,2] The electronic structures of the complexes range from Ru(IV)-Ru(IV),[1] Ru(III)-Ru(IV),[2] to Ru(III)-Ru(III),[3] in the same tridentate ligand (ethylbis(2-pyridylmethyl)amine; ebpma) system.

In this work, a HPO_4^{2-}-bridged Ru(III)-Ru(IV) complex having the $\{Ru_2(\mu\text{-}O)_2\}$ core, $[\{Ru^{III,IV}(ebpma)\}_2(\mu\text{-}O)_2(\mu\text{-}O_2PO_2H)]ClO_4$ ([**III,IV**(**HPO$_4$**)]ClO_4), was synthesized in water-acetone (pH of around 8) at room temperature, showing the $S = 1/2$ state ($\mu_{eff} / \mu_B = 1.70$ at 297 K). The electronic structures and electrochemical and spectroscopic properties of [**III,IV**(**HPO$_4$**)]$^+$ were investigated and the comparisons were made with a series of Ru(III)-Ru(IV) complexes having the $\mu\text{-}O_2XY^{m-}$ ligand (**Table**). The redox potentials ($E_{1/2}$) of the $Ru^{IV}\text{-}Ru^{IV}/Ru^{III}\text{-}Ru^{IV}$ couple and the maximum absorption bands (λ_{max}) of the $\{Ru_2(\mu\text{-}O)_2\}\text{-}\{Ru_2(\mu\text{-}O)_2\}^*$ transitions in CH_3CN showed correlations, indicating that the stronger electron-donating characters of the $\mu\text{-}O_2XY^{m-}$ ligand on the $\{Ru_2(\mu\text{-}O)_2\}$ core destabilize the SOMO energy levels.

The pK_as were observed at 8.8 for the equilibrium between [**III,IV**(**HPO$_4$**)]$^+$ and [**III,IV**(**PO$_4$**)], and 3.5 for that between $\{Ru_2(\mu\text{-}O)(\mu\text{-}OH)\}$ ([**III,IV**(**HPO$_4$**)**_1H**]$^{2+}$) and $\{Ru_2(\mu\text{-}O)_2\}$ ([**III,IV**(**HPO$_4$**)]$^+$) by the spectroscopic studies in water at 298 K. The redox behaviors in water and the one-electron oxidation of [**III,IV**(**HPO$_4$**)]$^+$ will be reported as well.

Table. Properties of Ru(III)-Ru(IV) complexes with the $\{Ru_2(\mu\text{-}O)_2\}$ core bridged by the O_2XY^{m-} ligand at 298 K.

$\mu\text{-}O_2XY^{m-}$	μ_{eff} / μ_B (295 ~ 298 K)	pK_a *	$E_{1/2}$**($Ru^{IV}\text{-}Ru^{IV}/Ru^{III}\text{-}Ru^{IV}$) / V	E_{pa}**($Ru^{IV}\text{-}Ru^{V}/Ru^{IV}\text{-}Ru^{IV}$) / V	λ_{max} (ε) / nm (M^{-1} cm^{-1})
CO_3^{2-} [1,2a]	2.01	†	0.15	†	1067 (660)
HPO_4^{2-}	**1.70**	**3.5**	**0.22**	**2.22**	**1016 (1020)**
SO_4^{2-}	1.79	2.1	0.31	2.02	945 (1440)
$CH_3CO_2^-$ [2b]	2.19	1.5	0.57	†	977 (1440)
HCO_3^- [1,2a]		2.4	0.60	†	972 (1490)
NO_3^- [2b]	2.17	†	0.93	†	762 (1300)

*between $\{Ru_2(\mu\text{-}O)(\mu\text{-}OH)\}$ and $\{Ru_2(\mu\text{-}O)_2\}$. ***vs*. Ag|0.01 M $AgNO_3(CH_3CN)$, 100 mV s^{-1}. † not observable.

1) T. Misawa-Suzuki, H. Nagao, *Dalton Trans*. **2023**, *52*, 2863.

2) a) T. Misawa-Suzuki, H. Nagao *et al*., *Inorg*. *Chem*. **2021**, *60*, 9996. b) T. Misawa-Suzuki, H. Nagao *et al*., *Inorg*. *Chem*. **2020**, *59*, 612. c) T. Suzuki, H. Nagao *et al*., *Inorg*. *Chem*. **2016**, *55*, 6830.

3) T. Misawa-Suzuki *et al*., 10th Asian Biological Inorganic Chemistry Conference, **2022**.

α-シクロデキストリン（CDX）に糸通しした 1,12-ジアミノドデカン（don）の両末端に異なるコバルト(III)錯体をもつロタキサンの合成

(東北大院理 [1]・福島大共生システム理工 [2]・宮教大教育 [3])
○荻野 博 [1]・猪俣慎二 [2]・笠井香代子 [3]

The Synthesis of Rotaxanes Consisting of α-Cyclodextrin (CDX) Threaded by 1,12-Diaminododecane (don) Bearing Two Different Cobalt(III) Complexes as Stoppers

([1]Tohoku University, [2]Fukushima University, [3]Miyagi University of Education)

○Hiroshi Ogino[1], Shinji Inomata[2], Kayoko Kasai[3]

The title rotaxanes were synthesized by the following two routes:
Route 1: $[CoCl(en)_2(monodentate\ don)]^{2+} + [Co(H_2O)(NH_3)_5]^{3+}$ + CDX →
$[2]$-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane A)
Route 2: $[Co(monodentate\ don)(NH_3)_5]^{3+} + [CoCl_2(en)_2]^{+}$ + CDX →
$[2]$-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane B)
Where en denotes 1,2-diaminoethane. ^{13}C-NMR spectra of the rotaxanes indicate that those of A and B are largely different. It is suggested that the direction of CDX in the rotaxane A is opposite to that in the rotaxane B.

Keywords：Synthesis of Rotaxanes; Cyclodextrin Rotaxane; Cobalt(III) Complexes

CDX はバケツの底を抜いた形の筒状の分子である。本研究の発表者(H.O.)は 1979 年に CDX に糸通しした don (1,12-diaminododecane)の両末端に$[CoCl(en)_2]^{2+}$を結合させたロタキサンを合成し、発表した。[1, 2] 両末端に異なる錯体をもつロタキサンを合成すると、CDX の向きの違いによる異性体が生成するはずである。本研究では、次の２つのルートでロタキサンを合成した（溶媒は DMSO）。

ルート１：$[CoCl(en)_2(monodentate\ don)]^{2+} + [Co(H_2O)(NH_3)_5]^{3+}$ + CDX →
$[2]$-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane A)
ルート２：$[Co(monodentate\ don)(NH_3)_5]^{3+} + [CoCl_2(en)_2]^{+}$ + CDX →
$[2]$-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane B)

ロタキサン A と B の ^{13}C-NMR スペクトルは大きく異なっており、ロタキサンに取り込まれた CDX の向きは A と B とで逆向きであることを示唆している。

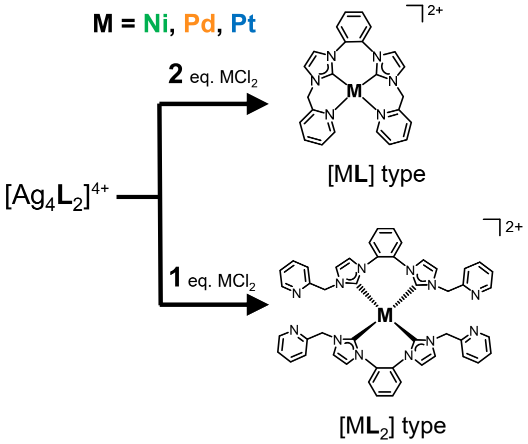
1) 荻野博、第 29 回錯体化学討論会(1979).
2) H. Ogino, *J.Am.Chem.Soc.*, **23**, 1303-1304(1981).

Synthesis and reactivity of group 10 transition metal complexes bearing a NHC/Pyridyl hybrid ligand.

([1]*Faculty of Chemistry and Biochemistry*, *Kanagawa University*) ○Masaya Okamura[1], Saki Kobana[1], Kota Imaizumi[1], Misa Kitahara[1], Rena Suzuki[1], Shiro Hikichi[1]

Keywords: N-Heterocyclic Carbene; Chelating Ligand; Catalyst; CO_2 Reduction

Recently, transition metal complexes bearing NHC/Pyridyl hybrid ligands, which have electron-donating NHCs with π-electron accepting pyridyl sites, have attracted attention for their excellent catalytic activity in a variety of reactions. In such mixed system ligands, it is known that the length and flexibility of the linker moiety connecting each functional group significantly affect their steric structure and catalytic activity. In this study, a hybrid chelating ligand, **L** was developed by connecting two NHC groups with a rigid phenylene linker and introducing a pyridyl group via a methylene spacer to provide flexibility in the coordination mode, and group 10 transition metal complexes with **L** as the ligand were synthesized and characterized.



Scheme 1. Synthesis of the complexes.

The imidazolium precursor, $H_2\mathbf{L}^{2+}$ was synthesized according to the procedure reported for a similar compound. The Br^- salt of $H_2\mathbf{L}^{2+}$ was then treated with an excess of Ag_2O at 80° in CH_3CN to form an Ag-**L** intermediate. X-ray structural analysis of this crystal revealed a $[Ag_4\mathbf{L}_2]^{4+}$ structure consisting of linear Ag_4 chains. Next, the reaction of the BF_4^- or ClO_4^- salts of the $Ag_4\mathbf{L}_2$ complex with metal-halides ($NiCl_2$, $PdCl_2$, K_2PtCl_4) in CH_3CN at 80ºC led to the formation of two types of complexes depending on the equivalent amount of metal ions (Scheme 1). Upon the reaction of $[Ag_4\mathbf{L}_2]^{4+}$ complexes with two equivalents of metal ions, complexes with [M**L**]-type compositions were formed. Single crystal X-ray analysis revealed a distorted square planar structure with a tetradentate coordination of **L**. On the other hand, $[M\mathbf{L}_2]$-type complexes were obtained when one equivalent of the metal ion was used. The crystal structures showed that the two **L** ligands were bidentate to the metal center via NHC moieties, while the four pyridine moieties were free without coordination. Due to the different orientations of the phenylene groups, the Ni(II) and Pd(II) complexes form an almost perfect square planar structure, while the Pt(II) complex has a distorted square planar structure. The electrochemical properties of the obtained complexes were evaluated by cyclic voltammetry, and a large increase in cathodic current was observed in the [M**L**]-type complexes upon reductive scanning in a CO_2 atmosphere, suggesting their catalytic activity.

ホウ素置換シリルリチウムの合成，反応および構造

(法政大院理工[1]・法政大生命[2])小和田 雄太[1]・○河内 敦[2]

Preparation, Reactions, and Structure of Boron-substituted Silyllithium

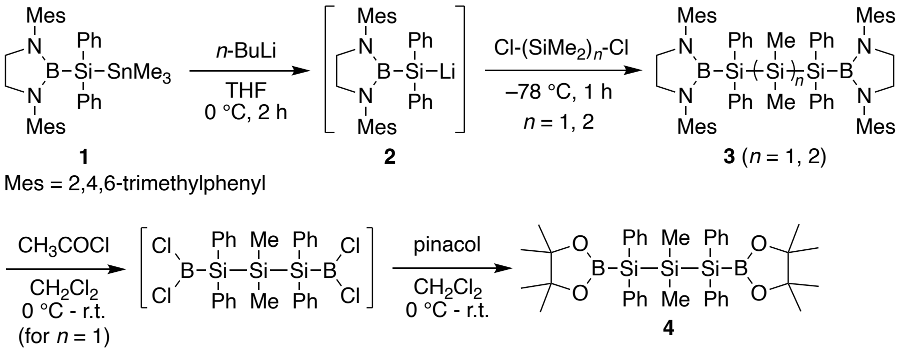
([1]*Graduate School of Science and Engineering, Hosei University,* [2]*Faculty of Bioscience and Applied Chemistry, Hosei University*) Yuta Kowada,[1] ○Atsushi Kawachi[2]

We previously reported the preparation of boron-substituted silyllithium **2** via the Sn-Li exchange reaction between silylstannane **1** and *n*-BuLi and the preparation of boron-substituted oligosilanes **3** by the reaction of **2** with dichlorosilanes. Herein, we report the structural analysis of oligosilanes **3** and the transformation of the substituents on the boron atoms in oligosilanes **3**. Some findings about the preparation of **2** and the structural study on silyllithium **2** in THF solution by NMR spectroscopies are also reported.

Keywords: Borylsilane, Silylstannane, Silyllithium, Oligosilane, Silane, Borane

当研究室ではすでに，ボリルシリルスタンナン **1** と *n*-ブチルリチウムとの Sn-Li 交換反応によるホウ素置換シリルリチウム **2** の合成とそれを用いたホウ素置換オリゴシラン **3** の合成について報告している1)。本発表では，オリゴシラン **3** の詳細な構造解析およびオリゴシランのホウ素原子上の置換基変換反応によるオリゴシラン **4** の合成について報告する。また，ホウ素置換シリルリチウム合成におけるホウ素原子上の置換基についての知見および各種 NMR スペクトル測定による THF 中でのシリルリチウム **2** の構造解析についても報告する。

Scheme 1



1) 小和田雄太，河内敦，日本化学会第 103 春季年会，K503-2am-06(2023).

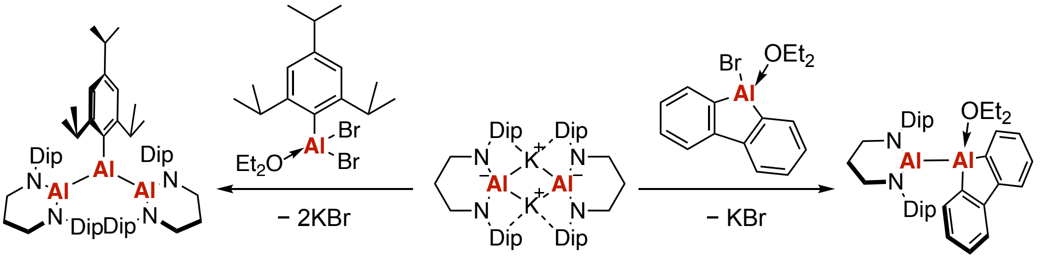
Synthesis of linear trialumane and unsymmetrical dialumane using Al anion

([1]*Graduate School of Engineering, Nagoya University*) ○Ryotaro Yamanashi,[1] Kanata Mizutani,[1] Makoto Yamashita[1]

Keywords: Aluminum; Dialumane; Trialumane; Catenation

Catenation is a term that refers to a property of an element to form the linear linkage of bonds between identical elements. It is a common phenomenon for group 14 elements as found in polyolefins and polysilanes. In contrast, no linear aluminum linkage with three or more aluminum atoms has been reported. In molecular chemistry of aluminum, three methods have been known to construct Al-Al bonds: (1) reduction of Al-H or -halogen bonds;[1] (2) insertion of alumylene, neutral Al(I) species, into the Al-halogen bond;[2] and (3) generation of neutral CpAl species and its spontaneous oligomerization to form Al clusters.[3] Recently, the first nucleophilic Al anion was reported to initiate a rapid advance in chemistry of Al nucleophiles.[4] Herein, we report the synthesis of dialumane and trialumane using our newly reported amino-substituted Al anion[5] and electrophilic aluminum reagents.

A linear trialumane was synthesized by reaction of our amino-substituted Al anion with $\mathrm{TipAlBr_2{\cdot}OEt_2}$ (Tip = 2,4,6-$^{i}\mathrm{Pr_3C_6H_2}$) (Scheme 1, left). Following the same strategy, we synthesized an unsymmetrical dialumane by reaction of the Al anion with *Al*-bromoaluminafluorene-ether complex (Scheme 1, right). In the presentation, the synthesis, structure, and reactivity of the resulting alkyl-, aryl substituted trialumanes and the unsymmetrical dialumane will be discussed.



Scheme 1. left: Synthesis of trialumane, right: Synthesis of unsymmetrical dialumane

1) A) Uhl, W. Z. *Naturforsch. B* **1988**, *43b*, 1113. B) Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nat. Chem.* **2010**, *2*, 865. 2) A) Li, B.; Kundu, S.; Zhu, H.; Keil, H.; Herbst-Irmer, R.; Stalke, D.; Frenking, G.; Andradac, D. A.; Roesky, H. W. *Chem. Commun.* **2017**, *53*, 2543. B) Hofmann, A.; Tröster, T.; Kupfer, T.; Braunschweig, H. *Chem. Sci.* **2019**, *10*, 3421. 3) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem. Int. Ed.* **1991**, *30*, 564. 4) A) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Nature 2018, 557, 92. B) Hobson, K.; Carmalt, C. J.; Bakewell, C. Chem. Sci. 2020, 11, 6942. C) Zhang, X.; Mei, Y.; Liu, L. L. *Chem. Eur. J.* **2022**, *28*, e202202102. 5) Feng, G.; Chan, K.L.; Lin, Z.; Yamashita, M. *J. Am. Chem. Soc.* **2022**, *144*, 22662.

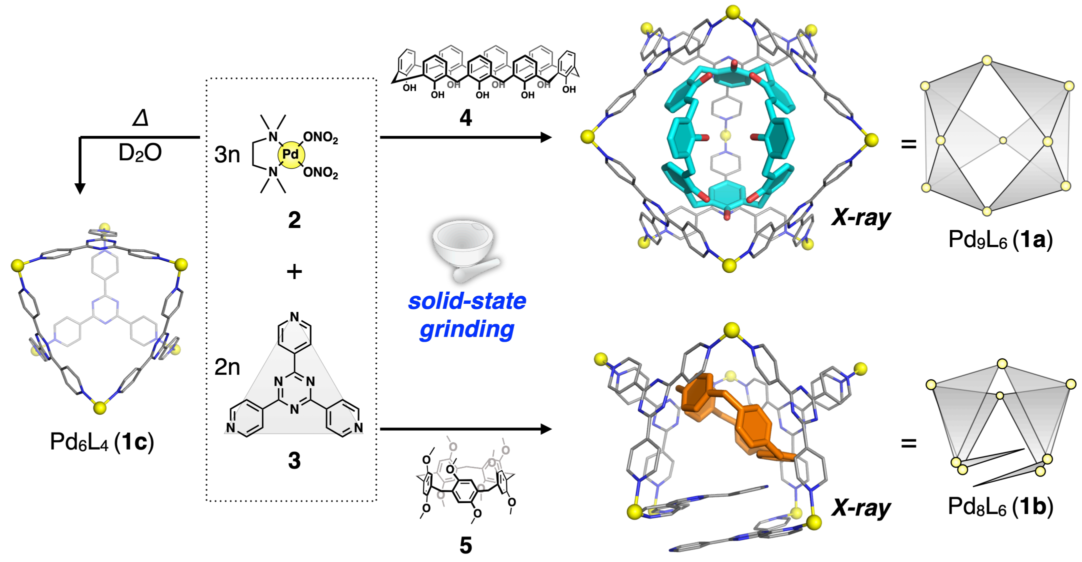
Construction of Expanded Hollow Cages by Templated Self-assembly in the Solid State for Conformation Control of Organic Macrocycles

([1]*School of Engineering, The University of Tokyo*, [2]*Division of Advanced Molecular Science, Institute for Molecular Science,* [3]*UTIAS, The University of Tokyo*)
○Kenta Iizuka,[1] Hiroki Takezawa,[1] Makoto Fujita[1,2,3]

Keywords: Self-assembly; Hollow cage; Conformational manipulation; Macrocycle; Solid-state reaction

Conformational manipulation by inclusion in host molecules is effective for controlling reactivities and properties of the guest molecule. However, the conformation fixing of middle molecules in a confined cavity has not been explored because of the absence of a suitable artificial host that has a large enough hydrophobic cavity. In this work, we achieved the construction of two types of expanded hollow cages **1** for conformational fixation of middle molecules by templated self-assembly in a solid state.

Powders of palladium complex **2**, tripodal ligand **3**, and macrocycle **4** were ground in a mortar with a pestle, and the resulting solid was suspended in D_2O and heated for several minutes. NMR and single-crystal X-ray diffraction studies revealed the formation of an inclusion complex of **4** with novel Pd_9L_6 cage **1a** in 46 % yield. The symmetry of **4** was degraded from apparent D_{8h} to C_{2v}, which reflects the conformational fixation of flexible macrocycle **4** by confinement. When **2**, **3**, and **4** were heated in D_2O without grinding, known M_6L_4 cage **1c** was solely obtained, suggesting no template effect of **4** in the solution state. When macrocycle **5** was used instead of **4**, Pd_8L_6 cage **1b** was formed with a similar protocol. In this case, D_5 symmetry of **5** was completely degraded to C_1 by inclusion.



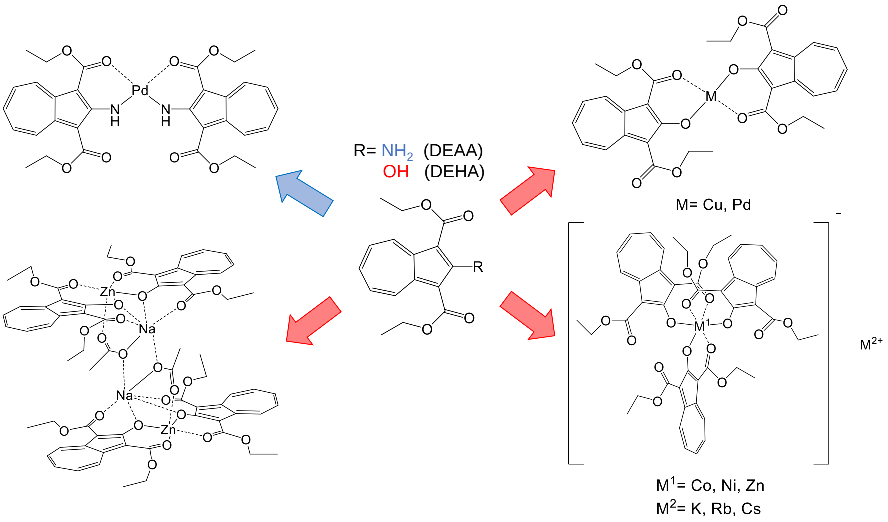
Synthesis and Structural Analysis of Metal Complexes with Azulene Derivatives as Ligands

([1]*Tokyo University of Science*) ○Tatsuya Iwashina,[1] Kazuki Yamamoto,[1] Takahiro Gunji[1]

Keywords: Azulene; Metal complexes; Coordination polymer; Double salt; Complexation reaction

Azulene is a structural isomer of naphthalene and is known as a unique compound that exhibits blue coloration with a simple structure. Azulene and its derivatives have attracted attention in the fields of organic synthesis and photochemistry because of their unique reactivity derived from their electronic states and optical properties 1), 2). However, there are few reports on metal complexes with azulene derivatives as ligands, and their structures and properties are of great interest. Therefore, we investigated the synthesis of metal complexes with azulene derivatives, diethyl 2-aminoazulene-1,3-dicarboxylate (**DEAA**) and diethyl 2-hydroxyazulene-1,3-dicarboxylate (**DEHA**), as ligands.

When **DEAA**, an azulene derivative with nitrogen, was used as a ligand, stable complexes were formed only with Pd. On the other hand, stable complexes with Co, Ni, Cu, Zn, and Pd were formed when **DEHA**, an azulene derivative with oxygen, was used as a ligand. In the Pd complexes, a change in coordination structure was observed between DEAA and DEHA as ligands. In the Co, Ni, and Zn complexes, hetero-complexes with Cs^+ used as a base were formed. In the synthesis of Zn complexes, when the base was changed from Cs_2CO_3 to Rb_2CO_3, K_2CO_3, Na_2CO_3, coordination polymers were formed for Cs, Rb, and K, but in the case of Na, the complexes had a cluster structure. Identification was performed by ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometries, elemental analysis, single crystal X-ray structure analysis, and UV-Vis spectra.



1) A. C. Razus, *Symmetry*. **2023**, *15*, 1391. 2) D. Dunlop, L. Ludviková, A. Banerjee, H. Ottosson, T. Slanina, *J. Am. Chem. Sos*. **2023**, *145*, 21569-21575.

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21日(木) 13:00 ~ 15:10 F1232(12号館 [3階] 1232)

[F1232-4pm] 09. 錯体化学・有機金属化学

座長：浦 康之、中島 裕美子

英語

13:00 ~ 13:20

[F1232-4pm-01]

Ruレドックス光増感部の還元力がRu(II)-Re(I)超分子光触媒のCO_2還元光触媒能に及ぼす影響

○鴨川 径[1]、石谷 治[1,2] (1. 東工大理、2. 広島大院先進理工)

英語

13:20 ~ 13:40

[F1232-4pm-02]

Electrocatalytic Reduction of Low Concentration CO_2 to CO Using Phenol and a Re(I) complex

○Siby Mathew[1], Osamu Ishitani [1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

英語

13:40 ~ 14:00

[F1232-4pm-03]

トリオルガノヒドロシランからのシリレン発生を利用したイリジウム触媒分子間シリレントランスファー反応

○宋 ユンハオ[1]、杉野目 道紀[1] (1. 京都大学)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[F1232-4pm-04]

三配位ホウ素ルイス酸部位を有する弱配位アニオンによるイリジウム触媒反応の選択性制御

○萬代 遼[1]、岩﨑 孝紀[1]、野崎 京子[1] (1. 東大)

英語

14:30 ~ 14:50

[F1232-4pm-05]

Electrochemical Homogeneous CO_2 Reduction Catalyzed by N-Heterocyclic Carbene Stabilized Au-Nanoclusters

○Samuel Jacob[1], Joey DeJesus[1], Masakazu Nambo[1,2], Cathleen Crudden[1,3,4] (1. Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya, Aichi, Japan, 2. Department of Chemistry, Graduate School of Science, Nagoya University; Furo, Chikusa, Nagoya, Aichi, Japan, 3. Department of Chemistry, Queen’s University, Chernoff Hall, Kingston Ontario, Canada, 4. Carbon to Metal Coating Institute, Queen’s University, Kingston, Ontario, K7L 3N6, Canada)

英語

14:50 ~ 15:10

[F1232-4pm-06]

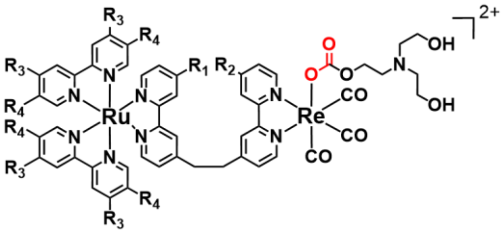
超分子反応場を有する金ナノクラスターの触媒的アルキン変換反応への応用

○井芹 建太[1]、磯﨑 勝弘[1]、中村 正治[1] (1. 京都大学)

Effects of the Reduction Potential of the Ru(II) Redox Photosensitizer Unit in Ru(II)-Re(I) Supramolecular Photocatalysts on their Photocatalysis for CO_2 Reduction

([1]*School of Science, Tokyo Institute of Technology*, [2]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kei Kamogawa,[1] Osamu Ishitani[1,2]

Keywords: *Carbon dioxide reduction, Photocatalyst, Metal Complex*



(1): R_1 R_2 R_3=Me, R_4=H
(2): R_1 R_3=OMe, R_2 R_4=H
(3): R_1=OMe, R_2=H, R_3 R_4=Me
(4): R_1=OMe, R_2 R_3 R_4=Me

Fig. 1 Structure of photocatalysts

A Ru(II)-Re(I) supramolecular photocatalyst (**1**) consisting of the $[Ru(diimine)_3]^{2+}$ redox photosensitizer and *fac*-$[Re(diimine)(CO)_3(OC(O)OC_2H_4N(CH_2CH_2OH)_2]$ as a catalyst can efficiently reduce CO_2 to CO with high selectivity, which has been applied to various combined systems with solid materials.[1] Recently, we fully clarified the photocatalytic CO_2 reduction mechanism by **1** detecting the reaction intermediates using various techniques such as time-resolved spectroscopy and liquid chromatography.[2,3] This mechanistic study suggests some important points for improving the photocatalysis of **1**. Two electron reduced intermediates of **1** which have carboxylic acid ligand (-COOH) or carboxylate ester ligand ($-COOCH_2CH_2N(CH_2CH_2OH)_2$) at axial position of Re catalyst unit show relatively low reactivity and are accumulated during the photocatalytic reaction. Importantly, reduction of the intermediates increases release of CO from the intermediates. Since, however, the Re units of these intermediates have a ~100 mV more negative reduction potential compared with the Ru photosensitizer unit, the accumulation of these intermediates causes the accumulation of one-electron reduced species (OERS) of Ru unit of which excitation induces ligand substation,[4] resulting in the decomposition of the photosensitizer unit.

To suppress the accumulation of the intermediates and accelerates the CO release from the intermediates, novel photocatalysts (**2-4**) of which the reduction potentials of the Ru and Re centers shift to negative and positive, respectively. By this adjustment of the potentials, the accumulation of OERS in the Ru unit was clearly suppressed, and the photocatalytic reaction speed increased. However, these structure changes of the photocatalysts induces another decomposition process. In this presentation, we will provide detailed insights into the photocatalytic activity of these photocatalysts.

[1] T. Nakajima, O. Ishitani, *et. al.*, *J. Am. Chem. Soc.*, 2016, **138**, 13818. [2] K. Kamogawa, O. Ishitani, *et. al., Chem. Sci.*, 2021, **12**, 9682. [3] K. Kamogawa, O. Ishitani, *et. al.*, *Chem. Sci.*, 2024 in press. [4] J. M. Lehn, *et. al.*, *J. Organomet. Chem.* 1990, **382**, 157.

Electrocatalytic Reduction of Low Concentration CO_2 to CO Using Phenol and a Re(I) Complex

([1]*Department of Chemistry, Tokyo Institute of Technology;* [1]*Department of Chemistry, Hiroshima University*) ○Mathew Siby,[1] Ishitani Osamu [1,2]

Keywords: CO_2 reduction; Electrocatalyst; Phenol; Low concentration CO_2; Re-complex catalyst

The electrocatalytic reduction of CO_2 into energy-rich chemicals is a pivotal strategy in the pursuit of sustainable energy solution. Although extensive efforts have been dedicated to the photo- and electro-catalytic reduction of pure CO_2, the reduction of low-concentration CO_2 remains a significant challenge, primarily due to the inefficient CO_2 capturing under these conditions. Our previous investigations on the Re(I) complex have unveiled a plausible approach for the capture of low concentration CO_2 using an axially ligated triethanolamine (TEOA) and its selective electrolytical reduction into CO.[1] In this presentation, we report the electrocatalytic reduction of CO_2 by fac-$[Re(bhmb)(CO)_3(H_2O)]^+$ (**Re(bhmb)**, bhmb = 4,4'-bis(hydroxymethyl)-2,2'-bipyridine), with the assistance of phenol in the absence and presence of water.

In a DMSO-PhOH (3M) mixed solution, **Re(bhmb)** selectively produces CO with a very high Faradic efficiency in 100% CO_2 atmosphere (Figure 1a). This electrocatalysis could be kept even under Ar containing 10% CO_2 (Figure 1b). In the case using 1% CO_2, formation speed of CO decreased (Figure 1c). The deprotonated phenol, i.e., the phenoxide anion was coordinated to the Re complex, forming Re(bhmb)-OPh complex and serving as CO_2 capturing ligand. The resulting CO_2 inserted complex Re(bhmb)-CO_2-OPh liberates CO. This transformation proceeds very efficiently, at a similar rate, even in the presence of water (5% v/v).

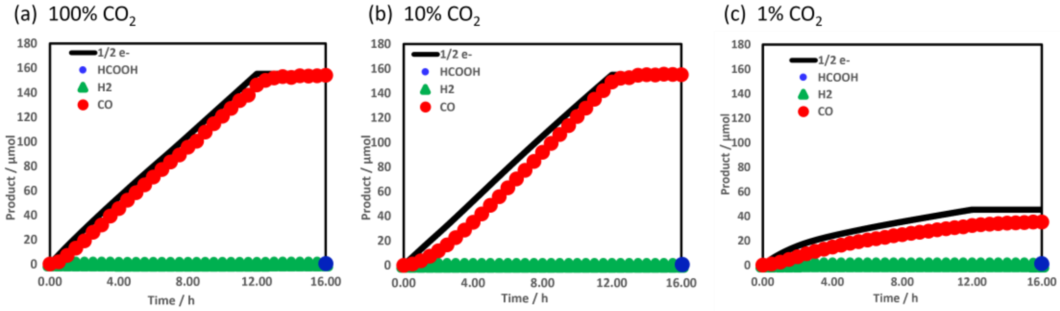


Figure 1 Time courses of generation of CO (red data point), H_2 (green triangle), and formic acid (blue data point) with half of the electrons flowing (line) during bulk electrolysis using the Re(bhmb) (0.5 mM) at -1.71 V vs $Ag/AgNO_3$ in a DMSO–PhOH (3M) solution containing Et_4NBF_4 (0.1 M) under (a) 1%, (b) 10% and (c) 100% CO_2 atmospheres.

1) Kumagai, H. and Ishitani, O. *et al.*, *Chem. Sci.* **2019**, *10*, 1597.

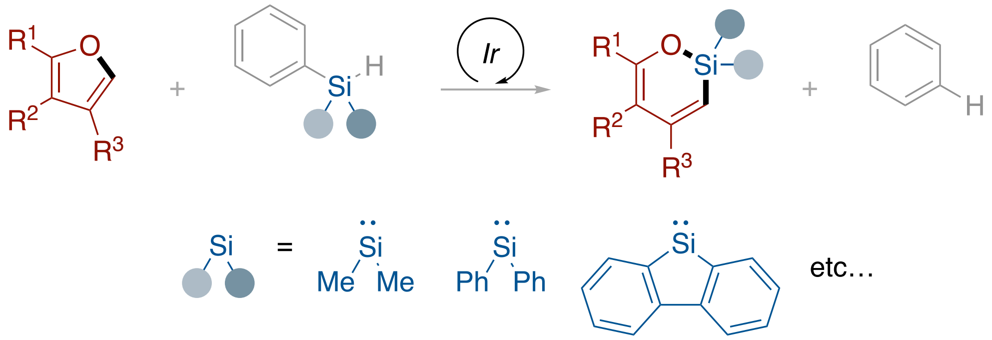
Iridium-Catalyzed Intermolecular Silylene Transfer Reaction Utilizing Silylene Generated from Triorganohydrosilanes

(*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University*) ○Yunhao Song, Michinori Suginome

Keywords: Silylene; Iridium Catalyst; Hydrosilane; Insertion Reaction; C-O Bond Cleavage

Silylene transfer reactions (STR) have attracted much attention in synthetic organosilicon chemistry, because two silicon-containing σ-bonds are formed in a single transformation either via insertion into σ-bonds or via cycloaddition to unsaturated bonds.[1,2] While a variety of silylene precursors for STR under catalytic and thermal reaction conditions have been developed, they are in most cases poorly handleable, less accessible, or requiring too harsh reaction conditions, hampering wide utilization of STR in the synthesis of organosilicon compounds. It is therefore highly desirable to explore new silylene precursors for more practical synthesis of organosilicon compounds and for the development of new STR. We herein report use of aryldiorganohydrosilanes as easily available and stable silylene precursors in the presence of iridium catalysts, leading to new STR in which diorganosilylene is inserted into the C−O bond of furan rings.

Furan derivatives and PhR_2SiH were heated in the presence of an iridium catalyst, affording 1,2-oxasiline derivatives via insertion of diorganosilylene (R_2Si:) into the C(sp^2)−O bond in the furan rings. It should be noted that formation of benzene was confirmed as a single byproduct in this intermolecular STR, indicating α-elimination of the phenyl group and the hydride on the silicon atom took place with cleavage of the Si-Ph bond.[3] Using this reaction protocol, a wide range of acyclic and cyclic diorganosilylenes including dimethylsilylene (Me_2Si:), diphenylsilylene (Ph_2Si:) and 9-silafluoren-9-ylidene were successfully generated.



1) I. Sasaki, A. Maebashi, J. Li, T. Ohmura, M. Suginome, *Eur. J. Org. Chem.* **2022**, *2022*, e202101573. 2) A. K. Franz, K. A. Woerpel, *Acc. Chem. Res.* **2000**, *33*, 813. 3) Y. Song, T. Ohmura, M. Suginome, #103 CSJ annual meeting, **2022**, K406-2am-03.

Weakly Coordinating Anions bearing Lewis Acidic Tri-coordinated Borons Induced Selectivity Control on Iridium Catalysis

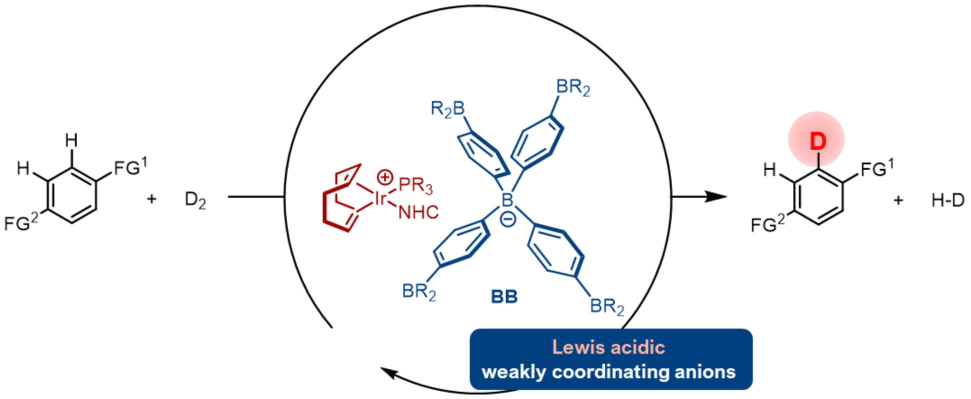
(*Graduate School of Engineering, The University of Tokyo*) ○Ryo Mandai, Takanori Iwasaki, and Kyoko Nozaki

Keywords: Cooperative Catalysts, Weakly Coordinating Anions, Catalytic C-H Bond Cleavage, Borates, Lewis acid

New class of transition metal catalysts owing activation sites in the second coordination sphere is drawing attractions with expectation that they enable challenging transformations by precise control of the molecular orientation by the acid/base residues incorporated in the ligands.[1] Realization of this concept, however, requires complicated design and synthesis to arrange activation sites in an appropriate location with a covalent and rigid linkage.

We envisioned that a novel weakly coordinating anion (WCA) endowed with Lewis acidic property would serve as a sterically flexible multi-activation site catalyst when combined with a cationic transition metal catalyst. A Lewis acidic WCA recognizes polar functional groups in substrates, such as halogens, carbonyls, and nitriles, by acid-base interaction to control orientation of the substrates. The electrostatic interaction between the ion pair approximates the captured substrate to the metal center and achieves unique chemo-, stereo- and regio-selectivity.

We newly synthesized tetraarylborates **BB**s featuring tri-coordinated boryl moieties. NMR analysis with the addition of $Et_3P{=}O$ to their tetrabutylammonium salts proved their Lewis acidity despite their anionic property. The mixture of $[Ir(cod)Cl]_2$, a phosphine ligand, and borate **BB** afforded the corresponding ion pair, where cationic Ir complex and anion BB separately exist but locates in the neighborhood of each other in DCM. When the ion pair was employed to hydrogen isotope exchange (HIE) of 1,4-difunctionalized arenes,[2] a unique regioselectivity was observed, being not observed with a commonly-employed WCA, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $\mathbf{BAr^F}$ under the same condition. This result may have demonstrated the concept of Lewis acidic WCA controlling selectivity.



1) H. J. Davis, R. J. Phipps, *Chem. Sci.* **2017**, 8, 864. 2) J. Atzrodt, V. Derdau, W. J. Kerr, M. Reid, P. Rojahn, R. Weck, *Tetrahedron* **2015**, *71*, 1924.

Electrochemical Homogeneous CO_2 Reduction Catalyzed by N-Heterocyclic Carbene Stabilized Au-Nanoclusters

([1]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya Unveristy*, [2]*Graduate School of Science, Nagoya University*, [3]*Department of Chemistry, Queen's University*) ○Samuel Jacob,[1] Joey DeJesus,[1] Masakazu Nambo,[1,2] Cathleen Crudden[1,3]

Keywords: Gold Nanocluster, Electrocatalyst, CO2 Reduction, Homogeneous, Carbene

Gold nanoclusters (AuNC) are well-studied and reputable for their ability to electrochemically catalyze several reactions of energy importance such as CO_2 reduction reaction (CO_2RR). Typically, AuNCs are stabilized by either phosphine or thiol-based ligands, however, our lab has focused on the synthesis and characterization of several new AuNCs stabilized by N-heterocyclic carbenes (NHC).[1-6] Due to their promising stability and facile means of structural modification, N-heterocyclic carbene (NHC) stabilized gold nanoclusters (AuNC) are a growing field of interest. Furthermore, their activity for electrocatalytic reduction of CO_2 to CO is notable compared to analogous thiol and phosphine supported AuNCs.[5,6] However, reaction mechanisms and means of catalyst optimization remain understudied. Herein, we present the homogeneous electrocatalytic CO_2 reduction activity of NHC stabilized AuNCs in nonaqueous solution. For this investigation we studied a family of AuNCs with varied ligand functionality and cluster sizes. Furthermore, the effect of solvent as well as protic and aprotic reaction conditions were explored. These studies provide insight for the structural optimization and mechanism for CO_2RR reactivity for AuNCs.

(1) Kawawaki, T.; Negishi, Y. Gold Nanoclusters as Electrocatalysts for Energy Conversion. *Nanomaterials (Basel)* **2020**, *10* (2). (2) Yi, H.; Osten, K. M.; Levchenko, T. I.; Veinot, A. J.; Aramaki, Y.; Ooi, T.; Nambo, M.; Crudden, C. M. Synthesis and enantioseparation of chiral Au13 nanoclusters protected by bis-N-heterocyclic carbene ligands. *Chem Sci* **2021**, *12* (31), 10436-10440. (3) Man, R. W. Y.; Yi, H.; Malola, S.; Takano, S.; Tsukuda, T.; Hakkinen, H.; Nambo, M.; Crudden, C. M. Synthesis and Characterization of Enantiopure Chiral Bis NHC-Stabilized Edge-Shared Au10 Nanocluster with Unique Prolate Shape. *J Am Chem Soc* **2022**, *144* (5), 2056-2061. (4) Lummis, P. A.; Osten, K. M.; Levchenko, T. I.; Sabooni Asre Hazer, M.; Malola, S.; Owens-Baird, B.; Veinot, A. J.; Albright, E. L.; Schatte, G.; Takano, S.; et al. NHC-Stabilized Au10 Nanoclusters and Their Conversion to Au25 Nanoclusters. *JACS Au* **2022**, *2* (4), 875-885. (5) Kulkarni, V. K.; Khiarak, B. N.; Takano, S.; Malola, S.; Albright, E. L.; Levchenko, T. I.; Aloisio, M. D.; Dinh, C. T.; Tsukuda, T.; Hakkinen, H.; et al. N-Heterocyclic Carbene-Stabilized Hydrido Au24 Nanoclusters: Synthesis, Structure, and Electrocatalytic Reduction of CO2. *J Am Chem Soc* **2022** *144* (20), 9000-9006. (6) Yang, D.; Wang, J.; Wang, Q.; Yuan, Z.; Dai, Y.; Zhou, C.; Wan, X.; Zhang, Q.; Yang, Y. Electrocatalytic CO2 Reduction over Atomically Precise Metal Nanoclusters Protected by Organic Ligands. *ACS Nano* **2022** *16* (10), 15681-15704.

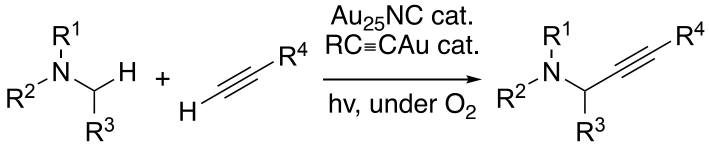
Catalytic Transformation of Alkynes Enabled by Gold Nanocluster Bearing Supramolecular Reaction Field

(*Institute for Chemical Research, Kyoto University*, *Graduate School of Engineering, Kyoto University*) ○Kenta Iseri, Katsuhiro Isozaki, Masaharu Nakamura

Keywords *: Gold Nanocluster, Catalyst, Supramolecular Reaction Field, Hydrogen Bond, Alkyne*

Thiolate-protected gold nanoclusters (AuNCs) consist of a superatomic core composed of tens of gold atoms and gold–thiolate staple motifs surrounding the core. Such AuNCs show photosensitization properties based on the superatomic core and catalytic activities based on the reactivity of gold–thiolate moieties. Although the strong gold–thiolate bond contributes to stabilizing the cluster structure, it tends to lower the catalytic activity of AuNCs. Our group has reported that the installation of peptide dendron thiolate ligands to Au_{25} nanoclusters ($Au_{25}NCs$) enables the construction of supramolecular reaction field, accelerating photocatalytic oxidation[1] and catalytic cyclization reactions.[2] Recently, we reported that the two structural components of AuNCs, the superatomic core and gold–thiolate staples, cooperatively participate in photooxidative alkynylation of amines to show unprecedented dual catalysis of AuNCs.[3] This reaction showed a long induction period due to the sluggish generation of catalytically active species, which bear σ,π-coordinated alkynyl ligands through ligand exchange between gold–thiolate staples and alkyne substrates. Herein, we report a new catalyst system for efficient catalytic transformation of alkynes enabled by mixing gold–alkynyl compounds with $Au_{25}NCs$ bearing supramolecular reaction field.

Typically, aliphatic tertiary amines and terminal alkynes are oxidatively cross-coupled by the irradiation of visible light in the presence of $Au_{25}NC$ and gold–alkynyl compounds under oxygen atmosphere, providing the corresponding propargylamine products regioselectively. The scope of substituent on gold–alkynyl compounds revealed the impact of electron-withdrawing groups on the rapid generation of catalytically active species. This presentation will also report screening of reaction conditions, scope of substrates, and applicability to other catalytic transformation of alkynes.



1) Isozaki, K.; Ueno, R.; Ishibashi, K.; Nakano, G.; Yin, H.; Iseri, K.; Sakamoto, M.; Takaya, H.; Teranishi, T.; Nakamura, M. *ACS Catal.* **2021**, *11*, 13180–13187.

2) Ueda, K.; Iseri, K.; Isozaki, K.; Nakamura, M. *The 103rd CSJ Annual Meeting,* **2023,** K502-3pm-13.

3) Isozaki, K.; Iseri, K.; Saito, R.; Ueda, K.; Nakamura, M. *Angew. Chem. Int. Ed.* **2024**, 63, e202312135.

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21日(木) 13:00 ~ 15:10 F1233(12号館 [3階] 1233)

[F1233-4pm] 09. 錯体化学・有機金属化学

座長：榎本 真哉、志賀 拓也

英語

13:00 ~ 13:20

[F1233-4pm-01]

二酸化炭素に応答する多孔性磁石：電荷移動型層状配位格子における常磁性相から反強磁性相の創出

○高坂 亘[1,2]、張 俊[3]、刘　新[1,2]、甘水 君佳[4]、北河 康隆[4] (1. 東北大金研、2. 東北大院理、3. 武漢大、4. 阪大院基礎工)

英語

13:20 ~ 13:40

[F1233-4pm-02]

Photoinduced magnetization in organometallic and organic compounds

○Verner Saeaesk[1] (1. Kyushu Universtiy)

英語

13:40 ~ 14:00

[F1233-4pm-03]

Thermal and Light-induced Switching Effects Based on Fe(II)-Hg(II) Spin-crossover Networks

○Guanping Li[1], Olaf Stefanczyk[1], Kunal Kumar[1], Koji Nakabayashi[1], Kenta Imoto[1], Guillaume Chastanet[2], Shin-ichi Ohkoshi[1] (1. Department of Chemistry, School of Science, University of Tokyo, 2. Université de Bordeaux, ICMCB)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[F1233-4pm-04]

水素結合型スピンクロスオーバー錯体を用いたプロトン伝導性超分子構造体の開発

○小林 文也[1]、田所 誠[1] (1. 東理大理)

日本語

14:30 ~ 14:50

[F1233-4pm-05]

1,2-ジチオシュウ酸配位子が架橋する2次元鉄混合原子価錯体における積層構造と磁気挙動の相関

○金友 拓哉[1]、澤柳 佑希[1]、遠藤 翼[1]、岡澤 厚[2]、榎本 真哉[1] (1. 東理大、2. 早大)

英語

14:50 ~ 15:10

[F1233-4pm-06]

S=1/2銅(II)置換Keggin型スルホタングステン酸のスピン-格子緩和挙動

○石崎 聡晴[1]、尾関 智二[1] (1. 日大)

CO_2-Sensitive Porous Magnet: Antiferromagnet Creation from a Paramagnetic Charge-Transfer Layered Coordination Framework

([1]*Institute for Materials Research, Tohoku University*, [2]*Graduate School of Science, Tohoku University,* [3]*Collage of Chemistry and Molecular Science, Wuhan University,* [4]*Graduate School of Engineering Science, Osaka University*) ○Wataru Kosaka,[1,2] Jun Zhang,[3] Qingxin Liu,[1,2] Naoka Amamizu,[4] Yasutaka Kitagawa,[4] Hitoshi Miyasaka[1,2]

Keywords: Metal–organic Framework; Charge-transfer complex; Gas-responsive magnetic property; Porous magnet; Antiferromagnet

Porous magnets that undergo a magnetic phase transition in response to gaseous adsorbates are desirable for the development of sustainable sensing and memory devices. However, a strong magnetic response to ubiquitous gases, such as O_2 and CO_2, is still rare and remains a significant challenge.[1,2,3] Especially, the creation of a magnet, meaning the change from a nonmagnet to a magnet by gas adsorption, has not yet been explored. Here, we demonstrate reversible control of the magnetic phase by cooperative CO_2 adsorption/desorption, which was achieved in a donor/acceptor metal-organic framework (D/A-MOF) $[\{Ru_2(2,4\text{-}F_2PhCO_2)_4\}_2TCNQ(OEt)_2]$ (**1**; $2,4\text{-}F_2PhCO_2^-$ = 2,4-difluorobenzoate; $TCNQ(OEt)_2$ = 2,5-diethoxy-7,7,8,8-tetracyanoquinodimethane).[4]

Compound **1** (Fig. 1a), which consists of two $[Ru_2(2,4\text{-}F_2PhCO_2)_4]$ units (abbreviated as $[Ru_2]$) and one $TCNQ(OEt)_2$ moiety, shows a two-electron transferred ionic state represented as $[\{Ru_2^{II,III}\}^+–TCNQ(OEt)_2^{2-}–\{Ru_2^{II,III}\}^+]$ below room temperature, resulting in the paramagnetic behavior (Fig. 1b). Meanwhile, **1** adsorbed three molar equivalents of CO_2, which is accompanied by the electronic state change into a one-electron transferred ionic state represented as $[\{Ru_2^{II,II}\}–TCNQ(OEt)_2^{\bullet-}–\{Ru_2^{II,III}\}^+]$. Strong intra-layer antiferromagnetic coupling between $[Ru_2^{II,II}]$ ($S = 1$) or $[Ru_2^{II,III}]^+$ ($S = 3/2$) and $TCNQ(OEt)_2^{\bullet-}$ ($S = 1/2$), as well as interlayer antiferromagnetic interaction, induced the onset of long-range antiferromagnetic ordering at $T_N = 62$ K (Fig. 1b). This is the first example of the creation of a CO_2-responsive magnet, which is promising for novel molecular multifunctional devices.[5]

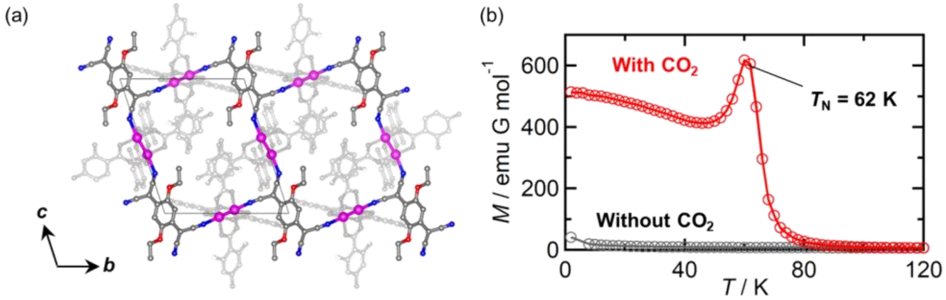


Fig. 1 (a) Crystal structure of **1**. (b) Temperature dependence of magnetization (100 Oe).

1) W. Kosaka et al., *Nat. Commun.* **2018**, *9*, 5420. 2) J. Zhang et al., *Nat. Chem.* **2021**, *13*, 191. 3) W. Kosaka et al., *Chem. Sci.* **2023**, *14*, 791. 4) J. Zhang et al., *J. Am. Chem. Soc.* **2021**, *143*, 7021. 5) J. Zhang et al., *J. Am. Chem. Soc.* **2023**, *145*, 26179.

Photoinduced magnetization in organometallic and organic compounds

([1]*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Verner Sääsk,[1]
Shengqun Su,[1] Osamu Sato[1]

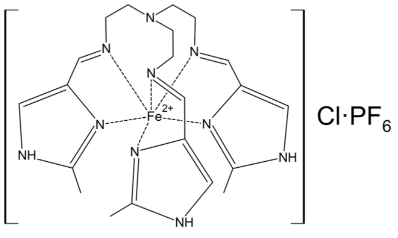
Keywords: Photoinduced magnetization, Soft crystals, Organometallics, Ultralong organic phosphorescence, Molecular crystals

Achievement of photoinduced magnetization phenomenon in two different molecular systems is reported.

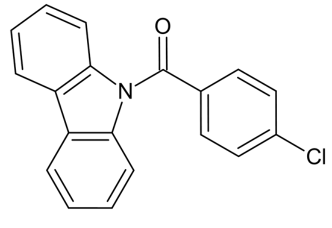
In system 1, photoinduced magnetization is achieved by exploiting a spin-crossover phenomenon in an iron complex $[Fe^{II}H_3L^{Me}]Cl\cdot PF_6$ (where H_3L^{Me} stands for tris[2-{[(2-methylimidazol-4-yl)methylidene]amino}ethyl]amine), first reported by Yamada *et al*. in 2006.[1] When this complex is irradiated with a 532 nm laser at a temperature of 5 K it undergoes a spin-crossover from a low-spin state to a high-spin state, resulting in a drastic change in its magnetic susceptibility. It was demonstrated that this metastable high-spin state can be trapped for hours at 5 K or reverted to the low-spin state by raising the temperature to 75 K. Moreover, the transition between low-spin and high-spin states of this iron complex also induces a change of polarity in its crystal lattice, which, in principle, should allow the realization of pyroelectric and photoelectric currents in this system.

In system 2, photoinduced magnetization is achieved in a purely organic molecule, 9H-carbazol-9-yl)(4-chlorophenyl)methanone (CPhCz), which was first described by Cai *et al*. in 2017.[2] A sufficient amount of triplet states to detect a change in the magnetic susceptibility of CPhCz was accumulated by exploiting the unique ability of this molecule to stabilize excited triplet states for a long time through H-aggregation.

Finally, structures of excited states and molecular mechanisms behind the photoinduced magnetization phenomenon in those two systems are compared and possible applications of such systems are suggested.



$[Fe^{II}H_3L^{Me}]Cl\cdot PF_6$



CPhCz

1. Yamada, M. et al. *Chem. – Eur. J.* **12**, 4536–4549 (2006).
2. Cai, S. et al. *Adv. Mater.* **29**, 1701244 (2017).

Thermal and Light-induced Switching Effects Based on Fe(II)-Hg(II) Spin-crossover Networks

([1]*Department of Chemistry, School of Science, University of Tokyo, [2]Université de Bordeaux, ICMCB*) ○Guanping Li,[1] Olaf Stefanczyk,[1] Kunal Kumar,[1] Koji Nakabayashi,[1] Kenta Imoto, Guillaume Chastanet,[2] Shin-ichi Ohkoshi[1]

Keywords: Fe(II) Complexes, Hg(II) Complexes, Terahertz spectroscopy, Spin-crossover

The pursuit of molecular switches with adjustable properties has been an ongoing objective of research for several decades.[1,2] In this context, a novel spin-crossover (SCO) compound (**1**) was synthesized, based on iron(II) complexes incorporating 4-acetylpyridine (4-acpy) and $[Hg(SCN)_4]^{2-}$ anions, and denoted as $[Fe(4\text{-acpy})_2][Hg(\mu\text{-SCN})_4]$ (**Figure 1**). Compound **1** is crystallized in a three-dimensional (3D) network in the non-centrosymmetric orthorhombic space group $Pna2_1$ with two distinct Fe centers (Fe1 and Fe2) and two tetrahedral $[Hg(SCN)_4]$ units. Moreover, magnetic measurements revealed an incomplete SCO exclusively at the Fe2 centers, with a transition temperature ($T_{1/2}$) of approximately 102 K. Photomagnetic studies conducted at 10 K, employing twelve lasers ranging from 405 to 1310 nm, elucidated both the light-induced excited spin-state trapping (LIESST) phenomenon with $T_{\mathrm{LIESST}} \approx 74$ K and the reverse-LIESST effect. Notably, a distinctive and highly responsive LIESST effect was observed under near-infrared light (1064 and 1310 nm). Optical and vibrational properties consistently supported the results from magnetic and photomagnetic studies. Additionally, the temperature and light-dependent terahertz (THz) absorption were associated with phonon vibrations around Fe2 centers, corroborating with the spin-crossover behavior, as confirmed by *ab initio* calculations. The Fe(II)-Hg(II) systems thus emerge as promising benchmarks for exploring synergistic switching effects across magnetic, photomagnetic, and spectroscopic properties.

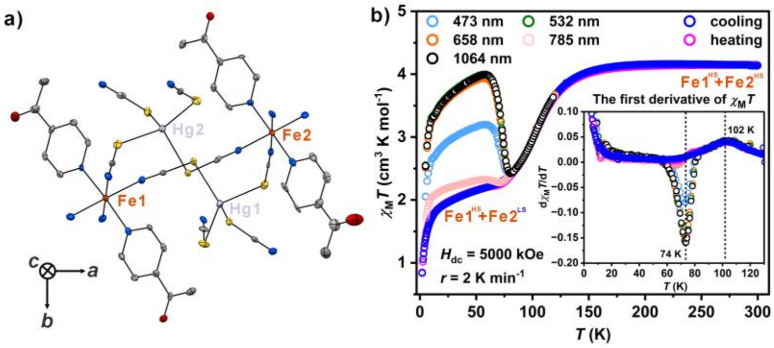


Figure 1. (a) Structural unit of **1** at 90 K. (b) Temperature dependences of $\chi_{\mathrm{M}}T$ before and after photoirradiation with selected lasers. The inset contains the first derivatives of the $\chi_{\mathrm{M}}T$ *vs*. T plots.

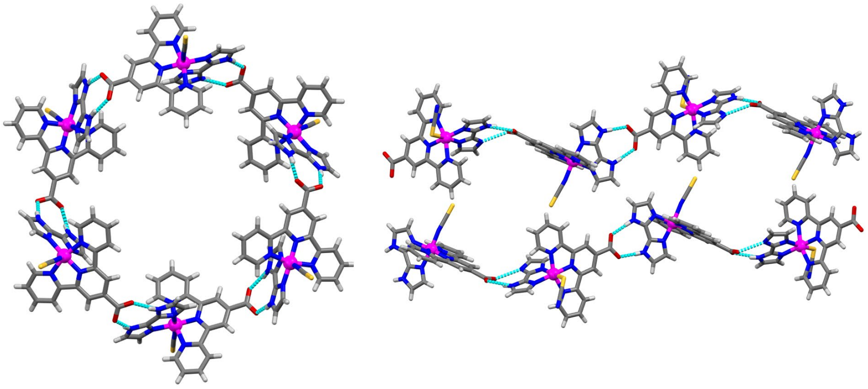
1) G. Li, O. Stefanczyk, K. Kumar, Y. Mineo, K. Nakabayashi, S. Ohkoshi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214673. 2) G. Li, O. Stefanczyk, K. Kumar, K. Imoto, K. Nakabayashi, S. Ohkoshi, *Chem. Mater.* **2023**, *35(22)*, 9613.

Proton Conductive Hydrogen-Bonded Architectures Constructed by Cobalt(II) Spin Crossover Complexes

(*Department of Chemistry, Faculty of Science, Tokyo University of Science*) ○Fumiya Kobayashi, Makoto Tadokoro

Keywords: Cobalt(II) Complex, Spin Crossover, Proton Conduction, Hydrogen Bonding

The development of molecule-based switchable multifunctional materials remains an important challenge in the field of molecular science. Achievement of a high proton conduction in spin crossover (SCO) compounds is of significant interest because of the possibility that the spin state can be controlled via proton transfer induced by an electric field, leading to the magnetoelectric effects, molecular spintronics and spin-protonics. However, there are few reports of proton conductive SCO molecules. Constructing hydrogen-bonding networks for efficient proton transport is important for achieving a high proton conductivity in such molecular compounds. To that end, high proton conductivities can be achieved via proton hopping along hydrogen-bonding networks. Controlling the molecular arrangement using hydrogen-bonding could also aid in the construction of advanced structures such as hydrogen-bonded organic frameworks (HOFs). In the present study, $[Co(COOH\text{-}terpy)_2]^{2+}$ (COOH-terpy = 4′-carboxyl-2,2′:6′,2″-terpyridine) was chosen as a hydrogen-bonded molecular unit since in prior studies several examples of SCO behavior involving $[Co(terpy)_2]^{2+}$ cation have been reported.$^{1)}$ Herein, we report the spin transition and proton conduction behaviors for hydrogen-bonded cobalt(II) SCO compounds $[Co(COOH\text{-}terpy)_2](ClO_4)_2\cdot 4H_2O$ (**1**)$^{2)}$ and $[Co(COO\text{-}terpy)(COOH\text{-}terpy)](ClO_4)\cdot 10H_2O$ (**2**). We also report the syntheses of hydrogen-bonded architectures of hydrogen-bonded hexamer $\{[Co(COO\text{-}terpy)(H_2bim)(SCN)](ClO_4)\cdot 6H_2O\}_6$ ([**3**]$_6$; H_2bim = 2,2′-biimidazole) and hydrogen-bonded mixed-valence 1D chain $\{[Co^{II/III}(COO\text{-}terpy)(H_2bim)(SCN)](ClO_4)\}_n$ ([**4**]$_n$).



