Communication

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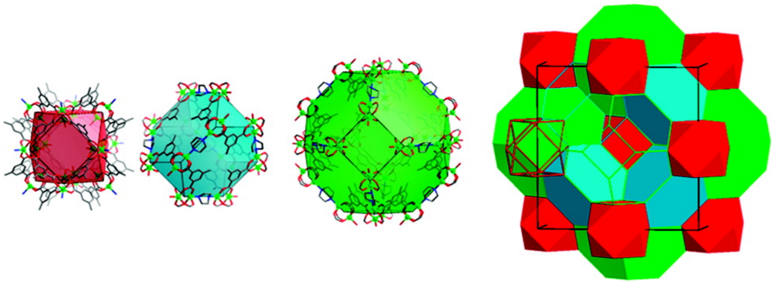

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Low-Level Self-Assembly of Open Framework Based on Three Different Polyhedra: Metal-Organic Analogue of Face-Centered Cubic Dodecaboride

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Coordination polymers or metal-organic frameworks (MOFs) with sustainable void structures enjoy the status as a new class of porous materials with high prospects for practical applications.[1] The network solids have inspired researchers due to the facile synthesis, high crystallinity, and predictable network topologies which collectively are keys for the design of functional materials.[2]

One of the topical issues in this area is a new type of MOFs with cage-like polyhedral building units.[3] Metal-organic polyhedral networks are different from typical MOFs having open-channel-type pores in that individual cages carrying large voids are interconnected through relatively small windows. These features could be potentially useful in the storage of small molecules because adsorbed guests may remain kinetically trapped inside the cages.

The rational synthesis of such polyhedron-based MOFs is challenging because information on the connectivity around secondary building units (SBUs) does not guarantee the successful prediction of the resulting polyhedra which in turn would form a three-dimensional (3D) net. In light of the new challenges, guidelines have been proposed by several groups. For example, Zaworotko recently reported covalently cross-linked "nanoballs" synthesized using extended organic ligands,[4] and Férey and co-workers used a combination of computational design and targeted synthesis to obtain highly porous MOFs with polyhedral building units.[5] Most of the other examples known in literature are based on synthetic ligands with a rigid and extended backbone.[6]

This communication shows that there may be an easier way to reach the same goal. The idea is based on the low-level self-assembly starting from metal ions and simple, unmodified ligands whose coordination modes are well-known. A polyhedron-based porous framework with a high symmetry and a unique topology is thus obtained and presented here.

The synthetic efforts have been guided by previous knowledge that dinuclear paddlewheels linked by isophthalate form various 2D nets with calixarene-like triangular or square motifs.[7] When additional linkages are added to such 4-connected nets by placing bridging ligands at the solvent sites of the paddlewheel SBUs, the resulting nets would have topologies somewhat different from typical MOFs with simple channel-type pores. Therefore, a mixture of Zn^{2+}, 5-methylisophthalic acid (H_2mip), and 1,4-diazabicyclo[2.2.2]octane (dabco) was allowed to react under solvothermal conditions in DMF.[8] The X-ray single-crystal analysis of the product revealed a non-interpenetrating 3D framework based on $Zn_2(O_2C)_4$ paddlewheel units.[9] The formula deduced from the X-ray structure is $[Zn_4(\text{mip})_4(\text{dabco})(OH_2)_2]$ (**1**).

In general, there are two solvent sites in a paddlewheel; however, only one of them is occupied by a bridging dabco ligand in the dinuclear SBU in **1**, and another site is coordinated by a water molecule (Figure 1a).

Therefore, the paddlewheels in **1** act as 5-connecting nodes with approximately a square pyramidal geometry (Figure 1a). The distances between the centers of paddlewheels separated by mip and dabco ligands are similar at 9.34 and 9.56 Å, respectively. This similarity and the bent angle imposed by mip result in the formation of triangles, squares, and hexagons in which the paddlewheels are located at each corner. The three kinds of polygons constitute the faces of three polyhedra, namely, cuboctahedron (CO), truncated tetrahedron (TT), and truncated octahedron (TO), as shown in Figure 1c. The three different semiregular polyhedra thus formed close pack sharing faces to result in the overall network structure of **1** (Figure 1b); CO and TT share a trigonal face, CO and TO a square, and TT and TO a hexagon. Therefore, the framework of **1** is best described as a space filling of CO, TT, and TO with a face-centered cubic symmetry. The underlying topology of **1** is a rare example of uninodal 5-connected nets[10] and has only been observed as the boron framework in UB_{12}[11] and other metal dodecaboride structures.[12]

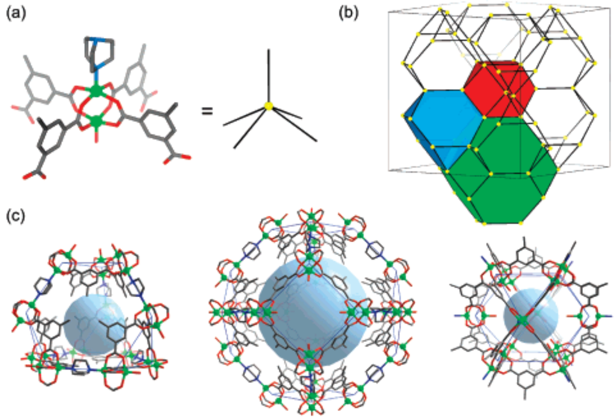

Figure 1. (a) The paddlewheel unit that acts as a 5-connecting node in **1** and its simplified model. (b) The 3D net of **1** stylized according to (a) reveals truncated tetrahedral (blue), truncated octahedral (green), and cuboctahedral cages (red). (c) Detailed views of the three polyhedra in (b) showing the voids. Blue spheres have diameters of 10, 18, and 9 Å from left to right, respectively.

