Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry- : Oral B

📅 Wed. Mar 26, 2025 1:30 PM - 3:40 PM JST | Wed. Mar 26, 2025 4:30 AM - 6:40 AM UTC 🏛 [F]2106(2106, Bldg. 2, Area 4 [1F])

# [[F]2106-1pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kenichi Kato, Yuya Tanaka

🏷 English
1:30 PM - 1:50 PM JST | 4:30 AM - 4:50 AM UTC
[[F]2106-1pm-01]

Ionic-Guests-Assisted Charge–Transfer Assemblies Based on the Electron-Donor Pillar[5]arene and the Electron-Acceptor Cyanostar

○Kiichi Yasuzawa[1], Nobuyuki Yamamoto[2], Alec J Sanchez[2], Shunsuke Ohtani[1], Kenichi Kato[1], Amar H Flood[2], Tomoki Ogoshi[1,3] (1. Kyoto University, 2. Indiana University Bloomington, 3. Kanazawa University WPI NanoLSI)

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🏷 English
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[[F]2106-1pm-02]

Construction of covalent organic frameworks based on pillar[*n*]arenes

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

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🏷 English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[[F]2106-1pm-03]

Versatile Protein Encapsulation in Crystals of Spherical Coordination Cages

○Hongkun Liu[1], Takahiro Nakama[1], Makoto Fujita[2,3] (1. Grad. School of Engineering, The Univ. of Tokyo, 2. UTIAS, The University of Tokyo, 3. Institute for Molecular Science)

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2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

Break

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🏷 English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[F]2106-1pm-04]

Formation of binaphthyl-based micelles capable of encapsulating metallodyes

○Yoshihisa Hashimoto[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Institute of Science Tokyo)

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🏷 English
3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC
[[F]2106-1pm-05]

Novel Tris(salen)-Type Metallocryptands for Selective Recognition Towards Biologically Active Compounds

○Syadza Firdausiah Syahruddin[1], Ryo Ide[2], Yoko Sakata[3], Masahiro Ehara[4], Shigehisa Akine[1,2,5] (1. Graduate School of Frontier Science Initiative, Kanazawa University, 2. Graduate School of Natural Science and Technology, Kanazawa University, 3. Graduate School of Engineering, Nagoya University, 4. Institute for Molecular Science, 5. Nano Life Science Institute, Kanazawa University)

English
3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC
[[F]2106-1pm-06]

### Emission Properties and Use of Multinuclear $Cu_nS_m$ Clusters within Aromatic Micelles

○Kazuki Toyama[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Science Tokyo)

# Ionic-Guests-Assisted Charge–Transfer Assemblies Based on the Electron-Donor Pillar[5]arene and the Electron-Acceptor Cyanostar

([1]*Kyoto University*, [2]*Indiana University Bloomington,* [3]*Kanazawa University WPI NanoLSI*)
○Kiichi Yasuzawa,[1] Nobuyuki Yamamoto,[2] Alec J. Sanchez,[2] Shunsuke Ohtani,[1] Kenichi Kato,[1] Amar H. Flood,[2] Tomoki Ogoshi.[1,3]

**Keywords**: Pillar[5]arene; Cyanostar; Charge–Transfer Assembly; Co-crystallization; Electrostatic Interaction

Macrocycle-based charge–transfer assemblies (MCTAs) have gained increasing interest due to their potentials for guest recognition and the structural aesthetics. In most cases, MCTAs have been created by co-crystallization, using the rigid steric structures of macrocyclic molecules as the main backbone. However, when the sizes or shapes of the electron-donor and acceptor molecules are quite different, achieving close assembly of the molecules to effectively form MCTAs becomes significantly challenging.

Herein, we report the creation of MCTAs based on two macrocycles with different sizes and shapes; pillar[5]arene (**PA**) and cyanostar (**CS**). **PA**, composed of five alkoxy benzene units, provides an electron-rich cavity, thus exhibiting electron donor property (Fig. 1a). In contrast, **CS**, containing electron-withdrawing cyanostilbene units, displays electron acceptor properties (Fig. 1b). Therefore, by mixing **PA** and **CS**, charge–transfer assemblies can be formed. However, MCTAs obtained by mixing only **PA** and **CS** could not achieve effective CT emission. This would be because the structures of **PA** and **CS** differ significantly– **PA** has a 3D pillar-like shape and **CS** has a 2D planar shape (Fig. 1c). To address these issues, we focused on the fact that **PA** and **CS** are excellent receptors for cation and anion guest molecules, respectively, due to their electron-rich or electron-deficient cavities. By introducing ionic guest molecules into the **PA**–**CS** system, the cationic guests can be encapsulated by **PA**, while the anionic guests can be sandwiched by two **CS** (Fig. 1d). The electrostatic interaction between ionic guests allowed the **PA** and **CS** to assemble closely, resulting in an improvement of the quantum yield and enabling the observation of CT emission even in the solution state, which cannot be accessed without ionic guests.

