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An unprecedented (3, 4)-connected self-penetrating metal–organic framework

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ABSTRACT

In this work, we obtained a highly rare three-dimensional Zn(II) MOF, namely $[Zn_2(BTC)_2(L)][(Me_2NH_2)_2]\cdot DMF$ (BTC^{3-} = 1,3,5-benzenetricarboxylate, L = N^1,N^4-bis(pyridin-3-ylmethyl)cyclohexane-1,4-dicarboxamide), and Me_2NH_2 = dimethylamine cation) by solvo(hydro)thermal method. This polymer was characterized by single-crystal X-ray diffraction, thermogravimetry and solid-state luminescence analysis. The outstanding structural feature of it is (3, 4)-connected net with unprecedented $(6\cdot 8^2)(6\cdot 8^5)(6^2\cdot 10)(6^2\cdot 8^3\cdot 10)$ topology and self-penetrating motif.

During the past decade, the construction of metal–organic frameworks (MOFs) is the current interest in the field of supramolecular chemistry and crystal engineering, and more and more people have paid considerable attentions to research it, due to its extensive potential applications in catalysis, separation, ion-exchange, magnetism, as well as their fascinating architectures and topological frameworks [1–5]. Currently, several extreme interests on MOFs were focused on designing new topological architectures, and pioneers have disclosed many kinds of topological structure, such as NbO, PtS, $CdSO_4$ net, diamond net, rutile net, boracite net, sodalite net, etc. [6–10] Carefully checking the structure characters of MOFs, most of them were constructed from the single type of node, and the MOFs assembled from the double type of nodes are relatively less developed, such as the (3, 4) and (3, 6)-connected MOFs [11]. To achieve this goal, the key factor is the choice of suitable organic ligands and metal centers; that is, to achieve the (3, 4)-connected net, one of the best ways is to choose metal centers with a low coordination number such as Zn, Cu, Co as 4-connected nodes and trigonal organic ligands as 3-connected nodes [12–15]. Fortunately, herein, we report a novel MOF, namely $[Zn_2(BTC)_2(L)]$ $[(Me_2NH_2)_2]$ DMF (Me_2NH_2 = dimethylamine cation, BTC^{3-} = 1,3,5-benzenetricarboxylate, L = N^1, N^4-bis (pyridin-3-ylmethyl)cyclohexane-1,4-dicarboxamide)), with (3, 4)-connected $(6\cdot 8^2)(6\cdot 8^5)(6^2\cdot 10)(6^2\cdot 8^3\cdot 10)$ topology and self-penetrating motif [16].

In this work, we selectively chose dipyridyl-amide ligands {[N^1,N^4-bis(pyridin-3-ylmethyl) cyclohexane-1,4-dicarboxamide)(L)} as organic linkers and polydentate O-donor H_3BTC (H_3BTC = 1,3,5-benzenetricarboxylic acid) to construction of MOFs, based on the following considerations: (i) up to date, the L ligand has not been utilized to construct MOFs until this work; (ii) the ligand L possesses a flexible backbone containing bifunctional binding sites (both pyridyl groups), as well as a strong capacity for hydrogen bonding from amide groups, which is anticipated to play a vital role in the assembly of flexible MOFs; [13] (iii) deprotonation of H_3BTC can produce multiple products of H_3BTC, $HBTC^{2-}$, and BTC^{3-}, with the number of potential donor oxygen atoms varying from one to six, are all versatile ligands for the construction of novel high-dimensional metal–organic hybrid compounds [2]; (iv) the high symmetry that it exhibits may be useful for the crystal growing of the product formed [15].

Polymer **1** was synthesized with $Zn(NO_3)_2$, 1,3,5-benzenetricarboxylic acid and the L ligand in DMF-water(3 mL/1 mL) solution by solvo(hydro) thermal reaction at 115 °C [17,18]. Single crystal X-ray diffraction reveals that polymer **1** crystallizes in $P2_1/c$ space group [19]. In this structure, the solvent molecules (DMF) and charge-balancing positive ions of $[Me_2NH_2]^+$ derived from the hydrolyzation of DMF are badly disordered and cannot be accurately determined, so they were squeezed by Platon Squeeze program [20]. Thereafter, we use the '1-squeese.cif' as the structure analysis data. The amount of them is estimated by EA and TG researches.

