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Metal–Organic Frameworks

A Mixed Molecular Building Block Strategy for the Design of Nested Polyhedron Metal–Organic Frameworks**

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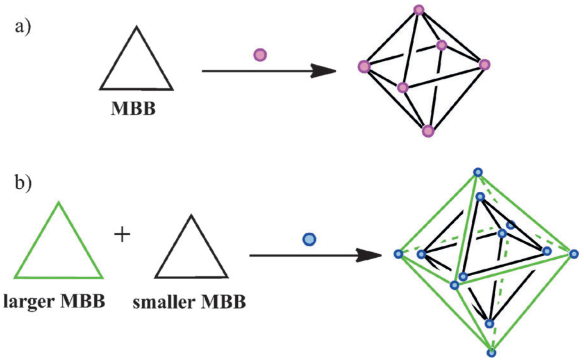
Abstract: *A mixed molecular building block (MBB) strategy for the synthesis of double-walled cage-based porous metal–organic frameworks (MOFs) is presented. By means of this method, two isostructural porous MOFs built from unprecedented double-walled metal–organic octahedron were obtained by introducing two size-matching C_3-symmetric molecular building blocks with different rigidities. With their unique framework structures, these MOFs provide, to the best of our knowledge, the first examples of double-walled octahedron-based MOFs.*

Metal–organic frameworks (MOFs) can be readily and conveniently synthesized from organic ligands and metal ions through a modular approach.[1] Microporous MOFs are of great interest because of their fascinating architectures and wide range of potential applications, especially in gas storage, chemical separation, drug delivery, catalysis, and chemosensing, among others.[2–6] Synthetic strategies of MOFs play a significant part in preparing new and distinctive materials. One of the most attractive targets in this field is to adjust and control the geometry and recognition properties of the pore. The use of metal–organic polyhedra (MOP)[7] as precursors has been shown to be an efficient strategy to build porous MOFs. The porosity of MOPs promises the porosity of the obtained MOFs, and the pore properties of the MOFs can be modulated by the selection and tuning of MOPs.[8]

The rational design of MOPs can be realized with edge-directed or face-directed self-assembly strategies,[9] in which the symmetry element and stoichiometry of the product could be predefined by the shape of the starting ligands applied. This is illustrated by the case of metal–organic octahedral cages, which are usually developed by face-directed connection of trigonal molecular building blocks (MBBs) at the corners (Scheme 1 a).[10–12] In MOFs constructed with trigonal MBBs, octahedral cages are universal supramolecular building blocks. For example, the classical HKUST-1 framework can be interpreted as the net of octahedra, in which four triangular benzene-1,3,5-tricarboxylate faces are connected by six paddle-wheel units at the corners.[10] Several discrete octahedral cages[11] of M_6L_4 or M_6L_8 composition, and the aggregation of octahedral cages[12] have thereby been generated. Furthermore, truncated octahedrons in sodalite-type MOFs have also been extensively investigated.[13] However, these reported metal–organic octahedra are invariably single-walled MOPs constructed with single trigonal organic ligands connected by single inorganic metal centers or clusters.



Scheme 1. The rational design of double-walled octahedra by means of two C_3-symmetric triangular MBBs.

For the practical application of MOP-based MOFs, especially in gas storage and separation, one of the problems that must be addressed is their stability. The practical applications of the high-surface-area porous MOFs have been severely restricted owing to their low thermal stabilities.[14] In the past decade, great efforts have been devoted to the design and synthesis of porous MOFs with high stability. Using double-walled MOPs instead of single-walled MOPs as supramolecular building blocks, may be one way to solve this problem, as the double walls of MOPs may contribute to the stabilization of the framework. A double-walled MOP containing outer and inner cages interconnected with covalent bonds could be classified as a cage-within-cage structure. Up to now, because of the difficulty in synthesizing such structures, only a few MOP-based MOFs with cage-within-cage motifs have been reported.[15] The assembly of these nested structures is based on intercage crosslinking by multifunctional organic ligands, which leads to the fact that the inside and outside cages usually have different shapes. According to this method, the symmetry and topology of the MOFs formed cannot be easily foreseen from the geometry of the organic building blocks.

