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

2024年3月19日(火) 13:00 ~ 15:10 E1131(11号館 [3階] 1131)

[E1131-2pm] 12. 有機化学—有機結晶・超分子化学

座長：重光 孟、堀内 新之介

日本語
13:00 ~ 13:20
[E1131-2pm-01]
トリスポルフィリンとゲスト分子の多成分自己集合により制御される分子配列

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

英語
13:20 ~ 13:40
[E1131-2pm-02]
Controlling the helicity of dynamic helical tricobalt(III) cryptands by tuning the diamine chain length at the aperture

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

日本語
13:40 ~ 14:00
[E1131-2pm-03]
液相・固相でのカゴ状金属酸化物{Mo_{132}}内部空間へのゲスト捕捉

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

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30
[E1131-2pm-04]
球状錯体の一義空間を用いたタンパク質の単分子包接

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

英語
14:30 ~ 14:50
[E1131-2pm-05]
ゲスト分子による箱型自己集合カプセルの構造異性の再配列とその構造変換

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

英語
14:50 ~ 15:10
[E1131-2pm-06]
アミドの水素結合を利用した位置選択的Diels-Alder反応系の開発

○倪 汪斌[1]、木原 伸浩[1] (1. 神奈川大学)

トリスポルフィリンとゲスト分子の多成分自己集合により制御される分子配列

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

Controlled molecular array in multi-component self-assembly of trisporphyrin and guests

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*, [2]*WPI-SKCM*[2]*, Hiroshima University*) ○Naoyuki Hisano,[1] Tomoki Kodama,[1,2] Takeharu Haino[1,2]

Our group developed a triple-layered trisporphyrin molecule **1** possessing two cleft cavities, which encapsulated electron-deficient aromatic molecules in a negative cooperative fashion.[1] In this study, we synthesized tris(zinc-porphyrin) **2**, capturing donor and acceptor guests **L1** and **G1** driven by dative bonds and donor-acceptor interactions, respectively. Tris(zinc-porphyrin) **1** showed homotropic negative cooperativity in the guest binding of **G1** and **L1**. The homotropic negative cooperativity led to the selective formation of a ternary host-guest complex. Upon the addition of **L2** into a solution of the ternary host-guest complex, a sequence-controlled multi-component supramolecular complex (**L1•2•G1**)$_2$**L2** was constructed.

Keywords : Molecular Recognition; Host–Guest Complex; Porphyrin

当研究室は, クレフト型ビスポルフィリンを二つ連結したトリスポルフィリン **1** が電子不足な芳香族分子の包接に負の協同性を示すことを見出した[1)]。本研究は，亜鉛を導入したトリスポルフィリン **2** を合成し，ゲスト包接挙動を調べた。亜鉛ポルフィリンの配位サイトは一つであるため，**2** は **L1** の包接に負の協同性が発現することが予想される。**2** のゲスト包接を調べたところ，**2** は **G1** および **L1** の包接にそれぞれホモトロピックな負の協同性を示すことがわかった。また，**2** はホモトロピックな負の協同性により, **G1** および **L1** を選択的に一分子ずつ包接した三元超分子錯体 **L1•2•G1** を形成することが分かった。^{1}H NMR および DOSY 測定により，三元超分子錯体 **L1•2•G1** は **L2** を添加することで二分子の **L1•2•G1** が架橋された多元超分子錯体 (**L1•2•G1**)$_2$**L2** が形成されることが分かった。

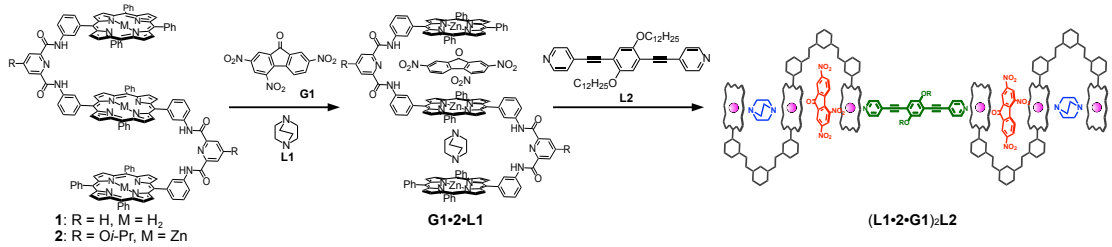


Figure 1. Molecular structures of trisporphyrin, ternary host–guest complex **G1•2•L1**, and multi-component host–guest complex (**L1•2•G1**)$_2$**L2**.

