An unprecedented twofold interpenetrated layered metal–organic framework with a MoS$_2$-H topology

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Metal–organic frameworks (MOFs) provide the opportunity to achieve the structural variety and interesting topological features observed in inorganic compounds and minerals.$^1$ Net topologies of two-dimensional (2D) networks are relatively simple compared with those of three-dimensional (3D) networks.$^2$ MOFs with a 2D network with a regular net topology (hcb,$^3$ sq,$^4$ and hxf)$^8$, a quasi-regular net topology (kgm)$^9$ and its dual net topology, Kagomé dual (kgd)$^7$ are well-known examples of 2D edge-transitive net topologies.

Two different polymorphs of the MoS$_2$ structure are known to exist (Fig. S1†).$^6$ Both of these consist of 2D structures having the same 3,6-connected edge-transitive net, but with different net topologies. One MoS$_2$ polymorph in the rhombohedral crystal system (the MoS$_2$-R structure) is a network of the CdCl$_2$ structure with a 2D 3,6-connected edge-transitive kgd net topology,$^{10}$ where the coordination geometry of the Mo ion is a 6-connected octahedron and the sulfide ion is in a 3-connected trigonal center.$^{11}$ The other MoS$_2$ polymorph structure forms in the hexagonal crystal system (the MoS$_2$-H structure), and also has a network composed of the same 2D 3,6-connected edge-transitive net, but with a different net topology.$^{12}$ The coordination geometry of the Mo ion in the MoS$_2$-H structure is 6-connected trigonal prismatic. Although several MOFs with a 2D 3,6-connected kgd net topology have been reported,$^7$ an MOF with the net topology of the MoS$_2$-H structure is unprecedented. This is probably because of the rarity of trigonal prismatic 6-connected nodes with a $D_{3b}$ site symmetry (Fig. 1).

Here, we report on an unprecedented twofold interpenetrated layered MOF having the net topology of the MoS$_2$-H structure using a $C_3$-symmetric ligand, $3,3',3''$-[1,3,5-benzenetriyltris(carbonylimino)] trisbenzoic acid (H$_3$L), as the 3-connected node and a Zn$_4$O(COO)$_6$ cluster as the “topological” trigonal prismatic 6-connected node.$^4$

In an effort to construct metal–organic polyhedra or MOFs containing a 3-connected node, we have carried out reactions using $C_3$-symmetric ligands as the 3-connected node with a metal ion or a metal cluster as a potential 6-connected node.$^{10}$ Surprisingly, the solvothermal reaction of H$_3$L with a potential 3-connected ligand with Zn(NO$_3$)$_2$ resulted in an MOF, I, with an unprecedented 2D 3,6-connected MoS$_2$-H net topology rather than the 2D 3,6-connected kgd$^7$ and the 3D 3,6-connected pyr,$^{11}$ rtl$^{10a,12}$ and qom$^{11}$ net topology. The Zn$_4$O(COO)$_6$ SBU in I is an octahedral node of an $O_h$ “geometrical” site symmetry (local site symmetry), but the “topological” site symmetry of the SBU is a trigonal prismatic $D_{3h}$ symmetry. The 3-connected ligand with its three flexible meta-carboxyphenyl groups allows the 6-connected node of the $O_h$ geometrical site symmetry to be the node of the $D_{3h}$ topological site symmetry.

The solvothermal reaction of the ligand H$_3$L and Zn(NO$_3$)$_2$·6H$_2$O in a $N,N'$-dimethylacetamide (DMA)/acetoni trile mixed solvent at 120 °C led to the formation of I. Structural analysis of I with an $R3c$ space group revealed that the asymmetric unit contained two thirds of the $L^-$ units, two zinc atom sites, a $μ_4$-O$^-$ group, and one DMA molecule.

An unprecedented twofold interpenetrated layered metal–organic framework with a two-dimensional 3,6-connected net topology has been prepared using a tricarboxylic acid as a 3-connected node and a Zn$_4$O(COO)$_6$ cluster as a 6-connected node, where the ligand flexibility and the combination of π–π stacking and hydrogen bonding interactions render the 6-connected node into a topological trigonal prismatic node.