1) F. Kobayashi, Y. Komatsumaru, R. Akiyoshi, M. Nakamura, Y. Zhang, L. F. Lindoy, S. Hayami, *Inorg. Chem.*, **2020**, 59, 16843–16852. 2) F. Kobayashi, T. Hiramatsu, K. Sueyasu, M. Tadokoro, *Cryst. Growth Des.*, **2023**, 23, 1633–1640.

1,2-ジチオシュウ酸配位子が架橋する 2 次元鉄混合原子価錯体における積層構造と磁気挙動の相関

（東理大 [1]・早大 [2]）○金友 拓哉 [1]・澤柳 佑希 [1]・遠藤 翼 [1]・岡澤 厚 [2]・榎本 真哉 [1]

Relationship between the stacking structure and magnetic behavior for two-dimensional mixed-valence iron(II,III) layered compounds bridged by a 1,2-dithiooxlate ligand

([1]*Tokyo University of Science*, [2]*Waseda University*) ○Takuya Kanetomo,[1] Yuki Sawayanagi,[1] Tsubasa Endo,[1] Atsushi Okazawa,[2] Masaya Enomoto[1]

1,2-Dithiooxalato (dto)-bridged mixed-valence iron complexes (cation)[Fe$^{\text{II}}$Fe$^{\text{III}}$(dto)$_3$] exhibit an alternating stacking structure with anionic layers and cations. Compound (^{n}Pr$_4$N)[Fe$^{\text{II}}$Fe$^{\text{III}}$(dto)$_3$] (**1**; ^{n}Pr$_4$N = tetra-*n*-propylammonium) displays a staggered stacking form and undergoes a charge-transfer phase transition (CTPT) behavior accompanied with electron transfer between the Fe centers.[1] Recently, our research revealed that (Ph$_4$P)[Fe$^{\text{II}}$Fe$^{\text{III}}$(dto)$_3$] (**2-Ph**; Ph$_4$P = tetraphenylphosphonium) and its derivatives adopt an eclipsed stacking form, demonstrating non-CTPT under ambient pressure.[2,3] In this study, we synthesized (A)[Fe$^{\text{II}}$Fe$^{\text{III}}$(dto)$_3$] (**2-Me**, A = methyltriphenylphosphonium (MePh$_3$P); **3**, A = triphenylsulfonium (Ph$_3$S)) and investigated crystal structures and cation-dependent magnetic behavior (Fig. 1). We will discuss a relationship between their stacking manners and CTPT.

Keywords : Molecular magnetism; Layered compounds; Magnetic phase transition; Mixed-valence iron complexes

鉄混合原子価錯体(cation)[Fe$^{\text{II}}$Fe$^{\text{III}}$(dto)$_3$]はアニオン性ハニカム層とカチオンの交互積層構造を示す。^{n}Pr$_4$N を用いた系 (**1**) は半周期ずれた staggered 積層を形成し、隣接する Fe 中心間の電荷移動による相転移 (CTPT) を示す [1]。一方、Ph$_4$P を用いた系 (**2-Ph**) とその類縁体は同周期で重なる eclipsed 積層を示し、常圧下で CTPT を示さない [2,3]。本研究では、積層様式と CTPT の相関を解明するため、MePh$_3$P と Ph$_3$S を用いた錯体 (**2-Me** と **3**) を合成し、構造及び物性を調べた。これらカチオンはハニカム環内へ貫入する置換基の立体が小さい/無いため、従来の系に比べて積層様式に自由度がある。実際、この特異性は結晶構造に反映されており、両物質共に eclipsed 積層でありながら常圧下で CTPT 由来の磁気挙動を示した (Fig. 1)。本発表では、対カチオンの分子構造がもたらす積層様式の変調と磁気挙動との相関について報告する。

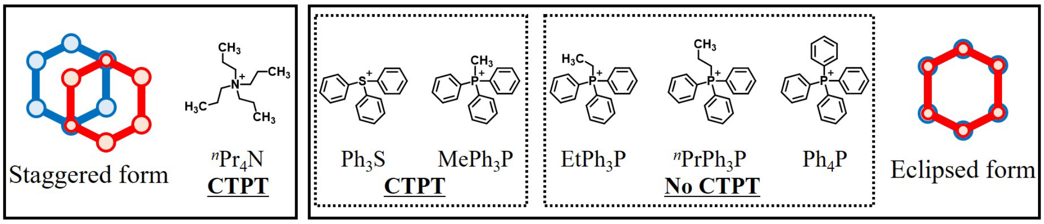


Fig. 1. Overview diagram illustrating the stacking forms and magnetic behaviors for **1**, **2**, and **3**.

1) M. Itoi et al. *Eur. J. Inorg. Chem.* **2006**, *2006*, 1198; 2) K. Nomura et al. *Cryst. Growth Des.* **2022**, *22*, 2139; 3) R. Taniai et al. *Dalton Trans.* **2023**, *52*, 8368.

Spin-lattice relaxation behavior of an *S*=1/2 copper(II)-substituted Keggin-type sulfotungstate

([1]*College of Humanities and Sciences, Nihon University*) ○Toshiharu Ishizaki,[1] Tomoji Ozeki[1]

Keywords: Molecular magnetism; Polyoxometalate; Copper(II); *S*=1/2; Magnetic relaxation

In terms of quantum bit (qubit) for quantum computation, *S*=1/2 mononuclear transition metal complexes have recently drawn much attention due to the long spin-lattice relaxation time and quantum coherent phenomena at even elevated temperatures.[1] Recently, we have revealed that the tetrabutylammonium salt of *S*=1/2 copper(II)-substituted Keggin-type silicotungstate $[(\text{n-C}_4\text{H}_9)_4\text{N}]_4\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Cu}]$ and phosphotungstate $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{O}_{39}\text{Cu}]$ exhibit slow magnetic relaxations in applied static magnetic field (H_{dc}).[2] The phosphorous(V) analogue showed significantly longer relaxation times at low temperature compared with the silicon(IV) analogue. In this presentation, magnetic properties of a tetrabutylammonium salt of copper(II)-substituted Keggin-type sulfotungstate[3] $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\text{SW}_{11}\text{O}_{39}\text{Cu}]$ was investigated.

AC magnetic susceptibility measurements for **1** revealed that out-of-phase (χ'') signals were successfully observed in an applied static magnetic field (H_{dc}) at low temperatures (Figure). This indicates that slow magnetic relaxation of **1**. The fitting using generalized Debye model showed that relaxation time up to 35.2 ms (1.8 K and H_{dc}=5000 Oe). The relaxation times were significantly elongated compared with the copper(II)-substituted silicon(IV) and phosphorous(V) analogues. In addition, the fitting parameter α that indicates dispersion of relaxation time is small (α≤0.16) compared with the copper(II)-substituted silicon(IV) and phosphorous(V) analogues. The small α indicates that magnetic relaxation of **1** has purer single relaxation phenomena compared with our previous results. The magnetic relaxation behavior of magnetically diluted **1** and discussion for the relaxation mechanism will be also reported.

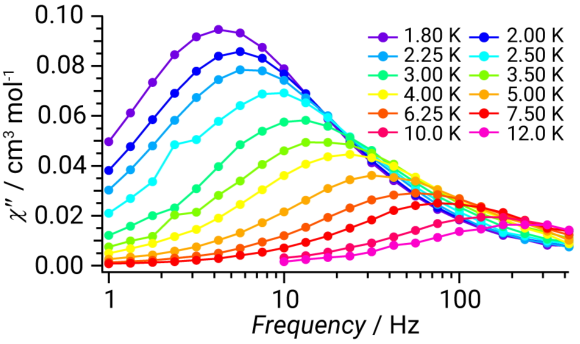


Figure The out-of-phase (χ'') signals measured in an applied static magnetic field (H_{dc}) of 3000 Oe at indicated temperatures.

1) M. Atzori, E. Morra, L. Tesi, A. Albino, M. Chiesa, L. Sorace, R. Sessoli, *J. Am. Chem. Soc.* **2016**, *138*, 11234. 2) T. Ishizaki, T. Ozeki, *Dalton Trans.* **2023**, *52*, 4678. 3). S. Azuma, T. Kadoguchi, Y. Eguchi, H. Hirabaru, H. Ota, M. Sadakane, K. Yanagisawa, T. Hasegawa, T. Ueda, *Dalton Trans.* **2020**. *49*, 2766.

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21日(木) 13:00 ~ 15:10 F1234(12号館 [3階] 1234)

[F1234-4pm] 09. 錯体化学・有機金属化学

座長：松岡 亮太、川守田 創一郎

英語
13:00 ~ 13:20

[F1234-4pm-01]

フェニルアゾメチンデンドリマーへの貴金属-卑金属の混合集積

〇飯塚 忠寿[1]、森合 達也[1]、塚本 孝政[2]、葛目 陽義[3]、今岡 享稔[1]、山元 公寿[1] (1. 東工大化生研、2. 東大生研、3. 山梨大学クリーンエネルギー研究センター)

英語
13:20 ~ 13:40

[F1234-4pm-02]

共焦点レーザー顕微鏡を用いたレニウム(Ｉ)錯体分子性結晶のベイポクロミック相転移及び微動の観察

〇馬 驍[1]、榎本 恭子[1]、石井 和之[1]、松田 雄貴[2]、阿部 正明[2] (1. 東大生研、2. 兵庫県立大院理)

英語
13:40 ~ 14:00

[F1234-4pm-03]

柔軟な発光性錯体ネットワーク結晶の創製と構造ダイナミクス観測

〇松田 雄貴[1]、中村 暸汰[1]、小澤 芳樹[1]、田原 圭志朗[1]、小野 利和[2]、吉成 信人[3]、今野 巧[3]、杉本 邦久[4]、小林 慎太郎[5]、河口 彰吾[5]、阿部 正明[1] (1. 兵庫県立大院理、2. 九大院工、3. 阪大院理、4. 近畿大理工、5. SPring-8/JASRI)

14:00 ~ 14:10

休憩

日本語
14:10 ~ 14:30

[F1234-4pm-04]

温度および圧力効果に基づく一次元d^8金属錯体の金属間距離と集積発光の詳細検討

〇吉田 将己[1]、三谷 開[1]、瀬川 海斗[1]、江口 大地[1]、玉井 尚登[1]、加藤 昌子[1] (1. 関学大)

日本語
14:30 ~ 14:50

[F1234-4pm-05]

塩基性水溶液中で二酸化炭素によって誘起されるN^C^N型白金(II)錯体の自己集合

〇服部 伸吾[1]、三田 博之[1]、篠﨑 一英[1] (1. 横浜市立大学)

英語
14:50 ~ 15:10

[F1234-4pm-06]

Au(I)錯体を基盤とした配位高分子の結晶サイズに依存した二重発光特性

〇芳野 遼[1]、江原 巧[2]、宮田 潔志[2]、恩田 健[2]、宮坂 等[1] (1. 東北大金研、2. 九大院理)

Multimetalic co-accumulation of precious and base metals in phenylazomethine dendrimer

([1]*Lab. Chem. Life Sci., Tokyo tech,* [2]*Institute of Industrial Science, University of Tokyo,* [3]*Clean Energy Research Center, University of Yamanashi*)
○Tadatoshi Iitsuka,[1] Tatsuya Moriai[1], Takamasa Tsukamoto[2], Akiyoshi Kuzume[3], Takane Imaoka[1], Kimihisa Yamamoto[1]

Keywords: *dendrimer; metallic accumulation*

We have developed various metal and alloy clusters using a phenylazomethine dendrimer (TPM-G4) as a template, examining their physical properties and functionalities (Figure 1) 1,2). However, synthesizing alloy clusters presents a challenge due to the requirement for multimetallic co-accumulation on the dendrimer. This process is complicated by the differing conditions necessary for each metal species combination (Figure 2). This challenge is particularly pronounced when combining precious (noble) metals with base metals, as they often necessitate distinct accumulation conditions. Moreover, the variety of metals that can be successfully integrated into multielemental clusters is currently limited.

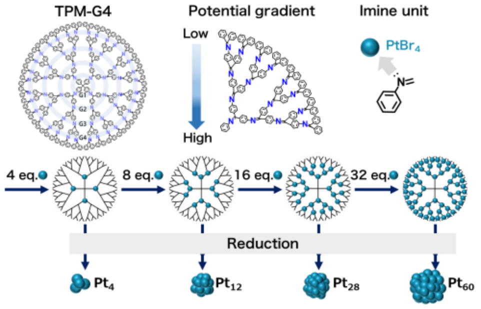


Figure 1 Accumulation on TPM-G4 and synthesis of metal clusters.

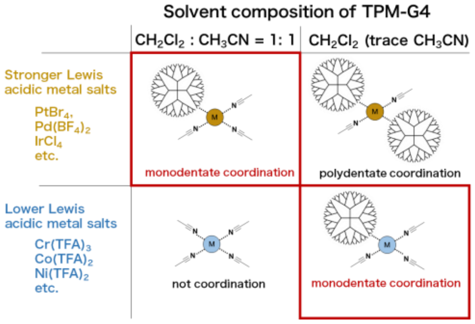


Figure 2 Difference of complexation conditions for TPM-G4 by metal salts.

In this study, our goal is to broaden the spectrum of multimetallic combinations of noble and base metals on the dendrimer. Our focus is on identifying noble metal complexes that can be co-accumulated under conditions amenable to base metals.

1) T. Imaoka *et al*., *Angew. Chem. Int. Ed*, **2015**, *54*, 9810.

2) T. Tsukamoto *et al*., *Nat. commun*, **2018**, *9*, 3873.

Observation of vapochromic phase transition and micro motions in molecular crystals using confocal laser microscopy

([1] *IIS, The Univ. of Tokyo*, [2] *Graduate School of Science, University of Hyogo*) ○XIAO MA[1], Kyoko Enomoto[1], Kazuyuki Ishii[1], Yuki Matsuda[2], Masaaki Abe[2]

Keywords : Re complex; Micro motions; Vapochromism; Single-crystal-to-single-crystal phase transition; Soft crystals

In recent years, molecular crystals undergo structural transformations in the presence of specific stimuli, which is called "Soft Crystals".[1] In relation to "Soft Crystals", various phenomena, such as vapochromism and mechanochromism, have been extensively investigated. In these studies, single-crystal-to-single-crystal phase transitions are one of important targets, because molecular structural transformations can be investigated by X-ray structural analyses in nanoscopic scale.

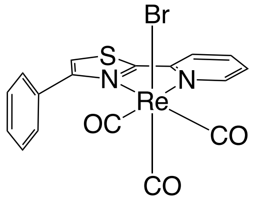


Figure 1. Molecular structure of $[Re(CO)_3Br(ppt)]$

In this study, we have investigated vapochromic single-crystal-to-single-crystal phase transition in microscopic scale by confocal laser microscopy, because our laboratory has previously demonstrated that super-resolution microscopy techniques are useful for directly observing time-dependent vapochromic behaviors.[2] Here, we employed *fac*-$[Re(CO)_3Br(ppt)]$ (Figure 1), whose molecular crystal exhibits chloroform vapor-induced single-crystal-to-single-crystal phase transition.[2] By modifying the attachment, dynamic, vapochromic behaviors were successfully observed in microscopic scale after $CHCl_3$ vapor exposure (Figure 2a). Importantly, the 1 μm-sized boundaries were found between the regions before and after vapochromism, i.e., initial and final phases (Figure 2b). The phosphorescence peak of the final phase (Figure 2e) becomes intense and shifts to the blue side compared with that of the initial phase (Figure 2c), while that of the boundary region was obviously weak (Figure 2d). The details will be discussed in the presentation.

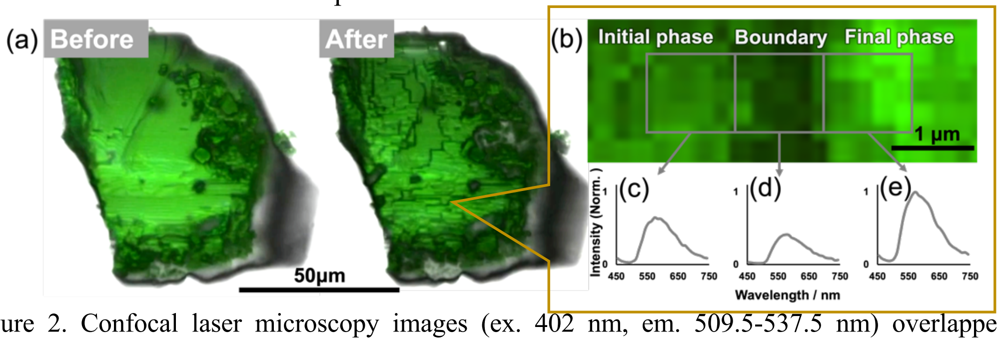


Figure 2. Confocal laser microscopy images (ex. 402 nm, em. 509.5-537.5 nm) overlapped with transmitted light microscopy images (402 nm) of a crystal of *fac*-$[Re(CO)_3Br(ppt)]$ before and after $CHCl_3$ vapor exposure (a), an expanded image (b), and phosphorescence spectra of initial phase (c), boundary region (d), and final phase (e).

1) M. Kato, *Soft Crystals*, K. Ishii, Eds., Springer Nature, Singapore, **2023**.
2) K. Ishii, *et al.*, *J. Phys. Chem. C.*, **2021**, *125*, 38, 21055–21061.
3) Y. Matsuda, *et al.*, *71st Conference of Japan Society of Coordination Chemistry,* **2021**, PF2-40.

Vapor-Induced Structural Transformation Dynamics of Photoluminescent Coordination Network Crystals

([1]*Graduate School of Science, University of Hyogo*, [2]*Graduate School of Engineering, Kyushu University*, [3]*Graduate School of Science*, *Osaka University*, [4]*Department of Chemistry*, *Faculty of Science and Engineering*, *Kindai University*, [5]*SPring-8/JASRI*) ○Yuki Matsuda,[1] Ryota Nakamura,[1] Yoshiki Ozawa,[1] Keishiro Tahara,[1] Toshikazu Ono,[2] Nobuto Yoshinari,[3] Takumi Konno,[3] Kunihisa Sugimoto,[4] Shintaro Kobayashi,[5] Shogo Kawaguchi,[5] Masaaki Abe [1]

Keywords: Photoluminescent Rhenium(I) Complex; Non-porous Crystal; Intramolecular Interactions; Gate-Open-Close Behaviors; In-situ Synchrotron Powder X-ray Diffraction

Noncovalent weak interactions among atoms and molecules, such as hydrogen bonds, halogen bonds, and CH/π interactions, are ubiquitous in natural and artificial systems from nanometer-to-micrometer scales and play vital roles especially in molecular assembly, recognition, catalysis, solid-state chemical processes, and biological events such as protein folding. As for porous crystalline solids, metal-organic frameworks (MOFs), extended 3D network solids via coordination bonds, may exhibit "gate-open-and-close" behavior upon guest-adsorption and desorption while retaining its crystallinity. Herein we report a new nonporous molecular solid to exhibit, besides MOFs, guest-induced structural transformation including reversible gate-open-and-close hysteresis or unidirectional gate-open behavior that is strictly guest-dependent under gaseous environments of volatile organic compounds (VOCs). The *in situ* and real-time probe for the transformation dynamics, unexplored in molecular crystals to date, was successfully carried out by photoluminescence (PL) spectroscopy, adsorption isotherms, and a sub-second *in situ* synchrotron PXRD method.

Complex **1**, *fac*-[Re(CO)$_3$Br(ppt)] (ppt = 2-pyridyl-4-phenylthiazole), was synthesized and characterized. Recrystallization of **1** with varied choice of solvents gave either guest-free nonporous **1** (denoted as Type O) or two types of guest (G)-inclusion crystals formulated **1•*n*G** with *n* = 0.5 and 1.0 which are denoted as Types A and B, respectively. All of those crystals contain highly extended network assemblies with noncovalent multiple intermolecular interactions in the crystal lattice (Fig. 1). In Type A, the guests were trapped in a discrete void, whereas in Type B were incorporated into a 1D channel void. We found that nonporous "desolvated" **1** showed vapor-dependent gate-open-and-close hysteresis upon VOC-exposure-and-pump cycles. Unidirectional guest-substitution, from Type B to A, was detected for specific VOCs (Fig. 1, bottom). Thermodynamic stability of the crystalline solids was determined by TG analysis. Crystal size-dependence in the vapochromic response will also be presented.

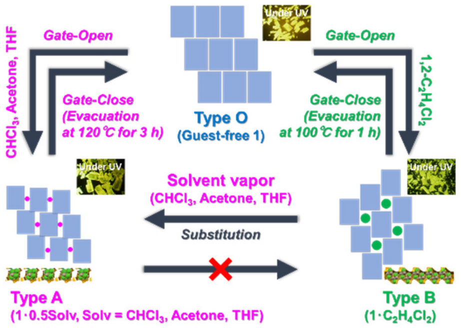


Fig. 1. Guest-induced transformation dynamics of nonporous molecular solids

日本化学会 第104春季年会 (2024)

温度および圧力効果に基づく一次元 d^8 金属錯体の金属間距離と集積発光の詳細検討

（関学大生命環境 [1]・関学大理 [2]）○吉田 将己 [1]・三谷 開 [1]・瀬川 海斗 [1]・江口 大地 [2]・玉井 尚登 [2]・加藤 昌子 [1]

Correlation Between Metal-Metal distance and Assembly-induced Luminescence of One-dimensional d^8 Metal Complexes Based on Temperature and Pressure Effects (Kwansei Gakuin University) ○Masaki Yoshida, Kai Mitani, Kaito Segawa, Daichi Eguchi, Naoto Tamai, Masako Kato

One-dimensional d^8 metal complexes such as Pt(II) and Pd(II) complexes are well known to show assembly-induced luminescence based on metal-metal interactions. However, there are still unresolved issues regarding the correlation of metal-metal distances and the delocalization of excited states via metal-metal interactions. In this study, we have investigated the excited states of a one-dimensional Pt(II) complex [Pt(dFppy)(pic)] (**1** in Fig. 1; dFppy = 2-(4,6-difluorophenyl)pyridinate, pic = α-picolinate) with a relatively long metal-metal distance (3.7053(3) Å) based on the variable-temperature and pressure measurements.

Keywords : Cyclometalated complexes, d^8 Metal complexes, Intermolecular interactions, Luminescence, Self-assembly

白金(II)錯体やパラジウム(II)錯体のような d^8 金属錯体は積層することで金属間相互作用に基づく特異な発光を示すため、光機能材料の基盤として盛んに研究がなされている。従来、この金属間相互作用を介した励起状態の形成・非局在化については慣例的に van der Waals 半径に基づいて議論されてきたが、詳細については未解明な点も多い。本研究では、結晶中で van der Waals 半径の和よりも長い金属間距離を有する一次元白金(II)錯体 **1**（図 1、上段）に対し、温度や圧力を用いて金属間距離を変化させることで、その励起状態の詳細を検討した。

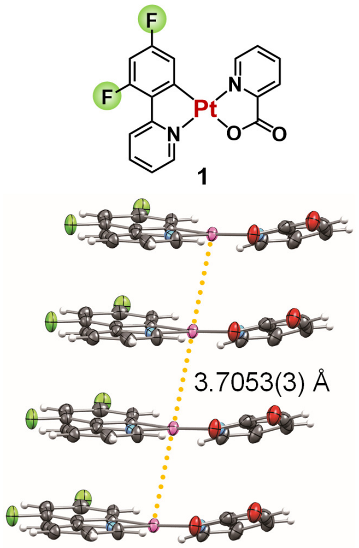


図 1. 錯体 **1** の分子構造と積層構造（水和水は省略）

錯体 **1** の 1 水和物結晶の 240 K における積層構造を図 1 に示す。この錯体は結晶中で白金の van der Waals 半径の 2 倍である 3.5 Å よりも長い 3.7053(3) Å という白金間距離を有する。それにもかかわらず、この結晶は室温において 623 nm 付近に発光極大を有する黄橙色発光を示し、種々の光物理測定からこの発光が金属間相互作用に由来することが判明した。さらに、この結晶に圧力を印加したところ、3.63 GPa 付近において発光極大波長が 721 nm 付近にまでシフトしたことから、白金間距離の収縮にともなう励起状態の多量化の促進 1)が示唆された。当日は、温度可変測定の結果および類似の積層型パラジウム(II)錯体の発光性についても報告し、金属間距離と励起状態の非局在化について詳細に議論を行う予定である。

1) M. Nakagaki, S. Aono, M. Kato, S. Sakaki, *J. Phys. Chem. C* **2020**, *124*, 10453–10461.

塩基性水溶液中で二酸化炭素によって誘起される N^C^N 型白金(II)錯体の自己集合

（横浜市大理 [1]）○服部 伸吾 [1]・三田 博之 [1]・篠﨑 一英 [1]

Self-Assembly of N^C^N-Coordinated Platinum(II) Complex Assisted by Carbon Dioxide in Basic Aqueous Solution

([1]*School of Science, Yokohama City University*) ○Shingo Hattori,[1] Hiroyuki Mita,[1] Kazuteru Shinozaki[1]

We report an unprecedented result of self-aggregation of Pt(II) complex triggered by CO_2 in basic aqueous solution. The color of basic aqueous solution containing Pt(II) complex changes from yellow to blue-green during the aggregation resulted from a reaction with CO_2 in air. Upon CO_2 gas bubbling, strong and broad absorption bands of aggregate assigned to the metal-metal-to-ligand charge transfer transition appeared at 701 and 1152 nm. Recrystallization of Pt(II) complex from Na_2CO_3 aqueous solution afforded polymorphic crystals of red and blue-green forms. A single X-ray crystallography revealed that the red form of crystal consists of a Pt-Pt stacked dimer bridged by CO_3^{2-} ion. An elemental analysis provided evidence that the blue-green crystal is constructed by linear array consisting of the Pt(II) complex.

Keywords : Self-assembly; Carbon dioxide; Pt(II) complex

CO_2 捕捉貯蔵技術は持続可能な社会を実現するために重要な概念である。これまで、金属錯体の CO_2 捕捉は報告されてきた一方、金属錯体の自己集合により劇的な色変化を伴って CO_2 捕捉した例はなかった。最近我々は、N^C^N 型白金(II)錯体($[Pt(L^1)Cl]^{2-}$, HL^1 = 1,3-di(5-carboxy-2-pyridyl)benzene)塩基性水溶液では CO_2 を捕捉することで白金(II)錯体が自己集合し、水溶液の色が黄色から青緑色へと変化することを見出した[1]。本発表ではその詳細について報告する。

CO_2 ガスバブリング前は、白金錯体のπ-π*/MLCT 遷移に由来する吸収帯が 400 nm 付近に観測された。一方、CO_2 ガスバブリング 10 秒後には、400 nm 付近にあった吸収帯のピークは短波長シフトし、600 nm 付近に二量体に由来する吸収帯が観測された。CO_2 ガスバブリング 30 秒後には、600 nm 付近の吸収帯は減少し、700 nm 付近と 1150 nm 付近に新たな吸収帯が観測された。観測された波長から、ブロードな吸収帯は四量体以上の会合度を持つ会合体であることが示唆された。また、Ar, N_2, O_2 ガスバブリングではこのようなスペクトル変化は起こらなかった。これより、$[Pt(L^1)Cl]^{2-}$ が CO_2 のみと反応することで会合体が形成されることが明らかとなった。

赤色結晶と青緑色結晶を作製した。赤色結晶は X 線単結晶構造解析により、CO_3^{2-} が白金に架橋配位子した二量体構造をとることが明らかとなった。青緑色結晶は X 線単結晶構造解析が困難であったが、元素分析により、$Na_3[Pt(L^2)(CO_3)]\ 6H_2O$ (HL^2 = 1,3-di(5-carboxylate-2-pyridyl)benzene)であることが示唆された。$[Pt(L^2)(CO_3)]^{3-}$の吸収スペクトルの時間変化を速度論解析と特異値分解を行うことにより、青緑色会合体が少なくとも３２量体であることが示唆された。

1) H. Mita, S. Hattori, T. Sasaki, S. Takamizawa, K. Shinozaki, *ChemSusChem*, **2023**, *16*, e202301174.

Crystal-downsizing Effect on Dual-emission Behavior in an Au(I)-based Coordination Polymer

([1]*Institute for Materials Research, Tohoku University*, [2]*Graduate School of Science, Kyushu University*) ○Haruka Yoshino,[1] Takumi Ehara,[2] Kiyoshi Miyata,[2] Ken Onda,[2] Hitoshi Miyasaka[1]

Keywords: Coordination polymer; Metal–organic framework; Metallophilic interactions; Dual-emission behavior; Crystal size control

Coordination polymers (CPs) and metal–organic frameworks (MOFs), a new class of crystalline and functional materials, are being extensively developed in the field of materials science. In addition, it has recently become clear that the particle size of the CPs/MOFs with flexible coordination networks impacts the functional properties of the framework. However, most of the studies have focused on gas adsorption, and the influence of domain size on the physical properties incorporated in CPs/MOFs and mechanical properties using physical stimulus has not been sufficiently investigated to date.

Herein, we report a novel luminescent CP $\{Cd^{II}(pmd)[Au^{I}(CN)_2]_2\}$ (pmd = pyrimidine; **1**) that exhibits an intense dual emission behavior (**Fig. 1**). The particle size of **1** can be controlled under various conditions such as solution diffusion, stirring, and reverse micelle method, yielding single crystals (**SC**; > 100 μm), microcrystalline (**bulk**; ~ 20 μm), and powder state (**W5**; < 10 μm), respectively (**Fig. 2(a)**). Importantly, the luminescence features of the **1** were strongly influenced by the domain size; the decrease in particle size (**SC**→**bulk**→**W5**) increases the fraction of low-energy emission (λ2 in **Fig. 2(b)**), which was also directly confirmed by the fluorescence microscope images (**Fig. 2(c)**). The details of dual emission behaviors for **1** was investigated through time-resolved photoluminescence analyses, demonstrating that the particle size of the resultant CP remarkably manipulated the excited state dynamics.

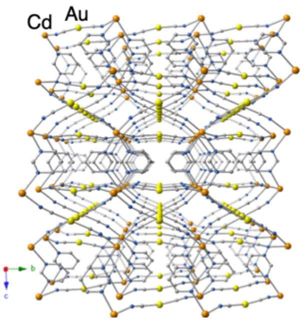


Fig. 1. Crystal structure of **1**

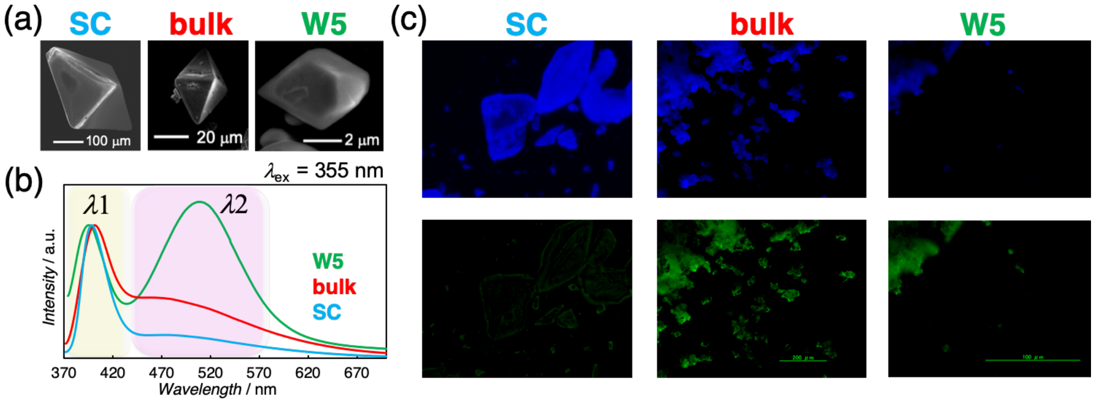


Fig. 2 **(a)** SEM images of **SC**, **bulk**, and **W5**. **(b)** Emission spectra of **SC**, **bulk**, and **W5**. **(c)** Fluorescence microscope images of **SC**, **bulk**, and **W5** (λ_{ex}= 365 nm).

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21日(木) 9:30 ~ 11:30 E1111(11号館 [1階] 1111)

[E1111-4am] 10. 有機化学―有機金属化合物

座長：小西 彬仁、上野 雅晴

英語
9:30 ~ 9:50
[E1111-4am-01]
芳香族基質の選択的活性化を指向したカゴ型ホウ素錯体の合成：π-ポケットへの複素環導入による効果

○筒井 裕哉[1]、小西 彬仁[1,2]、安田 誠[1,2] (1. 阪大院工、2. ICS-OTRI)

英語
9:50 ~ 10:10
[E1111-4am-02]
アミノ酸の還元的アルキル化を志向した、トリアリールボランライブラリーの構築および機械学習を用いた触媒構造最適化

○久田 悠靖[1]、鷲尾 隆[2]、滝澤 忍[3]、生越 専介[1]、星本 陽一[1,4] (1. 大阪大学大学院工学研究科、2. 大阪大学産業科学研究所、産業科学AIセンター、3. 大阪大学産業科学研究所、4. 大阪大学大学院工学研究科附属フューチャーイノベーションセンター)

英語
10:10 ~ 10:30
[E1111-4am-03]
カリウム還元剤を用いたアルキンの*anti*二重ホウ素化

○張 紫薇[1]、黒木 尭[1]、依光 英樹[1] (1. 京都大学)

10:30 ~ 10:50
休憩

英語
10:50 ~ 11:10
[E1111-4am-04]
シクロプロパノールを用いたシクロプロペンの立体選択的ヒドロキシアリル化：NHCによるエノール化亜鉛ホモエノラートの反応制御

○築地 健人[1]、金本 和也[1]、松本 有正[2]、吉戒 直彦[1] (1. 東北大学、2. 奈良女子大学)

日本語
11:10 ~ 11:30
[E1111-4am-05]
亜鉛/フッ素カルベノイド： 調製、安定性、構造および求核的モノフルオロアルキル化反応への応用

○宮本 公平[1]、川口 瑛美子[1]、森崎 一宏[1]、佐藤 美洋[1] (1. 北大院薬)

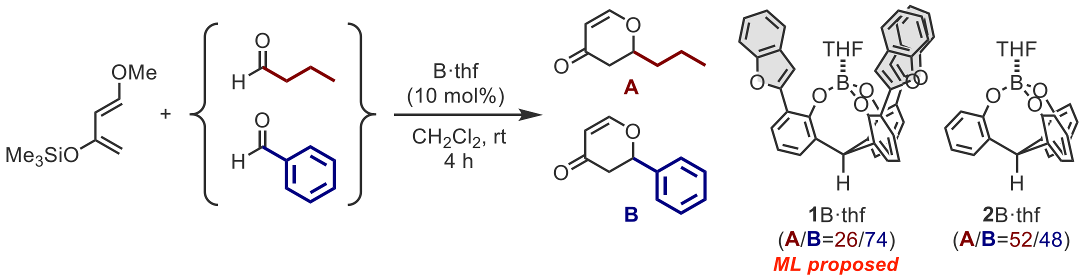
Synthesis of Cage-shaped Borate with Heteroaromatics for Selective Activation of Aromatic Aldehydes

([1]*Graduate School of Engineering, Osaka University*, [2]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI),Osaka University*)
○Yuya Tsutsui,[1] Akihito Konishi,[1,2] Makoto Yasuda[1,2]

Keywords: Lewis Acid Catalyst; Molecular Recognition; Boron Complex; Heterocyclic Ring; Machine Learning

A selective recognition of hydrocarbon moieties has been a longstanding issue for organic synthesis. We have been developing the π-pocket Lewis acid catalyst distinguishing between aliphatic and aromatic aldehydes with nearly identical electronic and steric properties.[1] Although the correlation between catalyst structure and selectivity have been confirmed by many experimental results,[2] conventional knowledge such as the steric or electrostatic environment of the π-pocket cannot explain this correlation. This may be because molecular recognition is defined by multiple cooperative non-covalent interactions within the π-pocket. Recent advances in machine learning (ML) applications to organic synthetic chemistry have significantly contributed to the predictions of yields and selectivities.[3] Since the underlying patterns and relationships in multiple chemical factors of the π-pocket catalyst should be analyzed and explored by data-driven methods, the application of ML may provide insight to design the π-pocket catalyst.

Using 7963 explanatory variables extracted from model hetero-Diels–Alder reactions, the ensemble algorithm predicted the chemoselectivity of unlearned borate catalysts. The catalyst **1**B·thf having three 2-benzofuryl groups around boron center, which is predicted to show high selectivity, exhibits the highest selective recognition of aromatic aldehydes in the inter- and intramolecular competitive hetero Diels-Alder reactions. Furthermore, a shapley additive explanations (SHAP) method clarified that the selectivity originates from the three-dimensional size weighted by the polarizability of the catalyst. These insights provide an evocative principle for the design of Lewis acid catalysts with non-covalent interactions.



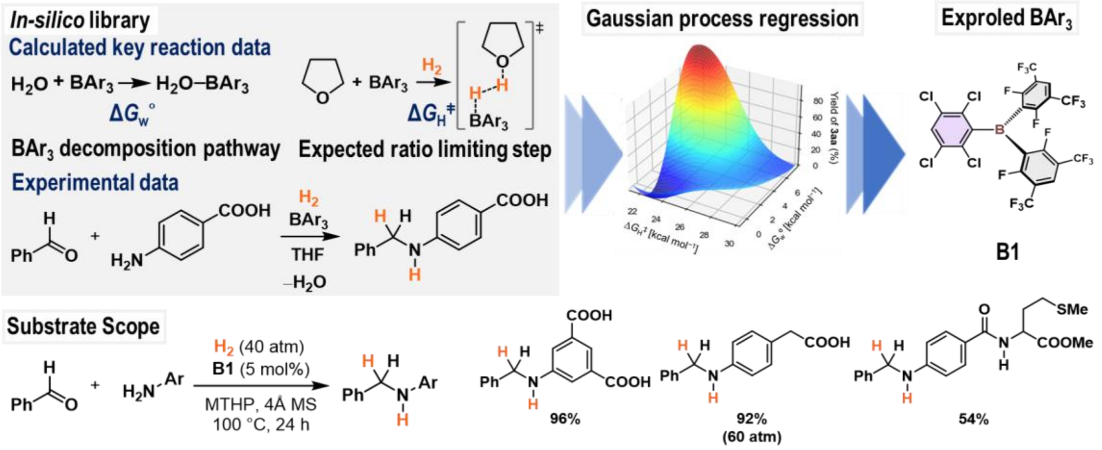
1) H. Nakajima, M. Yasuda, R. Takeda, A. Baba, *Angew. Chem. Int. Ed.* **2012**, *51*, 3867. 2) D. Tanaka, Y. Tsutsui, A. Konishi, K. Nakaoka, H. Nakajima, A. Baba, K. Chiba, M. Yasuda, *Chem. Eur. J.* **2020**, *26*, 15023. 3) a) A. Zahrt, J. Henle, B. Rose, Y. Wang, W. Darrow, S. Denmark, *Science*, **2019**, *363*, eaau5631. b) A. Żurański, J. Alvarado, B. Shields, A. Doyle, *Acc. Chem. Res.* **2021**, *54*, 1856. c) J. Crawford, C. Kingston, F. Toste, M. Sigman, *Acc. Chem. Res.* **2021**, *54*, 3136.

In-Silico-Assisted Derivatization of Triarylboranes for Catalytic Reductive Functionalization of Amino Acids with H_2

([1]*Department of Applied Chemistry, Faculty of Engineering, Osaka University,* [2]*Department of Reasoning for Intelligence and Artificial Intelligence Research Center, SANKEN, Osaka University,* [3]*Department of Synthetic Organic Chemistry and Artificial Intelligence Research Center, SANKEN, Osaka University,* [4]*Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University*) ○Yusei Hisata,[1] Takashi Washio,[2] Shinobu Takizawa,[3] Sensuke Ogoshi,[1] Yoichi Hoshimoto[1,4]

Keywords: Triarylboranes, Amino Acids, Gaussian process regression, Machine lerning, Reductive alkylation

Compared with the approach to the development of the Lewis base such as phosphine and *N*-heterocyclic carbenes, the application of machine learning (ML) in catalytic reactions using Lewis-acidic main-group elements has been constrained due to the absence of candidate library and effective parameters for the prediction of the activity of main-group elements. In this study, we report the development of a triarylborane (BAr_3) library and its application in an ML-assisted approach for the reductive alkylation of amine with H_2.[1] As reactions for collecting experimental data, amino acids containing carboxy groups that could potentially quench reactivity of FLP even under high-pressure H_2 and for long reaction time were applied. More than 50 kinds of BAr_3 from the library were theoretically applied for the prediction of turnover frequencies (TOF) based on the GPR analysis to demonstrate that the deformation energy can be a useful parameter.[2] The reaction system with optimal catalyst **B1** and 4-Methyltetrahydropyran (MTHP) as Lewis base and solvent showed a broad substrate scope, including aromatic amino acids with aniline moieties and peptide compounds.



1) Hisata, Y.; Washio, T.; Takizawa, S.; Ogoshi, S.; Hoshimoto, Y. *ChemRxiv. preprint* **2023**, DOI: 10.26434/chemrxiv-2023-3mwbd 2) Erdmann, P.; Greb, L. *Angew. Chemie - Int. Ed.* **2022**, 61, e202114550.

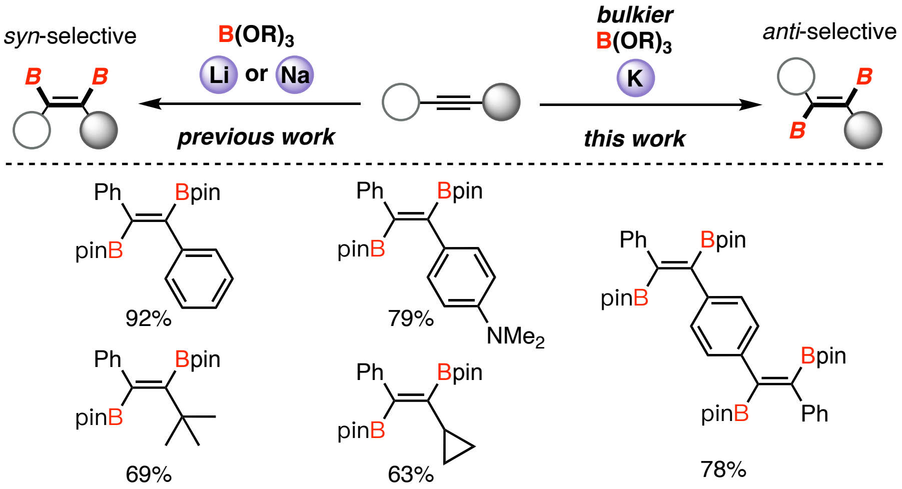
カリウム還元剤を用いたアルキンの *anti*-二重ホウ素化

（京大院理）○張 紫薇・黒木 尭・依光 英樹
Anti-Selective 1,2-Diboration of Alkynes by Using Potassium Reductants (*Graduate School of Science, Kyoto University*) ○Ziwei Zhang, Takashi Kurogi, Hideki Yorimitsu

The stereoselective synthesis of 1,2-diborylalkenes has attracted attention in organic synthesis since they can be further transformed into a diverse range of pharmaceuticals and functional materials. Therefore, the development of efficient stereoselective methods for synthesizing of 1,2-diborylalkenes is very important. Recently, we have developed a reductive *syn*-1,2-diboration of alkynes with lithium- or sodium-based reductants in the presence of trialkoxyborane as a reduction-resistant electrophile.[1] Herein, we report that the stereoselectivity is reversed by the use of potassium-based reductants instead of lithium- or sodium-based ones. Reduction of alkynes with potassium naphthalenide in the presence of bulky trialkoxyborane such as *i*PrOBpin resulted in *anti*-1,2-diboration exclusively to afford *trans*-1,2-diborylalkenes. The role of the countercation for the stereoselectivity will be discussed in this presentation.

Keywords : 1,2-diboration; stereocontrol; alkali metal arenide; single-electron reduction

1,2-ジボリルアルケンは医薬品や機能性材料中に多くみられる多置換アルケンの有用な合成前駆体であり、その立体選択的合成法の開発は重要である。近年我々は、一電子還元に耐えうるトリアルコキシボランの共存下、リチウムまたはナトリウム還元剤を用いたアルキンの還元的 *syn*-二重ホウ素化を報告した。[1] 今回我々は、カリウム還元剤を作用させると、二重ホウ素化の立体選択性が逆転することを発見した。すなわち、アルキンに対し嵩高いホウ素求電子剤である *i*PrOBpin の共存下でカリウムナフタレニドを作用させたところ、*anti*-二重ホウ素化が進行し、*trans*-ジボリルアルケンが単一の立体異性体として生成した。立体選択性に対する対カチオンの効果についても本発表中で議論する。



[1] S. Ito, M. Fukazawa, F. Takahashi, K. Nogi, H. Yorimitsu, *Bull. Chem. Soc. Jpn.* **2020**, *92*, 1171.

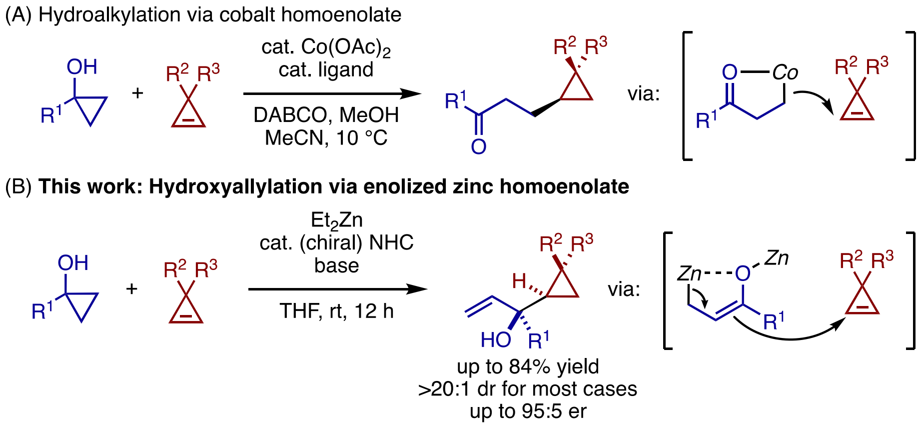
Stereoselective Hydroxyallylation of Cyclopropenes with Cyclopropanols via NHC Control of Enolized Zinc Homoenolate

([1]*Graduate School of Pharmaceutical Science, Tohoku University*, [2]*Faculty of Science, Nara Women's University*) ○Kento Tsukiji,[1] Kazuya Kanemoto,[1] Arimasa Matsumoto,[2] Naohiko Yoshikai[1]

Keywords: Cyclopropene; Cyclopropanol; Organozinc Compound; NHC

Cyclopropanes are important building blocks in medicinal chemistry and useful as versatile synthetic building blocks in organic synthesis. Besides the well-established methods for cyclopropanation, the addition to the C=C bond of cyclopropenes is an attractive approach to constructing densely functionalized cyclopropanes. While various stereoselective carbofunctionalization reactions of cyclopropenes have been developed over the last few decades, the addition reaction of cyclopropenes with prochiral nucleophiles, which generates a new stereogenic center outside the cyclopropane ring, remains rare.

Recently, Meng and co-workers reported a cobalt-catalyzed enantioselective hydroalkylation of cyclopropenes with cyclopropanols (**Scheme A**).[1] The reaction is believed to involve a cobalt homoenolate, which is generated through the ring-opening of a cobalt cyclopropoxide. Herein, we report on a zinc-mediated hydroxyallylation reaction of the same reactants that involves an "enolized zinc homoenolate,"generated in equilibrium via deprotonation of a zinc homoenolate, as a prochiral nucleophile (**Scheme B**). The reaction is enabled by *N*-heterocyclic carbene (NHC)-accelerated catalysis and affords densely functionalized cyclopropanes with excellent diastereocontrol over three contiguous stereocenters, including one outside the cyclopropane ring. Furthermore, an enantioselective variant of this hydroxyallylation has been achieved using a chiral NHC. In the presentation, we will discuss the details of the reaction optimization, the full substrate scope, the enantioselective variant, the plausible mechanism, and the synthetic utility.



(A) Hydroalkylation via cobalt homoenolate

(B) **This work: Hydroxyallylation via enolized zinc homoenolate**

1) W. Huang, F. Meng, *Angew. Chem. Int. Ed.* **2021**, *60*, 2694.

亜鉛/フッ素カルベノイド：調製、安定性、構造および求核的モノフルオロアルキル化反応への応用

（北大院薬 [1]）○宮本 公平 [1]・川口 瑛美子 [1]・森崎 一宏 [1]・佐藤 美洋 [1]

Zn/F Carbenoids: Preparation, Stability, Structure, and Application to Nucleophilic Monofluoroalkylation

([1]*Fac. Pharm. Sci., Hokkaido Univ.*) ○Kohei Miyamoto,[1] Emiko Kawaguchi,[1] Kazuhiro Morisaki,[1] Yoshihiro Sato[1]

Whereas carbenoids have been recognized as important reactive intermediates, studies on metal/fluorine carbenoids have been quite limited due to their instability. For example, lithium/fluorine carbenoids[1] have lifetime of 13 ms at −60 °C, limiting their synthetic utilities as well as investigation of their chemical properties.

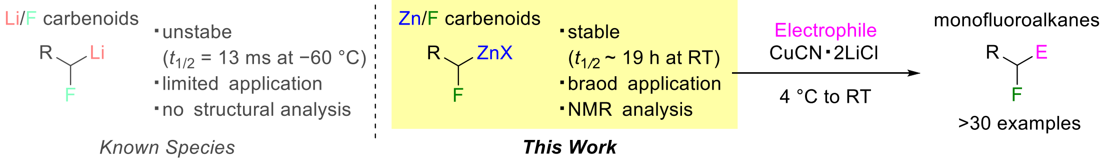
In this study, we have revealed that zinc/fluorine carbenoids can be prepared without cryogenic conditions. Their half-life times are around ten hours at ambient temperature, representing a more than 10^6-fold increase compared to that of lithium/fluorine carbenoids. Zinc/fluorine carbenoids can be applied to various coupling reactions with the assistance of copper reagents, offering a concise access to various monofluoroalkanes with functional groups at the α-position of the fluorine. We also succeeded in detailed NMR structural and kinetic analysis of zinc/fluorine carbenoids.

Keywords : Carbenoid; Fluorine; Zinc; Monofluoroalkylation

金属/フッ素カルベノイドは不安定であるため、その物性や応用に関する研究が限られていた。例えば、リチウム/フッ素カルベノイド [1] の寿命は−60 ℃でわずか 13 ms であり非常に安定性に乏しい。そのため反応に応用するためには、極低温で調製後速やかに他の求電子剤と反応させる必要がある。

そこで今回我々は、比較的電気陰性度の大きく、フッ素との結合エネルギーが小さい亜鉛に着目し、対応する金属/フッ素カルベノイドである「亜鉛/フッ素カルベノイド」に関する検討を行った。

検討の結果、亜鉛/フッ素カルベノイドは容易に調製可能であり、室温で数時間の半減期を有することが分かった。これは従来のリチウム/フッ素カルベノイドよりも 100 万倍以上の半減期である。また、本試薬はシアン化銅の存在下、様々なカップリング反応にも適応可能であった。これにより、フッ素の α 位に官能基を有する様々なモノフルオロアルカンの収束的合成が可能となった。さらに我々は、本カルベノイドの NMR 解析にも成功したので併せて報告する。



1. a) Pace, V.; Luisi, R. *et al. J. Am. Chem. Soc.* **2017**, *139*, 13648. b) Luisi, R.; Nagaki A. *et al. Angew. Chem. Int. Ed.* **2020**, *59*, 10924. c) Luisi R.; Degennaro L. *et al. Chem. Commun.* **2023**, *59*, 1373.

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21日(木) 9:30 ~ 11:30 E1112(11号館 [1階] 1112)

[E1112-4am] 10. 有機化学―有機金属化合物

座長：栗山 翔吾、藤田 健一

日本語

9:30 ~ 9:50

[E1112-4am-01]

アニオン性PCP型ピンサー配位子を有する鉄錯体を触媒としたエーテル類のC(sp^3)–H結合ホウ素化反応

○栗山 翔吾[1]、坂田 健[2]、西林 仁昭[1] (1. 東京大学大学院工学系研究科、2. 東邦大学薬学部)

英語

9:50 ~ 10:10

[E1112-4am-02]

鉄錯体を光触媒とする易酸化性の官能基を有するカルボン酸の脱炭酸－官能基化反応

○玉木 颯太[1]、草本 哲郎[1]、劒 隼人[1] (1. 阪大院基礎工)

英語

10:10 ~ 10:30

[E1112-4am-03]

エンインの環化反応を経る鉄触媒を用いた芳香族ケトンのC–H官能基化反応

○北澤 瑶一[1]、河内 卓彌[1]、垣内 史敏[1] (1. 慶大理工)

10:30 ~ 10:50

休憩

日本語

10:50 ~ 11:10

[E1112-4am-04]

Hoveyda-Grubbs型触媒のオレフィンメタセシス活性に対する配位子上のカルコゲン元素の効果

○衣川 翼[1]、廣田 俊[1]、松尾 貴史[1] (1. 奈良先端大・物質創成)

英語

11:10 ~ 11:30

[E1112-4am-05]

ルテナビシクロボロヒドリド錯体(RUCY®-BH)を用いた塩基無添加条件下でのケトンの不斉水素化反応およびアリルアルコールの不斉ヒドロアミノ化反応

○石坂 智洋[1]、中山 裕治[1]、峠 太一郎[1]、結城 大和[1]、松村 和彦[1]、百合野 大雅[2,3]、大熊 毅[2,3] (1. 高砂香料工業株式会社、2. 北大院工、3. 北大フロンティア化学教育研究センター)

アニオン性 PCP 型ピンサー配位子を有する鉄錯体を触媒としたエーテル類の $C(sp^3)$–H 結合ホウ素化反応

（東大院工[1]・東邦大薬[2]）○栗山 翔吾[1]・坂田 健[2]・西林 仁昭[1]

Catalytic Borylation of $C(sp^3)$-H Bonds of Ethers by Iron Complexes with Anionic PCP-type Pincer Ligands

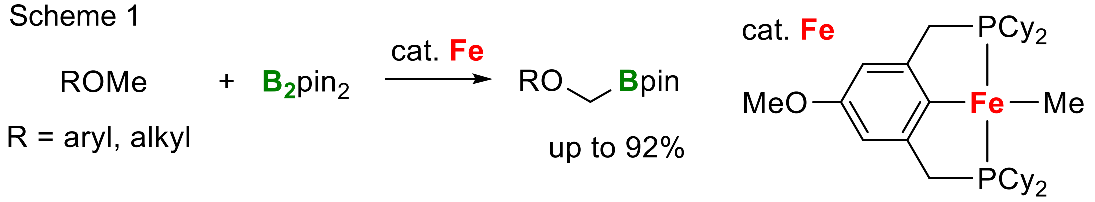
([1]*School of Engineering, The University of Tokyo,* [2]*Faculty of Pharmaceutical Sciences, Toho University*) ○Shogo Kuriyama,[1] Ken Sakata,[2] Yoshiaki Nishibayashi[1]

Recently, C–H borylation by earth-abundant metals such as iron has received much attention. We previously found that iron complexes with anionic PCP-type pincer ligands worked as effective catalysts toward C–H borylation of arenes. As an extensive study, we have found that novel iron complexes bearing anionic PCP-type pincer ligands with electron-donating groups worked as more efficient catalysts for C–H borylation, where various aryl and alkyl ethers underwent borylation at $C(sp^3)$–H bonds. The results of stoichiometric reactions of these iron complexes will be presented.

Keywords : Iron Complex; C–H Activation; C–H Borylation; Pincer Ligand

有機合成において有用な合成中間体である有機ホウ素化合物を直截的に得る手段として、遷移金属触媒を用いた C–H 結合ホウ素化反応が活発に研究されている。近年では、イリジウム等の貴金属触媒に代わり安価で豊富な鉄を触媒に用いた C–H ホウ素化反応が注目されている。最近、当研究室ではアニオン性 PNP 型ピンサー配位子を有する鉄メチル錯体が芳香環の $C(sp^2)$–H 及びアニソール類のメトキシ基 $C(sp^3)$–H ホウ素化に対して有効な触媒として働くことを報告した[1)]。また以前に我々はアニオン性 PCP 型ピンサー配位子を有する鉄錯体の合成と C–H 結合ホウ素化反応への反応性を報告した[2)]。今回、ピンサー配位子に電子供与性基を導入した鉄錯体がより高活性な C–H ホウ素化反応の触媒として働き、様々なアリールおよびアルキルエーテル類の $C(sp^3)$–H 結合のホウ素化反応が進行することを見出した (Scheme 1)。鉄錯体の化学量論反応によって反応中間体についての知見も得られたので、合わせて発表予定である。

Scheme 1



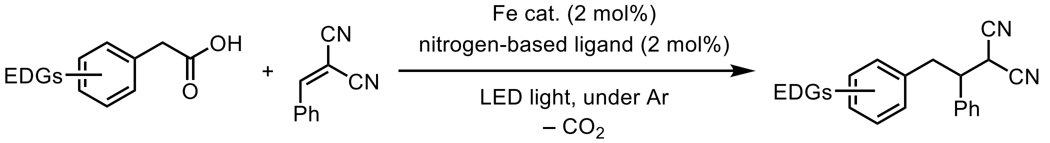
1) T. Kato, S. Kuriyama, K. Nakajima, Y. Nishibayashi, *Chem. Asian J.* **2019**, *14*, 2097.
2) Y. Suga, S. Kuriyama, Y. Nishibayashi, 102nd CSJ Annual Meeting, **2022**, J402-2pm-11.

Decarboxylative Functionalization of Carboxylic Acids with Easily Oxidizable Functional Groups Catalyzed by Iron Complexes under Photo-irradiation

(*Graduate School of Engineering Science, Osaka University*) ○ Sota Tamaki, Tetsuro Kusamoto, Hayato Tsurugi

Keywords: Photocatalyst; Iron Complex; Carboxylic Acid; Phenol; Amino Acid

Decarboxylation of aliphatic carboxylic acids for generating alkyl radicals has attracted attention in radical-mediated organic synthesis due to the abundance and versatility of the carboxylic acids.[1] Single-electron oxidation of carboxylate anions by anodic oxidation or photocatalysis has been developed for generating carboxylate radicals as the key intermediates prior to the decarboxylation; however, oxidation of the carboxylate anions leads to degradation of easily oxidizable functional groups such as phenol and indole groups bound to the carboxylic acids, resulting in a limitation of substrate applicability.[2] In this regard, photo-induced homolysis of metal–carboxylate covalent bonds is a suitable method to avoid the undesired oxidation of the easily oxidizable functional groups during the carboxylate radical generation.[3] Herein, we report that decarboxylative C–C bond formation of carboxylic acids having phenol and indole functionalities is achieved by a catalytic amount of iron(III) salt and nitrogen-based ligand under visible light irradiation. Treatment of 4-hydroxyphenylacetic acid with benzylidenemalononitrile (1.5 equiv.) in the presence of iron salt (2 mol%) and nitrogen-based ligand (2 mol%) under argon atmosphere with 427 nm blue LED irradiation (45 W) resulted in the formation of 2-(2-(4-hydroxyphenyl)-1-phenylethyl)malononitrile in 95% yield. Other arylacetic acids with electron-donating substituents on the aromatic ring were applicable under the similar reaction conditions by changing the wavelength of the light source. In addition, various *N*-protected amino acids served as functionalized alkyl radical sources. Optimization of the reaction conditions, scope of the substrates, and details on the catalytically active species are disclosed in this presentation.



EDGs = electron-donating groups

(1) Selected review: Li, L.; Yao, Y.; Fu, N. *Eur. J. Org. Chem.* **2023**, *26*, e202300166. (2) (a) Maeda, K.; Saito, H.; Osaka, K.; Nishikawa, K.; Sugie, M.; Morita, T.; Takahashi, I.; Yoshimi, Y. *Tetrahedron* **2015**, *71*, 1117. (b) Bloom, S.; Liu, C.; Kölmel, D. K.; Quio, J. X.; Zhang, Y.; Poss, M. A.; Ewing, W. R.; MacMillan, D. W. C. *Nat. Chem.* **2018**, *10*, 205. (3) Lu, Y.-C.; West, J. G. *Angew. Chem., Int. Ed.* **2023**, *62*, e202213055.

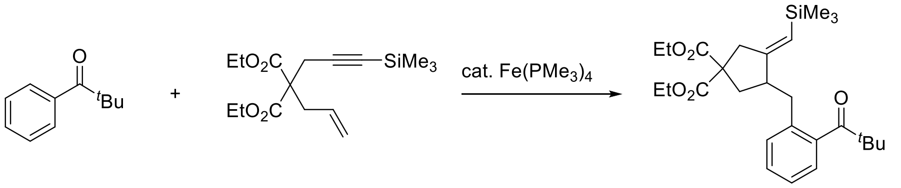
Iron-Catalyzed C–H Functionalization of Aromatic Ketones via Enyne Cyclization

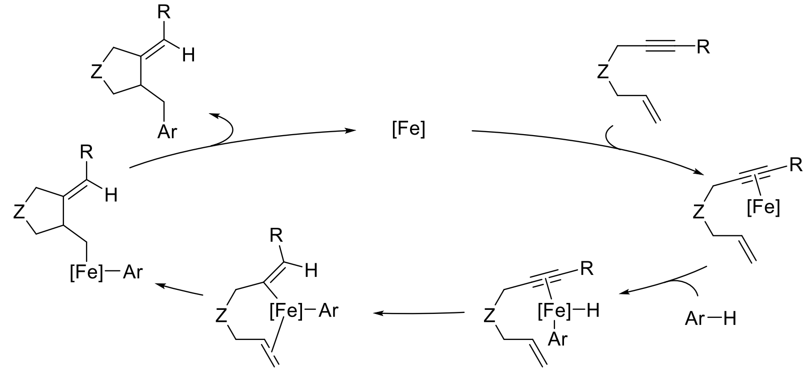
(*Faculty of Science and Technology, Keio University*) ○Yoichi Kitazawa, Takuya Kochi, Fumitoshi Kakiuchi

Keywords: *Iron Catalyst; C–H Bond Cleavage; Aromatic Ketones; Enynes; Cyclization*

C–H functionalizations using iron catalysts have been widely studied, but expansion of its scope is still desired.[1] Our group has found that an iron phosphine complex, $Fe(PMe_3)_4$, catalyzes ortho-selective C–H/olefin and C–H/alkyne couplings of aromatic ketones.[2] Here we report that the iron complex also catalyzes a C–H functionalization of aromatic ketones via enyne cyclization.