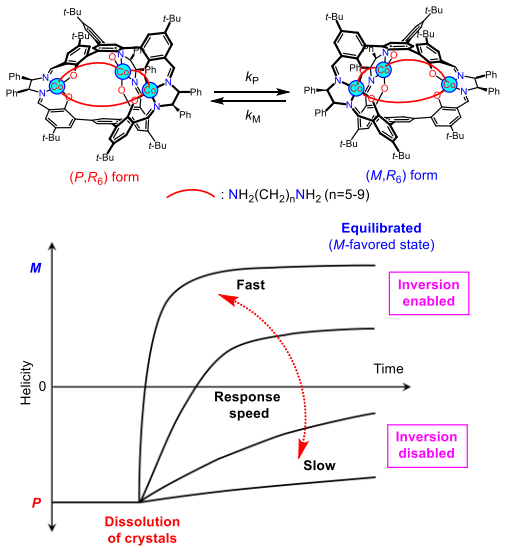
1) N. Hisano, T. Kodama, T. Haino, *Chem. Eur. J.* **2023**, *29*, e202300107.

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

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

Keywords: Helicity inversion, Dynamic structure conversion, Cobalt complex, Diamine, Cryptand

Development of artificial dynamic helical molecules with controllable helix inversion rate can be useful to make chiral memory materials.[1] Most of the previous reports of stimuli-responsive chiral molecules have been focused only on the equilibrium states before and after stimulation but not on controlling the kinetics.[1] We have already demonstrated that the helicity inversion kinetics of trinickel(II) cryptands can be controlled by guest recognition in the cryptand cavity.[2,3] In this research, novel chiral tris(salen)-type tricobalt(III) cryptands with diamines introduced at the aperture were synthesized. A series of diamines with different chain length were used (short 1,5-pentanediamine to long 1,9-nonanediamine). The tricobalt(III) complex is in dynamic equilibrium between *P* and *M* isomers in solution, preferring one isomer in major concentration. However, in single crystals the complexes were stabilized in one handed isomer (*P* isomer). We have investigated the time-dependent changes in the *P*/*M* ratios by spectroscopic techniques. The details of the energy diagrams for the *P*/*M* inversion will be discussed.



Scheme 1. Controlling the speed of helicity inversion by tuning the diamine chain length at the aperture.

1) S. Akine, H. Miyake, *Coord. Chem. Rev.* **2022**, *486*, 214582. 2) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front.*, **2014**, *1*, 53. 3) S. A. Ikbal, P. Zhao, M. Ehara, S. Akine *Sci. Adv.* **2023**, *9*, eadj5536.

液相・固相でのカゴ状金属酸化物{Mo132}内部空間へのゲスト捕捉

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

Guest Encapsulation within Metal Oxide Cage {Mo132} in Liquid and Solid Phases. ([1]*Grad. School of Env. Sci., Hokkaido Univ.*, [2]*Fac. of Env. Earth Sci., Hokkaido Univ.*) ○Akari Nakashuku,[1] Jaeseob Shin,[1] Chinatsu Murata,[1] Yukatsu Shichibu, [1,2] Katsuaki Konishi[1,2]

Metal oxide cluster of {Mo132} has 20 pores on the surface and its inner wall is coordinated with acetate ligands. Previous studies demonstrated the encapsulation of guest molecules within {Mo132} in solution phase. In this work, we performed such a guest encapsulation in solid phase. We evaluated the efficiency of solid grinding method with guest molecules through NMR measurements.

