

A designed metal–organic framework based on a metal–organic polyhedron†

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A C_3 symmetric ligand with three 1,3-benzenedicarboxylate units has been used to construct a metal–organic framework with a (3,24)-connected network topology, where the nanometre-sized metal–organic cuboctahedra (MOCs) have been incorporated solely into a cubic close packing (CCP) arrangement, which led to superoctahedral and supertetrahedral cavities.

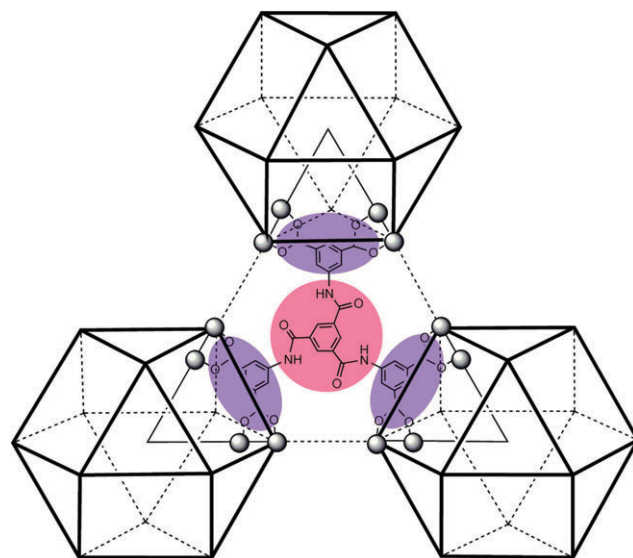
Great interest has developed in the synthesis of metal–organic frameworks (MOFs) because they offer opportunities for preparing materials with controllable functionalities.¹ Although remarkable progress has been made in this new field of chemistry and materials science, largely due to efficient design strategies,^{2,3} the preparation of MOFs with predictable structures is still a challenging problem.

Many metal–organic polyhedra^{4–6} and MOFs containing metal–organic polyhedra⁷ have been reported. Designed MOFs that are based on metal–organic polyhedra might provide very efficient ways for the construction of porous MOFs, because metal–organic polyhedra themselves have cavities, and the pore properties of the MOFs could be modulated at the level of the metal–organic polyhedra.^{7b} In most MOFs prepared that are based on metal–organic polyhedra, the metal–organic polyhedra were networked using additional linkers at the metal centers of the metal–organic polyhedra.

Recently, several discrete and networked metal–organic cuboctahedra (MOCs) as pseudo-spherical tectons have been achieved by linking transition metal ions with either nitrogen or carboxylate donor units.^{5,6} By linking the edges of three MOCs with large enough C_3 symmetric facial organic linkers (Scheme 1), a covalently networked MOF based on metal–organic polyhedra will come into being, and close packing arrangements of the MOCs will lead to additional octahedral and tetrahedral cavities besides the inherent inner cavities of the MOCs in the network. When the MOCs are used as a pseudo-spherical tecton for MOF construction, the networked packing arrangement of the MOCs will be restricted to a cubic close packing (CCP) arrangement, because 24 edges surrounding the center of a cuboctahedron are prepositioned for a CCP mode.

In this study we have used a C_3 symmetric facial ligand, 5,5',5''-[1,3,5-benzenetriyltris(carbonylimino)]tris-1,3-benzenedicarboxylic acid (H_6L) as a tritopic ligand. This contains three 1,3-benzenedicarboxylate (bdc) units, well known as a primary building unit for the construction of an edge-directed corner-linked MOC,⁶ and its planar C_3 symmetric tritopic character can force all of the resulting MOCs to the covalently linked triangular arrangement for a close packed structure.

Crystals of **1**, $[Zn_{24}(L)_8(H_2O)_{24}]_n$, were obtained *via* self-assembly of $Zn(NO_3)_2 \cdot 6H_2O$ and H_6L in dimethylacetamide (DMA). H_6L has a bdc moiety (purple region in Scheme 1), which can be coordinated to Zn^{2+} to form the paddle wheel secondary building unit, $Zn_2(COO)_4$, and is naturally bent, providing 120° angles for producing an edge-directed corner-linked MOC, where the bdc units are used for 24 edges and square paddle wheel units for 12 corners of the MOC (Fig. 1 and Fig. S1, ESI†). The interior cavity of the MOC can be accessed *via* triangular windows of ~ 4.1 Å in diameter or square windows of ~ 5.6 Å in diameter. The MOC, which acts as a 24-connected node, is linked by the tritopic node, 1,3,5-benzenetriyltris(carbonylimino) part of ligand L^{6-} (pink region in Scheme 1), to construct a 3-D network (Fig. S2, ESI†).



Scheme 1 A C_3 symmetric carboxylate ligand (L^{6-}) and three schematic cuboctahedra, $[Zn_{24}(bdc)_{24}]$; the bdc units (purple regions) of the ligand can be used to construct the cuboctahedra; 1,3,5-benzenetriyltris(carbonylimino) part (pink region) used as a tritopic linker; small gray balls indicate Zn^{2+} .

