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Unusual preservation of polyhedral molecular building units in a metal–organic framework with evident desymmetrization in ligand design†

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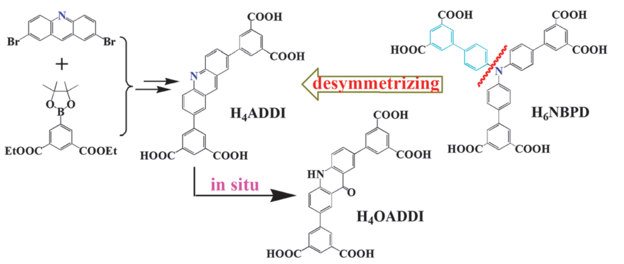
A new porous metal–organic framework (MOF) with three types of preserved polyhedral molecular building units, all of which have been observed in a series of isostructural MOFs constructed from highly symmetrical hexacarboxylic ligands, was formed even from a pre-designed related tetracarboxylic ligand with drastically reduced symmetry.

Metal–organic frameworks (MOFs) have attracted lots of interest because of their diverse compositions and framework aesthetic appeal, as well as their unique properties and various potential applications.[1] The architectural design of MOFs is mainly dependent on the assembly of metal centers and organic ligands.[2] Of particular importance are the design and use of organic ligands, which add flexibility and diversity to the chemical structures and functions of these materials.[3–6] Most of the carboxylate ligands used in MOF construction have been designed with a high symmetry for both aesthetic reasons and practical convenience in predicting the crystalline MOF structures. In comparison, ligands with lowered symmetry are rarely explored largely due to the uncertainty in MOF structure prediction. However, this could be considered as an advantage instead of a disadvantage because novel structures might be generated from desymmetrized ligands.

Recently, a new strategy called linker-directed vertex desymmetrization was proposed by Matzger and co-workers to construct MOFs by using reduced symmetry ligands, which were achieved through removing or adding chemical entities from/into high symmetry ligands.[7] The resulting MOFs presented diverse structures distinct from those constructed from the corresponding high symmetry ligands. To the best of our knowledge, a MOF with preserved original polyhedral molecular building units but assembled from desymmetrized ligands has not been reported to date. Here we wish to report such a case which demonstrates the complicated aspect of the desymmetrization in ligand design.

In our and other previous studies, a series of (3,24)-connected isoreticular MOFs (including PCN-61, -66, -68, -69, NOTT-113, -114, -115, PMOF-2, NU-100, *etc.*) with three types of metal–organic polyhedra (MOP) acting as building units were constructed from similar dendritic hexacarboxylate ligands and paddle-wheel Cu_2 nodes.[8] These MOFs exhibited not only graceful architecture but also excellent gas adsorption properties. To construct this series of MOFs, it was found that the hexacarboxylate ligands should have a C_3 symmetry and the three isophthalate moieties must be coplanar. In this work, we explored the construction of MOFs from a novel desymmetrized ligand 5,5′-(9-oxo-9,10-dihydroacridine-2,7-diyl)-diisophthalic acid (H_4OADDI), which was derived from the reported hexacarboxylate ligand 4′,4″,4‴-nitrilotribiphenyl-3,5-dicarboxylic acid (H_6NBPD)[8f] (Scheme 1). We employed a shearing strategy to desymmetrize H_6NBPD into 5,5′-(acridine-2,7-diyl)diisophthalic acid (H_4ADDI), which got oxidized *in situ* during the synthesis of a new MOF $[Cu_6(OADDI)_3(S)_6]\cdot n$S (**1**·*n*S, S represents non-assignable solvent molecules). Interestingly, **1**·*n*S preserved three types of MOP building units similar to those observed in NOTT-115,[8f] the corresponding MOF constructed from the high symmetry ligand H_6NBPD.

1·*n*S was solvothermally synthesized by the reaction of $Cu(NO)_2\cdot 2.5H_2O$ with H_4ADDI.‡ Its crystal structure was determined



Scheme 1 The design and *in situ* generation of the desymmetrized H_4OADDI ligand.

