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

2025年3月27日(木) 13:00 ~ 15:30 [F]2202(第4学舎 2号館 [2階] 2202)

[[F]2202-2pm] 12. 有機化学—有機結晶・超分子化学

座長：阿南 静佳、池本 晃喜

英語

13:00 ~ 13:20

[[F]2202-2pm-01]

Diastereoselective Synthesis of Topological Chiral Pillar[5]arenes: Unveiling the Unit and Macrocyclic Chirality Interplay

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

日本語

13:20 ~ 13:40

[[F]2202-2pm-02]

柔軟な大環状トリスレゾルシンアレーンの構造と分子認識

○久野 尚之[1]、井上 翔一朗[1]、下山 大輔[1]、関谷 亮[2]、Riyanka Das[3]、灰野 岳晴[1,3] (1. 広島大院先進理工、2. 弘前大院理工、3. 広島大 持続可能性に寄与するキラルノット超物質拠点)

日本語

13:40 ~ 14:00

[[F]2202-2pm-03]

トリス(フェニルイソオキサゾリル)ベンゼン誘導体の分子結晶中に現れる潜在的空孔を利用した選択的分子吸着

○小野 雄大[1]、平尾 岳大[2]、河田 尚美[3]、灰野 岳晴[1,2] (1. 広島大WPI-SKCM²、2. 広島大院先進理工、3. 広島大自然セ)

14:00 ~ 14:10

休憩

英語

14:10 ~ 14:30

[[F]2202-2pm-04]

反応性の異なる複数の状態をとる構造変換可能な相互貫入ケージ

○阿部 司[1]、張 雨桐[1]、竹内 啓介[1]、平岡 秀一[1] (1. 東京大学)

日本語

14:30 ~ 14:50

[[F]2202-2pm-05]

立方体形の自己集合体に形成される動的細孔による速度論ゲーティング

○陳 弘燁[1]、郭 一帆[1]、村田 萌[2]、小林 理[2]、島崎 智実[2]、立川 仁典[2]、平岡 秀一[1] (1. 東大院総合文化、2. 横浜市大院生命ナノ)

英語

14:50 ~ 15:10

[[F]2202-2pm-06]

Nearly perfect chirality inversion of a helical metallocryptand upon crystal dissolution assisted by guest binding as a booster stimulus

○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)

🏷 英語

15:10 ~ 15:30

[[F]2202-2pm-07]

Crystallographic Evidence of Water Repulsion in Fluorous Nanochannels

○Shuo Chen[1], Wei Yuan[1], Siyuan Ye[1], Yoshimitsu Itoh[1], Hiroshi Sato[3,2], Takeshi Uemura[1], Takuzo Aida[1,2] (1. the University of Tokyo, 2. RIKEN CEMS, 3. Hiroshima University)

Diastereoselective Synthesis of Topological Chiral Pillar[5]arenes: Unveiling the Unit and Macrocyclic Chirality Interplay

([1]*WPI-NanoLSI, Kanazawa University*, [2]*Graduate School of Engineering, Kyoto University,*) ○De-Hui Tuo,[1,2] Shigehisa Akine,[1] Kenichi Kato,[2] Shunsuke Ohtani,[2] Tomoki Ogoshi[1,2]