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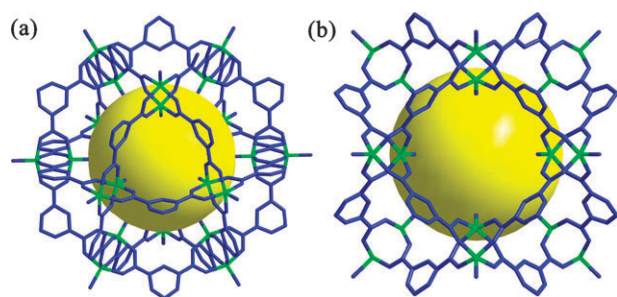


Fig. 1 MOC assembled from 24 bdc units and 24 Zn^{2+} ions, which has eight triangular windows (left) and six square windows (right). The yellow ball of 1.33 nm diameter represents the size of the cavity when the ligated water molecules are ignored.

In this network, each MOC is connected using 24 tritopic ligands, which results in 12 surrounding MOCs to the CCP arrangement, where all available tritopic positions in the CCP arrangement are occupied by the ligands (Fig. 2, Fig. S2, and Scheme S1, ESI†). Although the tritopic ligands on all 24 edges of the central MOC can result in up to 48 connectivities on the surrounding MOCs, each MOC in the CCP arrangement was interconnected to its 12 surrounding MOCs *via* quadruple covalent cross-linkages (Fig. 2 and Fig. S3a, ESI†). This linkage leads to the formation of a small square prismatic cage (Fig. S3b, ESI†). A similar linkage has been observed in the twofold interpenetrated simple cubic network of the MOCs $[\text{Cu}_{24}(\text{L}^2)_{12}(\text{H}_2\text{O})_{16}(\text{DMSO})_8]$, $\text{H}_4\text{L}^2 = 1,3\text{-bis}(5\text{-methoxy-1,3-benzenedicarboxylic acid})\text{benzene}$, where the ligand used contains two bdc units connected *via* a flexible linker.⁸

The CCP arrangement of the MOCs in net **1** led to superoctahedra and supertetrahedra, where the MOCs were used as vertices of the supercages and these vertices are connected *via* C_3 symmetric linkers as faces of octahedral and tetrahedral supercages, respectively (Fig. 3). Eight C_3 -symmetric facial

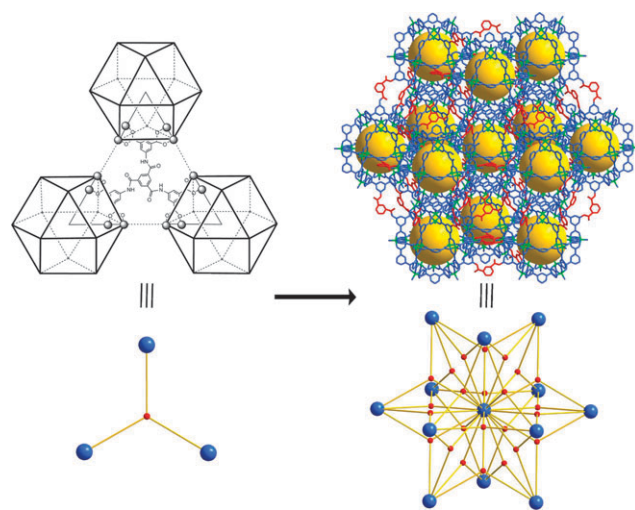


Fig. 2 Crystal structure of **1** composed of nano-sized MOCs covalently linked by C_3 symmetric organic moieties to construct a highly connected (3,24) network, in which the MOCs are cubic close packed. Two types of nodes are differentiated by colors: the red spheres refer to three-connected nodes and the blue spheres refer to 24-connected nodes.

ligands are connected at 12 octahedral edges using two paddle wheel units ($\text{Zn}_2(\text{COO})_4$) per edge to form a superoctahedron (Fig. 3a and c), the diameter of its inscribed sphere being ~ 1.88 nm, and the octahedral cavity volume is $\sim 4670 \text{ \AA}^3$. In a similar way four C_3 -symmetric facial ligands are engaged to form a supertetrahedron (Fig. 3b and d), and the diameter of the corresponding inscribed sphere is ~ 1.37 nm, the tetrahedral cavity volume being $\sim 1170 \text{ \AA}^3$. In net **1**, the three different types of cavities are interconnected through three different types of windows. While the MOC and the superoctahedral cavities are interconnected through square windows (Fig. S4, ESI†), the MOC and the supertetrahedral cavities are interconnected through narrow triangular windows (Fig. S5, ESI†). The two superoctahedral and two supertetrahedral cavities are also interconnected *via* the windows of the square prismatic junction-like cages formed at the common edge of the four supercages by using two paddle wheel units, where the window is partially blocked by the ligated solvent waters (Fig. S6, ESI†). The MOF prepared using a MOC leads to a high porosity network even in the close packing arrangement. The void volume of network **1** is 52481 \AA^3 per unit cell, which is $\sim 71\%$ of the total crystal volume (calculated by Platon).⁹

