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

2025年3月29日(土) 9:00 ~ 11:20 [B]A503(第2学舎 1号館 [5階] A503)

[[B]A503-4am] 09. 錯体化学・有機金属化学

座長：伊豆 仁、山田 鉄兵

英語
9:00 ~ 9:20
[[B]A503-4am-01]

ビス(ベンゾイミダゾール)配位亜鉛ジクロリド錯体を構築単位とする水素結合性有機構造体のゲスト交換を利用した合成

○太田 俊[1]、石井 萌々[1]、岡崎 雅明[1] (1. 弘前大院理工)

日本語
9:20 ~ 9:40
[[B]A503-4am-02]

ブロモスチリルピリジンを有するウェルナー型金属錯体の合成と光反応性

○陳 ユン[1]、齋藤 結大[1,2]、鄭 キン[1,2]、高橋 仁徳[3]、中村 貴義[3]、野呂 真一郎[1,2] (1. 北海道大学大学院環境科学院、2. 北海道大学大学院地球環境科学研究院、3. 北海道大学電子科学研究所)

日本語
9:40 ~ 10:00
[[B]A503-4am-03]

三核Zn錯体と電気化学セルによる大気CO_2吸脱着サイクル反応

○坂本 直柔[1]、村瀬 雅和[1]、宇山 健[1]、野中 敬正[1]、大橋 雅卓[1]、佐藤 俊介[1]、荒井 健男[1]、伊藤 敏幸[2] (1. 株式会社豊田中央研究所、2. 公益財団法人豊田理化学研究所)

英語
10:00 ~ 10:20
[[B]A503-4am-04]

CO_2の有効利用に向けたケージ化合物の合成とその性質

○北田 大樹[1]、小杉 健斗[1]、正岡 重行[2]、近藤 美欧[1] (1. 東京科学大学、2. 大阪大学)

英語
10:20 ~ 10:40
[[B]A503-4am-05]

微小な結晶スポンジを用いたナノグラムスケール試料の単結晶構造解析

○吉田 知史[1]、馬場 清喜[2]、仲村 勇樹[2]、佐藤 宗太[1,3]、藤田 誠[1,3,4] (1. 東大院工、2. JASRI、3. 分子研、4. 東大国際高等研)

英語
10:40 ~ 11:00
[[B]A503-4am-06]

Guest-regulated [2+2] photodimerization reactivity in Cd-including Werner clathrate

○Shi shi Du[1], Yuki Saito[1,2], Xin ZHENG[1,2], Shin-ichiro Noro[1,2] (1. Graduate School of Environmental Science, Hokkaido Univ., 2. Faculty of Environmental Earth Science, Hokkaido Univ.)

英語
11:00 ~ 11:20

[[B]A503-4am-07]

Engineering the Assembly and Elasticity of Isoreticular Dithiol-Based Metal-Organic Nanotubes

〇Kunyi Leng[1], Teppei Yamada[1] (1. The University of Tokyo)

Synthesis of hydrogen-bonded organic frameworks based on a bis(benzimidazole)-coordinated zinc dichlorido complex using guest exchange

(*Graduate School of Science and Technology, Hirosaki University*) ○Shun Ohta, Momo Ishii, Masaaki Okazaki

Keywords: Hydrogen Bond; Guest exchange; Porosity; Single-crystal X-ray Diffraction Analysis; Adsorption

Porous frameworks constructed through intermolecular hydrogen bonds are termed hydrogen-bonded organic frameworks (HOFs).[1] HOFs are mainly synthesized by recrystallization from solutions, including building block molecules; however, not all the solutions will give HOFs. For example, the crystallization solvents may prevent the building blocks from making the frameworks due to the formation of hydrogen bonds with the building blocks. Thus, methods for dealing with cases where HOFs are not obtained by recrystallization must be developed. In this presentation, with zinc complex **1** (Figure 1a),[2] we demonstrate that guest exchange, a process that replaces the guests in the porous frameworks with other molecules, is useful for converting non-HOF crystals to HOF.