Keywords: Pillar[*n*]arene; Diastereoselective synthesis; Chirality

Molecular topology, such as mechanically interlocked and entangled molecular architectures, has increasingly attracted attention in materials science and nanotechnology due to its fascinating topological features.[1] Herein, we present a series of topological chiral pillar[5]arenes (P5As) formed by combining two different planar chiralities (Figure 1a): paracyclophanes (S_p and R_p) and P5As (*pS* and *pR*). The topological chiral P5As were diastereoselectively synthesized using different paracyclophane units (Figure 1b). Topological P5As **a** and **b** were selectively formed from **1** or **2** racemates, while the chiral paracyclophane **2**-S_p selectively gave topological chiral P5A **a**-5(S_p-*pS*). From achiral paracyclophane **1'**, only topological P5A **b** was obtained due to the lack of hydroxymethyl directing groups. All the topological chiral molecules exhibited distinct CD spectra corresponding to the chiral units (Figure 1c), but closely resembled that of planar chiral P5A, indicating that macrocyclic chirality predominantly governs the chiroptical properties of these topological structures. TD DFT calculations revealed that the magnetic ($\boldsymbol{m}$) and electric ($\boldsymbol{\mu}$) transition dipole moments, along with their angles (θ), of the chiral paracyclophane units were rearranged and altered within the topological P5A structures (Figure 1d). This rearrangement significantly increased the overall magnitude of $|\boldsymbol{m}|$, reduced the θ angle, and resulted in tunable rotatory strength (R) and CD intensity of the topological chiral structures.

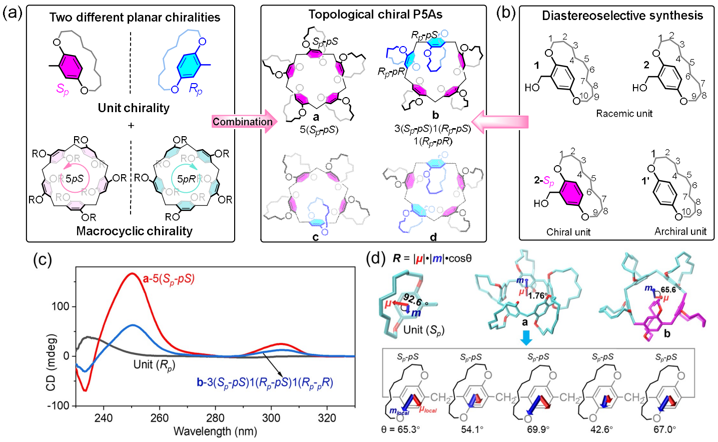


Figure 1. (a) Combination of two different planar chiralities. (b) Paracyclophane monomers. (c) CD spectra and (d) DFT calculation results of these topological chiral P5As.

1) W. Wang, S. Zhou, X. Yu *et al.*, *CCS Chem.* **2024**, *6*, 2084–2109.

柔軟な大環状トリスレゾルシンアレーンの構造と分子認識

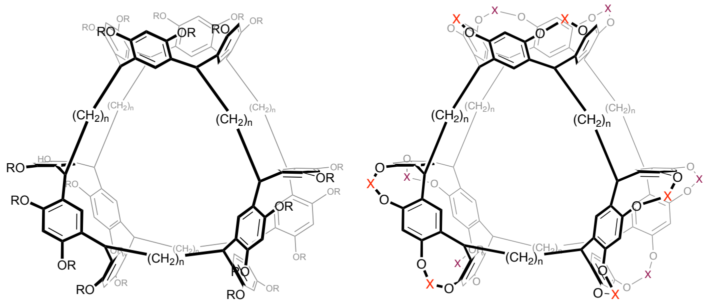
（広島大院先進理工 [1]・弘前大院理工 [2]・広島大持続可能性に寄与するキラルノット超物質拠点 [2]）○久野尚之 [1]・井上翔一朗 [1]・下山大輔 [1]・関谷亮 [2]・Riyanka Das[3]・灰野岳晴 [1,3]

Synthesis and molecular recognition of flexible macrocyclic trisresorcinarene

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*, [2]*Graduate School of Science and Technology, Hirosaki University*, [2]*WPI-SKCM*[2]*, Hiroshima University*) ○ Naoyuki Hisano,[1] Shoichiro Inoue,[1] Daisuke Shimoyama,[1] Ryo Sekiya,[2] Riyanka Das,[3] Takeharu Haino[1,3]

Our group developed macrocyclic trisresorcinarenes consisting of three resorcinarene units connected by odd-numbered alkyl chains.[1] However, the extremely low solubility of trisresorcinarenes in organic solvents hindered a detailed understanding of the molecular behavior in solution. In this study, we synthesized soluble trisresorcinarenes by introducing lipophilic protecting groups into the hydroxyl groups of resorcinarene units. Here, we report the structure and conformation of the trisresorcinarenes in solution. [2]

Keywords : Supramolecular Chemistry; Macrocyclic Molecule; Molecular Recognition; Calixarene



1: R = H, n = 5, 7, 11
2: R = piv, n = 5
3: X = Si(n-C_8H_{17})$_2$, n = 9

Figure 1. Molecular structures of trisrecorcinarene **1**–**3**.

