Two Zeolite-Type Frameworks in One Metal–Organic Framework with $Zn_{24}@Zn_{104}$ Cube-in-Sodalite Architecture**

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Over the past several decades, the self-assembly process driven by coordination chemistry has allowed the creation of many fascinating materials that range from discrete molecular cages to 3D porous frameworks.[1–3] A high level of synthetic control over such assembly processes has been achieved, as demonstrated by the increasing size of discrete assemblies (called coordination cages or metal–organic polyhedra (MOPs)) and the ever-increasing variety of topologies in metal-organic frameworks (MOFs).[4–10]

For several years, we have been interested in the development of synthetic methodologies for the engineering of geometric pore spaces. For example, we were able to use a number of extra-framework organic cations of different sizes to control the utilization of pore space in a series of porous anionic indium–BTC (H_3BTC = trimesic acid) frameworks (denoted CPM-1, CPM = crystalline porous materials), leading to a significant tunability in gas sorption properties.[1e] More recently, we created two types of cage-in-cage coreshell-like porous frameworks, called CPM-6 (or isostructural CPM-5) and CPM-24.[9c,12d] In both CPM-6 and CPM-24, the trifunctional ligand (BTC) interconnects outer and inner cages. Interestingly, the similar mechanism based on the intercage crosslinking by polyfunctional organic ligands was also found in the formation of discrete sphere-in-sphere coordination polyhedra with the same inside and outside cages as in CPM-24.[10d]

One of the most fundamental aspects in the assembly of the nested cages is the mechanism for the interconnection between inside and outside cages. Since the original discovery of the nesting mechanism based on trifunctional organic ligand in CPM-6, we have been faced with the question whether the use of a polyfunctional ligand is the only way to create the nested cage-in-cage architecture.[11–13] The work reported herein provides an unequivocal answer to this question by showing a new way in which the intercage connection is accomplished by monomeric Zn^{2+} sites anchored at the face center of eight hexagonal rings of the sodalite cage. In contrast, the original mechanism for the intercage connection as found in CPM-6 is based on the carboxy group anchored off the edge center of sodalite cages.

The new material (denoted CPM-7) was synthesized by solvothermal reaction between $Zn(NO_3)_2 \cdot 6H_2O$ and 2,5-furandicarboxylic acid (H_2FDA) in a binary solvent of diethylformamide (DEF) and methanol at 120° for three days. The chemical composition of CPM-7, determined by single-crystal X-ray analysis and formulated per sodalite cage in the sequence of [amine-template][monomer][trimer1-trimer2][tetramer][solvent], is $[(CH_3CH_2)_2NH_2]_{12} \cdot [Zn(FDA)_3]_4 \cdot [Zn_3(OH)(FDA)_{3/2} \cdot Zn_3(OH)(FDA)_{3/2} \cdot (H_2O)_6]_4 \cdot [Zn_4O(FDA)_4]_6 \cdot [(DEF)_{22}]$. Despite this apparently complicated formula, the topological structure of CPM-7 is in fact quite simple. In the above formula, $[Zn_4O(FDA)_4]_6$ represents a sodalite cage formed from the Zn_4O tetramer and FDA, while $[Zn_3(OH)(FDA)_{3/2} \cdot Zn_3(OH)(FDA)_{3/2} \cdot (H_2O)_6]_4$ is just a collection of eight $Zn_3(OH)$ trimers joined by FDA into a cube inside the sodalite cage. The $[Zn(FDA)_3]_4$ unit represents the monomeric Zn^{2+} site at the face center (6-ring face only) of the sodalite cage and has the role of cube-to-sodalite intercage connection. Note that because this is a 3D framework, the number of metal nodes and ligands in the above notation does not match with those based on zero-dimensional discrete cages.

CPM-7 crystallizes in a highly symmetric cubic space group I23 with a relatively large unit cell (*a* = 30.98 Å). Its structure is built from four crystallographically different building units, Zn_4O tetramer, two kinds of $Zn_3(OH)$ trimers, and Zn monomer (Figure 1). While the coexistence of all these different building blocks (from the same metal ion) is in itself very unusual, their very exotic bonding pattern is even more unusual. For example, the Zn_4O tetramer, in which Zn^{2+} sites occupy four tetrahedral corners and one oxygen is at the center of the tetrahedron, should "by default" be a six-connected tetramer, just like in MOF-5.[8a] Yet, it is eight-connected in CPM-7 (see Figure S2a in the Supporting Information). Such a bonding mode is very unusual and, to the best of our knowledge, has never been observed before.

