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Short communication

An unusual 8-connected self-penetrating metal–organic framework based on binuclear cadmium clusters

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ABSTRACT

A novel metal–organic framework based on binuclear cadmium clusters has been synthesized and characterized, which represents a new kind of 8-connected uninodal network topology presently known for self-penetrating systems.

Over the past few decades, aided by the network approach, entangled metal–organic frameworks have attracted increasing attention, not only because of their fascinating structures and topologies, but also for their potential applications as functional materials [1,2]. Among versatile entangled systems, interpenetrating network, which can be described as a number of individual nets participating in interpenetration with each other, has been extensively investigated, as evidenced by several comprehensive reviews [3]. Comparatively, the self-penetrating frameworks, as another type of tangled motifs, are single nets, having the peculiarity that the smallest topological rings are catenated by other rings belonging to the same network. Recently, amounts of self-penetrating frameworks with versatile connectivity have been reported, and some of them exhibit interesting properties, such as higher thermal stability, unusual adsorption behavior and nice nonlinear optical activity [4]. Thus, a further researching for the topological types of self-penetrating MOFs is helpful to a deep investigation of such materials.

To date, among all of the self-penetrating nets, 6-connected self-penetrating net is the most common prototype possibly owing to its variety of topological types and moderate numbers of connectivity [5]. While, examples of high-connected self-penetrating MOFs are relatively scarce, due to the limited coordination numbers of metal centers and steric hindrance issues of the organic ligands [6]. To construct such high-connected MOFs, the utilization of bi- or poly-nuclear metal clusters as the secondary building units (SBUs) has proved to be a feasible route, in view of that these SBUs generally possess larger sizes, more coordination sites, and smaller steric hindrance for ligands [7]. One common approach to the synthesis of bi- or poly-nuclear clusters is to control the hydrolysis of metal salts with the aid of carboxylate ligands. In this communication, we chose 1,4-cyclohexanedicarboxylic acid (H_2cdc) as the carboxylate-containing ligand because the carboxylate group may induce core aggregation. Meanwhile, in order to link discrete clusters into an extended network, we synthesized a new N-donor ligand, 1-(4-(4-(1H-imidazol-1-yl)benzyloxy)phenyl)-1H-imidazole (ibpi), for its long size and flexibility (Scheme S1, ESI) [8]. Herein, we report a novel metal–organic framework based on binuclear cadmium clusters, $[Cd_2(cdc)_2(ibpi)_2]\cdot 2H_2O$ (**1**), which represents a new kind of 8-connected uninodal network topology known for self-penetrating systems.

Compound **1** was prepared by hydrothermal reaction of $Cd(NO_3)_2\cdot 4H_2O$, 1,4-H_2cdc, ibpi and H_2O at 160 °C for 4 days [9]. The as-synthesized compound was characterized and formulated by elemental analysis and single-crystal X-ray diffraction studies [10]. Compound **1** crystallizes in a monoclinic space group $P2_1/c$. In the asymmetric unit, there exist one crystallographically unique Cd(II) atom, two half cdc^{2-} anions, one ibpi ligand and one uncoordinated water molecule. As shown in Fig. S1 in the ESI, the Cd(II) atom is seven-coordinated by five oxygen atoms from three cdc^{2-} anions (Cd–O 2.3428(18)–2.4946(19) Å) and two nitrogen atoms from two ibpi ligands (Cd–N 2.273(2)–2.419(2) Å). Cd(II) to O/N distances and bond angles are within the normal range (Table S1 in the supporting information). One cdc^{2-} anion bridges four Cd(II) atoms via two *syn,syn,anti*-μ_2 carboxylates, and the other cdc^{2-} anion connects two Cd(II) atoms by two chelate carboxylates. The ibpi ligand acts as a linker to join two Cd(II) atoms. In compound **1**, Cd1 and its symmetry-related Cd1A are bridged by two

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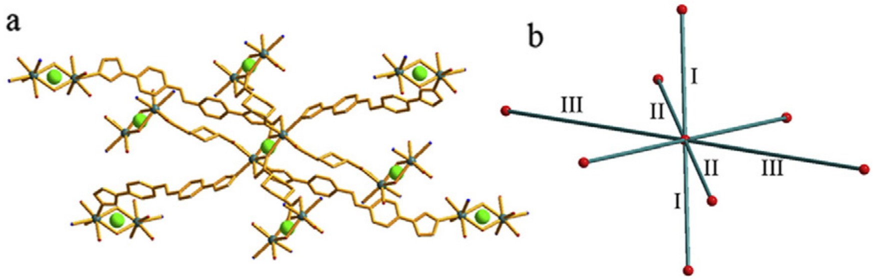

Fig. 1. a. The binuclear Cd(II) building unit of **1**. b. The linkages of the binuclear Cd(II) cluster with eight adjacent cores. The symbols of three types of linkers are I (10.30 Å), II (13.61 Å), and III (20.90 Å), respectively.

syn,*syn*,*anti*-μ_2 carboxylates to form a binuclear cadmium cluster, with the Cd1-μ_2-O2-Cd1A angle of 111.58° and Cd1⋯Cd1A distance of 4.00 Å. These clusters are connected by organic ligands to assemble a 3D framework. Within the framework, the neighboring clusters are separated by distances of 10.30 Å, 13.61 Å (through cdc^{2-}) and 20.90 Å (by ibpi). Based on the concept of topology, the binuclear cadmium clusters can be regarded as 8-connected nodes (Fig. 1), the organic ligands can be regarded as linear linkers, thus the whole structure can be simplified into a uninodal 8-connected network with a point symbol of ($4^{24}\cdot6^4$).