An unprecedented twofold interpenetrated layered metal–organic framework having the net topology of the MoS$_2$-H structure is a potential 6-connected node.$^{10}$ Surprisingly, the solvothermal reaction of H$_3$L with a potential 3-connected ligand with Zn(NO$_3$)$_2$ resulted in an MOF, I, with an unprecedented 2D 3,6-connected MoS$_2$-H net topology rather than the 2D 3,6-connected kgd$^7$ and the 3D 3,6-connected pyr,$^{11}$ rtl$^{10a,12}$ and qom$^{11}$ net topology. The Zn$_4$O(COO)$_6$ SBU in I is an octahedral node of an $O_h$ “geometrical” site symmetry (local site symmetry), but the “topological” site symmetry of the SBU is a trigonal prismatic $D_{3h}$ symmetry. The 3-connected ligand with its three flexible meta-carboxyphenyl groups allows the 6-connected node of the $O_h$ geometrical site symmetry to be the node of the $D_{3h}$ topological site symmetry.

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Fig. 1 Ball-and-stick drawings of two MoS$_2$ networks: (a) a network of the rhombohedral crystal system with a 2D 3,6-connected kgd net topology (the MoS$_2$-R structure), and (b) a network of the hexagonal crystal system with the 2D 3,6-connected net topology with a (44$^2$) point symbol (MoS$_2$-H structure).
In the network, the ligands are aligned along the crystallographic $C_3$-symmetry axes (Fig. 2a and S1†), and zinc atoms along with the carboxylate groups of the ligands form a well-known tetranuclear Zn cluster, [Zn₄O(COO)₆] as the 6-connected SBU (Fig. 2a). The geometrical site symmetry of the SBU is an octahedral $O_h$ symmetry, but the topological site symmetry is a trigonal prismatic $D_{3h}$ symmetry. In the network, three 6-connected SBUs are doubly connected via two $C_3$-symmetric ligands (Fig. 2b). The flexible amide linkage and the meta-positioned carboxylate group allow the two central phenyl groups of the doubly connected ligands to arrange in an eclipsed position, which leads to the topological site symmetry of the SBU having a trigonal prismatic $D_{3h}$ symmetry. When the Zn₄O(COO)₆ SBU is considered a 6-connected node and the ligand a 3-connected node, the MOF can be simplified as a network with a 2D 3,6-connected net topology with a $(4^3)_p(4^6)^2$ point symbol (Fig. 2c–f). This net topology is the same as that of the MoS₂–S structure.

In 1, a network composed of a 2D 3,6-connected net topology is interpenetrated by the other network with the same net topology via a twofold 2D–2D parallel interpenetration mode (Fig. 3).

The two interpenetrated networks are related to each other by a $D_3$ point symmetry to form an interpenetrated 2D layer. This 2D–2D parallel interpenetration of the two networks generates a $\pi–\pi$ stacking column composed of the four central phenyl rings of the ligands (Fig. 4). The two interplanar distances between the central phenyl groups are approx. 3.37 Å and approx. 3.45 Å. Another type of $\pi–\pi$ stacking interaction was observed between the carboxyphenyl groups of the doubly connected ligands of the two central ligands belonging to two different networks (Fig. S2†), where the carboxyphenyl interplanar distance was approx. 3.40 Å. The $\pi–\pi$ stacking interactions between the central phenyl groups of the four ligands in the twofold interpenetrated layer contribute to the stabilization of the eclipsed positioning of the central phenyl groups of the doubly connected ligands and the consequent unusual topological symmetry of the 6-connected SBU (the trigonal prismatic $D_{3h}$ symmetry).

The interactions between the twofold interpenetrated networks are further reinforced via internetwork hydrogen bonds (Fig. 4). The four ligands involved in the $\pi–\pi$ stacking interactions are also interconnected via six amide-to-amide N–H···O hydrogen bonds related by a $D_3$ point symmetry (Table S2†). The two networks in the interpenetrated 2D layer are tightly held together via a combination of $\pi–\pi$ stacking interactions and N–H···O hydrogen bonds.

The average thickness of the twofold interpenetrated layer is approx. 13.5 Å. The lattice DMA molecules are hydrogen bonded to the exposed amide groups at the layer surface (Fig. 5 and Fig. S3a and b and Table S2†). These DMA molecules are encapsulated in the pockets generated by the carboxyphenyl groups in the adjacent interpenetrated layer (Fig. 5 and Fig. S3c and d†). Within the pocket, a methyl group of the DMA molecule interacts with a carboxyphenyl group via a C–H···π interaction (closest C···C distance is 3.51(2) Å) (Fig. S4†). The solvent DMA molecules function as glue in holding the adjacent layers together via hydrogen bond interactions to one another.