When the reaction of pivalophenone with 1,6-enyne containing an internal alkyne and a terminal alkene moiety was carried out using a catalytic amount of $Fe(PMe_3)_4$, hydroarylative enyne cyclization proceeded to give a methylenecyclopentane derivative by regioselectively introducing hydro and phenyl groups onto the alkyne and the alkene moieties, respectively. This reaction is considered to proceed via coordination of the alkyne moiety of the enyne to the Fe center, oxidative addition of the ortho C–H bond of the ketone, regioselective insertion of the alkyne moiety into the Fe–H bond, cyclization by subsequent insertion of the alkene moiety, and reductive elimination.





1) R. Shang, L. Ilies, E. Nakamura, *Chem. Rev.* **2017**, *117*, 9086.

2) (a) N. Kimura, T. Kochi, F. Kakiuchi, *J. Am. Chem. Soc.* **2017**, *139*, 14849. (b) N. Kimura, S. Katta, Y. Kitazawa, T. Kochi, F. Kakiuchi, *J. Am. Chem. Soc.* **2021**, *141*, 4543. (c) Y. Kitazawa, T. Kochi, F. Kakiuchi, *J. Org. Chem.* **2023**, *88*, 1890.

Hoveyda-Grubbs 型触媒のオレフィンメタセシス活性に対するベンジリデン配位子上のカルコゲン元素の効果

（奈良先端大・物質創成 [1]）○衣川 翼 [1]・廣田 俊 [1]・松尾 貴史 [1]

Effect of a Sulfur Atom in the Benzylidene Ligand of Hoveyda-Grubbs-type Complexes on Their Catalytic Activities

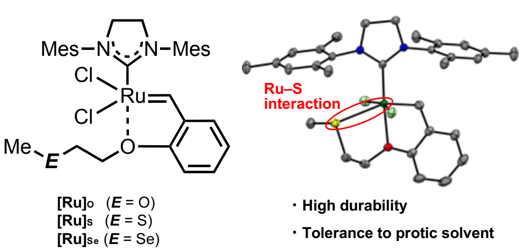
([1]*Dvision of Material Science of Science and Technology , Nara Institute of Science and Technology*) ○Tsubasa Kinugawa,[1] Shun Hirota,[1] Takashi Matsuo.[1]

Hoveyda-Grubbs second generation complex (HG-II) is a catalyst for olefin metathesis reactions. Various derivatives of HG-II have been developed to regulate the complex reactivities. We previously reported that an HG-type complex with an ethyleneamide group in the benzylidene ligand controls its reactivities through second-coordination sphere effect with a hydrogen bond between the amide moiety and a chlorido ligand.1) In this study, we have investigated the chalcogen atom effects in the phenoxy terminal of benzylidene ligand on the complex structures and reactivities. The complex with a sulfur atom at the phenoxy moiety was found to suppress the catalyst decomposition with the Ru–S interaction, resulting in the tolerance in polar solvents.2) Moreover, we extended the study to the HG-type complex with selenium atom (**[Ru]**$_{\mathbf{Se}}$) and investigated its reactivities.

Keywords : Hoveyda-Grubbs 2nd generation catalyst; *Olefin Metathesis*; *Chalcogen Elements*; *Ruthenium–Chalcogen Element Interaction*

Hoveyda-Grubbs 第 2 世代錯体(HG-II)は、*N*-ヘテロカルベン配位子とベンジリデン配位子を有するオレフィンメタセシス触媒であり、熱的安定性の高さに起因する利便性から、さまざまな構造修飾様式による反応性の制御が試みられている。以前、我々は、ベンジリデン配位子のフェノキシ部位末端にアミド部位を導入することで、第 2 配位圏効果によって錯体の安定性および反応性制御が可能であることを報告した 1)。そこで本研究では、16 族元素(O, S)を導入したベンジリデン配位子を有する錯体 **[Ru]**$_{\mathbf{O}}$, **[Ru]**$_{\mathbf{S}}$ を合成し、それらの構造と触媒活性について検証した 2)。

硫黄原子を有するベンジリデン配位子と HG-II 錯体を 1:1 の化学量論比で配位子交換反応を行ったところ、錯体**[Ru]**$_{\mathbf{S}}$ の収率が 50%を超えたことから、**[Ru]**$_{\mathbf{S}}$ は HG-II 錯体よりも安定であることが分かった。また錯体の結晶構造から、配位子末端の S 原子と中心金属の相互作用が錯体の安定化に寄与し、極性溶媒存在下における触媒反応では、触媒の分解が抑制され、HG-II 触媒よりも高い反応活性を示した 2)。さらに我々は、セレン (Se)元素を導入したホベイダ配位子と錯体 **[Ru]**$_{\mathbf{Se}}$ を合成し、その反応活性についても調査した。



1) T. Matsuo *et al*, *Dalton Trans*., **2020**, *49*, 11618. 2) T. Matsuo *et al*, *Dalton Trans*., **2023**, *52*, 9499.

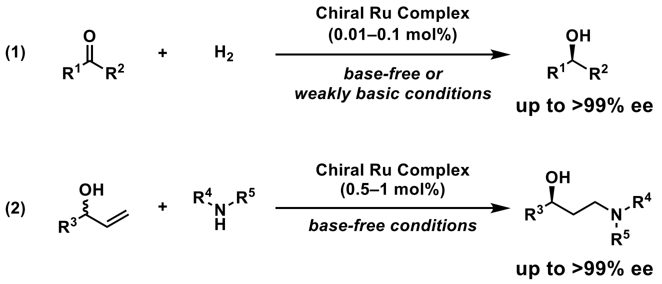
Ruthenabicyclic Borohydride Complexes (RUCY®-BH) for Asymmetric Hydrogenation of Ketones and Asymmetric Formal Hydroamination of Allylic Alcohols under Base-Free Conditions

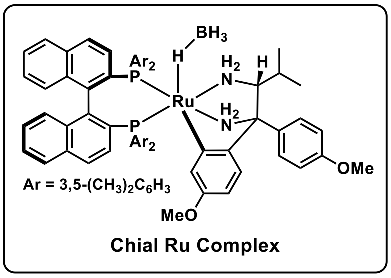
([1]*Takasago International Corporation*, [2]*Division of Applied Chemistry, Faculty of Engineering, Hokkaido University,* [3]*Frontier Chemistry Center, Hokkaido University*)
○ Tomohiro Ishizaka,[1] Yuji Nakayama,[1] Taichiro Touge,[1] Yamato Yuki,[1] Kazuhiko Matsumura,[1] Taiga Yurino,[2,3] Takeshi Ohkuma[2,3]

Keywords: Ruthenium; Borohydride Ligand; Base-Free Condition; Asymmetric Hydrogenation; Asymmetric Hydroamination

Catalytic asymmetric hydrogenation of ketones is a well-known method to obtain chiral secondary alcohols. We have previously reported an extremely rapid and enantioselective hydrogenation of ketones using the ruthenabicyclic complex RuCl(daipena)(xylbinap)/base catalyst system.[1] However, the need for a base puts restrictions on the asymmetric hydrogenation of base-labile ketones. In this study, novel ruthenabicyclic complexes bearing a η^1-BH_4 ligand, Ru(η^1-BH_4)(daipena)(diphosphine)[2] were developed to achieve asymmetric hydrogenation even under base-free conditions, based on the previous observation that RuH(η^1-BH_4)(diphosphine)(diamine)[3] catalyzed the reaction without addition of a base.

The hydrogenation of acetophenone using the borohydride complexes proceeded in high catalytic activity with >99% ee of the product under base-free conditions or weakly basic conditions. Under base-free conditions, base-labile ketones, such as α-chloroketone and trimethylsilyl-protected alkynyl ketone, were reduced to the corresponding alcohols in high yield and enantioselectivity. The borohydride complexes also catalyzed the asymmetric formal hydroamination of racemic allylic alcohols in the absence of an inorganic base. This reaction proceeds via a borrowing hydrogenation mechanism, which includes: (1) dehydrogenative oxidation of allylic alcohol, (2) aza-Michael addition, (3) asymmetric reduction of the β-amino ketone intermediate. This protocol provides a short-step process to give a variety of chiral γ-amino alcohols in high enantioselectivity (up to >99 % ee).





Chial Ru Complex

1) K. Matsumura, N. Arai, K. Hori, T. Saito, N. Sayo, T. Ohkuma, *J. Am. Chem. Soc.* **2011**, *133*, 10696. 2) T. Ishizaka, Y. Nakayama, T. Touge, Y. Yuki, K. Matsumura, T. Yurino, T. Ohkuma, *Tetrahedron* **2023**, *149*, 133705. 3) T. Ohkuma, M. Koizumi, K. Muñiz, G. Hilt, C. Kabuto, R. Noyori, *J. Am. Chem. Soc.* **2002**, *124*, 6508.

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21日(木) 13:00 ~ 14:20 E1122(11号館 [2階] 1122)

[E1122-4pm] 12. 有機化学―有機結晶・超分子化学

座長：井手 雄紀、湯浅 順平

英語

13:00 ~ 13:20

[E1122-4pm-01]

ロタキサン構造を介してメソゲンコアとフレキシブルテールとを一体化させたイオン性液晶の設計

○鷲野 豪介[1]、西村 涼[2]、宍戸 厚[1] (1. 東工化生研、2. 東工大物質)

英語

13:20 ~ 13:40

[E1122-4pm-02]

二次元COFの積層構造変形による蛍光スイッチング

○葉 思遠[1]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工)

英語

13:40 ~ 14:00

[E1122-4pm-03]

高出力する光駆動結晶の機械学習による材料設計と条件最適化

○石崎 一輝[1]、朝日 透[1]、谷口 卓也[1] (1. 早稲田大学)

日本語

14:00 ~ 14:20

[E1122-4pm-04]

偏光照射下における光駆動自励振動結晶の挙動の反応速度論に基づいた数理モデルからの解析

○景山 義之[1]、松浦 真紀子[1] (1. 北大)

Design of Ionic Liquid Crystals by Integrating a Mesogen Core with Flexible Tails via a Rotaxane Structure

([1]*Laboratory for Chemistry and Life Science, Institute of Innovative Research*, *Tokyo Institute of Technology,* [2]*School of Materials and Chemical Technology, Tokyo Institute of Technology*)
○Gosuke Washino,[1] Suzushi Nishimura[2], Atsushi Shishido[1]

Keywords: Rotaxane; Ionic Liquid Cyrtal; Supramolecule; Thermotropic Liquid Crystal; Crown ether

Ionic liquid crystals (iLCs) are attractive for creating unique material functions by arranging ionic molecules with higher-order structures and for the versatility of molecular design approaches in LCs. Besides introducing a mesogen core and flexible tails into a single molecule, iLCs can utilize counterions to enable LC phase expression by controlling a hydrophobic-hydrophilic balance. Rigid cations, known for crucial molecular structures in the iLC design, are also essential molecular components in the supramolecular field. For instance, in the synthesis of rotaxanes, typical mechanically interlocked structures, rigid cations like viologen derivatives serve as axle molecules to form threading structures with electron-rich ring molecules.[1] However, very few papers have reported syntheses of LC rotaxanes playing the dual roles of rigid cations in the two different fields.[2]

In this study, we present a design concept for iLCs where [2]rotaxane structure formation enables LC phase expression. We designed a [2]rotaxane (**Rtx12**) consisting of an axle molecule with only a mesogen core and a ring molecule with four flexible tails. Although neither the axle nor the ring has LC properties, **Rtx12** exhibits a smectic A phase due to integrating a mesogen core and flexible tails via a rotaxane structure. A 1:1 mixture of the axle and the ring without a rotaxane structure showed no thermotropic LCs; the rotaxane structure formation in **Rtx12** is crucial in exhibiting the LC phase. We further discuss developing this iLC design concept into a dynamic system: pseudo-rotaxane.

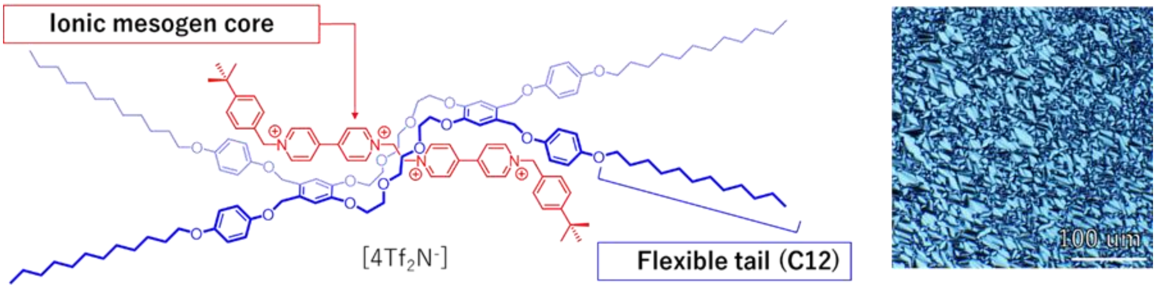


Figure 1. Chemical Structure of **Rtx12** and POM image of **Rtx12** at 140 °C upon cooling.

1) H. R. Wessels, C. Slebodnick, and H. W. Gibson, *J. Am. Chem. Soc.* **2018**, *140,* 7358. 2) N. D. Suhan, S. J. Loeb, and S. H. Eichhorn, *J. Am. Chem. Soc.* **2013**, *135,* 400.

Switching the Emission of Two-Dimensional COFs by Tuning Interlayer Stacking Arrangements

([1]*Graduate School of Engineering, The University of Tokyo*) ○Siyuan Ye,[1] Nobuhiko Hosono,[1] Takashi Uemura[1]

Keywords: COFs; Phase transition; Two-dimensional Materials; Through-space Charge transfer

The properties of two-dimensional (2D) materials are intrinsically linked to their stacking configurations. While scientists have controlled a limited array of these materials via operation under scanning tunneling microscope (STM),[1] a comprehensive exploration of their stacking modes remains elusive. Two-dimensional porous materials, such as Metal-Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs), have garnered significant interest for their adjustable properties and crystalline structures.[2] Traditionally, altering these materials' packing patterns necessitates intricate chemical modifications.[3] However, a novel approach has emerged with the discovery of guest-modulated interlayer slip in 2D COFs,[4] allowing for simpler manipulation of stacking patterns without altering the core structure.

This study introduces a new COF consisting of pyrene and cyanostilbene moieties in the framework, designated as **1**, which we successfully manipulated in terms of interlayer stacking via electron donor-acceptor alternation. When desolvated, **1** exhibits an ordered AA stacking arrangement. This configuration shifts to a quasi-AB stacking pattern upon introducing solvents with low surface tension (Figure 1). Conversely, high surface tension solvents and carbon dioxide lead to disordered stacking. These variations in stacking profoundly influence charge transfer between layers, markedly altering its fluorescence emission characteristics. Notably, **1** demonstrates non-emissive properties in AA stacking yet displays emissive fluorescence in quasi-AB stacking. By tailoring the size distribution of **1** in solution, we can fine-tune its emission color, achieving a unique single-component white light emission.

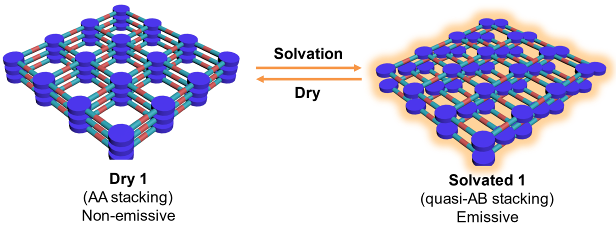


Figure 1. Schematic diagram of turning on fluorescence through changing the interlayer stacking of **1**

1) Y. Cao, V. Fatemi, and S. Fang, *Nature* 2018, **556**, 43, 2) S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem. Int. Ed.* 2004, **43**, 2334. 3) X. Wu, X. Han, Y. Liu, Y. Liu and Y. Cui, *J. Am. Chem. Soc.*, 2018, **140**, 16124. 4) C. Kang, Z. Zhang, V. Wee, A. K. Usadi, D. C. Calabro, L. S. Baugh, S. Wang, Y. Wang and D. Zhao, *J. Am. Chem. Soc.*, 2020, **142**, 12995.

Material design and condition optimization for generating higher force of photomechanical crystals by machine-learning

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*Center for Data Science, Waseda University*) ○Kazuki Ishizaki,[1] Toru Asahi,[1] Takuya Taniguchi[2]

Keywords: Generating force; Photomechanical crystal; Machine learning; Young's modulus

Photomechanical crystals show macroscopic motion under UV light irradiation. In our previous work, the generated force of the photomechanical salicylideneamine crystals was about 8.7 mN even under optimal conditions.[1] Searching a wide range of conditions is necessary to find the optimum conditions to increase generating force. In this study, photomechanical crystals with various Young's modulus were fabricated based on material design guidelines obtained by LASSO regression, and then conditions achieving larger generating force were explored by Bayesian optimization.

To design photomechanical crystals with various Young's moduli, we performed LASSO regression, one of the linear regression methods for variable reduction. LASSO regression was conducted to identify functional groups correlated with Young's modulus (Fig. 1a). Eleven types of salicylideneamine crystals were prepared based on the finding of the LASSO regression.

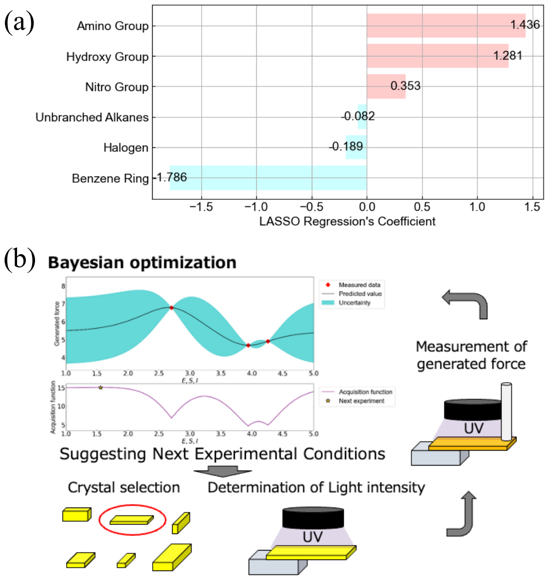


Fig. 1. (a) Molecular design by LASSO regression. (b) Condition search by Bayesian optimization.

The conditions corresponding to a larger generating force were searched using Bayesian optimization. Bayesian optimization suggests the following experimental conditions based on the value of the acquisition function calculated by the predictions and the uncertainty of the predictions. The condition of Young's modulus, crystal size, and light intensity were suggested by Bayesian optimization. Based on the suggested conditions, the crystal was selected, and light intensity was determined. After these steps, generating force was measured (Fig. 1b). The same operation was repeated to find the experimental conditions with the highest generating force. In this research, before the actual experiments, simulations were conducted to obtain an indication of the trial number.

1) K. Ishizaki, R. Sugimoto, Y. Hagiwara, H. Koshima, T. Taniguchi, T. Asahi, *CrystEngComm*, **23**, 5839-5847 (2021).

偏光照射下における光駆動自励振動結晶の挙動の反応速度論に基づいた数理モデルからの解析

（北大院理）○景山 義之・松浦 真紀子

Analysis of light-driven self-oscillatory crystal under polarized light irradiation from a mathematical model based on reaction velocity

(*Faculty of Science, Hokkaido University*) ○ Yoshiyuki Kageyama, Makiko Matsuura

We previously proposed that the light-driven self-oscillation of an azobenzene crystal is realized by the sequential behavior of the photoisomerization-triggered crystalline phase transition and its resultant alternation of the apparent photoisomerization rate constants1). In addition, we reported that the complexity of the self-oscillatory motion is derived when the excitation light is polarized2). Aiming to understand the origin of the complexity, we analyzed the observed frequency under polarization light excitation and constructed a math-model from the reaction equations. The observed behavior (**Fig. 1a**) can be explained by a kinetic model which is derived from the proposed mechanism (**Fig. 1b**). Moreover, we found that the existence of hysteresis contributes to the complexity of the behavior 3).

Keywords : Reaction Kinetics, Autonomous Motion, Far-from-equilibrium, Self-oscillatory Crystal, Hysteresis

演者らはアゾベンゼン誘導体を構成分子とした結晶の定常光照射下での継続的なフリップ運動を報告した。この現象では、光異性化が誘起する結晶構造転移が、見かけの光異性化速度定数を切り替えることで自己継続性を実現していると演者らは提案している 1)。また、照射光を偏光にした場合、偏光角度依存的な複雑な自励振動を示すことを明らかにしてきた 2)。その複雑性の起源の理解を目指し、本研究では、偏光照射下での自励振動の振動数について解析した。特徴的な振動数の偏光角度依存性(**Fig. 1a**)は、我々が提案する自励振動発現機構を基にした数理モデルの結果とよく一致した(**Fig. 1b**)。さらには、ヒステリシスの存在が挙動の複雑化に関与していることを発見した 3)。

1) T. Ikegami, Y. Kageyama, S. Takeda, *et al.*, *Angew. Chem. Int. Ed.* **55**, 8239 (2016).
2) Y. Kageyama, S. Takeda, *et al.*, *Chem. Eur. J.* **26**, 10759 (2020).
3) Y. Kageyama *et al.*, *arXiv* 2301.09873 (2023).

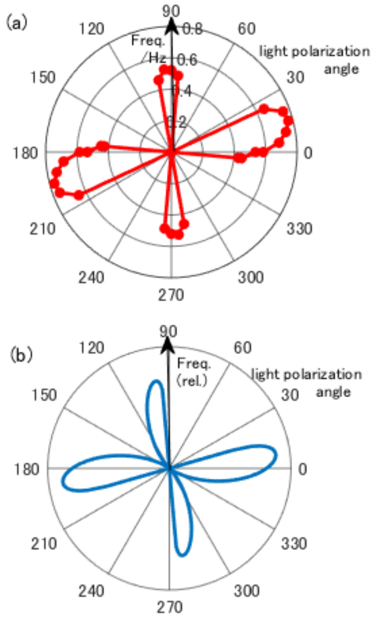


Fig. 1. Examples of the light polarization angle dependency on the frequency of the light-driven crystalline self-oscillation: (a) an experimental result and (b) a calculated result of the mathematical model.

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21日(木) 13:00 ~ 15:10 E1123(11号館 [2階] 1123)

[E1123-4pm] 12. 有機化学—有機結晶・超分子化学

座長：土戸 良高、木村 真也

日本語

13:00 ~ 13:20

[E1123-4pm-01]

超分子ゲルにより時空間的に制御されたフォトクロミック反応

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

日本語

13:20 ~ 13:40

[E1123-4pm-02]

アルキル化ジフェニルアントラセン液体の物性に及ぼすアトロプ異性体の効果

Xiao Zheng[1,2]、名倉 和彦[1]、松下 能孝[1]、○中西 尚志[1,2] (1. 物質・材料研究機構、2. 北海道大学)

英語

13:40 ~ 14:00

[E1123-4pm-03]

Chirality-controlling supramolecular assemblies of acidic and basic pillar[5]arenes

○Dehui Tuo[1,2], Shixin Fa[3], Seigo Tanaka [2], Kenichi Kato[2], Tomoki Ogoshi[2,1] (1. WPI-NanoLSI, Kanazawa Univ., 2. Grad.Sch.Eng., Kyoto Univ., 3. Northwestern Polytechnical Univ.)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[E1123-4pm-04]

固液界面におけるC_{3h}対称性コアを持つ分子の自己識別を利用した階層的なホモキラル分子集合体の構築

○前田 松祐[1]、Steven De Feyter[2]、田原 一邦[3] (1. 明大院理工、2. ルーバン大化、3. 明大理工)

日本語

14:30 ~ 14:50

[E1123-4pm-05]

温度に依存して左右にねじれた立体配座が変換する1:1ホスト-ゲストシステムの解析

○鈴木 望[1]、田浦 大輔[2]、古田 裕亮[2] (1. 神大、2. 名城大)

英語

14:50 ~ 15:10

[E1123-4pm-06]

イソオキサゾール骨格を側鎖にもつ白金錯体集合体の攪拌により誘導されるキロプティカル応答

○吉田 真也[1,2]、平尾 岳大[1]、灰野 岳晴[1,2] (1. 広島大院先進理工、2. 広島大WPI-SKCM²)

超分子ゲルにより時空間的に制御されたフォトクロミック反応

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

Spatiotemporally-controlled photochromic reactions using supramolecular gel

([1]*College of Life Sciences, Ritsumeikan University*, [2]*PRESTO JST*) ○Yuki Nagai,[1] Sota Fujisaki,[1] Yoshinori Okayasu,[1] Yoichi Kobayashi[1,2]

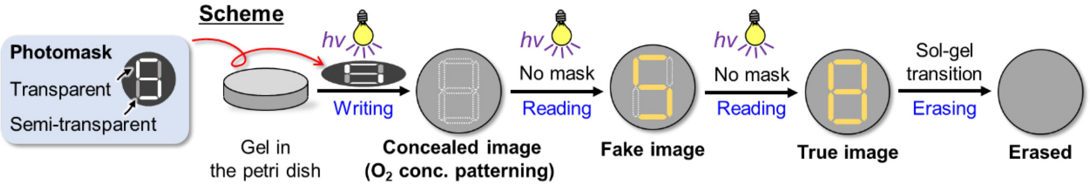
Controlling the time evolution of photochemical reactions leads to the development of temporally-programmed multiple photofunctions. In this study, we developed photochromic reactions showing unique time evolutions based on the regulation of oxygen (O_2) supply from the air by supramolecular gel. In photoirradiation to an air-saturated gel of anthraquinone (AQ), photoreduction of its colorless original form to yellow reduced form showed an induction period until coloration because the dissolved O_2 was consumed by quenching the photoreduction. While the reduced form was retained over an hour in the gel, the decoloration was completed instantly upon the solation by heating. This is because the sol state allows quick O_2 supply from the air in contrast to the gel state. Based on the unique photochromic dynamics, spatiotemporal photopatterning (Fig. 1) and multicolor photochromic reactions were achieved.

Keywords : Anthraquinone; Photopatterning; Triplet Excited State; Radical Anion; Nonlinear Response

光化学反応の時間発展の高度制御は、複数の機能が時間的にプログラムされた光機能材料の開発に繋がる。本研究では、超分子ゲルを用いて気相からの酸素供給を制御することにより特異な時間発展を示すフォトクロミック反応を開発した。

還元剤存在下でアントラキノン (AQ) に紫外光照射を照射すると、無色の酸化体から黄色の還元体へと光還元される。この光還元を空気飽和ゲル中において行うと、溶存酸素が光還元を阻害して次第に消費されていくため、光照射開始から着色までに誘導期間を示した。また、還元体由来の着色はゲルが空気からの酸素供給を抑制するために 1 時間以上も安定に存在した一方、加熱によってゾル化させると還元体の空気酸化により直ちに消色することができた。更に着色までの誘導期間を応用し、時空間的フォトパターニング (Fig. 1) やマルチカラーフォトクロミック反応を実現した。

Scheme



Sample images under white light

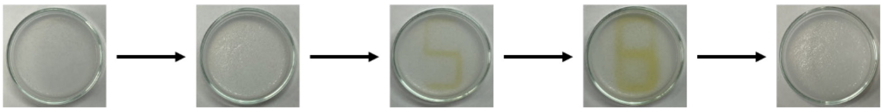


Fig. 1 (Top) The experimental scheme and (Bottom) the sample images in the spatiotemporal photopatterning.

アルキル化ジフェニルアントラセン液体の物性に及ぼすアトロプ異性体の効果

（物質・材料研究機構 ^{1}・北大院先端生命 ^{2}）Zheng Xiao^{1,2}・名倉 和彦 ^{1}・松下 能孝 ^{1}・○中西 尚志 ^{1,2}

Effect of atropisomer on the physical properties of alkylated diphenylanthracene liquids

(^{1}*National Institute for Materials Science*, ^{2}*Graduate School of Life Science, Hokkaido University*) Xiao Zheng,^{1,2} Kazuhiko Nagura,^{1} Yoshitaka Matsushita,^{1} ○Takashi Nakanishi,^{1,2}

By appropriate molecular design, π-conjugated molecules modified and protected with branched alkyl chains can be obtained as low-viscosity, practically stable, room-temperature liquids that do not solidify or become supercooled liquids[1-3]. For example, structural isomers with different substitution positions for the branched alkyl chain may have different viscosity of the alkyl-π molecular liquid and may even exhibit supercooling liquid properties[2,3]. In this study, we succeeded in separating and purifying *syn*- and *anti*-atropisomers of an alkylated diphenylanthracene liquid, which was unprecedented in π molecular liquids. We also investigated the structure-property relationships of each atropisomer and the effects of isomer mixtures on liquid properties by means of rheology, DSC, optical spectroscopies, and so forth.

Keywords : Functional Molecular Liquid; Atropisomer; Viscosity; Supercooled Liquid; Fragility

分岐アルキル鎖で修飾・保護されたπ共役分子は、適切な分子設計により、固化せず且つ過冷却液体とならない低粘性の常温液体として得ることができる[1-3]。例えば、分岐アルキル鎖の導入置換位置の違う構造異性体において、アルキル－π分子液体の粘度が異なる、更には過冷却性が生じることがある[2,3]。本研究では、アルキル化ジフェニルアントラセン液体を基材に、アルキル－π分子液体においてこれまで前例のなかったアトロプ異性体（*syn* 体、*anti* 体）を分離精製することに成功した。また、各アトロプ異性体の構造－物性相関、さらには異性体混合物の液体物性に与える影響に関して、レオロジー、DSC、分光測定等を用いて検討したので報告する。

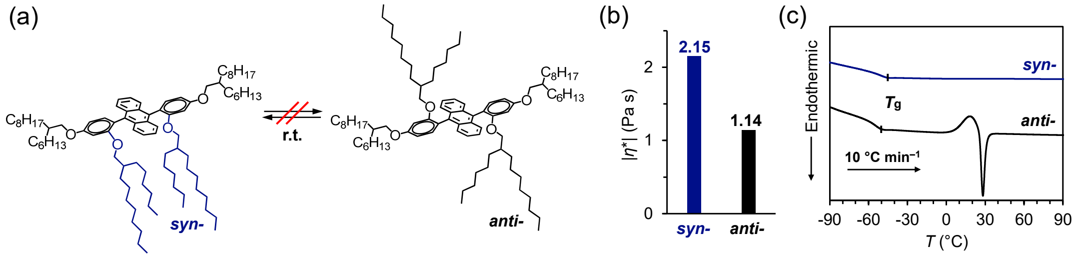


Fig. 1. (a) Chemical structure of *syn*- and *anti*-2,4-C_6C_{10}-diphenylanthracene; (b) complex viscosities ($|\eta^*|$) at 40 °C; (c) DSC thermograms under a heating scan of 10 °C min^{-1}.

1) F. Lu, T. Nakanishi et al., *Chem. Sci.* **2018**, *9*, 6774. 2) X. Zheng, K. Nagura, T. Takaya, K. Hashi, T. Nakanishi, *Chem. Eur. J.* **2023**, *29*, e202203775. 3) F. Lu, A. Shinohara, I. Kawamura, A. Saeki, T. Takaya, K. Iwata, T. Nakanishi, *Helv. Chim. Acta* **2023**, *106*, e202300050.

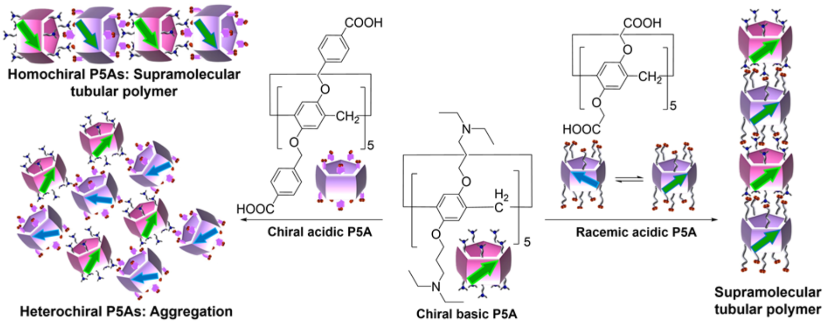
Chirality-controlling Supramolecular Assemblies of Acidic and Basic Pillar[5]arenes

([1]*WPI-NanoLSI, Kanazawa University*, [2]*Graduate School of Engineering, Kyoto University*, [3]*School of Chemistry and Chemical Engineering, Northwestern Polytechnical University*)
○ Dehui Tuo,[1,2] Shixin Fa,[3] Seigo Tanaka,[2] Kenichi Kato,[2] Tomoki Ogoshi[1,2]

Keywords: Pillar[*n*]arenes; Chirality; Supramolecular assembly

Chirality-controlled supramolecular assembly in multicomponent systems is important for the formation of complex self-assembled structures such as living organisms, and has the potential for applications in new functional materials. Pillar[*n*]arenes (PA) exhibit unique planar chirality, and interconversion of the chiral isomers (*pR* and *pS*) by units flipping make PAs intriguing platform for exploring chirality inversion, induction and transformation.[1] We previously achieved real-time monitoring of trimeric homochiral nanotube formation through multiple ion-pairing interactions between optically resolved peramino-pillar[5]arene (P5A) and a racemic rim-differentiated P5A pentaacid.[2] To this context, we envision such kind of acidic and basic P5As would be fascinating for investigating chirality-controlled supramolecular polymerization.

When chiral basic P5A co-assembled with chiral acidic P5A, chirality-controlled self-assembly morphologies were achieved depending on chirality of P5As, in which supramolecular gels are formed in P5As with homochirality, while P5As with heterochirality form turbid aggregations. The phenomena were probably because the acid-base interactions between the P5As are well matched in the homo combination where molecular chirality is aligned. By contrast, the hetero form takes random interaction forms due to mismatches of the interactions, resulting in the difference in the supramolecular formation. When chiral basic P5A co-assembled with racemic acidic P5A, chirality transfer by matching ten ion pairs between basic and acidic P5As occurs and chiral supramolecular tubular polymers are generated.



1) K. Kato, S. Fa, T. Ogoshi, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202308316. 2) S. Fa, T.-H. Shi, S. Akama, K. Adachi, K. Wada, S. Tanaka, N. Oyama, K. Kato, S. Ohtani, Y. Nagata, S. Akine, T. Ogoshi, *Nat. Commun.*, **2022**, *13*, 7378.

Construction of Homochiral Hierarchical Molecular Self-Assemblies Based on Self-Sorting of a Single Molecule with a C_{3h} Symmetric Core at the Liquid/Solid Interfaces

([1]*Graduate School of Science and Technology, Meiji University*, [2]*Department of Chemistry, KU Leuven*, [3]*School of Science and Technology, Meiji University*) ○Matsuhiro Maeda,[1] Steven De Feyter,[2] Kazukuni Tahara[3]

Keywords: Self-Assembled Molecular Networks; Scanning Tunneling Microscopy; Self-Sorting; Liquid/Solid Interface; Chirality Control

Self-sorting of multiple molecular components through orthogonal intermolecular recognition is a promising strategy for the construction of a hierarchical self-assembled molecular network (SAMN) on a surface. We recently reported that the dynamic self-sorting of the conformational isomers of a dehydrobenzo[12]annulene (DBA) derivative **DBA-OC14-OH** with achiral alkoxy chains and hydroxy groups in an alternating manner produces hierarchical triangular clusters of different sizes at the liquid/graphite interface (Fig. 1(a)).[1] In the self-sorting process, solvent molecules 1,2,4-trichlorobenzene and 1-hexanoic acid (HA) play significant roles. Namely, polarity modulation by changing the mixing ratio of the solvents and the co-adsorption of the HA molecules are keys for the size control of the triangular clusters.

We herein present the chirality control of these hierarchical triangular clusters using 1) a chiral molecular building block **cDBA-OC14(*S*)-OH** which has alternating chiral alkoxy chains and hydroxy groups (Fig. 1(c)),[2] and 2) a prochiral **DBA-OC14-OH** derivative in a chiral solvent 2-methyl-1-hexanoic acid (Fig. 1(b)). In both cases, the chirality information can be transferred from the single-molecule level to the hierarchical SAMN level via dynamic self-sorting (Fig. 1(c)).

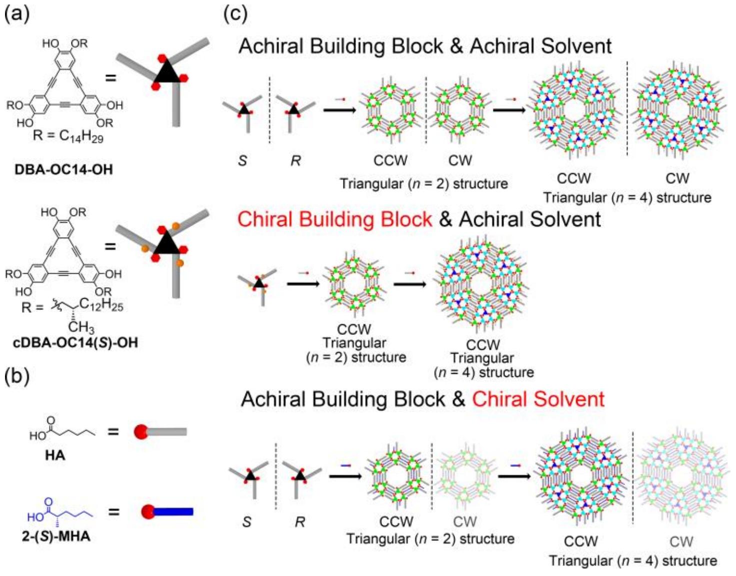


Figure 1. Chemical structures and schematic models of (a) DBA and (b) chiral solvents. (c) Formation of hierarchical triangular clusters.

1) Maeda, M.; Nakayama, R.; De Feyter, S.; Tobe, Y.; Tahara, K. *Chem. Sci*. **2020**, *11*, 9254. 2) Maeda, M.; Sato, K.; De Feyter, S.; Tobe, Y.; Tahara, K. *Nanoscale* **2023**, *15*, 19569.

温度に依存して左右にねじれた立体配座が変換する 1:1 ホスト-ゲストシステムの解析

（神大院工 [1]・名城大院理工 [2]）○鈴木 望 [1]・田浦 大輔 [2]・古田 裕亮 [2]

Analysis of 1:1 Host-Guest Systems with Temperature-Dependent Left- and Right-Twisted Conformational Changes ([1]*Graduate School of Engineering, Kobe University*, [2]*Graduate School of Science and Technology, Meijo University*) ○Nozomu Suzuki,[1] Daisuke Taura,[2] Yusuke Furuta[2]

In host-guest systems, the design of the host molecule with a twisted structure plays an essential role in the application of chiral materials (Figure 1).1) To evaluate and improve the functionality of the host molecule, the circular dichroism (CD) or ^{1}H-NMR spectroscopy is often used. However, the ^{1}H-NMR is not applicable when the interconversion between the diastereomeric left- and right-twisted conformations is faster than the timescale of the ^{1}H-NMR. In this work, we have developed a novel method that enables to analyze the 1:1 host-guest systems under the equilibrium between the left- and right-twisted conformations using the temperature-dependent CD spectra.

Keywords : Host-Guest; Chiral; Molecular Recognition

左右にねじれた立体配座を有するホスト分子とゲスト分子からなる分子認識システムは、キラル材料への応用が可能である 1)。左右にねじれた立体配座の定量化には、^{1}H-NMR を用いるが、ジアステレオメリックな左右の構造間の変化が ^{1}H-NMR のタイムスケールより速い場合には、^{1}H-NMR を利用することができない。本発表では、温度可変円二色性スペクトルを利用して、このような 1:1 ホスト-ゲストシステムを解析する新たな手法を開発したので、報告する。

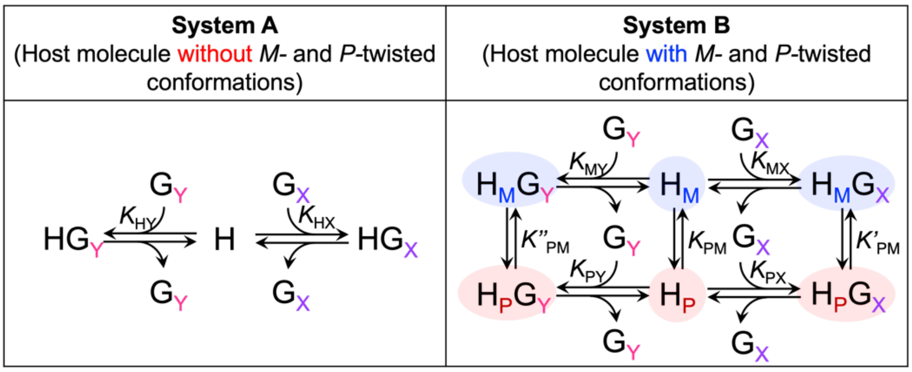


Figure 1. Host-guest systems. Guest molecules (G_X and G_Y) can be a pair of enantiomers or chiral and achiral molecules. System A: host molecule (H) *without* left- and right- (*M*- and *P*-) twisted conformations. System B: H *with* *M*- and *P*-twisted conformations (H_M and H_P).

1) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116*, 13752.

Vortex flow induced chiroptical response of self-assembled supramolecular objects of isoxazole-equipped platinum(II) complex

([1] *Graduate School of Advanced Science and Engineering, Hiroshima University,*
[2] *International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM²), Hiroshima University*) ○Masaya YOSHIDA,[1,2] Takehiro HIRAO,[1] Takeharu HAINO[1,2]

Keywords: Self-assembly; Circular dichroism; Nanostructure; Vortex flow; Orientation

Supramolecular assemblies exhibit photochemical properties unique to their assembled states. We reported that neutral platinum(II) complexes possessing isoxazole moieties were assembled to form one-dimensional fibers and micellar structures via π-π stacking, dipole-dipole, and metal-metal interactions.[1, 2] I will discuss the CD responses of the stacked assembly of platinum complex **1** (Figure 1a).

Complex **1** was self-assembled to form nanometric sheet-like structures in toluene, which did not show any CD response (Figure 1b dotted line). When the toluene solution of **1** was stirred, CD signals emerged. The intensity of the CD signals responded to the rotation frequencies of vortex flows. The rotation directions of vortices determined the signs of CD signals (Figure 1b, c). In contrast, complex **2** formed random aggregates in toluene, which did not show any CD response in vortex flows. Accordingly, the CD signals were most likely driven by the orientation of the sheet-like supramolecular objects in the solution.

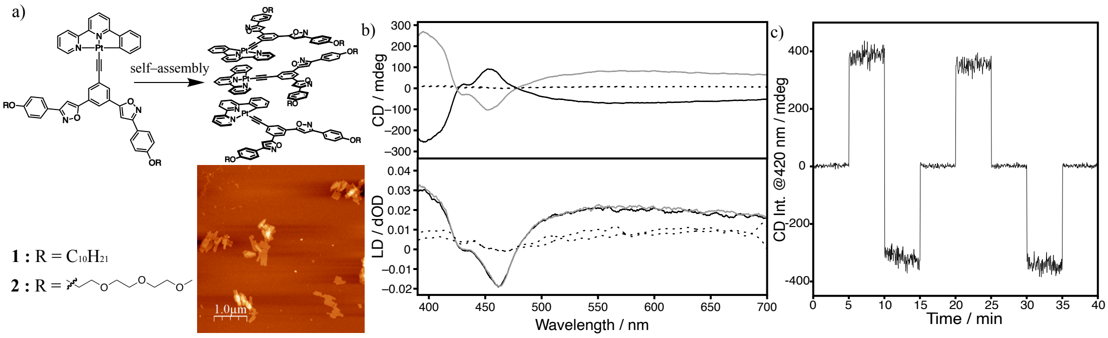


Figure 1. a) Structures of neutral Pt(II) complexes and AFM image of complex **1** on mica (5 µm × 5 µm). b) CD and LD spectra of complex **1** (0.3 mmol L^{-1}) (solid black line: clockwise 1000 rpm), (solid gray line: counterclockwise 1000 rpm), and (dotted black line: 0 rpm) at 25 °C in toluene. (C) Change in CD intensity at 420 nm in response to a stepwise variation of the stirring conditions of complex **1** (0.3 mmol L^{-1}) at 25 °C in toluene.

1) T. Ikeda, M. Takayama, J. Kumar, T. Kawai and T. Haino, *Dalton Trans.*, **2015**, *44*, 13156-13162.
2) M. Yoshida, T. Hirao, and T. Haino, *Org. Biomol. Chem.*, **2021**, *19*, 5303-5311.

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21日(木) 13:00 ~ 14:50 E1131(11号館 [3階] 1131)

[E1131-4pm] 12. 有機化学—有機結晶・超分子化学

座長：林 正太郎、燒山 佑美

英語

13:00 ~ 13:20

[E1131-4pm-01]

Triptycene Frameworks for Orientational Control over Electroactive Subunits in STM Break-Junction

○Colin John Martin[1], Tomoya Fukui[1], Ryosuke Takehara[1], Shintaro Fujii[2], Takanori Fukushima[1] (1. CLS, Tokyo Tech., 2. School of Science, Tokyo Tech.)

日本語

13:20 ~ 13:40

[E1131-4pm-02]

アルキル鎖長に依存した高移動度N字型有機半導体分子の結晶多形・相転移挙動の実測とシミュレーション

○三谷 真人[1]、Craig Yu[2]、沢辺 千鶴[2]、三津井 親彦[2]、關 拓和[3]、篠崎 雄大[3]、渡辺 豪[3]、橋爪 大輔[4]、熊谷 翔平[1]、竹谷 純一[2]、岡本 敏宏[1] (1. 東京工業大学、2. 東京大学、3. 北里大学、4. 理化学研究所)

13:40 ~ 13:50

休憩

英語

13:50 ~ 14:10

[E1131-4pm-03]

ハロゲンおよびエチニルを置換したカルド型芳香族ニトロキシド誘導体の固体磁気特性

○瀧井 優臣[1]、三浦 洋平[1]、吉岡 直樹[1] (1. 慶應義塾大学)

日本語

14:10 ~ 14:30

[E1131-4pm-04]

凝集誘起増強発光性を示すフマロニトリル系分子から成る低次元単結晶レーザー

○松尾 匠[1]、林 正太郎[1] (1. 高知工科大学)

日本語

14:30 ~ 14:50

[E1131-4pm-05]

ねじり天秤分子モデルを用いた芳香環–フラーレン間の非共有結合性相互作用の定量評価

○山田 道夫[1]、佐原 弘起[1]、栗原 幸代[1]、小泉 政彰[1]、辻 香澄[1]、成田 陽奈[1]、前田 優[1]、鈴木 光明[2] (1. 東京学芸大学、2. 城西大学)

Triptycene Frameworks for Orientational Control over Electroactive Subunits in STM Break-Junction

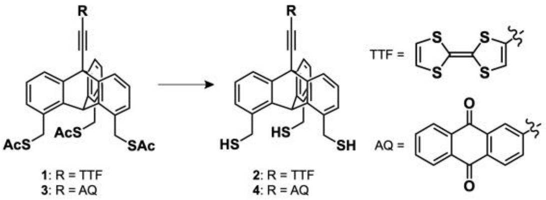
(*[1]Laboratory for Chemistry and Life Science, Tokyo Tech.*, *[2]School of Science, Tokyo Tech.)*
○Colin John Martin[1], Tomoya Fukui[1], Ryosuke Takehara[1], Shintaro Fujii[2], Takanori Fukushima[1]

Keywords: STM break junction, Self-assembled monolayers, Supramolecular scaffold, Noncovalent interactions, Triptycene

In the field of molecular electronics, quantifying the properties of discrete electroactive moieties remains an important goal, with numerous developments reported in recent years. Here, our approach which allows for accurate positioning of electroactive subunits with an upright configuration on substrate surfaces will be presented.[1] We have incorporated electron-donating tetrathiafulvalene or electron-accepting anthraquinone into existing triptycene-based supramolecular scaffolds[2] containing three thiol or thioacetate surface binding points. Self-assembled monolayers of these molecules have been prepared on Au(111) and characterized by XPS and STM, with the electronic properties particular to their attached subunits retained in the monolayers.

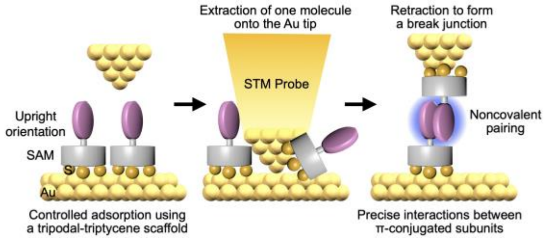
Using previously reported STM break junction techniques[3] we have conducted studies on these SAM materials as they undergo noncovalent donor-donor, and acceptor-acceptor interactions to explore their conductive behavior at the single molecular level. The triptycene scaffolds in these systems facilitate non-covalent face-to-face interactions between homodimers adsorbed on the two electrodes. Two electrical conduction regimes are observed: one arising from single molecules sandwiched between the electrodes, and the second from intermolecularly interacting homodimers bridging between electrodes.

This presentation demonstrates the validity of the approach using tripodal triptycene scaffolds to precisely direct electroactive subunits to undergo intermolecular pairing. We believe that this work will open a new avenue for evaluating heterodimers and lead to new pathways to evaluate both hetero- and homodimer interactions at the single molecular level.



1: R = TTF
3: R = AQ

2: R = TTF
4: R = AQ



1) C. J. Martin, T. Fukui, R. Takehara, S. Fujii, T. Fukushima, *Precis. Chem.* **2023**, *1*, 6, 388–394.
2) F. Ishiwari, Y. Shoji, T. Fukushima, *Chem. Sci.* **2018**, *9*, 8, 2028–2041.
3) S. Fujii, T. Fukushima, M. Kiguchi *et al. Jpn. J. Appl. Phys.* **2019**, *58*, 035003.

アルキル鎖長に依存した高移動度N字型有機半導体分子の結晶多形・相転移挙動の実測とシミュレーション

（東京工業大学[1]・東京大学[2]・北里大学[3]・理化学研究所[4]）○三谷 真人[1]・Craig P. Yu[2]・沢辺 千鶴[2]・三津井 親彦[2]・關 拓和[3]・篠崎 雄大[3]・渡辺 豪[3]・橋爪 大輔[4]・熊谷 翔平[1]・竹谷 純一[2]・岡本 敏宏[1]

Alkyl chain length-dependent polymorphism and phase transition behavior of N-shaped organic semiconducting molecules

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Graduate School of Frontier Science, The University of Tokyo,* [3]*School of Frontier Engineering, Kitasato University,* [4]*RIKEN Center for Emergent Matter Science (CEMS)*) ○Masato Mitani,[1] Craig P. Yu,[2] Chizuru Sawabe,[2] Chikahiko Mitsui,[2] Takuya Seki,[3] Yudai Shinozaki,[3] Go Watanabe,[3] Shohei Kumagai,[1] Jun Takeya,[2] Toshihiro Okamoto[1]

Control and prediction over aggregated structures of π-conjugated molecules are crucially important to effectively develop the high performance organic functional materials. During the study on the aggregated structures of alkyl-substituted N-shaped organic semiconductor (**C$_n$–DNBDT–NW**, Figure 1a) with high charge transporting capability, it was found that they exhibit polymorphism and unique phase transition behavior (Figure 1b). In the presentation, experimental details of crystal structure analyses and thermal analyses will be discussed, which will also compared with the results of MD simulations.

Keywords：Organic semiconducting molecules; Polymorphism; MD simulations

π共役系からなる材料の機能は集合体構造に大きく依存しており、高キャリア移動度などの高機能化に向けては集合体構造の制御・予測が極めて重要となる。我々の研究グループで開発されたN字型π共役系材料（**DNBDT–NW**, Figure 1a）は、導入するアルキル鎖長に応じて二つのヘリンボーン構造（HB1・HB3）を含む結晶多形を発現するほか、劇的な集合体構造変化を伴う相転移挙動を示し（Figure 1b）、薄膜形成過程で誘起される集合体構造（HB3）では世界最高レベルの高キャリア移動度を示すことが実験的に確かめられている1,2)。本発表では、本誘導体群の集合体構造の実測とMDシミュレーションによる予測結果について議論する。

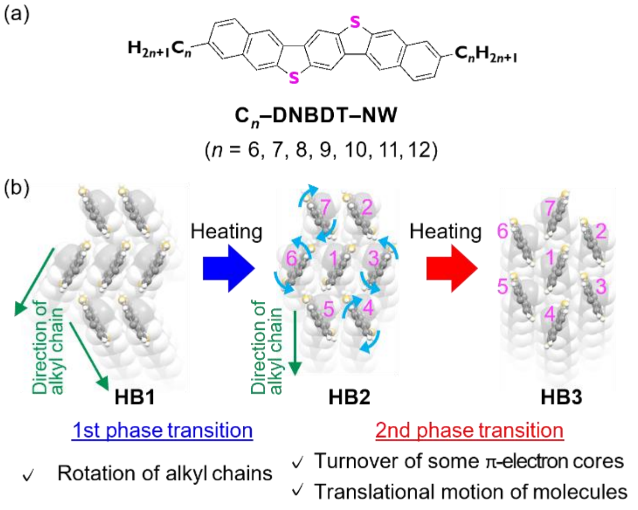


Figure 1. (a) Molecular structure of **C$_n$–DNBDT–NW**. (b) Phase transition behavior of **C$_n$–DNBDT–NW**.

1) T. Okamoto *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 9083. 2) C. Mitsui, T. Okamoto, J. Takeya *et al.*, *Adv. Mater.* **2014**, *26*, 4546.

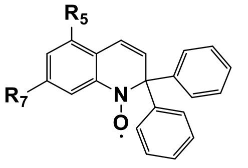
Solid-State Magnetic Properties of Halogen or Ethynyl Substituted Aromatic Nitroxide with Cardo Structure

(*Faculty of Science and Technology, Keio University*) ○Masaomi Takii, Youhei Miura, Naoki Yoshioka

Keywords: *Radical, Molecule-based Magnetism, Nitroxide, π-Conjugated System, Organic Crystal*

Aliphatic nitroxides such as TEMPO show high chemical stability, although it is difficult to be used as a spin center for molecule-based magnetic materials because of localization of SOMO and spin density around NO moiety. On the other hand, aromatic nitroxide derivatives where π-conjugated systems locate adjacent to NO moiety, often exhibit non-magnetic state through a disproportionation reaction or antiferromagnetic interaction due to close contact between NO moieties. In the case of 2,2-diphenyl-1,2-dihydroquinoline *N*-oxyl (DPQN, **1**), the steric effect of cardo structure consist of two phenyl rings at the 2-position has been found to suppress both the disproportionation reaction and the antiferromagnetic NO contact.[1)] At the 6-position of the quinoline ring where SOMO distribute, the introduced substituent may undergo further reactions. However, at the 5-position the node of the SOMO, the introduced substituent tends not to undergo further reactions.[2)]

In this study, DPQN derivatives substituted by halogen or ethynyl at 5- and 7-position **2**-**7** (**Scheme 1**) were synthesized to investigate the chemical modification effect on solid-state magnetic properties. According to DFT calculations, no SOMOs were observed on 5-substituents, however, 7- substituents had small SOMO distributions. A single crystal of **2** was obtained by recrystallization from ethanol/dichloromethane. Single crystal X-ray analysis reveals that **2** forms a halogen bonded chain with $d_{O\cdots I}$ = 3.154(5) Å (**Fig. 1**). SQUID measurement of **2** suggests weak antiferromagnetic interaction (**Fig. 2**).



1 : R_5 = H, R_7 = H
2 : R_5 = I, R_7 = H
3 : R_5 = −C≡C−TMS, R_7 = H
4 : R_5 = −C≡C−H, R_7 = H
5 : R_5 = H, R_7 = I
6 : R_5 = H, R_7 = −C≡C−TMS
7 : R_5 = H, R_7 = −C≡C−H

Scheme 1

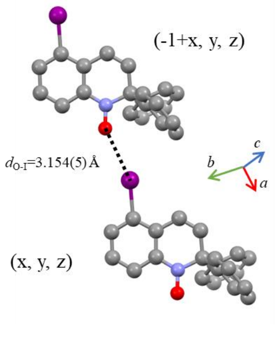


Fig. 1 Through I-O close contact of **2**.

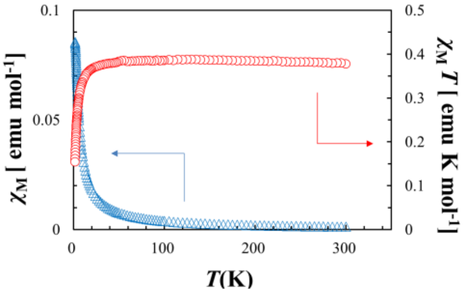


Fig. 2 Temperature dependence of $\chi_m T$ (○) and χ_m (△) for **2.**

---

1) M. Yao, N. Yoshioka, *et al.*, *Cryst. Growth Des.*, **2005**, *5*, 413-417.
2) M. Takii, Y. Miura, N. Yoshioka, The 103rd Annual Spring Meeting of the Chemical Society of Japan, K605-3pm-12 (March 2023, Tokyo Univ. Sci, Noda).

凝集誘起増強発光性を示すフマロニトリル系分子から成る低次元単結晶レーザー

（高知工科大 1)）○松尾 匠 1・林 正太郎 1

Low Dimensional Single Crystal Lasers Composed of Fumaronitrile-based π-Conjugated Molecules Exhibiting Aggregation Induced Enhanced Emission

([1]*School of Engineering Science, Kochi University of Technology*) ○Takumi Matsuo,[1] Shotaro Hayashi[1]

Fumaronitrile (FN) based π-conjugated molecules are known as aggregation induced enhanced emission (AIEE) luminogen. Although the photoluminescence quantum efficiency (Φ_{PL}) of FN solids is not so high, single crystals of bis(biphenyl)fumaronitrile (BPFN) showed higher Φ_{PL} of 0.46. Modifying the growth technique of self-assembly, BPFN was intentionally grown in various low dimensional micro-structures; crystalline 2D, 1D, and amorphous 0D. The revealed crystal structure suggested ideal conformation and molecular packing to achieve lasing; highly luminescent *E*-isomer conformation, uniaxial molecular orientations. As a result, we first achieved lasing in low dimensional structures of FN-based AIEE luminogen.

Keywords : Fumaronitrile; Aggregation Induced Enhanced Emission; Organic Solid State Lasers; Low Dimensional Structures

フマロニトリル(FN)系π共役分子は凝集誘起増強発光性(AIEE)を示す．しかし分子内電荷移動(ICT)によって固体状態の発光量子収率(Φ_{PL})はさほど高くなく，結晶材料としての光物性はほとんど知られていない.1,2) 我々は FN 系 π 共役分子のうち，bis(biphenyl)fumaronitrile(BPFN)が FN 系分子の中で高い Φ_{PL} 値を示すことを見出した(Φ_{PL}=0.46). BPFN は溶液中での再結晶法では二次元単結晶が得られ(図 1a)，一方で BPFN 溶液を KBr 単結晶にドロップキャストすると基板上へのエピタキシャル成長に基づき一次元結晶が形成された(図 1b). ガラス基板上への溶液のドロップキャストを行うとサイズが均一なアモルファスマイクロドットが形成された(図 1c). これら低次元構造体のうち二次元薄板状結晶と一次元ニードル構造は光励起レーザー発振が観測された(図 1d). 単結晶 X 線構造解析から BPFN は結晶内で FN 部位が発光性の高い *E* 体の配座をとり，分子が結晶内で一軸配向していた. 以上から BPFN 結晶は高い誘導放射効率が期待でき，故にレーザー媒質として優れることを示した.

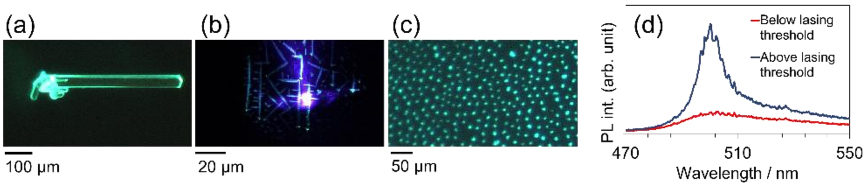


図 1 (a)-(c) 二次元薄板状結晶，一次元ニードル結晶，マイクロドットの蛍光像. (d)二次元薄板状結晶からのレーザー発振閾値前後での蛍光スペクトル.

1) In-situ photoisomerization for aggregation-induced emission of dibiphenyl fumaronitrile. H. Jeonga, K. M. Kima, S. Cho, J. K. Lee, *J. Photochem. Photobiol.* **2015**, 311, 199. 2) Fumaronitrile-Based Fluorogen: Red to Near-Infrared Fluorescence, Aggregation-Induced Emission, Solvatochromism, and Twisted Intramolecular Charge Transfer. X. Y. Shen, W. Z. Yuan, Y. Liu, Q. Zhao, P. Lu, Y. Ma, I. D. Williams, A. Qin, J. Z. Sun, B. Z. Tang, *J. Phys. Chem. C* **2012**, 116, 10541.