When complex **1** was crystallized from *N*,*N*-dimethylformamide (DMF), DMF-solvated crystals ($\mathbf{1}_2\cdot(\mathrm{DMF})_5$) were obtained (Figure 1b). A single crystal X-ray diffraction analysis of $\mathbf{1}_2\cdot(\mathrm{DMF})_5$ revealed that the hydrogen bonding sites of **1** are all occupied by the N–H···O hydrogen bonds with DMF, and any framework via hydrogen bonds is not constructed. Thus, $\mathbf{1}_2\cdot(\mathrm{DMF})_5$ can be concluded not to be a HOF. Next, $\mathbf{1}_2\cdot(\mathrm{DMF})_5$ were exposed to acetone. As a result, a partial guest exchange proceeded to yield the crystals of $\mathbf{1}\cdot(\mathrm{acetone})_{0.5}(\mathrm{DMF})_{0.5}$ (Figure 1b). $\mathbf{1}\cdot(\mathrm{acetone})_{0.5}(\mathrm{DMF})_{0.5}$ has pores characterized predominantly by intermolecular N–H···Cl hydrogen bonds, proving the conversion of non-HOF crystals to HOF (Figure 1c). We will also report the results of exposing $\mathbf{1}_2\cdot(\mathrm{DMF})_5$ to other organic vapors.

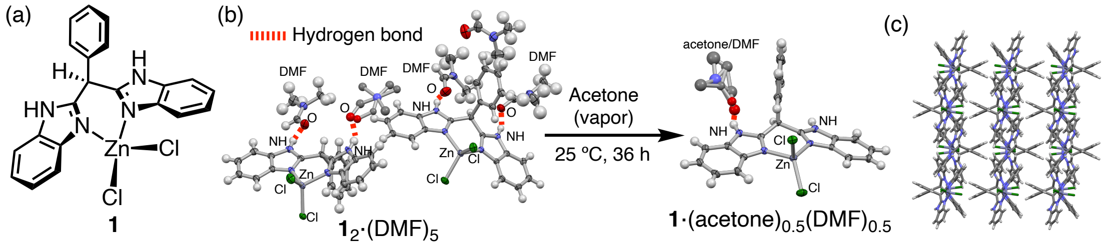


Figure 1. (a) Structure of **1**. (b) Conversion of $\mathbf{1}_2\cdot(\mathrm{DMF})_5$ to $\mathbf{1}\cdot(\mathrm{acetone})_{0.5}(\mathrm{DMF})_{0.5}$. (c) 3D packing of $\mathbf{1}\cdot(\mathrm{acetone})_{0.5}(\mathrm{DMF})_{0.5}$.

1) I. Hisaki *et al.*, *Angew. Chem., Int. Ed.* **2019**, *58*, 11160–11170. 2) S. Ohta *et al.*, *Inorg. Chem.* **2022**, *61*, 19890–19898.

ブロモスチリルピリジンを有するウェルナー型金属錯体の合成と光反応性

(北大院環境科学[1]・北大院地球環境科学[2]・北大電子研[3]) ○陳 ユン[1]・齋藤 結大[1,2]・鄭 キン[1,2]・高橋 仁徳[3]・中村 貴義[3]・野呂 真一郎[1,2]

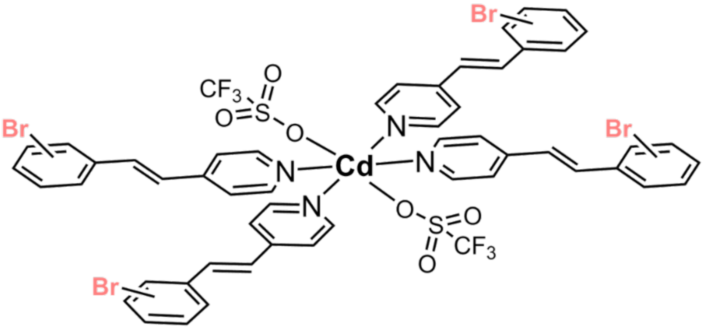
Synthesis and Photoreactivity of Werner-Type Metal Complexes with Bromostyrylpyridine

