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Two-folded interpenetrated metal-organic framework constructed by zinc(II) and mixed ligands

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The new two-fold interpenetrated three-dimensional zinc metal-organic framework $\{[Zn_3(timp)_2(oba)_2(HCOO)_2]\cdot 3DMF\cdot 6H_2O\}_n$ has been synthesized by a solvothermal reaction, and its Brunauer–Emmett–Teller surface area (334 $m^2\,g^{-1}$) was calculated by nitrogen adsorption at 77 K.

Metal-organic framework (MOF) materials are of considerable current interest due to unique solid-state properties, profoundly influencing their structural architecture and potential applications.[1–6] Porous MOFs are highly crystalline 3D organic-inorganic hybrids constructed by assembling metal ions or small metal-containing clusters with multidentate organic ligands *via* coordination bonds.[7] Due to their modular assembly for a rational design of a desired pore size and structural porosity of the materials, porous MOFs have witnessed explosive development and rapid progress in the past decade.[8–10] They are amenable to design and their pores can be functionalized for applications *via* either postsynthetic modification[11] or ligand design.[12] The most interesting feature of porous MOFs lies in their exceptional surface areas, and the record for highest reported surface area has been broken repeatedly over the past years. These merits of porous MOFs not only make them stand out from other porous materials, but also push them to the forefront of energy research, which has been particularly driven by increasing world energy demand.

The prediction of mixed-ligand architectures is still challenging; thus, it is a good choice for the construction of new frameworks.[13] Here, we described a new twofold interpenetrated framework $\{[Zn_3(timp)_2(oba)_2(HCOO)_2]\cdot 3DMF\cdot 6H_2O\}_n$ **1** based on Zn^{II}, tripodal ligand timp, 1,3,5-tris(1-imidazolyl)benzene and a bent carboxylate co-ligand [H_2oba is 4,4′-oxybis(benzoate)]. The new coordination polymer was obtained under solvothermal conditions.[†] The crystal structure,[‡] topological analysis and absorption performance were studied in detail. Additionally, complex **1** exhibits the microporous sorption of N_2.

The crystal structure determination revealed that complex **1** crystallizes in the triclinic system $P\bar{1}$. The asymmetric unit of **1** contains three Zn^{2+} ions, two timp molecules, two oba^{2-} anions, two coordinated water molecules, two coordinated formate anions decomposed from the dimethylamine,[18] three lattice DMF and six water molecules squeezed by PLATON, as shown in Figure 1. The Zn(1) atom is tetrahedrally coordinated and bound by one carboxylate O atom, one formate anion, and two N atoms from timp ligands, while Zn(2) and Zn(3) cations are five-coordinated, and the τ trigonality factors are 0.098 and 0.329, respectively, indicating that they are in the distorted square pyramidal coordination geometry.[19] Zn(2) center is bridged by two O atoms from one carboxylate, one coordinated formate molecule, and two N atoms from two timp ligands. Zn(3) is bound by three O atoms from two carboxylate groups and two N atoms. The Zn–O and

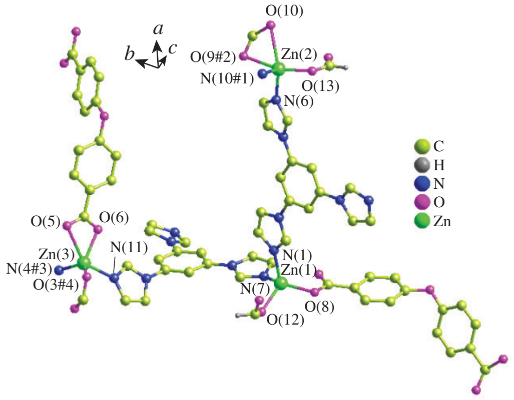

Figure 1 Coordination environments of complex **1**. Most hydrogen atoms and solvent molecules are omitted for clarity. Symmetry codes: #1 = *x*, *y*, 1 + *z*; #2 = 1 + *x*, 1 + *y*, *z*; #3 = *x*, 1 + *y*, –1 + *z*; #4 = –1 + *x*, *y*, *z*.

[†] Commercial reagents and solvents were used as received.

General procedure for the preparation of complex **1**. A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (59.4 mg, 0.2 mmol), timp (27.6 mg, 0.1 mmol) and H_2oba (25.8 mg, 0.1 mmol) was dissolved in DMF/H_2O, placed in a Parr Teflon-lined stainless steel vessel (25 ml) under autogenous pressure and heated at 95 °C for 3 days. Crystals were collected (yield based on timp ligand: ~70% for **1**).

