

An unprecedented stable self-penetrating metal-organic framework with solvent-dependent luminescence properties

Ya-Juan Xiao, Fu-Hong Liu, Liang Zhao*, Zhong-Min Su*

Institute of Functional Material Chemistry, Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

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ABSTRACT

A fascinating 3D pillared-layer structure, namely $[\text{Cd}_3(\text{bpea})_2(\text{trz})_2(\text{H}_2\text{O})_2] \cdot \text{DMF}$ (**1**), has been isolated under hydrothermal condition by reaction of cadmium salt, biphenylethene-4,4'-dicarboxylic acid (bpea) and 1,2,4-triazole (Htrz). Compound **1** presents an unusual self-penetrating network displaying uninodal seven-connected $\{4^{14} \cdot 5 \cdot 6^6\}$ topology with trinuclear cadmium clusters as seven-connected nodes, which exhibited exceptional resistance to acid/base aqueous solutions. Furthermore, solvent-dependent luminescence properties of **1** were investigated, and the results showed that **1** could serve as a potential luminescent sensor in detecting traces of the target species, such as toluene and nitrobenzene.

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Metal-organic frameworks (MOFs) are known for their variety of intriguing coordination architectures [1] and have qualified themselves for different applications ranging from gas adsorption/separation [2], luminescence [3], and sensing to drug delivery [4,5]. Much effort has been dedicated to explore efficient synthetic strategies for the preparation of novel MOFs [6], while selection/design of suitable organic ligands still plays a crucial role in the construction of MOFs with desired structures and functions. Azoles, the five-membered aromatic N-heterocyclic ligands, are very important building blocks in the development of diverse captivating topological networks, thus azolate ligands have been widely used in constructing new MOFs with fascinating structures and interesting properties [7]. On the other hand, as we all know, rigid aromatic polycarboxylate ligands have been proved to be promising candidates for syntheses of multidimensional frameworks owing to their excellent multidentate coordination ability to metal ions and easily adjustable length and geometry. In the progress of design and synthesis of MOFs, assembling multicarboxylate bridging ligands and azolate ligands together into a framework comes to be a good choice to construct MOFs with attractive topologies and applications.

Over the past years, more and more attention has been paid to the field of recognition and sensing applications of MOFs, especially for the luminescent MOFs [4]. The capability of transducing the host-guest chemistry to detectable changes in luminescence of MOFs provides an effective means for chemical sensing applications. Fluorescence-based detection of MOFs is gaining increasing attention in virtue of its high selectivity and sensitivity, simplicity and

fast response, both in solution and solid phase [8]. In fact, recently, a number of luminescent MOFs have successfully exhibited potential applications in sensor of ions, small molecules, explosives and temperature [9–11]. For example, Li and co-workers have systematically discussed the development of different types of luminescent MOFs on explosive detection and proposed the possible mechanisms, which give new insights into explosive sensing application of luminescent MOFs [12]. Therefore, synthesis of novel luminescent MOF materials, which are suitable for potential sensing applications, is an attractive and significant task.

Given the above considerations, we selected 1,2,4-triazole (Htrz) as multidentate N-donor ligands and well used rigid luminescent biphenylethene-4,4'-dicarboxylic acid (bpea), a ligand, as co-ligand to assemble with cadmium salt and fortunately a captivating 3D pillared-layer coordination polymer was obtained. It is formulated as $[\text{Cd}_3(\text{bpea})_2(\text{trz})_2(\text{H}_2\text{O})_2] \cdot \text{DMF}$ (**1**) based on elemental analysis, IR (Fig. S1), TG (Fig. S2) and an X-ray study (details in the ESI). Compound **1** displays the rare 3D self-penetrating network with an unprecedented uninodal seven-connected $\{4^{14} \cdot 5 \cdot 6^6\}$ topology. The stabilities of **1** have been investigated in the air, water, acid and base solutions. Moreover, the solvent-dependent luminescence properties of compound **1** were also studied in detail.

X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit contains three crystallographically unique Cd^{II} , two deprotonated trz ligands, two bpea ligands, two coordinated water molecules and one isolated DMF molecule. The three independent Cd^{II} atoms exhibit three different coordination spheres, as depicted in Fig. 1a. Cd1 and Cd3 both adopt pentagonal-bipyramid coordination mode, completed

* Corresponding authors.