Herein, we present a modified assembly strategy (the mixed MBB strategy; Scheme 1 b) for the synthesis of MOFs based on double-walled MOPs, in which two kinds of ligands

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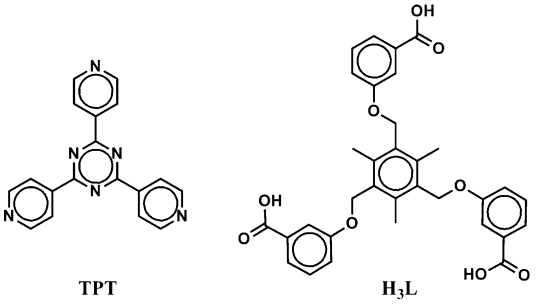

TPT

H_3L

Scheme 2. The structures of TPT and H_3L.

with the same shape are used (Scheme 2). The key point of this strategy is the size-matching between the molecular building blocks. The design and synthesis of two unprecedented double-walled octahedral cage-based MOFs, $[M_3L_2(TPT)_2{\cdot}x\,G]_n$ ($M = Ni$ for **1**, Co for **2**; TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine, H_3L = 2,4,6-tris[1-(3-carboxylphenoxy)ylmethyl]mesitylene, G = guest molecules), are presented as examples to illustrate this strategy. With similar trigonal configuration, TPT and L^{3-} could arrange in parallel to construct the double walls of an octahedron. The larger, flexible L^{3-} ligand is at the exterior of the octahedron, whereas the smaller, rigid TPT ligand serves as the inner scaffold to reinforce the octahedral cage and further stabilize the framework.

The $[Ni_3L_2(TPT)_2{\cdot}x\,G]_n$ (**1**) framework was obtained by solvothermal reaction of H_3L, TPT, and $Ni(NO_3)_2{\cdot}6\,H_2O$ in DMF/C_2H_5OH (DMF = *N*,*N*-dimethylformamide) at 85 °C for 72 h. When we used $Co(NO_3)_2{\cdot}6\,H_2O$ instead of $Ni(NO_3)_2{\cdot}6\,H_2O$ as the metal source, $[Co_3L_2(TPT)_2{\cdot}x\,G]_n$ (**2**), which is isostructural with **1**, was obtained. Single crystal X-ray analysis[16] reveals that **1** crystallizes in the cubic space group $P\bar{4}3m$ and exhibits a non-interpenetrated 3D structure. In **1**, each pair of adjacent Ni^{2+} ions (Ni···Ni: 3.356 Å) are bridged by the four carboxylate groups of the four L^{3-} ligands to form a paddle-wheel unit (Figure 1 a) with Ni–O distances in the range of 2.010–2.214 Å. In the paddle-wheel unit, the Ni^{2+} ion shows the distorted octahedral geometry completed by four carboxylic oxygen atoms from four L^{3-} ligands and two nitrogen atoms from two TPT ligands. Each L^{3-} ligand participates in the construction of three different paddle-wheel units (Figure 1 b). Moreover, the peripheral phenyl moieties are perpendicular to the central benzene ring, which makes the Ni_2 dinuclear cores arrange in an equilateral triangle mode, with an outer Ni···Ni distance of 17.957 Å and an inner Ni···Ni distance of 13.211 Å. The connection of six paddle-wheel units by four L^{3-} ligands induces an outer $Ni_{12}L_4$ octahedral cage (Figure 1 c), in which four of the eight faces are occupied by L^{3-} ligands, whereas the other four remain open. In addition, this type of octahedron can also be called tetrahemihexahedron, according to the faceted MOPs rule.[8a] For this octahedral chamber, the distances between diagonal Ni^{2+} ions are 18.683 and 25.395 Å for the inner and outer Ni^{2+} ions, respectively. On the other hand, four TPT ligands coordinate to the inner six Ni^{2+} ions and are parallel to the outer L^{3-} ligands with a center-to-center distance between the triazine ring of TPT and the central benzene ring of L^{3-} of 3.522 Å ($\pi\cdots\pi$ interactions). In this way, a "Russian-doll-type" double-walled octahedral cage (Figure 1 d; see also the Supporting Information, Figure S1) is constructed. It is worth noting that a hexa-coordinated Ni^{2+} ion in a paddle-wheel unit is quite unusual. A paddle-wheel unit constructed with carboxylates is well-known, and its rigid and well-defined geometry could strictly direct the assembly of building blocks and determine the topology of ordered networks.[17a] Normally, the metal ions in a typical paddle-wheel unit are penta-coordinated,[10,17] in which the axial position is occupied by only one atom. However, two atoms are observed in the