([1]*Graduate School of Environmental Science Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*, [3]*Research Institute for Electronic Science, Hokkaido University*) ○Yun Chen,[1] Yuki Saito,[1,2] Xin Zheng,[1,2] Kiyonori Takahashi,[3] Takayoshi Nakamura,[3] Shin-ichiro Noro[1,2]

Werner-type metal complexes show interesting host-guest properties. In our laboratory, Werner-type metal complexes with styrylpyridine ligands have been investigated to control their host-guest properties by a light stimulus1). In this study, the Werner-type metal complexes were synthesized using three types of bromostyrylpyridine with different positions of the bromine substituent, $[\mathrm{Cd(CF_3SO_3)_2(4\text{-}x\text{-}bspy)_4}]$ (4-x-bspy = (4-(x-bromostyryl)pyridine, x = 4 (**1**), x = 3 (**2**), x = 2 (**3**)). In the crystals, **1-3** showed the center-to-center distances of C=C double bonds shorter than Schmidt's upper threshold distance of 4.2 Å for the [2+2] photodimerization reaction, suggesting potential photoreactivity. The detailed photoreactivity will be discussed.

Keywords : Werner-type metal complexes; Bromine substituent; Photoreactivity

ウェルナー型金属錯体は興味あるホストーゲスト特性を示す。我々はこれまでホストーゲスト特性の光制御が可能なウェルナー型金属錯体を得るためにスチリルピリジンが配位したウェルナー型金属錯体の合成を検討してきた1)。本研究では、ブロモ基の位置が異なる三種類のブロモスチリルピリジン配位子を用いてウェルナー型金属錯体、$[\mathrm{Cd(CF_3SO_3)_2(4\text{-}x\text{-}bspy)_4}]$ (4-x-bspy = (4-(x-bromostyryl)pyridine, x = 4 (**1**), x = 3 (**2**), x = 2 (**3**))、を新規に合成した（下図）。得られた錯体 **1-3** はいずれも結晶中において配位子の中央の C=C 二重結合間距離が Schmidt の閾値 4.2Å よりも短いため、光反応を起こす可能性がある。当日は、光反応性について詳細に報告する。



1) Y. Zhang, X. Zheng, Y. Saito, T. Takeda, N. Hoshino, K. Takahashi, T. Nakamura, T. Akutagawa, S. Noro, *Angew. Chem. Int. Ed.* **2024**, *63,* e202407924

三核 Zn 錯体と電気化学セルによる大気 CO_2 吸脱着サイクル反応

([1]豊田中研, [2]豊田理研) ○坂本 直柔 [1]・村瀬 雅和 [1]・宇山 健 [1]・野中 敬正 [1]・大橋 雅卓 [1]・佐藤 俊介 [1]・荒井 健男 [1]・伊藤 敏幸 [2]

Atmospheric CO_2 adsorption/desorption by trinuclear Zn complexes with electrochemical reactors.

([1]*Toyota Central R&D Labs., Inc.,*[2] *Toyota Physical and Chemical Research Institute*) ○Naonari Sakamoto,[1] Masakazu Murase,[1] Takeshi Uyama,[1] Takamasa Nonaka,[1] Masataka Ohashi,[1] Shunsuke Sato,[1] Takeo Arai,[1] and Toshiyuki Itoh[2]

Carbon dioxide (CO_2) separation and capture technology represent a pivotal approach for curbing increases in atmospheric CO_2 concentrations. In a previous study, we synthesized a trinuclear zinc cryptand complex (Zn_3**L**) through inspiration derived from the function of carbonic anhydrase. The Zn_3**L** complex was observed to facilitate a more rapid absorption of CO_2 in comparison to the conventional alkaline aqueous solutions that are commonly utilized as CO_2 absorbents [1]. However, stable cycling during CO_2 adsorption and desorption could not be achieved because the addition of acids and bases, required for CO_2 desorption and complex regeneration. In this study, we present the CO_2 absorption-desorption cycle that employs a metal complex material in conjunction with an electrochemical reactor utilizing an ionic liquid as the supporting electrolyte. The application of Zn_3**L** with the electrochemical reactor resulted in the attainment of both high cycle stability and effective absorption-desorption performance. Through ex-situ nuclear magnetic resonance (NMR) analysis, attenuated total reflectance-Fourier transform far-infrared/infrared spectroscopy (ATR-FT-FIR/IR), and ex-situ/*operando* X-ray absorption spectroscopy (XAS) [2], the chemical species involved in CO_2 adsorption, desorption, and complex reconstruction over six cycles were monitored. Our findings indicate that the coordination state of the central zinc ion undergoes a change with each cycle. Furthermore, even in later cycles, the formation of water-coordinated species with Zn enables the complex to maintain its CO_2 adsorption performance [3].