ねじり天秤分子モデルを用いた芳香環–フラーレン間の非共有結合性相互作用の定量評価

（東学芸大教[1]・城西大理[2]）〇山田 道夫[1]・佐原 弘起[1]・栗原 幸代[1]・小泉 政彰[1]・辻 香澄[1]・成田 陽奈[1]・前田 優[1]・鈴木 光明[2]

Quantification of Noncovalent Arene–Fullerene Interactions Using a Molecular Torsion Balance

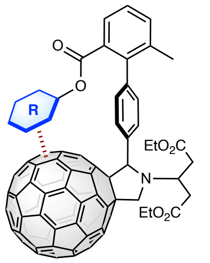
([1]*Department of Chemistry, Tokyo Gakugei University*, [2]*Department of Chemistsry, Josai University*) 〇Michio Yamada,[1] Koki Sahara,[1] Yukiyo Kurihara,[1] Masaaki Koizumi,[1] Kasumi Tsuji,[1] Haruna Narita,[1] Yutaka Maeda,[1] Mitsuaki Suzuki[2]

The unique structure of fullerenes is of great interest in numerous fields, including materials chemistry and medicinal chemistry, owing to their peculiar hydrophobic structure and excellent electron-accepting properties. The intermolecular interactions on fullerene surfaces are intricately linked with the macroscopic properties of fullerene-based materials; hence, a quantitative understanding of these interactions is required. In this study, we designed and synthesized fullerene-based torsion balances and quantitatively evaluated the non-covalent interactions between the fullerene surface and substituted arenes by analyzing their conformational isomerism based on restricted rotation around the biphenyl C–C bond. We disclosed that the experimentally observed arene–fullerene interaction can be explained mainly by the contribution of the dispersion and electrostatic terms. Although the dispersion term is effective throughout the interaction, especially for electron-rich arenes, the electrostatic term also has a significant impact.[1–4]

Keywords : π–π interactions; anion–π interactions; dispersion interaction; electrostatic interaction; Hammett analysis

フラーレンは，優れた電子受容能や疎水性構造を有することから，材料科学や医薬品化学などの分野で興味が持たれている。そのマクロな物性には分子間相互作用が大きく関与することから，フラーレンの応用を目指す上で，フラーレン表面に働く相互作用に対する定量的な理解が求められる。しかし，このような分子間相互作用は弱いため，その計測は容易ではない。

本研究では、フラーレンを用いたねじり天秤型のモデル分子 **1** を設計・合成し，そのビフェニル構造部の C–C 結合における束縛回転に起因する配座異性を解析することによって，種々の置換アレーン **(R)** とフラーレン表面との間に働く分子間相互作用の定量評価を行った。その結果，アレーン–フラーレン間に働く相互作用は主として分散相互作用の項と静電相互作用の項によることを明らかにした。また，全体を通じて分散相互作用の項が支配的であるものの，特に電子豊富なアレーンの場合には静電相互作用の項も充分に大きいことを見出した[1–4)]。



Folded **1**

---

1) M. Yamada, et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 16133–16140. 2) M. Yamada et al., *Angew. Chem. Int. Ed.* **2022**, *61*, e202212279. 3) M. Yamada, et al., *Chem. Eur. J.* **2023**, *29*, e202300877. 4) M. Yamada, *ChemPlusChem* **2023**, *88,* e202300062.

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21日(木) 13:00 ~ 14:00 E1132(11号館 [3階] 1132)

[E1132-4pm] 13. 有機化学―反応機構・光化学・電気化学

座長：臼井 聡、高橋 明

日本語

13:00 ~ 13:20

[E1132-4pm-01]

フッ素置換アクリジニウムをフォトレドックス触媒としたベンゼンの空気酸化反応

〇赤尾 祐介[1,2]、大野 祥平[2]、板橋 勇輝[3]、淺原 時泰[1]、小泉 靖明[1]、田井 国憲[1]、近藤 一見[1]、長瀬 剛[1]、井上 豪[2]、大久保 敬[3,4] (1. 大塚製薬（株）、2. 阪大院薬、3. 阪大先導的学際研、4. 阪大高等共創研)

英語

13:20 ~ 13:40

[E1132-4pm-02]

Mechanisms and the Role of Lewis Acids in Transition Metal Catalysts for C-O, C-F, and H-H Activation

〇Panida Surawatanawong[1] (1. Mahidol University, Faculty of Science)

日本語

13:40 ~ 14:00

[E1132-4pm-03]

ラジカルジホスフィン化による歪んだ小分子からのリン配位子合成

〇美多 剛[1,2]、Chandu G. Krishnan[1,2]、髙野 秀明[1,2]、勝山 瞳[1,2]、林 裕樹[1,2]、神名 航[3]、前田 理[1,2,3] (1. 北大WPI-ICReDD、2. JST-ERATO、3. 北大院理)

フッ素置換アクリジニウムをフォトレドックス触媒としたベンゼンの空気酸化反応

(大塚製薬（株）[1]・阪大院薬[2]・阪大先導的学際研[3]・阪大高等共創研[4]) ○赤尾 祐介[1,2]・大野 祥平[2]・板橋 勇輝[3]・淺原 時泰[2]・小泉 靖明[1]・田井 国憲[1]・近藤 一見[1]・長瀬 剛[1]・井上 豪[2]・大久保 敬[3,4]

Aerobic Oxygenation of Benzene Using Fluorine-Substituted Acridinium as a Photoredox Catalyst

([1]*Otsuka Pharmaceutical Co., Ltd.*, [2]*Osaka Univ.*,[3]*Osaka Univ. OTRI*, [4]*Osaka Univ. IACS*) ○ Yusuke Akao,[1,2] Shohei Ohno,[2] Yuki Itabashi,[3] Haruyasu Asahara,[2] Yasuaki Koizumi,[1] Kuninori Tai,[1] Kazumi Kondo,[1] Tsuyoshi Nagase,[1] Tsuyoshi Inoue,[2] Kei Ohkubo,[3,4]

A series of fluorine-substituted acridinium were designed and synthesized to develop a photoredox catalyst with strong oxidation power. There is a linear relationship between the electron affinity (EA) values calculated by quantum chemical calculations and the one-electron reduction potentials at the singlet excited state determined by the electro- and photochemical measurements (Figure 1). This results indicate that computational chemistry can sufficiently predict the experimental oxidation power of acridinium derivatives without synthesis. The hydroxylation of benzene was successfully achieved under visible-light irradiation by utilizing the strong electron-transfer oxidation property of acridinium ion (AC-18), and the highest yield of phenol was observed to be 80%. The reaction mechanism was clarified by the time-resolved transient absorption spectroscopic measurements. The photochemical reaction is initiated by electron transfer from benzene to the singlet excited state of acridinium.

Keywords : Photoredox catalyst; Oxygenation; Acridinium; Benzene; Phenol

フッ素基を導入した種々のアクリジニウムイオンを設計・合成し，フォトレドックス触媒として広く用いられている 9-メシチル-10-メチルアクリジニウム（AC-01）に比べ強力な酸化力を示すアクリジニウム触媒の開発を目指した．量子化学計算から大きな電子親和力 (EA) 値を有するアクリジニウム触媒を予測し，それらの中から合成できた化合物の一重項励起状態還元電位を実験的に求めプロットしたところ，図 1 に示すような比例関係が認められた．この結果よりアクリジニウム化合物の酸化力の実験値を計算化学で十分に予測できることがわかった．その中でも強力な電子移動酸化特性を有する AC-18 を光触媒として用いた場合、ベンゼンの水酸化反応が可視光照射下で進行し，フェノールの最高収率は 80％に達した． レーザー過渡吸収分光解析などを用いて反応機構の詳細について明らかにした．

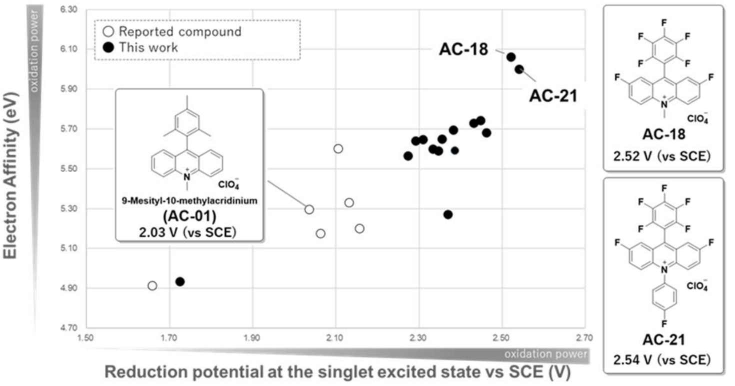


Figure 1. Relationship of reduction potential at singlet excited state *vs* electron affinity

Mechanisms and the Role of Lewis Acids in Transition Metal Catalysts for C-O, C-F, and H-H Activation

[1]Department of Chemistry and Center of Excellence for Innovation in Chemistry,
Faculty of Science, Mahidol University, Bangkok 10400, Thailand
Panida Surawatanawaong[1], Thanapat Worakul[1], Kajjana Boonpalit[1], Chayapat Uthayopas[1]

Keywords: Transition Metal; Lewis Acid; C-O Activation; C-F Activation; Hydrogenation

Density functional calculations were performed to give insights into the mechanisms and the role of Lewis acids in transition metal catalysts for C-O, C-F, and H-H activation. In the first process, nickel complex with N-heterocyclic carbene (Ni-SIPr) has been shown to selectively catalyze C−O bond hydrogenolysis of aryl methyl ether to obtain arene and alcohol as the only products. The Lewis acid $AlMe_3$ was found to facilitate aryl C–O bond activation via the five-centered transition state by forming a Lewis acid/base adduct with 2-methoxynaphthalene (NaphOMe) with the interaction from the Me group of $AlMe_3$ to Ni. Then, we investigated the C-F activation in the hydrodefluorination of CF_3-substituted aniline derivatives, $CF_3(C_6H_4)NMe_2$, by the Ru–S complex, $[(PEt_3)Ru(DmpS)]^+$ (DmpS = 2,6-dimesitylphenyl thiolate) with $HSiMe_2Ph$ and with HAl^iBu_2. The Si-H activation on Ru-S generates Ru–H with thiosilane ligand, in which the Si-S bond must be cleaved to generate the active silylium moiety for the fluoride abstraction. In contrast, the Al-H activation of HAl^iBu_2 leads to the formation of Ru–H with the alumenium ($^+Al^iBu_2$), stabilized by the donation from both σ(Ru–H) and sulfur lone pair. For the H_2 activation, the nickel-borane complex, $Ni[(Mes)B(o\text{-}Ph_2PC_6H_4)_2]$, has been reported as an efficient catalyst for styrene hydrogenation. Following the H_2 activation, the resulting *trans*-dihydride nickel-alane complex has higher negative charges on both terminal and bridging hydrogen atoms than the corresponding nickel-borane complex. With the higher hydricity of hydrogen, nickel−alane is expected to be more reactive toward hydrogenation of styrene than nickel-borane. The role of Lewis acids in forming different types of interaction with transition metals affects their catalytic activities toward C-O, C-F, and H-H activation.

1) Worakul, T.; Surawatanawong, P. *Organometallics* **2023**, *42*, 896-907.
2) Boonpalit, K.; Uthayopas, C.; Surawatanawong, P. *Organometallics* **2022**, *41*, 259-269.
3) Uthayopas, C.; Surawatanawong, P. *Dalton Trans.* **2019,** *48,* 7817-7827.
4) Wititsuwannakul, T.; Tantirungrotechai, Y.; Surawatanawong, P. *ACS Catal.* **2016,** *6*, 1477-1486.
5) Sawatlon, B.; Wititsuwannakul, T.; Tantirungrotechai, Y.; Surawatanawong, P. *Dalton Trans* **2014,** *43*, 18123-18133.

ラジカルジホスフィン化による歪んだ小分子からのリン配位子合成

（北大 WPI-ICReDD[1]・JST-ERATO[2]・北大院理[3]）○美多　剛[1,2]・Chandu G. Krishnan[1,2]・高野　秀明[1,2]・勝山　瞳[1,2]・林　裕樹[1,2]・神名　航[3]・前田　理[1,2,3]

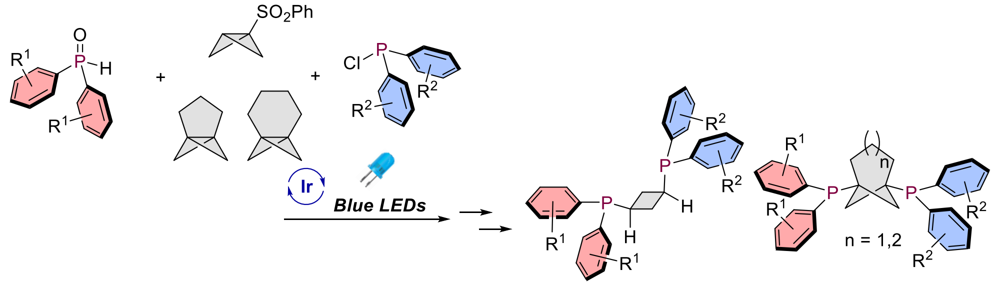
Synthesis of Phosphine Ligands through Radical Diphosphination of Strained Small Molecules

([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*) ○Tsuyoshi Mita,[1,2] Chandu G. Krishnan,[1,2] Hideaki Takano,[1,2] Hitomi Katsuyama,[1,2] Hiroki Hayashi,[1,2] Wataru Kanna,[3] Satoshi Maeda[1,2,3]

The chemical synthesis of diphosphinated cyclobutene, bicyclo[3.1.1]heptane, and bicyclo[4.1.1]octane-based diphosphine ligands was successfully accomplished starting from the corresponding strained molecules such as bicyclo[1.1.0]butane, [3.1.1]propellane, and [4.1.1]propellane by employing a calculation-guided ring-opening diphosphination. The feasibility of the initial radical addition can be estimated through DFT calculations using the AFIR method. This study greatly focuses the importance of integrating experimental and computational methods in the design and synthesis of new diphosphination reactions involving strain-containing small molecules.

Keywords : Radical; Cyclobutane; Propellane; Diphosphination; DFT Calculations

我々の研究グループでは以前、エチレンや[1.1.1]プロペランに対するジホスフィン化の検討を行い、非対称、および対称のリン配位子の合成に成功している[1,2]。今回、これら以外の歪んだ様々な化合物に対して $Ph_2P(O)$・がラジカル付加を進行させる活性化障壁を、AFIR 法を駆使し DFT 計算で見積もったところ、ビシクロ[1.1.0]ブタン、[3.1.1]プロペラン、および[4.1.1]プロペランの単結合もラジカル的に開環できることを見出した。その結果に基づき、新たなジホスフィン化反応を実現すべく、原料として $Ar_2P(O)H$ と $ClPAr_2$ を用いたラジカル三成分反応を実施したところ、対応するジホスフィン化合物を高収率で得ることに成功した。本反応では対称のみならず、非対称のリン化合物も効率良く合成することができた。



1) Takano, H.; Katsuyama, H.; Hayashi, H.; Kanna, W.; Harabuchi, Y.; Maeda, S.; Mita, T. *Nat. Commun.* **2022**, *13*, 7034.

2) Takano, H.; Katsuyama, H.; Hayashi, H.; Harukawa, M.; Tsurui, M.; Shoji, S.; Hasegawa, Y.; Maeda, S.; Mita, T. *Angew. Chem., Int. Ed.* **2023**, 62, e202303435.

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21日(木) 13:00 ~ 14:20 E1141(11号館 [4階] 1141)

[E1141-4pm] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：隅田 有人、土肥 寿文

日本語

13:00 ~ 13:20

[E1141-4pm-01]

酵素反応を利用した光学活性なデルタラクトン類の合成と香気評価

〇川崎 正志[1]、岡田 卓哉[2]、田中 康雄[3]、豊岡 尚樹[2] (1. 富山県立大学、2. 富山大学、3. 大洋香料株式会社)

英語

13:20 ~ 13:40

[E1141-4pm-02]

水素結合供与触媒による、α位ヘテロ原子置換アミノニトリルの不斉合成

〇小山田 悠介[1]、藤井 未来[1]、中村 修一[1] (1. 名古屋工業大学)

英語

13:40 ~ 14:00

[E1141-4pm-03]

重金属応答性新規C4N4蛍光プローブの創製

〇公平 実希[1,2]、Harald Gröger[2]、熊谷 直哉[1,3] (1. 慶大院薬、2. Bielefeld University、3. 微化研)

英語

14:00 ~ 14:20

[E1141-4pm-04]

自己集合環状3量体分子$[HyAl\text{-}Py]_3$の合成と機能開発

〇鶴岡 航太朗[1]、熊谷 直哉[1,2] (1. 慶應義塾大学大学院、2. 微生物科学研究所)

酵素反応を利用した光学活性なデルタラクトン類の合成と香気評価

（富山県大工[1]・富山大院理工[2]・大洋香料[3]）○川崎 正志[1]・岡田 卓哉[2]・田中 康雄[3]・豊岡 尚樹[2]

Synthesis of optically active delta-lactones using enzymatic reaction and evaluation of their odors

([1]*Faculty of Engineering*, *Toyama Prefectural University*, [2]*Graduate School of Science and Engineering*, *University of Toyama*, [3]*Taiyo Corporation*)○Masashi Kawasaki,[1] Takuya Okada,[2] Yasuo Tanaka,[3] Naoki Toyooka[2]

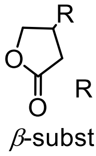
Numerous lactones have been discovered in nature and synthesized. Among them, *γ*-lactones and *δ*-lactones are considered essential compounds in the preparation of flavors and fragrances.[1] Inspired by this, we synthesized the enantiomers of eight *β*-substituted *γ*-lactones and reported on the relationship between the structures and the odors, as well as the olfactory differences between the enantiomers within the same lactone.[2] In this study, we synthesized the enantiomers of *δ*-lactones **1**, **2**[3] and evaluated the odors.

In the synthesis of the enantiomers of **1**, racemic primary alcohol (±)-**4** was optically resolved, and the resulting optically active alcohols, (*R*)- and (*S*)-**4**, were utilized as synthetic intermediates. Lipase, a kind of hydrolase, was employed for the enantioselective acetylation of (±)-**4** during the optical resolution. Similarly, utilizing racemic secondary alcohol (±)-**9**, the enantiomers of **2** were synthesized. The details of the results of odors evaluations for the enantiomers of **1** and **2** will be presented in the session.

Keywords: Lactone; Lipase; Odor

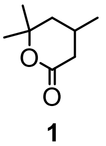
多くのラクトン類が天然から見出され、合成されている。その中の *γ*-ラクトン類、*δ*-ラクトン類はフレーバー、フレグランスの調香において必要不可欠な香料とされている 1)。そのようなことに触発され、我々は以前、8 種の *β*-置換 *γ*-ラクトンそれぞれの両鏡像異性体を合成し、構造と香気の関係および同一ラクトンにおける鏡像異性体間での香気の差異について調査、報告をした 2)。今回はラセミ体での香気が報告されている *δ*-ラクトン **1**, **2**3)それぞれの両鏡像異性体を合成し、香気評価を行った。

δ-ラクトン **1** の両鏡像異性体の合成では、ラセミ体の 1 級アルコール(±)-**4** を光学分割し、得られた光学活性アルコール(*R*)-**4**, (*S*)-**4** を合成中間体として利用した。光学分割の際には加水分解酵素であるリパーゼを不斉触媒としたエナンチオ選択的なアセチル化反応を利用した。また、ラセミ体の 2 級アルコール(±)-**9** を利用し同様の手法で、*δ*-ラクトン **2** の両鏡像異性体を合成した。香気評価の結果は講演にて報告する。

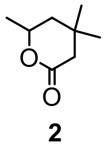


R = CH_3 - n-C_8H_{17}

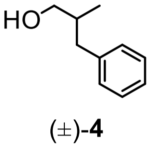
β-substituted *γ*-lactones



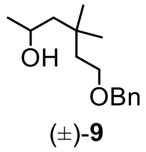
1



2



(±)-**4**



(±)-**9**

1) 伊藤信彦、香りの技術動向と研究開発、中島基貴編、pp. 117-143、フレグランスジャーナル社、(2004). 2) M. Kawasaki *et al.*, *Tetrahedron*, **2020**, *76*, 130984. 3) U. -A. Schaper *et al.*, European Patent Organization, EP 0 004 978 A1 (1979).

Asymmetric Synthesis of α-Heteroatom-substituted Aminonitriles by Hydrogen-Bonding-Donor Catalysis

(*Graduate School of Engineering, Nagoya Institute of Technology*) ○Yusuke Oyamada, Miku Fujii, Shuichi Nakamura

Keywords: nitriles; thiol; organocatalyst; enantioselective; ketals

Chiral α-aminonitriles are essential precursors to α-amino acids. In the field of aminonitrile synthesis, Strecker reaction has emerged as the most straightforward and powerful method.[1] However, several limitations remain for this type of reaction. One of the primary limitations is that this reaction is unsuitable for synthesizing α-heteroatom-substituted chiral α-amino nitriles due to the lack of electrophilicity of the electrophilic reactant (ester, amide, thioamide, etc.). Furthermore, this reaction sometimes requires the use of toxic cyanide precursors such as KCN, NaCN, $Zn(CN)_2$, etc. It should be noted that α-sulfur-substituted chiral α-amino nitriles and their derivatives are important structures because they are present in penicillin and other biologically active molecules.[2] These facts led us to become interested in the asymmetric synthesis of α-sulfur-substituted α-aminonitriles. We hypothesized that α-sulfur-substituted chiral aminonitriles could be obtained by using α-iminonitrile as a novel precursor to synthesize amino acid derivatives. Herein, we describe the first asymmetric synthesis of α-sulfur-substituted α-amino acid derivatives bearing a tetrasubstituted stereocenter (**Figure 1**).

When we used iminonitrile as an electrophile, benzyl thiol as a model nuclephile and 10 mol% of thiourea catalyst in CH_2Cl_2 for 30 minutes, we obtained the α-thio-substituted aminonitrile in 95% yield, 99% ee and only 1 mol% of the catalyst loading is still quite good for this reaction. We are delighted to find that this method enable for the construction of not only various *N*,*S*-ketal aminonitriles maintaining extremely high stereoselectivities in most cases but also *N*,*Se*-ketals. Some control experiments described the presence of nitrile plays an important role for both controlling enantioselectivity and enhancing electrophilic reactivity. This work can provide a powerful strategy for overcoming the limitation of synthesizable α-aminonitriles.

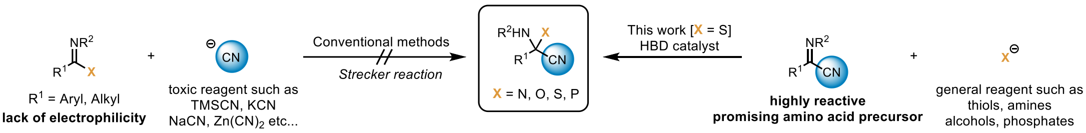


Figure 1

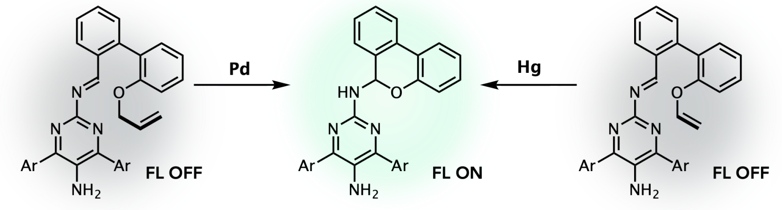
1) Wang, J.; Liu, X.; Feng, X. *Chem. Rev.* **2011**, *111*, 6947–6983. 2) Kohn, H.; Sawhney, K. N.; LeGall, P.; Robertson, D. W.; Leander, J. D. *J. Med. Chem.* **1991**, *34*, 2444–2452.

Engineering the C4N4 Fluorophore to Develop Turn-On Fluorescent Probes for Heavy Metal Detection

([1]*Graduate School of Pharmaceutical Sciences, Keio University,* [2]*Fuculty of Chemistry, Bielefeld University,* [3]*Institute of Microbial Chemistry*) ○ Miki Kohei,[1,2] Harald Gröger,[2] Naoya Kumagai[1,3]

Keywords: C4N4; Fluorescence; Probe; Palladium; Heavy Metal

Since heavy metals significantly expand the scope of chemical transformations, their use as catalysts and reagents is indispensable in the chemical industry. On the other hand, heavy metal residues are potentially harmful and subject to strict control, especially in the production of active pharmaceutical ingredients. Therefore, the development of a simple, fast, and efficient fluorometric analytical method for reliable detection of minute amounts of heavy metals is in high demand. C4N4, having free amino groups at the 2- and 5-positions of the pyrimidine core, is a new class of fluorescent materials that exhibits high quantum yield and large Stokes shift. We revealed that C4N4 can be rendered non-fluorescent by forming an imine with the 2-amino group, which can be exploited to design turn-on fluorescent probes in response to specific conditions of interest. Forming an "R^1-NH-CH(R^2)-OR^3"-subunit proved effective to regain intense fluorescence, thereby we synthesized the new derivative suitable to detect minute amounts of palladium. As a result, we confirmed that this new probe was capable to detect palladium by 30 minutes of stirring in the presence of $NaBH_4$ as a reductant in MeOH at room temperature. To note, this derivative displayed a decent selectivity form palladium among various metal cations. Furthermore, we found that the present turn-on mechanism was valid for other stimuli e.g. enzymes or other metal cations by employing appropriate substituents on the phenolic OH group, expanding the scope of probe applications. For example, mercury can be detected by switching the substituent from an allyl group to a vinyl group. The opportunity of probe application can be significantly leveraged by the orthogonal nature of absorption/emission properties, which can be independently manipulated by aromatic attachment at 4 and 6 positions. They also would be suitable in aqueous media making use of natural cofactors, opening up a perspective for being used in biological systems.



Ar = 3,5-$(CF_3)_2C_6H_3$ λ_{em} 500 nm, Φ_F 0.22
Ar = 3,5-$Ph_2C_6H_3$ λ_{em} 480 nm, Φ_F 0.25

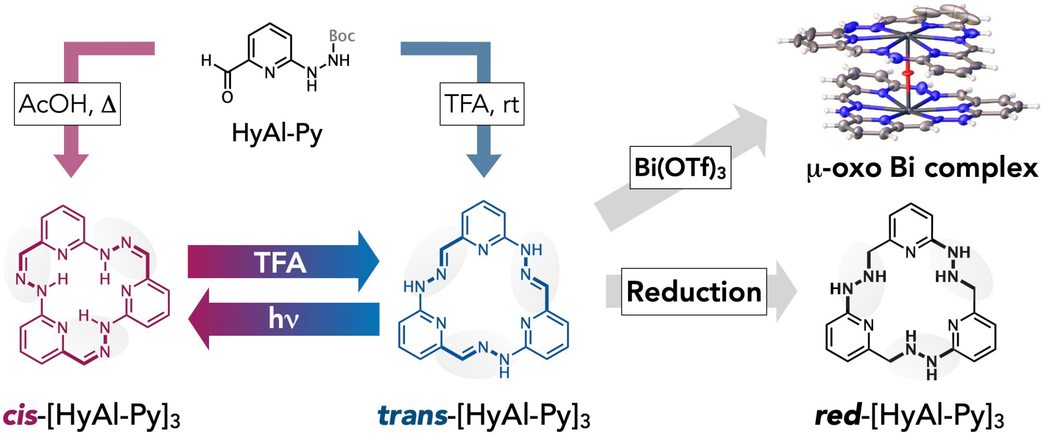
Design and Synthesis of Self-Assembling Cyclic Trimer $[\text{HyAl-Py}]_3$ and its Strategic Applications

([1]*Graduate School of Pharmaceutical Sciences*, *Keio University*, [2]*Institute of Microbial Chemistry*) ○ Kotaro Tsuruoka[1], Masato Nozaki[1], Naoya Kumagai[1,2]

Keywords: Pyridine; Hydrazone; Macrocyclic molecule; Metal complex; Photoisomerization

Hydrazone is used in various fields of chemistry due to its ease of synthesis, high stability, and unique structural properties. The facile hydrolytic cleavage of hydrazone also allows for its use as a key functional group in dynamic combinatorial chemistry (DCC). We have designed and synthesized a bifunctional pyridine monomer, HyAl-Py, bearing a hydrazine and a formyl group at the 2- and 6-positions for use in DCC. Exposure of HyAl-Py to TFA acidic conditions gave rise to cyclic trimer *trans*-$[\text{HyAl-Py}]_3$ in quantitative yield by triple head-to-tail *trans*-hydrazone formation. *trans*-$[\text{HyAl-Py}]_3$ has six inwardly oriented sp^2 nitrogen atoms capable to capture metal cations and formed complexes with rare earth and bismuth cations. In contrast, exposure of HyAl-Py to AcOH acidic conditions selectively gave *cis*-$[\text{HyAl-Py}]_3$ in which *cis*-configured hydrazono protons formed intramolecular hydrogen bonds to acquire a contracted planar structure. Upon irradiation with blue LED, photoexcited *trans*-$[\text{HyAl-Py}]_3$ isomerized to *cis*-$[\text{HyAl-Py}]_3$. The *cis*-$[\text{HyAl-Py}]_3$ reverted to the *trans* isomer by acidic treatment with TFA. *trans*-$[\text{HyAl-Py}]_3$ and *cis*-$[\text{HyAl-Py}]_3$ have contrasting physical properties such as solubility and fluorescence properties.

Reduction of the *trans*-$[\text{HyAl-Py}]_3$ hydrazone structure afforded a new cyclic hydrazine compound with six amino groups. Hydrazone formation was barely compromised by the presence of substituents at the 4-position of the pyridine moiety, furnishing various *trans*-$[\text{HyAl-Py}]_3$ derivatives. Each derivative is capable of reversible *trans*/*cis* isomerization, as well as metal complexation and fluorescence property.



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21日(木) 13:00 ~ 14:50 E1142(11号館 [4階] 1142)

[E1142-4pm] 15. 有機化学—脂肪族・脂環式化合物，新反応技術

座長：齋藤 由樹、浅野 圭佑

英語
13:00 ~ 13:20

[E1142-4pm-01]

テトラコナゾールの連結・連続フロー合成

○笹谷 将洋[1]、石谷 暖郎[1]、小林 修[1] (1. 東京大学)

英語
13:20 ~ 13:40

[E1142-4pm-02]

ビーズミル法を用いたポリエチレンテレフタレートの触媒的低温解重合反応

○川瀬 智也[1]、石谷 暖郎[1]、小林 修[1] (1. 東大)

英語
13:40 ~ 14:00

[E1142-4pm-03]

ジアザベンゾアセナフテン光酸化還元触媒によるエステルの多電子還元

○服部 修佑[1,2]、奥村 慎太郎[1,2]、魚住 泰広[1,2] (1. 分子研、2. 総研大)

14:00 ~ 14:10

休憩

英語
14:10 ~ 14:30

[E1142-4pm-04]

トランスシクロオクテンを利用した触媒的臭素化におけるBr_2捕捉剤の開発

○村田 竜一[1]、下道 謙太[1]、平松 将嗣[1]、松原 誠二郎[1]、浦口 大輔[2]、浅野 圭佑[2] (1. 京大院工、2. 北大触媒研)

英語
14:30 ~ 14:50

[E1142-4pm-05]

光酸化還元/コバルト協働触媒によるアルケンの分岐選択的ヒドロハロゲン化反応

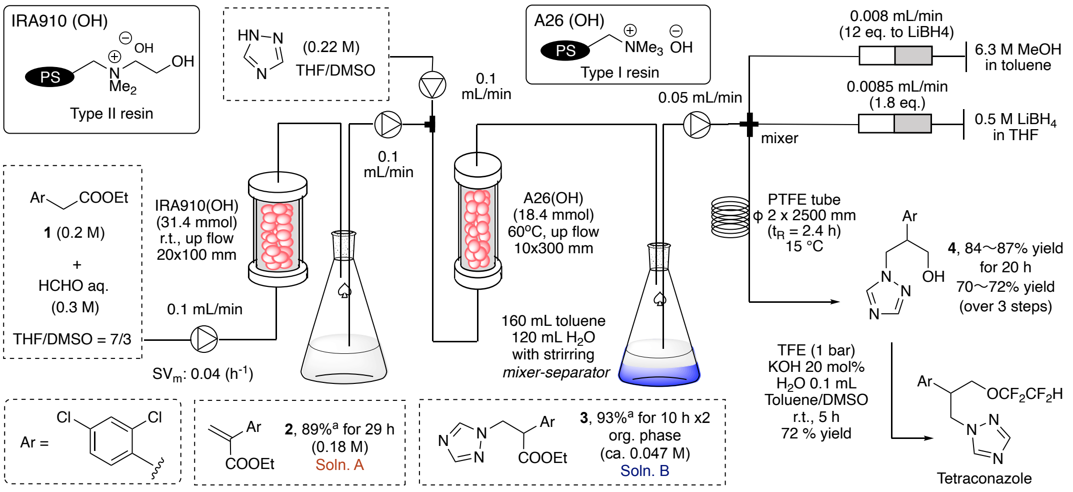
○渋谷 将太郎[1]、長尾 一哲[1]、大宮 寛久[1] (1. 京大化研)

Sequential- and continuous-flow synthesis of tetraconazole by integrating heterogeneous catalytic processes and organometallic reactions

(*School of Science*[1] *and GSC Social Cooperation Laboratory,*[2] *The Univ. of Tokyo*)
○ Masahiro SASAYA,[1] Haruro ISHITANI,[2] Shū KOBAYASHI[1, 2]

Keywords: Sequential-flow reaction; Heterogeneous catalyst; α-Methylenation; Aza-Michael addition; Ester reduction

Tetraconazole, a demethylation inhibitor fungicide in high global demand, is typically synthesized through a base-promoted construction of its molecular framework through α-methylenation reaction and aza-Michael addition of 1,2,4-triazole, followed by a functional group conversion from ester to fluoroalkyl ether. In our pursuit of a sequential and continuous-flow synthesis of this valuable compound, we initially focused on exploring heterogeneous catalyses for the molecular scaffold construction. Contrary to our experience with solid base-catalyzed flow reactions,[1] a commercially available ethanol amine-type ammonium hydroxide resin exhibited the best results in terms of both selectivity and durability for the α-methylenation of ester **1** using formalin. Interestingly, the choice of solvent and ester moiety also notably influenced product selectivity. Following optimization of the two-step transformation including aza-Michael addition, we faced a challenge of reconciling the water-based reactions used for the initial scaffold construction with the ester reduction employing metal hydride reagents, which require hydrophobic conditions. Screening of reductants and fine-tuning to minimize undesirable side reactions led to the development of optimized sequential-flow system depicted below. Under these optimized conditions, alcohol **4**, a key precursor to tetraconazole, was obtained in 72% yield over 20 hours without any offline manipulation. Subsequently, tetrafluoroalkyl etherification with tetrafluoroethylene under batch conditions successfully completed the synthesis, yielding the target tetraconazole molecule.



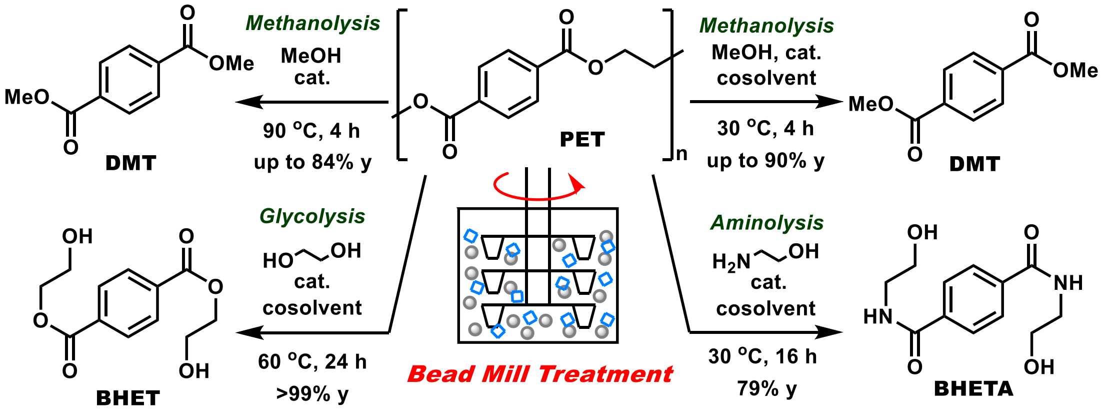
1) Laroche, B.; Saito, Y.; Ishitani, H.; Kobayashi, S. *Org. Process Res. Dev.* **2019**, *23*, 961.

Bead Mill-Driven Acceleration of Catalytic Depolymerization Reactions of Poly(ethylene terephthalate) under Mild Reaction Conditions

(*School of Science* [1] *and GSC Social Cooperation Laboratory* [2]*, The Univ. of Tokyo*)
○Tomoya KAWASE[1], Haruro ISHITANI[2], Shū KOBAYASHI[1,2]

Keywords: Bead Milling; Poly(ethylene terephthalate); Depolymerization; Chemical Recycling; Carbon Neutral

Chemical recycling of post-consumer plastics offers a promising approach to convert waste into renewable chemical raw materials, thereby contributing to a sustainable society. However, the requirement of high temperature often renders the process economically unviable. Mass transfer limitations due to the insolubility of plastics in solvents present a significant bottleneck. We propose that pulverization technology, especially bead milling, can address this challenge. By utilizing this technology, we envisioned plastics to be physically and/or mechanochemically broken down into fine particles, which can increase the surface area and accelerate the reactions even at low temperatures. To validate this concept, we investigated depolymerization reactions of PET under mild reaction conditions. When bead milling was applied as a pretreatment, catalytic methanolysis of PET under 90 °C were remarkably accelerated to give high yields of its monomer DMT,[1] despite conventional reactions requiring temperatures exceeding 180 °C.[2] We revealed that solvent and bead material under bead mill conditions had an impact on acceleration of the subsequent methanolysis reaction: using toluene as a solvent with ZrO_2 beads was the most effective. Particle size distribution and GPC analyses disclosed that both particle size and molecular weight reduction progressed under the specified bead mill conditions. It is assumed that these changes contribute to the reaction acceleration. The optimized method employing bead milling and the identified catalyst proved successful not only for methanolysis but also for glycolysis and aminolysis reactions, all under remarkably mild conditions, showcasing the versatility of our approach. This work provides valuable insights for tackling the low-temperature recycling of other plastics.



1) T. Kawase, H. Ishitani, S. Kobayashi, *Chem. Lett*. **2023**, *52*, 745.
2) J. Chen, *et al. ACS Catal*. **2022**, *12*, 4659.

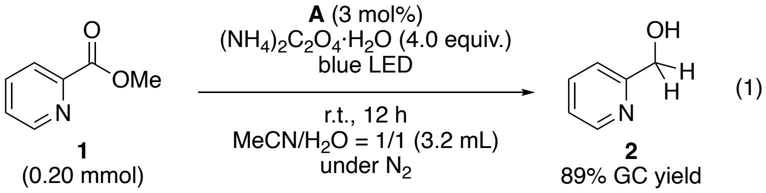
Multi-electron Reduction of Esters by Diazabenzoacenaphthene-based Photoredox Catalysts

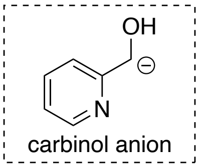
([1]*Institute for Molecular Science,* [2]*SOKENDAI*) ○Shusuke Hattori,[1,2] Shintaro Okumura,[1,2] Yasuhiro Uozumi[1,2]

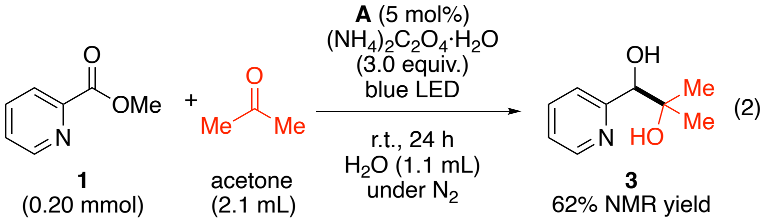
Keywords: Photoredox Catalysis; Multi-electron Reduction; Diazabenzoacenaphthenes; Esters

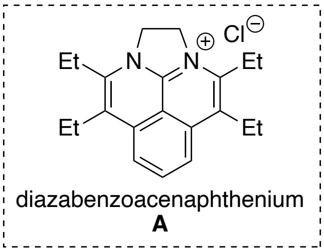
During the last decade, photocatalysis has been becoming a rapidly growing field in chemistry. However, photocatalytic reduction of esters remains a formidable challenge due to the poor electrophilicity of their carbonyl carbons. Photocatalytic reduction of esters into alcohols should be achieved via the carbinol anion intermediates where almost simultaneous four-electron transfer to esters is required. We have developed a novel diazabenzoacenaphthene-based photocatalyst which realized the four-electron reduction of esters, and the resulting carbinol anion intermediates underwent protonation as well as 1,2-addition with the second carbonyl compounds to give the corresponding alcohols and *vic*-diols, respectively.

Diazabenzoacenaphthenium photocatalyst **A** bearing high photoredox ability was designed in silico and prepared. Diazabenzoacenaphthenium **A** catalyzed the four-electron reduction of methyl picolinate **1** in the presence of ammonium oxalate monohydrate in acetonitrile/water under blue light irradiation for 12 hours to afford 2-pyridinemethanol **2** in 89% GC yield (eq. 1). When the reduction was conducted in acetone under similar conditions, ester **1** reacted with acetone to afford *vic*-diol **3** in 62% NMR yield (eq. 2).





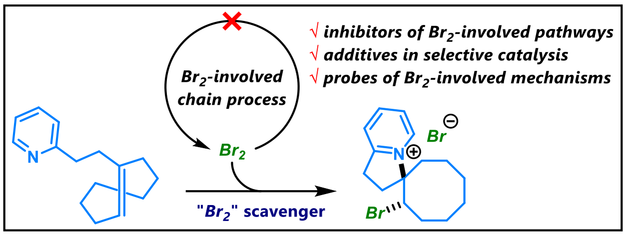




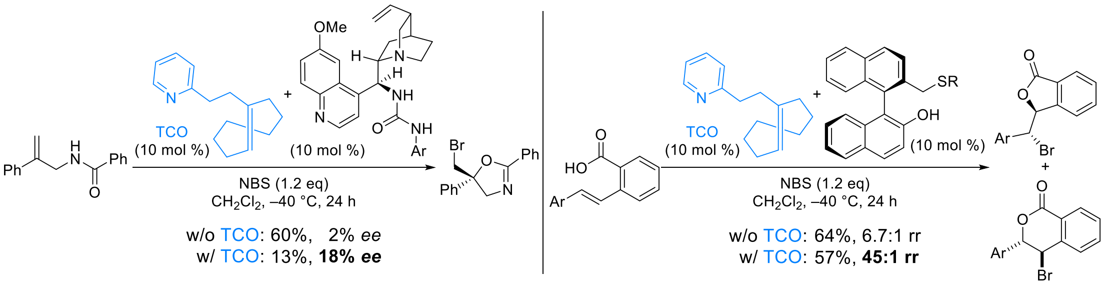
trans-Cyclooctenes as Scavengers of Bromine Involved in Catalytic Bromination

([1]*Graduate School of Engineering, Kyoto University*, [2]*Institute for Catalysis, Hokkaido University*, [3]*List Sustainable Digital Transformation Catalyst Collaboration Research Platform, Institute for Chemical Reaction Design and Discovery (ICReDD List-PF), Hokkaido University*) ○ Ryuichi Murata,[1] Kenta Shitamichi,[1] Masatsugu Hiramatsu,[1] Seijiro Matsubara,[1] Daisuke Uraguchi,[2,3] Keisuke Asano[2]

Keywords: *trans*-Cyclooctene; Scavenger; Bromine; Bromination



Scavengers that capture reactive chemical substances are used to prevent the decomposition of materials. However, in the field of catalysis, the development of scavengers that inhibit background pathways has attracted little attention, although the concept will open up an otherwise inaccessible reaction space. In catalytic bromination, fast non-catalyzed background reactions disturb the catalytic control of the selectivity, even when using *N*-bromoamide reagents, which have a milder reactivity than bromine (Br_2). Here, we developed a *trans*-cyclooctene (TCO) bearing a 2-pyridylethyl group to efficiently retard background reactions by capturing Br_2 in bromocyclization using *N*-bromosuccinimide.[1] The use of less than a stoichiometric amount of the TCO was sufficient to inhibit non-catalyzed reactions, and mechanistic studies using the TCO revealed that in situ-generated Br_2 provides non-catalyzed reaction pathways based on a chain mechanism. The TCO was useful as an additive for improving enantioselectivity and regioselectivity in catalytic reactions. Cooperative systems using the TCO with selective catalysts offer an alternative strategy for optimizing catalyst-controlled selectivity during bromination. Moreover, it also served as an indicator of Br_2 involved in catalytic reaction pathways; thus, the TCO was useful as a probe for mechanistic investigations into the involvement of Br_2 in bromination reactions of interest.



1) R. Murata, K. Shitamichi, M. Hiramatsu, S. Matsubara, D. Uraguchi, K. Asano, *Chem.—Eur. J.* Early View, e202303399.

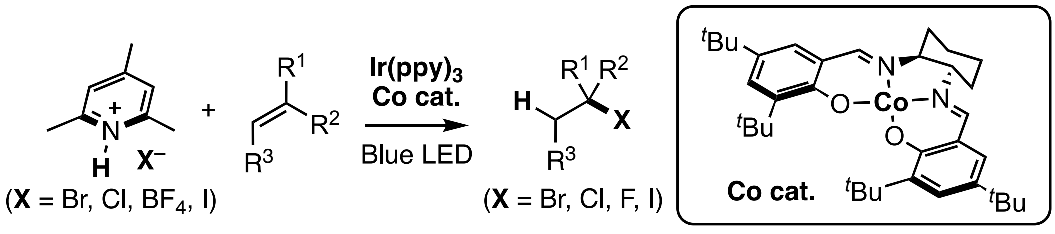
A Dual Cobalt and Photoredox Catalysis for Hydrohalogenation of Alkenes

(*ICR, Kyoto Univ.*) ○Shotaro Shibutani, Kazunori Nagao, Hirohisa Ohmiya

Keywords: Photoredox catalyst; Cobalt catalyst; Single-electron transfer; Alkene; Hydrohalogenation

Alkyl halides have been classified to one of most fundamental and important organic compounds due to the high reactivity as coupling reagents and ubiquitous structures in natural products and pharmaceutical drugs. Therefore, synthetic methods for preparation of alkyl halides have been intensively studied. Hydrohalogenation of alkenes using hydrogen halide (HX) is a simple, atom-economical and cost-effective approach for preparation of alkyl halides. However, such conventional methods suffered from strong acidic and harsh reaction conditions, resulting in low functional group compatibility. To overcome this problem, Carreira and others demonstrated a radical approach to hydrohalogenation of alkenes using a cobalt catalyst, hydrosilanes and electrophilic halogen sources.1) Therein, the catalysis allows to deliver the hydrogen and halogen atoms from hydrosilanes and halogen sources through metal hydride hydrogen atom transfer and $S_\mathrm{H}2$ reactions, respectively. Since these protocols enable to avoid the use of strong acidic HX, high functional group compatibility is ensured. However, low atom economy remained as an unresolved problem.

We demonstrate an alternative radical-based approach for hydrohalogenation of alkenes ensuring high atom economy and chemoselectivity. A dual photoredox/cobalt catalysis2) enables to convert a proton and a halide anion from collidine·HX salt to a nucleophilic hydrogen radical equivalent and an electrophilic halogen radical equivalent through single electron reduction and oxidation and deliver them to an alkene moiety. This protocol allows for introduction of fluorine, chlorine, bromine, or iodine atom to alkene, producing highly functionalized alkyl halides by changing the halide anion source. The method was able to tolerate functional groups that are unstable under acidic conditions, such as methoxymethyl, esters, silyl ethers, and amides. This was also applicable to hydrohalogenation of alkenes derived from pharmaceuticals and natural products.



1) Gaspar, B.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 5758.

2) Nakagawa, M.; Matsuki, Y.; Nagao, K.; Ohmiya, H. *J. Am. Chem. Soc.* **2022**, *144*, 7953

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21日(木) 13:00 ~ 14:20 E1143(11号館 [4階] 1143)

[E1143-4pm] 15. 有機化学―脂肪族・脂環式化合物，新反応技術

座長：村田 貴嗣、波多野 学

日本語

13:00 ~ 13:20

[E1143-4pm-01]

ジボロン酸無水物触媒によるアミン水溶液を用いた脱水縮合アミド化反応の開発

○岩澤 太陽[1]、高橋 那央也[2]、嶋田 修之[1] (1. 日本大、2. 北里大)

日本語

13:20 ~ 13:40

[E1143-4pm-02]

N-トリフルオロメタンスルホニルイミダゾールを用いる高化学選択的トリフリル化反応

○平田 翼[1]、波多野 学[1]、新田 純基[2]、山﨑 貴子[2]、富田 廉[2]、秋山 勝宏[2] (1. 神戸薬科大学、2. セントラル硝子株式会社)

日本語

13:40 ~ 14:00

[E1143-4pm-03]

Weinrebアミド型Horner–Wadsworth–Emmons（HWE）試薬を用いたHWE反応の実験的機構解析研究

村田 貴嗣[1]、○筒井 久澄[1]、椎名 勇[1] (1. 東京理科大学)

日本語

14:00 ~ 14:20

[E1143-4pm-04]

第三級脂肪族アミンのγ位選択的な官能基化[2]

○榊原 陽太[1]、濱脇 康佑[1]、平手 和希[1]、千葉 将真[1]、寺田 昂祐[1]、木之下 拓海[1]、村上 慧[1] (1. 関西学院大学)

ジボロン酸無水物触媒によるアミン水溶液を用いた脱水縮合アミド化反応の開発

（日本大文理 [1]・北里大薬 [2]）○岩澤 太陽 [1]・高橋 那央也 [2]・嶋田 修之 [1]

Development of Diboronic Acid Anhydride-Catalyzed Dehydrative Amidations Using Aqueous Amine Solutions ([1]*Department of Chemistry, Nihon University*, [2]*Department of Pharmaceutical Sciences, Kitasato University*) ○ Hinata Iwasawa,[1] Naoya Takahashi,[2] Naoyuki Shimada,[1]

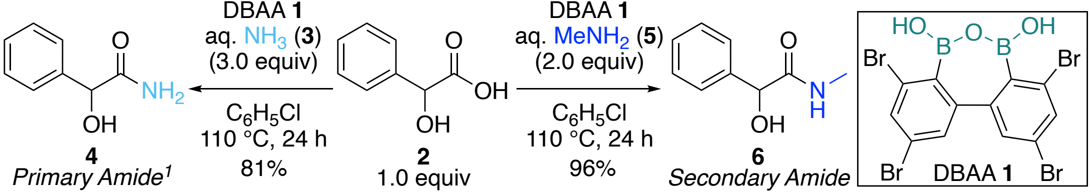
Catalytic amidation of carboxylic acids with amines is an ideal synthetic method for constructing amide bonds, which is universally found in pharmaceuticals and agrochemicals. However, this synthetic method requires strict dehydrative conditions, making it difficult to use commercially available and easy to handle aqueous amine solutions as amine substrates. In this study, we have succeeded a development of an unprecedented catalytic dehydrative amidations using aqueous amine solutions catalyzed by diboronic acid anhydride, which was originally developed in our laboratory. We found the amidation reaction of mandelic acid (**2**) with aqueous ammonia solution (**3**) in the presence of DBAA **1** in chlorobenzene at 110 °C gave the corresponding amide **4** in high yield. In addition, aqueous methylamine solution (**5**) was also applicable to give secondary amide **6** in excellent yield.

Keywords : Dehydrative condensation; Organoboron Catalysis; Amide

アミドは医農薬品や天然物骨格に普遍的に含まれる重要な化学結合様式であることから，効率的な合成手法の開発が強く望まれている。これまでに，有機ホウ素触媒によるカルボン酸とアミンからの直截的なアミド化反応の開発研究が精力的に行われてきた。しかしながら，本手法は厳密な脱水操作を必須としていることから，市販で取扱容易なアミン水溶液をアミン基質として用いることは困難であった。今回我々は，当研究室で独自に開発したジボロン酸無水物触媒 DBAA **1** による前例のない，アミン水溶液を用いた触媒的脱水縮合アミド化反応の開発に成功した。

検討の結果， DBAA **1** 存在下，マンデル酸 (**2**)とアンモニア水溶液 (**3**)とのアミド化反応を行ったところ，クロロベンゼン加熱条件下，目的とする第一級アミド **4** が高収率で得られることを見出した(Scheme 1)[1)]。さらにメチルアミン水溶液 (**5**)をアミン基質とした場合にも第二級 *N*-メチルアミド **6** が得られることを明らかにした。

Scheme 1. Diboronic Acid Anhydride–Catalyzed Amidation Using Aqueous Amine Solutions



1) Takahashi, N.; Iwasawa, H.; Kinashi, T.; Makino, K.; Shimada, N. *Chem. Commun.* **2023**, *59*, 7391–7394.

N-トリフルオロメタンスルホニルイミダゾールを用いる高化学選択的トリフリル化反応

（神戸薬大薬[1]・セントラル硝子株式会社[2]）○平田 翼[1]・波多野 学[1]・新田 純基[2]・山﨑 貴子[2]・富田 廉[2]・秋山 勝宏[2]

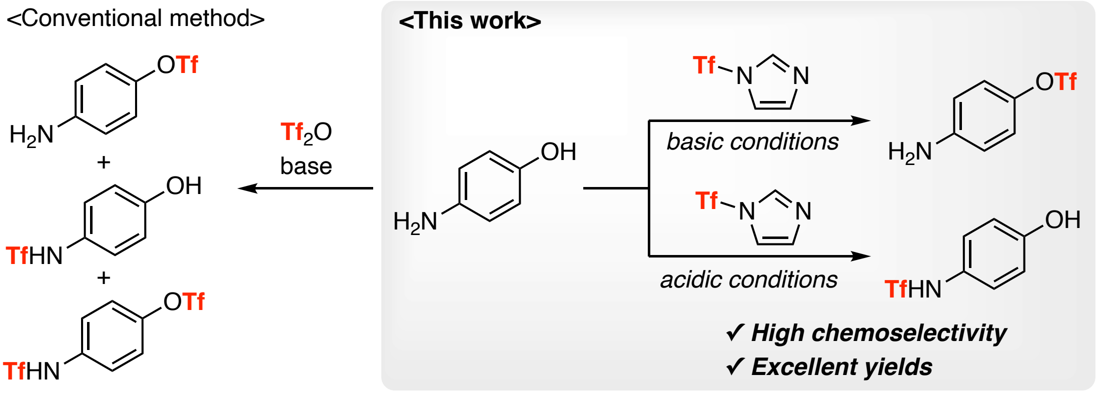
Highly Chemoselective Triflation Using *N*-Trifluoromethanesulfonylimidazole

([1]*Faculty of Pharmaceutical Sciences, Kobe Pharmaceutical University*, [2]*New-STEP Research Center, Central Glass Co. Ltd.*) ○Tsubasa Hirata,[1] Manabu Hatano,[1] Junki Nitta,[2] Takako Yamazaki,[2] Ren Tomita,[2] Katsuhiro Akiyama[2]

Aryl triflates (ArOTf), which can be synthesized by trifluoromethanesulfonylation (triflation) of the hydroxy groups of phenols, are used as substrates for transition metal-catalyzed coupling reactions such as the Suzuki-Miyaura reaction, and are therefore important in organic synthesis. However, the reaction using conventional trifluoromethanesulfonic anhydride (Tf_2O) is often non-selective when the substrates have other reactive functional groups, and undesired byproducts are given. In this study, we developed a highly chemoselective triflation using *N*-trifluoromethanesulfonylimidazole. Under basic conditions, the reactions proceeded selectively at the hydroxy groups of phenols. On the other hand, under acidic conditions, the reactions proceeded selectively at the amino groups of anilines. We will propose the reaction mechanism of these chemoselective triflations of phenols and anilines.

Keywords: *Triflation; Chemoselectivity; Phenol; Aniline; Sulfonylation*

フェノール類のヒドロキシ基をトリフルオロメタンスルホニル化（トリフリル化・Tf化）することで合成できるアリールトリフラート（ArOTf）は、鈴木-宮浦反応に代表される触媒的カップリング反応の基質として用いられるため、有機合成上重要である。ところが、反応性の高いトリフルオロメタンスルホン酸無水物（Tf_2O）を用いるトリフリル化反応では、目的以外の競合する官能基も非選択的に反応しうるため、しばしば混合物を与える。本研究では、*N*-トリフルオロメタンスルホニルイミダゾールを用いて、塩基性条件下におけるフェノール類の高化学選択的 *O*-Tf 化、および酸性条件下におけるアニリン類の高化学選択的 *N*-Tf 化に成功した。発表では高化学選択性の発現機構についても考察する。



Weinreb アミド型 Horner–Wadsworth–Emmons（HWE）試薬を用いた HWE 反応の実験的機構解析研究

(東理大理) 村田 貴嗣・○筒井 久澄・椎名 勇

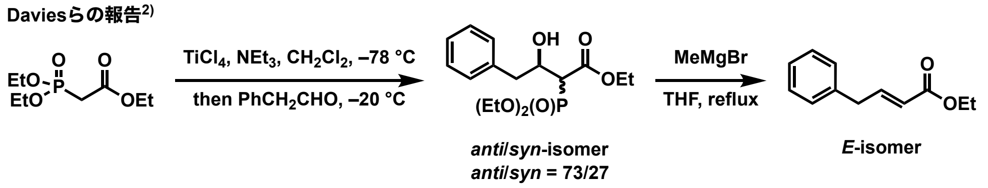
Experimentally Mechanistic Study of Horner–Wadsworth–Emmons (HWE) Reaction with Weinreb Amide-type HWE Reagent

(*Faculty of Science, Tokyo University of Science*) Takatsugu Murata, ○Hisazumi Tsutsui, Isamu Shiina

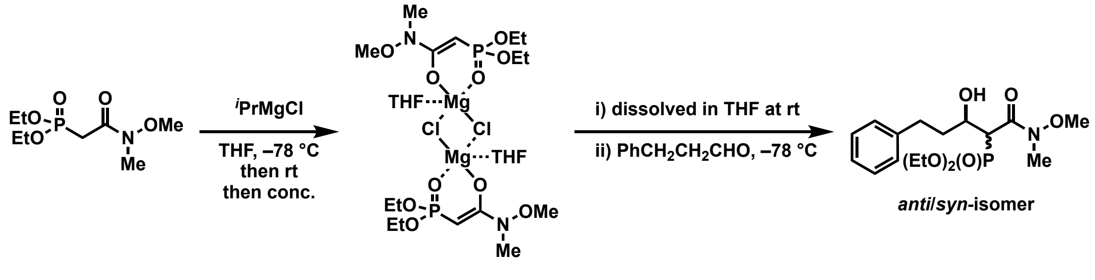
Horner–Wadsworth–Emmons reaction has been employed in a number of syntheses. In many syntheses of them, the products are subjected to the conditions of functional transformations. In the other hand, the reaction mechanism and the selectivity of HWE reaction have not been elucidated. In this study, we experimentally researched the mechanism of HWE reaction.

Keywords : Horner–Wadsworth–Emmons Reaction; Elongation Reaction; Weinreb Amide

Horner–Wadsworth–Emmons 試薬の開発や利用に関する報告例は数多く存在するが、その詳細な反応機構については解明されていない。2006 年に田辺らは、ルイス酸を用いたアルドール反応条件下にて HWE 反応中間体が単離できたことを報告している $^{1)}$。また、S. G. Davies らは田辺らが単離した中間体から HWE 反応成績体への変換が可能であることを報告している $^{2)}$。



我々は、Weinreb アミド構造を有する HWE 試薬 $^{3)}$を用いた反応の中間体であるホスホノエノラートの初の単離について報告している $^{4)}$。今回、HWE 反応の条件を制御することによって HWE 反応中間体の単離に成功した。さらに、その中間体を用いた実験化学的な反応機構の調査を行った。本講演ではこれらの詳細を報告する。



1) M. Katayama, R. Nagase, K. Mitarai, T. Misaki, Y. Tanabe, *Synlett*, **2006**, *1*, 129–132.
2) S. G. Davies *et al*., *Org. Lett.*, **2008**, *10*, *23*, 5437–5440.
3) J.-M. Nuzillard, A. Boumendjel, G. Massiot, *Tetrahedron Lett.*, **1989**, *30*, 3779–3780.
4) 村田貴嗣、筒井久澄、平石真太郎、臼倉大輝、岡野宙輝、椎名勇、日本化学会第103 春季年会、K705-2vn-04 (2023).

第三級脂肪族アミンのγ位選択的な官能基化[2]

（関西学院理工）○榊原 陽太・濱脇 康佑・平手 和希・千葉 将真・寺田 昂祐・木之下 拓海・村上 慧

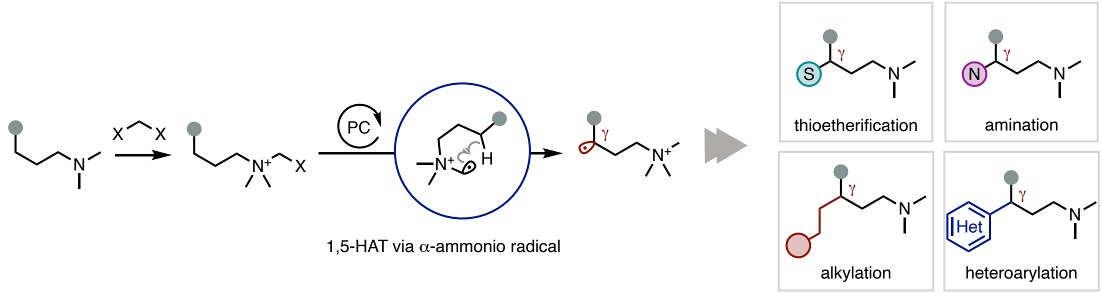
γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [2]

([1]*Graduate Department of Chemistry, School of Science and Engineering, Kwansei Gakuin University*) ○Yota Sakakibara, Kosuke Hamawaki, Kazuki Hirate, Shoma Chiba, Kosuke Terada, Takumi Kinoshita, Kei Murakami

Regioselective C–H functionalization reactions of tertiary aliphatic amines, which are frequently used in pharmaceuticals and agrochemicals, are powerful tools to simplify the synthesis of complex amines. For this reason, numerous reactions using photocatalysis or transition metal catalysis have been developed. However, there are still limitations on the positions that can be functionalized, and in particular, there is no reliable method which can selectively functionalize the γ-position of the nitrogen atom. Herein, we have developed a new method to selectively functionalize the γ-position of the nitrogen atom of tertiary aliphatic amines.

Keywords : Photoredox catalysts; Radical; Ammonium salts ;C–H functionalization; Hydrogen atom transfer

第三級脂肪族アミンの位置選択的なC–H官能基化反応は複雑なアミンの合成を簡便にする強力なツールである[1]。そのため、これまでに数多くの反応が開発されている。しかし、いまだに官能基化できる位置には制限があり、特に窒素原子のγ位の官能基化は困難である。このような背景の中、今回我々は第四級アンモニウム構造を利用することで窒素原子のγ位を選択的に官能基化する手法を開発した。具体的には、α-ハロゲノアンモニウム塩から発生させたラジカル種[2]が引き起こす分子内水素原子移動(1,5-HAT)により、窒素原子のγ位に選択的にラジカル種を発生させることに成功した。なお、α-ハロゲノアンモニウム塩は、第三級脂肪族アミンから容易に調製可能である。 この活性種を用いることで多様な官能基を導入可能であることを見いだし、さらには第三級アミンへと誘導するための適切な脱メチル化条件も発見した。



[1] Dutta, S.; Li, B.; Richertsen, D. R. L.; Valles, D.; Seidel, D. *SynOpen* **2021**, *5*, 173.