当研究室は，3 つのレゾルシンアレーン分子が奇数のアルキル鎖により連結された大環状トリスレゾルシンアレーン **1** を報告した 1)。しかしながら，トリスレゾルシンアレーン **1** は有機溶媒への溶解性が極めて低いため, 溶液中での分子挙動については詳細がわかっていない。本研究では，レゾルシンアレーンの水酸基に脂溶性の保護基を導入することで，可溶性のトリスレゾルシンアレーン **2,3** を合成し，溶液中のトリスレゾルシンアレーンの構造について調べた。ピバロイル基を導入したトリスレゾルシンアレーン **2** は溶媒の種類に応じて二種類の配座をもつことがわかった 2)。また，水酸基をジオクチルシランで架橋したトリスレゾルシンアレーン **3** は，ヘキサンやペンタンに対しても高い溶解性を示した。

1) Shimoyama, D.; Sekiya, R.; Kudo, H.; Haino, T. *Org. Lett.* **2020**, *22*, 352.
2) Shimoyama, D;. Sekiya, R.; Inoue, S.; Hisano, N.; Tate, S.; Haino, T. *Chem. Eur. J.* **2024**, *30*, e20240922.

トリス(フェニルイソオキサゾリル)ベンゼン誘導体の分子結晶中に現れる潜在的空孔を利用した選択的分子吸着

（[1]広島大 WPI-SKCM^2・[2]広島大院先進理工・[3]広島大自然セ）○小野 雄大[1]・平尾 岳大[2]・河田 尚美[3]・灰野 岳晴[1,2]

Selective Molecular Adsorption Using Latent Porosity in a Molecular Crystal of Tris(phenylisoxazolyl)benzene Derivatives

([1]*International Institute for Sustainability with Knotted Chiral Meta Matter/WPI-SKCM^2, Hiroshima University*, [2]*Graduate School of Advanced Science and Engineering, Hiroshima University,* [3]*Natural Science Center for Basic Research and Development/N-BARD, Hiroshima University*) ○Yudai Ono,[1] Takehiro Hirao,[2] Naomi Kawata,[3] Takeharu Haino[1,2]

Porous organic compounds have great potential for the adsorption and separation of molecular mixtures. Our group has reported flat molecule tris(phenylisoxazolyl)benzene formed self-assembled structure via intermolecular interactions in organic solvents.[1] In this study, we designed and synthesized tris(phenylisoxazolyl)benzene derivative **1** possessing methoxy group. The latent pores were found in the molecular crystal of **1**, which can be used for *cis*-selective molecular adsorption against the *cis*-/*trans*-decalin mixture (Figure 1).[2]

Keywords : Organic Crystal; X-Ray Diffraction Analysis; Porosity; Adsorption

空間·空隙を有する有機結晶は，その空間を利用した選択的な分子吸着や分離への応用が期待され，これまで盛んに研究が行われてきた。当研究室では，平面分子トリス(フェニルイソオキサゾリル)ベンゼンが分子間相互作用を駆動力として溶液中で自己集合することにより形成される超分子ポリマーについて報告している[1]。本研究では，側鎖にメトキシ基を導入することで結晶性を向上させたトリス(フェニルイソオキサゾリル)ベンゼン **1** を設計·合成し，その分子結晶中に選択的分子吸着に利用可能な潜在的空孔が存在することを見出した (Figure 1a)[2]。**1** は結晶中で積層構造を形成しており，その積層構造間には溶媒分子を包接可能な空間が存在していた(Figure 1b)。さらに，シス-トランスデカリン混合物を用いた吸着実験では，**1** の結晶中に存在する包接空間がシスデカリンを高選択的に吸着できることが明らかになった(Figure 1c)。