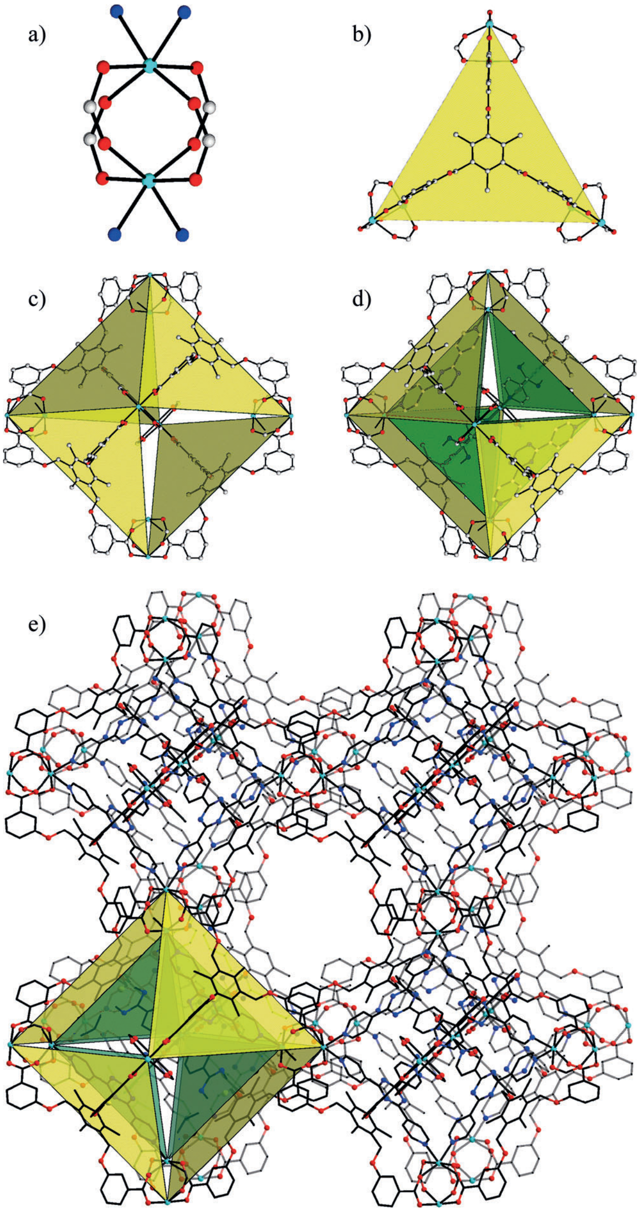

Figure 1. Portions of the crystal structure of **1**. a) The unique paddle-wheel unit. b) The triangular face defined by the L^{3-} linked to three $Ni_2(CO_2)_4$ units. c) The outer $Ni_{12}L_4$ octahedral cage. d) A double-walled octahedral cage. e) A cube of eight double-walled octahedral cages sharing $Ni_2(CO_2)_4$ paddle-wheel units. Ni turquoise, C black, N blue, O red. Solvent molecules and hydrogen atoms omitted for clarity.

paddle-wheel unit of **1**, which may be a key factor in the formation of the novel double-walled octahedral cage. Finally, by sharing the $Ni_2(CO_2)_4$ paddle-wheel units at the vertexes, the cages are packed to give a three dimensional framework (Figure 1e; see also Figure S2a).