[‡] *Crystallographic data for* **1** *after squeeze by PLATON*: $C_{63}H_{49}N_{13}O_{15}Zn_3$, M = 1424.26, triclinic, space group $P\bar{1}$, a = 14.366(2), b = 15.189(2) and c = 18.833(3) Å, V = 3750.7(10) Å^3, Z = 2, d_{calc} = 1.261 g cm^{-3}, μ(MoKα) = 1.017 mm^{-1}, T = 296(2) K, 27832 reflections measured, 8727 independent reflections (R_{int} = 0.0621), final R_1 = 0.0608 [$I > 2\sigma(I)$], $wR(F^2)$ = 0.1597, GOF = 1.008. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[14] The distributions of peaks in the channels of **1** was chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON.[15] The number of solvent water molecules in **1** was determined by elemental analysis. Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. A semiempirical absorption correction was applied using SADABS.[16] The topological analysis and some diagrams were produced using the TOPOS 4.0 program.[17]

CCDC 1054617 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

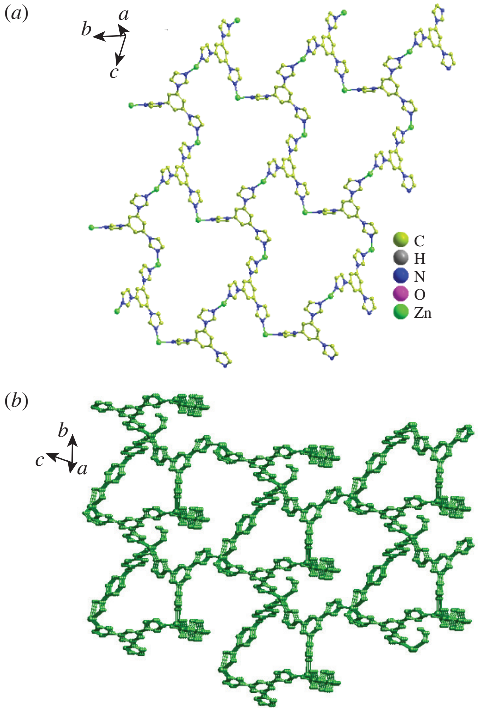

Figure 2 (*a*) The 2D layer constructed by timp ligands and Zn ions along the *a* axis; (*b*) a view of 3D network of **1** along the *a* axis.

Zn–N bond lengths are 1.924(9)–2.499(5) and 2.012(4)–2.070(5) Å, respectively, similarly to those in other Zn^{II} compounds.[20]

The timp ligands link the Zn cations to form a 2D layer with the $Zn_6(timp_{2/3})_6$ ring [Figure 2(*a*)]. Then, the oba^{2-} ligands connect these 2D sheets to generate a 3D framework [Figure 2(*b*)].

A better insight into the nature of this intricate framework is provided by the TOPOS analysis software, reducing multidimensional structures to simple nodes and connection nets. The metal cations Zn(1) and Zn(2) can be regarded as 3-connected nodes; Zn(3) can be regarded as a 4-connected node; the timp ligand connects to three Zn cations and acts as a 3-connected node. Therefore, the whole structure can thus be represented as a 3,3,4-c net topology [Figure 3(*a*)]. The framework **1** occupies 66.7% of the total crystal volume calculated by Platon; the remaining space is occupied by the DMF and water molecules. The potential voids are large enough to be filled *via* mutual interpenetration of an independent equivalent framework, generating a 2-fold interpenetrating architecture [Figure 3(*b*)]. Further analysis of interpenetration, according to a recent classification, reveals that it belongs to Class IIa.[21,22] The two identical interpenetrated nets are generated by symmetry element, that is, the inversion center of $P\bar{1}$ space group.

To check the permanent porosities for complex **1**, N_2 sorption isotherms at 77 K were measured for the desolvated samples obtained by soaking **1** in methanol, and then vacuum-drying at 80 °C overnight. As shown in Figure 4, **1** displays typical type-I adsorption isotherms and adsorbs 130 $cm^3\ g^{-1}$ of N_2 at 77 K, and the Brunauer–Emmett–Teller (BET) and Langmuir surface areas are 334 and 468 $m^2\ g^{-1}$, respectively.

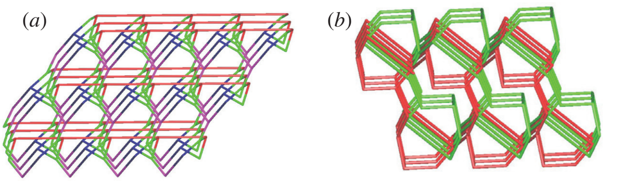

Figure 3 Schematic view of (*a*) the topology of structure **1** (oba^{2-} ligands were simplified into linkers); (*b*) two interpenetrating frameworks with topology structure.

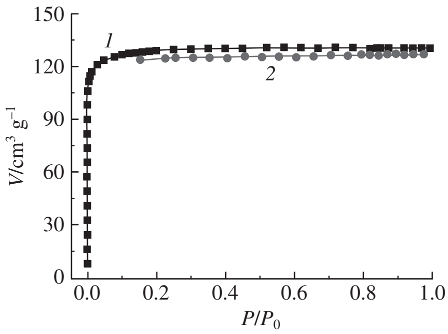

Figure 4 Nitrogen (*1*) adsorption and (*2*) desorption isotherms measured at 77 K.

In conclusion, we have successfully prepared a 3D porous network (Zn-MOF) based on timp and H_2oba as co-ligands under solvothermal conditions. The structure of the Zn-MOF is a doubly interpenetrated framework with $\{6.10^2\}_4\{6^2.10^3.12\}$ net. In addition, the obtained complex exhibits microporous sorption for N_2.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.01.022.

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