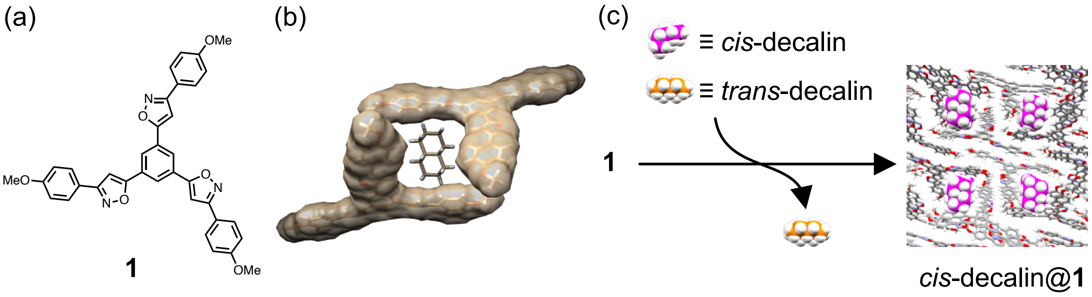


Figure 1. (a) Molecular structure of **1**. (b) Molecular surface of *cis*-decalin@**1**. (c) Schematic representation of *cis*-selective adsorption of **1** against the *cis*-/*trans*-decalin mixture.

1) M. Tanaka, T. Ikeda, J. Mack, Y. Kobayashi, T. Haino, J. Org. Chem., **2011**, *76*, 5082-5091.
2) Y. Ono, T. Hirao, N. Kawata, T. Haino, *Nat. Commun.*, **2024**, *15*, 8314.

Transformable quadruply interpenetrated cage with multiple states of different reactivities

(*Graduate School of Arts and Sciences, The University of Tokyo*) ○Tsukasa Abe, Yutong Zhang, Keisuke Takeuchi, Shuichi Hiraoka

Keywords: Interpenetrated cages; Halide ions; Anion matching index; Kinetic control; Lewis acid

Molecular self-assemblies with tunable multi-pockets are potentially functional molecules that generate multiple states. Pd_4L_8 interpenetrated cages (ICs), in which two Pd_2L_4 cages are quadruply interpenetrated, have three correlating, tunable pockets for anions. Here, we report that ICs binding three F^- or Cl^- ions, (F·F·F)- and (Cl·Cl·Cl)-ICs, were self-assembled from ditopic ligand L in high yields. The outer anions in the ICs were selectively exchanged with F^- or Cl^- under kinetic control, resulting in the quantitative formation of the thermodynamically most stable (Cl·F·Cl)-IC from the (F·F·F)-IC. The (F·Cl·F)-IC, which was produced from the (Cl·Cl·Cl)-IC with F^- by selective anion exchange, is a metastable transient species. The three thermodynamically stable ICs showed different reactivities in the presence of BF_3 and Ag^+. The addition of BF_3 to the (Cl·Cl·Cl)-IC afforded heteroleptic [2]-catenane via unusual ligand exchanges, whereas the outer F^- ions in the (F·F·F)-IC were removed by BF_3 to form a metastable (⊗·F·⊗)-IC. The heteroleptic [2]-catenane was converted into the (Cl·Cl·Cl)-IC by addition of Lewis base (F^- or Py*). The addition of Ag^+ to the (Cl·Cl·Cl)-IC caused dethreading to form the Pd_2L_4 cages, whereas the (F·F·F)-IC was intact against Ag^+. The thermodynamically most stable (Cl·F·Cl)-IC did not react with either BF_3 or Ag^+. As a result, a total of seven states were generated, affording a complicated network in response to halide ions, Lewis acids and bases, and Ag^+.[1]