[2] Rios, L. A.; Dolbier, Jr. W. R.; Paredes, R.; Lusztyk, J.; Ingold, K. U.; Jonsson, M. *J. Am. Chem. Soc.* **1996**, *188*, 11313.

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

2024年3月21日(木) 13:00 ~ 15:40 H935(9号館 [3階] 935)

[H935-4pm] 16. 天然物化学・ケミカルバイオロジー

座長：高橋 大介、佐々木 要

日本語

13:00 ~ 13:20

[H935-4pm-01]

アルドール反応を用いたN末端アミノ酸の化学修飾

○花屋 賢悟[1]、和田 雄貴[2]、河野 正規[2]、田口 和明[1]、松元 一明[1]、東林 修平[1]、須貝 威[1] (1. 慶應義塾大学、2. 東京工業大学)

英語

13:20 ~ 13:40

[H935-4pm-02]

α-ヒドラジノ酸含有大環状ペプチドのin vitroセレクションと薬剤候補の探索

○松本 聡美[1]、加藤 敬行[1]、菅 裕明[1] (1. 東京大学)

13:40 ~ 13:50

休憩

英語

13:50 ~ 14:10

[H935-4pm-03]

分子内水素結合により加速される2,5-ジケトピペラジン形成反応を用いたタグ付きチオエステル合成

○中津 幸輝[1]、林 剛介[1]、村上 裕[1,2] (1. 名大院工、2. 名大ナノライフ)

日本語

14:10 ~ 14:30

[H935-4pm-04]

光応答性RNA結合低分子を用いたUGGAAリピートRNAの相分離体形成の光誘導とメカニズム解析

○藤原 侑亮[1,2]、柴田 知範[1,2]、堂野 主税[1,2]、中谷 和彦[1,2] (1. 大阪大学　産業科学研究所、2. JST, CREST)

14:30 ~ 14:40

休憩

英語

14:40 ~ 15:00

[H935-4pm-05]

脂質ナノ粒子化セルフアジュバンティングがんワクチンの調製と機能評価

○伊藤 啓太[1]、真鍋 良幸[1,2]、大島 志乃[3]、亀谷 美恵[3]、真栄城 正寿[4]、渡慶次 学[4]、深瀬 浩一[1,2] (1. 阪大院理、2. フォアフロント研究センター、3. 東海大医、4. 北大院工)

英語

15:00 ~ 15:20

[H935-4pm-06]

酢酸菌由来リポ多糖部分構造の化学合成および機能評価

○山浦 遼生[1]、下山 敦史[1]、深瀬 浩一[1] (1. 大阪大学大学院)

🏷 英語

15:20 ~ 15:40

[H935-4pm-07]

4分枝シアリル*N*-グリカンの化学合成

○矢野 君晟[1]、真鍋 良幸[1,2]、深瀬 浩一[1,2] (1. 阪大院理、2. 阪大院理FRC)

アルドール反応を用いたN末端アミノ酸の化学修飾

（慶大薬[1]・東工大理[2]）○花屋 賢悟[1]・和田 雄貴[2]・河野 正規[2]・田口 和明[1]・松元 一明[1]・東林 修平[1]・須貝 威[1]

N-terminal modification of polypeptides via metal-mediated aldol reaction

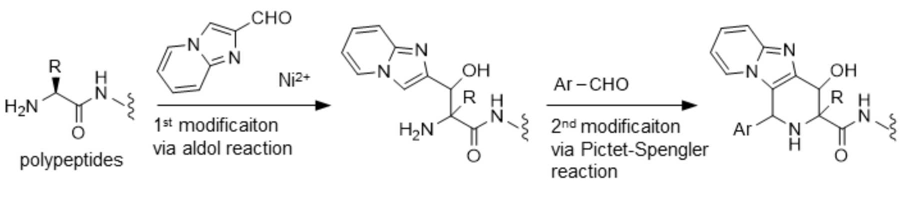
([1]*Faculty of Pharmacy, Keio University*, [2]*Department of Chemistry, Tokyo Institute of Technology*) ○Kengo Hanaya,[1] Yuki Wada,[2] Masaki Kawano,[2] Kazuaki Taguchi,[1] Kazuaki Matsumoto,[1] Shuhei Higashibayashi,[1] Takeshi Sugai[1]

Bioconjugation reactions have been continuously developed to fulfill the growing demand for applications in both industrial applications and fundamental chemical biology research. Since the most polypeptides possess the N-terminus as a unique reactive site, N-terminal selective modifications can provide modified polypeptides with uniform properties and structures. We present here the N-terminal selective dual modification via nickel(II)-mediated aldol reaction with imidazo[1,2-*a*]pyridine-2-carboxaldehyde at neutral pH and the following Pictet-Spengler reaction with heteroaromatic aldehydes at weakly acidic pH. The methodology allows to attach two artificial molecules such as drugs, fluorophores, and PEG in various combination to a therapeutic antibody consisting of more than 1300 residues as well as short peptides.

Keywords：Polypeptide; Chemical modification; N-terminus; Nickel; Aldol reaction

創薬やケミカルバイオロジーにおいて、ポリペプチドの特定のアミノ酸残基上に薬物や蛍光分子などの人工分子を導入する手法（化学修飾法）の開発が求められている。N末端アミノ酸は一本のポリペプチド鎖につき1箇所存在する。そのため、N末端アミノ酸の化学修飾法は、さまざまなポリペプチドに適用可能であると考えられる。本研究では、含窒素芳香族アルデヒドと金属イオンを組み合わせたアルドール反応を活用することにより、中性緩衝液中でN末端アミノ酸を選択的に化学修飾する手法を開発した。

8残基のペプチドに対し、pH 7.5の緩衝液中、イミダゾ[1,2-a]ピリジン-2-カルボキシアルデヒド（IMPC）誘導体とニッケルイオンを組み合わせて用いると、それぞれアルドール反応した生成物が得られた。約1300残基からなるIgGに対してもアルドール反応はN末端アミノ酸上で進行した。アルドール反応の生成物に弱酸性条件下、別途アルデヒドを作用させるとPicgtet-Spengler反応が進行し、2種類の人工分子を導入することができた。



In Vitro Selection of Macrocyclic Peptides Containing α-Hydrazino Acid for Exploration of Drug Candidates

([1]*Graduate School of Science, The University of Tokyo*) ○Satomi Matsumoto,[1] Takayuki Katoh,[1] Hiroaki Suga[1]
Keywords: α-Hydrazino acid; Nonstandard peptide drug

α-Hydrazino acid (α-Hza, **Fig. a**) is a β-amino acid analog with its β-carbon replaced by nitrogen. Introduced into a peptide chain, α-Hza is able to induce a turn structure by forming an intramolecular bifurcated hydrogen bond (**Fig. b**), allowing the peptide to fold into a reinforced hairpin structure[1] (**Fig. c**). Such α-Hza-containing peptide ligands are expected to exhibit excellent properties as drug candidates: improved binding affinity to target proteins, proteolytic resistance, and membrane permeability.

Non-proteinogenic amino acids (npAAs) like α-Hza face challenges in ribosomal peptide synthesis primarily due to the following two reasons: 1) slow accommodation of npAA-tRNA onto the ribosomal A site and 2) slow peptidyl transfer of npAA. However, our group recently achieved successful incorporation of α-Hza into model peptides by taking advantage of an engineered tRNA, $\mathrm{tRNA}^{\mathrm{Pro1E2}}$, in an *Escherichia coli* reconstituted translation system called the Flexible *In Vitro* Translation (FIT) system[2]. $\mathrm{tRNA}^{\mathrm{Pro1E2}}$ has optimized T-stem and D-arm motifs for efficient binding to elongation factors EF-Tu and EF-P[3], respectively, to enhance the incorporation of npAAs by accelerating accommodation and peptidyl transfer, respectively[4].

In this research, α-Hza-containing macrocyclic peptide libraries with more than 10^{13} diversities were constructed by optimizing conditions of FIT system. These libraries were then applied to *in vitro* selection by means of RaPID system for exploration of novel peptide drug candidates with rigid structures. Here, human factor XIIa (FXIIa) and Janus kinase 2 (JAK2) were selected as model extra- and intracellular target proteins, respectively. Consequently, α-Hza-containing binder peptides with low-nanomolar K_D values were obtained and showed high inhibitory activity against these targets. In addition, membrane permeability of the JAK2 binder peptides was also confirmed.

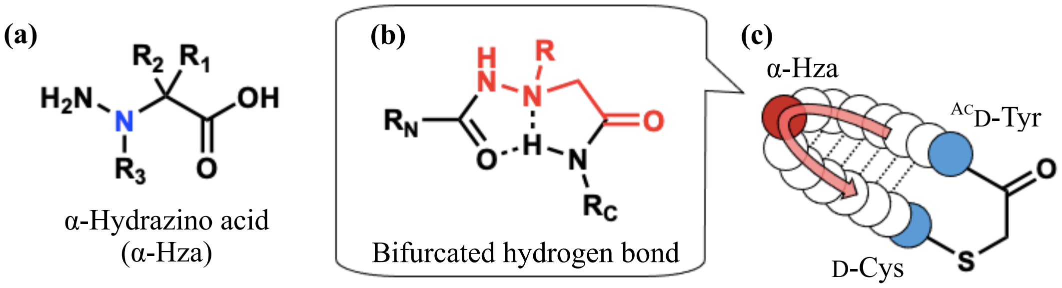


Fig. Construction of α-Hza-containing peptide library with rigid structure.
(a) Structure of α-Hza. α-Nitrogen is shown in blue.
(b, c) α-Hza in peptide chain forms intramolecular bifurcated hydrogen bond **(b)** and folds the peptide into a rigid hairpin structure **(c)**.

[1] Günther, R.; Hofmann, H-J. *J. Am. Chem. Soc.* **2001,** *123,* 247-255.
[2] Katoh, T.; Suga, H. *J. Am. Chem. Soc.* **2021,** *143,* 18844-18848.
[3] Katoh, T.; Iwane, Y.; Suga, H. *Nucleic Acids Res.* **2017,** *45,* 12601-12610.
[4] Katoh, T.; Suga, H. *J. Am. Chem. Soc.* **2018,** *140,* 12159-12167.

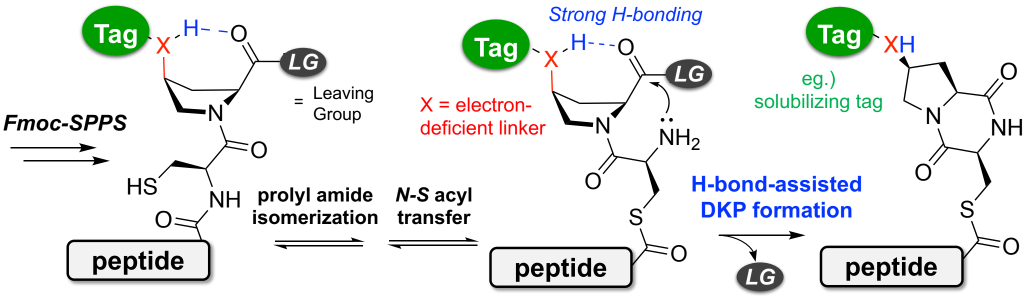
Intramolecular Hydrogen-Bonding-Accelerated 2,5-Diketopiperazine Formation for Facile Synthesis of Tag-Attached Peptide Thioester

(1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.) ○Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2]

Keywords: Proline derivatives; Thioester, Diketopiperazine; Peptide Ligation; Fmoc Solid-Phase Peptide Synthesis

Native chemical ligation (NCL) is a promising strategy to ligate side-chain unprotected peptides between an N-terminal cysteine peptide and a C-terminal peptide thioester in neutral aqueous conditions.[1] To introduce a thioester moiety through Fmoc solid-phase peptide synthesis (SPPS), various thioester surrogates have been designed and reported by peptide chemists. The moiety of cysteinyl-prolyl-leaving group (Cys-Pro-*LG*) is readily introduced to a peptide in Fmoc SPPS and converts into thioester through diketopiperazine (DKP) formation. The effect of leaving group to reaction rate in DKP formation has been explored intensively.[2–4] Proline substitutions at γ-position greatly affect the cis-trans conversion of prolyl amide and puckering of the pyrrolidine ring of proline.[5] We hypothesized that Cγ-modified proline is an effective tool to investigate the nature of DKP formation.

Herein, we demonstrate the use of prolyl 4*S* modifications for Cys-Pro-*LG* to achieve facile synthesis of tag-attached peptide thioester through Fmoc-SPPS. By conducting comparative analyses of 4*S*-NHR and 4*S*-OR substitutions, we have found that modifications bearing a hydrogen donor improve the rate of DKP-thioester formation. In addition, we performed density functional theory (DFT) calculations and indicated that intramolecular hydrogen bonding between 4*S*-substitutions and prolyl carbonyl stabilizes the transition states of DKP formation. Finally, we report chemical protein synthesis using peptide DKP-thioester with a solubilizing tag connected via an optimized linker at the prolyl γ-position.



1) Dawson, P. E.; Muir, T. W.; Clark-Lewis, I.; Kent, S. B. *Science* **1994**, *266*, 776. 2) Kawakami, T.; Kamauchi, A.; Harada, E.; Aimoto, S. *Tetrahedron Lett.* **2014**, *55*, 79. 3) Yanase, M.; Nakatsu, K.; Cardos, C. J.; Konda, Y.; Hayashi, G.; Okamoto, A. *Chem. Sci.* **2019**, *10*, 5967. 4) Nakatsu, K.; Yanase, M.; Hayashi, G.; Okamoto, A. *Org. Lett.* **2020**, *22*, 4670. 5) Newberry, R. W.; Raines, R. T. *Top. Heterocycl. Chem.* **2017**, *48*, 1.

光応答性 RNA 結合低分子を用いた UGGAA リピート RNA の相分離体形成の光誘導とメカニズム解析

（阪大産研[1]・JST, CREST[2]）○藤原 侑亮[1,2]・柴田 知範[1,2]・堂野 主税[1,2]・中谷 和彦[1,2]

Mechanism of phase separation of UGGAA repeat RNA induced by photoswitchable RNA binding ligands

([1]*SANKEN, Osaka University*, [2]*CREST, JST*) ○Yusuke Fujiwara,[1,2] Tomonori Shibata,[1,2] Chikara Dohno,[1,2] Kazuhiko Nakatani[1,2]

RNAs containing r(UGGAA) repeat sequences form structures called RNA foci. Although RNA foci have been shown to change their components and localization depending on the surrounding environment, their individual functions are yet to be identified. Therefore, spatiotemporal control of RNA foci formation is needed for understanding their dynamics. We have reported that NCD (Naphthyridine Carbamate Dimer) binds to r(UGGAA) repeats and inhibits RNA foci formation1). In this research, we introduced NCTA, a photoswitchable RNA ligand that binds to r(UGGAA) repeats. UV irradiation enhances NCTA's binding to UGGAA/UGGAA mismatches, while visible light irradiation reduces the affinity. In model cells, NCTA increased the size of r(UGGAA) RNA foci within 1 hour after UV irradiation, which is reversed by subsequent visible light irradiation within the same timeframe. These results indicated that NCTA functions as a "photoswitch" facilitating reversible changes in foci. We will also discuss the mechanisms by which NCTA promotes RNA foci formation.

Keywords : Photoswitch; Nucleic Acid; RNA foci; Phase separation; Repeat RNA

r(UGGAA)反復配列をもつ RNA は、細胞内で RNA foci と呼ばれる相分離体を形成し、転写や翻訳に影響を及ぼす。RNA foci は環境や時間変化に応じてその構成や局在を変化させるが、それらの機能の解明のためには RNA foci の時空間的な形成制御技術が必要である。当研究室ではこれまでに、r(UGGAA)反復配列に結合するリガンド NCD を開発し、NCD が細胞内で RNA foci を阻害することを報告した 1)。そこで本研究では、２分子の NCD をアゾベンゼンで繋げた光応答性リガンド NCTA2)を用いることで、光刺激による RNA foci の時間選択的な形成制御を目指した。

NCTA は 365 nm (UV) 光および 460 nm (可視) 光照射により、UGGAA/UGGAA 二本鎖に対する結合親和性がそれぞれ活性化、および抑制された。r(UGGAA)反復配列を発現するモデル細胞に NCTA を処理したところ、 UV 照射によって RNA foci の形成が促進され、続く可視光照射によって RNA foci は UV 照射前の状態まで回復した。これらの過程はそれぞれ 1 時間で完了し、NCTA が細胞内 RNA foci 形成の"光スイッチ"として働くことを示している。発表では、NCTA が細胞内 RNA foci 形成を促進するメカニズムについても議論したい。

1) Shibata T. *et al. Nat. Commun.* **2021**, *12*, 236.
2) Dohno C. *et al. Nucl. Acid. Res,* **2023**, *51*, 9533.

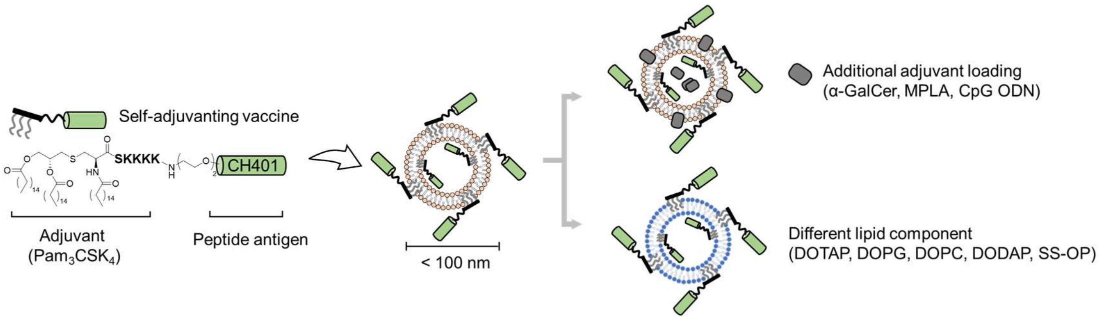
Preparation and Immunological Evaluation of Lipid Nanoparticle-based Self-adjuvanting Cancer Vaccine

([1]*Graduate School of Science, Osaka University*, [2]*Forefront Research Center, Osaka University*, [3]*School of Medicine, Tokai University*, [4]*Faculty of Engineering, Hokkaido University*) ○Keita Ito,[1] Yoshiyuki Manabe,[1,2] Shino Oshima,[3] Yoshie Kametani,[3] Masatoshi Maeki,[4] Manabu Tokeshi,[4] Koichi Fukase[1,2]

Keywords: Peptide vaccine; Adjuvant; Lipid nanoparticle

Cancer vaccine therapy garners a great attention because they expect to prevent recurrence. Especially, peptide vaccines are useful due to the easy preparation as homogeneous materials. However, the practical application of cancer peptide vaccines has been impeded by the low antigenicity of the peptide antigen. To induce robust immune responses, vaccine materials should be smoothly taken up by immune cells. Furthermore, antigen-specific immune responses should be induced to realize high potency without adverse effects. In this study, we developed antigen/adjuvant (immune stimulant)-loaded lipid nanoparticle (LNP) as a novel vaccine material. Formulation of vaccine materials to 100 nm spherical particle is expected to enable their efficient delivery to lymph nodes, and co-loading of antigen and adjuvant is expected to realize antigen-specific immune response.

We prepared the LNP that is loaded the conjugate of CH401 peptide (tumor-associated antigen of breast cancer) with an adjuvant. This LNP-based vaccine was prepared using the iLiNP microfluidic device, which allows precise size control below 100 nm.[1] In addition, to achieve the fine-tuning of immune responses, additional adjuvants were co-loaded to this vaccine material. We further investigated the lipid components of LNPs to enhance the vaccine efficacy. The *in vivo* experiments of these vaccine materials provided a guideline of efficient peptide vaccine development.



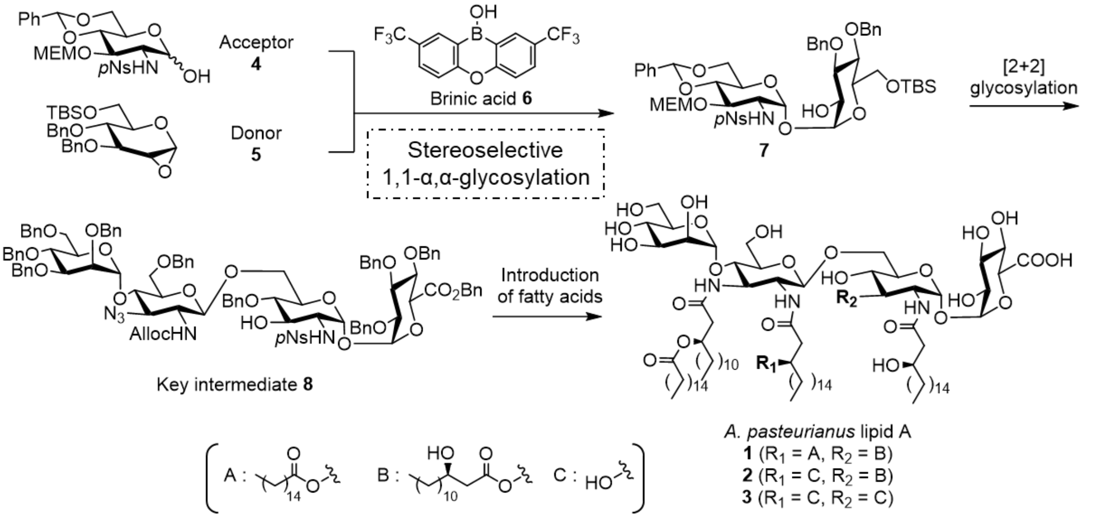
1) Kimura, N., Maeki, M., Sato, Y., Note, Y., Ishida, A., Tani, H., Harashima, H., Tokeshi, M., *ACS Omega* **2018**, *3*, 5044.

Chemical synthesis and functional evaluation of acetic acid bacterial lipopolysaccharide partial structures

(*Graduate School of Science, Osaka University*) ○Haruki Yamaura, Atsushi Shimoyama, Koichi Fukase

Keywords: innate immunity; lipid A; *Acetobacter pasteurianus*; acetic acid bacteria; kurozu

Lipopolysaccharide (LPS), one of the cell surface components of Gram-negative bacteria, activates innate immunity. *Acetobacter pasteurianus* is a Gram-negative bacterium used for the fermentation process of traditional Japanese black rice vinegar (kurozu). *Acetobacter pasteurianus* LPS, which is a candidate of immunostimulatory component of kurozu, contains lipid A with a distinctive structure[1]. Here, we achieved the first synthesis of three kinds of *A. pasteurianus* lipid A **1**-**3** to identify active principle of *A. pasteurianus* LPS. We investigated the efficient construction of 2-trehalosamin skeleton of **7** and found that 1,2-*cis*-glycosylation using borinic acid **6**[2] between **4** and **5** afforded **7** in high yield and stereoselectivity. We next performed [2+2] glycosylation to synthesize the key intermediate **8** with an orthogonal protecting group pattern. We introduced various fatty acids into appropriate positions of **8**, and removed all protecting groups by catalytic hydrogenolysis to achieve the first chemical synthesis of **1**-**3**. We further identified that the active principles of the immunostimulating activity of *A. pasteurianus* LPS is the lipid As **1**-**3**, confirming that LPS is an immunostimulatory component of kurozu. Structure-activity relationship studies revealed that the glucuronic acid residue, a characteristic structure of *A. pasteurianus* lipid A, is important for immune function and acid resistance ability.



[1] M. Hashimoto, K. Fukase, Y. Fujimoto, et al., *J. Bio. Chem.*, **2016**, *291*, 21184–21194. [2] Y. Takemoto, et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 14054–14059.

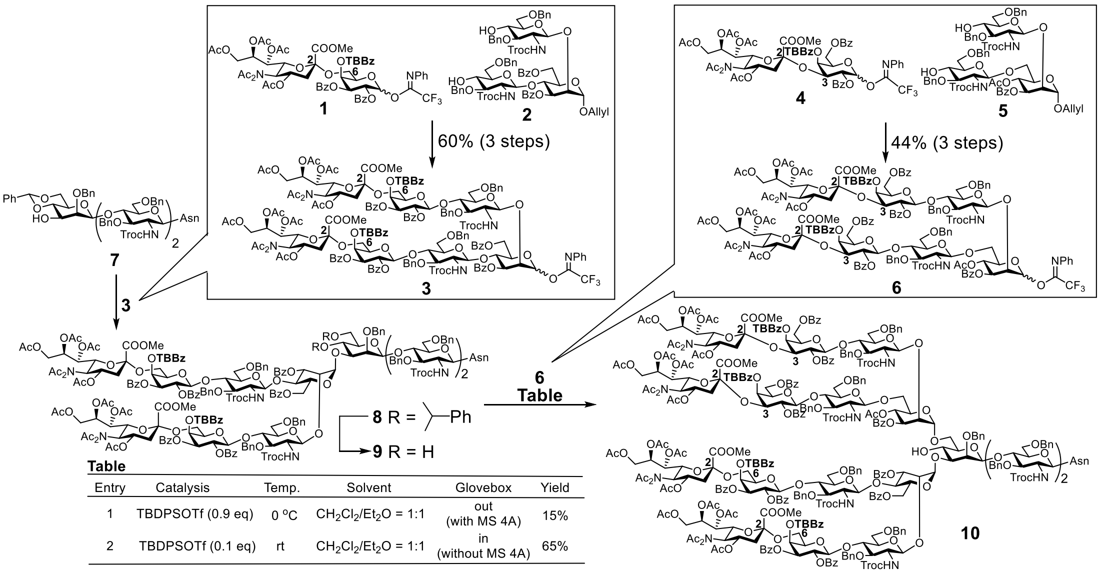
Chemical synthesis of tetraantennary sialyl *N*-glycans

([1]*Graduate School of Science, Osaka University,* [2]*Project Research Center for Fundamental Sciences, Osaka University*) ○Kumpei Yano,[1] Yoshiyuki Manabe,[1,2] Koichi Fukase[1,2]

Keywords: Sialyl *N*-glycan; glycosylation; glovebox; protecting group

Asparagine-linked glycans (*N*-glycans) play important roles in various biological events. For example, sialyl *N*-glycans interact with sialic acid-binding immunoglobulin-like lectins (Siglec) and are involved in regulation of the immune responses.

In this study, we investigated the synthesis of the fully sialylated tetraantennary *N*-glycans. Sialic acid containing fragments tend to form supramolecular aggregates, leading to reduced reactivity in glycosylations. Herein, to access this issue, we employed diacetyl protection of acetamide as well as *p*-*tert*-butyl benzoyl (TBBz) protection of hydroxy group to enhance the solubility of sialyl fragments.[1] First, heptasaccharides **3** and **6** were synthesized by the glycosylation using TBBz-protected siaα(2,6)gal **1** and siaα(2,3)gal **4**, respectively. The [7+3] glycosylation between **3** and **7** smoothly proceeded at low temperature to give **8** in good yield. After cleavage of benzylidene group, we found that glycosylation between **6** and **9** proceeded using mixed solvent of CH_2Cl_2 and Et_2O to obtain **10** probably due to the stabilization effect of the oxocarbenium ion intermediate by Et_2O.[2] Notably, the glycosylation without MS 4A in glovebox enabled catalytic glycosylation to afford **10** in good yield. We also investigated the synthesis of symmetric tetraantennary *N*-glycans via [7+7+3] glycosylations.



Table

Entry	Catalysis	Temp.	Solvent	Glovebox	Yield
1	TBDPSOTf (0.9 eq)	0 °C	$CH_2Cl_2/Et_2O = 1:1$	out (with MS 4A)	15%
2	TBDPSOTf (0.1 eq)	rt	$CH_2Cl_2/Et_2O = 1:1$	in (without MS 4A)	65%

1) Sachi Asano, Hide-Nori Tanaka, Akihiro Imamura, Hideharu Ishida, Hiromune Ando. *Org. Lett.* **2019**, *21*, 4197. 2) Masahiro Nagasaki, Yoshiyuki Manabe, Naoya Minamoto, Katsunori Tanaka, Alba Silipo, Antonio Molinaro, Koichi Fukase. *J. Org. Chem.* **2016**, *81,* 10600.

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21日(木) 9:00 ~ 11:30 H931(9号館 [3階] 931)

[H931-4am] 17. 生体機能関連化学・バイオテクノロジー

座長：岡村 秀紀、石渡 明弘

日本語

9:00 ~ 9:20

[H931-4am-01]

毛髪トリートメント効果を有する有機酸とアミンの新規化合物合成

〇片山 耕太郎[1]、宮本 紘幸[1]、望月 佑次[2]、新 菜摘[2]、山崎 祥子[3]、堀田 弘樹[1,4]、辻野 義雄[4] (1. 神戸大学大学院海事科学研究科、2. ロート製薬株式会社、3. 奈良教育大学、4. 神戸大学大学院科学技術イノベーション研究科)

日本語

9:20 ~ 9:40

[H931-4am-02]

神経分化の誘導および蛍光特性を有するチエノピリジン誘導体

〇園田 健登[1]、浅尾 和弥[1,2]、川口 真一[1,2]、川添 嘉徳[1,2] (1. 佐大農、2. 佐大院先進)

日本語

9:40 ~ 10:00

[H931-4am-03]

金触媒反応を引き金とする超分子ハイドロゲル形成

〇山本 智也[1,2]、中村 亜希子[2]、向峯 あかり[2]、田中 克典[2,3] (1. 大阪大学・大学院工学研究科、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室、3. 東京工業大学・物質理工学院・応用化学系)

英語

10:00 ~ 10:20

[H931-4am-04]

NIR Fluorescence analysis of the trypsin enzyme using unsymmetrical squaraine dye- peptide conjugate.

〇PRIYANKA Priyanka[1,2], Shekhar Gupta[1], Tamaki Kato[1] (1. Kyushu Institute of Technology,Japan, 2. Kyushu Institute of Technology, Japan)

10:20 ~ 10:30

休憩

英語

10:30 ~ 10:50

[H931-4am-05]

Near Infrared Fluorescent Detection of Protease Activity using Peptide-Bound Squaraine Dye

〇Shekhar Gupta[1], Priyanka Balyan [1], Sai Kiran Mavileti[1], Shyam Sudhir Pandey[1], Tamaki Kato[1] (1. Kyushu Institute of Technology)

英語

10:50 ~ 11:10

[H931-4am-06]

がん代謝物との[3+2]付加環化反応を利用したRI内用療法

〇大出 雄大[1]、石渡 明弘[2]、プラディプタ アンバラ[1]、田中 克典[1,2] (1. 東京工業大学・物質理工学院・応用化学系、2. 理化学研究所・開拓研究本部・田中生体機能合成化学研究室)

🏷 英語

11:10 ~ 11:30

[H931-4am-07]

RNA標的創薬を指向した新規RNA結合分子探索システムの開発

〇長澤 瞭佑[1,2]、鬼塚 和光[1,2]、岩田 遼平[1,2]、小松 馨[3,4]、宮下 映見[3,4]、壇辻 さやか[4]、村瀬 裕貴[1,2]、小澤 眞美子[1]、齊藤 博英[3]、永次 史[1,2] (1. 東北大多元研、2. 東北大院理、3. 京大CiRA、4. xFOREST Therapeutics)

日本化学会 第104春季年会 (2024)

毛髪トリートメント効果を有する有機酸とアミンの新規化合物合成

(神戸大学大学院海事科学研究科 [1]・ロート製薬株式会社 [2]・奈良教育大学 [3]・神戸大学大学院科学技術イノベーション研究科 [4]) ○片山 耕太郎 [1]・宮本 紘幸 [1]・望月 佑次 [2,4]・新 菜摘 [2]・山崎 祥子 [3]・堀田 弘樹 [1,4]・辻野 義雄 [4]

Synthesis of new compounds composed of organic acids and amines with hair treatment effects

(*[1]Graduate School of Maritime Sciences, Kobe University, [2]ROHTO Pharmaceutical Co., Ltd., [3]Nara University of Education, [4]Graduate School of Science, Technology and Innovation, Kobe University*) ○Kohtaro Katayama[1], Hiroyuki Miyamoto[1], Yuji Mochizuki[2,4], Natsumi Shin[2], Shoko Yamazaki[3], Hiroki Hotta[1,4], Yoshio Tsujino[4]

Many people are concerned about the age-related hair "waviness" and loss of shine, and techniques for treating hair to improve this are available. We have discovered that a new compound obtained from muconic acid and 2-aminoethanethiol (cysteamine) has a high ability in improving the habit and swell of the hair, Muconic acid is naturally occurring and used as a precursor for plastics and fibers1). Cysteamine, on the other hand, is already a substance used as cosmetics and perm solution.

Two types of the new compounds obtained were identified, mono-adducts and bis-adducts2), and it was discovered that it was possible to change the proportion of the compounds produced by adjusting the equivalent amount of cysteamine in the raw material and the heating time. It was also confirmed that the bis-adducts has higher effects on hair, such as hair straightening. These compounds are expected to be applied in hair cosmetics.

Keywords：Muconic Acid, Cysteamine, Michael Addition, Hair Straightening, Hair Treatment Agent

加齢に伴う髪の毛の「うねり」とツヤの低下に悩みを抱える人は多く、これを改善する毛髪処理技術が美容院等で提供されている。我々は、天然に存在し、プラスチックや繊維などの前駆体として利用されるムコン酸 1）と、化粧品やパーマ液として使用される 2-アミノエタンチオール（システアミン）を混合・加熱することによって得られた新規化合物に、毛髪の癖やうねりを改善させる高い機能があることを発見した。

得られた新規化合物はモノ付加体とビス付加体の 2 種類が確認され、原料のシステアミンの当量および加熱時間を調整することにより生成される化合物の割合を変えることが可能であることが発見された。また、縮毛矯正をはじめとする毛髪に対する効果はビス付加体の方がより高いことも確認された。

これらの化合物は頭髪化粧品への応用が期待される。

1）Curr. Opin. Biotechnol. 2017, 45:136–143
2）特許第 7232484 号

神経分化の誘導および蛍光特性を有するチエノピリジン誘導体

(1. 佐大農、2. 佐大院先進) ○園田 健登 [1]・浅尾 和弥 [1,2]・川口 真一 [1,2]・川添 嘉徳 [1,2]

The thieno[2,3-*b*]pyridine derivative that is a neural differentiation inducer and a fluorescent molecule

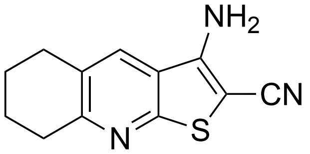
([1]*Faculty of Agriculture, Saga University,* [2]*Graduate School of Advanced Health Sciences, Saga University)* ○Kento Sonoda[1], Kazuya Asao[1,2], Shin-ichi Kawaguchi[1,2], Yoshinori Kawazoe[1,2]

Neurotrophins are proteins that have been implicated in the pathogenesis of various neurodegenerative diseases. However, due to several problems with protein reagents, alternative small molecule inducers of neural differentiation are needed. We found that small molecules of thieno[2,3-*b*]pyridine derivatives induced neural differentiation. Particularly, two derivatives exhibited significant neuritogenic activity in rat pheochromocytoma (PC12) cells. Moreover, one of the two derivatives displayed fluorescence and a discernible Stokes shift. Furthermore, several experiments indicated that this derivative induced neural differentiation in a manner independent of NGF. Therefore, this derivative has the potential as a novel neurotrophic factor and as a fluorescent reagent including bioimaging.

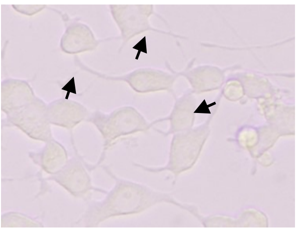
Keywords : Thienopyridine; Neural differentiation; Fluorescent reagent; PC12 cell; Bioimaging

神経成長因子（NGF）や脳由来神経栄養因子（BDNF）は神経細胞の成長や再生に関与するタンパク質であり、様々な神経変性疾患への関与が指摘されている。しかし、タンパク質試薬には価格や安定性などの問題点があるため、低分子化合物による神経分化誘導剤が必要とされている。我々は、チエノ[2,3-*b*]ピリジン誘導体が神経分化を誘導することを見出した。これを元に 13 種類の誘導体を合成し、ラット褐色細胞腫（PC12）細胞を用いて神経分化能を評価したところ、2 種類の誘導体が有意に神経分化を誘導することを示した。さらに、2 種類の誘導体のうち 3-Amino-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-2-carbonitrile（下図）は Stokes shift の大きい蛍光を示すことを確認した。

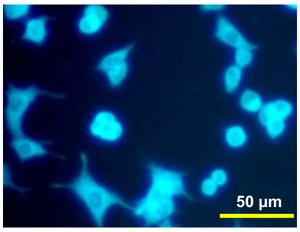
作用機序については NGF の受容体である TrkA の発現が少ない細胞でも神経分化を誘導すること、誘導体を添加した際の蛍光観察において、この誘導体は細胞膜内へ透過することが確認できたことなどから、この誘導体が NGF とは異なる作用機序で神経細胞の分化を誘導することが示唆された。したがって、この誘導体は新規の神経栄養因子としてだけでなく、化合物の蛍光特性による神経分化のバイオイメージング試薬への応用も期待される。



3-Amino-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-2-carbonitrile



Neural Differentiation



Fluorescence Imaging

金触媒反応を引き金とする超分子ハイドロゲル形成

（阪大院工[1]・理研開拓研究本部　田中生体研[2]・東工大物質理工[3]）◯山本智也[1,2]・中村亜希子[2]・向峯あかり[2]・田中克典[2,3]

Supramolecular hydrogelation triggered by gold catalysis ([1]*Graduate School of Engineering, Osaka University*, [2]*Biofunctional Synthetic Chemistry Laboratory, Cluster for Pioneering Research, RIKEN,* [3]*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ◯ Tomoya Yamamoto,[1] Akiko Nakamura,[2] Akari Mukaimine,[2] Katsunori Tanaka[2,3]

Low-molecular-weight gelators construct gels with supramolecular fibril formation. While enzyme-triggered supramolecular hydrogelation has been extensively developed to selectively construct gels in targeted organs and cells *in vivo*, there are few enzymes that localize in targeted sites. Therefore, novel triggers for supramolecular gelation are important to expand its applicability.

In this study, we developed the low-molecular-weight gelator whose gelation is triggered by gold catalysis, aiming at the *in vivo* construction of biomaterials with biocompatible transition-metal catalysts. Gold catalysis transforms the structure of the hydrophobic core of our gelator, which induces the transformation of the fibril morphology to construct a supramolecular gel. This fibril transformation alters the cytotoxicity against cancer cells, demonstrating its potential use in cancer therapy.

Keywords : Supramolecular gel, Gold catalysis, in vivo synthesis, Cancer therapy, Self-assembly

低分子ゲル化剤は、分子間での水素結合や疎水性相互作用によって超分子繊維構造を構築し、溶媒分子を包摂することでゲルを形成する。近年は酵素反応を引き金として、疾患部位でゲルを形成するゲル化剤が広く研究されているが、疾患部位で選択的に進行する酵素反応は限定される。我々はこれまでに、生体適合性の高い遷移金属触媒を生体内に導入し、プロドラッグの活性化に応用する研究を行ってきた。このような生体内に導入された遷移金属触媒による反応は、低分子ゲル化剤のゲル化の引き金としても応用可能であると考えられる。

本研究では、生体内での遷移金属触媒反応によってバイオマテリアルを構築する手法の確立を目指して、金触媒反応を引き金としてハイドロゲルを構築する低分子ゲル化剤を開発した[1)]。金触媒反応によって構造変換される保護基を疎水性部分として導入した低分子ゲル化剤を合成し、金触媒反応を引き金としてゲル化する条件を見出した。このゲル化剤は近触媒反応によって超分子繊維構造が変化し、この構造変化がゲル化の機構に重要であることが電子顕微鏡観察により示された。形成されたゲルはこの繊維構造変化によってがん細胞に対する毒性が顕著に変化し、がん治療への応用可能性が示された。

1) T. Yamamoto, A. Nakamura, A. Mukaimine, K. Tanaka, *Tetrahedron Chem.* in press, DOI:10.1016/j.tchem.2023.100058.

NIR fluorescence analysis of the trypsin enzyme with Unsymmetrical Squaraine Dye-Peptide Conjugate

Priyanka*, Shekhar Gupta, Shyam S. Pandey, and Tamaki Kato

Graduate School of Life Science and System Engineering, Kyushu Institute of Technology, 2-4, Hibikino, Wakamatsu, Kitakyushu, Japan, 808-0196

E-mail:priyankabalyan1705@gmail.com

Keywords: Squaraine dye, Dye-peptide conjugate, aggregation, bio-imaging

For imaging applications, fluorescent probes are immensely appreciated owing to their deep tissue penetration as well as autofluorescence of biomolecules is highly diminished. Dye probes having absorption and emission in the NIR region have great potential for biosensing and bio-imaging applications. A simple and effective solid-phase peptide synthesis method was used to design a near-infrared (NIR) sensitive fluorescent probe based on the dye-peptide conjugate (USQ 1 PC) for the detection of trypsin activity. Photophysical characterization was done using absorption and emission spectroscopies in different solvents. In phosphate buffer dye's absorption intensity decreased drastically due to the formation of dye aggregation and also fluorescence intensity was effectively quenched in PBS because of a strong dye-dye interaction. Added 2U/ml of trypsin enzyme in 10uM of dye-peptide conjugate USQ-1-PC showed more than a 2-fold increase in the fluorescence intensity. Hence, the trypsin enzyme hydrolyzed the peptide-dye combination, causing an efficient and quick recovery of the quenched fluorescence of USQ 1 PC. By efficiently and quickly detecting their activities, the currently developed NIR-sensitive substrate offers potential application for the diagnosis of protease-related disorders.

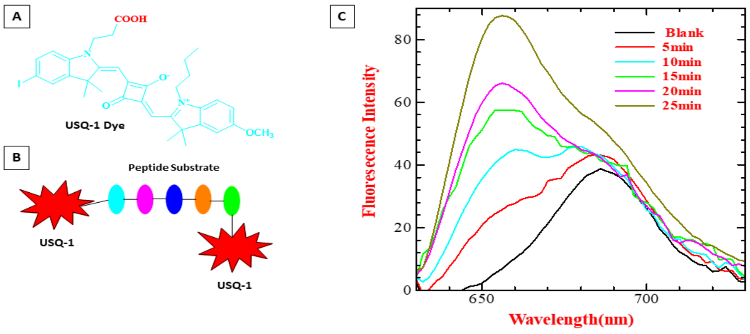


Figure 1 A) Structure of USQ-1dye B) Dye-Peptide conjugate C) Fluorescence emission spectra USQ-1 PC (10 μM) in PBS(0.1M) at pH 7.4 as a function of time after the addition of 2U/ml of trypsin enzyme.

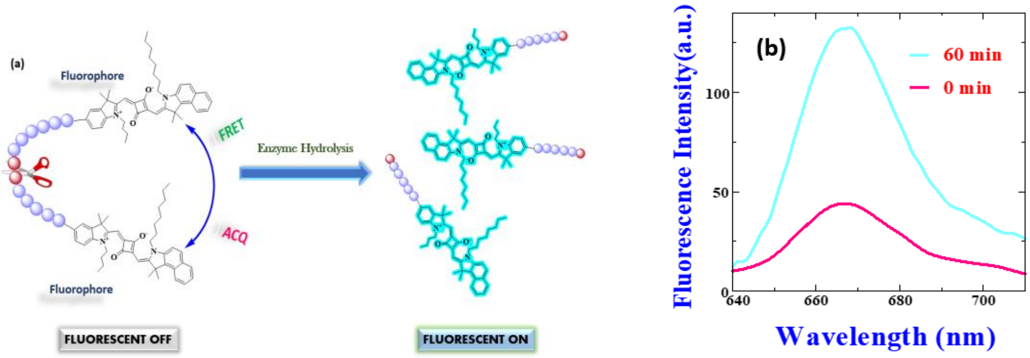
Near Infrared Fluorescent Probes for Detection of Protease Activity using Peptide-Bound Squaraine Dye

([1]*Graduate School of Life Science and System Engineering, Kyushu Institute of Technology,2-4 Hibikino, Wakamatsu-Ku, Kitakyushu-Shi, Fukuoka,808-0196, Japan*) ○Shekhar Gupta,[1] Priyanka,[1] Sai Kiran Mavletti,[1] Shyam S. Pandey,[1] Tamaki Kato[1]

Keywords: Squaraine Dye; Dye Peptide Conjugate; NIR; Aggregation; FRET

The majority of biomarkers for diseases are enzymes, and the regulation of these enzymes is both fundamental and crucial. Abnormal enzymatic activity can lead to disorders and diseases within biological systems. Recognizing the significance of enzymes in biology, researchers have developed numerous tools to map the activity of specific enzymes, aiming to understand their function and distribution. Near-infrared (NIR) fluorescence probe studies on enzymes offer a valuable approach to gaining insights into their roles within living systems, leveraging the natural advantages of NIR probes. There is high need of designing NIR fluorescent probes, aiming to create sensors capable of visualizing enzyme activity in the NIR region.

Squaraine dyes have excellent potostability with intensive absorption and strong fluorescence in the NIR region. In this work, dye peptide conjugate, SQ122-Lys-βAla-Ala-Phe-Ala-βAla-Lys-SQ122 has been developed as an NIR-fluorescent probe that can detect chymotrypsin activity. The probe showed complete quenching in PBS buffer but after the addition of enzyme re-aapearance of fluorescence emission was observed. Addition of 40 nM of enzyme in 5μM solution of dye peptide conjugate shows >3 fold increase in fluorescence intensity within 60 minutes. This increase in fluorescence emission can be attributed to both the FRET mechanism and the quenching behavior induced by aggregation in the dye-peptide conjugate.



(a)Schematic representation for the fluorescence turn-off/turn-on mechanism. (b)Fluorescen-ce spectra upon addition of 40 nM of enzyme in 5μM dye peptide conjugate solution.

がん代謝物との[3+2]付加環化反応を利用した RI 内用療法

（東工大物質理工 [1]・理研 開拓研究本部 田中生体研 [2]）○大出 雄大 [1]・石渡 明弘 [2]・プラディプタ アンバラ [1]・田中 克典 [1,2]

Internal radioisotope therapy utilizing [3+2] cycloaddition reaction with cancer metabolites

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Biofunctional Synthetic Chemistry Laboratory*, *Cluster for Pioneering Research, RIKEN*) ○Yudai Ode,[1] Akihiro Ishiwata,[2] Ambara R. Pradipta,[1] Katsunori Tanaka[1,2]

Adverse drug reactions are a major risk factor associated with cancer chemotherapy. However, the development of internal radioisotope (RI) therapy in recent years has been impressive in overcoming this problem. Our previous research has shown that acrolein is produced in large amounts in cancer cells but is negligible in healthy cells. Furthermore, we have discovered that aryl azides can react selectively with the acrolein of cancer cells to produce diazo compounds, which can then react with the nearby organelle to form a covalent bond within the cancer cells. In this study, we have designed an internal RI therapy using the azide-acrolein reaction and have utilized various RIs. We have investigated their antitumor effects, and the details of our findings will be discussed in the symposium.

Keywords: Internal radiotherapy; Cancer; Acrolein; [3+2] Cycloaddition; Aryl azide

がん治療分子の開発において、副作用の問題を避けるため、標的がん細胞のみを攻撃する分子標的治療（ミサイル療法）の研究が盛んである [1]。この一つとして、放射性治療分子を投与して、がん組織近傍から放射線治療を行う RI 内用療法が挙げられる。今回我々は、この RI 内用療法の新候補として、がん細胞内での有機合成化学反応と様々な RI(放射性同位体)を融合させた方法を考案した。

これまでに我々の研究室では、がん細胞内でアクロレインが大量に発生していることを発見した [2]。さらにアジド分子ががんから産生されるアクロレインと選択的に反応することにより、アジド由来分子ががん細胞内に効果的に留まる現象を見出している。これはがん患者のサンプルでも効果的に起こり、ヒトにも一般的な現象である。そこで、アジド分子に対して様々な RI で標識した新規分子をデザインし、がん細胞内での生体内合成反応による集積効果と RI を用いた分子によるがん殺傷効果を期待した。本研究では、放射性前駆体分子の合成、RI による標識効率の検討、さらに動物実験による腫瘍増加の抑制評価と生体内分布の評価を行なったので、これらの経緯について報告する [3]。

1) K. Fujiki, Y. Kanayama, S. Yano, N. Sato, T. Yokokita, P. Ahmadi, Y. Watanabe, H. Haba, K. Tanaka, *Chem. Sci.* **2019**, *10*, 1936.
2) T. Tanei, A. R. Pradipta, K. Morimoto, M. Fujii, M. Arata, A. Ito, M. Yoshida, E. Saigitbatalova, A. Kurbangalieva, J.-I. Ikeda, E. Morii, S. Noguchi, K. Tanaka, *Adv. Sci.* **2019**, *6*, 1801479.
3) Y. Ode, A. R. Pradipta, P. Ahmadi, A. Ishiwata, A. Nakamura, Y. Egawa, Y. Kusakari, K. Muguruma, Y. Wang, X. Yin, N. Sato, H. Haba, K. Tanaka, *Chem. Sci.*, **2023**,*14*, 8054-8060.

Development of a new screening system to discover RNA-binding small molecules for RNA-targeting therapeutics

(*[1]IMRAM, Tohoku University, [2]Graduate School of Science, Tohoku University, [3]CiRA, Kyoto University, [4]xFOREST Therapeutics*)○Ryosuke Nagasawa[1,2], Kazumitsu Onizuka[1,2], Ryohei Iwata[1,2], Kaoru R. Komatsu[3,4], Emi Miyashita[3,4], Sayaka Dantsuji[4], Hirotaka Murase[1], Mamiko Ozawa[1], Hirohide Saito[3], Fumi Nagatsugi[1,2]

Keywords: RNA-binding small molecule, Large scale analysis, Screening, Chemical probe, FID assay

RNA-binding molecules are attractive targets as therapeutic drugs for treatments of gene-related diseases and infections. Fluorescent indicator displacement (FID) assay is a method to identify novel RNA-binding molecules (**Fig. A**). To perform FID assays for various RNAs, the identification of the targetable RNAs that indicators bind to is required due to the lack of information on RNA binding of indicators. Therefore, a method to obtain binding profiles of indicators to different RNAs can provide useful information to identify a large number of targetable RNAs and make screening more efficient.

In this study, we utilized microarray technology[1] to obtain the binding profiles of fluorescent indicators, thiazole orange (TO) type probes[2] known as a light-up probe. Based on the obtained profiles, we selected targetable disease-related RNAs and identified several RNA-binding small molecules by FID assays. Interestingly, we found that different indicators provided different hit compounds, which encouraged us to develop new indicators to obtain novel hit compounds without missing them.

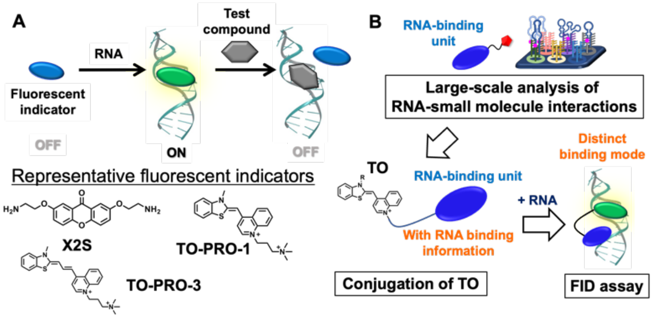


Fig. (**A**) FID assay, (**B**) novel fluorescent indicators.

We next aimed to develop new fluorescent indicators that have distinct binding modes from known indicators and discover novel RNA-binding small molecules by FID assays with the new indicators (**Fig B**). We synthesized TO-conjugated RNA-binding molecules with the large-scale data of RNA binding selectivity obtained by microarray technology, and their binding selectivity were generally retained even after conjugation with TO moiety. Furthermore, we conducted FID assays using disease-related RNAs and developed the indicators and successfully identified new hit compounds that were not detected with known TO-based indicator. In this presentation, we will report the detailed data on the novel indicators and the results of the FID assays.

1) H. Saito, et al., *Nat. Commun.* **2020**, *11*, 6275. 2) S. Nishizawa, et al., *Chem. Commun.* **2019**, *55*, 3183.

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21日(木) 9:00 ~ 11:30 🏛 H936(9号館 [3階] 936)

[H936-4am] 17. 生体機能関連化学・バイオテクノロジー

座長：細野 暢彦、川上 了史

🏷 英語
9:00 ~ 9:20
[H936-4am-01]
内部表面にピレンを化学修飾したタンパク質ナノケージTIP60の物性評価

○山下 舞佳[1]、宮本 憲二[1]、川上 了史[1] (1. 慶應義塾大学)

🏷 英語
9:20 ~ 9:40
[H936-4am-02]
オキシダーゼ模倣触媒作用のためのフェリチンケージ内でのヒスチジンクラスターの構築

○Tian Jiaxin[1]、Maity Basudev[1]、Pan Tiezheng[1]、Abe Satoshi[1]、Ueno Takafumi[1] (1. 東京工業大学)

🏷 英語
9:40 ~ 10:00
[H936-4am-03]
ナノ細孔への選択的吸着による変性タンパク質の除去

○武富 大空[1]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工)

🏷 英語
10:00 ~ 10:20
[H936-4am-04]
Tau由来ペプチドを融合した光応答性4量体タンパク質による微小管構造の光操作

○渡 宗英[1]、稲葉 央[1]、岩崎 崇[2]、角五 彰[3]、松浦 和則[1] (1. 鳥取大院工、2. 鳥取大院農、3. 京大院理)

10:20 ~ 10:30
休憩

🏷 日本語
10:30 ~ 10:50
[H936-4am-05]
蛍光タンパク質修飾人工ウイルス殻の細胞内自己集合

○坂本 健太郎[1]、山本 優香[1]、稲葉 央[1]、松浦 和則[1] (1. 鳥大院工)

🏷 日本語
10:50 ~ 11:10
[H936-4am-06]
SARS-CoV-2由来スパイクタンパク質を搭載したエンベロープウイルスレプリカの構築

○古川 寛人[1]、中村 圭祐[2]、稲葉 央[1]、佐々木 善浩[2]、秋吉 一成[2]、松浦 和則[1] (1. 鳥取大院工、2. 京大院工)

🏷 英語
11:10 ~ 11:30
[H936-4am-07]

Accurate Prediction of Protein pK_a by Geometric Deep Learning

○Shijie Xu[1], Akira Onoda[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

Characterization of protein nanocage TIP60 with pyrene-modified interior surface

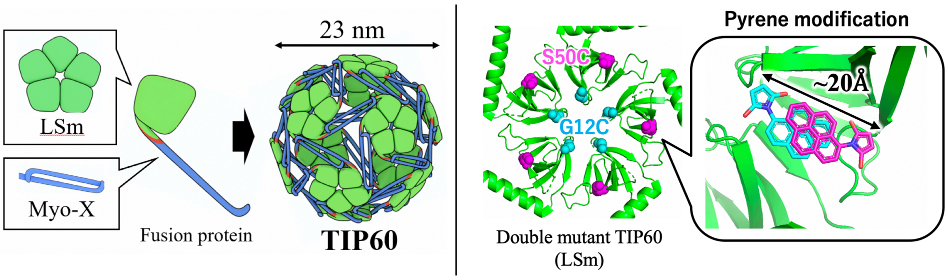
([1] *Keio University*) ([2] *Shinshu University*) ○Maika Yamashita,[1] Norifumi kawakami,[1] Ryoichi Arai,[2] Kenji Miyamoto[1]

Keywords: *Protein Nanoparticles; TIP60; Pyrene; molecular encapsulation; Thermostability*

Synthetic fluorescent molecules are widely used in various fields, from pure biology to medicine. For example, they are employed in detecting macromolecules of interest and serving as photosensitizers in photodynamic therapy. However, the poor water solubility limits their application range. The varieties of molecular materials to dissolve the hydrophobic fluorescent molecules in aqueous phase have thus developed thus far. Protein-based nanocages are one of the most promising materials for this purpose. Although natural proteins have hydrophilic surfaces, effort to hydrophobize the interior surface of nanocages provide confined hydrophobic compartments for encapsulating hydrophobic fluorescent molecules[1,2].

We recently produced a nanocage having hydrophobic interior surface based on an artificially designed 60-mer protein nanocage, TIP60[3,4](figure, left panel). The interior surface is modified by pyrenes. The singly modified TIP60, containing 60 pyrenes on the interior surface, allows for the accommodation of aromatic fluorescent molecule (Nile Red) through π-stacking[5]. However, the low encapsulation efficiency (2-3 mol./cage) is needed to improve.

In this study, to improve the efficiency, we aimed to increase the hydrophobicity of the interior surface of TIP60 by augmenting the number of modified pyrene molecules. Specifically, we designed a double mutant G12C and S50C as modification sites (figure, right panel). The modified TIP60 could encapsulate 20-30 mol./cage of Nile Red. We found that the doubly modified TIP60 exhibited higher thermostability than both unmodified and singly modified TIP60. This improvement is attributed to the π-stacking of pyrene molecules on the interior surface of TIP60. As shown in the figure, two pyrenes are positioned where they can interact with each other. Indeed, we found the excimer formation of pyrene molecules. Accordingly, the developed doubly modified TIP60 could be used as the potential nanocarrier for hydrophobic fluorescent molecules and as a component of a light harvesting system.



1.) T.G.W. Edwardson *et al., Natt. Commun.* **2020** 2.) D. Ren *et al., Adv. Function. Mater..* **2012** 3.) N. Kawakami *et al., Angew. Chem. Int. Ed.* **2018** 4.) J. Obata *et al., Chem. Commun.*, **2021** 5.) M. Yamashita *et al., ChemPlusChem,* **2023**

Construction of histidine clusters within a ferritin cage for oxidase-mimetic catalysis

([1]*Grad. School of Life Sci. and Technol., Tokyo Institute of Technology)*
○Jiaxin Tian[1], Basudev Maity[1], Tiezheng Pan[1], Satoshi Abe[1] and Takafumi Ueno[1]

Keywords: Ferritin cage; Histidine cluster; X-ray crystal structure; Peroxidase activity.

Developing materials that mimic the enzyme, Horseradish peroxidase (HRP) [1] has a huge practical importance as oxidative catalysis to break down harmful substances in the environment, especially the organic pollutants. Most peroxidase mimetic materials rely on metal complexes or nanoparticles, with only a few being metal-free [2]. This is due to the lack of systematic investigations to create peroxidase mimics, like how to position the side chains and other elements. With this background, we aimed to develop a simple metal-free artificial peroxidase mimic by rational design of catalytic sites on a robust protein surface.

To achieve the goal, we employed the 24-mer ferritin cage as a suitable template due to the high stability and unique structural features, especially the confined environment, which is known to be beneficial for catalytic performance. Since histidine is known to activate H_2O_2, we systematically introduced a series of histidine residues near the 2-fold symmetric interface, which is the most stable part of the ferritin cage and characterized the mutants by X-ray crystallography. Peroxidase activities were evaluated in presence of H_2O_2 and re-designed the mutants to find the key requirements for catalysis.

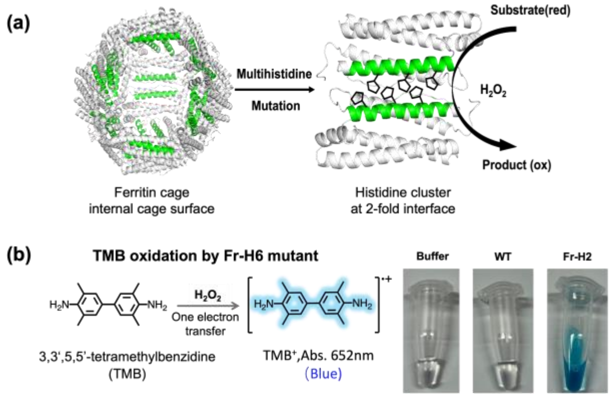


Figure1. Overview of the work. (a) Schematic representation showing the construction of a catalytic histidine-rich site near 2-fold symmetric interface (b) Oxidation of TMB substrate by a histidine-rich ferritin mutant in the presence of H_2O_2.

This presentation will describe the systematic design of metal-free peroxidase mimetic by suitable positioning of Histidine in B-helix near the 2-fold symmetric interface of the ferritin cage (Fig.1a). We evaluated the catalytic oxidation of 3,3,5,5-Tetramethylbenzidine (TMB) as a model substrate by Ferritin mutants in the presence of H_2O_2 (Fig. 1b). The detailed X-ray crystal structure analysis with comparison of catalytic activities by various ferritin mutants will be discussed.

Reference. 1) E. Derat et al., *J. Phys. Chem. B,* 2006. 2) Y. Z. Li *et al.*, *ACS Appl. Matter. Interfac*es, 2017. 3) J. Fan, *et al.*, *Biomaterials*, 2012. 4)Taher, M, et al., *Angew. Chem. Int. Ed.*, 2022

Removing Denatured Proteins by Selective Adsorption in Nanopores

([1]*Graduate School of Engineering, University of Tokyo*) ○Hirotaka Taketomi,[1] Nobuhiko Hosono,[1] Takashi Uemura[1]

Keywords: Metal–organic frameworks; Nanopore; Denatured protein; Adsorption; Purification

Denatured proteins tend to form aggregates and inhibit the function of other proteins, causing serious diseases. Purification of proteins to eliminate such denatured fraction is an important technique in protein engineering and research on protein drug discovery. Although size exclusion chromatography (SEC) is commonly employed to remove denatured proteins, its limited scalability poses challenges for industrial applications.[1] In this study, we present a highly efficient and scalable technique for selectively removing denatured proteins from a mixture of native and denatured proteins using metal–organic frameworks (MOFs) (**Figure 1a**).