**Fig. 2** Illustrations of 1. (a) The L⁻ ligand unit as a 3-connected node and the Zn₄O(COO)₆ SBU as a 6-connected node. (b) The 6-connected SBUs are doubly interconnected via $C_3$-symmetric 3-connected ligands to a binodal 3,6-connected 2D network. A single network is shown viewed along the crystallographic (c) $a$-axis and (d) $b$-axis. A schematic view of the 2D network with a net topology with a $(4^3)_p(4^6)^2$ point symbol is shown viewed along the approximate crystallographic (e) $c$-axis and (f) $b$-axis.

**Fig. 3** A layer of the 2D–2D parallel twofold interpenetrated networks in 1. The layer is represented along the top and side views using (a) and (b) a ball-and-stick model, respectively, (c) and (d) a space-filling model, respectively, and (e) and (f) a schematic representation, respectively. The two interpenetrated networks are denoted by red and blue.

**Fig. 4** Ball-and-stick diagrams showing $\pi–\pi$ stacking interactions and amide-to-amide hydrogen bonds between the interpenetrated networks in 1 viewed along the crystallographic (a) $b$-axis and (b) $c$-axis. The hydrogen bonds are denoted by green dotted lines.
layer and via C–H⋯π interactions to the other layer in a 3D packed layered structure. In the crystal structure of I, the interpenetrated 2D layers are packed in a staggered fashion. The MoS$_2$H structure is a non-interpenetrated layered structure, whereas I has a twofold interpenetrated layered structure. Further, there is a difference in the 3D packing of the layers. The layers in the MoS$_2$H structure are packed in a (ABC)$_h$ repeating order, whereas those in I are packed in a (A$_1$B$_1$C$_1$A$_2$B$_2$C$_2$)$_h$ repeating order (Fig. S5†).

**Conclusions**

A solvothermal synthesis of the C$_3$-symmetric tricarboxylic acid ligand, H$_2$L, and a zinc(II) ion in DMA led to a twofold interpenetrated 2D–2D parallel layered MOF with a 3,6-connected net topology, where the ligand serves as a 3-connected node and the tetranuclear zinc carboxylate cluster, Zn$_4$(O$_2$(COO)$_6$)$_h$, serves as a 6-connected SBU node. Although the geometrical site symmetry of the 6-connected SBU has an octahedral $O_h$ symmetry, the topological site symmetry of the SBU has a trigonal prismatic $D_{3h}$ symmetry. The trigonal prismatic 6-connected SBUs are doubly connected via $2\times3$ connected ligands, which leads to a network having the MoS$_2$H net topology, a 2D 3,6-connected edge-transitive net topology with a $(4)_2(4'6)_2$ point symbol. The flexible amide linkage between the central phenyl residue and the DMA molecules are shown in the ball-and-stick model (denoted by aqua and green) seen along (a) the top view and (b) the side view. The 2D–2D parallel interpenetration of the networks is limited to two dimensions and results in a layered MOF structure.

The formation of a 2D–2D parallel interpenetrated layered MOF structure with a rare 2D 3,6-connected edge-transitive MoS$_2$H net topology sets an example that MOFs with a simple, but unprecedented, net topology can be obtained when an appropriate metal ion and ligands with the desired geometrical characteristics are employed.

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**Notes and references**

† It is well known that the tetranuclear μ₃-oxo-zinc carboxylate cluster, Zn$_4$(O$_2$(COO)$_6$)$_h$, in MOF-5 and its isoreticular MOF structures are 6-connected SBUs that have an octahedral $O_h$ site symmetry. However, although the Zn$_4$(O$_2$(COO)$_6$)$_h$ secondary building unit (SBU) in I is the 6-connected node and the “geometrical” (or local) site symmetry of the SBU has the same $O_h$ symmetry, the site symmetry of the SBU in the topologically idealized 3,6-connected net (the “topological” site symmetry of the SBU) has a trigonal prismatic $D_{3h}$ symmetry.

‡ Crystal data for MOF I: [Zn$_4$(O$_2$(COO)$_6$)$_h$]: 6DMA (C$_{14}$H$_{12}$N$_{18}$O$_{44}$Zn$_8$), $f_{\text{w}}$ = 3335.59 g mol$^{-1}$, rhombohedral, space group $R3c$, $a = b = 17.837(5)$ Å, $c = 81.04(5)$ Å, $V = 22327(15)$ Å$^3$, Z = 6, μ(MoKα, λ = 0.71073 Å) = 1.354 g cm$^{-3}$, 34 661 reflections were collected, 4408 were unique ($R_{int} = 0.1134$), $R_f(wR_f) = 0.1257 (0.2593)$ for 3312 reflections ($I > 2σ(I)$).