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by single-crystal X-ray diffraction. The phase purity of the product was confirmed by powder X-ray diffraction (PXRD), where the experimental pattern matches well with the simulated one (Fig. S3, ESI†). Thermogravimetric analysis (TGA) of the as-synthesized **1**·*n*S indicated a weight loss of 50% before about 250 °C, above which the compound starts to decompose (Fig. S5, ESI†).

As reported previously,[8] all (3,24)-connected MOFs crystallized in a highly symmetric cubic space group of $Fm\bar{3}m$ as represented by NOTT-115.[8f] The structure of these MOFs can be described as the packing of three types of polyhedra: cuboctahedra (C-Oh), truncated tetrahedra (T-Td), and truncated octahedra (T-Oh). In comparison, single-crystal X-ray diffraction analysis revealed that **1**·*n*S crystallized in the centrosymmetric tetragonal space group of $P4/mnc$. Similar to NOTT-115, **1** also possessed dimeric paddle-wheel $[Cu_2(COO)_4]$ nodes. All the carboxylate groups in $OADDI^{4-}$ took part in the coordination in the same mode. It is quite interesting that in **1** three kinds of polyhedra are formed (Fig. 1a): twelve Cu_2 nodes are connected together by twenty isophthalate moieties of different $OADDI^{4-}$ ligands to give a C-Oh polyhedron; twelve Cu_2 entities are connected together by ten $OADDI^{4-}$ ligands to form a T-Td polyhedron; and twenty-four Cu_2 entities are assembled together by sixteen $OADDI^{4-}$ ligands to form a T-Oh polyhedron. All these polyhedra are similar to those observed in NOTT-115, but distorted for T-Td and T-Oh ones because the carboxylate groups are not coplanar in $OADDI^{4-}$. Furthermore, as shown in Fig. 1b, the truncated triangular face (distorted hexagon) of the T-Td or the T-Oh polyhedron is constructed from three ligands with each linked to four shared Cu_2 nodes, even if fully occupied by only one. This is different from that in NOTT-115, where only one ligand links six Cu_2 nodes in each hexagonal face.[8f] The capability of forming these hexagonal faces in both MOFs should be key for the similar polyhedral structural features of **1** and NOTT-115. In the polyhedral packing of **1**, similar to that in NOTT-115, eight trigonal faces of each C-Oh polyhedron are shared by eight T-Td polyhedra, and the remaining six square faces are shared with six T-Oh polyhedra. Simultaneously, each T-Td polyhedron shares its four hexagonal faces with four T-Oh polyhedra and its four trigonal faces with four C-Oh polyhedra. Finally, these three types of polyhedra share their faces and extend to form a three-dimensional (3D) framework with pores (Fig. 1c). The pore volume ratio in **1** is about 70% without guest solvent molecules, as calculated using the PLATON program.

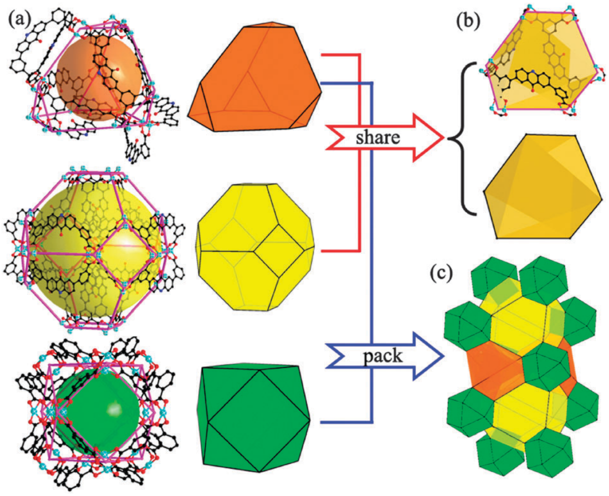

Fig. 1 The structural presentation of **1**: (a) the T-Td, T-Oh, and C-Oh polyhedra; (b) the hexagonal face shared by T-Td and T-Oh polyhedra; (c) the face-shared polyhedral packing.

