Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Tue. Mar 19, 2024 3:55 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:55 AM - 8:15 AM UTC F1234(1234, Bldg. 12 [3F])

[F1234-2vn] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Nobuhiko Hosono, Shinpei Kusaka

English
3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC
[F1234-2vn-01]
Isotropic expansion of a polyaromatic capsule and its multi-guest binding ability
○Ryuki Sumida[1], Ryuto Nabata[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

English
4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC
[F1234-2vn-02]
Construction of a two-dimensional metal-organic framework composed of C_1-symmetric macrocyclic ligands and interlayer arrangement control of functional small molecules
○Keiichi NAKAGAWA[1], Shohei TASHIRO[1], So YOKOMORI[2], Nobuyuki MATSUSHITA[2], Mitsuhiko SHIONOYA[1] (1. Graduate School of Science, The University of Tokyo, 2. College of Science, Rikkyo University)

English
4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC
[F1234-2vn-03]
Green Synthesis of a Flexible Metal-Organic Framework $[Cu(BF_4)_2(4,4'\text{-bipyridine})_2]$ (ELM-11) for Selective CO_2 Adsorption
○Shivakumar Kilingaru Ishwara[1], Shin-ichiro Noro[1] (1. Hokkaido University)

English
4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC
[F1234-2vn-04]
Highly Selective Separation of Isoprene from C5 Hydrocarbons Mixture Using Pyridyl-based Metal-Organic Frameworks containing copper(I) iodide cluster.
○Joonsik KIM[1], Pavel M Usov[1], Yuki Wada[1], Hiroyoshi Ohtsu[1], Takaya Matsumoto[1,2], Masaki Kawano[1] (1. Tokyo Institute of Technology, 2. ENEOS Corporation)

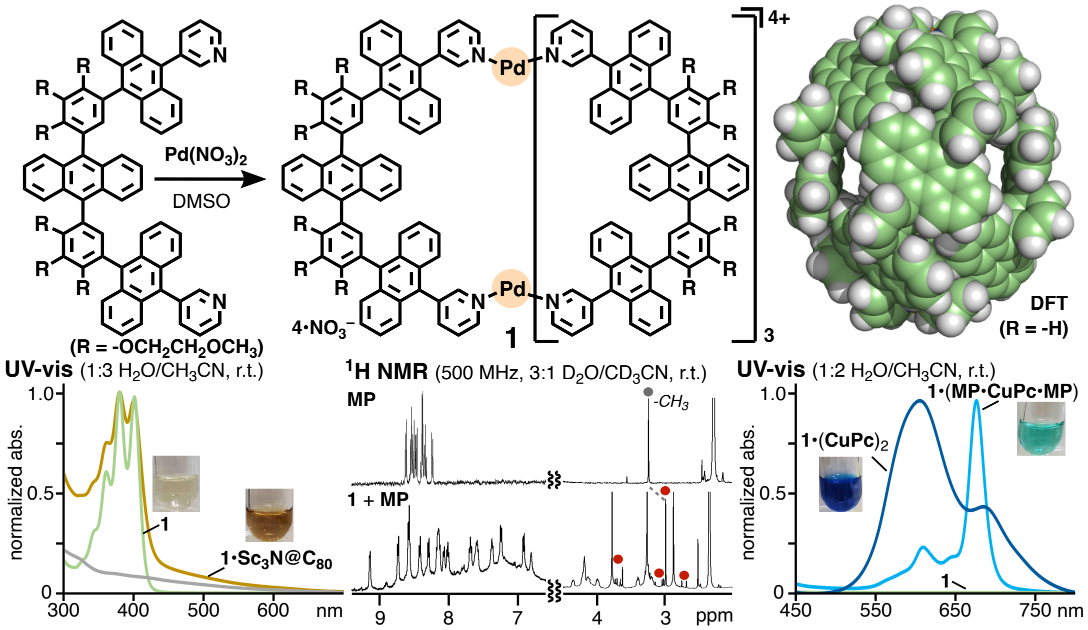
Isotropic Expansion of a Polyaromatic Capsule and its Multi-Guest Binding Ability