We chose a MOF (Cr-MIL-101) as the porous adsorbent due to its appropriate window/pore size for selectively sieving polypeptide chains. Lysozyme was chosen as the model protein, and we measured the adsorption isotherms for the lysozymes in both its native and denatured states in the solution. Interestingly, denatured lysozyme exhibited a significantly higher adsorption amount compared to its native form. We fitted the isotherms to the Langmuir model and determined the maximum loading capacity for native and denatured lysozymes to be 0.04 g/g and 0.42 g/g, respectively. Given the MOF's pore window size of approximately 1.5 nm, the denatured and fully unfolded (reduced) lysozyme, with a thickness of ~1 nm, was selectively inserted and captured in the pore, while the native folded form, with a diameter of 2-4 nm, was rejected. We performed selective adsorption experiments using a mixture of native and denatured lysozyme (at a ratio of 2:8, w/w). By adding the MOF to the protein mixture, we successfully removed only the denatured protein from the solution, achieving a purity level of >99% based on activity (**Figure 1b**).

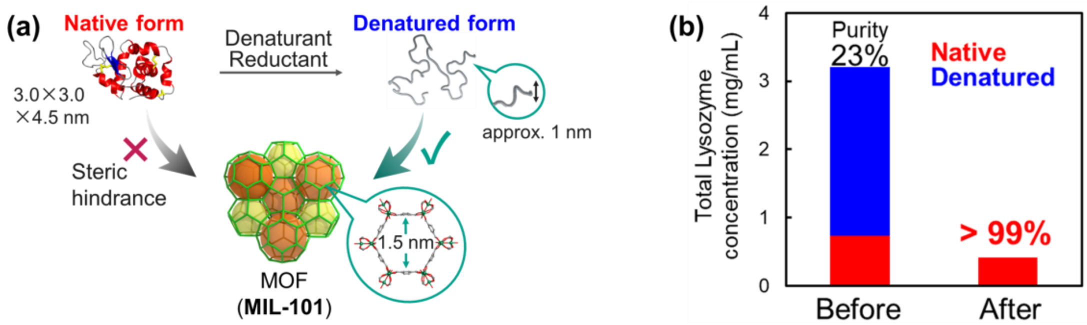


Figure 1. (a) Schematic illustration of the selective protein adsorption in the MOF. (b) Fraction of native (red) and denatured (blue) lysozyme in the solution before and after adding the MOF.

1) A. P. J. Middelerg, *Trends Biotechnol.* **2002**, *20*, 437–443.

Optical manipulation of microtubule structures by Tau-derived peptide-fused light-responsive tetrameric protein

([1]*Graduate School of Engineering*, *Tottori University*, [2]*Graduate School of Agricultural Science*, *Tottori University*, [3]*Graduate School of Science*, *Kyoto University*) ○Soei Watari,[1] Hiroshi Inaba,[1] Takashi Iwasaki,[2] Akira Kakugo,[3] Kazunori Matsuura[1]

Keywords: Microtubule; Tubulin; Tau-derived peptide; Light-responsive protein; Optical manipulation

Microtubules are tubular cytoskeletons with a 15 nm inner diameter, which are formed by polymerization of tubulin proteins. Microtubule involves crucial cell functions such as cell division, cell deformation, and cell migration. We have previously developed a Tau-derived peptide (TP) which bound to the inner surface of microtubules.1) We also have succeeded in generation of various microtubule superstructures such as doublet and branched microtubules by multivalent binding of TP-fused tetrameric protein (Azami Green).2) Herein, we focused on other tetrameric protein Dronpa, which converts reversibly monomer and tetramer by irradiation of light with different wavelengths (Fig. 1a). In this study, we constructed TP-fused Dronpa (TP-Dronpa) to manipulate microtubule accumulation and dispersion states by light irradiation (Fig. 1b).

Firstly, we assessed binding site of TP-Dronpa to microtubules. It is indicated that TP-Dronpa can bind to microtubule outer surface by incubation with formed microtubules. Strikingly, we could observe bundled microtubules when TP-Dronpa (tetramer) bound to microtubules, while the TP-Dronpa (monomer) showed no effect to form bundled microtubules (Fig. 1b). Furthermore, we have succeeded in manipulating microtubule accumulation and dispersion states by light irradiation through changing the assembly number (tetramer and monomer) of microtubule-bound TP-Dronpa.

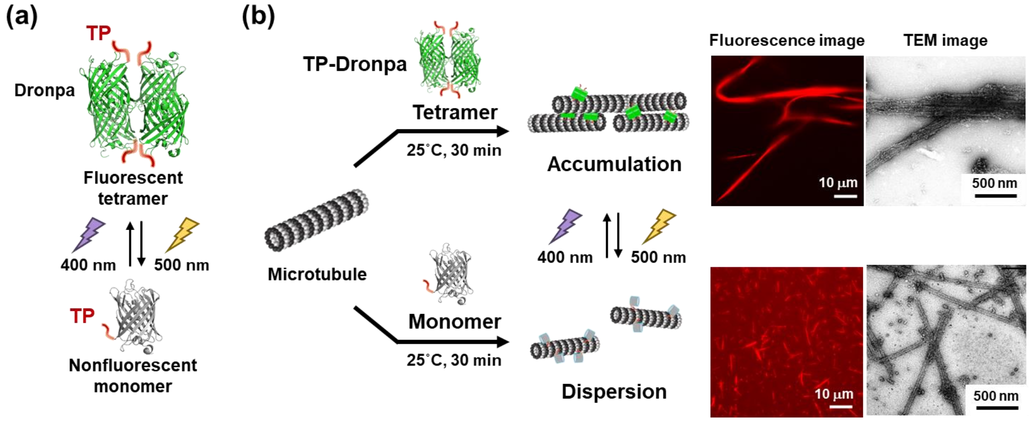


Fig. 1. (a) Photo-conversion of TP-Dronpa. (b) Optical manipulation of microtubule structures by TP-Dronpa.

1) H. Inaba, T. Yamamoto, A. M. R. Kabir, A. Kakugo, K. Sada, K. Matsuura, *Chem. Eur. J.*, **24**, 14958 (2018).

2) H. Inaba, Y. Sueki, M. Ichikawa, A. M. R. Kabir, T. Iwasaki, H. Shigematsu, A. Kakugo, K. Sada, T. Tsukazaki, K. Matsuura, *Sci. Adv.*, **8**, eabq3817 (2022).

蛍光タンパク質修飾人工ウイルス殻の細胞内自己集合

（鳥大院工 [1]）○坂本 健太郎 [1]・山本 優香 [1]・稲葉 央 [1]・松浦 和則 [1]

In-cell self-assembly of fluorescent protein-modified artificial viral capsid

([1]*Graduate School of Engineering, Tottori University*) ○Kentarou Sakamoto[1], Yuka Yamamoto[1], Hiroshi Inaba[1], Kazunori Matsuura[1]

Peptide/protein-based self-assembling nanocages are expected to be utilized in many fields, however, they are mainly used extracellularly, and there are few papers reporting in-cell self-assembly. We have developed “artificial viral capsid” self-assembled from β-Annulus peptide derived from capsid protein of tomato bushy stunt virus.1) While we have been reporting intracellular delivery of artificial viral capsid self-assembled at outside of cells, it is still unknown whether the delivered capsid retain its spherical structure, and there is no report showing in-cell self-assembly of artificial viral capsid. In this presentation, we report in-cell self-assembly of the capsid and evaluation method of the assembly (Fig. 1). β-Annulus conjugated with fluorescent protein (FP) (β-Annulus-FP) is expected to form artificial viral capsid decorated with FPs. β-Annulus-FP expressed in cells were isolated and purified. The in vitro self-assembly was assessed by dynamic light scattering, transmission electron microscopy, and fluorescence polarization measurements. Fluorescence polarization measurement of cells expressing β-Annulus-FP suggested the in-cell self-assembly of the capsid. FRET measurement, TEM observation of the cells and super-resolution microscopy also implied the in-cell self-assembly.

Keywords：In-Cell Self-Assembly, Artificial Viral Capsid, Fluorescence Polarization

ペプチド／タンパク質からなる自己集合性ナノケージは多方面への応用が期待される超分子集合体であるが、これらはあくまで「細胞外」での利用が主であり、「細胞内」で自己集合するナノケージの報告例は数少ない。我々は、トマトブッシースタントウイルス由来の 24 残基β-Annulus ペプチドが水中で自己集合し「人工ウイルス殻」を形成することを見出している 1)。人工ウイルス殻を用いた「細胞外」から「細胞内」への送達の例は複数存在する一方で、送達された人工ウイルス殻が細胞内でその形状を保持しているかどうかは不明である。本発表では人工ウイルス殻の細胞内自己集合の実現及びその評価系の構築について報告する(Fig. 1)。蛍光タンパク質 (FP) とβ-Annulus を結合したβ-Annulus-FP を培養細胞内で発現させ、単離精製した後、動的光散乱・電子顕微鏡観察・蛍光異方性測定により人工ウイルス殻の形成が確認された。β-Annulus-FP 発現細胞の蛍光異方性測定により細胞内自己集合による人工ウイルス殻の形成が示唆され、また細胞内自己集合は FRET 測定、発現細胞の電子顕微鏡観察および超解像顕微鏡観察からも示唆することができた。

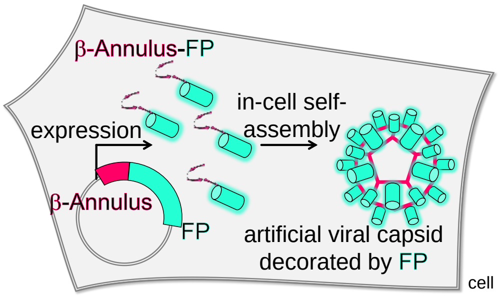


Figure 1. Schematic illustration of in-cell self-assembly of artificial viral capsid.

1) K. Matsuura, *Chem. Commun.*, **2018**, *54*, 8944–8959.

SARS-CoV-2 由来スパイクタンパク質を搭載したエンベロープウイルスレプリカの構築

（鳥取大院工[1]・京大院工[2]）〇古川 寛人[1]・中村 圭祐[2]・稲葉 央[1]・佐々木 善浩[2]・秋吉 一成[2]・松浦 和則[1]

Construction of enveloped viral replica equipped with spike protein derived from SARS-CoV-2. ([1]*Graduate School of Engineering, Tottori University*, [2]*Graduate School of Engineering, Kyoto University*) 〇Hiroto Furukawa,[1] Keisuke Nakamura,[2] Hiroshi Inaba,[1] Yoshihiro Sasaki,[2] Kazunari Akiyoshi,[2] Kazunori Matsuura[1]

Previously, we have demonstrated that β-annulus peptide derived from TBSV self-assembled into artificial viral capsids in water, which can encapsulate some guest macromolecules and can be modified with some functional materials at the surface. Recently, we have succeeded in constructing the artificial enveloped capsid via electrostatic interaction of cationic lipid bilayer and anionic capsid. In this study, we constructed enveloped viral replica equipped with spike protein derived from SARS-CoV-2 and evaluated its interaction with ACE2 receptor by imaging flow cytometry and quartz crystal microbalance. In addition, we evaluated interaction between S protein-equipped viral replica and ACE2 receptor expressed on cell membrane.

Keywords : β-Annulus peptide; Artificial Viral Capsid; Envelope; Self-assembly; SARS-CoV-2

SARS-CoV-2 は、膜上のスパイクタンパク質(S protein)が宿主細胞表面の ACE2 受容体と結合し、細胞内に侵入する 1)。最近、Ferritin や *de novo* タンパク質集合体表面へ S protein 又はその Receptor binding domain (RBD)を直接修飾した研究が報告されているが、エンベロープ型集合体表面への S protein の搭載は未だ達成されていない。我々はこれまで、TBSV 由来β-Annulus ペプチドの自己集合により構築される人工ウイルスキャプシドにカチオン性脂質二分子膜を複合化したエンベロープウイルスレプリカの構築に成功した 2)。本研究では、無細胞タンパク質発現系により SARS-CoV-2 由来 S protein を搭載したエンベロープ型ウイルスレプリカを構築し(Fig. 1)、ACE2 受容体との結合評価をイメージングフローサイトメトリー及び水晶振動子マイクロバランス (QCM) 法により詳細に解析した。さらに、膜局在 mlACE2-EGFP を強制発現させた HeLa 細胞への蛍光標識 S protein 搭載エンベロープウイルスレプリカの結合を CLSM 観察により評価した。その結果、ウイルスレプリカ上に搭載した S protein のおいても遊離・固定化 ACE2 受容体に nM オーダーの解離定数で強く結合し、HeLa 細胞膜上の ACE2 受容体に対しても結合することが確認された。以上の結果より、ACE2 受容体結合能を有する S protein 搭載エンベロープウイルスレプリカの構築が示唆された。

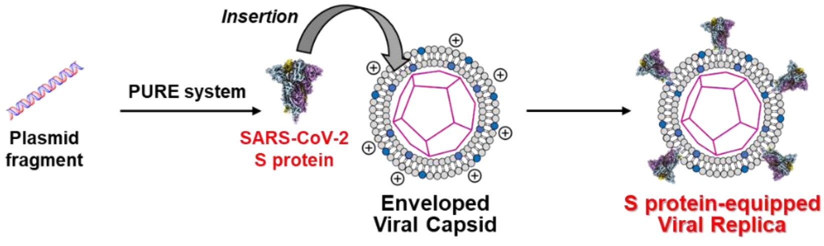


Figure 1. Schematic illustration of construction of SARS-CoV-2 S protein-equipped viral replica.

1) L. Duan et al., *Front. Immunol.*, **11**, 576622 (2020).
2) H. Furukawa et al., *Chem. Commun.*, **56**, 7092 (2020).

Accurate Protein pK_a Prediction by Geometric Deep Learning

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Shijie Xu,[1] Akira Onoda [1,2]

Keywords: Protein pK_a prediction; Geometric deep learning

Protein pK_a plays a crucial role in many biological processes, such as protein folding, protein-ligand binding, and enzyme catalysis, by regulating the protonation states of ionizable residues. Unlike the residues in the solvent, the deeply buried residues in the protein interior are probably largely affected by the electrostatic interactions with the surrounding residues, and thus their pK_a values are often shifted from the standard values in the solvent. However, modeling such interactions is intractable due to the complexity of the protein structure and remains a challenging problem.

In the past decades, many computational methods have been developed to predict protein pK_a values and achieved great success. Among them, the most popular approach includes the continuum electrostatics methods [1], which are based on the Poisson-Boltzmann equation (PBE), and the empirical methods [2]. However, PBE methods are computationally expensive while the empirical methods are not accurate enough. Recently, machine learning methods [3] have been proposed to predict protein pK_a values, which show a great superiority in the trade-off between prediction accuracy and computational cost. Besides, most of these methods are based on black-box machine learning models, which are not capable of providing physical insights into protein pK_a values. Therefore, a new method that is both accurate, fast, and explainable is needed.

In this work, we propose a novel approach to predict protein pK_a based on geometric deep learning, termed EquipKa, which not only exhibits high prediction accuracy at a fast speed but also explains how the protein structure determines the protein pK_a shift through the learned geometric features. We demonstrate the effectiveness of our approach on a benchmark dataset and show that our approach outperforms the state-of-the-art methods, including the PBE, empirical, and machine learning methods, as shown in Fig. 1a. Besides, the pK_a shift contributions from different neighboring atoms are also visualized as cylinders in Fig. 1b where the thickness represents the strength and colors represent the direction of contributions.

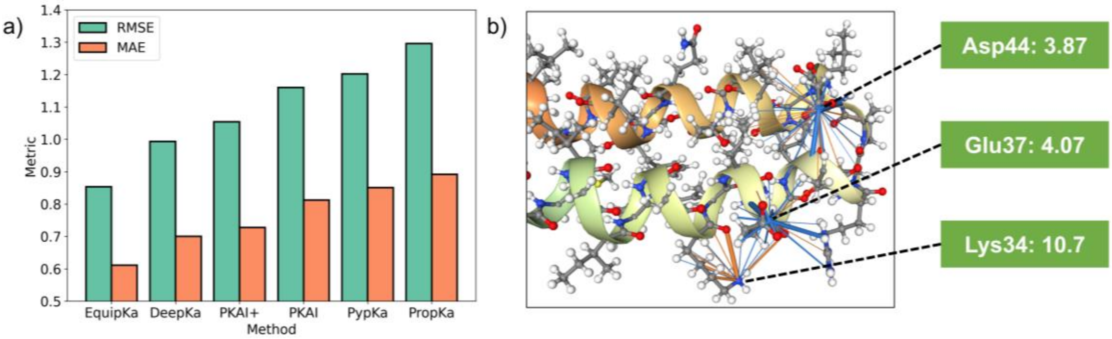


Figure 1. a) The performance of state-of-the-art pK_a predictors. Our EquipKa achieved the best score on the RMSE (root-mean-square error) and MAE (mean absolute error). b) The predicted pK_a values of Lys34, Glu37, and Asp44 in protein (1a91) by EquipKa. Blue represents higher than model pK_a while orange is lower. pK_a shift contributions from neighboring atoms are also plotted as llines with blue color (positive shift) or orange color (negative shift).

1) Reis P. B.P.S. *et al. J. Chem. Inf. Model.* 2020, *60*, 4442-4448. 2) Søndergaard, C. R. *et al. J. Chem. Theory Comput.* 2011, *7*, 525-537. 3) Cai, Z., *et al. ACS omega* 2021, *63*, 34823-34831.

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21日(木) 13:00 ~ 15:30 H931(9号館 [3階] 931)

[H931-4pm] 17. 生体機能関連化学・バイオテクノロジー

座長：森廣 邦彦、神谷 由紀子

英語
13:00 ~ 13:20

[H931-4pm-01]

FRETを応用した抗miRNA核酸の作用機序解析法の開発

〇朱 紅宇[1]、神谷 由紀子[1,2]、浅沼 浩之[1] (1. 名古屋大学、2. 神戸薬科大学)

日本語
13:20 ~ 13:40

[H931-4pm-02]

非環状型人工核酸からなる抗miR-21核酸の開発

〇神谷 由紀子[1,2]、佐藤 史経[2]、浅沼 浩之[2] (1. 神薬大、2. 名大)

英語
13:40 ~ 14:00

[H931-4pm-03]

アゾベンゼン塩基含有DNAアプタマーによる受容体活性の可逆的光制御

〇若野 将大[1]、村山 恵司[2]、植木 亮介、浅沼 浩之[2]、山東 信介[1] (1. 東京大学大学院工学系研究科、2. 名古屋大学大学院工学系研究科)

14:00 ~ 14:10

休憩

英語
14:10 ~ 14:30

[H931-4pm-04]

メチル化DNAが鎖置換能を持つDNAポリメラーゼに与える影響

〇富澤 美月[1]、渡邊 貴和子[1]、塚越 かおり[1]、池袋 一典[1] (1. 東京農工大学)

英語
14:30 ~ 14:50

[H931-4pm-05]

Vinyl-quinazolione derivatives-based RNA alkylation and the single-nucleotide resolution analysis by next generation sequencing

〇Yutong Chen[1,2], Kazumitsu Onizuka[1,2], Kaoru Richard Komatsu[3], Emi Miyashita[3,4], Kaho Maeta[3], Hirohide Saito[4], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku University, 2. Department of Chemistry, Graduate school of Science, Tohoku University, 3. xFOREST Therapeutics, 4. CiRA, Kyoto University)

英語
14:50 ~ 15:10

[H931-4pm-06]

弱酸性微小環境応答性人工核酸塩基を用いたがん選択的DNAアプタマーの開発

〇陳 鈺媛[1]、森廣 邦彦[1]、根本 祐衣[1]、市村 晃人[1]、植木 亮介[1]、山東 信介[1]、岡本 晃充[1] (1. 東京大学)

日本語

15:10 ~ 15:30

[H931-4pm-07]

フッ素官能基修飾核酸における修飾基の数とリンカー構造が細胞取り込みおよびsiRNAノックダウン機能に与える影響

○高津 正子[1]、森廣 邦彦[1]、太田 有羽[1,2]、相川 光介[1]、岡添 隆[1,2]、岡本 晃充[1] (1. 東京大学、2. AGC株式会社)

Developing the intracellular FRET imaging approach to elucidate the mechanism of anti-miRNA oligonucleotides

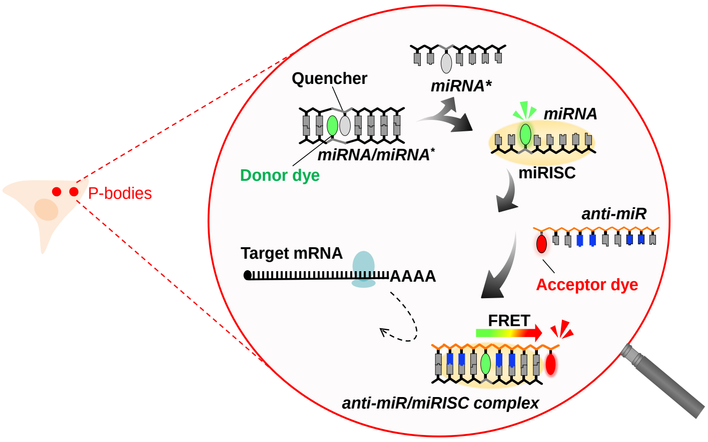
([1]*Graduate School of Engineering, Nagoya University,* [2] *Laboratory of Bioanalytical Chemistry, Kobe Pharmaceutical University*) ○Hongyu Zhu,[1] Yukiko Kamiya,[1,2] Hiroyuki Asanuma

Keywords: Anti-miRNA Oligonucleotide; Imaging analysis; FRET

The aberrant expression of microRNA (miRNA) such as miR-21 has been implicated in many human diseases, especially cancer. Therefore, miRNA inhibition has emerged as an attractive therapeutic strategy. For instance, anti-miRNA oligonucleotides (anti-miRs) are chemically modified synthetic oligonucleotides that complement and inhibit aberrant miRNA function. To enhance anti-miR efficacy, our lab has developed enzyme-resistant and effective SNA-anti-miRs with our original acyclic nucleic acid, serinol nucleic acid (SNA), backbone, and the artificial nucleobase 2,6 - diaminopurines (D) for increasing miRNA affinity.[1]

While anti-miRs exhibit efficacy in suppressing miRNA function, the molecular details of anti-miR-mediated miRNA inhibition in cells remain unclear. Key questions remain regarding the interaction between the anti-miRNA and target miRNA and the subcellular localization of the complex. To address this, we developed a Förster resonance energy transfer (FRET) system to monitor the anti-miR and miRNA interactions in cells.[2]

In this system, we designed and optimized the miRNA/miRNA* probe with the donor dye (BO) on miRNA and quencher (methyl red; MR) on miRNA*. Additionally, we paired miRNA on miRISC with Cy3 labeled SNA-anti-miR acceptor to enable FRET upon anti-miRNA and miRNA on miRISC binding. This system provides a novel application for exploring the mechanisms underlying anti-miR action and the intracellular interactions of therapeutic agents, including anti-miRs and siRNAs in cells. More details of the FRET system properties will be presented at the conference.



1) Y. Kamiya *et al.*, *ChemBioChem.*, **2017**, 18, 1917–1922.
2) Z. Hongyu *et al.*, *ACS Chem Biol,* **2023**, 18, 10, 2281–2289.

非環状型人工核酸からなる抗 miR-21 核酸の開発

(神薬大 [1]、名大工 [2]) ○神谷 由紀子 [1,2]、佐藤 史経 [2]、浅沼 浩之 [2]

Development of Anti-miR-21 Oligonucleotide by Acyclic Nucleic Acids

([1]*Faculty of Pharmaceutical Sciences, Kobe Pharmaceutical University*, [2]*Graduate School of Engineering, Nagoya University*) ○Yukiko Kamiya,[1,2] Fuminori Sato,[2] Hiroyuki Asanuma[2]

Artificial nucleic acids that have high nuclease resistance and affinity to natural oligonucleotides are promising as nucleic acid drugs. We have been attempted to develop anti-miRNA oligonucleotide (AMO) by using Serinol nucleic acid (SNA).[1] To develop SNA-based AMO against miR-21 (AMO21) which has complementary region, SNA-SNA hybridization should be avoided. For this, we prepared AMO having 2,6-diaminopurine (D) and 2-thiouracil (sU) known as the pseudo-complementary base pairs.[3, 4] As a result, self-association of the SNA-based AMO was inhibited and anti-miR21 activity was enhanced. Then, we evaluated the properties of the SNA-AMO21 in vivo using model mice. Tumor growth in the xenograft model mice was suppressed upon injection of SNA-based AMO. No significant hepatotoxicity was observed.

Keywords：Antisense; artificial nucleic acid; miR-21; miRNA

酵素耐性能や RNA 親和性を向上させる人工核酸は核酸医薬への応用が期待されている。非環状型人工核酸 Serinol nucleic acid (SNA)は、非常に高い酵素耐性を示すことから、核酸医薬品のプラットフォームとして有望である。そこで、癌や線維症などの疾患組織において過剰発現する miR-21 を標的とした SNA からなる Anti-miRNA oligonucleotide(SNA-AMO21)の開発に取り組んでいる[1]。しかし、SNA は自己親和性が高いために、自己相補配列を有する miR-21 を標的とした場合、自己相補領域を介した SNA 自身の相互作用によって、anti-miRNA 活性が低下してしまう問題があった。そこで本研究では、自己相互作用を抑制する手法を開発し、高い miR-21 阻害活性をもつ SNA-AMO21 の開発を目指した。

本研究の目的のために、まずは Pseudo-complementary 塩基対である 2,6-ジアミノプリン（D）と 2-チオウラシル（sU）の SNA アミダイトモノマーの新規合成法を確立した[2,3] 。開発した手法を用いて D, sU を導入した SNA-AMO21 を調製し、自己相互作用ならびに anti-miRNA 活性を評価した。その結果、D と sU を導入することにより、期待通りに SNA-AMO21 の二次構造形成の阻害、さらに miR-21 阻害活性の劇的な向上を達成した。そこで、D, sU を導入した SNA-AMO21 の in vivo 評価を実施した。Xenograft モデルマウスに対し、SNA-AMO21 を投与した結果、SNA-AMO21 投与群にて有意に腫瘍増殖が抑制された。また、特段の肝毒性や腎毒性は観察されなかった。以上、我々は高活性で安全性の高い SNA-AMO21 の開発に成功した。

[1] Y. Kamiya, *et al.*, *ChemBioChem*, **2017**, *18*, 1917-1922.

[2] Y. Kamiya, *et al.*, *Chem. Asian J.*, **2020**, *15*, 1266-1271.

[3] F. Sato, *et al.*, *J. Org. Chem.*, **2023**, *88*, 796-804.

アゾベンゼン塩基含有 DNA アプタマーによる受容体活性の可逆的光制御

（東京大学大学院工学系研究科[1]、名古屋大学大学院工学研究科[2]）○若野 将大[1]・村山 恵司[2]・植木 亮介・浅沼 浩之[2]・山東 信介[1]

Reversible optical control of receptor activity by azobenzene base-containing DNA aptamer.

([1] *Graduate School of Engineering, The University of Tokyo*, [2] *Graduate School of Engineering, Nagoya University*) ○Masahiro Wakano,[1] Keiji Murayama,[2] Ryosuke Ueki, Hiroyuki Asanuma,[2] Shinsuke Sando[1]

Certain cellular functions are regulated by dimerization and activation of receptor tyrosine kinases, followed by the cell signaling circuits.[1] DNA aptamers have the ability to bind to target receptors specifically, and are attracting attention as a new molecular technology for the regulation of receptor dimerization due to their ease of synthesis and potential application of DNA nano technology. However, conventional DNA aptamers generally activate the target receptors only once. To address this issue, we developed a Met-aptamer whose agonistic activity can be optically controlled by introducing azobenzene bases.[2] The azobenzene base undergoes *cis-trans* isomerization upon photoirradiation, switching between the active dimeric and inactive monomeric structures of the aptamer, allowing its activity and activation time to be reversibly regulated in response to light. We have confirmed that Met phosphorylation and downstream cell signaling in Hela cells can be regulated by the aptamer and light irradiation pattern.

Keywords: DNA aptamer, azobenzene, artificial DNA, receptor, optical control

ある種の細胞機能は、受容体チロシンキナーゼの二量体化と活性化、それに続く細胞シグナル伝達回路によって制御されている[1]。この動態を解明するため、受容体の二量化を人工的に制御する手法が求められている。DNA アプタマーは、標的受容体と特異的に結合する機能を持ち、合成の容易さや DNA ナノ工学の応用可能性から、受容体を制御する新しい分子技術として注目されている。しかし、従来の DNA アプタマーは基本的に一度しか受容体を活性化できない。この問題に対し、我々は、アゾベンゼン塩基[2]を DNA アプタマーに導入し、光によってアゴニスト活性を可逆的に制御できる Met 受容体アプタマーを開発した。本アプタマーは、光照射によりアゾベンゼン塩基が *cis-trans* 異性化し、アプタマーの活性な二量体構造と非活性な単量体構造とが切り替わることで、その活性や活性化時間を光に応じて可逆的に調整できる。このアプタマーを用い、Hela 細胞の Met のリン酸化や下流細胞シグナルをアプタマーおよび光照射パターンによって制御できることを確かめた。

1) M. A. Lemmon and J. Schlessinger, *Cell.* **2010**, *141*, 1117–1134.
2) H. Asanuma et al., *Angew. Chem.* **2001**, *40*, 14, 2671–2673.

The influence of methylated DNA on DNA polymerase with strand displacement ability

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*)
○Mizuki Tomizawa,[1] Kiwako Watanabe,[1] Kaori Tsukakoshi,[1] Kazunori Ikebukuro[1]

Keywords: DNA methylation, DNA polymerase with strand displacement ability

DNA methylation is an important epigenetic event which alters gene expression without a change in nucleotide sequence. The methylated cytosine bearing methyl group to the carbon 5 position of the cytosine ring is common in eukaryotes. Cytosine methylation usually occurs in CpG islands in promoter regions which CpG oligodeoxynucleotides densely present. The aberrant CpG methylation relates to inborn disorder, cancer, mental disorder and so on. Therefore, it is required to develop a method to detect CpG methylation in target genomic regions rapidly for the clinical diagnosis.

We reported that DNA structure, G-quadruplexes (G4)[1] and i-motif [2] changed by CpG methylation, and the initial elongation efficiency of PCR[3] of the template DNA bearing those structures also changed by CpG methylation. G4 and i-motif are the non-canonical steric structures formed by guanine-rich or cytosine-rich nucleic acids. Based on these findings, we developed methylated DNA detection methods by detecting DNA structure differences. In addition, it was reported that double-stranded DNA (dsDNA) cause stabilization[4] or destabilization[5] by CpG methylation recently.

Therefore, we assumed that amplification efficiency of DNA polymerase with strand displacement ability changes by CpG methylation. This DNA polymerase can displace the DNA encountered during elongation. We used loop-mediated isothermal amplification (LAMP) for use of DNA polymerase with strand displacement ability, one of the methods that amplifies DNA under isothermal conditions with strand displacement DNA synthesis[6] and have been used widely in infection test. LAMP reaction was performed to synthetic DNA bearing the sequence of upstream region of dopamine receptor D2 (DRD2) which associated with schizophrenia, and the androgen receptor (AR) promotor region which associated with hormone-independent prostate cancer of the human genomic DNA. LAMP products were measured by turbidity, fluorescence intensity and electrophoresis analysis. We observed that significant differences of amplification time from unmethylated DNA and methylated DNA. It is possible that detection of CpG methylation becomes easy and rapid by our findings.

1) H. Hasegawa, *Int. J. Mol. Sci.*, **2021**, *22*, 13159. 2) D. Oshikawa, *Int. J. Mol. Sci.*, **2022**, *23*, 6467. 3) W. Yoshida, *Anal. Chem.* **2016**, *88*, 7101-7107. 4) J. Yoo, *Nat. Commun*., **2016**, *7*, 11045. 5) A. Furukawa, *Nucleic Acids Res.*, **2021**, *49*, 2. 6) T. Notomi, *Nucleic Acids Res.*, **2000**, *28*, 12.

Vinyl-quinazolinone derivatives-based RNA alkylation and the single-nucleotide resolution analysis by next generation sequencing

([1]*IMRAM, Tohoku University*, [2]*Department of Chemistry, Graduate School of Science, Tohoku University,* [3]*xFOREST Therapeutics,* [4]*CiRA, Kyoto University*) ○Yutong Chen,[1,2] Kazumitsu Onizuka,[1,2] Kaoru R. Komatsu,[3] Emi Miyashita,[3,4] Kaho Maeta,[3] Hirohide Saito,[4] Fumi Nagatsugi[1,2]

Keywords: Vinyl-quinazolinone (VQ); RNA alkylation; Next generation sequencing.

RNA transcripts largely participated various processes in cellular biology and disease onset, providing unlimited potential for RNA-targeted therapeutics. Small molecules with good cell-permeability and structural adaptation have been extensively studied for RNA biology investigation and regulation. Chemically reactive compounds which can form covalent bond with RNAs were exploited for probing and labeling to target RNA.

Previously, we reported that vinyl-quinazolinone (VQ) derivatives converted to a reactive-ON state and selectively reacted with higher-ordered RNA by the elimination of leaving groups (Figure 1).[1] In this study, we would report the optimization of VQ's reactivity and investigated the protonation-accelerated reaction mechanism.[2] Furthermore, we synthesized azide-functionalized VQ with two different RNA binder and analyzed the alkylation reactivity towards RNA library. In this approach, the reverse transcription to record mutations induced by probe adduct into cDNA and amplification followed by next generation sequencing analysis, enabled detection of alkylation frequency along the sequence and alkylation location at single-nucleotide resolution. We will report these results in detail.

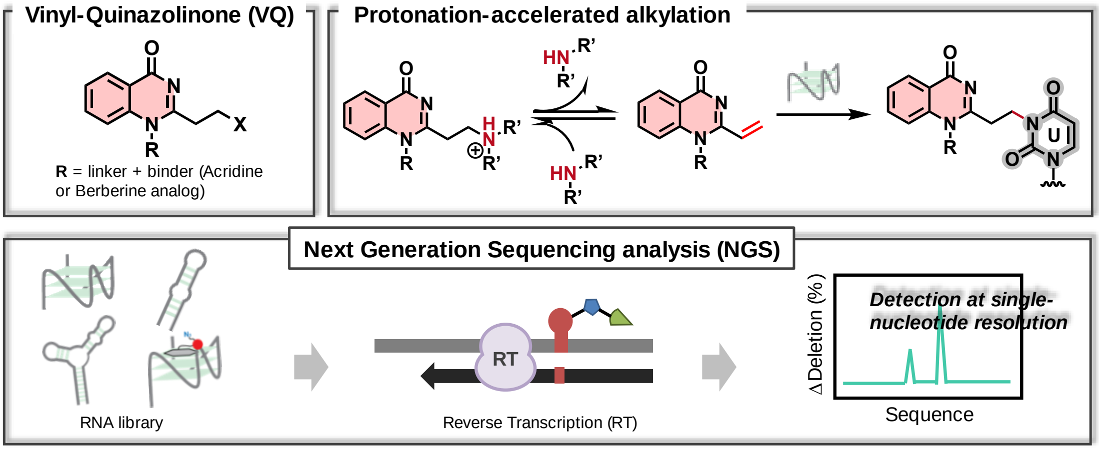


Figure 1. VQ-based RNA alkylation and large-scale analysis by next generation sequencing

1) K. Onizuka, M. E. Hazemi, F. Nagatsugi, *et al.*, *Nucleic Acids Res*. **2019**, *47*, 6578–6589.
2) Y. Chen, K. Onizuka, M. E. Hazemi, F. Nagatsugi, *Bioconjugate Chem*. **2022**, *33*, 2097–2102.

Development of cancer-selective DNA aptamer using weakly acidic microenvironment-responsive artificial nucleobase

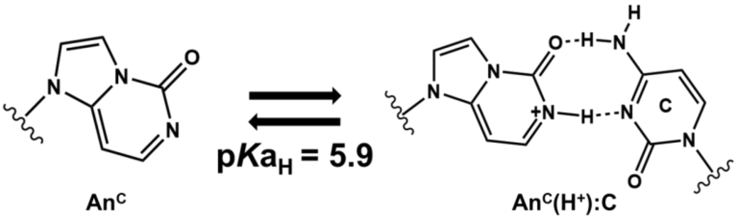
([1]*Graduate School of Engineering, The University of Tokyo*) ○Yuyuan Chen,[1] Kunihiko Morihiro,[1] Yui Nemoto,[1] Akito Ichimura,[1] Ryosuke Ueki,[1] Shinsuke Sando,[1] Akimitsu Okamoto[1]

Keywords: DNA Aptamer; pH-responsive; Artificial Nucleobase

Since the pH around cancer cells is biased to be weakly acidic (approximately 6.2-6.9) compared to that around normal cells, where the pH is maintained at approximately 7.4[1], the use of pH-responsive nucleic acid molecules in cancer drugs is expected to enhance cancer selectivity and reduce adverse effects on patients. **An^{C}**, an artificial nucleobase previously developed in this laboratory, was found to have a pKa$_{H}$ of 5.9, and it is thought to be capable of reversibly forming a base pair with cytosine by protonation at pH around cancer cells[2].Therefore, we thought that it would be possible to develop highly cancer-selective nucleic acid drugs by using this artificial nucleobase **An^{C}** to the formation of versatile duplexes.

In our research, **An^{C}** nucleotides are introduced into DNA aptamer CSL1 to equip them with weakly acidic microenvironment responsiveness and cancer cell selectivity. The sequence of CSL1 was designed on the basis of SL1, which has been reported as an antagonist of C-Met.[3] We synthesized three types of DNA aptamers **CSL1s**, **CSL1-I**, **CSL1-II**, and **CSL1-III** which containing 1, 2, and 3 **An^{C}** nucleotides, respectively.

To evaluate the stabilization of **CSL1** under acidic environment, the melting temperature (T_m) of each **CSL1** was measured in PBS (pH 7.4 or pH 6.4). **CSL1-I** showed higher T_m in pH 6.4 than in pH 7.4, indicating stabilization in acidic condition by **An^{C}** introduction. We also evaluated the pH-responsive inhibitory effects of **CSL1s** by quantifying phosphorylated C-Met with ELISA in A549 cells in buffer (pH 7.4 or pH 6.4) mimicking microenvironment of normal and tumor tissue. The wound healing assay also be used to evaluate the inhibitory effect of **CSL1s** on cancer cell migration.



1) Anderson N M, Simon M C. *Current Biology*, **2020**, *30*, 921.
2) Morihiro, K, Moriyama, Y, Nemoto, Y, Osumi, H. Okamoto, A, *Journal of the American Chemical Society*, **2021**, *143*, 14207.
3) Ueki R, Sando S. *Chemical Communications*, **2014**, *50*, 13131.

フッ素官能基修飾核酸における修飾基の数とリンカー構造が細胞取り込みおよび siRNA ノックダウン機能に与える影響

（東大院工[1]・AGC 株式会社[2]）○高津 正子[1]・森廣 邦彦[1]・太田　有羽[1,2]
・相川 光介[1]・岡添 隆[1,2]・岡本 晃充[1]

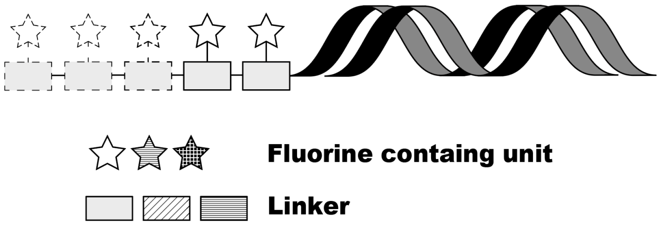
The Impact of Linker Structure and the Number of Fluorine-containing Functional Groups of Nucleic Acids on Cellular Uptake and siRNA Knockdown Efficacy

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*AGC Inc.*) ○Masako Takatsu[1], Kunihiko Morihiro[1], Yu Ota[1,2], Kosuke Aikawa[1], Takashi Okazoe[1,2], Akimitsu Okamoto[1]

The cellular uptake and knockdown efficacy of chemically modified siRNA are critical factors in the development of effective nucleic acid-based therapeutics. We investigated the cellular uptake of perfluoroalkyl-modified DNA and observed variations in the mode of cellular entry based on the number of conjugated perfluoroalkyl units 1). In this study, we designed a series of siRNAs modified with fluorine-containing functional groups, incorporating varying linker structures and numbers of modified groups. Cellular uptake was assessed through flow cytometry analysis, and knockdown efficacy was evaluated by measuring target gene expression levels. This insight will contribute to the rational design of nucleic acid therapeutics.

Keywords : Nucleic acid therapeutics; Conjugated-DNA/RNA; Drug delivery; Fluorine; Cellular uptake

核酸医薬開発において、目的に応じた細胞内送達機能を付与する化学修飾設計のためには、化学構造による細胞取り込みの違いや機能への影響を測定評価することが重要である。私たちは最近、ペルフルオロアルキル基（PFC 基）を化学修飾した DNA の細胞膜透過性を評価し、PFC 基の数により細胞内導入効率や導入形態が異なることを見出した 1)。本研究では、siRNA のセンス鎖に環境負荷の少ないフッ素官能基を修飾し、そのリンカー構造や修飾ユニット数を変えた場合に細胞取り込み効率とノックダウン効果がどのように影響を受けるかを、フローサイトメトリーおよび標的 mRNA の定量により評価した。



1) Cellular Penetration and Intracellular Dynamics of Perfluorocarbon-Conjugated DNA/RNA as a Potential Means of Conditional Nucleic Acid Delivery. Takatsu. M, Morihiro. K, Watanabe. H, Yuki. M, Hattori. T, Noi. K, Aikawa. K, Noguchi. K, Yohda. M, Okazoe. T, Okamoto. A, *ACS Chem. Biol.* **2023**, 18(12), 2590–2598.

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21日(木) 13:00 ~ 15:30 H932(9号館 [3階] 932)

[H932-4pm] 17. 生体機能関連化学・バイオテクノロジー

座長：中田 栄司、堂浦 智裕

日本語

13:00 ~ 13:20

[H932-4pm-01]

アデノシンA_{2A}受容体サブタイプ選択的な光応答性リガンドの開発およびその構造基盤

○鈴木 啓文[1]、堂浦 智裕[1]、荒谷 剛史[2]、浅田 秀基[2]、岩田 想[2]、清中 茂樹[1] (1. 名古屋大学、2. 京都大学)

日本語

13:20 ~ 13:40

[H932-4pm-02]

新規イメージングプローブによるシナプス可塑性時のAMPA受容体の精密動態解析

○曽我 恭平[1]、柴田 晃大[1]、Hansel Adriel[2]、藤原 孝彰[2]、南後 恵理子[2,3]、清中 茂樹[1] (1. 名古屋大学大学院・工、2. 東北大学・多元研、3. 理研 SPring-8)

日本語

13:40 ~ 14:00

[H932-4pm-03]

BODIPY類を骨格とする赤色および深赤色蛍光性分子による細胞および組織内脂質滴の可視化

○吉原 利忠[1]、宇田 梨紗[1]、飯島 鈴七[1]、嶋貫 真由子[1]、塩崎 秀一[1] (1. 群馬大)

日本語

14:00 ~ 14:20

[H932-4pm-04]

細胞内酸化還元ホメオスタシスを制御し得る低分子アロステリックジスルフィド/ジセレニド試薬

○三神 瑠美[1]、金村 進吾[2]、奥村 正樹[3]、荒井 堅太[1] (1. 東海大、2. 関学大、3. 東北大)

14:20 ~ 14:30

休憩

英語

14:30 ~ 14:50

[H932-4pm-05]

蛍光や生物発光を利用した生細胞内RNA動態の可視化解析

○吉村 英哲[1]、江口 正敏[1]、上田 善文[1]、小澤 岳昌[1] (1. 国立大学法人東京大学)

日本語

14:50 ~ 15:10

[H932-4pm-06]

組織内チオール代謝物イメージング及び組成解析を実現するTLC蛍光ラベル化剤の開発

○西原 達哉[1]、鈴木 我空[1]、西田 光輝[1]、塚目 莉加[1]、田邉 一仁[1] (1. 青山学院大学)

日本語

15:10 ~ 15:30

[H932-4pm-07]

新規ミスマッチ認識分子の創生とその特性

○武井 史恵[1]、山田 直生[1]、比留間 寿美代[1] (1. 防衛医科大学校)

アデノシン A_{2A} 受容体サブタイプ選択的な光応答性リガンドの開発およびその構造基盤

（名大院工[1]・京大院医[2]）○鈴木 啓文[1]・松葉 佑弥[1]・堂浦 智裕[1]・荒谷 剛史[2]・浅田 秀基[2]・岩田 想[2]・清中 茂樹[1]

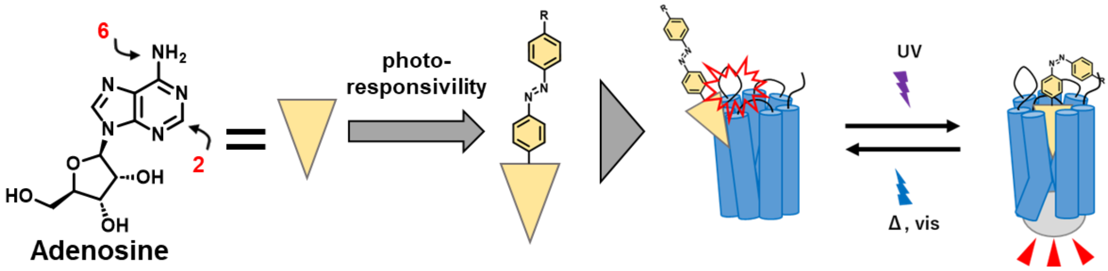
Development and structural analysis of subtype-selective photoresponsive ligands for adenosine A_{2A} receptor

([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Medicine, Kyoto University*) ○Harufumi Suzuki,[1] Yuya Matsuba,[1] Tomohiro Doura,[1] Tsuyoshi Araya,[2] Hidetsugu Asada,[2] So Iwata,[2] Shigeki Kiyonaka[1]

Adenosine A_{2A} receptor ($A_{2A}R$), a member of the class A G protein-coupled receptor (GPCR) family, is widely expressed *in vivo*. Elucidation of the physiological function of $A_{2A}R$ is highly desirable, because $A_{2A}R$ is involved in various diseases such as insomnia and Parkinson's disease. Here, we focused on photopharmacology, which enables the control of the activity of target molecules with high spatiotemporal resolution by light irradiation. We designed and synthesized adenosine derivatives with a photoresponsive azobenzene moiety at the 2- or 6-position of the purine group. Cell-based screening of these compounds identified $A_{2A}R$-selective photoresponsive ligands. Of note, the crystal structure of $A_{2A}R$ with the $A_{2A}R$-selective photoresponsive ligand revealed the photoresponsive mechanism and the subtype-selectivity of the ligand.

Keywords : Adenosine receptors; Photopharmacology; Azobenzene; optical control; GPCR

アデノシン A_{2A} 受容体（$A_{2A}R$）は G タンパク質共役型受容体（GPCR）の class A に属し、アデノシンを共通の内在アゴニストとする 4 つのサブタイプ（A_1、A_{2A}、A_{2B}、A_3）の 1 種である。$A_{2A}R$ は生体内で広範に発現し、不眠症やパーキンソン病をはじめとする様々な疾患に関与するため、$A_{2A}R$ が持つ生理機能のより詳細な解明が望まれる。サブタイプ選択的なリガンドは $A_{2A}R$ の生理機能の解明に有用であるが、生体内に発現する $A_{2A}R$ に広く作用するため、特定細胞における $A_{2A}R$ の生理機能の解明には適していない。そのため、$A_{2A}R$ の活性を部位特異的に制御する手法が求められる。私達は光照射により高い時空間分解能で標的分子の活性制御が可能な光薬理学に着目し、アデノシンの 2 位または 6 位に光応答性部位となるアゾベンゼン部位を持つ光応答性リガンドを設計および合成した。細胞応答に基づくスクリーニングより $A_{2A}R$ 選択的な光応答性リガンドを見出し、光応答性リガンドと $A_{2A}R$ の複合体の共結晶構造解析より光応答性リガンドの光作動性と $A_{2A}R$ に対するサブタイプ選択性の構造基盤を解明した。



新規イメージングプローブによるシナプス可塑性時の AMPA 受容体の精密動態解析

（名大院工[1]・東北大 多元研[2]・理研 SPring-8[3]）〇曽我 恭平[1]・柴田 晃大[1]・Hansel Adriel[2]・藤原 孝彰[2]・南後 恵理子[2,3]、清中 茂樹[1]

A novel imaging probe to quantify AMPA receptors trafficking during synaptic plasticity

([1]*Graduate School of Engineering, Nagoya University*, [2]*IMRAM, Tohoku University,* [3]*RIKEN SPring-8*) 〇Kyohei Soga[1], Akihiro Shibata[1], Hansel Adriel[2], Takaaki Fujiwara[2], Eriko Nango[2,3], Shigeki Kiyonaka[1]

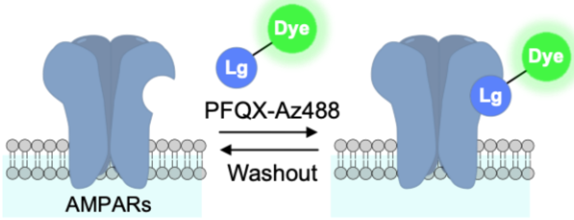
Synaptic activities are regulated by various stimuli in our brain. In the case of memory formation, the strength of synaptic transmission is changed, which is called synaptic plasticity. In this research, we developed a novel imaging probe, PFQX-Az488, to easily and reversibly visualize AMPA receptors which play a pivotal role in synaptic plasticity.

The labeling of endogenous AMPA receptors in neuronal cells with PFQZ-Az488 is accomplished within a brief 30-second. Of note, the effect of labeling to neuronal cells is minimal because PFQX-Az488 can be easily washed out after observation. In cultured hippocampal neurons, this probe allowed to quantify the change of expression levels of AMPA receptors during synaptic plasticity. Furthermore, we achieved a detailed quantification of AMPA receptors trafficking by combining PFQX-Az488 labeling method with a conventional method which we have reported previously.

Keywords : Fluorescent imaging probe; AMPA receptor; Synaptic plasticity

我々の脳内では神経細胞は様々な刺激に応じて、その活動が制御されている。特に記憶形成時にはシナプス可塑性と呼ばれる神経活動の変化が生じる。今回、我々はシナプス可塑性に密接に関与することが知られる、AMPA 型グルタミン酸受容体（AMPA 受容体）を簡便かつ可逆的に可視化可能な蛍光イメージングプローブ PFQX-Az488 を開発した。AMPA 受容体結合部位を用いた X 線結晶構造解析により、PFQX-Az488 結合の分子基盤も明らかにした。

PFQX-Az488 は神経細胞に添加するだけで AMPA 受容体を標識可能であり、その結合飽和時間は 30 秒以内と非常に高速である。また、簡便に washout を行うことができるため、AMPA 受容体のスナップショットイメージングに適している。実際に、PFQX-Az488 を用いて、海馬培養神経細胞でシナプス可塑性時における AMPA 受容体の発現量変化を解析することに成功した。また、以前に我々が報告した AMPA 受容体ケミカルラベル化法1)と組み合わせることで、シナプス可塑性時の AMPA 受容体の動態解析にも成功したので、本講演ではその詳細も報告する。



1) Ojima *et al. Nat. Commun.* 2021.

BODIPY 類を骨格とする赤色および深赤色蛍光性分子による細胞および組織内脂質滴の可視化

（群馬大院理工）○吉原 利忠・宇田 梨紗・飯島 鈴七・嶋貫 真由子・塩崎 秀一

Visualization of lipid droplets in cells and tissues by using red and deep-red fluorescent molecules based on BODIPY (*Graduate School of Science and Technology, Gunma University*)

○Toshitada Yoshihara, Risa Uda, Suzuna Iijima, Mayuko Shimanuki, Shuichi Shiozaki

We have designed and synthesized red and deep-red fluorescent molecules based on BODIPY to visualize lipid droplets in living cells and tissues using fluorescence microscopy. The developed molecules exhibited high fluorescence quantum yields in solution. We demonstrated that these molecules selectively accumulated into lipid droplets in living cells and could be visualized lipid droplets in the liver of healthy and fatty liver model mice.

Keywords : Lipid Droplet; Fluorescence; Cell; Tissue; NAFLD

近年、アルコールを摂取しない成人において、過剰な脂質が肝臓に蓄積して発症する非アルコール性脂肪肝疾患(NAFLD)が世界中で急増している。NAFLD の初期過程では肝臓への過剰な脂質蓄積によって、肝細胞内に多数の脂質滴(LD)の発現が見られる。このため脂質滴をイメージングする方法の開発が進められている。特に脂質滴に選択性を示す小分子蛍光性色素と蛍光顕微鏡を用いた方法は、細胞内の脂質滴を高感度に検出・イメージングすることが可能である。我々は、クマリン類を用いて培養細胞だけでなく生きたマウス肝臓内の脂質滴をイメージングできる青色および緑色蛍光色素を開発した[1, 2]。本研究では、BODIPY 骨格を有する化合物 1(Fig. 1)の 2, 8 位に芳香族置換基を導入することで、赤色および深赤色領域に蛍光を示す分子(2〜5、Fig. 1)を開発し、それらを用いた培養細胞およびマウス肝臓内の脂質滴イメージングについて報告する。

ジブチルエーテル中において化合物 1 は 515 nm に蛍光極大波長(λ_{flu})を示した。一方、化合物 2〜5 のλ_{flu} は 623、605、674、658 nm であり、化合物 2 および 3 では赤色蛍光、化合物 4 および 5 では深赤色蛍光を示した。よって、化合物 1 の 2、8 位に芳香族置換基を導入することでπ共役系が拡張し、蛍光極大波長が大きく長波長シフトすることが明らかとなった。化合物 2〜5 を HeLa 細胞の培地に添加し 30 分培養後、共焦点蛍光顕微鏡で観察したところ、多数の顆粒状のオルガネラがイメージングされた。市販の脂質滴蛍光色素との共染色から化合物 2〜5 は、脂質滴に選択的に分布することが示された。化合物 2〜5 を麻酔下にある脂肪肝モデルマウスに尾静脈投与し、共焦点蛍光顕微鏡で肝臓表面を観察したところ、化合物 3、5 では投与 30 分後において、肝臓内の脂質滴をイメージングできることが示された。

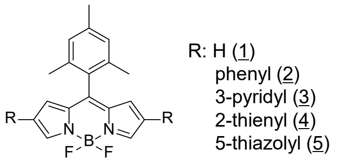


Fig. 1 Chemical structures of LD probe

1) K. Purevsuren et al., *J. Photochem. Photobiol A: Chem.* **2023**, *438*, 114562.
2) T. Yoshihara et al., *Anal. Chem.* **2020**, *92*, 4996.

細胞内酸化還元ホメオスタシスを制御し得る低分子アロステリックジスルフィド/ジセレニド試薬

（東海大理化[1]・東海大先進生命研[2]・東北大際研[3]・関学大理化[4]）○三神 瑠美[1,2]・金村 進吾[3,4]・奥村 正樹[3]・荒井 堅太[1,2]

Small allosteric disulfinde/diselenide reagents may regulate cellular redox homeostasis

([1]*School of Science, Tokail University*, [2]*Institute of Advanced Biosciences, Tokai University,* [3]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University,* [4]*School of Science and Technology, Kwansei Gakuin University*)○Rumi Mikami,[1, 2] Shingo Kanemura,[3, 4] Masaki Okumura,[3] Kenta Arai[1, 2]

Enzymes adroitly regulate their own enzymatic activities by altering peptidyl conformations around the active sites through association of a cofactor or partial chemical modification. Mimicking such the allosteric regulation mechanism of the actual enzymes would be useful in controlling the activity of artificial catalysts to accordingly exert the catalytic functions in cells. Therefore, this study aims to develop biocompatible artificial catalysts, which mimic an allosteric enzyme and modulate their catalytic activities by changing their molecular structure with Ca^{2+} as an allosteric effector. First, diselenide (SeSe)- and disulfide (SS)-containing compounds fused with a Ca^{2+}-chelator was prepared. Coordination of Ca^{2+} into the molecules altered their own structures, decreasing the thermodynamic stability of the SeSe and SS bonds and hence readily converting into corresponding catalytically active selenol and thiol states. The compounds effectively catalyzed oxidative folding and reduction of reactive oxygen species in the presence of Ca^{2+}, and similar regulation of the activities was observed in cells.

Keywords : Pritein folding; Antioxidant; Diselenide; Disulfide; Allosteric catalyst

酵素は、補因子の会合や化学修飾を受けることで、活性部位周辺のタンパク質立体構造を変化させ、酵素活性を巧みに制御している。このような実際の酵素のアロステリック制御機構を模倣することは、低分子触媒の活性を制御し、細胞内で適切に機能を発揮させるうえで有効であると考えられる。そこで、本研究では、生体内のアロステリック酵素を模倣し、アロステリック因子とするCa^{2+}によって分子構造を変化させることで、触媒活性を変調する生体適合型の人工触媒の開発を目指した。初めに、Ca^{2+}キレーターを融合させた含ジセレニド（SeSe）およびジスルフィド（SS）化合物を合成した。合成化合物は、Ca^{2+}がその分子内に配位することで分子構造が変化し、SeSe および SS 結合部位の熱力学的安定性が低下し、触媒活性なセレノールおよびチオール体へと変換された。合成化合物は、Ca^{2+}存在下で酸化的フォールディングならびに活性酸素種の還元を良好に促進するとともに、細胞内においても同様の触媒活性の制御が観測された。

Monitoring of RNA motility in living cells using fluorescence/bioluminescence and "mPUM technology"

(*School of Science, The University of Tokyo*) ○Hideaki Yoshimura, Masatoshi Eguchi, Yoshibumi Ueda, Takeaki Ozawa

Keywords: Live-cell Imaging; RNA; Fluorescence; Bioluminescence

The importance of intracellular location and motion of RNA in cell physiological phenomena has been widely recognized. For a detailed understanding of the mechanisms in these phenomena, RNA monitoring techniques are required to analyze the time course of RNA localization and distribution in living cells. Moreover, RNAs are a direct target molecule in various technologies for gene expression analysis. Technological advances in various comprehensive gene expression analyses have promoted the discovery of genes associated with a variety of physiological events by identifying and quantifying the corresponding RNAs. However, these methods are not applicable to obtain spatiotemporal information on RNAs in living cells because of their destructive properties. This emphasizes the need for non-destructive live-cell imaging techniques for spatiotemporal analysis of RNAs.

In this presentation, we introduce an RNA labeling technique named “mPUM technology” that is applicable to live cell imaging of RNA. The mPUM technology is a selective and universal RNA labeling method using RNA-binding protein PUM-HD mutants. PUM-HD can be modified in a custom-made manner to recognize and capture an 8-base RNA sequence of interest. The combination of the mPUM technology with microscopy techniques allows monitoring of localization and motility of target RNAs in living cells.

To monitor target molecules in living cells, the use of fluorescence is a major approach. The mPUM technology was applied to labeling RNAs in living cells for fluorescence microscope imaging by making a fusion protein of mPUM and fluorescent protein [1]. In this approach, a split fluorescent protein reconstitution method was often used for reducing of fluorescence background from excess probes not attached to the target RNA. The split fluorescent protein reconstitution reaction is, however, an irreversible process, and the accumulation of reconstituted fluorescent proteins prevents precise observation. To overcome the drawback in the fluorescence protein reconstitution method, we also adopted bioluminescent protein reconstitution, which is based on a reversible reaction in recovering the full-length bioluminescent protein. In this presentation, two examples of mPUM-based RNA monitoring studies will be introduced and discussed, which use fluorescence and bioluminescence to visualize endogenous target RNAs in living cells.

1) T. Yamada, H. Yoshimura, R. Shimada, M. Hattori, M. Eguchi, T. K. Fujiwara, A. Kusumi, T. Ozawa, *Sci. Rep.* **2016**, 6, 38910. 2) M. Eguchi, H. Yoshimura, Y. Ueda, T. Ozawa., *ACS Sens.* **2023**, 8, 4055.

組織内チオール代謝物イメージング及び組成解析を実現する TLC 蛍光ラベル化剤の開発

（青山学院大理工）○西原 達哉・鈴木 我空・西田 光輝・塚目 莉加・田邉 一仁

Distribution Analysis of Thiol Metabolites in the Frozen Tissue by Using Fluorescent Labelling Reagent Coated TLC Plate

(*College of Science and Engineering, Aoyama Gakuin University*)
○Tatsuya Nishihara, Gaku Suzuki, Koki Nishida, Rika Tsukame, Kazuhito Tanabe

Distribution of thiol metabolites in the tissues gives very important information for the disease assessment. However, the mass spectrometry imaging (MSI) has the drawbacks such as time-consuming steps and expensive equipment. To solve these limitations, in this study, we attempted to develop a new methodology, which imaged the distribution of thiol metabolites rapidly and easily. Toward the imaging and analysis of thiol metabolites, we developed the fluorescent labelling reagent coated TLC plate, which shows the fluorescent signal after the reaction with the thiol metabolites in the tissue slice on the TLC plate. In fact, we successfully detected the fluorescent signals derived from the adducts of thiol metabolites in the frozen liver tissue.

Keywords：Metabolite, Thin Layer Chromatography, Labelling Regent

近年、組織内の代謝物分布解析にあたり、質量分析イメージング (MSI) が有力な方法論として用いられている。しかしながら、MSI はピクセルごとの質量分析を前提としているため、測定、及び解析に膨大な時間を要する。また、反応性の高い分子種の解析に困難を伴う点も課題として挙げられる。そのため、簡便かつ、迅速な代謝物分布解析を実現可能にする新たな方法論の構築が現在求められている。

本研究では、生体内の酸化還元を担う重要な生体分子であるチオール代謝物に着目した。これまでに我々は、組織内のチオール代謝物を薄層クロマトグラフィー (TLC) へトレースし、その場で蛍光標識することで、チオール代謝物の分布イメージング可能であることを報告してきた。本研究では、新たに、リシンを母核構造とし、蛍光色素としてピレン酪酸、光切断部位としてニトロベンジル、反応部位としてマレイミドを備えたラベル化剤を設計した。本ラベル化剤をコートした TLC に対して、生体組織内物質をトレースすることで、チオール代謝物の付加体がその場で生成する。本ラベル化剤は、チオール代謝物とのマイケル付加反応、及び UV 照射によるニトロベンジルの解離の 2 条件で蛍光回復する特性を新たに付与している。そのため、TLC 全体を光照射することで、組織内に含まれるチオール代謝物の分布イメージングが未反応のラベル化剤を除去することなく実現する。さらに、解析対象領域に対して局所的に UV 照射を行った後に、展開操作を行うことにより、照射領域内に含まれるチオール代謝物の組成解析も可能となる。実際に、本ラベル化剤を塗布した機能化 TLC を用いることで、食肉用豚肝臓内に含まれるチオール代謝物の検出に成功した。本発表では、ラベル化剤の特性評価、及び組織内チオール代謝物解析についての詳細について報告する。

新規ミスマッチ認識分子の創生とその特性

（防衛医大）○武井 史恵、山田 直生、比留間 寿美代

Synthesis and Characterization of Novel DNA Mismatch-Binding Molecule. (Faculty of Medicine, National Defense Medical College) ○Fumie Takei, Naoki Yamada, Sumiyo Hiruma

Molecules that bind specifically to special structures of DNA and emit fluorescence are of interest as molecular probes used to reveal biochemical processes. A variety of fluorescent molecules have already been developed which bind to specific structures of DNA. In particular, a fluorescent molecule with a diamino-naphthyridine derivative (DANP), which we have previously developed, binds specifically to the cytosine bulge structure of DNA and exhibits characteristic fluorescence. In this study, we synthesized a novel DNA binding ligand, DANP derivatives with the organometallic compound ferrocene as a substituent, and found to be fluorescent molecules that bind to DNA mismatch structures.