MOC is ideal for the construction of a highly-connected network because it can be used as a 6-connected, 8-connected, 12-connected, or 24-connected node based on different strategies for self-assembly (face-directed, edge-directed or vertex-directed). The (3,24)-connected MOF, $[\text{Zn}_{24}(\text{L})_8(\text{H}_2\text{O})_{24}]_n$, to the best of our knowledge, represents the highest connected topology presently known for frameworks (Fig. 2).¹⁰ The Schläfli symbol of the (3,24) net is: $(4^3)_{24}(4^{72}.6^{132}.8^{72})_3$.^{2b,11}

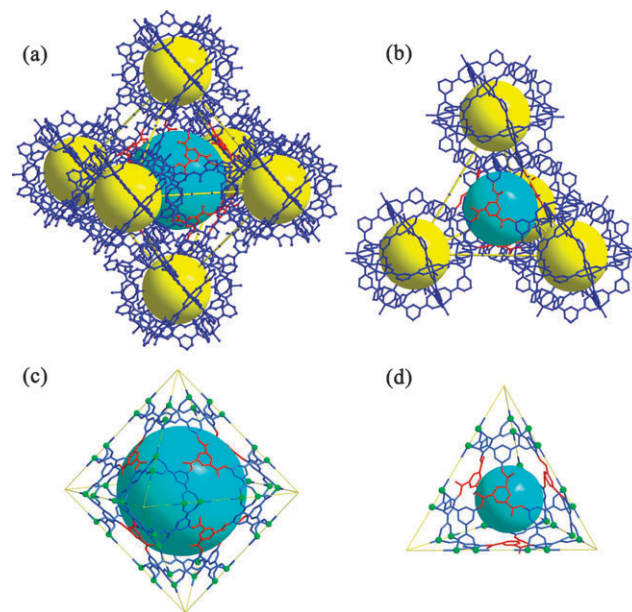


Fig. 3 Superoctahedral (a) and supertetrahedral (b) cavities formed using MOCs at the vertex of either the octahedral or the tetrahedral cavity are shown in cyan. The C_3 symmetric linker moieties of the ligands are shown in red and the MOCs are shown in blue with a yellow dummy ball in the center. (c) and (d): the face-directed edge-connected nature of the superoctahedral and supertetrahedral cages is presented.

Thermogravimetric analysis (TGA) of **1** (Fig. S7, ESI†) reveals a weight loss of ~48.3% in the region 25–300 °C in at least more than two steps. This weight loss corresponds to 84 water (observed 10.2%, calcd 10.4%) and 76 DMA molecules (observed 38.1%, calcd 38.0%).[‡] Decomposition of the framework is observed above 380 °C. The TGA of **1a** that has been prepared by treatment of **1**, repeatedly soaking and desolvating in methanol and vacuum drying at 110 °C overnight, shows only a small weight loss (~2.8%) up to 200 °C. The similarity of the powder X-ray diffraction (PXRD) pattern of **1** with the simulated PXRD pattern from the single crystal structure, as shown in Fig. S8 (ESI†), suggests its stability with solvent DMA in its cavity. However, substitution of the DMA by methanol and the subsequent removal of the methanol lead to the loss of its crystallinity. A typical Type II isotherm of **1a** for N₂ sorption indicates that the desolvated framework is a nonporous material (Fig. S9, ESI†).

In conclusion, we have prepared a predesigned MOF using a C₃ symmetric tritopic ligand, 5,5',5''-[1,3,5-benzenetriyltris(carbonylimino)]tris-1,3-benzenedicarboxylic acid, where the bdc units have been combined with Zn(II) ions to construct edge-directed corner-linked MOCs, and these polyhedra have been used to construct a MOF with (3,24)-connected network topology. In the network, the nanometre-sized MOCs have been constrained to a CCP arrangement *via* the covalent tritopic interlinkage using the 1,3,5-benzenetriyltris(carbonylimino) part of the ligand at all 24 edges of the cuboctahedron. The non-interpenetrating CCP arrangement of the MOCs led to superoctahedral and supertetrahedral cavities. Further investigation on the sorption behavior of **1** using polar organic vapors and various gaseous molecules is in progress.

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Notes and references

[‡] Even though the TGA of **1** suggests that the crystals contained two different types of solvent molecules, probably ~84 water molecules and ~76 DMA molecules as structural solvents in the cavity, the elemental analyses were not consistent with the TGA result, despite several attempts. The extent of the solvent molecules in the cavity might vary depending on the exposure time of the sample to air.

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