Topologically, the framework of **1** can be simplified as a novel (3,4)-connected ternary net (*i.e.*, trinodal) when considering each Cu_2 entity as a planar 4-connected node and each tetracarboxylate $OADDI^{4-}$ ligand as two 3-connected nodes (Fig. S1, ESI†). For NOTT-115, each hexacarboxylate ligand is considered as four 3-connected nodes to give also a (3,4)-connected net, but being different from that of **1** (Fig. S2, ESI†).

The permanent porosity of **1** was demonstrated by N_2 gas adsorption at 77 K. Before the gas adsorption experiment, a freshly prepared sample was activated by supercritical carbon dioxide (SCD). The N_2 adsorption isotherm showed the characteristics of a microporous material (Fig. 2). The maximum N_2 uptake at 1 bar for **1** is 568 $cm^3\ g^{-1}$. The Brunauer–Emmett–Teller (BET) and Langmuir surface areas of **1** are evaluated to be 1475 and 1736 $m^2\ g^{-1}$, respectively. The pore size distribution evaluation (by PSD theory) demonstrated three kinds of pores in the material with the pore size of about 9.1, 11.8, and 14.8 Å, respectively, corresponding to the T-Td, T-Oh, and C-Oh polyhedral cages in the structure of **1** (Fig. 1).

Another interesting aspect of this work is the *in situ* oxidation of H_4ADDI to H_4OADDI during the formation of **1**. This has been confirmed by single-crystal X-ray diffraction of **1** and NMR analysis of the recovered ligand after acidic decomposition of **1** (Fig. S7, ESI†). This *in situ* reaction was also observed in the process of using a relevant dicarboxylic acid ligand to construct a MOP as discussed below.

Further removal of two carboxylate groups from H_4ADDI gave the ligand 3,3′-(acridine-2,7-diyl)dibenzoic acid (H_2ADDB, Fig. 3a), from which a new MOP, $[Cu_4(OADDB)_4(DMA)_4]\cdot nS$ (**2**·*n*S, OADDB = 3,3′-(9-oxo-9,10-dihydroacridine-2,7-diyl)dibenzoate), with the same Cu_2 nodes in **1** was constructed. **2**·*n*S was solvothermally synthesized by the reaction of $Cu(NO)_2\cdot 2.5H_2O$ with H_2ADDB.‡ Single-crystal X-ray diffraction revealed that **2**·*n*S crystallized in the triclinic space group $P\bar{1}$ and possesses a molecular cage structure (Fig. 3b). In the structure two Cu_2 entities are connected by four

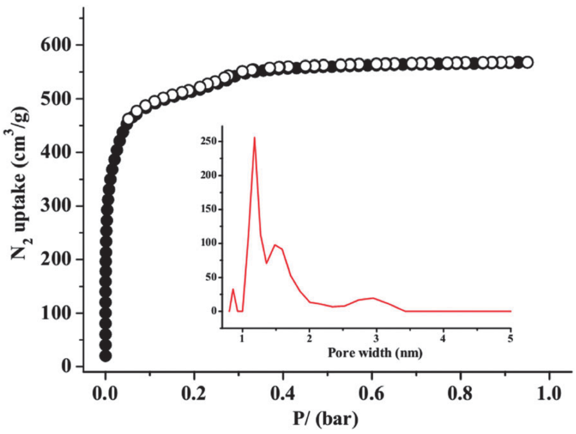

Fig. 2 N_2 adsorption and desorption isotherms at 77 K and pore size distribution (inset) of **1**.

