

Interconversion between Molecular Polyhedra and Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) have attracted a great deal of attention in the past decade because of their captivating structural diversities and intriguing potential applications, such as gas storage and separation, catalysis, drug delivery, and chemical sensing.^{1,2} Likewise, the study of the assembly and reactivity of molecular polyhedra has also emerged as an exciting new branch of supramolecular chemistry.³ However, there exists very little overlap between the two. While some of the MOFs can be viewed structurally as interlinked polyhedra,^{4,5} and hypotheses such as “hierarchical assembly” and the “supramolecular building block approach” have been invoked to illuminate the mechanism of the assembly of such MOFs, direct experimental evidence for the proposed mechanisms has not been reported prior to this work.

MOFs are always synthesized by a “one-pot” procedure. Stepwise assembly of a MOF from a molecular polyhedron precursor is difficult because the intermediate molecular polyhedra are not always soluble, even if they can be interlinked.⁵ As a result, a “bottom-up” synthesis of MOFs from molecular polyhedra cannot start from the bottom, though a conceptual design has been elaborated.⁶

Herein, we report the design and synthesis of a rare example of a soluble and robust molecular polyhedron and the unprecedented reversible assembly of a MOF from such a molecular polyhedron (Figure 1). Additionally, other reactions of the molecular polyhe-

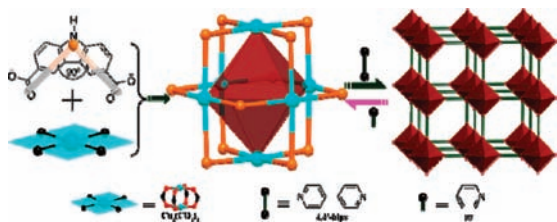


Figure 1. Schematic representation of the assembly of a molecular octahedron and its interconversion with a MOF.

dron, such as terminal-ligand exchange and deconstruction into a 1D coordination polymer, are also demonstrated.

Among potential MOF building units, a molecular octahedron is ideal because it can be extended into a 3D MOF simply by interlinking the six vertices through a ditopic ligand. As demonstrated in MOP-28,⁷ a molecular octahedron can be prepared from an angular (90°) dicarboxylate ligand and a paddlewheel $\text{Cu}_2(\text{CO}_2)_4$ cluster. Herein, the ligand adopted for such a purpose was 9H-carbazole-3,6-dicarboxylate (CDC, Figure 1), which can be synthesized by following a modified literature method.⁸ It was anticipated that the N–H functional groups of the ligands would form hydrogen bonds with appropriate solvent molecules, improving the solubility of the ensuing molecular polyhedron. The $\text{Cu}_2(\text{CO}_2)_4$ paddlewheel clusters should occupy the six corners of an octahedron while labile terminal ligands cap the two axial positions of each

paddlewheel unit. Ligand substitution of the labile axial ligands with ditopic organic linkers should lead to the formation of an extended structure.

A solvothermal reaction between H_2CDC and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in a 1:1 DMA/EtOH (DMA = *N,N*-dimethylacetamide) mixed solvent system afforded $[\text{Cu}_2(\text{CDC})_2(\text{DMA})(\text{EtOH})]_6 \cdot x\text{S}$ (S = noncoordinated solvent molecule) (**1**) as blue-green crystals.⁸ Single-crystal X-ray diffraction studies⁸ showed that **1** crystallizes in the monoclinic space group $P2_1/n$. The molecular octahedron is composed of six axially coordinated $\text{Cu}_2(\text{CO}_2)_4$ paddlewheel clusters joined by 12 CDC linkage units (Figure 2 and Figure S8 in the

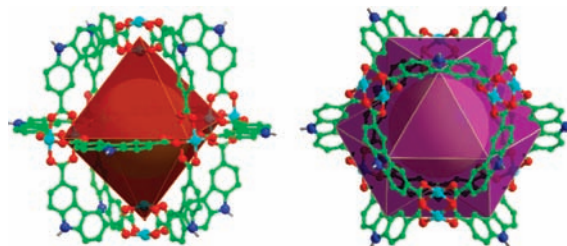


Figure 2. Polyhedral representations of **1**: (left) paddlewheel $\text{Cu}_2(\text{CO}_2)_4$ clusters act as vertices; (right) CDC ligands act as vertices. Axial ligands and most of the H atoms have been omitted for clarity.

Supporting Information) and is structurally very similar to MOP-28.⁷ The idealized symmetry for the molecular octahedron should be O_h , but the crystallographic symmetry is lowered by the existence of three different pairs of axial ligands (DMA/DMA, DMA/EtOH, and EtOH/EtOH) for the $\text{Cu}_2(\text{CO}_2)_4$ clusters in an asymmetric unit. The molecular octahedron resides on a symmetry-imposed inversion center. The longest dimension of **1** is ~ 24.0 Å (atom-to-atom distance throughout this communication). The internal spherical cavity of **1** has a diameter of ~ 13.8 Å ignoring coordinated solvents, and the size of the triangular aperture is ~ 10.0 Å. Alternatively, this molecular polyhedron can also be described as a cuboctahedron when the CDC linkers are viewed as the vertices (Figure 2, right).

Other $\text{M}_2(\text{CO}_2)_4$ -based molecular polyhedra have been synthesized, but few of them are soluble.⁹ Compound **1** dissolves in DEF, DMF, DMA, and DMSO; the molecular polyhedra are preserved in solution, but they undergo axial-ligand substitution upon dissolution.