Keywords : Metal Oxide ; Guest Encapsulation; Solid State

金属酸化物クラスター $[Mo_{132}O_{372}(H_2O)_{72}(CH_3COO)_{30}]^{42-}$（以下{Mo132}）は表面に20箇所の空孔が存在し（**Fig. 1**）[1]、水溶液中でこの空孔を通じたゲストの取り込みが報告されている[2]。当研究室でも、溶液中でベンゼン誘導体をはじめとするゲストがアニオン-π相互作用によって内部に取り込まれることを見出している[3]。一方、水への溶解性が著しく低いゲストの{Mo132}への取り込みの報告はない。そこで本研究では、固相混合を用いて{Mo132}へのゲスト内包を検討した。

{Mo132}とベンゾフェノンの粉体を固相混合し、得られた粉体に D_2O を加えてフィルターでろ過した。このろ液を ^{1}H-NMR で測定するとブロードなピークが 5.8 ppm に見られた。このブロードピークの拡散係数が{Mo132}のアセテート配位子と同程度の値を示すことが DOSY NMR 測定からわかり、ベンゾフェノンの内包を確認した（**Fig. 2**）。さらに、本手法によって一度{Mo132}に取り込まれたゲストは有機溶媒下においても内包状態を維持していることがわかった。

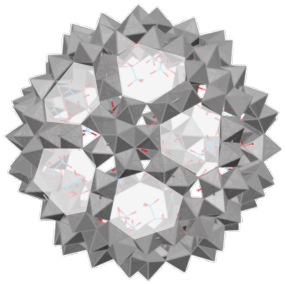


Fig. 1 Skeletal structure of {Mo132}.

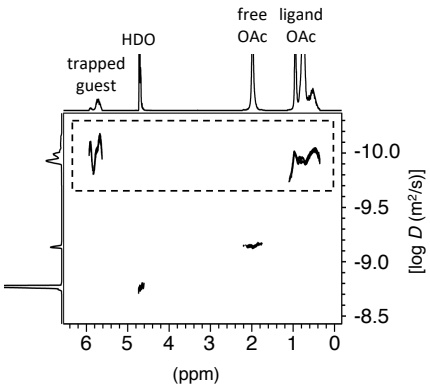


Fig. 2 ^{1}H-NMR and DOSY spectra of {Mo132} mixed with benzophenone.

[1] A. Müller *et al*., *Chem*. *Soc*. *Rev*. **2012**, *41*, 7431.
[2] R. Newman *et al*., *Chem*. *Eur*. *J*. **2016**, 22, 15231.
[3] C. Murata *et al*., *Chem*. *Commun*. **2023**, *59*, 2441.

球状錯体の一義空間を用いたタンパク質の単分子包接

(東大院工[1]・京大複合研[2]・分子研[3]・東大国際高等研[4]) ○海老原 梨沙[1]・中間 貴寛[1]・守島 健[2]・杉山 正明[2]・矢木 真穂[3]・藤田 誠[1,3,4]

Single protein encapsulation in well-defined cavities of spherical complexes ([1]*Grad. School of Engineering, The Univ. of Tokyo*, [2]*Inst. for integrated Radiation and Nuclear Science, Kyoto Univ.*, [3]*Inst. for Molecular Science*, [4]*UTIAS, The Univ. of Tokyo*) ○Risa Ebihara,[1] Takahiro Nakama,[1] Ken Morishima[2], Masaaki Sugiyama[2], Maho Yagi-Utsumi[3], Makoto Fujita[1,3,4]

Protein encapsulation within artificial hosts is useful for protein functional modulation and stabilization, but precise control of encapsulation is difficult due to the inhomogeneity of host cavities. In this work, we have reported single protein encapsulation in well-defined cavities of $M_{12}L_{24}$ cages constructed by self-assembly of bis-pyridine ligands (L) and Pd(II) ions (M)[1,2]. ^{1}H diffusion-ordered spectroscopy (DOSY) NMR and analytical ultracentrifugation (AUC) verify precise protein encapsulation in a single-molecule state. By using different sizes of cages, 15 kinds of proteins with 3-6 nm diameter were encapsulated within the cage in a single-molecule state. By isolating proteins within their cavity, the interactions and aggregation of the proteins were inhibited, thus significantly stabilizing them against organic solvents.