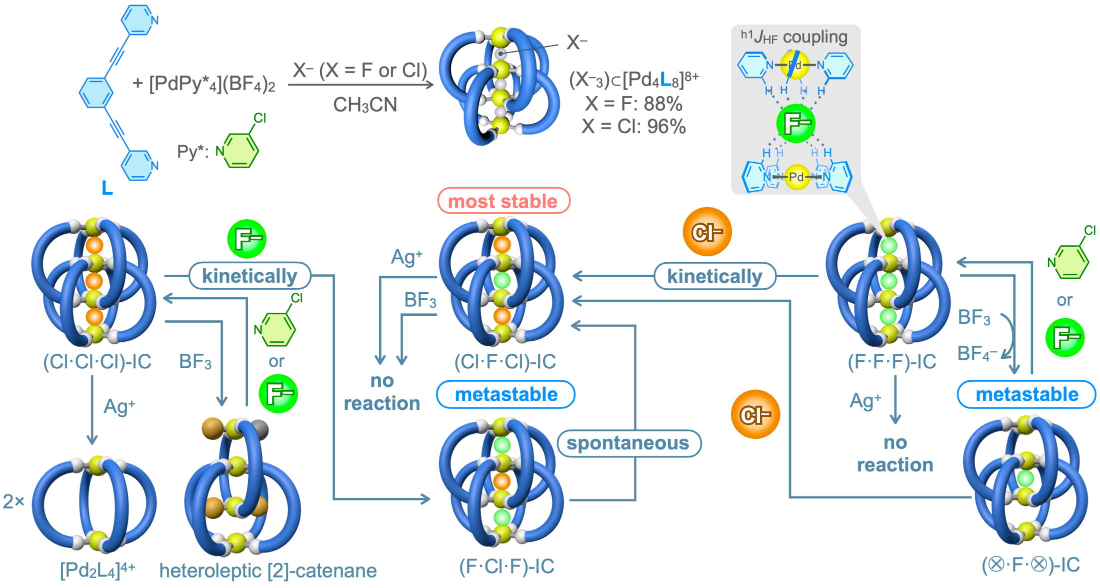


Figure Anion exchanges of quadruply interpenetrated cage (IC).

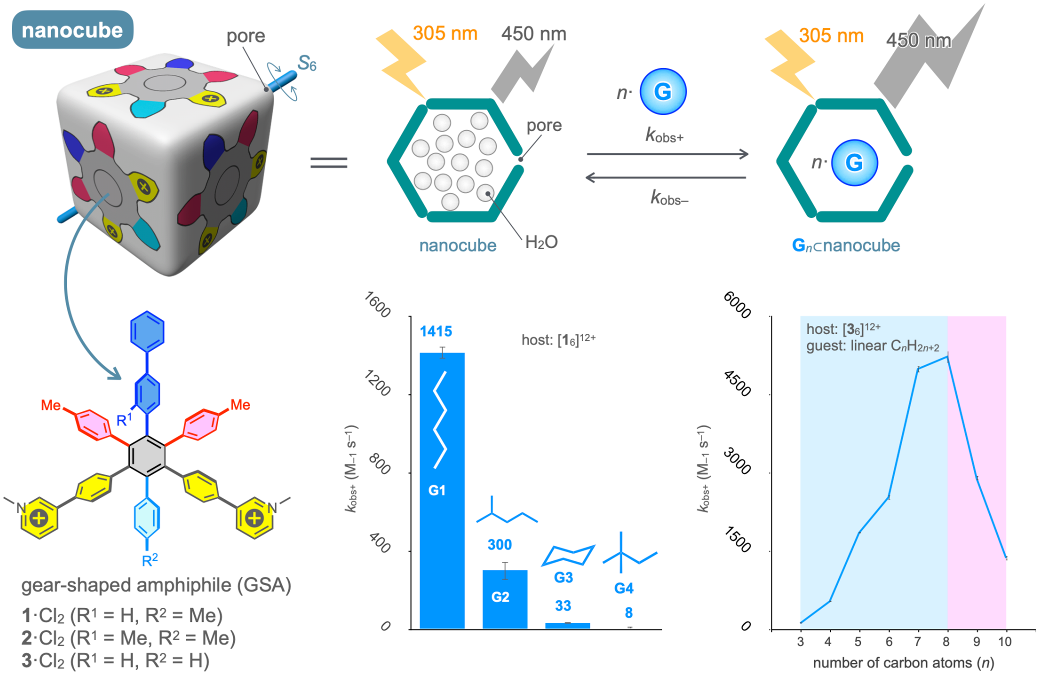
1) Tsukasa Abe, Yutong Zhang, Keisuke Takeuchi, and Shuichi Hiraoka, *Chem*, accepted.

