

An unprecedented twofold interpenetrated layered metal–organic framework with a MoS₂-H topology†

Lalit Rajput,^a Seunghye Hong,^b Xinfang Liu,^{ab} Minhak Oh,^a Dongwook Kim^a and Myoung Soo Lah^{*a}

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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 Zn₄O(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.

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 **sql**,⁴ and **hxl**⁵), a quasi-regular net topology (**kgm**)⁶ and its dual net topology, Kagomé dual (**kgd**)⁷ are well-known examples of 2D edge-transitive net topologies.

Two different polymorphs of the MoS₂ structure are known to exist (Fig. S1†).⁸ Both of these consist of 2D structures having the same 3,6-connected edge-transitive net, but with different net topologies. One MoS₂ polymorph structure in the rhombohedral crystal system (the MoS₂-R structure) is a network of the CdCl₂ structure with a 2D 3,6-connected edge-transitive **kgd** net topology,^{1c} where the coordination geometry of the Mo ion is a 6-connected octahedron and the sulfide ion is in a 3-connected trigonal center.^{8a,c} The other MoS₂ polymorph structure forms in the hexagonal crystal system (the MoS₂-H structure), and also has a network composed of the same 2D 3,6-connected edge-transitive net, but with a different net topology.^{8b,c} The coordination geometry of the Mo ion in the MoS₂-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 MoS₂-H structure is unprecedented. This is

probably because of the rarity of trigonal prismatic 6-connected nodes with a D_{3h} site symmetry (Fig. 1).

Here, we report on an unprecedented twofold interpenetrated layered MOF having the net topology of the MoS₂-H structure using a C_3 -symmetric ligand, 3,3',3''-[1,3,5-benzenetriyltris(carbonylimino)] trisbenzoic acid (H₃L), as the 3-connected node and a Zn₄O(COO)₆ cluster as the “topological” trigonal prismatic 6-connected node.‡

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 H₃L as a potential 3-connected ligand with Zn(NO₃)₂ resulted in an MOF, **1**, with an unprecedented 2D 3,6-connected MoS₂-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**¹³ net topology. The Zn₄O(COO)₆ SBU in **1** is an octahedral node of an O_h “geometrical” site symmetry (or 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 H₃L and Zn(NO₃)₂·6H₂O in a *N,N'*-dimethylacetamide (DMA)/acetonitrile mixed solvent at 120 °C led to the formation of **1**. Structural analysis of **1** with an $R\bar{3}c$ space group§ revealed that the asymmetric unit contained two one-thirds of the L³⁻ units, two zinc atom sites, a μ_4 -O²⁻ group, and one DMA molecule.

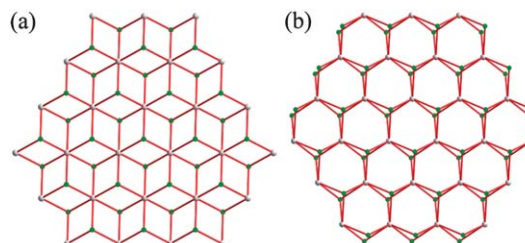


Fig. 1 Ball-and-stick drawings of two MoS₂ networks: (a) a network of the rhombohedral crystal system with a 2D 3,6-connected **kgd** net topology (the MoS₂-R structure), and (b) a network of the hexagonal crystal system with the 2D 3,6-connected net topology with a $(4^3)_2(4^3 6^{12})$ point symbol (MoS₂-H structure).