(Lab. for Chem. & Life Sci., Tokyo Tech) Ryuki Sumida, Ryuto Nabata, Michito Yoshizawa

Keywords: Polyaromatic capsule; Isotropic expansion; Large cavity; Binding ability; Pairwise encapsulation

Higher fullerenes, which are expanded analogues of fullerene C_{60}, provide closed, large polyaromatic cavities. Whereas the isotropic expansion of spherical M_nL_{2n} cages has been achieved using metal ions and elongated wire-like ligands, its host properties remain unclear because of large openings.[1] Here we report the synthesis of an isotropically expanded polyaromatic capsule and its binding abilities.

Expanded capsule **1** was obtained by the treatment of Pd(II) ions and tri-anthracene-based bent ligand **2** in DMSO (Figure, top). When capsule **1** and higher fullerene **$Sc_3N@C_{80}$** were stirred in 1:3 H_2O/CH_3CN at 80 °C, the solution color was changed from pale yellow to brown (Figure, bottom left), due to the quantitative formation of 1:1 host-guest complex **1•$Sc_3N@C_{80}$**. In the similar way, capsule **1** quantitatively bound four 1-methylpyrene (**MP**) molecules in the cavity of **1** (Figure, bottom middle). In addition, capsule **1** encapsulated two Cu(II)-phthalocyanines (**CuPc**) to give a blue solution of **1**•(**CuPc**)$_2$. The combination of **1**•(**CuPc**)$_2$ and **MP** gave rise to **1**•(**MP•CuPc•MP**) as a bluish green solution (Figure, bottom right). UV-visible, ESI-TOF MS, and theoretical studies indicated the selective formation of an unusual sandwich-like stack **MP•CuPc•MP** within **1**.



[1] K. Harris, D. Fujita, M. Fujita, *Chem. Commun.* **2013**, *49*, 6703–6712.

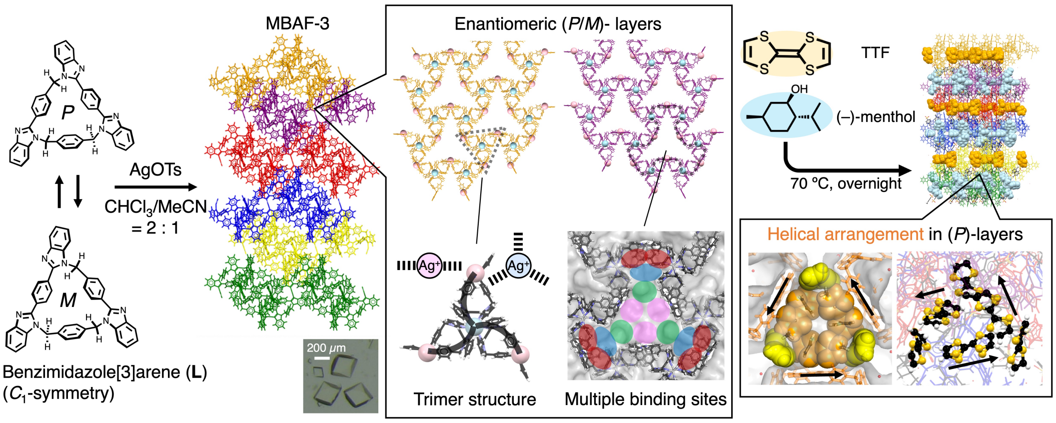
Construction of a two-dimensional metal-organic framework composed of C_1-symmetric macrocyclic ligands and interlayer arrangement control of functional small molecules

([1]*Graduate School of Science, The University of Tokyo*, [2]*College of Science, Rikkyo University*) ○Keiichi NAKAGAWA,[1] Shohei TASHIRO,[1] So YOKOMORI,[2] Nobuyuki MATSUSHITA,[2] Mitsuhiko SHIONOYA[1]

Keywords: Porous crystal; Molecular recognition; Metal-organic framework; Macrocycle; Molecular arrangement

Metal-organic frameworks (MOFs) exhibit highly excellent molecular adsorption capacity due to their high porosity and molecular recognition ability. In particular, 2D MOFs have attracted much attention because their dimensionally restricted arrangement of guest molecules allows them to be applied to various functions such as template synthesis, separation, and sensing. For precise arrangement of guest molecules, it is important to construct multiple binding sites on the 2D MOFs. However, it remained difficult because conventional MOFs use simple, flat-shaped ligands to control their dimensionality, providing only a few interaction points for molecular recognition.