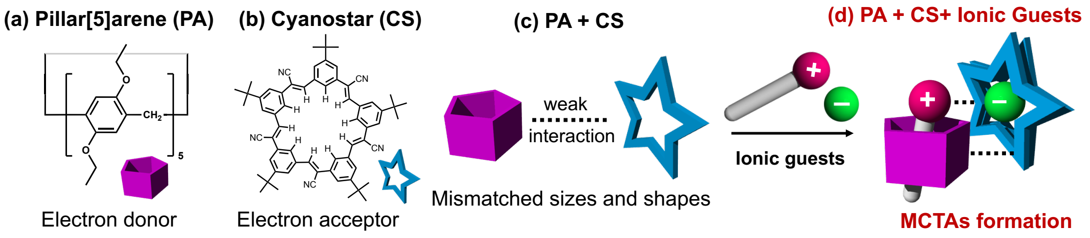


Fig.1 Chemical structures of (a) pillar[5]arene (**PA**) and (b) cyanostar (**CS**). CT assembly formation of (c) **PA**+**CS** and (d) **PA**+**CS**+ionic guests.

Reference: 1) J.-R. Wu, G. Wu, D. Li, Y.-W. Yang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218142.

# Construction of Covalent Organic Frameworks Based on Pillar[*n*]arenes

([1]*Grad. Sch. of Eng., Kyoto Univ.,* [2]*WPI-NanoLSI, Kanazawa Univ.*)
○Katsuto Onishi,[1] Shunsuke Ohtani,[1] Kenichi Kato,[1] Tomoki Ogoshi[1,2]

**Keywords**: Pillar[*n*]arene; Covalent Organic Framework; Dynamic Covalent Bond

Pillar[*n*]arenes are pillar-shaped macrocyclic compounds. They have reaction sites on both rims of the pillar structures. Consequently, crosslinking at the reaction sites results in the formation of porous polymer networks. However, connecting pillar[*n*]arenes with irreversible covalent bonds affords amorphous solids because of random crosslinking.1) Recent studies reported that the nucleophilic aromatic substitution ($S_N$Ar) reaction afforded covalent organic frameworks (COFs).2) This was due to structural corrections facilitated by dynamic $S_N$Ar reactions, which enabled the formation of ordered network structures.

In this study, we successfully constructed pillar[*n*]arene-based COFs by connecting pillar[*n*]arenes through $S_N$Ar reaction (**COF-P5A** and **COF-P6A**, **Figure 1a**). Powder X-ray diffraction (PXRD) patterns revealed that they were crystalline solids (**Figure 1b**). Scanning electron microscope (SEM) images suggested the formation of the one-dimensional frameworks (**Figure 1c**). In addition, gas adsorption analyses revealed that the frameworks exhibited microporosity with pore sizes at the Ångstrom level.