So far, compound **1** has the same point symbol with the 8-connected body-centered cubic (**bcu**) lattice and two 8-connected self-penetrating structures, namely [$(Cu_4(bpp)_4V_4O_{12})\cdot3H_2O$] (bpp = 1,3-bis(4-pyridyl)propane) and [$Pb_6(\mu_4\text{-}O)_2(L)_4]_n$ [H_2L = 4,4′-(hexafluoroisopropylidene)bis-(benzoic acid)] [11]. However, they actually show different network topologies with the long vertex symbols (Table S2, ESI). To further understand these complicated high-connected structures, a new approach is adopted here, which was proposed by Hill et al., namely the visualization of structures as combinations of interconnected 2D sheets or subnet tectons instead of considering 3D structures solely in terms of topology via "schläfli" symbols [12]. In this way, for the **bcu** net, the zigzag chain bridges across the diagonal of a single [2 × 2] window of the (4,4) layers and thus no self-catenation occurs; for [$(Cu_4(bpp)_4V_4O_{12})\cdot3H_2O$], the zigzag chains between the parallel adjacent (4,4) nets bridge across the diagonal of eight windows, and catenations of one 4-membered shortest circuit by other six 4-membered shortest circuits are observed in the inter-layer connections; for [$Pb_6(\mu_4\text{-}O)_2(L)_4]_n$, the self-penetrating architecture is constructed from sets of 2-fold parallel interpenetrating undulated 2D (4,4) nets, which are alternately linked by the interlamellar zigzag chains, and can be also viewed as generating from the cross-linking of two interpenetrating 6-connected **pcu** nets; while, in compound **1**, the zigzag chains between the parallel adjacent (4,4) nets bridge across the diagonal of three windows, and catenations of one 4-membered shortest circuit by other four 4-membered shortest circuits are observed in the inter-layer connections (Fig. 2). Obviously, such a unique connection inevitably results in a new kind of 8-connected self-penetrating architectures (Fig. 3a).

Further insight into the nature of this intricate architecture can be obtained if one can imagine removing one at a time from the three types of links of different lengths. On removing type II, the remainder is a 3D 6-connected framework based upon binuclear nodes, exhibiting a 3-fold interpenetrating **pcu** substructure. For any n-fold interpenetrated net, it is always true that if the extra edges that could connect all the n-fold interpenetrated nets together are added, a single self-penetrating net with higher connectivity will be obtained. Therefore, the overall framework of **1** is definitely a self-penetrating net and can be considered as derived from three interpenetrating **pcu** nets that are cross-linked by two extra connections along the cube diagonals (Fig. 3b).

The purities of compound **1** was confirmed by PXRD analyses, in which the main peaks of experimental data are basically in good agreement with the corresponding simulated one (Fig. S2, ESI). Its thermal behavior was performed on samples consisting of numerous single crystals of **1** under nitrogen atmosphere with a heating rate of 10 °C/min. The weight loss in the range of 25–93 °C attributes to the gradual release of uncoordinated water molecules (obsd 3.1%, calcd 2.9%). The destruction of the framework occurs at ca. 290 °C with the residue corresponding to CdO (obsd 21.0%, calcd 20.8%) (Fig. S3, ESI). Given that the d^{10} metal complexes have interesting photoluminescent properties, the luminescent property of compound **1** has been investigated in the solid state at room temperature. Compound **1** displays a single peak at ca. 475 nm upon excitation at 399 nm. This emission is neither metal to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Cd^{2+} ion is difficult to oxidize or reduce due to its d^{10} configuration [13]. In view of that the free ligand ibpi exhibits an emission at 390 nm upon excitation at 333 nm, this emission can probably be

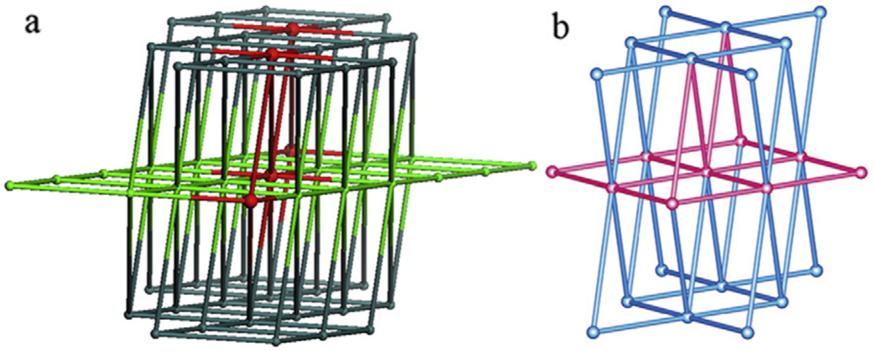

Fig. 2. Schematic representations of the topologies observed in **1** (a) and the **bcu** network (b), highlighting the essential differences between them.