There are eight FDA ligands attached to the Zn_4O tetramer and they can be divided into two sets. The first set consists of four bidentate chelating COO–Zn links in which

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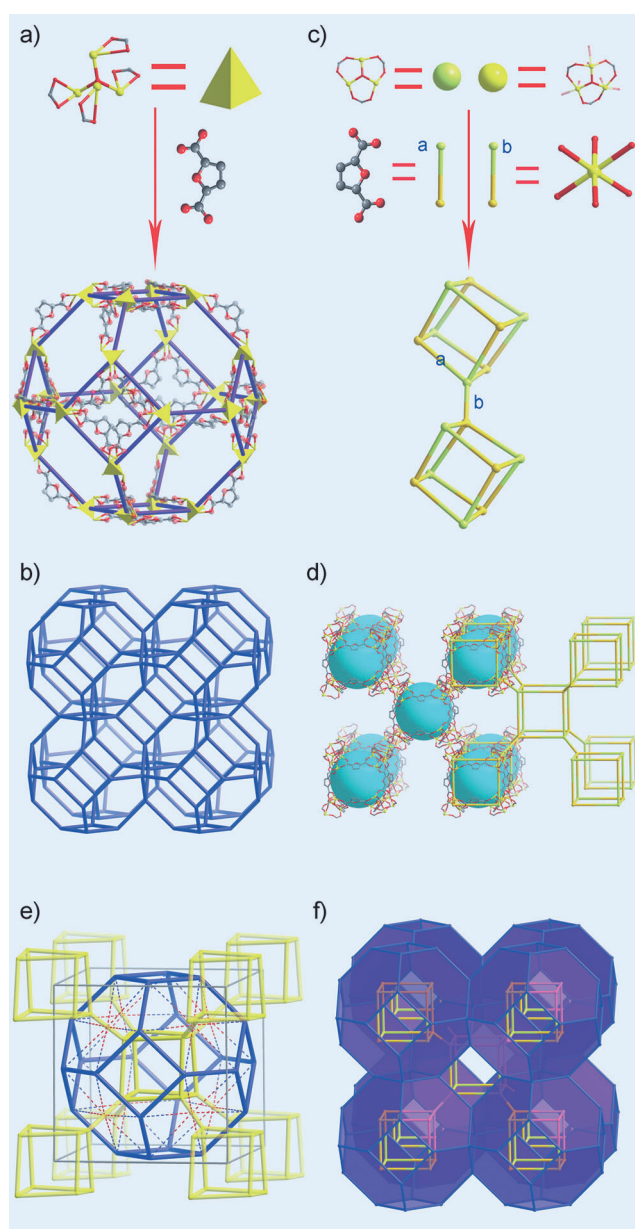California State University
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Figure 1. a) 24 Zn_4O tetramers are connected by FDAs to form a sodalite cage, b) 3D sodalite-type framework, c) Four trimers **1** (green) and four trimers **2** (yellow) are joined into a cube by FDA ligands (shown as type **a** linkage). Two adjacent cubes are linked through one Zn^{2+} monomer (shown as type **b** linkage), d) 3D ACO-type framework (Zn: yellow, O: red, C: grey), e) Nested $Zn_{24}@Zn_{104}$ cages joined together by monomeric Zn^{2+} sites (shown as dashed lines) at the center of the hexagonal windows of the sodalite cage, f) 3D nested cage-in-cage and framework-in-framework structure of CPM-7.

one COO group of FDA chelates to one Zn site in the Zn_4O tetrahedron (Figure 1a). This bonding pattern is common in indium MOFs,[1e, 9c] but it is quite unusual for Zn^{2+}. In the second set, there are four bidentate bridging COO–Zn_2 links in which one COO group of FDA bridges two Zn sites on the edge of the Zn_4O tetrahedron (as in MOF-5). These two sets of ligands play very different roles in the framework construction. Through four chelating COO–Zn links, each

Zn_4O tetramer is joined to four other Zn_4O tetramers to form a sodalite framework (Figure 1b). On the other hand, each bridging COO–Zn_2 link uses the other end of FDA to also bridge two Zn sites that come from one Zn monomer and one Zn trimer, respectively (see Figure S2a).

There are in fact two crystallographically different trimers: water-free $[Zn_3(OH)(O_2CR)_3]^{2+}$ (trimer **1**) and water-containing $[Zn_3(OH)(O_2CR)_3(H_2O)_6]^{2+}$ (trimer **2**). In trimer **1**, each Zn is four-coordinated, while in trimer **2**, each Zn is six-coordinated because of the presence of two terminal water molecules (Figure 1c and S2b). Topologically, however, trimer **1** and trimer **2** are equivalent, because the presence of water molecules does not affect the intercluster connectivity in any way.

Each trimer **1** is connected to six bridging FDA ligands. Three of these FDA ligands connect to three separate trimers **2**, thus leading to a cube (in a cube, each corner is always connected to three other corners) with four trimers **1** and four trimers **2** as corners of the cube (Figure 1c). The other three FDA ligands bridge between trimer **1** and the Zn monomer. Similarly, each trimer **2** is also connected to the Zn^{2+} monomer by three bridging FDA ligands, thus leading to the six-coordinated monomeric Zn^{2+} site.