In this study, a 2D MOF with multiple guest binding sites, metal-benzimidazole[3]arene framework-3 (MBAF-3, $[\mathrm{Ag}_{1.17}\mathbf{L}](\mathrm{OTs})_{1.17}$), was developed based on a C_1-symmetric macrocyclic ligand ((*P*/*M*)-benzimidazole[3]arene, **L**) and AgOTs. In the crystal structure of MBAF-3, three (*P*)- or (*M*)-**L** molecules are tricoordinated with two Ag^+ ions, forming homochiral trimers $[\mathrm{Ag}_2((P/M)\text{-}\mathbf{L})_3]^{2+}$. These are further connected with two-coordinate Ag^+ to form enantiomeric (*P*)- and (*M*)-layers, which are stacked alternately to form a crystal. Crystallographic analysis revealed that the enantiomeric layers with multiple binding sites enable helical and diastereoselective arrangement of TTF (= tetrathiafulvalene) using (–)-menthol as a chiral auxiliary. (–)-Menthol was only introduced into the (*M*)-layers of MBAF-3 by hydrogen bonding, and TTF molecules were adsorbed to the (*P*)-layers to form a right-handed helical cluster.



Green Synthesis of a Flexible Metal-Organic Framework [$Cu(BF_4)_2$(4,4´-bipyridine)$_2$] (ELM-11) for Selective CO_2 Adsorption

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Keywords: Green Chemistry; Metal-Organic Framework; CO_2 Capture; Gas Separation

Developing cost-effective and eco-friendly adsorbents is crucial for reaching the 2050 carbon neutrality goal. Elastic Layer-structured Metal-organic framework-11 (ELM-11), a flexible MOF with the formula [$Cu(BF_4)_2(bpy)_2$] (bpy = 4,4´-bipyridine), exhibits energy-efficient carbon capture potential with high working capacity and intrinsic thermal management.[1] However, the conventional synthesis of its precursor, pre-ELM-11 [$Cu(BF_4)_2(bpy)(H_2O)_2$]·bpy, involves organic solvents in addition to H_2O. In this research, we achieved pre-ELM-11 synthesis using only H_2O at room temperature and studied the CO_2 adsorption and CO_2/N_2 gas separation behaviors of its dehydrated form ELM-11.

The pre-ELM-11 was synthesized in 85-87% yield at 25 °C using only H_2O as the reaction solvent and as the washing solvent during filtration. The CO_2 uptake of H_2O-synthesized ELM-11 was 78 $cm^3(STP)\cdot g^{-1}$ at 298 K, slightly lower than 85 $cm^3(STP)\cdot g^{-1}$ for MeOH/H_2O-synthesized ELM-11 (**Fig. 1a**). Both samples exhibited high selectively for CO_2 adsorption over N_2 at 298 K under mixed CO_2/N_2 gas condition (**Fig. 1b**). Moreover, the H_2O-synthesized ELM-11 showed a slightly lower gate-opening pressure compared to MeOH/H_2O-synthesized ELM-11 (**Fig. 1a**). Our synthetic method is economical and environmentally friendly for scalable, real-world CO_2 sequestration applications.