Kinetic gating by dynamic synthetic pores created in cuboid self-assemblies in water

([1]*Graduate School of Arts and Sciences, The University of Tokyo*, [2]*Graduate School of Nanobioscience, Yokohama City University*) ○Hongye Chen,[1] Yifan Guo,[1] Moe Murata,[2] Osamu Kobayashi,[2] Tomomi Shimazaki,[2] Masanori Tachikawa,[2] Shuichi Hiraoka[1]

Keywords: self-assembly; kinetic gating; dynamic pore; dispersion force; hydrophobic effect.

Passing through a pore is an elementary process for binding target molecules. Although the encapsulation of molecules in host molecules has been extensively discussed in thermodynamics, the effect of the pore and its dynamism on the binding kinetics is not fully understood. In this study, we designed and synthesized synthetic dynamic pores as cuboid assemblies (nanocubes) from gear-shaped amphiphiles (GSAs), $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$, and the encapsulation processes were monitored by emission spectroscopy to determine the passage rate constants (k_{obs+}). The dynamic pores of $[\mathbf{1}_6]^{12+}$ exhibited a highly kinetic preference for linear alkanes over branched ones. Molecular dynamics simulations of the three types of nanocubes indicated that the difference in their pore dynamics is the origin of the kinetic selection for alkanes with different bulkiness. In addition, the passage speed increased with increasing chain length of the guest molecules. The introduction of an unsaturated bond at the hydrocarbon terminal further enhanced the passage speed, whereas the introduction of a hydrophilic oxygen atom slowed the passage speed. These results can be explained by the longer lifetime of the encounter complexes originating from the dispersion force and CH-π interaction between the hydrophobic outer surface of the pores and the hydrocarbons.



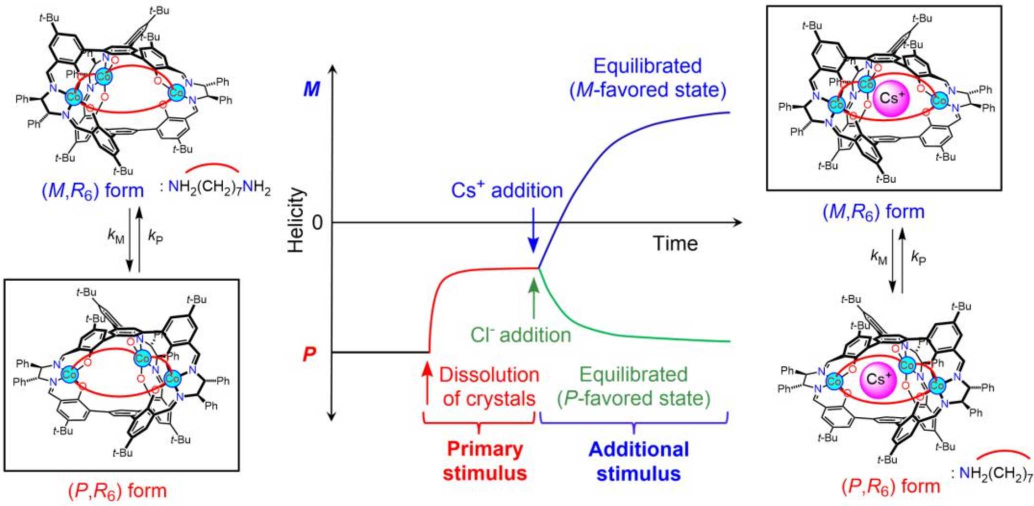
Nearly perfect chirality inversion of a helical metallocryptand upon crystal dissolution assisted by guest binding as a booster stimulus