Keywords: CO_2 capture, Operando analysis, Metal complex, Electrochemical reaction, Mechanism

大気中二酸化炭素（CO_2）濃度低減に向け、CO_2 を分離回収し資源として有効利用する取り組みが注目されている。これまでに、炭酸脱水酵素に着想を得た三核亜鉛クリプタント錯体(Zn_3**L**)が、一般的な CO_2 吸収剤であるアルカリ水溶液よりも優れた CO_2 吸収速度を実現できることを見出している[1]。一方で、CO_2 の脱離と再吸収のために錯体構造の再構築が必要である。そのために必要な酸と塩基の添加が、系中における Zn_3**L** の溶解性低下の原因となり、安定した CO_2 吸脱着サイクルの実現には至っていなかった。本研究では、支持電解質にイオン液体を用いた電気化学リアクターを Zn_3**L** の反応場として使用することで、安定したサイクル性と高い吸脱着特性の両立を実証した。また、Zn_3**L** における CO_2 吸着種、脱離種、錯体再構築種の構造状態について、Ex-situ 核磁気共鳴分析(NMR)、減衰全反射-フーリエ変換遠赤外/赤外分光分析(ATR-FT-FIR/IR)および、ex-situ/*operando* X 線吸収分光法(XAS)[2]を用いて明らかにした。サイクル動作毎に、中心金属 Zn への配位種が変化する一方で、水分子配位種の継続的な形成が、CO_2 吸収性能の維持に寄与していることが明らかとなった[3]。

[1] M. Murase *et al.*, *ChemSusChem* **2023**, 16, e202300679.
[2] N. Sakamoto, K. Sekizawa *et al., Nat. Catal.,* **2024**, 7, 574-584.
[3] M. Murase, N. Sakamoto *et al.*, *Angew. Chem. Int. Ed.* **2024***,* e202420703.

Synthesis and Properties of Cage Compounds for CO_2 conversion

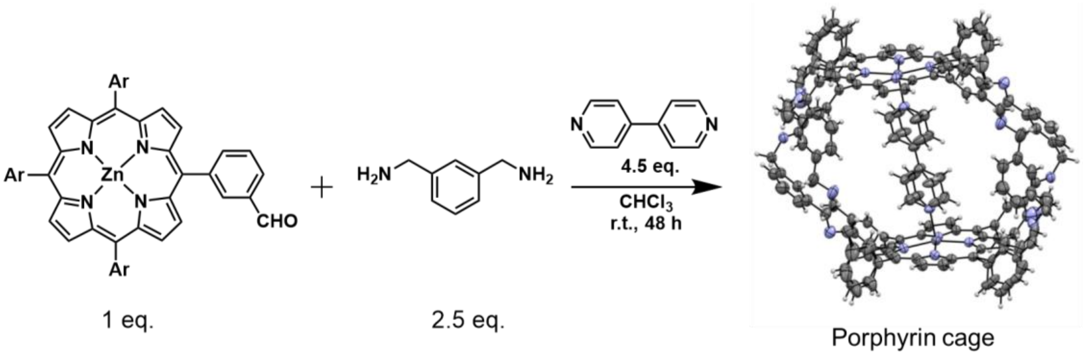
([1]*School of Science, Institute of Science Tokyo*, [2]*Graduate School of Engineering, Osaka University*) ○Masaki Kitada,[1] Kento Kosugi,[1] Shigeyuki Masaoka,[2] Mio Kondo[1]

Keywords: Self-Assembled Cages, Catalyst, CO_2 Reduction

Recently, CO_2 conversion has attracted attention as a solution to energy and environmental problems such as the depletion of fossil fuels and global warming. The aim of this study is the construction of a catalytic system that promotes efficient photo/electro-chemical CO_2 conversion reactions. For this purpose, we newly designed molecular cages based on porphyrin complexes.