The novel molecule ferrocene DANP (FeDANP) was synthesized from DANP and ferrocene carboxylic acid. The melting temperature (T_m) of DNA containing bulge structures were little changed with or without FeDANP. On the other hand, the ΔT_m of the cytosine-cytosine mismatch structure (C-C mismatch structure) was larger than that of other mismatch DNA. Furthermore, the addition of FeDANP to the C-C mismatch DNA structure increased the fluorescence intensity. In particular, the fluorescence change in the C-C mismatch structure was greater than in the other mismatch structures, suggesting that FeDANP specifically recognises the C-C mismatch DNA structure.

Keywords : DNA Mismatch Binding ligand; Fluorescent molecule

DNA の特殊構造に特異的に結合し蛍光を発する分子は、生化学的プロセスを明らかにする際に使われる分子プローブとして注目され、すでに様々な DNA の特殊構造に結合する蛍光分子が開発されている。特に我々が以前開発したジアミノナフチリジン骨格を有する蛍光分子（DANP）は DNA のシトシンバルジ構造に特異的に結合して、特徴的な蛍光を示す。本研究ではこの DANP に有機金属化合物であるフェロセンが結合した分子を合成し、その特徴について調べた。

DANP とフェロセンカルボン酸から合成したフェロセン DANP (FeDANP)とバルジ構造を含む DNA との結合を DNA の融解温度(T_m)を用いて調べたところ、いずれのバルジ構造においても、FeDANP の有無による T_m の変化はほとんど観測されなかった。一方、シトシンと各種塩基のミスマッチ構造 DNA の組み合わせでは シトシン－シトシンミスマッチ構造(C-C ミスマッチ構造)の T_m 変化が他のミスマッチ構造に比べ大きく、FeDANP が C-C ミスマッチ構造特異的に結合していることが示唆された。蛍光についても、C-C ミスマッチ構造に FeDANP を加えると、蛍光強度は増大したことから、今までの蛍光分子では不可能であった C-C ミスマッチ構造の蛍光検出が可能となった。

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21日(木) 13:00 ~ 14:50 🏛 H936(9号館 [3階] 936)

[H936-4pm] 17. 生体機能関連化学・バイオテクノロジー

座長：田村 朋則、野中 洋

🏷 英語

13:00 ~ 13:20

[H936-4pm-01]

化学合成タンパク質のハイスループット合成を志向した、Diketopiperazineチオエステルペプチドの固相合成法開発

〇中嶋 雄哉[1]、中津 幸輝[1]、林 剛介[1]、村上 裕[1,2] (1. 名大院工、2. 名大ナノライフ)

🏷 英語

13:20 ~ 13:40

[H936-4pm-02]

4量化する抗体軽鎖の会合挙動と3Dドメインスワッピング構造の解明

〇酒井 隆裕[1]、山口 将平[1]、真島 剛史[1]、小林 直也[1]、段 練[2]、藤木 涼[2]、Kowit Hengphasatporn[2]、重田 育照[2]、緒方 英明[3]、一二三 恵美[4]、宇田 泰三[5]、廣田 俊[1] (1. 奈良先端大・先端科技、2. 筑波大・計算科学研究センター、3. 兵庫県大・院理、4. 大分大・研究マネジメント機構、5. 九州先端研・ナノテク)

🏷 英語

13:40 ~ 14:00

[H936-4pm-03]

ミセル形成チオール化合物による高濃度でのタンパク質フォールディング促進

〇喜多村 真衣[1]、村岡 貴博[1,2] (1. 東京農工大学、2. 神奈川県立産業技術総合研究所)

14:00 ~ 14:10

休憩

🏷 日本語

14:10 ~ 14:30

[H936-4pm-04]

構造変化を干渉する分子ストッパーによるAMPA受容体のケモジェネティック制御

〇三浦 裕太[1]、小島 憲人[1,2]、宮下 治[3]、堤 尚孝[4]、浜地 格[2]、山下 敦子[4]、清中 茂樹[1] (1. 名大、2. 京大、3. 理研、4. 岡大)

🏷 日本語

14:30 ~ 14:50

[H936-4pm-05]

N-acyl-N-aryl sulfonamide(ArNASA)反応基: タンパク質の化学修飾と不可逆阻害

〇河野 正晴[1]、村川 駿介[1]、杉原 大[2]、田村 朋則[1]、浜地 格[1,3] (1. 京都大学大学院、2. 京都大学、3. JST ERATO)

Solid-Phase Synthesis of Diketopiperazine Thioester Peptide for High-throughput Chemical Protein Synthesis

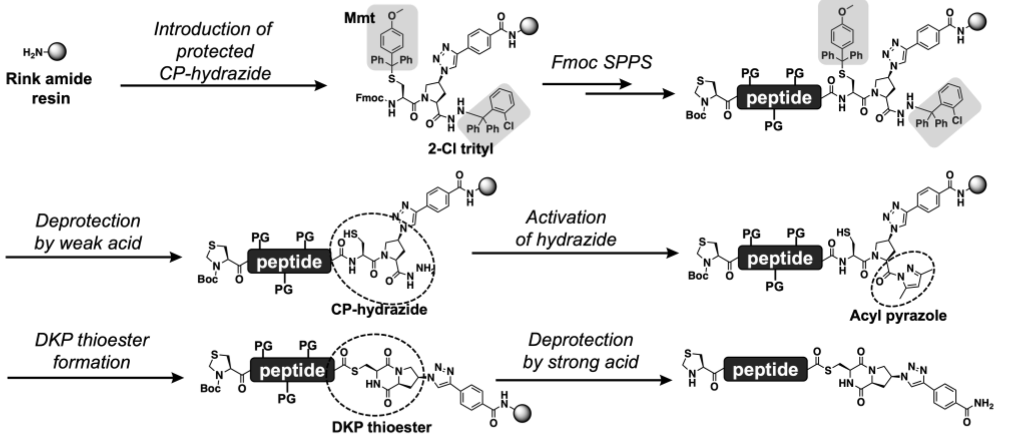
([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University*) ○Yuya Nakajima,[1] Koki Nakatsu,[1] Gosuke Hayashi,[1] Hiroshi Murakami[1,2]

Keywords: Chemical Protein Synthesis; Fmoc Solid-Phase Peptide Synthesis; Thioester Peptide; Native Chemical Ligation; Combinatorial Synthesis

C-terminal thioester peptides are frequently used for peptide ligation in chemical protein synthesis. Facile preparation of multiple thioester peptides is key for the efficient synthesis of various target proteins. However, conventional Fmoc solid-phase peptide synthesis (SPPS) cannot be applied to the direct synthesis of *C*-terminal thioester peptides due to the lability of thioester moiety in Fmoc SPPS, especially in the Fmoc deprotection procedure.

We have studied diketopiperazine (DKP) thioester peptide, which is converted from *C*-terminal cysteinylprolyl ester[1] or cysteinyl prolyl imide[2,3] by *N*-*S* acyl rearrangement of the cysteine residue followed by intramolecular cyclization. Although the DKP formation-mediated thioester synthesis proceeds almost quantitatively regardless of *C*-terminal amino acid residues, this thioesterification reaction has been exclusively performed in the liquid-phase so far.

Here, we developed a solid-phase strategy for synthesizing DKP thioester peptides, which are immobilized to resin by anchoring the γ -position of proline via CuAAC reaction. The activation of the *C*-terminal hydrazide to acylpyrazole[4] and the subsequent conversion to DKP thioester with an optimized condition gave a reliable Fmoc SPPS method for direct preparation of thioester peptides, which enables parallel synthesis of protein fragment peptides.



1) T. Kawakami, S. Aimoto, *Chem. Lett.*, **2006**, *36*, 76-77. 2) M. Yanase, K. Nakatsu, C. J. Cardos, Y. Konda, G. Hayashi, A. Okamoto, *Chem. Sci.*, **2019**, *10*, 5967-5975. 3) K. Nakatsu, M. Yanase, G. Hayashi, A. Okamoto, *Org. Lett.*, **2020**, *22*, 4670-4674. 4) D. T. Flood, J. C. J. Hintzen, M. J. Bird, P. A. Cistrone, J. S. Chen, P. E. Dawson, (2018) *Angew. Chem. Int. Ed. Engl*. **2018**, *57*, 11634-11639.

機能超分子化学研究室

ドメインスワッピングにより 4 量化する抗体軽鎖の会合挙動と X 線結晶構造

酒井 隆裕

【序論】

近年、抗体医薬品は、がんやアルツハイマー病などあらゆる疾患に対して成功を収めています。しかし、抗体は不安定であり、互いに会合することで凝集体を形成しやすく、**凝集形成により抗原認識能が低下する場合があります。**また、生体内での抗体の凝集は疾患の原因となる場合もあり、過剰に発現された抗体の軽鎖が凝集すると、臓器に障害を及ぼします。このように、抗体の凝集機構を解明することは大変重要ですが、**凝集体の原子レベルでの情報はほとんどありません。**

一方、タンパク質会合機構の一つに 3D-ドメインスワッピング (3D-DS) という現象があります。3D-DS は、同じ分子間で、同じ構造領域を交換して会合する機構です。3D-DS による多量化は凝集を促進する報告もあります。抗体の凝集に関して広く研究されているにも関わらず、3D-DS に関する情報は非常に少なく、**抗体軽鎖が 3D-DS で多量化する報告は未だありません。**

本研究では、多量化するヒト抗体軽鎖#4 に着目し、その**会合メカニズムの解明を目指します。**まず、抗体軽鎖#4 の変異体#4C214A を調整し、溶液中での会合挙動を調べました。さらに、#4 の可変領域#4V_L の X 線結晶構造解析により、**抗体軽鎖の 3D-DS 構造を初めて明らかにしました。**

【結果・考察】

抗体軽鎖#4C214A は、大腸菌を用いて培養・発現し、各種クロマトグラフィーにより精製しました。精製した#4C214A のサイズ排除クロマトグラフィー (SEC) 分析により、#4C214A は溶液中で 4 量体を形成し、**単量体と 4 量体の平衡であることが明らかになりました (図 1a)。**

詳細に多量化挙動を調査するため、抗体軽鎖#4C214A の熱力学的解析を行いました。解離定数の温度依存性から、熱力学的パラメーターを算出すると、温度上昇に伴い、4 量体から単量体へ解離する際の標準エンタルピー変化量が増大しました。一般的に、温度が上昇すると水素結合や静電相互作用は弱くなり、標準エンタルピー変化量は減少します。しかし、増大したことから、#4C214A は**疎水性相互作用により 4 量体を形成することが示唆されました。**

4 量化メカニズムを原子レベルで解明するため、抗体軽鎖#4C214A の 4 量体の X 線結晶構造解析を行ったが、十分な分解能を得ることができなかった。そこで、定常領域を切除した抗体軽鎖可変領域#4V_L を調整しました。#4V_L は#4C214A と同様に溶液中で 4 量体を形成し、その結晶構造では、**3D-DS した 2 量体がさらに 2 量化することで、4 量体を形成していました (図 1b)。**2 量体同士の相互作用界面には多くの疎水性残基が存在し **(図 1c)**、4 量化に疎水性相互作用が大きく寄与することが結晶構造からも確認されました。本研究成果は、抗体の安定性向上と新規抗体医薬品の開発に役立つ研究として期待されます。本成果は筆頭著者として Nature Communications 誌に出版し (https://www.nature.com/articles/s41467-023-43443-4)、プレスリリースも発行されています (https://www.jst.go.jp/pr/announce/20231208/pdf/20231208.pdf)。

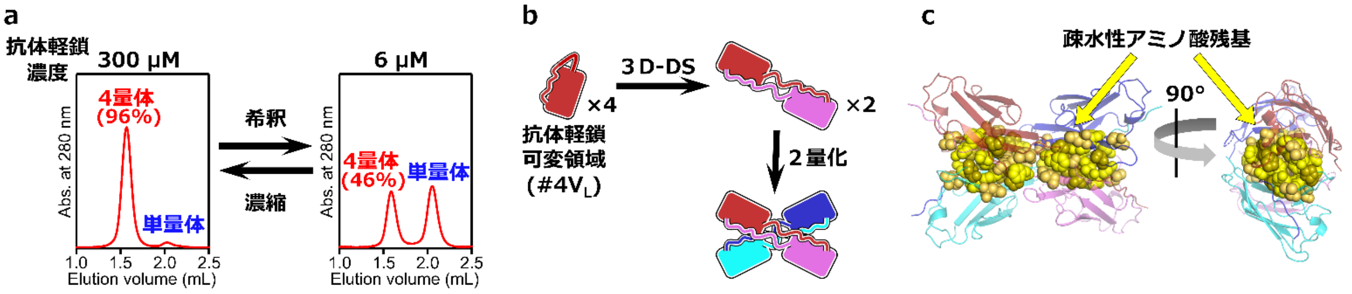


図1. これまでの研究結果。**a** 抗体軽鎖#4C214AのSEC溶出曲線。**b** 抗体軽鎖可変領域#4V_Lの4量化メカニズム。**c** #4V_Lの4量体結晶構造。2量体間に存在する疎水性アミノ酸残基を黄色で示す。

Development of micelle bearing thiol groups to promote oxidative protein folding under crowded environment

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Kanagawa Institute of Industrial Science and Technology*) ○ Mai Kitamura,[1] Takahiro Muraoka [1, 2]

Keywords: Crowded condition; Oxidative protein folding; Disulfide bonds; Micelles

Protein folding is a posttranslational modification process to gain their biological functions by forming native structures. During the folding process, proteins can be aggregated through intermolecular hydrophobic interactions and disulfide bond (SS-bond) formation, which is particularly facilitated in the crowded condition, such as the interior of cells. In cells, chaperones and oxidoreductases play important roles in inhibiting protein aggregation and promoting oxidative folding, respectively, as quality control systems of protein expression. Mimicking the mechanisms and functions of those quality-controlling proteins can be, thus, a promising approach to developing practically useful synthetic materials for preventing protein misfolding diseases, such as Parkinson’s disease.

In this study, we developed a novel synthetic material to promote oxidative folding even under crowded condition. We focused on protein disulfide isomerase (PDI), which is one of the representative oxidoreductases involving in the oxidative folding. The major roles of PDI contain 1) introduction and exchange of SS-bonds for folding promotion of the client proteins and 2) aggregation inhibition of client proteins with its hydrophobic pocket. Inspired by these functions of PDI, here we developed a supramolecular PDI-mimic, CTAB-SS$_{\text{out}}$ micelle, based on a micelle-forming lipid bearing a redox-active functionality. In the interior of CTAB-SS$_{\text{out}}$ micelle, there is the hydrophobic space (Fig. 1).

To investigate the reactivities of the thiol groups of CTAB-SS$_{\text{out}}$ in the oxidative folding, the chemical properties were evaluated following the previous study.[1] As a result, CTAB-SS$_{\text{out}}$ showed better performance than cysteine-containing dipeptides conjugated with amino acids possessing amino groups.[2] Based on the evaluation of thiol groups of CTAB-SS$_{\text{out}}$, folding assay was conducted in a crowded condition using bovine pancreatic trypsin inhibitor (BPTI), which is a protein with three SS-bonds. In this assay, both protein aggregation inhibition effect and SS-bond introduction and exchange effect were observed with CTAB-SS$_{\text{out}}$. Neither CTAB micelle nor a mixture of a redox-active thiol and CTAB micelle showed such a high activity of the folding promotion. CTAB-SS$_{\text{out}}$ micelle successfully demonstrated oxidative protein folding promotion in highly concentrated conditions.

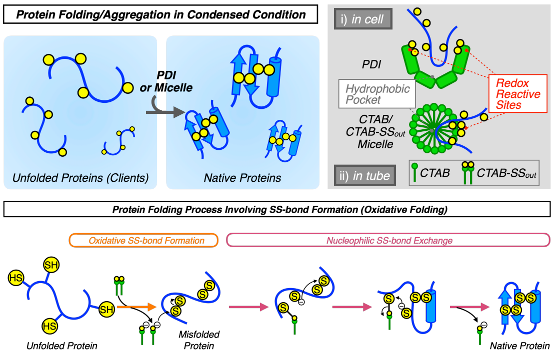


Fig. 1 Schematic illustration of the oxidative protein folding in a condensed condition.

1) S. Okada *et al.*, *Chem. Sci.*, **2023**, *14*, 7630–7636. 2) H. Nishino,† M. Kitamura† *et al.*, *RSC Adv.*, **2022**, *12*, 26658–26664 (†: equal contribution).

構造変化を干渉する分子ストッパーによる AMPA 受容体のケモジェネティック制御

（名大院工[1]・京大院工[2]・理研[3]・岡大院薬[4]）○三浦 裕太[1]・小島 憲人[1,2]・宮下 治[3]・堤 尚孝[4]・浜地 格[2]・山下 敦子[4]・清中 茂樹[1]

Chemogenetic Control of the AMPA Receptor Activity Using the Molecular Stopper Approach

([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*RIKEN Center for Computational Science,* [4]*Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Okayama University*) ○Yuta Miura,[1] Kento Ojima,[1,2] Osamu Miyashita,[3] Naotaka Tsutsumi,[4] Itaru Hamach,[2] Atsuko Yamashita,[4] Shigeki Kiyonaka[1]

AMPA receptors (AMPARs) mediate fast excitatory neurotransmission in the central nervous system and play vital roles such as synaptic plasticity. Four subunits, GluA1-4, assemble into tetramers to make up the core functional cation channel, with different combinations conferring unique trafficking behaviors and biophysical characteristics. Subunit-specific regulation is difficult due to high homology. Activation of AMPARs is triggered by structural changes in the ligand binding domain from open to closed-form. Previously, we reported novel activation methods for AMPARs termed A-CBC (allosteric activation via coordination-based chemogenetics), in which artificial coordination sites were introduced near the ligand-binding site for artificial activation by Pd(II) complex.

Here, we developed a new method for chemogenetic inhibition of AMPARs. We utilized coordination of Pd(II) complex with two of mutated His residues in the vicinity of the ligand-binding site for interfering with the structural change upon activation.

Keywords :Chemogenetics; Glutamate Receptor; Palladium; Coordination Chemistry; AMPAR

AMPA 受容体(AMPAR)は、中枢神経系での速い興奮性神経伝達を担う 4 量体カチオンチャネルであり、その発現様式が記憶や学習に大きく関連している。AMPAR には GluA1-4 と呼ばれる 4 種サブユニットが存在し、それぞれ異なる機能を有するとされるが、構造的相同性の高さからサブユニット選択的活性制御が難しい。これまでに我々は、遺伝子工学と配位化学を融合させた配位ケモジェネティクスを開発した。AMPAR は、活性化の際にリガンド結合部位が開から閉構造へと変化する事が知られている。我々は、リガンド結合部位近傍に配位性アミノ酸である His の変異導入を行い、Pd 錯体との配位結合によって人為的に閉構造へと変化させて受容体の選択的活性化に成功した 1)。

本研究では、活性化の先行研究とは異なり、錯体の嵩高さに着目した受容体選択的な阻害を行った。具体的には、2 つの His 残基をリガンド結合部位近傍に変異導入し、そこへ立体障害となる嵩高い Pd 錯体を配位させる事で、閉構造への変化を妨げて受容体の活性を阻害する新たな「ケモジェネティック活性阻害」を開発した。

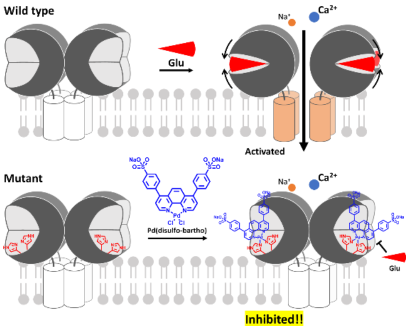


Fig. 1 Chemogenetic inhibition of AMPARs.

1) S. Kiyonaka *et al. Nat. Chem.* (2016)

N-acyl-*N*-aryl sulfonamide(ArNASA)反応基：タンパク質の化学修飾と不可逆阻害

（京大院工[1]・JST ERATO[2]）○河野 正晴[1]・村川 駿介[1]・杉原 大[1]・田村 朋則[1], 浜地 格[1,2]

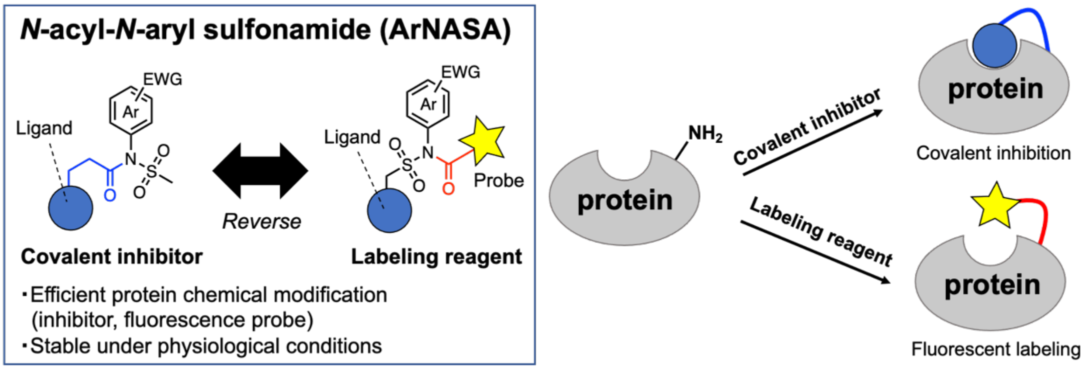
Development of *N*-acyl-*N*-aryl sulfonamide warheads for covalent protein modification and inhibition ([1]*Graduate School of Engineering, Kyoto University*, [2]*ERATO JST*) ○Masaharu Kawano,[1] Shunsuke Murakawa,[1] Dai Sugihara[1], Tomonori Tamura,[1] Itaru Hamachi[1, 2]

Recently, we discovered that lysine-reactive *N*-acyl-*N*-aryl sulfonamide (ArNASA) warheads are promising for covalent inhibition strategy.[1] ArNASA warheads exhibited superior stability and biocompatibility in water compared to conventional lysine-reactive warheads. ArNASA groups can be easily introduced into ligands for target proteins by one-step coupling reaction. Contrary to this molecular design, when the ligand moiety is linked to the leaving group side (*N*-aryl sulfonamide) of ArNASA and the functional probe is introduced to the *N*-acyl group side, this molecule is expected to function as a ligand-directed labeling reagent – an affinity labeling agent that does not inhibit the protein activity. In this study, we designed and synthesized ArNASA-based labeling reagents for selective labeling of endogenous membrane proteins overexpressed in cancer cells.

Keywords : Covalent inhibitors, N-acyl-N-aryl sulfonamide, Lysine-reactive, Warhead

ごく最近、我々はリジン残基標的型不可逆阻害剤の新しい反応基として *N*-acyl-*N*-aryl sulfonamide (ArNASA)を開発した。1) ArNASA は既存のリジン標的型反応基と比較して優れた水中安定性・生体適合性を示し、標的タンパク質に対するリガンドのカルボン酸誘導体とワンステップで連結することで、容易に不可逆阻害剤を合成可能である。こうした分子設計とは逆に、リガンド部分を ArNASA の脱離基側(*N*-aryl sulfonamide)に連結し、機能性プローブを *N*-acyl 基側に導入すれば、その分子はリガンド指向性ラベル化剤（タンパク質活性を阻害しないアフィニティラベル化剤）として機能すると予想される。そこで本研究では、ArNASA を基盤とするリガンド指向性ラベル化剤を設計・合成し、がん細胞に過剰発現する内在性膜タンパク質の選択ラベリングを試みた。本講演ではこれらの詳細について発表する。

1) M. Kawano *et al. JACS*, 2023, 145, 26202-26212.



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21日(木) 9:00 ~ 11:30 D342(3号館 [4階] 342)

[D342-4am] 18. 高分子

座長：樋口 昌芳、福元 博基

日本語

9:00 ~ 9:20

[D342-4am-01]

有機アルミニウム触媒による不飽和炭化水素モノマーの重合・共重合

〇木村 なな子[1]、竹内 大介[1] (1. 弘前大学)

英語

9:20 ~ 9:40

[D342-4am-02]

Substituent effects of ether-functionalized propylenes on scandium-catalyzed copolymerization with ethylene

〇Mingjun Chi[1,2], Hao Wang[2], Masayoshi Nishiura[2], Lin Huang[2], Haoran Zhang[2], Zhaomin Hou[1,2] (1. Saitama University, 2. RIKEN)

英語

9:40 ~ 10:00

[D342-4am-03]

耐アルカリ特性に優れたトリアリールスルホニウム塩を含む高分子材料の開発と応用

〇今井 智大[1]、一二三 遼祐[1]、稲木 信介[1]、冨田 育義[1] (1. 東京工業大学)

英語

10:00 ~ 10:20

[D342-4am-04]

Synthesis of functional polyesters containing cleavable linkages and AIE luminogen via Passerini-type multicomponent polymerizations

〇Chih-Feng HUANG[1], Li-Chieh CHOU[1], Yi-Shen HUANG[1] (1. National Chung Hsing University)

10:20 ~ 10:30

休憩

英語

10:30 ~ 10:50

[D342-4am-05]

過酸化水素を酸化剤として用いたベンゼンからヒドロキノン重合体の一段階合成

〇杉本 秀樹[1]、宮田 憲伸[1]、中野 晟志[2]、東村 秀之[2]、伊東 忍 (1. 大阪大学、2. 岡山理科大学)

英語

10:50 ~ 11:10

[D342-4am-06]

A New Synthetic Approach of Metallosupramolecular Polymer and its Electrochromic Application

〇Satya Ranjan Jena[1], Masayoshi HIGUCHI[1], Chih-Wei Hu[1] (1. National Institute for Materials Science)

日本語

11:10 ~ 11:30

[D342-4am-07]

主鎖骨格に含フッ素ベンゾジチオフェンを用いたπ共役高分子の開発および光学特性評価

○奥崎 秀俊[1]、佐藤 世良[1]、吾郷 友宏[2]、久保田 敏夫[1]、福元 博基[1] (1. 茨城大学大学院理工学研究科、2. 兵庫県立大学大学院理学研究科)

・有機アルミニウム触媒による不飽和炭化水素モノマーの重合・共重合

（弘前大院理工）○木村なな子・竹内大介

Polymerization and Copolymerization of Unsaturated Hydrocarbon Monomers by Organoaluminum Catalysts

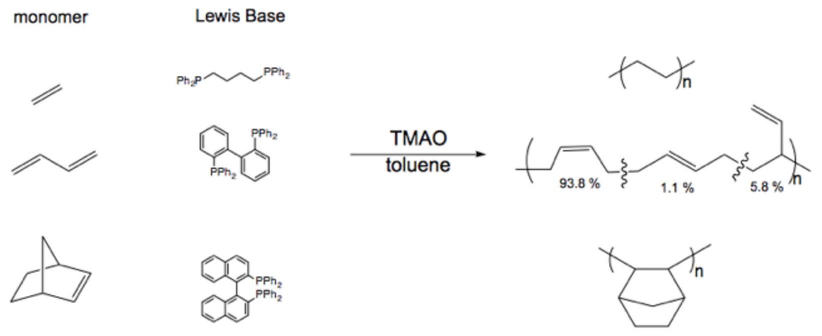
(*Graduate School of Science and Technology, Hirosaki University*) ○Nanako Kimura, Daisuke Takeuchi

Transition metal catalysts have been extensively used for the polymerization of olefins and conjugated dienes. Herein we report that TMAO in combination with phosphines catalyze polymerization of some unsaturated hydrocarbon monomers.

TMAO in combination with phosphines such as DPPB catalyze polymerization of ethylene. TMAO/phosphine systems are also effective for the polymerization of 1,3-butadiene. Especially, TMAO/DPPBiPh system produces polybutadiene with high cis-1,4 selectivity. TMAO/rac-BINAP system bring about norbornene polymerization efficiently. Copolymerization of these monomers was also investigated.

Keywords : Organoaluminum; Phosphine; Ethylene; Butadiene; Norbornene

エチレンやブタジエンなどの不飽和炭化水素モノマーの重合には、従来、遷移金属触媒や希土類触媒が主に用いられてきた。一方で、エチレン重合に活性を示すカチオン性有機アルミニウム触媒の例がいくつか知られている1)。ごく最近、アルミニウム触媒によるブタジエン重合の例も報告されている2)。最近、我々は、一般的に助触媒として用いられているTMAO（メチルアルミノキサン）とLewis塩基であるNHCを組み合わせた触媒系が、エチレンの重合に有効であることを見出している3)。本研究では、有機アルミニウムとホスフィンを組み合わせた触媒系による不飽和炭化水素モノマーの重合について検討を行った。



TMAOとホスフィンを組み合わせた触媒系はエチレンの重合に有効であった。特に、DPPBを用いた場合に活性が向上した。TMAOとホスフィンを組み合わせた触媒系はブタジエンの重合にも有効であった。DPPBiPhを用いた場合には、高いcis-1,4選択性を示すポリブタジエンが得られた。ノルボルネンの重合には、TMAOとrac-BINAPを組み合わせた触媒系が有効であった。これらのモノマーの共重合についても検討を行った。

References 1) R. F. Jordan, *et al. JACS* **1997**, *119*, 8125; R. F. Jordan, *et al. JACS* **1998**, 120, 8277; V. C. Gibson, *et al. Chem. Commun.* **1998**, 2523. 2) T. Jian, *et al. Polym. Chem.* **2023**, *14*, 980. 3) N. Kimura, *et al. Des. Monomers Polym.* **2023**, *26*, 182.

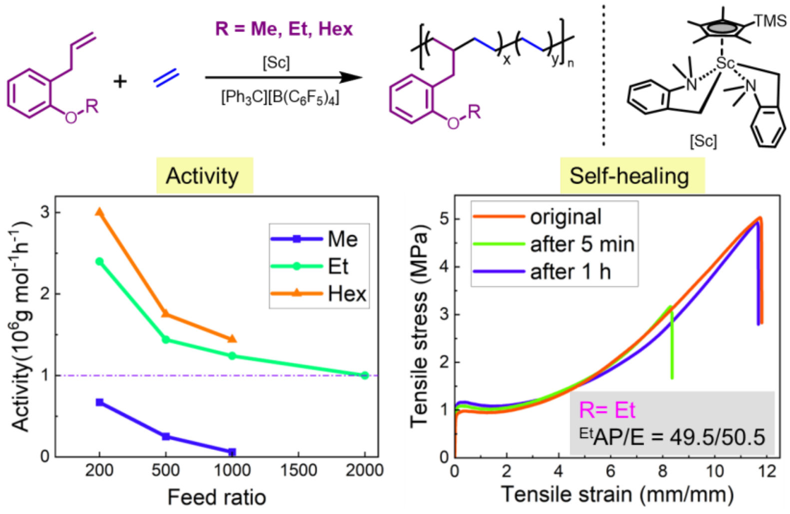
Substituent Effects of Ether-Functionalized Propylenes on Scandium-Catalyzed Copolymerization with Ethylene

([1]*Graduate School of Science and Engineering, Saitama University; [2]Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science*) ○Mingjun Chi,[1,2] Hao Wang,[2] Masayoshi Nishiura,[2] Lin Huang,[2] Haoran Zhang[2], Zhaomin Hou[1,2]

Keywords: Copolymerization; Substituent effects; Self-healing properties; Scandium catalysts

The copolymerization of nonpolar and polar olefins in a controlled fashion is of great interest and importance. We recently reported the sequence-controlled copolymerization of ethylene (**E**) and anisylpropylene (**^{Me}AP**) by a half-sandwich scandium catalyst, which afforded unique multiblock copolymers composed of relatively long **E**-*alt*-**^{Me}AP** sequences and short **E-E** sequences.[1,2] Such microstructure-regulated polymers exhibited excellent elasticity and self-healing properties because of the microphase separation of nanodomains of the crystalline **E-E** segments from a flexible **E**-*alt*-**^{Me}AP** matrix. To further investigate the influences of ether-functional groups on the copolymerization behaviors and the self-healing properties of the resulting copolymers, we then examined the analogous copolymerization by using ether-functionalized propylenes with various substituents on the oxygen atom.

Herein we report the scandium-catalyzed copolymerization of ethylene (**E**) with ether-functionalized propylenes (**AP**) having different substituents (Et ((**^{Et}AP**), *n*-Hex(**^{Hex}AP**)) at the oxygen atom. The copolymerization afforded unique multi-block copolymers with relatively long alternating **E**-*alt*-**$^{Et/Hex}$AP** and **E-E-$^{Et/Hex}$AP** sequences and short **E**－**E** blocks. Significant substituent effects were observed on the copolymerization activity and self-healing properties. We found that **^{Et}AP** and **^{Hex}AP** showed much higher activity than that of **^{Me}AP**. The copolymers with ethyl substituent (**^{Et}AP**) exhibited much improved elasticity and self-healing property compared with Me group (**^{Me}AP**).



1) Wang, H.; Yang, Y.; Nishiura, M.; Higaki, Y.; Takahara, A.; Hou, Z. *J. Am. Chem. Soc.* **2019**, *141*, 3249.

2) Yang, Y.; Wang, H.; Huang, L.; Nishiura, M.; Higaki, Y.; Hou, Z. *Angew. Chem. Int. Ed.* **2021**, *60*, 26192.

Synthesis and Applications of Polymers Containing Highly Alkaline-resistant Triarylsulfonium.

([1]*School of Materials and Chemical Engineering, Tokyo Institute of Technology*)
○Tomohiro Imai[1], Ryoyu Hifumi[1], Shinsuke Inagi[1], Ikuyoshi Tomita[1]

Keywords: Polycondensation; Polymer Reaction; Triarylsulfonium Salts; Anion-exchange Membrane

To realize the low-cost hydrogen production system, the water splitting module that operates under alkaline conditions is paid much attention to, since it does not require noble metals such as Pt for electrodes. However, due to the low chemical stability of the anion-exchange membrane (AEM) which consists of polymers possessing positively charged functional groups, no module that exhibits sufficient durability has been realized yet.

To develop an AEM with high alkaline resistance, we focused on the triarylsulfonium (**TAS**) structures as ion exchange groups and they were synthesized from sulfur compounds by means of the addition reaction to arynes[1,2] or by the Friedel-Crafts arylation reaction, from which the alkaline resistant feature of the **TAS** salts proved to be strengthened dramatically by introducing sterically demanding substituents.[3] Under the conditions of 1 M KOH/CD_3OD at 80 ℃, for example, **TAS 3cH**, prepared by the Friedel-Crafts reaction, exhibits 33 times higher stability compared to benzyltrimethylammonium (BTMA), the commonly used cationic functional group (**Fig.1**).[4]

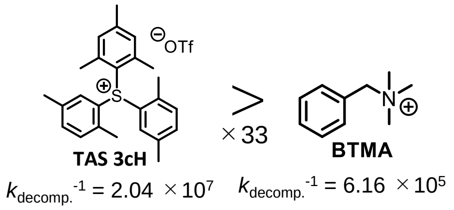
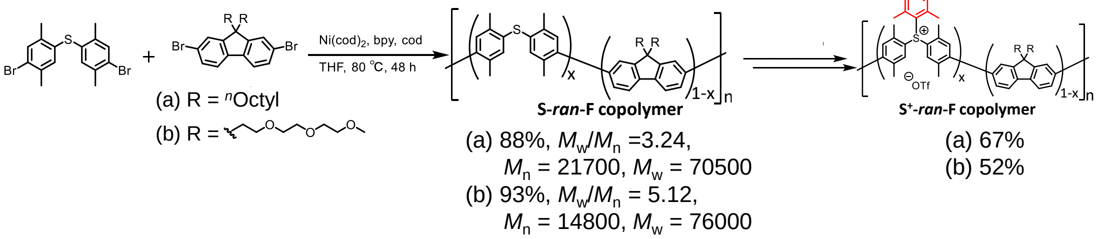


Fig. 1 Highly alkaline-resistant **TAS**

Various polymers containing highly alkaline-resistant **TAS** units in the main chain have been synthesized by the transition metal-catalyzed coupling followed by polymer reactions (**Scheme 1**). Properties of the polymers for the AEM applications will also be described.



Scheme 1 Synthesis of polymers containing highly alkaline-resistant **TAS**

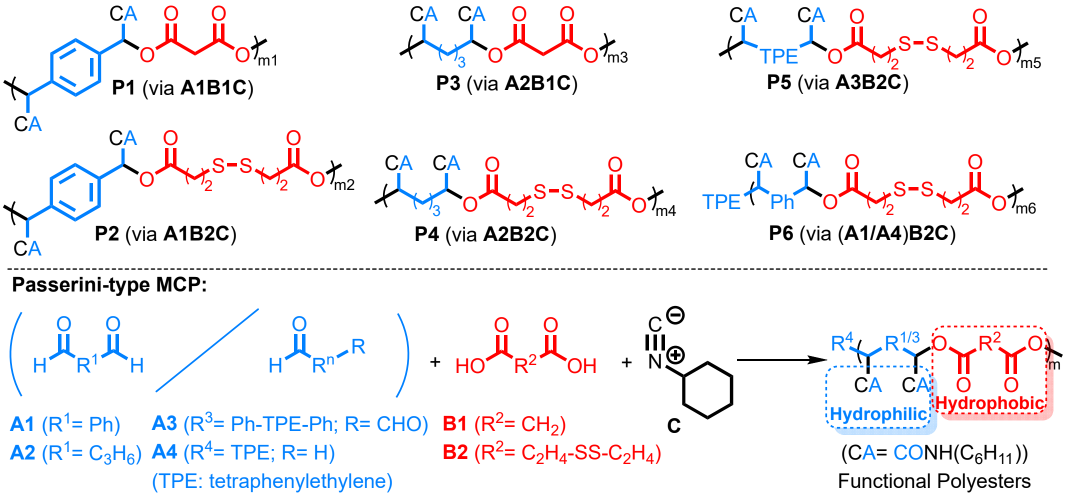
1) T. Hsu, *et al.*, *J. Am. Chem. Soc.*, **2017**, *142*, 11983-11987. 2) L. Xiajin, *et al.*, *Org. Lett.*, **2017**, *19*, 838-841. 3) T. Imai, R. Hifumi, S. Inagi, I. Tomita, *71st SPSJ Symp. Macromol.*, **2022**, 3E07. 4) T. Imai, R. Hifumi, S. Inagi, I. Tomita, *72nd SPSJ Symp. Macromol.*, **2023**, 2B18.

Synthesis of Functional Polyesters Containing Cleavable Linkages and an AIE Luminogen via Passerini-type Multicomponent Polymerizations

([1] *Dep. Chem. Eng., National Chung Hsing University (NCHU), Taichung 402, Taiwan*)
○Chih-Feng HUANG[1,*], Li-Chieh CHOU[1], Yi-Shen HUANG[1] (HuangCF@nchu.edu.tw)

Keywords: Passerini-type multicomponent polymerizations; Polyesters; AIE luminogen

Introduction to polymer chemistry from old reactions, new catalogs of polycondensations which are so-called “multicomponent polymerizations (MCPs)”.[1] As shown in **Scheme 1**, we conducted Passerini-type multicomponent polymerizations (P-MCPs) with various monomer combinations (i.e., dialdehydes, dicarboxylic acids, and cyclohexyl isocyanide) and afforded a series of functional polyester with dual-cleavable linkages of ester and disulfide groups and an aggregation-induced emission (AIE) luminogen of tetraphenylethylene (TPE).[2] Significant AIE features were acquired in TPE-containing polyesters with increases in the H_2O contents in various DMSO/H_2O mixtures. By striking the redox and AIE features together, intriguingly, the AIE behavior of the TPE-containing polymeric micelles was “switched off” with dithiothreitol treatment. We demonstrated an efficient, diverse, and facile approach through Passerini-type MCPs to design amphiphilic-typed polyesters with dual-cleavable linkages and an AIE feature.



Scheme 1. Synthesis of P1–P6 functional polyesters via P-MCP of (di)aldehydes, diacids, and isocyanide compounds (TPE: tetraphenylethylene; CA: cyclohexyl amide).

1. a)O. Kreye, T. Tóth and M. A. R. Meier, *J. Am. Chem. Soc.*, 2011, **133**, 1790; b)J. O. Holloway, K. S. Wetzel, S. Martens, F. E. Du Prez and M. A. R. Meier, *Polym. Chem.*, 2019, **10**, 3859; c)X. X. Deng, L. Li, Z. L. Li, A. Lv, F. S. Du and Z. C. Li, *ACS Macro Lett.*, 2012, **1**, 1300; d)L. Li, A. Lv, X. X. Deng, F. S. Du and Z. C. Li, *Chem. Commun.*, 2013, **49**, 8549.
2. L.-C. Chou, M. G. Mohamed, S.-W. Kuo, Y. Nakamura and C. F. Huang, *Chem. Commun.*, 2022, **58**, 12317.

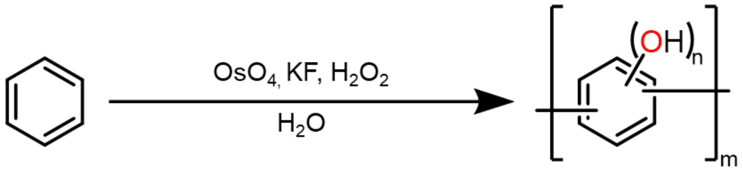
One-pot synthesis of hydroquinone-polymers from benzene with hydrogen peroxide

([1]*Graduate School of Engineering, Osaka University*, [2] *Graduate School of Science, Okayama University of Science*) ○Hideki Sugimoto[1], Kenshin Miyata[1], Akiyuki Nakano[2], Hideyuki Higashimura[2], Shinobu Itoh

Keywords: *hydroquinone-polymer, osmium tetroxide, hydrogen peroxide*

Hydroquinone-polymer can be a conducting polymer because it has unhybridized *p*-orbitals which lie perpendicular to its benzene ring [1)]. However, there is no method for preparing a hydroquinone-polymer in a convenient manner. We have reported an efficient phenol production from benzene using osmium tetroxide (OsO_4) as a catalyst and hydrogen peroxide (H_2O_2) as an oxidant [2)]. In this study, we find direct formation of a hydroquinone-polymer from benzene as a result of re-examination of the experimental conditions.

First, using benzene as a substrate, OsO_4 as a catalyst, potassium fluoride (KF) as a co-catalyst, and H_2O_2 as an oxidant, a reaction was conducted in water (Scheme 1). As a result, a brown solid was obtained in a 24wt% yield after isolation procedures. The polymeric structure was identified by UV-Vis and FT-IR spectra as well as GPC analysis. The analyses revealed that the obtained material was a hydroquinone-based polymer with M_n = 2400 and M_w = 6600, where benzene rings were connected through C–C bonds. The hydroxyl groups of the polymer were acetylated and the acetyl derivative was analyzed by ^{1}H-NMR spectrum, which showed that it has about 2.5 hydroxyl groups per one benzene ring. This is the first report of one-pot synthesis of a hydroquinone-polymer from benzene. Electrochemical property of the polymer in water was studied by cyclic voltammetry. At pH 9, an oxidation peak and a reduction peak based on the hydroquinone moiety were observed at 0.49 V and -0.80 V, respectively, indicating its redox-active nature as expected. As this polymer has also phenol moieties, a potentially use of this polymer as a curing agent for epoxy resin was examined. When EP4 with four epoxy groups was treated with this polymer at 250 °C and then cooled to room temperature, a black solid was obtained. On the other hand, only EP4 did not cure when treated in the same method. The results showed that this polymer has functionality as a curing agent for epoxy resins.



Scheme 1. Synthesis of phenol-polymers.

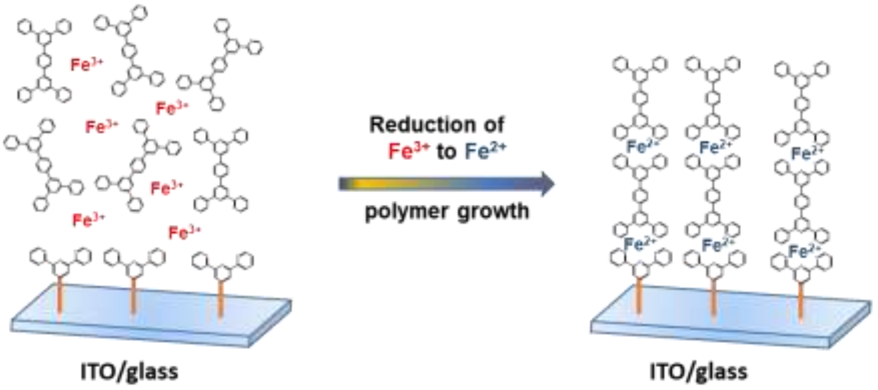
1) N. Mahato, H. Jang, A. Dhyani, S. Cho, *Polymers*, 2020, 12, 2480.
2) 植田悠太, 藤本智広, 杉本秀樹, 伊東忍, 第 54 回酸化反応討論会, 2021

A New Synthetic Approach of Metallosupramolecular Polymer and its Electrochromic Application

([1]*Electronic Functional Macromolecules Group, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan*) ○ Satya Ranjan Jena,[1] Chih-Wei Hu,[1] Takashi Sato,[1] Jian Zhang,[1] Satoshi Moriyama,[1] Masayoshi Higuchi*[1]

Keywords: Electropolymerization, Metallosupramolecular polymers, Electrochromic, Coloration efficiency, Switching time.

The potential uses of surface functionalization make it a crucial topic in the realm of materials research. In that aspect, electropolymerization is a valuable approach to surface functionalization because it offers controlled and convenient synthetic pathways. The exploration of in-situ synthesis for metallosupramolecular polymers (MSPs), involving the utilization of coordination-driven metal ions and coordinating ligands, as well as the investigation of their potential applications through electropolymerization, has been limited. Herein, we present the formation of MSPs on a pre-terpyridine-functionalized indium tin oxide (ITO) glass substrate using Fe(III) ions and 4′,4′′′′-(1,4-phenylene)-bis(2,2′:6′,2″-terpyridine) ligand. The application of an anodic potential facilitated polymer growth, driven by the robust coordination between the reduced metal ions (Fe(II)) and the bis-terpyridine ligand. The polymer's formation was confirmed by the appearance of corresponding peaks in the cyclic voltammogram and UV-vis spectral profile. Surface morphology was characterized through atomic force microscopy (AFM). Electrochromic (EC) properties of the electro-polymerized MSP (EP-MSP) were investigated, utilizing the redox-active Fe(II)-(terpyridine)$_2$ unit. The film demonstrated an optical switching coloring time of 2.1 seconds and 5.7 seconds for bleaching, a transmittance change of 54%, and a coloration efficiency of 142.6 cm^2 C^{-1}.[1] In addition, we designed and synthesized a pyrimidylamine derivative which could be a great opportunity to explore this system in the formation of metallosupramolecular polymers.



1) C.-W. Hu, S. R. Jena, T. Sato, J. Zhang, S. Moriyama, M. Higuchi *ACS Appl. Polym. Mater.* **2023**.

主鎖骨格に含フッ素ベンゾジチオフェンを用いたπ共役高分子の開発及び光学特性評価

(茨大院理工[1]・兵庫県大院理[2]) ○奥崎 秀俊[1]・佐藤 世良[1]・吾郷 友宏[2]・久保田 俊夫[1]・福元 博基[1]

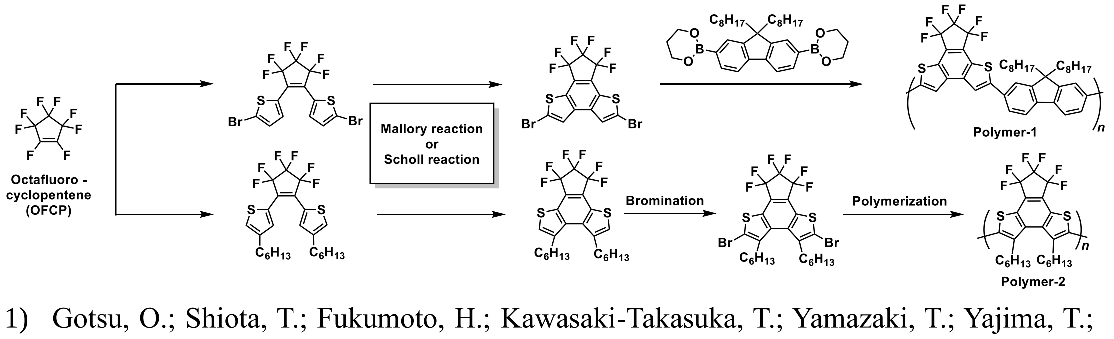
Synthesis and Optical Properties of π-Conjugated Polymers with Fluorine-containing Benzodithiophene

([1]*Graduate School of Science and Engineering, Ibaraki University,* [2]*Graduate School of Science, University of Hyogo*) ○ Hidetoshi Okuzaki[1], Sera Sato[1], Tomohiro Agou[2], Toshio Kubota[1], Hiroki Fukumoto[1]

Polymers including benzodithiophene (BDT) skeleton have a small band gap derived from a rigid planar π-electron system, however, they are unstable under atmospheric conditions due to their high HOMO energy levels. Recently, we found that the introduction of cyclic fluorine substituents into polycyclic aromatic hydrocarbons lowers their HOMO and LUMO energy levels and improves their antioxidant capacity[1)]. In this study, polymers containing fluorinated BDT units were synthesized and their optical properties were evaluated. Comparison of the fluorescence spectra of **Polymer-1** in solution and film revealed a red shift of the emission wavelength maximum in the film state indicating the interaction between polymer chains is considered to be stronger in the film state. On the other hand, no fluorescence was observed in **Polymer-2** in both solution and film, because of its distorted structure along the polymer main chain.

Keywords：*π-Conjugated polymer; Fluorine-containing polymer; Benzodithiophene*

ベンゾジチオフェン(BDT)は機能性π共役系ポリマーの母骨格として用いられている。BDT 骨格を有するポリマーの多くは高い HOMO エネルギー準位を持つため大気下で不安定である。当研究室では、多環芳香族炭化水素に環状フッ素置換基を導入すると HOMO 及び LUMO エネルギー準位が低下することを見出している。本研究では、含フッ素 BDT ユニットを含むポリマーを合成し、その光学特性を評価した。**Polymer-1** の溶液およびフィルムの蛍光スペクトルの比較から、フィルム状態における発光波長極大のレッドシフトを確認した。すなわち、フィルム状態では高分子鎖間同士の相互作用がより強く生じたと考えられる。一方、高分子主鎖がねじれた骨格である **Polymer-2** では蛍光は確認できなかった。



1) Gotsu, O.; Shiota, T.; Fukumoto, H.; Kawasaki-Takasuka, T.; Yamazaki, T.; Yajima, T.; Agou, T.; Kubota, T. *Molecules* **2018**, *23*, 3337.

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21日(木) 13:00 ~ 15:10 D341(3号館 [4階] 341)

[D341-4pm] 18. 高分子

座長：松岡 慶太郎、西村 達也

日本語
13:00 ~ 13:20

[D341-4pm-01]

水溶性ナイロンの系統的評価に基づくLCST型温度応答性の理解

○菅野 明梨[1]、松岡 慶太郎[1,2]、佐田 和己[1,2] (1. 北大院総化、2. 北大院理)

英語
13:20 ~ 13:40

[D341-4pm-02]

精密ラジカル重合法による液晶高分子修飾ZnOナノロッドの合成と配向挙動

○中野 果穂[1]、久保 祥一[1]、宍戸 厚[1] (1. 東工大化生研)

英語
13:40 ~ 14:00

[D341-4pm-03]

Mechano-responsive supramolecular hydrogel driven by stretch induced phase separation

○Sooyeon Noh[1], Akihide Sugawara[1], Yoshinori Takashima[1], Hiroshi Uyama[1] (1. Osaka Univ.)

14:00 ~ 14:10

休憩

日本語
14:10 ~ 14:30

[D341-4pm-04]

次世代イメージングツールへの応用を指向した撥水性ナノ薄膜の大量調製法の確立と機能評価

○内田 頼[1]、平塚 達也[2]、青木 拓斗[3]、岡村 陽介[1,3,4] (1. 東海大学院工、2. 東海大学工、3. 東海大院総理工、4. 東海大マイクロ・ナノ研)

日本語
14:30 ~ 14:50

[D341-4pm-05]

カーボン複合可動性架橋材料を用いた応力-ひずみセンシング

○以倉 崚平[1,2]、梶本 晃太[1]、朴 峻秀[1,2]、高島 義徳[1,2,3] (1. 阪大院理、2. 阪大FRC、3. 阪大OTRI)

日本語
14:50 ~ 15:10

[D341-4pm-06]

両親媒性ジブロックポリペプチドとDawson型ポリオキソメタレートとの複合化による三角形ナノプレート構造とその触媒活性の評価

宮本 翔唯[1]、○黒岩 敬太[1] (1. 崇城大学)

水溶性ナイロンの系統的評価に基づく LCST 型温度応答性の理解

（北大院総化 [1]・北大院理 [2]）○菅野 明梨 [1]・松岡 慶太郎 [1,2]・佐田 和己 [1,2]

Clarification of LCST-type thermo-responsiveness based on systematically evaluation of water soluble soft nylons

([1]*Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ.*, [2]*Fac. of Sci., Hokkaido Univ.)* ○Akari Sugano,[1] Keitaro Matsuoka,[1,2] Kazuki Sada[1,2]

Nylon is the oldest man-made fiber developed in 1935 as an alternative to silk. Research of nylon has focused on improving their physical properties in bulk to produce tough fibers. Consequently, the physical properties and functions in the solution of nylon have received little attention because of low solubility. In previous study, we developed water-soluble *N*-methylated nylon with a flexible main chain. Moreover, we determined the ideal unit formula per one tertiary amide group, $C_6H_{11}NO$, for realizing lower critical solution temperature (LCST) -type thermo-responsiveness in water. Under this criterion, we can find numerous LCST-type thermo-responsive polymer containing an amide group in the side chain for example Poly(*N*-isopropylacrylamide)[1]. Therefore, the balance of hydrophilic tertiary amide groups and hydrophobic alkyl chain C_5H_{11} is important to LCST-type thermo-responsiveness in water. In this study, we investigate the influence of the location of alkyl chain C_5H_{11} by replacing *N*-methyl groups to other *N*-alkyl groups such as Et and Pr.

Keywords : Thermo-responsive polymer, Nylon, Polyamide, Lower Critical Solution Temperature, LCST

ナイロンは世界で初めて合成された化学繊維である。ナイロンの研究は、繊維としての高い機械的強度を求めた固体物性に集中しており、溶液物性については低い溶解性のためにほとんど研究がなされていない。当研究室では、ナイロンの第二級アミド結合を *N*-メチル化した、主鎖が柔軟な水溶性の *N*-メチル化ナイロンを開発した。さらに、アミド基１つあたりの組成式が $C_6H_{11}NO$ である *N*-メチル化ナイロン（*N*-Me-2,8/-3,7/-4,6/-5,5/-6,4）について、ある温度以上で不溶となる下限臨界共溶温度（LCST）型温度応答性を示すことを見出した。LCST 型温度応答性高分子の代表例である、ポリ（*N*-イソプロピルアクリルアミド）[1]についても側鎖にアミド基を有しており、その組成式は $C_6H_{11}NO$ である。したがって LCST 型温度応答性の発現にはアミド基による親水性とアルキル鎖 C_5H_{11} による疎水性とのバランスが重要であることが示された。本研究では、*N*-メチル基を *N*-アルキル基（Et, Pr）とすることでアルキル基 C_5H_{11} の配置による LCST 型温度応答性への影響について検討した。

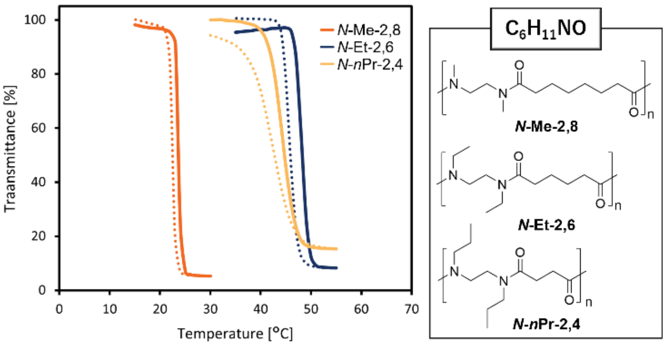


Figure. Transmittance change at 800 nm of *N*-Me-2,8, *N*-Et-2,6, *N*-*n*Pr-2,4 in H_2O (10 mg/mL) by the temperature changes (scan rate: 1.5 °C/min).

1) Aseyev, V.; Tenhu, H.; Winnik, F. M. *Adv. Polym. Sci.* **2010**, *242* (1), 29–89.

Synthesis of ZnO Nanorods Grafted with Liquid-crystalline Polymers by Controlled Radical Polymerization and their Alignment Behavior

(*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*)
○Kaho Nakano, Shoichi Kubo, Atsushi Shishido

Keywords: Nanorod; Liquid-crystalline Polymer; Surface Modification; Alignment; Controlled Polymerization

Anisotropic inorganic nanomaterials, such as nanorods and nanotubes, have attracted great attention and have been extensively researched due to their highly anisotropic properties applicable to the development of functional devices.[1] To take advantage of the anisotropic properties, it is essential to control their alignment. Very few papers have reported achieving large-area alignment among various nanorod alignment methods. We demonstrated the unidirectional alignment of ZnO nanorods over large areas with the assistance of liquid crystals (LCs).[2,3] LC polymers were grafted from the surface of ZnO nanorods to make nanorods miscible with host LCs and to align cooperatively with surrounding host LCs over a surface-treated substrate. Increasing the fraction of nanorods could fully utilize the functions of nanorods; however, the alignment behavior of LC polymer-grafted nanorods alone remains unclear. In this study, we synthesized ZnO nanorods grafted with different LC polymers and investigated the alignment behavior of LC polymer-grafted nanorods depending on the molecular structures of the LC polymers.

ZnO nanorods were synthesized according to our previous report.[4] LC polymers with phenyl benzoate moieties in the side chains were grafted from the surface of the ZnO nanorods by controlled radical polymerization. Atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization were employed for polymers with methoxy and cyano groups at the terminal of the phenyl benzoate moiety, respectively. The LC polymer-grafted ZnO nanorods were sheared over a glass substrate under elevated temperature. The alignment behavior of mesogens in LC polymers and nanorods was evaluated by polarized optical microscopy and polarized UV-visible absorption spectroscopy.

1) S. Zhang *et al.*, *Adv. Mater.* **2018**, *30*, 1705794. 2) S. Kubo, M. Nakagawa, *et al.*, *ACS Appl. Mater. Interfaces* **2014**, *6*, 811. 3) K. Ogata, S. Kubo, A. Shishido, *et al.*, *Molecules* **2022**, *27*, 689. 4) S. Kubo, M. Nakagawa, *Chem. Lett.* **2012**, *41*, 1137.

Mechano-responsive supramolecular hydrogel driven by stretch induced phase separation

([1]*Graduate School of Engineering, Osaka University,* [2]*Graduate School of Science, Osaka University*) ○Sooyeon Noh[1], Akihide Sugawara[1], Yoshinori Takashima[2], Hiroshi Uyama[1]

Keywords: Supramolecule, Hydrogel, Cellulose, Host–Guest Interaction, Mechano-responsiveness

Introduction: Mechano-responsive hydrogels that can induce changes in their appearance with the applied force have attracted much attention because they can visualize the mechanical stress. Supramolecular host–guest interaction is composed of hetero-molecular pairs, enabling to produce changes in the network properties in its associated and dissociated states[1]. Therefore, it can be used as a molecular switch in response to external mechanical force. In this study, mechano-responsive supramolecular hydrogels were prepared utilizing cellulose modified with adamantane (Ad) as a guest group. The hydrogels were cross-linked by host–guest complex between β-cyclodextrin (β-CD) and Ad.

Experimental: Ad-modified cellulose (Ad-cellulose) was synthesized by esterification reaction between hydroxy group of cellulose and 1-adamantanecarbonyl chloride (**Fig. 1a**). The CD-AdC*x* hydrogels were prepared by free-radical copolymerization of acrylamide (AAm) and 6-acrylamido-β-CD (β-CD-AAm) in the presence of Ad-cellulose. (*x* refers to the weight percentage of Ad-cellulose in the pre-gel solution) (**Fig. 1b**). The mechano-responsive properties of the CD-AdC*x* hydrogels upon stretching were analyzed by evaluating the opacity of the gels.

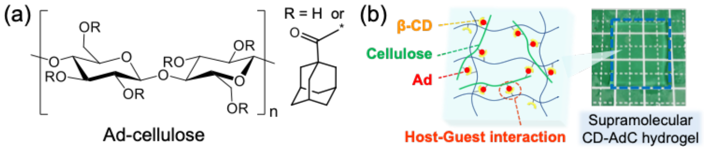


Figure 1. (a) Chemical structure of Ad-cellulose (b) Schematic illustration and photograph of the CD-AdC hydrogel.

Results and Discussion: The synthesized Ad-cellulose showed the solubility in an aqueous solution of β-CD derivatives. This result indicates that host–guest complex was formed between Ad group and host molecule, and Ad-cellulose with the complex hydrated in the aqueous media due to the enhancement of the hydrophilicity of the polymer. The appearance of the hydrogel changed from transparent to opaque upon stretching and returned to its original state upon releasing (**Fig. 2a**). The mean gray value, which indicates the opacity, showed that the opacity of the hydrogels gradually increased upon stretching to 600% strain (**Fig. 2b**). This property is due to the phase separation of the Ad-cellulose in the gel network induced by dissociation of the host–guest complex under mechanical force.