Keywords : protein encapsulation, self-assembly, $M_{12}L_{24}$ cage, protein stabilization, nano space

人工ホストへのタンパク質包接は、安定化などタンパク質機能制御に有用だが、ホスト空間の不均一性のため精密な包接は難しい。本研究では、巨大球状錯体の一義空間へのタンパク質の単分子包接を報告する。配位子(L)と Pd(II)イオン(M)の自己集合により形成する $M_{12}L_{24}$ 中空錯体[1,2] は、配位子の設計に基づき大きさの異なる一義的な内部空間(内径 4-6 nm)を構築するため、精密なタンパク質単分子包接が可能である(Fig. 1a)。^{1}H DOSY NMR や分析超遠心(AUC)の測定から錯体へ 1 分子のタンパク質が選択的に包接されたことが示された。適したサイズの球状錯体を用いることで最大径 3-6 nm の計 15 種類のタンパク質の単分子包接を達成した(Fig. 1b)。包接されたタンパク質は、タンパク質間の相互作用・凝集が抑制されて安定性が著しく向上した。

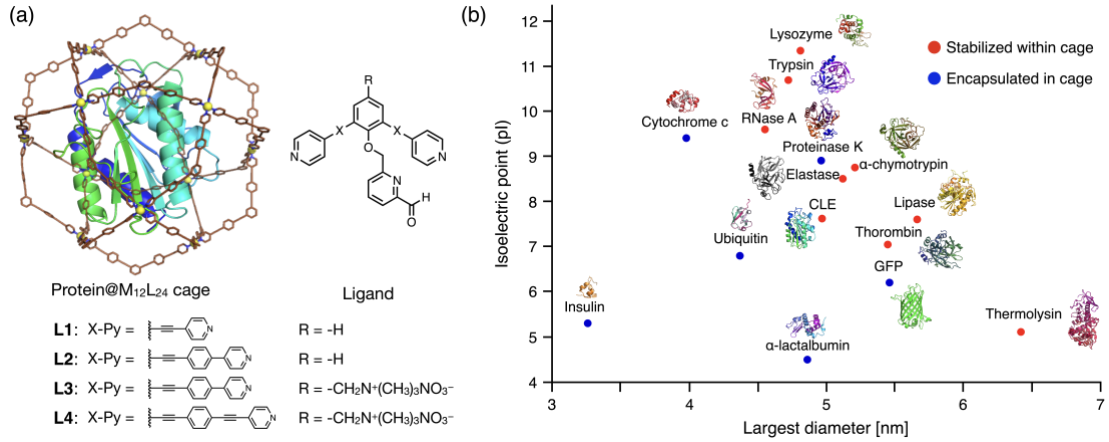


Fig. 1 (a) Protein encapsulated in $M_{12}L_{24}$ cages. (b) Scope of single protein encapsulation in the cages.

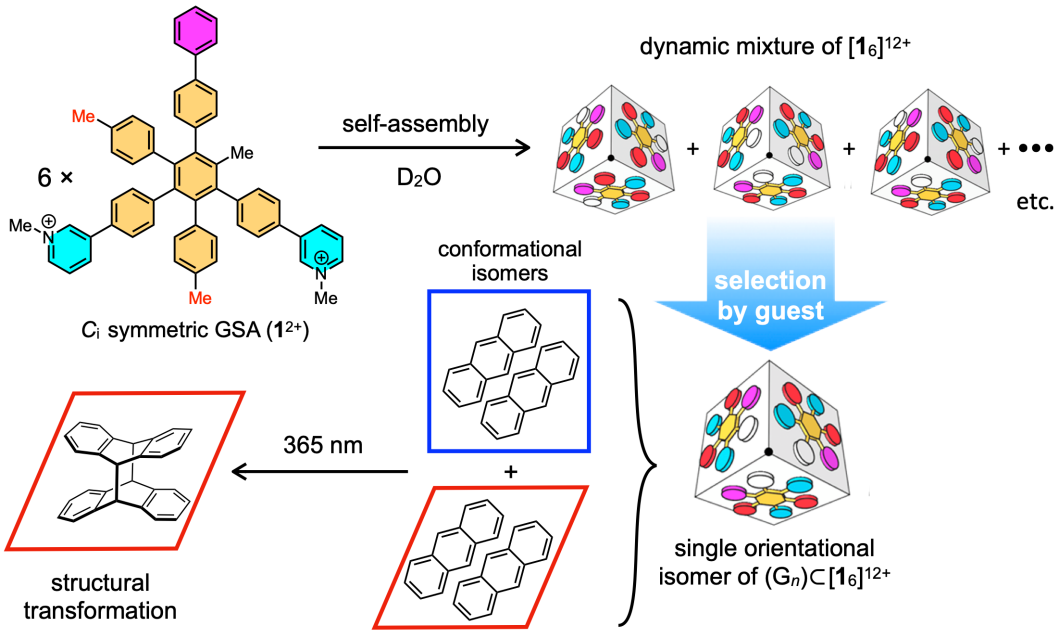
1) D. Fujita, *et al., Chem* **2021**, *7*, 2672. 2) T. Nakama, R. Ebihara, *et al.*, *Chem. Sci.* **2023**, *14*, 2910.