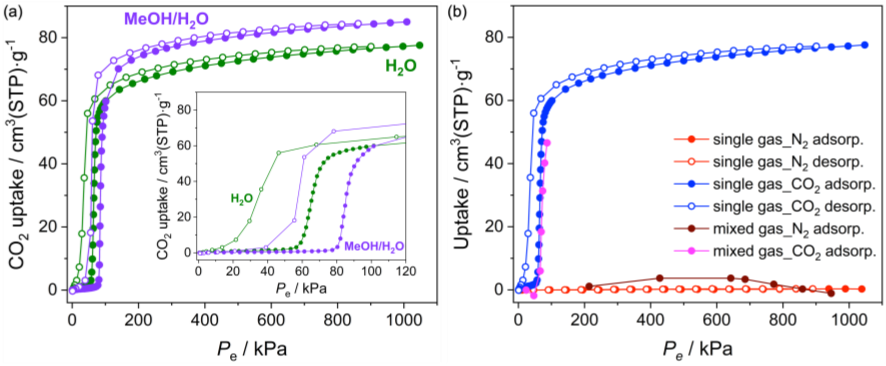


Fig. 1 (a) CO_2 sorption isotherms measured at 298 K for ELM-11 samples synthesized from MeOH/H_2O and H_2O. (b) Single gas (CO_2 and N_2) and mixed gas ($CO_2:N_2$ = 1:9) sorption isotherms measured at 298 K for ELM-11 sample synthesized from H_2O.

1) a) D. Li, K. Kaneko, *Chem. Phys. Lett.* **2001**, *335*, 50. b) A. Kondo, H. Noguchi, S. Ohnishi, H. Kajiro, A. Tohdoh, Y. Hattori, W.-C. Xu, H. Tanaka, H. Kanoh, K. Kaneko, *Nano Lett.* **2006**, *6*, 2581. c) S. Hiraide, Y. Sakanaka, H. Kajiro, S. Kawaguchi, M. T. Miyahara, H. Tanaka, *Nat. Commun.* **2020**, *11*, 3867.

Highly Selective Separation of Isoprene from C5 Hydrocarbons Mixture Using Pyridyl-based Metal-Organic Frameworks containing copper(I) iodide cluster

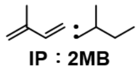
([1]*School of Science, Tokyo Institute of Technology*, [2]*ENEOS Corporation*) ○Joonsik Kim,[1] Pavel M Usov,[1] Yuki Wada,[1] Hiroyoshi Ohtsu,[1] Takaya Matsumoto,[1,2] Masaki Kawano[1]

Keywords: Metal-organic frameworks; Hydrocarbon separation; X-ray crystallography, Structural optimization calculations

Unsaturated hydrocarbons are widely used in industry as raw materials, but they typically require the use of extractive distillation processes for purification, which consume large amounts of energy. To address this challenge, several metal-organic frameworks (MOFs) based on copper iodide were developed.[1] The presence of accessible pores inside these frameworks could be used for separating and isolating specific molecules from hydrocarbon mixtures. However, there have not been many studies on the separation of olefin mixtures, especially including diene. Therefore, several pyridyl-based ligands were employed for MOF formation, providing promising candidates with high selectivity for olefins.

Three pyridyl-based (3- and 4-pyridyl) metal-organic frameworks (MOF) with copper(I) iodide cluster were used to selectively separate three structurally related C5 hydrocarbons (isoprene, 2-methyl-1-butene and 2-methylbutane). The separation is especially challenging due to close similarity of the molecules geometric shapes and have not been investigated in detail in the past. One of those MOF displayed over 3267 times higher selectivity for adsorption of isoprene over 2-methylbutane making it a promising candidate for industrial scale separation. Structural optimization calculations using Matlantis software, an atomistic simulator, revealed the reason of the high affinity for isoprene.

Table 1. Guest uptake and selectivity of each MOFs.

Material	Isoprene uptake, mmol/g	IAST Selectivity at 50 kPa	Reference
		 IP : 2MB	
MOF1	1.7	**3267 : 1**	This work
MOF2	0.65	327 : 1	Previous work
MOF3	1.4	9.5 : 1	Previous work
MIL-125	4.4	1.1 : 1	2
NH_2-MIL-125	4.6	1.1 : 1	2

1) R. Robson, *J. Am. Chem Soc*. **1989**, *111*, 5962-5964.
2) S. Kim, W. Ahn, *Catalysis Today*. **2013**, *204*, 85-93.