^aInterdisciplinary School of Green Energy, Ulsan National Institute of Science & Technology, Ulsan, 689-798, Korea. E-mail: mslah@unist.ac.kr; Fax: +82 52 217 2019; Tel: +82 52 217 2931

^bDepartment of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do, 426-791, Korea

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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, $[Zn_4O(COO)_6]$, 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 $Zn_4O(COO)_6$ 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 $(4^3)_2(4^36^{12})$ point symbol (Fig. 2c–f).¹⁴ This net topology is the same as that of the MoS_2 -H 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 π – π stacked 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 π – π stacking interaction was observed between the carboxyphenyl groups of the two central ligands belonging to two different networks (Fig. S2†), where the carboxyphenyl interplanar distance was approx. 3.40 Å. The π – π stacking interactions between the central phenyl groups of the four ligands in the twofold interpenetrated layer

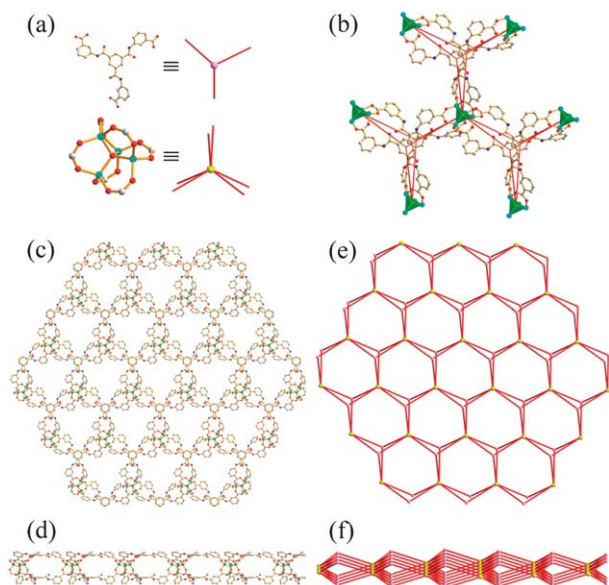


Fig. 2 Illustrations of **1**. (a) The L^3 - ligand unit as a 3-connected node and the $Zn_4O(COO)_6$ SBU as a 6-connected node. (b) The 6-connected SBUs are doubly interconnected *via* C_3 -symmetric 3-connected ligands to a binodal 3,6-connected 2D network. A single network is shown viewed along the crystallographic (c) c -axis and (d) b -axis. A schematic view of the 2D network with a net topology with a $(4^3)_2(4^36^{12})$ point symbol is shown viewed along the approximate crystallographic (e) c -axis and (f) b -axis.

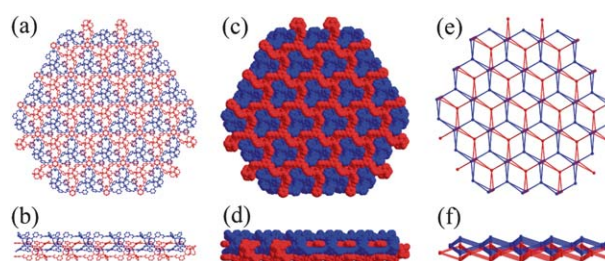


Fig. 3 A layer of the 2D–2D parallel twofold interpenetrated networks in **1**. The layer is represented along the top and side views using (a) and (b) a ball-and-stick model, respectively, (c) and (d) a space-filling model, respectively, and (e) and (f) a schematic representation, respectively. The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

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 π – π stacking interactions are also interconnected *via* six amide-to-amide $N-H\cdots O$ 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 $\pi\cdots\pi$ stacking interactions and $N-H\cdots O$ 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 $C-H\cdots\pi$ interaction (closest $C\cdots C$ 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

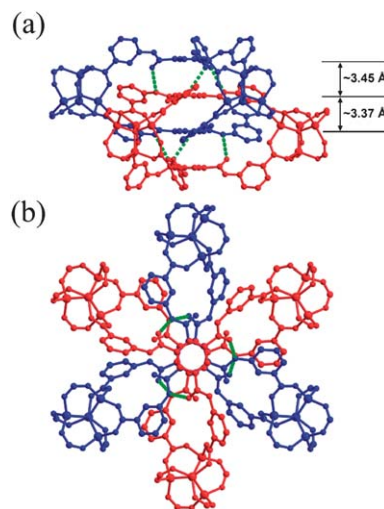


Fig. 4 Ball-and-stick diagrams showing π – π stacking interactions and amide-to-amide hydrogen bonds between the interpenetrated networks in **1** viewed along the crystallographic (a) b -axis and (b) c -axis. The hydrogen bonds are denoted by green dotted lines.

