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Interpenetrating Polyhedral MOF with a Primitive Cubic Network Based on Supermolecular Building Blocks Constructed of a Semirigid C_3-Symmetric Carboxylate Ligand

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By application of a newly developed C_3-symmetric tripodal carboxylate ligand, 1,1′,1″-(benzene-1,3,5-triyl)tripiperidine-4-carboxylic acid (H_3BTPCA) to assemble with zinc ion in the presence of pyridine, a novel 2-fold interpenetrating polyhedral metal−organic framework with a primitive cubic network based on supermolecular building blocks (SBBs) has been synthesized. The basic paddlewheel secondary building units (SBUs) are connected by deprotonated BTPCA ligands to generate an octahedron as the SBB, which is further connected through the six vertexes by sharing the paddlewheel SBUs to give rise to the 3D primitive cubic network.

In the past decades, the field of functional metal−organic frameworks (MOFs) has grown rapidly because of their interesting topologies and special applications such as in catalysis, gas storage, and nonlinear optical materials.[1−5] By careful selection of multifunctional organic carboxylate ligands, many porous MOFs containing polyhedra such as trigonal bipyramids, hexagonal bipyramids, truncated tetrahedra, truncated octahedra, truncated cuboctahedra, cuboctahedra, small rhombihexahedra, cubohemioctahedra, and octahedra have been synthesized and reported.[6−8] The polyhedra in these porous MOFs play important roles in their functionalities such as gas storage, etc. Most of the ligands in the reported polyhedra-containing MOFs mentioned above are limited to rigid tri- or tetratopic carboxylate ligands, such as 1,3,5-benzenetricarboxylic acid and its derivatives, but reports on polyhedral MOFs based on flexible carboxylate ligands are quite rare. Recently, Hong and co-workers reported a novel porous polyhedral MOF containing four types of interconnected polyhedral cages based on flexible

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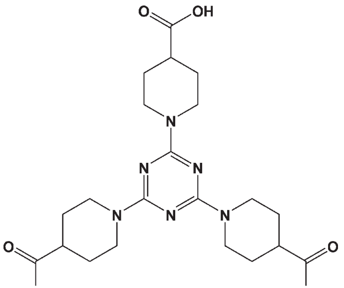
hexacarboxylate ligands.[9] However, there are no examples of polyhedral MOFs based on flexible C_3-symmetric carboxylate ligands.

Recently, an effective strategy for the construction of porous polyhedral MOFs, that is, the use of supermolecular building blocks (SBBs), has been defined and developed.[10] The metal cluster or the basic secondary building unit (SBU) was connected by the organic ligands to generate polyhedra as SBBs, which were further connected through the vertexes of the polyhedra to form high-dimensional frameworks. By application of these polyhedral SBBs, highly porous MOFs can be achieved.[11] Herein reported is an interpenetrating polyhedral MOF with a primitive cubic network based on SBBs.



H_3BTPCA

In our work, we selected the semirigid C_3-symmetric carboxylate ligand 1,1′,1″-(benzene-1,3,5-triyl)tripiperidine-4-carboxylic acid (H_3BTPCA) as the assembly ligand. Because of the flexibility of the three arms of the piperidine rings, this new tripodal ligand may possess two different conformations: cis,cis,cis and cis,cis,trans. In particular, the cis,cis,cis conformation will favor the formation of polyhedral SBBs. However, single-crystal X-ray diffraction (XRD) reveals that the free H_3BTPCA adopts the cis,cis,trans conformation (Figure 1, left) with the formula of $[H_4BTPCA]Cl\cdot 2H_2O$ (Supporting Information, Figure S1). The proton locates on one of the nitrogen atoms of the central triazine ring, and the chlorine ion locates close to one of the carboxyl oxygen atoms to form a O−H···Cl bond (2.963 Å). The two uncoordinated water molecules form strong hydrogen bonds with the carboxyl oxygen atoms (2.695 Å). The hydrogen-bonding interactions between the carboxyl oxygen atom and the protonated nitrogen atom of the central triazine ring connect H_3BTPCA to generate a 1D supramolecular chain (Supporting Information, Figure S2). It has been reported that the flexible ligand can change its conformation to meet the requirement of coordination geometries of metal ions or the 3D packing.[12] The cis,cis,cis conformation of H_3BTPCA may be generated when they coordinate to metal ions to form MOFs.

