

Onion-Shell Metal–Organic Polyhedra (MOPs): A General Approach to Decorate the Exteriors of MOPs using Principles of Supramolecular Chemistry

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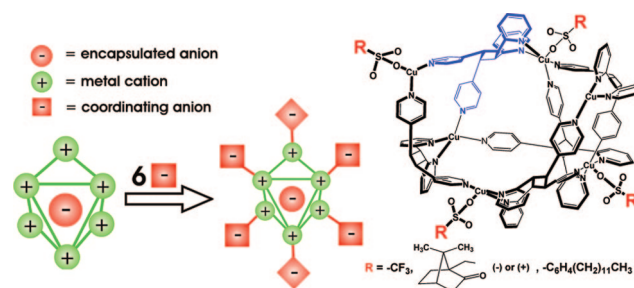
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The design and construction of complex supramolecular architectures requires an understanding of how to control arrangements of noncovalent forces between multiple components to allow functionalities to be expressed. In this context, metal–organic polyhedra (MOPs)¹ are attractive platforms to present surface-exposed organic groups in synthetic supramolecular chemistry. These capsular assemblies form *via* coordination-driven self-assembly of metal ions with organic subunits of predefined geometries. Much attention has focused upon inner cavities of MOPs to elucidate behaviors of guests.² Comparatively little attention, however, has been paid to develop the exteriors,³ which could enable these cages to interact selectively with their environments and deliver their contents.⁴

Here, we introduce a simple and general method to decorate the exteriors of MOPs with organic groups using principles of supramolecular chemistry. We show how noncovalent decoration of MOPs, in the form of trigonal antiprisms,⁵ give novel onion-shell capsules with alternating negative–positive–negative charges (Scheme 1, left). These capsules are complements to MOPs described by Fujita that involve alternating positive–negative–positive charges associated with interior, versus exterior, environments.⁶ Our strategy uses anions, in the form of organosulfonates RSO_3^- [$\text{R} = -\text{CF}_3$, (+ or –)-10-camphor-sulfonate (CPS), -dodecylbenzenesulfonate (DBS)], to radially decorate the nanometer-scale cationic MOP $[\mathbf{1}(\text{H}_2\text{O})_6]^{12+}$ (where: $\mathbf{1} = \text{Cu}_6(2,4\text{'-tpcb})_6$ with $2,4\text{'-tpcb} = \text{rctt-1-bis(2-pyridyl)-2-bis(4-pyridyl)cyclobutane}$).⁵ The resulting cages possess three concentric shells with a core of anionic guests, a cationic shell, and an anionic exterior. The strategy affords novel homochiral polyhedra with up to 18 components. We show how subtleties of the self-assembly process can be tuned so that the encapsulated anions are different than the decorators.⁷

Host $[\mathbf{1}(\text{H}_2\text{O})_6]^{12+}$ consists of six Cu(II) ions, six molecules of $2,4\text{'-tpcb}$, and six water molecules that form a capsule *ca.* 1 nm in diameter. The topology conforms to a trigonal antiprism.⁵ The cavity encapsulates polyatomic anions (e.g., ClO_4^-) while the water molecules coordinate Cu(II) ions along the corners of the polyhedron. Owing to the positioning of the waters, we expected that the exterior of the capsule could be decorated noncovalently by replacing the waters with organic anions (Scheme 1, right). The MOP would, thus, be programmable in terms of the number and spacing of points of attachment of anions along the exterior. In an ideal case, a one-pot reaction would result in radial assembly of six organic anions. Such an approach would obviate a covalent synthesis of a decorating ligand, which is the established method.⁸ Single or multiple anions could assemble within the polyhedron. The structural diversity and widespread availability of organosulfonates,⁹ as well as the ability to engage in Cu–O bonds, made the anions attractive as decorating units. The +12 charge of $\mathbf{1}$ could

Scheme 1. Onion-Shell Antiprisms with Noncovalent Decorators



augment the weak association¹⁰ of $\text{Cu}(\text{II})$ and RSO_3^- ions to give cages of general composition $[\mathbf{1}(\text{RSO}_3)_n]^{12-n}$.

To test our hypothesis, equimolar $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and $2,4\text{'-tpcb}$ were mixed in MeCN. Addition of diethyl ether produced a powder. An IR spectrum gave a band at 1267 cm^{-1} , which corresponds to the CF_3SO_3^- ion. Single crystals of $[\mathbf{1}(\text{CF}_3\text{SO}_3)_6](\text{CF}_3\text{SO}_3)_6 \cdot 18\text{H}_2\text{O}$ ($\mathbf{2}$) suitable for X-ray analysis were grown *via* slow diffusion of diethyl ether into a solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and $2,4\text{'-tpcb}$ (1:1 ratio) in MeCN.