A blue-green solution of **1** in DEF has an absorption peak at 704 nm, almost identical to that of $\text{Cu}_2(\text{OAc})_4$ in DEF (Figure S6). In DEF solution, **1** undergoes a ligand-substitution reaction to yield **2**, which can be crystallized by layering the solution with EtOH or MeCN. Compound **2** can also be synthesized by a procedure similar to that for **1** but using DEF instead of DMA. **2** has a crystal structure similar to that of **1** except for the axial ligands but crystallizes in the space group $R\bar{3}$ (Figure 3).⁸ All of the external axial Cu sites are coordinated with DEF molecules, whereas water molecules occupy all of the internal Cu sites. Evidently, the larger size of a DEF molecule (compared to DMA) precludes it from entering the polyhedron.

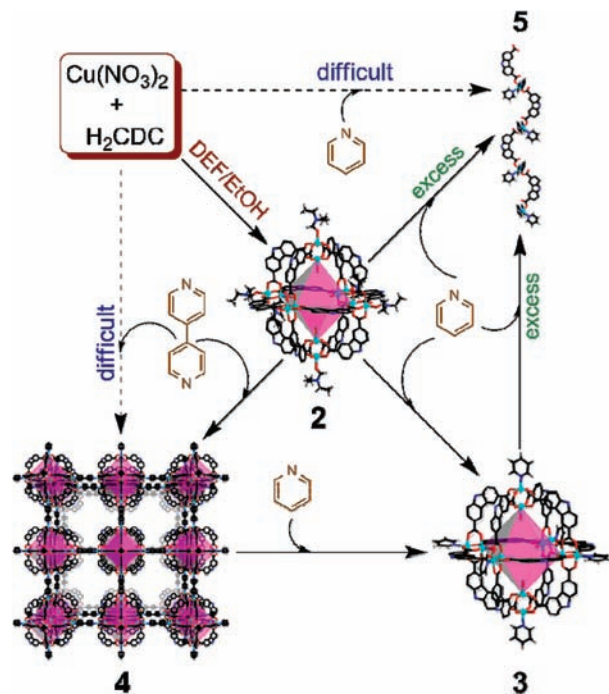


Figure 3. Reaction scheme and drawings of crystal structures of coordination assemblies 2–5. Most of the H atoms have been omitted for clarity. Color scheme: Cu, aqua; O, red; N, blue; C, black.

Another derivative of **1** was prepared by introducing a small quantity of pyridine (py) into a DEF solution of **2**. The absorption peak for this newly formed green solution is shifted from 704 to 716 nm and matches well with that of $\text{Cu}_2(\text{OAc})_4$ in DEF/py (Figure S7). When allowed to stand at room temperature for several days, the solution afforded green crystals. X-ray diffraction studies⁸ confirmed that **3** also crystallizes in the space group $R\bar{3}$ and that the molecular octahedron is intact with the external Cu sites now coordinated by py ligands (Figure 3).

A polyhedron-based MOF, **4**, was constructed by treating a solution of **1** in DEF with an EtOH solution of 4,4'-bipyridine (4,4'-bipy). The MOF possesses a twofold-interpenetrated 3D framework structure, as shown in Figure S10. Each single network adopts an augmented **pcu** (**pcu-a**) topology, and one is shown in Figure 3. The window size of the single net is ~ 14.4 Å, and the cubic chamber, inhabited by octahedron building blocks from the other network, has a side length of ~ 30.5 Å. In the framework, each octahedron is a six-connected node linked by crystallographically disordered 4,4'-bipy ligands at all six external Cu sites, and each disordered 4,4'-bipy lies along a pseudo-fourfold axis and was refined at half occupancy over each of two equivalent orientations. Remarkably, though interpenetrated, the framework of **4** still preserves a 76% solvent-accessible area (as calculated using the PLATON routine), in large part as a result of the porosity of the octahedron building block.¹⁰ To the best of our knowledge, this is the first example of a truly stepwise construction of a MOF using a molecular polyhedron precursor.

Reversible transformation/conversion between a molecular polyhedron and a polyhedron-based MOF was also realized for the first time when **4** was disassembled back into the molecular octahedron by dissolution in a 4:1 DEF/py solvent mixture. The ensuing solution had the same absorption feature as that of **3**, and the formation of **3** was further confirmed by X-ray diffraction studies on the green crystals isolated.⁸

Furthermore, the molecular octahedra can be deconstructed by addition of an excess of pyridine to a DEF solution of them. A 1D

helical chain, **5**, in which pentacoordinated Cu centers are coordinated by three py molecules and interlinked by CDC ligands, was crystallized. Each CDC ligand coordinates to two Cu ions using only one O atom of each carboxyl group.

Figure 3 also shows that the stepwise MOF synthetic routes (for **4** and **5**) using molecular polyhedra can lead to new MOFs, which may be difficult or impossible to synthesize using the one-pot reaction method.

In summary, an unprecedented stepwise dimensional modification has been realized for metal–organic coordination assemblies. A judicious choice of ligand resulted in a soluble molecular octahedron that formed a series of derivatives through axial-ligand substitution reactions. The axial ligand was also replaced by a ditopic ligand, resulting in interlinking of the octahedra and the formation of a MOF. This MOF was dimensionally reduced back to a molecular octahedron and further deconstructed to form a 1D chain. The assembly of other MOFs using the molecular octahedron and the design and synthesis of new polyhedra and their extension into MOFs are in progress.

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Supporting Information Available: Synthesis and general characterizations (PXRD, EA, IR, and TGA), crystallographic data in CIF format, absorption spectra, and additional structural figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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