While each monomeric Zn^{2+} site is six-coordinated, it is topologically eight-connected. This is because six FDA ligands around the monomeric Zn^{2+} site contribute a total of twelve oxygen sites (at the other end of FDA ligands) around the Zn monomer. Six of these connect to the Zn_4O tetramers, while the other six oxygen sites work in two groups and connect directly to the Zn sites in trimer **1** and trimer **2**, respectively. As a result, the eight-connected Zn monomer has two roles. It uses two connections to join the cubes into the zeolitic ACO topology (in the ACO topology, primitive cubes are packed into a body-centered cubic pattern; Figure 1d). And it uses the remaining six connections to join to the six nodes of the hexagonal rings of the sodalite cage (Figure 1e).

The aforementioned unusual coexistence of various inorganic building blocks and unusual bonding patterns between them lead to the unprecedented nested $Zn_{24}@Zn_{104}$ cage-in-cage architecture in which a larger sodalite cage encapsulates a smaller cubic cage. In this case, the larger Archimedean cage (sodalite) with an overall negative charge is formed by Zn_4O tetramers, while the smaller neutral Platonic cage (cube) is formed by $Zn_3(OH)$ trimers. Each cube in the ACO network is connected to adjacent cubes through hexagonal windows of sodalite. The monomer is at the center of the window and is bonded to six vertices of the hexagon (Figure 1f).

Thermogravimetric analysis of CPM-7 shows that the removal of solvents occurs in the temperature range of 100–140°C (Figure S5 in the Supporting Information). Powder X-ray diffraction further confirms that CPM-7 retains its crystallinity up to approximately 240°C (Figure S6 in the Supporting Information). The as-synthesized sample was activated by immersing crystals in methanol for three days. The sample was then degassed at 160°C for 24 hours prior to gas adsorption/desorption measurements (Figure 2). The CO_2 uptake reached 28.6 $cm^3 g^{-1}$ at 760 Torr and 273 K. In
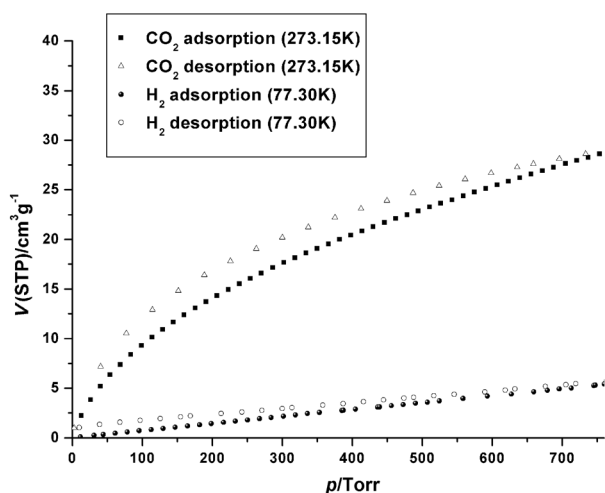
Figure 2. CO_2 and H_2 adsorption and desorption isotherms of CPM-7. STP = standard temperature and pressure.

comparison, H_2 adsorption only gave an uptake of 5.4 $cm^3 g^{-1}$ at 760 Torr and 77 K. We observed that for many MOFs, the H_2 uptake in $cm^3 g^{-1}$ at 760 Torr and 77 K is often significantly higher than (sometimes approximately twice) the CO_2 uptake (also in $cm^3 g^{-1}$) at 760 Torr and 273 K. For example, CPM-5 exhibits a CO_2 uptake capacity of 81.3 $cm^3 g^{-1}$ at 273 K and 760 Torr while for H_2 gas, CPM-5 can adsorb 139.2 $cm^3 g^{-1}$ of H_2 at 77 K and 760 Torr. Apparently, there is a significant difference between CPM-5 and CPM-7, in terms of the interactions between gas molecules and frameworks.

So far there are very few cage-within-cage structures. Our main interest in such a configuration is to accomplish efficient partition of pore space to optimize usage of pore space for gas sorption, based on the assumption that excessively large pore cavity has its own limitations, particularly for low-pressure gas sorption applications. There are, however, a number of parameters in the cage-in-cage configuration that strongly affect the gas sorption properties. In addition to variations in intercage connectivity, strategies for achieving different types of outside and inside cages are critically important for enhanced gas sorption.

In conclusion, we reported a cage-within-cage porous material that has highly unusual building blocks, such as eight-connected Zn_4O tetramer, and combines multiple different building blocks (tetramer, trimer, as well as monomer). Two types of polyhedral cages are formed (sodalite cage from tetramers and cubic cage from trimers), each of which forms a different zeolite-type topology (sodalite and ACO). This is the first example of two types of zeolite frameworks nested in the same material, and it also demonstrates a new mechanism for the formation of nested cage structure that is distinctly different from the previously reported mechanism based on polyfunctional ligands.[14–16] This new type of intercage linking mechanism through metal sites might be adapted for the synthesis of discrete coordination polyhedra as well, which may lead to the creation of sophisticated coordination assemblies, and perhaps a better understanding of self-assembly processes in both synthetic and natural systems.

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