Guest-induced redistribution of conformational isomers of self-assembled box-shaped capsule and their structural transformation

([1]*Graduate School of Arts and Science, The University of Tokyo*)
○Hongye Chen,[1] Shinnosuke Horiuchi,[1] Shuichi Hiraoka,[1]
Keywords: amphiphile; self-assembly; induced-fit; structure transformation

Biological receptors such as enzymes are structurally flexible, which allows them to adapt to target molecules. In contrast, most synthetic receptors are relatively rigid because rigid building blocks are connected through strong and highly directional interactions. Previously, our group reported box-shaped water-soluble capsules, nanocube,[1] assembled from six gear-shaped amphiphiles (GSAs). Although only less directional, weak interactions exist between the six GSAs, the nanocubes are thermally very stable but show adaptive properties, responding to the size, shape, and charge state of the guest molecules in an induced-fit manner.[2]

In this study, we designed and synthesized a C_i-symmetric GSA ($\mathbf{1}^{2+}$). Because of its asymmetrical structure, the peripheral methyl groups can be placed at both the poles or the equator when it assembles into the nanocube. As a result, a D_2O solution of GSA showed a complicated ^{1}H NMR spectrum, indicating the formation of a mixture of 16 possible isomers of $[\mathbf{1}_6]^{12+}$. Upon the encapsulation of guest molecules (G), the ^{1}H NMR spectrum became sharp, indicating a single orientational isomer of $(G_n)\subset[\mathbf{1}_6]^{12+}$. Upon the encapsulation of a couple of anthracenes in the nanocube, two types of conformational isomers were produced and photodimerization of the anthracenes in the nanocube induced one of the conformations.



1) Y.-Y. Zhan *et al. Commun. Chem.* **2018**, *1*, 14. 2) Y.-Y. Zhan *et al. Nat. Commun.* **2018**, *9*, 4530.

Regioselective Diels-Alder reaction using hydrogen bonding of amides

(*Graduate School of Science, Kanagawa University*) ○Wang-Bin Ni, Nobuhiro Kihara

Keywords: Diels-Alder reaction, hydrogen bonding, regioselectivity, reaction field, molecular recognition

In the Diels-Alder reaction of a diene with an electron-donating group and a dienophile with an electron-withdrawing group, one of the two possible regioisomers is formed selectively because the overlap of frontier molecular orbitals controls the regioselectivity. Therefore, the regioselective Diels-Alder reaction of diene **1** with dienophile **2** is difficult because ester and amide functional groups in **2** exhibit similar electronic effects. When the Diels-Alder reaction is carried out in the presence of xanthene derivative **3**, a regioselective formation of **4** is expected because **1** and **2** will be aligned on **3** by the hydrogen bonding between amides. Formamide **1** was synthesized from **6** by the reductive amidation using formamide in the pressure of formic acid. Diacylhydrazine **2** was synthesized by the acylation of formhydrazide with the half ester derived from **7**. Cu(I)-catalyzed condensation of **8** and uracil **9** afforded **3**. While direct Diels-Alder reaction of **1** and **2** did not occur, regio-selective Diels-Alder reaction of **1** and **2** was investigated in the presence of **3**.