Molecular cages are the class of compounds formed by self-assembly of multiple molecular components. Thanks to their flexible molecular designability and unique internal cavities, they are expected to have a variety of applications.[1] Especially, the use of molecular cages as catalysts has attracted considerable attention these days.[2] As catalytic sites to be embedded into molecular cages, we focused on metal porphyrin complexes. Porphyrin complexes have been widely used as functional molecules.[3] They are also known to promote CO_2 reduction reactions.[4] Therefore, incorporating porphyrins into molecular cages is important for developing the catalytic system that promotes efficient photo/electro-chemical CO_2 reduction reactions.

Our strategy to obtain molecular cages containing metal porphyrin complexes are shown in the Scheme 1. In our strategy, we expected that reversible dynamic covalent bond, imine bond, enables entropy driven assembly to afford the cage compounds selectively. By the condensation of metal porphyrin complexes bearing aldehyde moieties with diamine linkers in the presence of template molecule successfully afforded the targeted molecular cage and the obtained cage was characterized by single crystal X-ray analysis.



Scheme 1. Synthetic strategy for the metal porphyrin based cage compounds.

1) A. R. Stefankiewicz *et al*., *Coord. Chem. Rev*., **2021**, *434*, 213820.
2) H.-C. Zhou *et al*., *Chem. Soc. Rev.*, **2019**, *48*, 4707.
3) W.-D Jang *et al., Acc. Chem. Res.*, **2021**, *54*, 2249.
4) J. Zhong *et al*., *Chemical Engineering Journal*, **2023,** *470*, 144249.

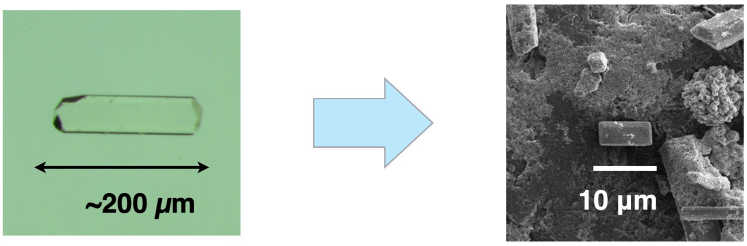
Nanogram scale single crystal X-ray diffraction analysis by using micro crystalline sponge.

([1]School of Engineering, The Univ. of Tokyo, [2]JASRI, [3]IMS, [4]UTIAS) ○Satoshi Yoshida[1], Seiki Baba[2], Yuki Nakamura[2], Sota Sato[1,3], Makoto Fujita[1,3,4]

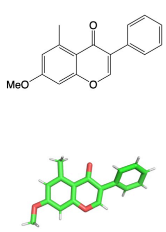
Keywords: Crystalline Sponge Method, Single Crystal X-ray Diffraction, Coordination Complex, Nanogram-Scale Analysis

Structure analysis method less than nanogram scale is limited while it has great demand in the various area like natural chemistry, metabolomics. Crystalline sponge (CS) method[1], where guest structure can be determined by applying the single crystal X-ray diffraction method to the a porous crystalline metal organic framework including the analyte molecule, has a potential to analyze such nanogram-scale compounds. In this work, we focused on the relationship that the required guest amount in CS method was proportional to the crystal size, and tried to reduce the guest amount in CS method by the down-sizing of CS crystals.

CS crystals with 5–10 μm (microCS) were synthesized by mixing ligand and zinc metal solution. Guest compounds were absorbed into microCS crystals by using a glass capillary as a vial. The guest introduction was completed faster than the conventional CS method due to the improvement of the diffusion. As a result of the automatic measurement in synchrotron, three guest compounds **1**, **2**, and **3** can be observed with 100% occupancy by using 30 ng of the guest compounds. For guest compound **4**, the guest structure was clearly observed even when 3 ng of **4** was used.