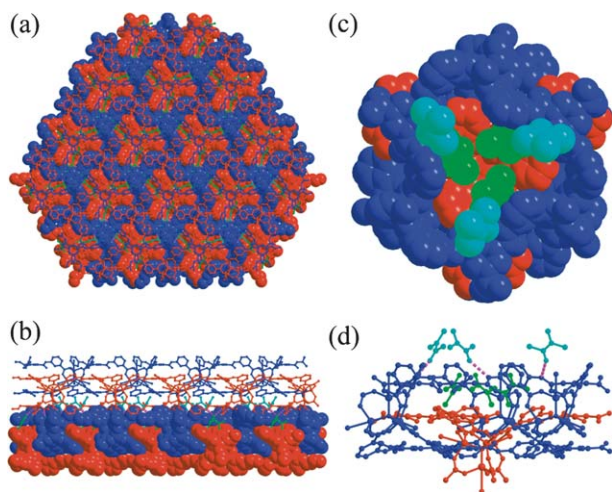


Fig. 5 Packing diagrams of the two adjacent 2D layers (one layer is shown as a ball-and-stick model and the other as a space-filling model, and the DMA molecules are shown in the ball-and-stick model (denoted by aqua and green) seen along (a) the top view and (b) the side view. The DMA molecules are hydrogen bonded (denoted by aqua) and involved in C–H $\cdots\pi$ interactions (denoted by green) in the pockets of the interpenetrated 2D layer seen along (c) the top view (using the space-filling model) and (d) the side view (using the ball-and-stick model).

layer and *via* C–H $\cdots\pi$ interactions to the other layer in a 3D packed layered structure. In the crystal structure of **1**, the interpenetrated 2D layers are packed in a staggered fashion. The MoS₂-H structure is a non-interpenetrated layered structure, whereas **1** has a twofold interpenetrated layered structure. Further, there is a difference in the 3D packing of the layers. The layers in the MoS₂-H structure are packed in a $-(ABC)_n-$ repeating order, whereas those in **1** are packed in a $-(A_1B_1C_1A_2B_2C_2)_n-$ repeating order (Fig. S5†).

Conclusions

A solvothermal synthesis of the C₃-symmetric tricarboxylic acid ligand, H₃L, 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, Zn₄O(COO)₆, 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* two 3-connected ligands, which leads to a network having the MoS₂-H net topology, a 2D 3,6-connected edge-transitive net topology with a (4³)₂(4³6¹²) point symbol. The flexible amide linkage between the central phenyl residue and the terminal carboxyphenyl group and the *meta*-positioning of the carboxylate group allow the two central phenyl groups of the doubly connected ligands to be in an eclipsed position. This renders the 6-connected Zn₄O(COO)₆ SBU towards the unusual trigonal prismatic D_{3h} topological site symmetry in the network. In the MOF, 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 MoS₂-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 μ^4 -oxo-zinc carboxylate cluster, Zn₄O(COO)₆, in MOF-5 and its isorecticular MOF structures⁹ are a 6-connected SBU that has an octahedral O_h site symmetry. However, although the Zn₄O(COO)₆ secondary building unit (SBU) in **1** is the same 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 **1**: [Zn₄OL₂]₂·6DMA (C₁₄₄H₁₂₆N₁₈O₄₄Zn₈), $f_w = 3335.59 \text{ g} \cdot \text{mol}^{-1}$, rhombohedral, space group R3c, $a = b = 17.837(5) \text{ \AA}$, $c = 81.03(5) \text{ \AA}$, $V = 22\,327(15) \text{ \AA}^3$, $Z = 6$, μ (MoK α , $\lambda = 0.71073 \text{ \AA}$) = 1.354 mm⁻¹, 34 661 reflections were collected, 4408 were unique ($R_{\text{int}} = 0.1134$). $R_1(wR_2) = 0.1257$ (0.2593) for 3312 reflections [$I > 2\sigma(I)$], $R_1(wR_2) = 0.1608$ (0.2772) for all reflections.

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