As shown in Fig. 1, the asymmetric unit consists of two unique Zn(II) ions. Each zinc ion shows the four-coordinated ZnO_3N tetrahedral geometry completed by BTC^{3-} oxygen atoms and L nitrogen atom. The coordination surrounding them is described in detail as follows. Zn_1 is coordinated by O_3, O_6, and O_{11}, from three BTC^{3-} groups and N4 from L ligand; Zn2 is coordinated by O_1, O_7, and O_{10} from three BTC^{3-} groups

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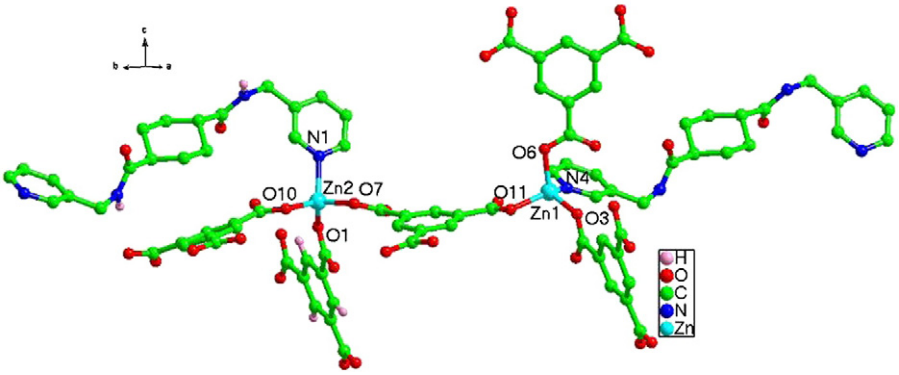

Fig. 1. View of the coordination surrounding around metal ions in polymer **1**.

and N_1 from the L ligand. The Zn – O bond lengths range from 1.922 Å to 2.015 Å, and the bond lengths of Zn_1-N_4 and Zn_2-N_1 are 2.014 Å, and 2.064 Å, respectively, comparable with that reported in other Zn(II) compounds [15]. For the BTC^{3-} ligand, it adopts the tri(monodentate) coordinated mode [17]. On the other hand, the L ligand shows the bridging mode to link two zinc ions together.

As shown in Fig. 2, the combination of zinc centers and BTC^{3-} groups forms a 2D three-connecting bilayered structure. And further through L ligand, these 2D bilayers are integrated together to form a 3D layer-pillared net [Fig. 3]. Note that herein the L ligands not only act as pillars to support the 2D bilayered net, but also they are deeply embedded in the bilayered net, playing the penetrating role, thus resulting in the overall 3D self-penetrating net. Furthermore, the volume of void space (occupied by DMF and $[Me_2NH_2]^+$ ions) observed in polymer **1** is estimated by Platon program, giving 1684.5 $Å^3$, equal to 33.0% of the cell volume, indicating potential porous framework of it [21].

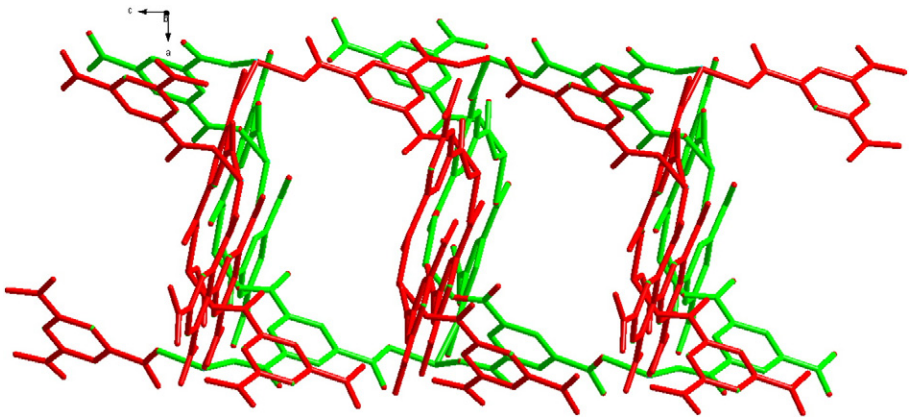

Fig. 2. View of a 2D bilayered structure formed by Zn ions and BTC^{3-} groups (each color presents a single layer).

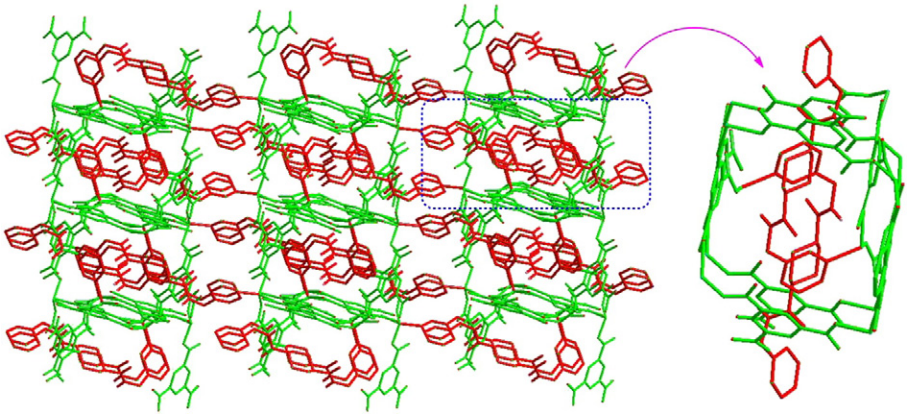

Fig. 3. View of the 3D net built on 2D bilayered structure and L pillars. The highlighted at the right presents the penetrating manner.