Perspective views of $\mathbf{2}$ are shown in Figure 1. The metal and organic components assembled to form the polyhedron $\mathbf{1}$, which sits around a crystallographic -3 position. Six CF_3SO_3^- ions lie along the exterior of $\mathbf{1}$, interacting with the polyhedron *via* six Cu–O bonds (Cu–O bond length 2.24 \AA) (Figure 1a). Two additional CF_3SO_3^- ions interact with the exterior of the polyhedron *via* electrostatic forces. These two ions cap the antiprism, with each $-\text{SO}_3$ group pointing toward the cavity (Figure 1b). A single CF_3SO_3^- anion, which lies disordered over six positions, also assembled within $[\mathbf{1}(\text{CF}_3\text{SO}_3)_6]^{6+}$ and, thus, serves as a guest (Figure 1b). The exterior decorators and encapsulated anion are, thus, of the same chemical type. The remaining three CF_3SO_3^- ions, along with 18 water molecules, lie exterior to the MOP, participating in a network of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

With a noncovalent decoration of $\mathbf{1}$ established, we turned to complex functionality in the form of chiral anions. Of the few chiral MOPs, most are composed of achiral components and typically afford racemates.^{11,12} We expected a one-pot entry to a homochiral MOP wherein six homochiral groups assemble along $\mathbf{1}$. For a chiral decorator, we chose camphorsulfonate (CPS), a common chiral auxiliary.¹³ Molecular modeling suggested a single CPS ion would be too large to fit in $\mathbf{1}$. Since the ClO_4^- ion is a tight-fitting guest,⁵ reaction of $\text{Cu}(\text{CPS})_2$, $2,4\text{'-tpcb}$, and ClO_4^- ions would afford $\mathbf{1}$ with radially decorating CPS ions *and* encapsulated ClO_4^- ions. We would, thus, use size to fine-tune the self-assembly to give a superassembly with guests different than the decorators.

To test our hypothesis, equimolar $[\text{Cu}(\text{H}_2\text{O})_6][(+)\text{-CPS}]_2$, $2,4\text{'-tpcb}$, and NaClO_4 were mixed in MeCN. Addition of diethyl ether

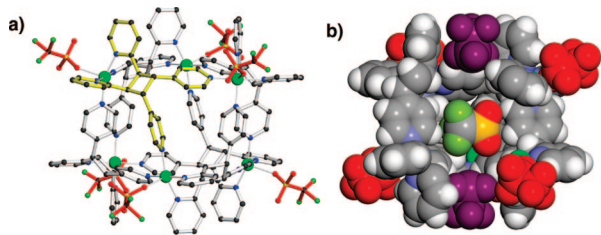


Figure 1. X-ray structure of decorated **2**: (a) Ball-and-stick (2,4'-tpcb, yellow; CF_3SO_3^- , red) and (b) cut-away showing capping CF_3SO_3^- anions (purple) and CF_3SO_3^- guest (green = Cu, yellow = S, yellow-green = F, red = O, blue = N, gray = C, white = H).

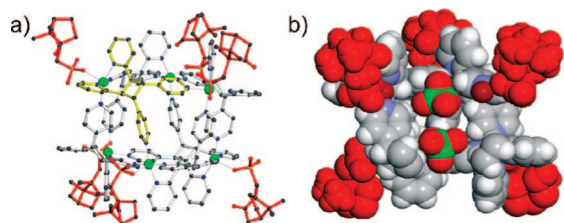


Figure 2. X-ray structure of homochiral **3**: (a) Ball-and-stick and (b) cut-away showing ClO_4^- guests (100% and 50% occupied).

produced a blue powder. An IR spectrum gave bands at 1270, 1146, 1120, and 1087 cm^{-1} , which correspond to the CPS and ClO_4^- ions. Single crystals of $[\mathbf{1}(+-)\text{CPS}]_6(\text{ClO}_4)_6 \cdot 6.5\text{H}_2\text{O} \cdot 11.5\text{CH}_3\text{CN} \cdot 3\text{C}_4\text{H}_{10}\text{O}$ (**3**) suitable for X-ray analysis were grown *via* diffusion of diethyl ether into a solution of $[\text{Cu}(\text{H}_2\text{O})_6][(+)\text{-CPS}]_2$, 2,4'-tpcb, and NaClO_4 (1:1:1 ratio) in MeCN.