From the viewpoint of topology, each TPT–L^{3-} wall can be represented as a planar 3-connected node, and each paddle-wheel unit can be regarded as a distorted tetragonally 4-connected node. Thereby, an infinite (3,4)-connected network, exhibiting boracite (*bor*) topology with Schläfli symbol $(6^3)_4(6^28^4)_3$, is produced, as shown in Figure S3a. This topology is different from *tbo* net of HKUST-1[10] and porph@MOM-4 framework (Figures S3 and S4).[18] Aside from the octahedral chamber of the $Ni_6(TPT)_4@Ni_{12}L_4$ cage, the large accessible voids of the total lattice volume delineate another distinct truncated cube of $Ni_{24}(TPT)_{28}L_{28}$ (Figure S2b), which is built from the packing of eight $Ni_6(TPT)_4@Ni_{12}L_4$ cages. Thus, the network of **1** contains two distinct molecular cage environments (Figure S2): smaller double-walled octahedral cages (internal diameter of ca. 12 Å; Figure S5a) and larger truncated cubic cages (internal diameter of ca. 18 Å; Figure S5b). Channels with dimensions of 11 × 11 $Å^2$ (without taking van der Waals radii into consideration) run along the *a*, *b*, and *c* directions (Figure S6). The solvent-accessible volume of **1** is estimated to be 67.6% per unit cell by PLATON.[19]

In **1**, both L^{3-} and TPT ligands are C_3-symmetric, and form the faces of an octahedral cage. C_3-symmetric ligands have been shown to be superior precursors for constructing octahedral and tetrahedral cages.[20] With regard to the flexible L^{3-} ligand, the central benzene ring and peripheral flexible phenyl carboxyl groups are linked by -CH_2-O- groups, the distortion of which through the rotation of single bond can make this ligand form a flat tripodal configuration. Moreover, the *meta* position of the carboxyl groups of L^{3-} ligand makes the two L^{3-} ligands linked by $Ni_2(CO_2)_4$ units non-coplanar (the dihedral angle between the two central benzene rings of two L^{3-} ligands is 70.53° in the cage formed), which is adapted to form a closed polyhedral structure. Compared with L^{3-}, the slightly smaller TPT ligand (Figure S7) ensures that it can be encapsulated to coordinate with the inner Ni^{2+} ions, resulting in the smaller inner cage. In summary, the equilateral triangular shape and size-matching of ligands, as well as the flexibility of the larger ligand, promise the construction of double-walled cage. This mixed MBB strategy could be considered as a revised version of the face-directed self-assembly method, in which double-layer walls, instead of single-layer wall, are connected by metal clusters.

To the best of our knowledge, to date all of the reported metal–organic octahedrons have invariably been single-walled;[10–12] moreover, in most MOFs with cage-within-cage structures, the cages are connected by multifunctional organic ligands and have different shapes.[15] $[Ni_3L_2(TPT)_2{\cdot}x\,G]_n$ (**1**) is the first example of a double-walled octahedron-based MOF, and is also the first example of cage-within-cage based MOF, in which the outer and inner cages have the same shape.