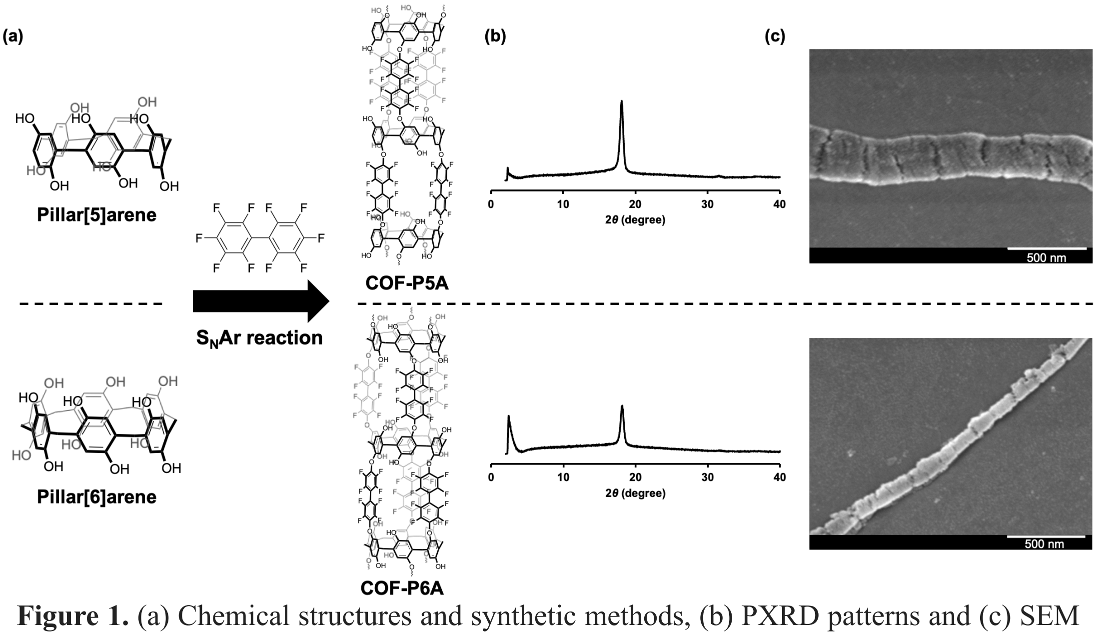


**Figure 1.** (a) Chemical structures and synthetic methods, (b) PXRD patterns and (c) SEM images of **COF-P5A** (upper) and **COF-P6A** (lower).

1) Y. Togari, S. Ohtani, E. Kanao, K. Sato, M. Mizuno, K. Kato, R. Mizuta, Y. Sasaki, T. Ogoshi, *ACS Appl. Mater. Interfaces,* **2024**, *16*, 69963–69972. 2) W. J. Ong, T. M. Swager, *Nat. Chem.* **2018**, *10*, 1023–1030.

# Versatile Protein Encapsulation in Crystals of Spherical Coordination Cages

([1]*Grad. School of Engineering, The Univ. of Tokyo*, [2]*UTIAS, The Univ. of Tokyo*, [3]*Institute for Molecular Science*) ○Hongkun Liu,[1] Takahiro Nakama,[1] Makoto Fujita[2,3]

**Keywords**: Protein immobilization; Coordination cage; Crystallization; Enzymatic reaction; Heterogeneous catalysis

Protein immobilization in solid supports is a promising approach to improve the practical performance of enzymes as heterogeneous catalysts. Despite successes with various matrices, they often suffer from limited protein scope, low loading capacity, and ambiguous environments around the protein. Previously, we reported protein encapsulation in $M_{12}L_{24}$ spherical coordination cages, leading to significant stabilization of the caged protein.[1,2,3]

Here, we demonstrate a versatile method to immobilize proteins in porous single crystals by encapsulation in the $M_{12}L_{24}$ coordination cages (**Fig. 1**). Each protein was encapsulated in a well-defined cavity of $M_{12}L_{24}$ cages prior to crystallization by the conjugation with bis(pyridine) ligands (**L**) and subsequent self-assembly with Pd(II) ions (**M**). Crystals of the caged proteins were then obtained by vapor diffusion (**Fig. 1A,B**). This pre-encapsulation strategy allowed us to immobilize more than 10 different proteins in the crystal of $M_{12}L_{24}$ cages without any significant changes in conditions. Fourier-transform infrared (FTIR) and X-ray absorption fine structure (XAFS) spectroscopy provided structural information on immobilized proteins. The superoxide dismutase 1 (SOD1) immobilized in the cage crystal catalyzed superoxide ($\mathrm{O2}^{\bullet -}$) disproportionation with an 82% residual activity. Remarkably, the co-immobilization of two enzymes, SOD1 and cytochrome c (cyt c), in a single crystal has enabled a cascade reaction with a proximity-induced 4.2-fold increase in catalytic performance compared to the enzymes immobilized in different cage crystals (**Fig. 1C**).