Other than being a rare example with a unique topology which is unknown to date in MOFs, the structure of **1** possesses the following characteristics. First, the large voids inside the three polyhedra are interconnected through relatively narrow passages since the hexagonal window is effectively blocked by methyl groups of mip ligands. This feature prevents the interpenetration of the framework of **1** allowing a large pore volume. Second, the inner space of the CO cage is decorated by coordinated water molecules which may be replaced by other coordinating solvents or even removed to expose the open metal sites. Finally, the CO cages are connected to TT and TO only through dabco ligands. This implies that new MOFs based on interconnected CO cages of such may be synthesized using diamine ligands longer than dabco.

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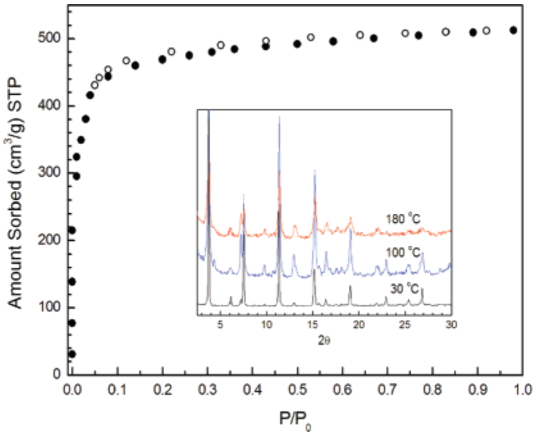

Figure 2. N_2 sorption isotherms of **1** measured at 78 K. Filled and open circles denote adsorption and desorption, respectively. Inset shows X-ray powder diffraction patterns of as-synthesized **1** at 30, 100, and 180 °C.

The porous net of **1** is estimated to have 66.7% of its crystal volume accessible by small guest molecules. The largest free passage measured after considering the van der Waals surface of the framework is 6.6 Å which corresponds to the free opening of the square window. The free opening of the trigonal window is much smaller at 3.7 Å. However, there exist large void spaces inside each polyhedron. For example, an imaginary sphere with the diameter as large as 18 Å can fit inside the TO cage without touching the van der Waals surface of the inner wall. Similarly, spheres with 10 and 9 Å diameters can fit inside the TT and CO cages, respectively (Figure 1c).

The polyhedron-based network **1** is considered permanently porous based on the results of variable-temperature X-ray powder diffractions and gas sorption measurements. The as-synthesized material maintains its powder diffraction patterns at 180 °C in the air (Figure 2).[13]

The N_2 sorption isotherms measured after guest exchange with $CHCl_3$ followed by evacuation under a dynamic vacuum reveals type I behavior typical for microporous materials and most MOFs.[14] The BET and Langmuir surface areas obtained from the adsorption branch of the isotherm are 1533 and 2178 m^2/g, respectively. The total pore volume is 0.793 cm^3/g. The high surface area and large pore volume are comparable to those of a series of pillared layer frameworks [$Zn_2(xbdc)_2(dabco)$], where xbdc is terephthalate or its derivative.[15] Therefore, it would be interesting to compare these MOFs having similar chemical compositions in terms of their sorption behavior and storage capacities for various guests.

In conclusion, the synthesis and basic characterizations of a highly symmetric polyhedron-based MOF are shown. The framework is based on $Zn_2(O_2C)_4$ paddlewheels interconnected through dabco ligands and possesses a uninodal 5-connected net in which three types of space-filling Archimedean polyhedra share faces. The 3D net maintains its structural integrity even after a complete evacuation. Also, the title framework has rooms for derivatizations at the coordinating solvent and the auxiliary methyl group of mip ligand. The approach taken in this work does not require presynthesis of organic linkers or sophisticated computational aid but judicious choice of metal ions and ligands.

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Supporting Information Available: Experimental procedures, analytical data, figures, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) See Supporting Information.

(9) Crystal data for **1**: space group $Fm\bar{3}m$, $a = 39.938(6)$ Å, $V = 63705(15)$ Å^3, $Z = 24$, $T = 173$ K, $\rho_{calcd} = 0.702$ g/cm^3, μ(Mo K$_\alpha$) $= 0.93$ mm^{-1}, 2449 reflections observed [$I > 2\sigma(I)$]; $R_1 = 0.0892$ (observed), $wR_2 = 0.2195$ (all data).

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