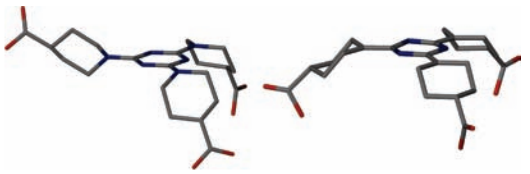


Figure 1. cis,cis,trans and cis,cis,cis conformations of the semirigid H_3BTPCA ligand in the free ligand (left) and **1** (right), respectively.

The solvothermal reaction of H_3BTPCA and $Zn(NO_3)_2\cdot 6H_2O$ in DMSO/H_2O (2:1, v/v) in the presence of pyridine gave rise to a large amount of colorless block crystals of **1**.[13] The formula of $Zn_3(BTPCA)_2(H_2O)_3\cdot py\cdot 3DMSO$ was further confirmed by elemental analysis and thermogravimetric analysis (TGA).

Single-crystal XRD[14] reveals that complex **1** is a 3D interpenetrating polyhedral MOF with the paddlewheel $Zn_2(COO)_4$ as the basic SBU. The central zinc ion is five-coordinated by four oxygen atoms from different BTPCA ligands and a one-coordinated water molecule in a square-pyramidal geometry. Four carboxylate groups from different BTPCA ligands connect two zinc ions to generate the paddlewheel SBU, in which the axial positions are occupied by coordinated water molecules. The BTPCA ligand adopts the cis,cis,cis conformation (Figure 1, right) to link three paddlewheel SBUs, and all of the piperidine rings of BTPCA adopt stable "chair" configurations. Thus, each SBU attaches to four BTPCA ligands, and every BTPCA binds three SBUs to form a T_d octahedron, in which four ligands cover the alternating triangular faces of the octahedron and the paddlewheel SBU occupies each vertex (Figure 2).

The octahedron can be considered as the SBB of the whole structure. The six paddlewheel SBUs locate at the six vertexes of the octahedron, similar to a six-coordinated octahedral metal ion, providing the possibility of extending into a high-dimensional polyhedral framework. The SBBs are connected to one another through the six vertexes by sharing the paddlewheel SBUs to generate a 3D porous polyhedral MOF (Figure 3). The dimensions of the resulting square channels are 9.1 × 9.1 Å (from atom to atom), and the distance from one octahedron to its adjacent one is 19.0 Å. If the SBB of the octahedron can be considered as a single node, the resulting topology of **1** would be a primitive cubic network (Figure 3).

The overall structure of **1** contains two identical interpenetrating nets. The second net is generated by a translation of the first by 16.472 Å in the [111] direction (Figure 4a). The translation allows the paddlewheel SBUs of the second net

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(13) Synthesis of **1**: H_3BTPCA (20 mg, 0.04 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (18 mg, 0.06 mmol) were dissolved in 4 mL of mixed solvents of DMSO and H_2O (2:1, v/v) in a beaker. After 3 drops of pyridine was added, the resulting colorless solution was sealed in a glass tube, heated to 120 °C at a rate of 16 °C/h, kept at 120 °C for 7 h, and then cooled to room temperature at a rate of 6 °C/h. The resulting colorless block crystals of **1** were collected by filtration, washed several times with DMSO, and dried in the air. (Yield: 55%.) Elem anal. Calcd for **1**: C, 42.94; H, 5.64; N, 12.28. Found: C, 43.32; H, 4.95; N, 11.94.

(14) Crystallographic data for **1**: $C_{14}H_{20}N_4O_5Zn$, $M = 389.71$, cubic, space group $I\bar{4}3m$, $a=b=c=19.0203(12)$ Å, $U=6881.0(8)$ Å^3, $Z=12$, $D_{calcd}=1.129$ g cm^{-3}, $\mu=1.094$ mm^{-1}, $F(000)=2424$, crystal size $= 0.10 \times 0.10 \times 0.10$ mm^3; 4640 reflections were measured with 944 unique reflections ($R_{int} = 0.0848$), of which 597 [$I > 2\sigma(I)$] were used for the structure solution. Final R1 (wR2) = 0.0842 (0.2406), 69 parameters.

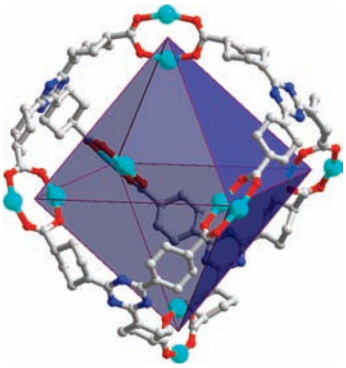

Figure 2. T_d octahedron: the six SBUs (only half of each paddlewheel is shown) occupy all of the vertexes, and the four BTPCA ligands cover every other face of an octahedron.