It has been reported that some double-walled MOFs that contain a large pore space show good stability during the desolvation process before gas sorption.[21] We expected that the double-walled **1** and **2** could exhibit better stability and have potential applications in gas sorption. To confirm the stability of **1** and **2**, thermogravimetric analyses (TGAs) were performed. The results reveal that almost all of the guest molecules in the pores were removed below 150 °C, and no further weight loss was observed until 300 °C (Figure S8). Variable-temperature powder X-ray diffraction (PXRD) shows that the samples retain their crystallinity up to about 220 °C and 100 °C for **1** and **2**, respectively (Figures S9 and S10). These results indicate that **1** is stable upon removal of encapsulated solvent molecules. Furthermore, DFT calculations (see the Supporting Information) were carried out to compare the stability of **1** and **2**, the results show complex **1** is more stable than complex **2**, which is consistent with experimental observations. In order to address the porosities of **1** and **2**, gas sorption measurements were conducted. The N_2 adsorption isotherm of activated **1** was measured at 77 K (Figure 2). The Brunauer–Emmett–Teller (BET) surface area of **1** is about 1206 m^2g^{-1} and the Langmuir surface area is about 1600 m^2g^{-1}. The fit of the adsorption data using the Horvath–Kawazoe method demonstrates the pore width distribution from about 0.6–1.5 nm (Figure S11). Additionally, **1** shows average CO_2 adsorption capacity of about 9.7 wt% (49.40 cm^3g^{-1}) at 273 K and 1 atm, 5.43 wt% (27.69 cm^3g^{-1}) at 298 K and 1 atm (Figure S12), respectively. **1** can also adsorb a considerable amount of H_2 (107.8 cm^3g^{-1}, 0.96 wt%, at 77 K and 1 atm). CH_4 adsorption at high pressure was also measured (Figure S13), the result shows that CH_4 uptake at 52 bar and 298 K is 9.28% for **1**. As seen from Figure S14, the PXRD patterns of **1** (as-synthesized, activated with supercritical drying, and after gas adsorption) are in good agreement with each other, indicating the stability of the framework of desolvated samples. The adsorption properties of **2** are similar to those of **1** and are given in the Supporting Information.

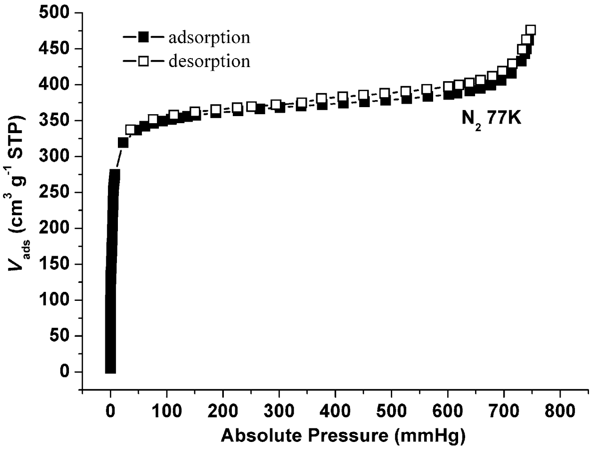

Figure 2. N_2 sorption isotherms for **1** at 77 K.

In conclusion, complexes **1** and **2** exemplify a mixed MBB strategy for the synthesis of MOFs with a cage-within-cage structure. The key element of this strategy is the selection of MBBs with complementary symmetry, shape, size, and flexibility. Complexes **1** and **2** obtained with this strategy have outer and inner cages with the same shape, and the cages are interlinked by unique metal clusters. Though these complexes only show moderate surface area and stability, the formation of a double-walled structure and the incorporation of a rigid inner cage still show the potential of the mixed MBB strategy for improving the stability of MOFs. Further investigations with this strategy for the construction of stable MOFs with cage-within-cage structures are underway in our lab.

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[16] Crystal and refinement information: **1**: cubic, $P\bar{4}3m$, $a = 22.039(2)$, $b = 22.039(2)$, $c = 22.039(2)$ Å, $V = 10704(2)$ Å^3, $T = 113$ K, $Z = 2$, $R_1 = 0.0558$, $wR_2 = 0.1287$, GOF = 0.948; **2**: cubic, $P\bar{4}3m$, $a = 22.249(3)$, $b = 22.249(3)$, $c = 22.249(3)$ Å, $V = 11014(2)$ Å^3, $T = 133$ K, $Z = 2$, $R_1 = 0.0470$, $wR_2 = 0.1342$, GOF = 1.009. CCDC 937831 (**1**) and 917265 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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