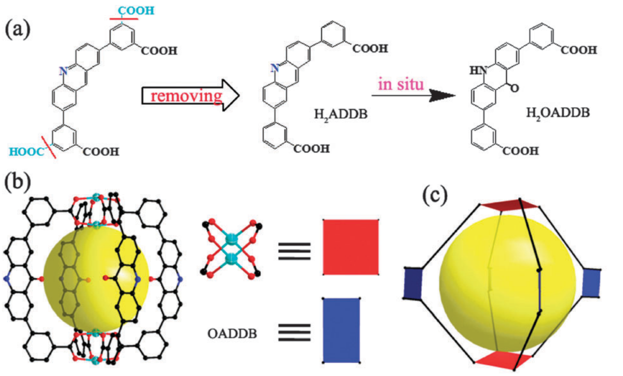

Fig. 3 (a) The design and *in situ* generation of H_2OADDB; (b) the structure of **2** (yellow sphere shows the internal cavity); (c) lantern shaped configuration of **2**.

$OADDB^{2-}$ ligands to form a big paddle-wheel with the distance between two Cu_2 nodes being about 5.2 Å. The overall molecular cage can also be considered to have a lantern shaped configuration as presented in Fig. 3c. The H_2ADDB ligand was *in situ* oxidized to H_2OADDB during the formation of **2**, similar to what happened during the synthesis of **1**. The oxidation of an acridine to an acridin-9(10*H*)-one compound is a well-documented organic transformation.[9]

Despite the similarity between H_4OADDI and H_2OADDB, the molecular cage of MOP **2** is not a structural unit of MOF **1**. It should be pointed out that based on a similar system of tetracarboxylate and dicarboxylate ligands we have recently successfully designed and constructed several MOPs and MOFs for targeted application including CO_2 capture.[3c] In that work the dicarboxylate ligand gave a molecular cage structurally similar to the one present in **2**, however, the molecular cage was directly incorporated as supramolecular building units into the corresponding MOFs synthesized from the related tetracarboxylate ligands. These results demonstrated that a slight modification of a ligand can lead to drastically distinct MOFs.

In summary, the ligand design based on desymmetrization through gradual removal of two and four carboxyl groups from a high symmetry hexacarboxylate ligand has led to two new ligands, from which a MOF and a MOP were constructed respectively. Unpredictably, the formed MOF has a polyhedron-based structure with three kinds of preserved polyhedral molecular cage building units as observed in the corresponding MOF (NOTT-115) constructed from the highly symmetrical hexacarboxylic ligand. The MOP has a lantern shaped structure, but it was not incorporated into the MOF like what was observed in a similar system reported by us. These results demonstrate both the power of the ligand desymmetrization strategy in generating novel MOFs and the challenge in the precise design and control of MOFs, in which even a slight perturbation of ligand structures may lead to drastically distinct MOFs.

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‡ Synthesis of **1**·*n*S. A solution of $Cu(NO)_2{\cdot}2.5H_2O$ (116 mg, 0.5 mmol) and H_4ADDI (101 mg, 0.2 mmol) in the mixed solvent of 8 mL of dimethyl sulfoxide (DMSO) and 1 mL of methanol was sealed in a 20 mL glass vial and heated at 100 °C for 6 days. Dark-green block crystals were collected, washed with DMSO and acetone, and then dried in air (yield 43%). The PXRD pattern of as-synthesized **1**·*n*S is shown in Fig. S3 (ESI†). For TGA and FT-IR, see Fig. S5 and S9 (ESI), respectively. Synthesis of **2**·*n*S. A mixture of $Cu(NO)_2{\cdot}2.5H_2O$ (46 mg, 0.2 mmol), H_2ADDB (83 mg, 0.2 mmol), and 3 drops of HBF_4 (48% aqueous solution) in 3 mL of *N*,*N*-dimethylacetamide (DMA) was sealed in a 20 mL glass vial and heated at 85 °C for 3 days. The resulting dark-yellow solution was allowed to stand at room temperature for 6 days to obtain dark-green block crystals, which were washed with DMA and then dried in air (yield 52%). The PXRD pattern of as-synthesized **2**·*n*S is shown in Fig. S4 (ESI). For TGA and FT-IR, see Fig. S6 and S10 (ESI), respectively.

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