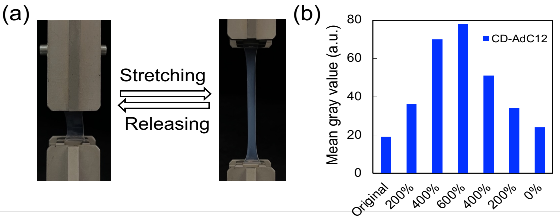


Figure 2. (a) Mechano-responsive behavior and (b) Opacity value of the CD-AdC12 gel upon stretching.

1) Sugawara, A. *et al. ACS Macro Letters* **2021**, 10 (7), 971-977.

次世代イメージングツールへの応用を指向した撥水性ナノ薄膜の大量調製法の確立と機能評価

(東海大院工[1]・東海大工[2]・東海大院総理工[3]・東海大マイクロ・ナノ研[4]) ○内田 頼[1]・平塚 達也[2]・青木 拓斗[3]・岡村 陽介[1,3,4]

Establishment of Massive Fabrication of Water-Repellent Nanosheets and Their Evaluation for Next-Generation Imaging Tools. ([1] *Graduate School of Engineering, Tokai University*, [2] *School of Engineering, Tokai University,* [3] *Graduate School of Science & Technology, Tokai University,* [4] *Micro/Nano Technology Center, Tokai University*) ○Rai Uchida,[1] Tatsuya Hiratsuka,[2] Takuto Aoki,[3] Yosuke Okamura[1,3,4]

Polymer nanosheets with a thickness of less than 100 nm represent unique properties such as high level of adhesiveness to the various interfaces 1). In fact, water-repellent nanosheets composed of a fluoropolymer prevented drying and blurring of biological tissues during microscopic observation, resulting in high-resolution deep tissue imaging 2,3). In this study, we propose massive fabrication of water-repellent nanosheets by using Roll-to-Roll method and evaluate their characterizations as imaging tools. Roll-to-Roll method was used to successfully massive fabrication of water-repellent nanosheets. The nanosheet was uniquely capable of providing a coverslip-free imaging. In fact, by wrapping the tissue with a nanosheet, an extra distance of 170 μm for the movement of objective lens was obtained. We thus demonstrated that nanosheet wrapping acts as a powerful tool for high quality deep imaging of tissues.

Keywords: Water-Repellent Nanosheet, Massive Fabrication, Roll-to-Roll Method, Deep Tissue Imaging

高分子薄膜の膜厚を 100 nm 以下に加工するとナノ厚特有の高接着性が発現し、反応性官能基や接着剤を使用することなく物理吸着のみで種々の界面に対して貼付できる 1)。この特性を活用し、撥水性高分子からなるナノ薄膜を用いて生体組織をラッピングすると、観察時に生じる乾燥やブレが抑制され、高解像度のイメージングが可能になる 2,3)。現在、撥水性ナノ薄膜の調製法としてスピンコート法が提案されている。この方法は、均質なナノ薄膜が調製可能であり高い膜厚制御性を有する利点があるものの、生産性に乏しいため大量調製法の確立が急務である。本研究では、大面積かつ連続的に調製可能であるロール・ツー・ロール方式を活用した撥水性ナノ薄膜の大量調製法を確立し、次世代イメージングツールへの応用を目指す。

ロール・ツー・ロール方式は以下の工程で行った。μコーターを用いて、ポリビニルアルコール水溶液 (PVA, 4.0 wt%)をポリプロピレンフィルム (PP, 幅: 10 cm, 長さ: 100 m)に塗工 (搬送速度: 1.0 m/min) し、犠牲膜とした。次いで、フッ素系高分子溶液 (CYTOP, 1.5 wt%)を PVA-PP フィルム上に塗工 (搬送速度: 2.0 m/min)した。その後、純水に浸漬させ、CYTOP ナノ薄膜を剥離、回収した。電顕観察及び表面粗さ解析を行ったところ、ナノ薄膜には欠損が見られず、平滑性の高いことが示唆された。したがって、撥水性ナノ薄膜の大量調製に成功した。 透明化試薬によって屈折率 1.52 に統一したマウスの脳切片にナノ薄膜をラッピングした。共焦点レーザー顕微鏡を用いて、ナノ薄膜を介して神経細胞 (eYFP 発現)を撮像したところ、作動距離が劇的に向上し、従来のガラス基板を介した観察では困難である 300 μm 付近の深部まで観察可能であった。従って、ロール・ツー・ロール方式にて大量調製した撥水性ナノ薄膜を活用し、生体深部イメージングツールとして応用できる可能性を実証した。

1) Okamura Y. *et al. Adv. Mater.* **21**, 4388 (2009). 2) Zhang H. *et al. Adv. Mater.* **29**, 1703139 (2017). 3) H. Zhang *et al. PLoS ONE* **15**, e0227650 (2020).

日本化学会 第104春季年会 (2024)

カーボン複合可動性架橋材料を用いた応力-ひずみセンシング

（阪大院理 [1]・阪大 FRC[2]・阪大 OTRI[3]）○以倉 崚平 [1,2]・梶本 晃太 [1]・朴 峻秀 [1,2]・高島 義徳 [1,2,3]

Stress-strain sensing using carbon composites with movable cross-links

([1]*Graduate School of Science, Osaka University*, [2]*FRC, Osaka University,* [3]*OTRI, Osaka University*) ○ Ikura Ryohei,[1,2] Kota Kajimoto,[1] Junsu Park,[1,2] Takashima Yoshinori[1,2,3]

We designed two kinds of composite materials with Ketjenblack (KB) and movable cross-linked elastomers to achieve high toughness, high conductivity, and strain-sensing functions. One approach is mixing a linear polymer (poly(ethyl acrylate), PEA), EA-based movable cross-linked material, and KB to obtain the stress-strain sensor showing stable responses for over 100 loading and unloading cycles. The other approach is a composite made with KB and a movable cross-network elastomer, where movable cross-links connect the CD-modified polystyrene (PSCD) and PEA. The obtained composite acts as a highly sensitive stress-strain sensor.

Keywords : Carbon composites; Movable cross-links; Toughness; Conductivity; Stress-strain sensing

本研究では、主鎖がシクロデキストリン(CD) の空孔に高分子鎖が貫通した可動性架橋 [1] を有する導電性カーボンフィラー(KB)複合材料超分子材料を 2 種類開発し、強靭性･導電性･ひずみ応答性を付与した [2]。可動性架橋高分子材料(SC)と直鎖状高分子(PEA: Poly(ethyl acrylate)、KB をボールミル混合し、複合材料 SC/PEA/KB(10)を得た(**Fig. 1a**)。延伸ひずみに対して線形的に電気抵抗が増加するひずみセンサー(**Fig. 1b**)が得られ、100 回の繰り返しの延伸にも安定な応答性を示した(**Fig. 1d**)。もう一つの設計として、アセチル化 CD 修飾 Polystyrene の CD 環を PEA が貫通した材料と KB を THF 中に溶解後、乾燥して複合材料 PSCD⊃PEA/KB(10)を得た。PSCD⊃PEA/KB(10)は延伸時に被包接高分子 PEA が CD 環から脱離することで、より高いひずみ応答性を示した(**Fig. 1c**)。また、100 回の延伸により、安定的な応答に近づいた(**Fig. 1e**)。

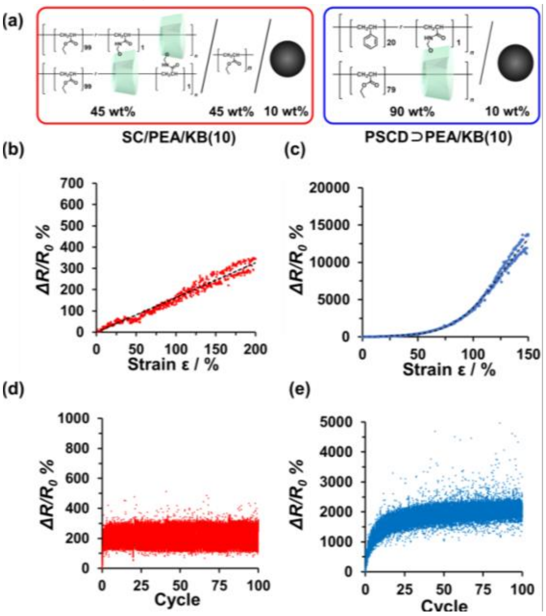


Fig. 1. (a) Chemical components of SC/PEA/KB(10) and PSCD⊃PEA/KB(10). $\Delta R/R_0$ of **(b)** SC/PEA/KB(10) and **(c)** PSCD⊃PEA/KB(10) upon tensile deformation. $\Delta R/R_0$ of **(d)** SC/PEA/KB (10) and **(e)** PSCD⊃PEA/KB (10) during 100 stretch-release cycles at 100% strain.

【参考文献】1) Fabrication and Mechanical Properties of Knitted Dissimilar Polymeric Materials with Movable Cross-Links. R. Ikura, Y. Takashima, et. al. *Mol. Syst. Des. Eng.* **2022**, *7*, 733-745. **2)** Highly stretchable stress-strain sensor from elastomer nanocomposites with movable cross-links and ketjenblack. R. Ikura, Y. Takashima, et. al. *ACS Polymers Au* **2023**, *3*, 394-405.

両親媒性ジブロックポリペプチドと Dawson 型ポリオキソメタレートとの複合化による三角形ナノプレート構造とその触媒活性の評価

(崇城大院工 1))宮本 翔唯 1・○黒岩 敬太 1

Triangular nanoplate formed from hybrids of Dawson-type polyoxometalates with amphiphilic diblock polypeptides and their catalytic properties.

([1]*Graduate School of Engineering, Sojo University*) Kai Miyamoto,[1] ○Keita Kuroiwa,[1]

Diblock copolypeptide amphiphiles can form a variety of structures depending on the ratio and type of amino acids in the hydrophilic and hydrophobic regions.1) Polyoxometalates (POM) exhibit characteristic structures that depend on their constituents, along with multi-electron redox reactions. The goal of this study was to hybridize $[P_2W_{18}O_{62}]^{6-}$ with polypepitdes to develop functional nanomaterials with enhanced catalytic properties. The specific structures resulting from the self-assembly process and their respective catalytic effects were evaluated. Scanning Electron Microscopy (SEM) observations confirmed that the resulting hybrid material formed a distinctive triangular structure based on the triple symmetry of $[P_2W_{18}O_{62}]^{6-}$. The reaction using the hybrid material was successfully carried out in a homogeneous system under water. The hydrophilic and hydrophobic layers within the specific triangular structure are thought to be crucial elements in the reaction process.

Keywords : Diblock Copolypepitde Anphiphiles; Supramolecular Hybrid; Polyoxometalate; Nanostructure; Triangular nanoplate

両親媒性ジブロックコポリペプチドは、親水部と疎水部のアミノ酸の比率や種類、重合度に応じて、様々なナノ構造が形成される。1) ポリオキソメタレート（POM）は、多電子酸化還元反応とともに、その構成成分に依存した特徴的な構造と性質を示す。本研究では、$[P_2W_{18}O_{62}]^{6-}$をポリペプチドとハイブリッド化し、触媒特性を向上させた機能性ナノ材料の開発を行った。自己組織化プロセスから得られる特徴的なナノ構造を評価し、それぞれの触媒効果を評価した。走査型電子顕微鏡（SEM）観察の結果、得られたハイブリッド材料は、$[P_2W_{18}O_{62}]^{6-}$の三回対称性に基づく特徴的な三角形ナノプレート構造を形成していることが確認された。このハイブリッド材料を触媒として用いた有機合成反応では、水中の均一系で可能となった。ハイブリッド材料の特異な三角形構造内の親水層と疎水層が、反応プロセスにおける重要な要素になっていると考えられる。

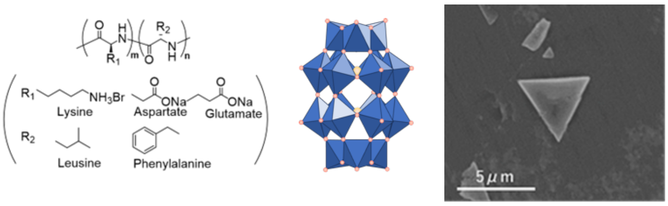


Fig.1 Chemical structure of polypeptides, schematic illustration of $[P_2W_{18}O_{62}]^{6-}$, and SEM image of hybrid $[P_2W_{18}O_{62}]^{6-}$ / Lys$_{33}$-*b*-Leu$_1$

1) Y. Tanimura, K. Miyamoto, T. Shiga, M. Nihei, K. Kuroiwa, *J. Phys. Chem. C* **2023**, *127*, 16525-16537. and references therein.

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

2024年3月21日(木) 13:00 ~ 15:10 A1442(14号館 [4階] 1442)

[A1442-4pm] 19. コロイド・界面化学

座長：亀山 達矢、神戸 徹也

英語

13:00 ~ 13:20

[A1442-4pm-01]

機械学習を用いた多元素合金ナノ粒子における高活性水素発生反応触媒の探索

○丸田 悠斗[1]、草田 康平[1,2]、Seo Okkyun[5]、坂田 修身[5]、河口 彰吾[5]、久保田 佳基[6]、金子 弘昌[7]、鳥山 誉亮[3]、山本 知一[3]、村上 恭和[3,4]、北川 宏[1] (1. 京大院理、2. 京大白眉センター、3. 九大URC、4. 九大院工、5. 高輝度光科学研究センター、6. 阪公大院理、7. 明大院理工)

英語

13:20 ~ 13:40

[A1442-4pm-02]

Machine learning guided development of size and shape controlled inorganic nanoparticles

○Quan ZOU[1], Kiyoshi Kanie[1,2] (1. International Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai, Miyagi 980- 8577, Japan, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan)

英語

13:40 ~ 14:00

[A1442-4pm-03]

多元系合金ナノ粒子触媒によるCO_2水素化反応における元素–電子構造–生成物選択性相関

○中村 雅史[1]、Dongshuang Wu[1]、向吉 恵[1]、草田 康平[1,2]、鳥山 誉亮[3]、山本 知一[3]、村上 恭和[3,4]、河口 彰吾[5]、伊奈 稔哲[5]、久保田 佳基[6]、北川 宏[1] (1. 京大院理、2. 京大白眉セ、3. 九大URC、4. 九大院工、5. JASRI/SPring-8、6. 阪公大院理)

14:00 ~ 14:10

休憩

日本語

14:10 ~ 14:30

[A1442-4pm-04]

Au-Fe_3O_4ヤヌスナノ粒子の液液界面における自己組織化によるベシクル形成

○谷地 赳拓[1,2]、三友 秀之[2,4]、蟹江 澄志[3,4]、居城 邦治[2] (1. 日本学術振興会、2. 北大電子研、3. 東北大SRIS、4. 東北大多元研)

英語

14:30 ~ 14:50

[A1442-4pm-05]

Highly ordered $L1_0$-type Pt-*M*-Zn Nanoparticles for Electrocatalysts

○Wu Tian[1], Ryota Sato[2], Yoshiharu Uchimoto[3], Toshiharu Teranishi[1,2] (1. Grad. Sch. of Sci., Kyoto Univ., 2. Inst. for Chem. Res., Kyoto Univ., 3. Grad. Sch. of Human and Environ. Stud., Kyoto Univ.)

英語

14:50 ~ 15:10

[A1442-4pm-06]

三次元銀ナノ粒子超格子の合成と構造特異的機能

○ZHU LINGKAI[1]、猿山 雅亮[2]、寺西 利治[1,2] (1. 京都大学　理学研究科、2. 京都大学 化学研究所)

Exploration of highly active catalysts for hydrogen evolution reaction in multi-element alloy nanoparticles by machine learning

(*[1]Grad. Sch. Sci., Kyoto Univ., [2]Hakubi Center, Kyoto Univ., [3]URC, Kyushu Univ.,[4]Grad. Sch. Eng., Kyushu Univ, [5]Japan Synchrotron Radiation Research Institute [6]Grad. Sch. Sci., Osaka Pref. Univ. [7]Grad. Sch. Tech., Meiji Univ.)* ○Yuto Maruta[1], Kohei Kusada[1, 2], Tomokazu Yamamoto[3], Takaaki Toriyama[3], Yasukazu Murakami[3, 4], Okkyun Seo[5], Shogo Kawaguchi[5], Osami Sakata[5], Yoshiki Kubota[6], Hiromasa Kaneko[7], Hiroshi Kitagawa[1]

Keywords: Nanoparticles, Multi-element alloys, Catalysts, Machine learning, Hydrogen evolution reaction

Multi-element solid-solution alloy nanoparticles (NPs) have attracted much attention as a new class of catalysts because they have both high activities and stabilities for many kinds of reactions. For example, equimolar platinum-group metal (PGM) quinary alloy NPs show extremely high catalytic activity for electrochemical hydrogen evolution reaction (HER)[1,2]. However, it is quite difficult to find their optimized compositions because of their compositional complexities. One possible way to overcome this difficulty is to use machine learning, and here, we explored a PGM multi-element alloy HER catalyst by machine learning.

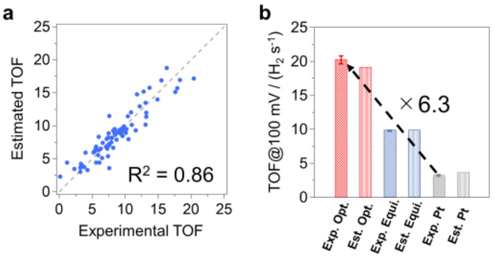


Figure 1 (a) Parity plot of TOF at 100 mV (b) Experimental and estimated TOF at 100 mV of the optimized sample (red), equimolar sample (blue) and Pt NPs (grey).

We firstly synthesized PGM quinary alloy NPs with more than 70 different compositions directly on carbon support. Turnover frequency (TOF) which shows an activity normalized by electrochemical active surface area was used as a target variable to discuss the intrinsic activity. Cross terms and three-factor interaction terms of compositions from XRF were used as descriptors to search multi-element alloy compositions. It is found that the Gaussian-process regression (GPR) model using only experimental variables shows a very high generalization performance (Fig.1-a). The virtual experiment with 10,000 compositions was conducted using the obtained model to predict the optimal composition. A catalyst with the predicted optimal composition was synthesized and showed 6.3 times higher HER activity than Pt NPs (Fig.1-b). Moreover, this activity value is consistent with the estimated value from the GPR model, indicating that the optimal composition was successfully predicted by using a simple dataset consisting only of the experimental results. Since there are more than 10,000 compositions covering the quinary alloys in increments of 5%, our method can make compositional optimization more than 100 times more efficient. This method could be applied to other complex alloy systems.

1) D. Wu et al., *Chem. Sci.*, 2020,11, 12731-12736. 2) Y. Maruta et al., *Chem Commun.*, 2022, 58, 6421-6424.

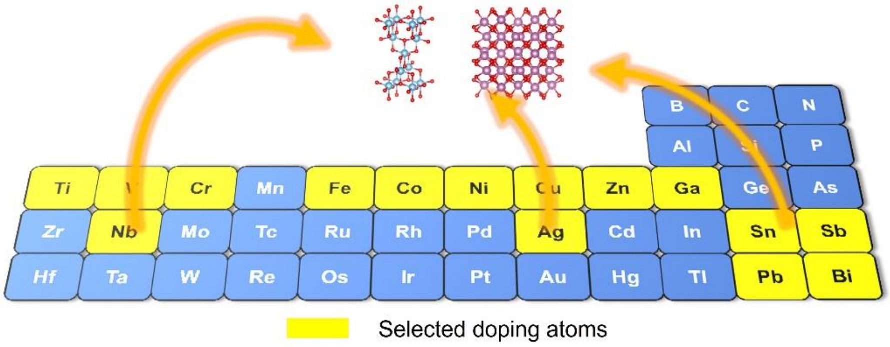
Machine learning guided development of size and shape controlled inorganic nanoparticles

(¹ *International Center for Synchrotron Radiation and Innovation Smart (SRIS), Tohoku University, Sendai, 980-8577, Japan,* [2] *Institute of Multidisciplinary Research for Advanced Materials Institution, Tohoku University, Sendai, 980-8577, Japan*)

○Quan Zou[1], Kiyoshi Kanie[1,2]

Key words: inorganic nanoparticles, size and shape, machine learning

Controlling the size and shape of nanoparticles (NPs) was deemed as an effective method to ameliorate their properties[1,2]. Thus, it was adopted as a controllable strategy to synthesize functional materials. However, conventional methods of controlling the size and shape of inorganic NPs involve a wide range of factors, which led to a dilemma that development of inorganic NPs was mainly focused on the trail-and-error method. Lack of theoretical guidance in controlling the size and shape of NPs was regarded as one of the most crucial bottlenecks hindering the development of NPs. On the other hand, artificial intelligence (AI), considered as a rising power to surpass human and further develop novel materials from a new perspective, attracted our interests. Machine learning (ML) was adopted to develop promising and novel NPs.



In this work, 2 metal oxides and 13 doping atoms were selected to prepare size and shape-controlled NPs. All the NPs were synthesized in a unified procedure, from which the features for database construction were extracted. XRD and TEM were used to investigate the structural and compositional information and determine the synthesis of NPs. Finally, ML was adopted to analyze the database and predict promising candidates for practical applications.

1) *J. Am. Chem. Soc.* 2011, 133, 39, 15743–15752

2) *J. Am. Chem. Soc.* 2014, 136, 396–404

Element–Electronic Structure–Product Selectivity Relationship in CO_2 Hydrogenation over Multi-Element Alloy Nanoparticle Catalysts

([1]*Grad. Sch. Sci., Kyoto Univ.*, [2]*Hakubi Center, Kyoto Univ.*, [3]*URC, Kyushu Univ.*, [4]*Grad. Sch. Eng., Kyushu Univ.*, [5]*JASRI/SPring-8*, [6]*Grad. Sch. Sci., Osaka Metro. Univ.*)
○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Shogo Kawaguchi[5], Toshiaki Ina[5], Yoshiki Kubota[6], Hiroshi Kitagawa[1]

Keywords: Multi-Element Alloy Nanoparticles; CO_2 Hydrogenation; Selectivity; XANES

Multi-element alloys nanoparticles (MEA NPs) are now one of the dominant subjects of catalyst development.[1] Recent studies have demonstrated their attractive catalytic properties; extraordinary enhancement in activity,[2] realization of complicated catalysis[3] or excellent durability.[4] Nevertheless, the product selectivity control has poorly been studied in the field of MEA NPs catalysts. It would require systematic understanding about how elemental combinations in alloys affect their electronic structures and catalytic properties.

Here, we targeted a series of alloy NPs composed of elements with different electronic natures, platinum-group metals (PGMs) and base metals (*p*-block or 3*d* metals), and developed their versatile synthesis method. Then, their electronic structures and catalytic activities as CO_2 hydrogenation catalysts (**Fig.**) were investigated. As a result, we found the evident correlation between the whiteline peak heights in XANES of PGM *L* egdes and CO/CH_4 selectivities. This indicates that the elemental interaction in the alloy would affect their electronic structures, consequently leading to the change in their catalytic properties.

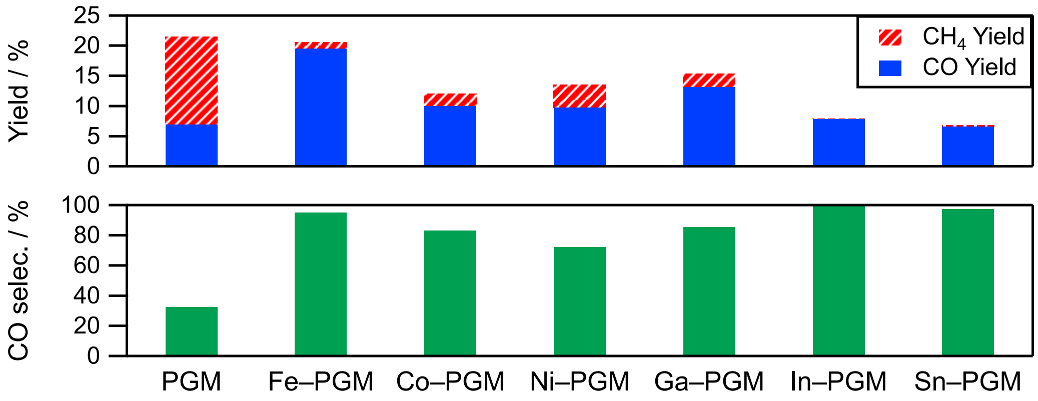


Fig. CH_4 and CO yields (top) and CO selectivity (bottom) in CO_2 hydrogenation over PGM quinary NPs and X–PGM senary NPs (X=Fe, Co, Ni, Ga, In and Sn) at 450 °C.

1) Y. Sun and S. Dai, *Sci. Adv.*, **2021**, *7*, eabg1600. 2) D. Wu *et al.*, *Chem. Sci.*, **2020**, *11*, 12731. 3) D. Wu *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 13833. 4) K. Mori *et al.*, *Nat. Commun.*, **2021**, *12*, 3884.

日本化学会 第104春季年会 (2024)

$Au\text{-}Fe_3O_4$ ヤヌスナノ粒子の液液界面における自己組織化によるベシクル形成

（日本学術振興会 [1]・北大電子研 [2]・東北大 SRIS [3]・東北大多元研 [4]） ○谷地 赳拓 [1,2]・三友 秀之 [2,4]・蟹江 澄志 [3,4]・居城 邦治 [2]

Vesicle Formation via Self-Assembly of $Au\text{-}Fe_3O_4$ Janus Nanoparticles at a Liquid-Liquid Interface

([1]*JSPS*, [2]*RIES, Hokkaido University,* [3]*SRIS, Tohoku University,* [4]*IMRAM, Tohoku University,*) ○ Takehiro Yachi,[1,2] Hideyuki Mitomo,[2,4] Hideyuki Mitomo,[2,4] Kiyoshi Kanie,[3,4] Kuniharu Ijiro[2]

Au-magnetic Janus nanoparticles (NPs) have great potential in bioapplication because they show unique optical and electromagnetic properties as well as high biocompatibility. In addition, the assembled state can be controlled by modifying each surface differently, allowing for further functionalization through self-assembly. In this study, we synthesized $Au\text{-}Fe_3O_4$ Janus NPs with hydrophilic ligands on the Au surface and hydrophobic ligands on the Fe_3O_4 surface to form self-assembled vesicle structures at the liquid-liquid interface. The results showed that vesicles of about 100 nm are stably formed at the interface of $CHCl_3$/sodium citrate aqueous. The resulting vesicles are expected to be used for applications such as drug delivery.

Keywords : Au nanoparticles, Magnetic nanoparticles, Self-assembly, Janus nanoparticle, Vesicles

金ナノ粒子と磁性ナノ粒子からなるヤヌスナノ粒子は，それぞれの光学特性や磁気特性を併せ持ち，高い生体適合性を示すことから生体応用などにおいて注目を集めている．また，それぞれの表面に対して異なる表面修飾が可能であるため，異なる表面特性を利用した自己集合化によるさらなる機能化が期待される．本研究では，$Au\text{-}Fe_3O_4$ ヤヌスナノ粒子の合成と表面修飾を行い，自己組織化によるベシクルの形成を行った．

【実験】まず，オレイルアミンで被覆された Au ナノ粒子の合成を行い，これを種粒子として $Au\text{-}Fe_3O_4$ ヤヌスナノ粒子を合成した [1,2)]．次いで得られた粒子の Au 表面を親水性の 11-Mercaptoundecanol hexaethyleneglycol ether で修飾し，親水面と疎水面を併せ持つ粒子を得た．その後，$CHCl_3$ とクエン酸ナトリウム水溶液の界面にて粒子を自己組織化させることによってベシクル構造の形成を行った．

【結果・考察】**Fig. 1a** に得られた粒子の TEM 像を示す．結果として，8.8 ± 0.8 nm の Au 粒子，13.5 ± 1.7 nm Fe_3O_4 粒子からなるヤヌス粒子が得られた．また，Au 表面を親水性配位子で修飾した粒子では，$CHCl_3/H_2O$ の界面に集合する様子が見られ，親水・疎水表面の双方を有することが示唆された．**Fig. 1b** に液液界面における自己組織化によって形成されたベシクルの TEM 像を示す．結果より，100 nm 程度のベシクル構造の形成が確認され，親水面・疎水面を併せ持つ $Au\text{-}Fe_3O_4$ ナノ粒子の自己組織化によってベシクルの形成が可能であることが示された．本手法では，ベシクル内部への薬物内包を利用した薬物送達への応用などが期待されるほか，Fe_3O_4 粒子表面を有機分子で修飾することでさらなる機能化が期待される．

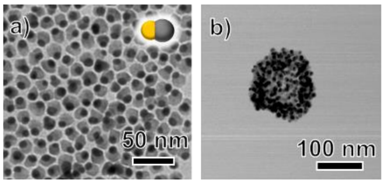


Fig. 1 a) $Au\text{-}Fe_3O_4$ ナノ粒像および b) 自己組織化により形成されたベシクルの TEM 像

1) H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White, S. Sun, *Nano Lett.*, 5, 379 (**2005**)
2) M. Niehues, S. Engel, B. J. Ravoo, *Langmuir*, 37, 11123 (**2021**)

Highly Ordered $L1_0$-Type Pt–M–Zn Nanoparticles for Electrocatalysts

([1]*Graduate School of Science, Kyoto University*, [2]*Institute for Chemical Research, Kyoto University*, [3]*Graduate School of Human and Environmental Studies, Kyoto University*) ○Wu Tian,[1] Ryota Sato,[2] Yoshiharu Uchimoto,[3] Toshiharu Teranishi[1,2]

Keywords: Inorganic Nanoparticle; $L1_0$-Type Ordered Alloy; Low-Temperature Ordering; Strain Effect; Electrocatalyst

$L1_0$-ordered PtM (M is typically a 3d transition metal) intermetallic compounds (IMCs) have been regarded as promising electrocatalysts for sluggish reactions like oxygen reduction reaction (ORR) for fuel cells because of their superior acid corrosion resistance and much higher activity in acid media. Although there are many reports on the synthesis of binary $L1_0$-PtM or ternary $L1_0$-type Pt(M_1,M_2) nanoparticles (NPs) as electrocatalysts, they require high-temperature annealing to induce the phase transformation from disordered Pt–M alloy into ordered Pt–M IMCs.[1] However high-temperature annealing of supported NP catalysts causes severe sintering of NPs, which is unfavorable to electrocatalytic performance. Taken in consideration that $L1_0$-PtZn possesses much lower phase transformation temperature, we envisioned that the incorporation of Zn as an ordering promoter would allow the phase transformation of $L1_0$-PtM NPs to be initiated at relatively low temperature without sintering.

In this study, we used organometallic zinc complexes to incorporate the hard-to-reduce Zn into Pt–M NPs by a facile wet-chemical way (Fig. 1). This method allowed us to precisely control the composition of the NPs. The addition of Zn reduced the ordering temperature of Pt–M–Zn NPs and made it possible to transform into ordered IMCs at lower temperature, which helps to suppress sintering and achieves higher ordering degree. To improve ORR activity, i.e., to optimize the strain effect on the Pt outermost layer formed by acid treatment, compositionally controlled $L1_0$-type Pt(M,Zn) (M = Co and/or Ni) NPs with high ordering degree were synthesized through low temperature annealing. This approach is expected to address simultaneous improvements in ORR activity and durability.

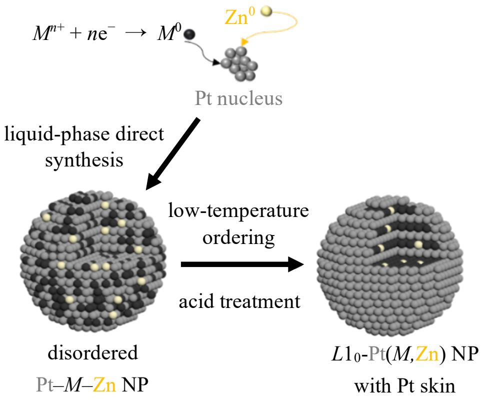


Figure 1. Schematic illustration of the synthetic route to core-shell $L1_0$-Pt(M,Zn) NP

This work is supported by NEDO (JPNP 20003).

1) J. Li *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 19209.

三次元 Ag ナノ粒子超格子の合成と構造特異的機能

（京大院理 ^{1}・京大化研 ^{2}）○Zhu Lingkai[1]・猿山 雅亮 [2]・寺西 利治 [1,2]
Synthesis of 3D Ag nanoparticle superlattices and their structure-specific functions ([1]*Graduate School of Science, Kyoto University,* [2]*Institute for Chemical Research, Kyoto University*) ○ Lingkai Zhu[1], Masaki Saruyama[2], Toshiharu Teranishi[1,2]

Nanoparticle (NP) superlattices show unique concerted properties which are not exhibited by isolated NPs. Especially, the superlattices consisting of NPs with localized surface plasmon resonance properties have been expected as a new type of plasmonic materials due to their unique optical properties derived from plasmon coupling. In this study, we investigated the simple one-pot synthesis of 3D Ag NP superlattices and their structure-specific functions. Ag NP superlattices were obtained as a blue powder, which showed broad optical absorption from visible to near-infrared region due to the plasmon coupling. The film of the superlattice showed superhydrophobicity derived from the micro-meter scale surface roughness and has a potential as a substrate for highly sensitive Raman scattering measurements.

Keywords：Self-assembly, LSPR, Ag nanoparticles, Small-angle X-ray scattering

局在表面プラズモン共鳴（LSPR）特性をもつナノ粒子の超格子は、プラズモンカップリング現象によって共鳴波長の変化や局所増強電場の形成を示すことから、新しい光学応用が期待される。本研究では、Ag ナノ粒子の三次元超格子を一段階反応で合成する方法を開発するとともに、その構造特異的な機能について検証した。

$AgNO_3$ をドデシルアミン中で加熱することで青色の沈殿物が得られ、これが約 10 nm の Ag ナノ粒子が最密充填した多面体構造をもつ数 μm の三次元超格子であることを確認した（Fig. 1）。Ag ナノ粒子分散液が 400 nm にのみ LSPR 吸収を示すのに対して、この超格子はプラズモンカップリングにより可視～近赤外域にかけて幅広い光を吸収できることが分かった（Fig. 2a）。また、三次元超格子を基板上に成膜することで、自然に形成される μm オーダーの凸凹によって超撥水性が発現することを見出しており（Fig. 2b）、基質濃縮効果をもつ高感度ラマン散乱用の基板としての利用も検討したので報告する。

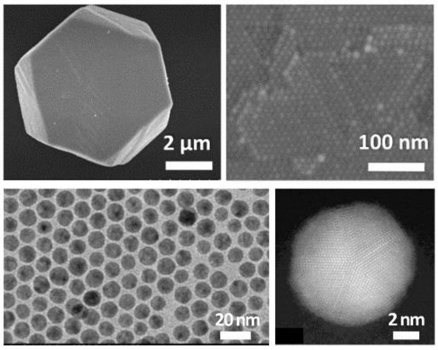


Fig. 1. (upper) SEM images of Ag NP superlattice. (lower) TEM images of Ag NPs.

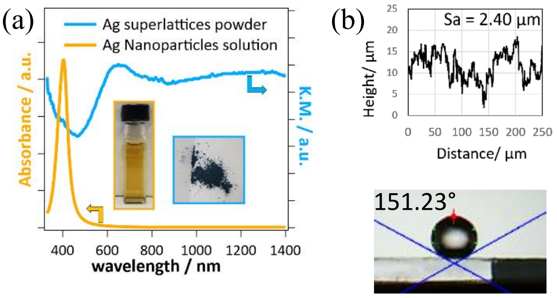


Fig. 2. (a) Absorption spectra of Ag NPs and their superlattices. (b) Surface roughness of Ag NP superlattices film and the contact angle with water droplet.

1) F. Nakagawa, M. Saruyama, T. Teranishi *et al.*, *J. Am. Chem. Soc.* **2022**, 144, 5871–5877.

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

2024年3月21日(木) 9:00 ~ 11:30 A1455(14号館 [5階] 1455)

[A1455-4am] 21. エネルギーとその関連化学，地球・宇宙化学

座長：前田 和彦、鳥本 司

日本語
9:00 ~ 9:20
[A1455-4am-01]
膜蒸留と気液交換を融合したHTOのH_2Oからの効率的分離

〇三好 弘一[1]、藤原 正浩[2] (1. 徳島大学、2. 大阪大学)

英語
9:20 ~ 9:40
[A1455-4am-02]
Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

〇Susmita Roy[1], Masayoshi Higuchi Higuchi[1], Sanjoy Mandal[1] (1. National Institute for Materials Science (NIMS), 1 -1 Namiki)

英語
9:40 ~ 10:00
[A1455-4am-03]
有機薄膜太陽電池材料における自発的対称性の破れによる電荷分離

〇在間 嵩朗[1,2]、大田 航[1,2]、春田 直毅[1,2]、 上島 基之[3]、大北 英生[2]、佐藤 徹[1,2] (1. 京大福井セ、2. 京大院工、3. （株）MOLFEX)

英語
10:00 ~ 10:20
[A1455-4am-04]
Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

〇Wentao Zhang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)

10:20 ~ 10:30
休憩

英語
10:30 ~ 10:50
[A1455-4am-05]
層状ペロブスカイト酸フッ化物$Pb_3Fe_2O_5F_2$を電極触媒とした水の酸化反応

〇水落 隆介[1]、菅原 勇貴[1]、山口 猛央[1]、前田 和彦[1] (1. 東京工業大学)

日本語
10:50 ~ 11:10
[A1455-4am-06]
CO_2と水からギ酸を生成する電気化学リアクタの長期耐久性向上

〇加藤 直彦[1]、河合 泰明[1]、野尻 菜摘[1]、塩澤 真人[1]、菊澤 良弘[1]、鈴木 伸明[1]、小坂 悟[1]、濱口 豪[1]、竹田 康彦[1] (1. 株式会社　豊田中央研究所)

🏷 日本語
11:10 ~ 11:30
[A1455-4am-07]

光触媒型膜-電極接合体へのプロトン伝導性配位高分子の適用

〇竝木 裕司[1,2]、田部 博康[1]、堀毛 悟史[1] (1. 京大、2. ポーラ化成工業)

膜蒸留と気液交換を融合したHTOのH_2Oからの効率的分離

（徳島大放セ[1]・阪大環境安全セ[2]）○三好 弘一[1]・藤原 正浩[2]

Efficient separation of HTO from H_2O by membrane distillation using gas-liquid exchange

([1] *Adv. Rad. Res., Edu., Mgmt. Ctr., Tokushima University*, [2]*Res. Ctr. Environ. Preserv., Osaka University*) ○Hirokazu Miyoshi,[1] Masahiro Fujiwara[2]

H_2O containing HTO loaded on a hydrophobic membrane with a photothermal black dye was exposed to an artificial sunlight for 1.5 h. The heat generated from the sunlight vaporized the water to penetrate the vapor through the membrane. The water vapor thus permeated was mixed in H_2O impregnated in hydrophilic filters under the membrane. Gas-liquid exchange occurred in these filters to decrease the content of HTO in the recovered water under all filters. The increases both of the filter number and the water content of the hydrophilic filters further enhanced the separation effect of HTO. When four hydrophobic membranes and four water-containing hydrophilic filters were set alternately, the ratio of HTO recovered under these filters was reduced to 12%.

Keywords : Tritiated water; Membrane distillation; Light irradiation; Gas-liquid exchange; rectification

光熱変換性の色素ソルベントブラック 5(SB-5)を塗布した疎水性膜(PTFE 製 PF100)上にHTO含有水(HTO濃度: 3026 Bq/mL)を導入し、上方から人工太陽光(994 Wm^{-2})を1.5時間照射した（図左）。光熱変換効果によりHTO含有水は蒸気となり疎水性膜を透過する。その際、膜下にセットした含水の親水性フィルター中で気液交換が起き、全てのフィルター下部に回収された水中のHTO濃度は減少していた。親水性フィルターの枚数や含水量を増やすことで、回収水中のHTO濃度をさらに下げることができた。親水性フィルターであるガラスフィルター(GB-140)にH_2Oを約2.5 g含水させた場合、フィルター下部に回収された水中のHTO濃度は約77%まで減少した。さらに、含水ガラスフィルターと疎水性膜の組み合わせを4セット計8枚まで増やしたところ、HTO量を約12%までに減少させることに成功した（図右）。一方、水を含まないフィルターではHTO濃度はほとんど減少しなかった。

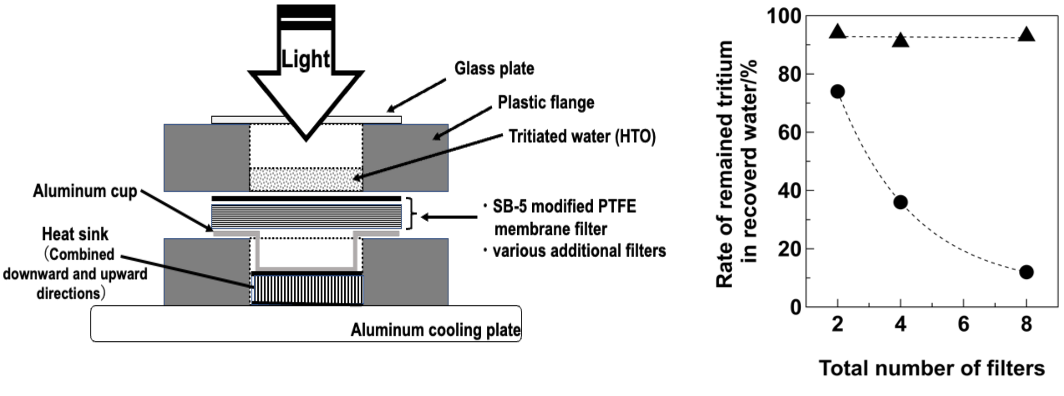


Figure (Left) Schematic diagram of experimental apparatus of tritiated water separation. (Right) Relation between the remained tritiated water rate in recovered water and the total number of PF100 and GB-140. ▲: Dry GB-140. ●: GB-140 with 1 g of water.

Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

([1]*National Institute for Materials Science (NIMS), 1 -1 Namiki*) ○Susmita Roy,[1] Sanjoy Mandal,[1] Masayoshi Higuchi[1]

Keywords: Electrochromism; Metallo-supramolecular Polymer; Electrochromic Device; Durable Electrochromic Device; Electrochromic memory

An solid-state electrochromic device (ECD) of Fe(II)-based metallo-supramolecular polymer (polyFe) with excellent durability was fabricated by incorporating Nickel hexacyanoferrate (NiHCF) as a charge-balancing layer. The solid-state ECD displayed bleaching and coloring at small potential window, with maximum optical contrast. The minimalization of the potential difference during EC changes enabled ultra-high cycle stability and improved optical memory. For the further improvement of the EC properties, it was revealed that the optimization of the film thickness of the polyFe and NiHCF is critical to maintaining the charge balance between the working and counter electrodes. At last, the cyclic stability for the repeated color changes over 100,000 cycles were achieved.[1] This finding will help engineers and scientists to fabricate a low-voltage-driven, long-lasting ECD for real-life application in smart electrochromic window technology.

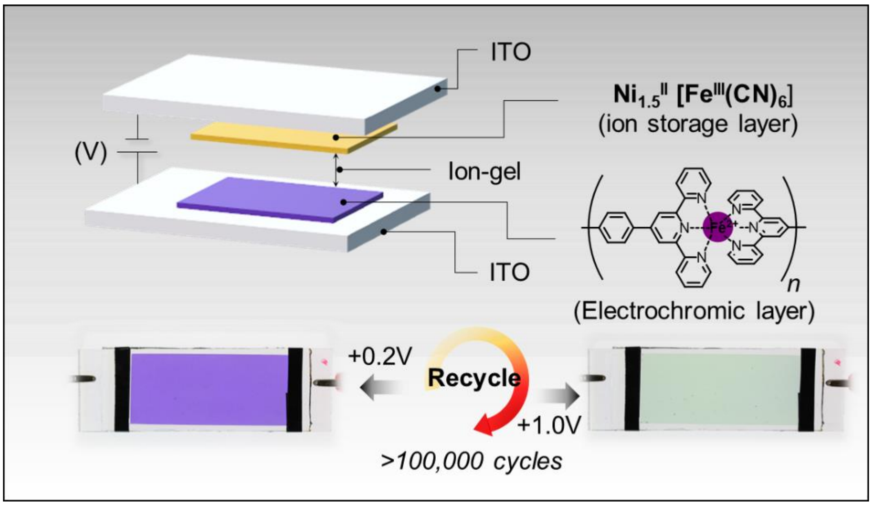


Figure 1. Highly Durable Electrochromic Device of Fe(II)-Based Metallo-Supramolecular Polymer

1) S. Mondal, S. Roy, Y. Fujii, M. Higuchi *ACS Appl. Electron. Mater.* **2023**, *5*, 6677–6685.

Spontaneous-Symmetry-Breaking Charge Separation in Organic Photovoltaic Material

([1]*Fukui Institute for Fundamental Chemistry, Kyoto University,* [2]*Graduate School of Engineering, Kyoto University,* [3]*MOLFEX, Inc.*) ○Takeaki Zaima,[1,2] Wataru Ota,[1,2] Naoki Haruta,[1,2] Motoyuki Uejima,[3] Hideo Ohkita,[2] Tohru Sato[1,2]

Keywords: Photovoltaic conversion; ITIC; Density functional theory; Pseudo-Jahn–Teller effect; Vibronic coupling

In organic photovoltaics (OPV), the driving force of the charge separation has been considered to be an energy offset, i.e., the LUMO (or HOMO) energy difference between donor and acceptor materials.[1] However, highly efficient OPV materials with small energy offsets were recently reported.[2,3] In such OPV materials, the driving force of the charge separation remains unclear. Symmetry-breaking charge separation (SB-CS) that causes the intra- or intermolecular charge separation between identical fragments could be an initial charge separation step in small offset systems.[4] This study aims to theoretically identify the driving force of charge separation in the small offset system using ITIC[3], a non-fullerene acceptor material for OPV devices.[5]

In the previous study, ITIC has been considered packed through the terminal π-π stacking.[6] Hence, we constructed the edge-stacking dimer model of ITIC. According to our density functional theory calculations, the pseudo-Jahn–Teller (PJT) distortion[4] of the S_1 excimer state induces spontaneous SB-CS (SSB-CS) between the identical ITIC molecules even without the asymmetry of the surrounding environment (Fig. 1). The strong PJT effect arises from the vibronic coupling between the pseudo-degenerate S_1 and S_2 excited states with different irreducible representations, i.e., A_u for S_1 and A_g for S_2, via the asymmetric vibrational mode of A_u. The vibrational mode responsible for the spontaneous polarization is the intramolecular C-C stretching vibration between the core IT and terminal IC units. These results suggest that the charge separation efficiency in the initial photovoltaic conversion process can be improved by controlling the PJT effect.

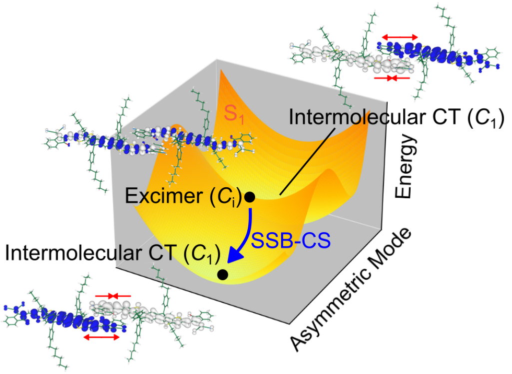


Fig. 1: Schematic illustration of the SSB-CS in ITIC dimer.

1) P. Peumans *et al.*, *J. Appl. Phys.* **2003**, *93*, 3693. 2) K. Kawashima *et al.*, *Nat. Commun.* **2015**, *6*, 1. 3) Y. Lin *et al.*, *Adv. Mater.* **2015**, *27*, 1170. 4) A. N. Bartynski *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 5397. 5) T. Zaima *et al.*, *J. Phys. Chem. Lett.* **2023**, *14*, 9706. 6) G. Han *et al.*, *J. Mater. Chem. C* **2017**, *5*, 4852. 7) I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, 1989).

Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

(*Graduate School of Engineering, Nagoya University*) ○Wentao Zhang, Kazutaka Akiyoshi, Tatsuya Kameyama, Tsukasa Torimoto

Keywords: Semiconductor nanocrystal; Quantum size effect; $AgBiS_2$; Light energy conversion; Low toxicity

The energy structure and light absorption properties of semiconductor quantum dots (QDs) can be controlled by changing their size and composition. The QDs have been intensively investigated for the application to photovoltaic, photocatalysis, and bio-imaging. In recent years, I-V-VI semiconductors (e.g. $NaBiS_2$[1], $AgBiS_2$[2]), composed of low-toxic elements, are regarded as potential alternatives to toxic IV-VI and II-VI semiconductors (PbSe[3], CdS[4]). Notably, $AgBiS_2$ QDs are expected to be an excellent light absorber for photovoltaic application due to their remarkable light-harvesting capabilities from the visible to the near-IR regions. However, there are limited reports on controlling their particle size and composition to enhance light-electricity conversion efficiency. In this study, we report a solution-phase synthesis of Ag-Bi-S QDs and their utilization in sensitized solar cells.

Ag-Bi-S QDs were prepared by heating the precursors of Ag(OAc), $Bi(OAc)_3$ and S in a mixture solution of oleylamine and dodecane thiol at different temperatures. As the preparation temperature increased from 100 °C to 200 °C, the particle size increased from 2.7 to 8.1 nm, accompanied by the change in particle composition from Ag-deficient ones to the stoichiometric $AgBiS_2$. The energy gap of QDs decreased from 1.45 to 1.05 eV with an increase in the particle size from 2.7 to 8.1 nm.

Figure 1a shows the electronic energy structure of Ag-Bi-S QDs prepared at different temperatures. The level of valence band was negatively shifted with an increase in the reaction temperature, while the level of conduction band was almost constant. The level of defect sites in the energy gap was evaluated by measuring the photocurrent onset potential of QD-immobilized electrodes: The defect sites were present in the energy gap for QDs prepared at 100 and 120 °C, but they were absent for the QDs with almost the stoichiometric composition, prepared at temperatures higher than 150 °C. Sensitized solar cells were fabricated by immobilizing Ag-Bi-S QDs on porous TiO_2 electrodes. Figure 1b shows the *J-V* curves of resulting cells. The use of the QDs prepared at 150 °C gave the highest performance, the power conversion efficiency reaching 0.76%.

[1] J. Vela *et al.*, *Chem. Mater.* **2020**, *32*, 6085. [2] Y. Wang *et al*, *Nat. Photon.* **2022**, *16*, 235. [3] S. Liu *et al.*, *ACS Nano* **2021**, *15*, 3376. [4] R. Zeng *et al.*, *Anal. Chem.*, **2019**, *91*, 2447.

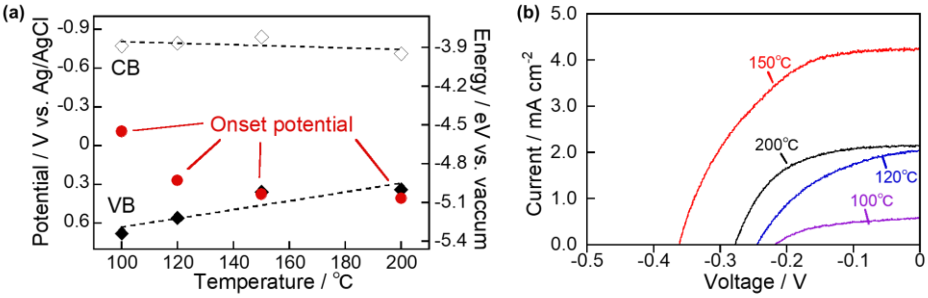


Fig. 1 (a) Energy structures of Ag-Bi-S QDs. (b) *J-V* curves of Ag-Bi-S QD-sensitized solar cells under the irradiation of AM1.5G simulated solar light.

Electrochemical water oxidation by layered-perovskite oxyfluoride $Pb_3Fe_2O_5F_2$

([1]*School of Science, Tokyo Institute of Technology*, [2]*Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology*) ○Ryusuke Mizuochi,[1] Yuuki Sugawara,[2] Takeo Yamaguchi,[2] Kazuhiko Maeda[1]

Keywords: Electrochemical water splitting; Oxygen evolution reaction electrocatalyst; Layered material; Mixed-anion compound

Hydrogen production by water electrolysis has attracted attention as a sustainable way to achieve carbon neutrality in the future, with a strong focus on oxygen evolution reaction (OER), compared to hydrogen evolution reaction (HER). It is because the OER is more sluggish with four-electron transfer than the HER. An OER electrocatalyst without noble metal is desired from the viewpoint of industrial application for cost-effectiveness. We have focused on iron-based oxyfluorides as OER electrocatalysts and, indeed, found that a lead-iron oxyfluoride, $PbFeO_2F$, achieved the functionality.[1] Oxyfluorides are mixed anion compounds, which include oxide and fluoride anions coordinated to a metal center. They have physical and chemical properties, which do not appear in a single anion counterpart (i.e., oxides and fluorides).[2] In this study, we investigated another lead-iron oxyfluoride, $Pb_3Fe_2O_5F_2$, with layered double perovskite structure as an OER electrocatalyst. 2D-layered compounds have attracted attention not only as electrocatalysts but also in other applications due to their unique structural and electronic properties. However, there is no report utilizing a single-phase 2D-layered oxyfluoride as an OER electrocatalyst. Therefore, we focused on the 2D-layered $Pb_3Fe_2O_5F_2$ as the OER electrocatalyst and compared to the $PbFeO_2F$ with 3D-cubic perovskite structure.

Electrodes of the lead-iron oxyfluorides were fabricated by drop-casting oxyfluoride particle suspension with a conductive carbon support onto a carbon substrate. Electrochemical OER activities and properties were investigated for the as-prepared electrodes. It was found that $Pb_3Fe_2O_5F_2$ had relatively high OER activity and superior electrochemical property compared to $PbFeO_2F$ and even general iron-based perovskite oxides (such as $SrFeO_3$, $LaFeO_3$ and $BiFeO_3$). Comparison between $Pb_3Fe_2O_5F_2$ samples with different parameters in the synthesis revealed that the presence of (0*k*0) crystal facets on the $Pb_3Fe_2O_5F_2$ enhanced the OER activity. Furthermore, density functional theory calculations in the OER process indicated that the higher activity of $Pb_3Fe_2O_5F_2$ than $PbFeO_2F$ was attributed to the greater exposed area of the crystal facets with lower OER overpotential, supporting the results confirmed by the above electrochemical investigation.

1) R. Mizuochi, K. Izumi, Y. Inaguma, K. Maeda, *RSC Adv.* **2021,** *11*, 25616.

2) H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun.* **2018,** *9*, 772.

CO_2と水からギ酸を生成する電気化学リアクタの長期耐久性向上

（豊田中研 [1]）〇加藤直彦 [1]・河合康明 [1]・野尻菜摘 [1]・塩澤真人 [1]・菊澤良弘 [1]・鈴木伸明 [1]・小坂悟 [1]・濱口豪 [1]・竹田康彦 [1]

Improvements in long-term durability of electrochemical reactors producing formate from CO_2 and water

([1] Toyota Central R&D Labs., Inc.) 〇Naohiko Kato*, Yasuaki Kawai, Natsumi Nojiri, Masahito Shiozawa, Yoshihiro Kikuzawa, Nobuaki Suzuki, Satoru Kosaka, Tsuyoshi Hamaguchi and Yasuhiko Takeda.

We previously developed a 1 m^2-sized artificial photosynthetic cell consisting of an electrochemical (EC) reactor featuring a Ru-complex polymer (RuCP) cathode catalyst integrated with Si solar cells to convert CO_2 to formate, and realized a solar-to-chemical energy conversion efficiency of 10.5%$^{1,2)}$. In this study, we improved the durability of the EC reactor. A pyrrole derivative containing amino group introduced in the RuCP and carboxyl group created on the carbon supports by a UV-ozone treatment formed strong chemical bond, reducing the detachment of the RuCP catalyst. A newly developed chemically-resistant graphite adhesive prevented the carbon supports from peeling off from the conductive substrates. We constructed 75 cm^2-sized EC reactors facing the cathodes and durable IrO_x-TaO_x/Pt-Metal oxide/Ti anodes with porous separators between them. High Faradaic efficiency (*FE*) of formate production over 80% was secured under inclined installation even after 3000 h intermittent operation (Figure 1). *Keywords: Solar fuels; Long-term durability; Artificial photosynthesis; Electrochemical reactors; Solar-driven CO_2 reduction; Formate.*

我々は、これまでに、Ru 錯体ポリマー（RuCP）からなる CO_2還元触媒を用いた電気化学(EC)リアクタと Si 太陽電池を組み合わせた 1 m^2 サイズの人工光合成セルを構築し、太陽光-化学エネルギー変換効率 10.5%を達成した$^{1,2)}$。今回、EC リアクタの耐久性を向上させた。アミノ基を含むピロール誘導体を RuCP に導入し、炭素担体への UV オゾン処理により生成するカルボキシル基と化学結合させることによって、RuCP の脱離を抑制した。更に、高化学耐性のグラファイト接着剤を開発し、炭素担体の導電基板からの剥離を防止した。対向させたカソードと高耐久性の IrO_x-TaO_x/Pt-Metal oxide/Ti アノードの間に多孔質セパレータを挿入した 75cm^2 の EC リアクタを、屋外環境を想定した傾斜設置で間欠動作させた 3000 時間後にギ酸生成ファラディー効率（*FE*）80%以上が維持された（図 1）。

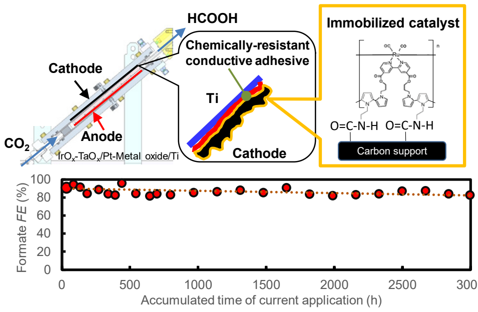


Fig.1 EC reactor designed for integration with solar cells and *FE* of formate production for 3000 h.

1)N. Kato, et al., *Joule*, **2021**, 5, 687. 2)N. Kato, et al., *ACS Sustain. Chem. Eng.*, **2021**, 9,16031.

光触媒型膜-電極接合体へのプロトン伝導性配位高分子の適用

（京大院工 [1]・ポーラ化成 [2]・京大高等研究院 [3]・京大院理 [4]）〇竝木 裕司 [1,2]・田部 博康 [3]・堀毛 悟史 [4]

Photocatalytic membrane electrode assemblies with proton conductive coordination polymers

([1]*Graduate School of Engineering, Kyoto University*, [2]*POLA Chemical Industries, Inc.*,[3]*Institute for Advanced Study, Kyoto University*, [4]*Graduate School of Science, Kyoto University*,) 〇Yuji Namiki[1,2], Hiroyasu Tabe[3], Satoshi Horike[4]

Photocatalytic solar cells are a promising power supply system because of their higher cell voltage than conventional solar cells.[1] The photocatalytic solar cells consist of membrane-electrode assemblies composed by electrolyte membranes, electrodes, and photocatalysts. In this study, we used proton (H^+)-conductive coordination polymers as solid electrolytes.[2,3] Electric power was generated under the solar irradiation by MEAs with coordination polymers consisting of Zn^{2+} ions, phosphate ions, and alkylamines for 72 hrs, while the current decrease was observed in the MEAs consisting of conventional electrolyte membranes such as Nafion®.

Keywords : Photocatalytic reaction, Coordination polymer, Proton conductivionl, Solar cell

従来の太陽電池と比べ高い起電力を特長とする光触媒式太陽電池に注目が集まっている [1)]。光触媒式太陽電池は、電解質膜と光触媒電極によって構成される膜ー電極接合体（MEA）からなり、負極側に加湿アルゴンを、正極側に加湿酸素をフローさせ、太陽光を照射することで作動する。光触媒式太陽電池の安全面や省スペース性を向上させるには、固体電解質の利用が望ましい。本研究では機械的耐久性と耐湿性に優れ、光触媒との融合も近年報告された配位高分子（CP）を固体電解質として適用した [2)]。亜鉛イオン、リン酸イオン、アルキルアミンからなる CP[3)] から構築される MEA に疑似太陽光を照射したところ 72 時間にわたり安定に発電できることを確認した（図 1）。一方、Nafion®を適用すると、72 時間後の電流出力は初期値と比較して 75%低下した。

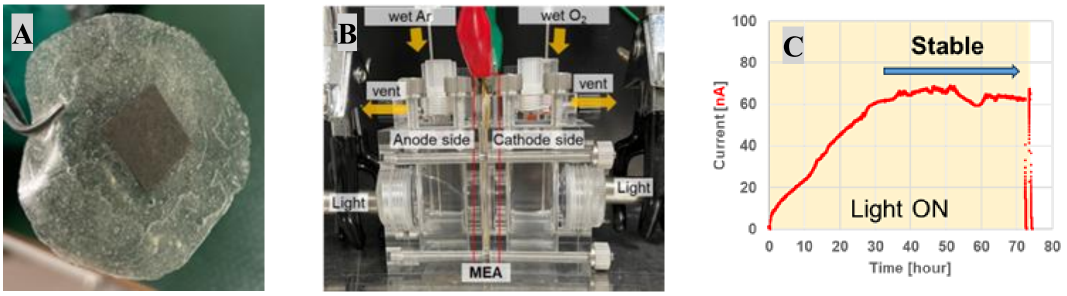


Figure 1. MEA with CP(A), H-type cell system(B), Stability test of MEA with CP(C)

1) Y. Ogura, S. Okamoto, T. Itoi, Y. Fujishima, Y. Yoshida, Y. Izumi, *Chem. Commun.*, **2014**, *50*, 3067.
2) H. Izu, H. Tabe, Y. Namiki, H. Yamada, S. Horike, *Inorg. Chem.*, **2023**, *62*, 11342.
3) T. Ogawa, K. Takahashi, S. S. Nagarkar, K. Ohara, Y. Hong, Y. Nishiyama, S. Horike. *Chem. Sci.*, **2020**, *11*, 5175.