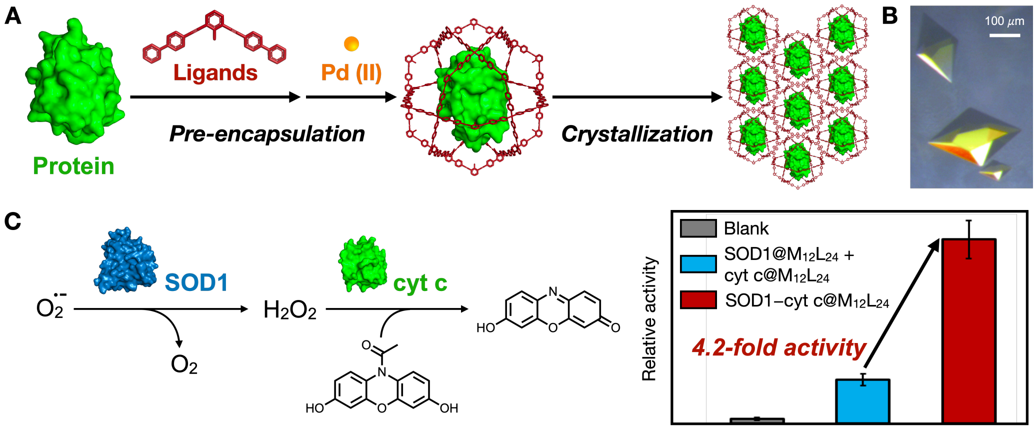


**Fig. 1** (**A**) Schematic diagram of protein immobilization in crystals of $M_{12}L_{24}$ cages. (**B**) Crystals of caged SOD1. (**C**) Cascade reaction by two enzymes immobilized in the $M_{12}L_{24}$ cage crystal.

1) *Chem* **2021**, *7*, 2672. 2) *Chem. Sci.* **2023**, *14*, 2910. 3) *Angew. Chem. Int. Ed.* **2024**, e202419476.

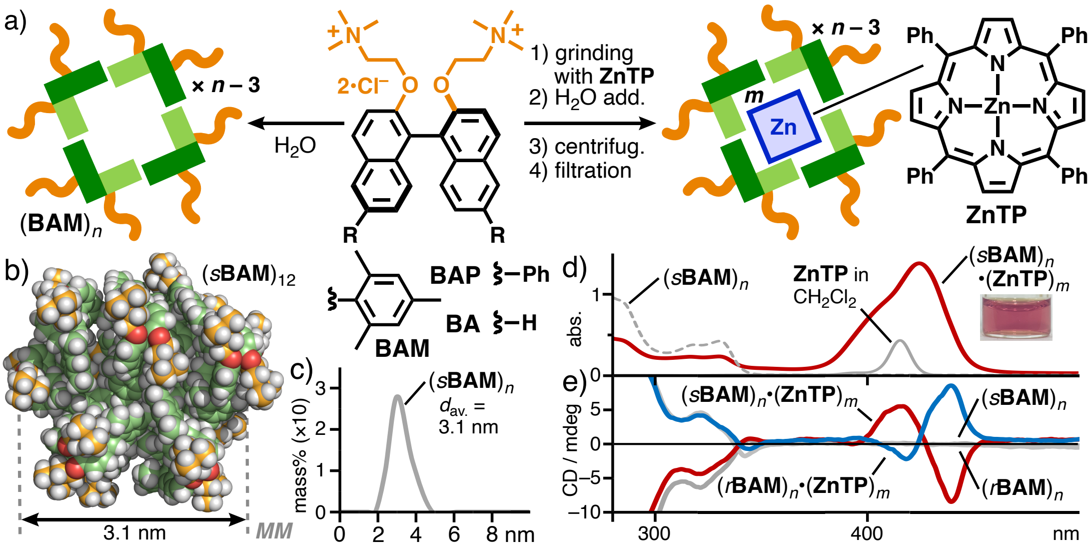
# Formation of Binaphthyl-based Micelles Capable of Encapsulating Metallodyes

(*Lab. for Chem. & Life Sci., Science Tokyo*) Yoshihisa Hashimoto, Yuya Tanaka, and Michito Yoshizawa

**Keywords**: binaphthyl; bent amphiphile; aromatic micelle; chiroptical properties; metallodyes

BINOL (1,1’-binaphthyl-2,2’-diol) is an excellent, chiral aromatic compound due to its characteristic axial chirality, versatile functionality, and synthetic accessibility in supramolecular chemistry. Although various BINOL-based macrocyclic and cage-like compounds generate chiral cavities, their host functions have been largely limited so far, owing to the open and rigid frameworks.