~ microgram	sample amount	**~ nanogram**
typically 1–7 days	soaking time	**typically < 4 h**



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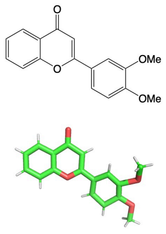

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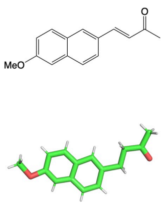

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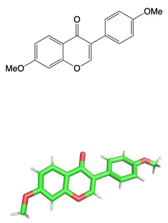

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[1] Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen & M. Fujita, *Nature* **495**, 461–466.

Guest-regulated [2+2] photodimerization reactivity in Cd-including Werner clathrate

([1]*Graduate School of Environmental Science, Hokkaido University,* [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Shishi Du,[1] Yuki Saito,[1,2] Xin Zheng,[1,2] Shin-ichiro Noro[1,2]

Keywords: Werner clathrate; [2+2] photodimerization; Single-crystal-to-single crystal transformation

Werner clathrates are inclusion complexes with the composition of $[M(A)_2(L)_4]$ (M = divalent metal ion, A = monovalent anion, L = pyridine derivative ligand). Our laboratory has recently focused on Werner complexes/clathrates with photoreactive ligands because a light stimulus may control their porous properties.[1] Previously, we reported that the Werner complex $[Cd(CF_3SO_3)_2(1\text{-sim})_4]$ (**1**) (1-sim = 1-styrylimidazole) exhibited [2+2] photodimerization reaction to form a two-dimensional coordination polymer **1′** with *syn*-head-to-tail (*syn*-HT) photodimers. In this study, the photoreactivity of the Werner clathrate with dioxane guests, $[Cd(CF_3SO_3)_2(1\text{-sim})_4]\cdot 3$dioxane (**1**·3dioxane), was investigated.

1·3dioxane was obtained by the slow diffusion of hexane to the dioxane solution containing $Cd(CF_3SO_3)_2$ and 1-sim. In the crystal of **1**·3dioxane, there were only *trans* 1-sim ligand. Focusing on the overlapping between 1-sim ligands, we found the parallel stacking between the 1-sim ligands with the center-to-center distance of 3.75 Å between C=C double bonds, shorter than Schmidt's threshold distance of 4.2 Å for the [2+2] photodimerization reaction.[2] Upon irradiating **1**·3dioxane with 365 nm UV light for 10 h, ca. 50% of 1-sim ligands were dimerized to form a one-dimensional coordination polymer **1″** (Figure 1). Unlike the structure of **1′**, **1″** included not only *syn*-HT dimers but also *cis* isomers.

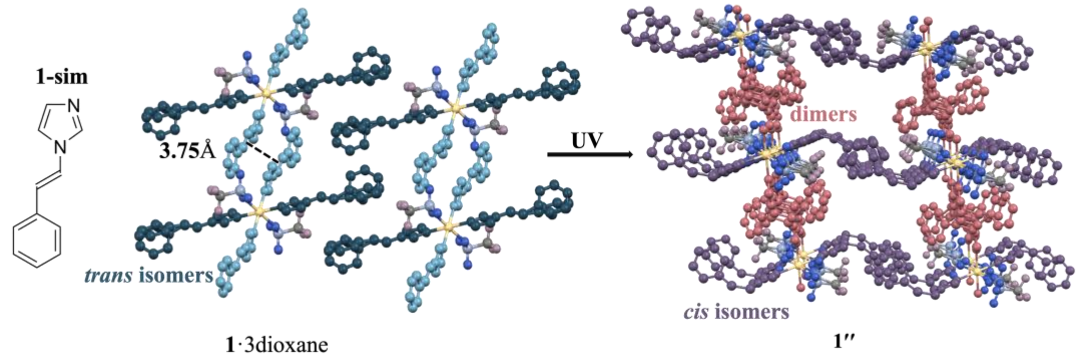

Figure 1. Packing state of **1**·3dioxane before and after UV irradiation.