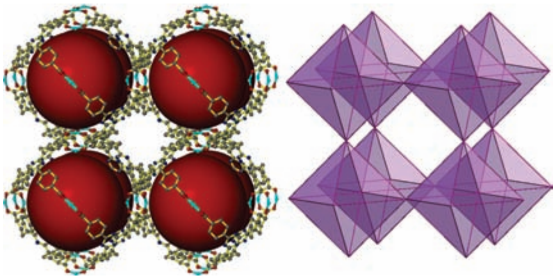

Figure 3. Left: the 3D framework of **1**. Right: the primitive cubic network after considering the octahedron as the octahedral node.

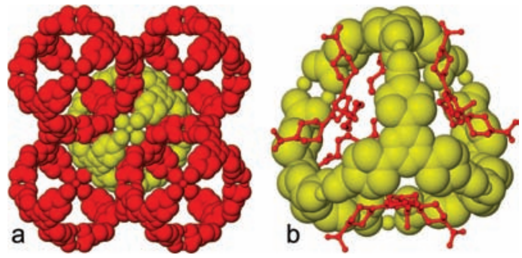

Figure 4. (a) Interpenetrating net showing that one octahedron in the first net was surrounded by four octahedra in the second net. (b) Four opening windows in the octahedron of the first net are blocked by four BTPCA ligands in the second net.

just located in the square channels of the first net to block the void. Despite the interpenetration of the two nets, **1** still possesses a large solvent-accessible volume (36.1% calculated from *PLATON*).[15] Although the voids inside the octahedron are large enough, there are no opening windows on the octahedron because of interpenetration (Figure 4b). Elemental analysis reveals that there are three additional uncoordinated dimethyl sulfoxide (DMSO) molecules and one pyridine molecule located inside the octahedron.

TGA shows that complex **1** can be stable up to 415 °C. There is no weight loss from 50 to 250 °C. The weight loss of 22.9% from 250 to 320 °C corresponds to the loss of three coordinated water molecules, one pyridine molecule, and three uncoordinated DMSO molecules (calcd: 24.2%). There is no weight loss from 320 to 415 °C, and after 415 °C, **1** starts to decompose. The loss of the coordinated water molecules and uncoordinated DMSO molecules at higher temperature may derive from the fact that the coordinated water molecules and uncoordinated DMSO molecules locate inside the cages without any openings.

Two MOFs with topologies similar to those of **1** exist in the literature: HKUST-1[16] and $[Cu_3(tpt)_4](ClO_4)_3$.[17] In HKUST-1, the rigid benzenetricarboxylate (BTC) ligand was used to link the paddlewheel SBUs to form a noninterwoven cuboctahedral network due to the rigidity and smaller size of BTC. However, in $[Cu_3(tpt)_4](ClO_4)_3$, the rigid 2,4,6-tri-4-pyridyl-1,3,5-triazine was used to connect tetrahedral zinc ions to generate the 3D interpenetrating framework because of the larger size of the ligand. These comparisons also indicate that the flexible and large organic ligands are apt to connect metal ions or clusters to form interpenetrating frameworks.

Complex **1** crystallizes in cubic space group $I\bar{4}3m$, belonging to a noncentrosymmetric structure, which prompts us to measure its second-harmoninc-generation (SHG) properties. SHG measurements on the powder samples reveal that complex **1** displays a SHG response in the powder state 0.6 times that of KDP (KH_2PO_4), which is weaker than other reported noncentrosymmetric MOFs.[18]

In conclusion, a novel 2-fold interpenetrating polyhedral MOF with a primitive cubic network based on the SBBs has been synthesized and characterized. The cis,cis,cis conformation of the semirigid C_3-symmetric BTPCA plays an important role in the formation of the polyhedral SBBs. To the best of our knowledge, complex **1** represents the first polyhedral MOF with a primitive cubic network constructed from a semirigid C_3-symmetric carboxylate ligand. Current research provides a new strategy to construct polyhedral MOFs by use of semirigid C_3-symmetric tripodal carboxylate ligands. Further studies will focus on the synthesis of noninterpenetrating porous polyhedral MOFs with this semirigid BTPCA ligand.

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Supporting Information Available: Experimental procedures and structural figures for H_3BTPCA and **1**, TGA, XRD, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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