Perspective views of **3** are shown in Figure 2. The components assembled to give the homochiral polyhedron $[\mathbf{1}(+-)\text{CPS}]_6^{6+}$, which sits around a crystallographic 32 position. The six (+)-CPS ions decorate the exterior of the antiprism, interacting with **1** *via* six Cu–O bonds (Cu–O bond length 2.19 Å) (Figure 2a). In contrast to **2**, the cavity of **3** is filled with anions chemically different than the decorators. Each cavity is filled with up to two ClO_4^- anions (Figure 2b), while each end of the antiprism is capped by one ClO_4^- ion. The encapsulated ClO_4^- ions are disordered such that each cavity is occupied by either two ClO_4^- ions or a ClO_4^- ion and a water molecule. The remaining ClO_4^- ions, along with the solvent, are disordered and lie exterior to **1**. We also generated the homochiral enantiomer of $[\mathbf{1}(+-)\text{CPS}]_6^{6+}$. Specifically, reaction of $[\text{Cu}(\text{H}_2\text{O})_6][(-)\text{-CPS}]$, 2,4'-tpcb, and NaClO_4 afforded crystalline $[\mathbf{1}((-)\text{-CPS})_6(\text{ClO}_4)_6 \cdot 8\text{H}_2\text{O} \cdot 7.5\text{CH}_3\text{CN} \cdot 3\text{C}_4\text{H}_{10}\text{O}$ (**4**). An X-ray analysis revealed **1** decorated with six (–)-CPS ions and encapsulated ClO_4^- ions.

Although organosulfonates are weakly coordinating,⁹ evidence supporting the decorators associating with **1** in solution comes from electrospray mass spectrometry (ESMS) and solubility experiments.¹⁴ In particular, the ESMS spectrum of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and 2,4'-tpcb in MeCN gave only a single peak at m/z 364, which corresponds to free 2,4'-tpcb. However, upon addition of NaClO_4 , peaks form in the low and high m/z region. The most abundant peaks are m/z 576 and 526, which correspond to $[(\mathbf{1}(\text{CF}_3\text{SO}_3)_6)]^{+6}$ and $[(\mathbf{1}(\text{ClO}_4)_6)]^{+6}$. Doubly and triply charged peaks are also present, with the most prominent being $[(\mathbf{1}(\text{CF}_3\text{SO}_3)_6)]^{+3}$ (m/z 1303). From the structure of **2**, the triply charged peak is assigned as decorated **1** with the corners, capping sites, and cavity occupied by six, two, and one CF_3SO_3^- ion, respectively. Remaining peaks (Supporting Information) are assigned to decorated $[\mathbf{1}(\text{CF}_3\text{SO}_3)_6]^{6+}$ with two encapsulated ClO_4^- guests and surface-exchanged $-\text{CF}_3\text{SO}_3^-$ ions.¹⁵ Solubility experiments conducted in CHCl_3 using DBS also

support the decorators associating with **1** in solution. Specifically, an attempt to dissolve nondecorated $[\mathbf{1}][(\text{ClO}_4)_{12}]$ in CHCl_3 resulted in a blue suspension and no visible color change to the solvent following Ultrafine filtration. However, when NaDBS (ratio of **1**/DBS = 1:10) was added to the suspension of solid $[\mathbf{1}][(\text{ClO}_4)_{12}]$, a blue solution formed within minutes. When $\text{Cu}(\text{ClO}_4)_2$ and NaDBS were added, in a separate experiment, to CHCl_3 , a solution with no visible color change formed. Given that CHCl_3 is relatively nonpolar and noncoordinating and that the components of the MOP are charged, these observations are consistent with **1** forming in solution with the negatively charged end of each DBS ion being directed to the exterior of the polyhedron. The decorated MOP would, in effect, resemble a reverse-micelle¹⁶ with the charged groups sequestered to the core and the hydrophobic groups pointing away from the cavity.

In summary, we have presented a method to noncovalently decorate exteriors of MOPs involving shells of alternating negative–positive–negative charges. In addition to chiral and hydrophobic groups, we plan to study a wide range of decorators that bestow additional properties. That we can selectively modify guests is expected to give MOPs of enhanced complexity.

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Supporting Information Available: Crystallographic data (CIF) and experimental preparations for **2**, **3**, and **4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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