Here we report novel chiral aromatic micelles bearing BINOL frameworks and their ability of efficient chirality transfer to metallodyes. Three types of bent amphiphiles *s*/*r***BAM**, *s***BAP**, and *s***BA** were designed using different substituents at the 6,6’-positions of the BINOL framework. The bent amphiphiles were synthesized in 4-5 steps including Negishi or Suzuki-Miyaura coupling. Amphiphile *s***BAM** having mesityl groups quantitatively formed a chiral aromatic micelle in water (Fig. a, right), as confirmed by NMR, PL, UV-visible, and CD analyses. The DLS and molecular modeling studies revealed a spherical structure composed of 12•*s***BAM** with a diameter of ~3 nm (Fig. b,c). Aromatic micelle (*s***BAM**)$_n$ efficiently encapsulated Zn-porphyrin **ZnTP** *via* grinding method (Fig. a, left). The CD spectra of the resulting host-guest composite (*s*/*r***BAM**)$_n$•(**ZnTP**)$_m$ displayed mirror CD bands at 390-450 nm (Fig. e), attributed to chirality transfer from the host to the bound guests, with absorption dissymmetry factors ($|g_{\mathrm{abs}}|$) being ~3 × $10^{-4}$.



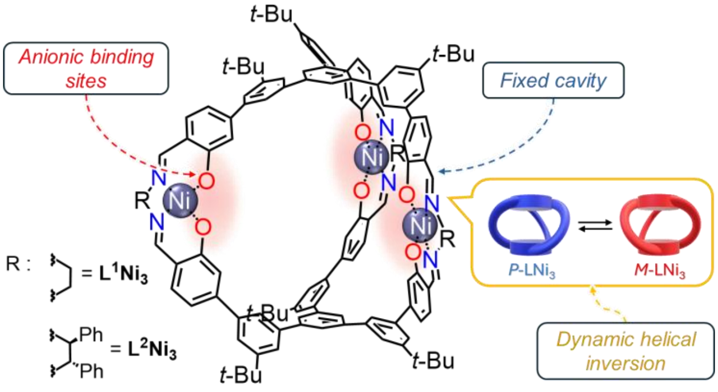
# A Novel Tris(salen)-Type Metallocryptand for Selective Recognition Towards Biologically Active Compounds

(*[1]Graduate School of Frontier Science Initiative, Kanazawa University, [2]Graduate School of Natural Science and Technology, Kanazawa University, [3]Graduate School of Engineering, Nagoya University, [4]Institute for Molecular Science, [5]Nano Life Science Institute, Kanazawa University*) ○Syadza Firdausiah,[1] Ryo Ide,[2] Yoko Sakata,[3] Masahiro Ehara,[4] Shigehisa Akine[1,2,5]

**Keywords**: Amino acids, chirality, covalent cage, molecular recognition, saccharides.

The advancement of host-guest chemistry has enabled the design of novel supramolecular structures with enhanced functional properties. We have demonstrated that metallocryptands containing three salen (*N*,*N*′-disalicylideneethylenediamine)-type coordination structures showed an excellent binding affinity to cationic guest species such as alkali metal ions.[1,2] In this study, we report larger analogue of the metallocryptand, $LNi_3$, and its selective molecular recognition of bioactive compounds, including guanidinium salts, amino acid derivatives, and monosaccharides.

The synthesis involved seven reaction steps to produce the imine cage precursor ($H_6L$), followed by complexation with $Ni^{2+}$ to yield $LNi_3$. Single-crystal X-ray diffraction revealed the formation of helical enantiomers (*M*- and *P*-forms), consistent with the stability difference between the helical and meso diastereomers estimated by the DFT calculations. The binding studies showed that $LNi_3$ exhibited size- and structural-dependent affinities, with 1:3, 1:2, or 1:1 host-guest ratio depending on the guest properties. Its fixed cavity architecture facilitated size discrimination, while its dynamic *P*/*M* helical equilibrium elicited chiroptical responses for selective guests, indicating its potential for enantioselective recognition.



This work underscores the utility of tris(salen)-type metallocryptand in molecular recognition and enantiomeric sensing, offering insights for future applications in supramolecular chemistry.

1) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front*. **2014**, 1, 53.
2) S. Asif Ikbal, P. Zhao, M. Ehara, S. Akine, *Sci. Adv.* **2023**, 9, eadj5536.