1) Y.-Y. Zhang, X.Zheng, Y. Saito, T. Takeda, N. Hoshino, K, Takahashi, T, Nakamura, T. Akutagawa, S. Noro, *Angew. Chem., Int. Ed* .**2024**, *63,* e202407924. 2) G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647.

Engineering the Assembly and Elasticity of Isoreticular Disulfide-Based Metal–Organic Nanotubes

(*School of Science, The University of Tokyo*) ○Kunyi Leng, Teppei Yamada

Keywords: Metal–Organic Nanotube; Hydrogen Bond; Crystal Engineering; Elastic Crystal, Disulfide Ligand

Metal–organic nanotubes (MONTs), a fascinating subclass of metal–organic frameworks (MOFs), have garnered significant attention due to their unique tubular 1D architectures and tunable physicochemical properties.[1] Compared with the well-developed 2D[2] and 3D[3] MOFs, MONTs are still in their infancy due to the synthetic difficulties. A limited number of MONTs have been synthesized, and while a majority of reports have focused solely on structural details. Regulating the elasticity of MONTs through precise modulation of their inter-tube interactions remains a significant challenge, as it requires a deep understanding of their assembly mechanisms.

In this study, we reported the rational design and synthesis of isoreticular MONTs through the self-assembly of cadmium ions (Cd^{2+}), 4,4'-Dipyridyl Disulfide(^{py}DS), and isophthalate derivatives (Hip^{2-} or $OHip^{2-}$). The crystal structures revealed that two Cd^{2+} were connected by two ^{py}DS to form a coordination square $[Cd^{2+}(^{py}DS)_2]^{4+}$, which one-dimensionally connected with the assistant of isophthalate to form a metal−organic nanotube. Moreover, the substituents at 5 positions of isophthalate pointed out to the adjacent nanotube, offering a powerful strategy for tuning the inter-tube interactions. In MONT-DS-OHip, robust hydrogen bonding between neighboring nanotubes, with hydroxyl groups as donors, enhanced mechanical properties and minimized solvent effects on elasticity (Fig. 1a). In contrast, MONT-DS-Hip, lacking this network, displayed solvent-dependent stacking and significant variability in elasticity (Fig. 1b). This approach provides a versatile strategy for designing responsive MONT systems.

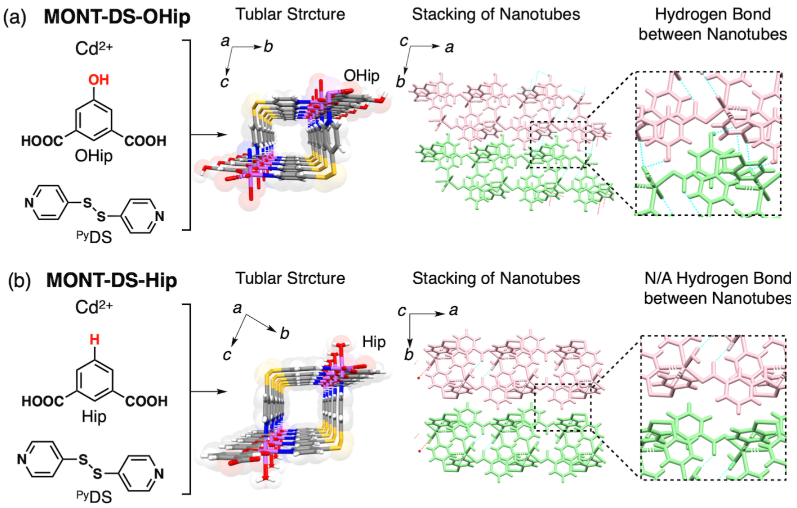

Fig. 1 The constituent components and crystal structures of (a) MOF-DS-OHip and (b) MOF-DS-Hip.

1) K. Otsubo, H. Kitagawa et al., *Nat. Mater.* **2011***, 10,* 291–295. 2) J. Dou, M. Dincă et al., *Nat. Mater.* **2021**, *20*, 222–228. 3) H. Li O. M. Yaghi et al., *Nature* **1999**, *402*, 276–279.