([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; Cation encapsulation; Cryptand

Development of artificial dynamic helical molecules with controllable helix inversion rate can be useful to make chiral memory materials.[1] In literature, chirality inversion has been mostly studied and discussed as equilibrated states both before and after inversion without focusing on equilibration 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]

We have synthesized chiral tris(salen)-type tricobalt(III) metallocryptands with diamines at the aperure. In this work, we observed time dependent changes for nearly perfect chirality inversion of the helical tricobalt metallocryptand from pure P form in the crystalline state to M-major in solution, which is assisted by binding with a cation as a booster stimulus. The metallocryptand has both cation and anion binding sites; the cation binding in its closed binding cavity enabled the chirality inversion, while anion binding preserved the same chirality as that in the crystalline state.



Scheme 1. Helicity inversion control in a dynamic tricobalt(III) cryptand by two step stimulus.

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.

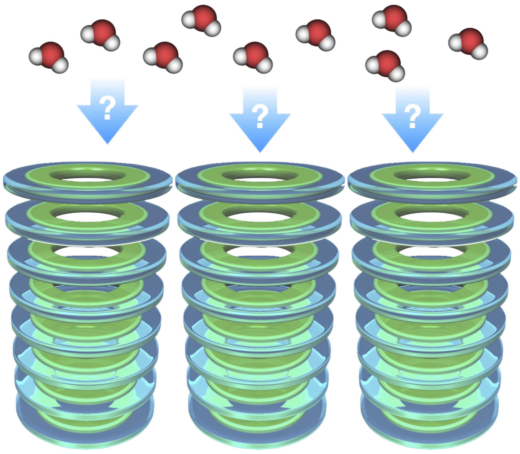
Crystallographic Evidence of Water Repulsion in Fluorous Nanochannels

([1]*the University of Tokyo*, [2]*RIKEN CEMS*, [3]*Hiroshima University*)
〇Shuo Chen[1], Wei Yuan[1], Siyuan Ye[1], Yoshimitsu Itoh[1], Hiroshi Sato[3,2], Takeshi Uemura[1], Takuzo Aida[1,2]

Keywords: Fluorous Nanochannel; Crystal Engineering; Super Hydrophobicity; Hydrogen Bonding

Fluorous nanochannels have demonstrated unprecedented potential for ultrafast water desalination as transmembrane single-channels, offering groundbreaking opportunities to address global water scarcity.[1] Their exceptional ability to rapidly and efficiently separate water from salts stems from their superhydrophobic fluorous interiors, which can break water clusters into smaller species that permeate faster while rejecting salts completely through an electrostatic barrier.[2,3] Although these properties have been extensively studied at the single-channel level, their behavior and functionality in aggregated or bulk states remain largely unexplored, leaving a significant gap in our understanding of their practical applications.

In this presentation, we report the successful synthesis of porous crystals featuring fluorous nanochannels. Crystallographic analyses revealed the influence of fluorine moieties within these nanochannels on hydrogen-bonding networks between the channels and water molecules. The precise control of fluorous nanochannels in crystalline structures enables rational material design and bridges the gap between laboratory discoveries and practical applications.



1) Y. Itoh, S. Chen, T. Aida *et al.*, *Science*. **2022**, *376*, 738-743. 2) J. Zhang *et al.*, *J. Am. Chem. Soc.* **2023**, *145*, 26925-26931. 3) Z. Gu, M. Duan, Y. Tu, *Desalination* **2022**, *523*, 115452.