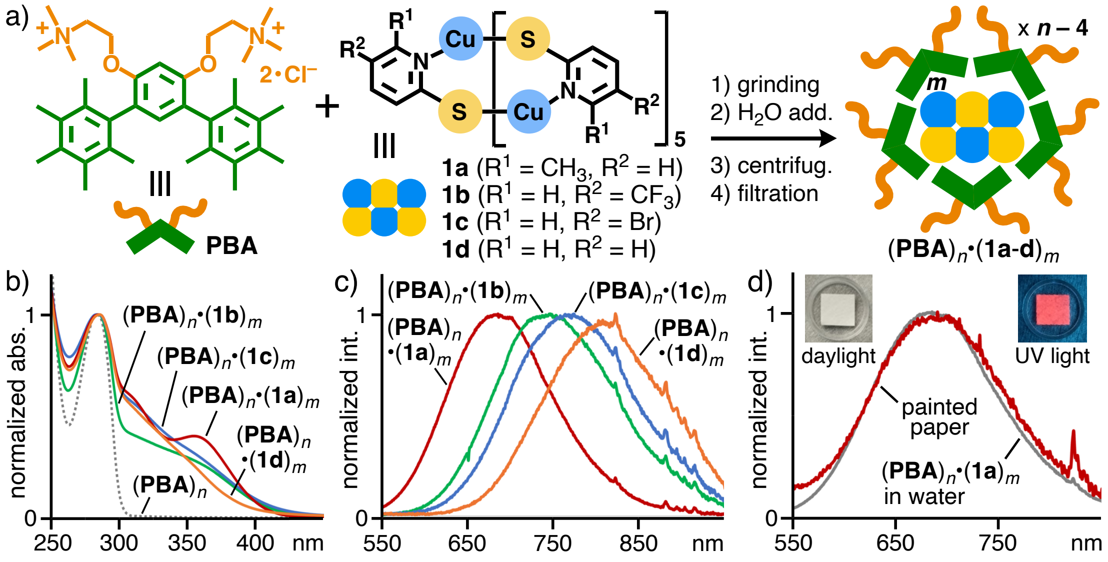
# Emission Properties and Use of Multinuclear $Cu_nS_m$ Clusters within Aromatic Micelles

(*Lab. for Chem. & Life Sci., Science Tokyo*) ○Kazuki Toyama, Yuya Tanaka, Michito Yoshizawa

**Keywords**: Multinuclear Copper-sulfur Cluster; Aromatic Micelle; Encapsulation; Red-to-NIR Emission; Security Ink

Multinuclear $Cu_nS_m$ clusters have been attracted interest, due to their characteristic photophysical properties.[1] However, the majority of $Cu_nS_m$ clusters are insoluble and/or unstable in organic solvents as well as in water, which interferes with their applications. Aromatic micelle displays wide-ranging host ability toward aromatic compounds as well as metal-complexes.[2] On the other hand, its encapsulation ability toward multinuclear $M_n$ clusters ($n > 3$) has not been unrevealed to date.

Here we report the solution-state red-to-near-infrared (NIR) emission of $Cu_6S_6$ clusters upon encapsulation by aromatic micelles in water. The resultant solution served as potential security ink. $Cu_6S_6$ cluster **1a**-**d** were efficiently incorporated by aromatic micelle $(\textbf{PBA})_n$ in water through a grinding method (Fig. a). The UV-visible spectra of the resultant solutions showed new absorption bands derived from **1a**-**d** ($\lambda$ = 300-420 nm; Fig. b), indicating their water solubilization upon encapsulation. Host-guest complexes $(\textbf{PBA})_n\text{•}(\textbf{1a-d})_n$ displayed various red-to-NIR emission in water, depending on the substituents on the clusters ($\lambda_{max}$ = 685-805 nm; $\phi$ = 16-31%; Fig. c). The aqueous $(\textbf{PBA})_n\text{•}(\textbf{1a})_n$ solution was used as writing and painting ink on paper, which is colorless under daylight yet red-to-NIR emissive under UV-light irradiation (Fig. d). Furthermore, this protocol was applicable to $Cu_{12}S_6$ and $Cu_4I_4$ clusters.



[1] A. Baghdasaryan, T. Bürgi, *Nanoscale* **2021**, *13*, 6283–6340. [2] M. Yoshizawa, L. Catti, *Acc. Chem. Res.* **2019**, *52*, 2392–2404.