E-mail address: zmsu@nenu.edu.cn (Z.-M. Su).

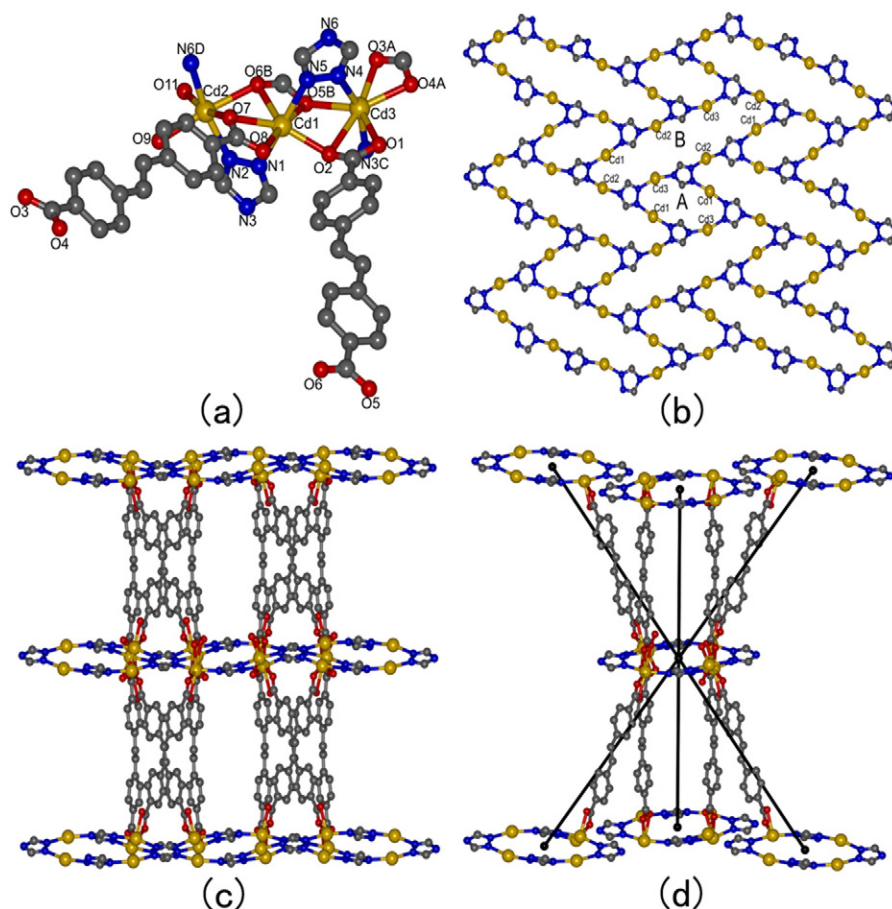


Fig. 1. (a) Coordination environment of Cd centers in **1**. Symmetry operation: A, $-1 + x, 0.5 - y, -1.5 + z$; B, $-1 + x, y, z$; C, $-x, -y, 1 - z$; D, $x, 0.5 - y, 0.5 + z$. Color codes: Cd, yellow; C, gray; N, blue; O, red. (b) Representations of the 2D layers by trz and Cd ions in **1**. A and B represent the tetra-nuclear Cd-trz loops and octa-nuclear Cd-trz loops, respectively. (c) The overall 3D pillared-layer structure of **1**. DMF molecules and H atoms are removed for clarity. (d) Concise representation of the extension directions of the pillared bpea ligands.

by five carboxylate oxygen atoms from three different bpea ligands and two nitrogen atoms from two distinct trz ligands. While the coordination geometry of Cd2 centers is a distorted octahedron with two N atoms from two discrete trz ligands, two carboxylate oxygen atoms from two separate bpea ligands, and two O atoms from two aqua ligands. Despite the extremely similar coordination environment of Cd1 and Cd3, five coordinated carboxylate oxygen atoms are distinguishing because three bpea of them offer different coordination modes, bidentate chelate, tri- and tetra-dentate, while trz presents the sole $\mu_{1,2,4}$ -bridging mode in **1**.

The structure of **1** could be best described as a 3D pillared network in which the layers are formed by the connection of trz ligands and Cd atoms (Fig. 1b). Such layers are further pillared by the aromatic backbones of bpea ligands to generate an overall 3D pillared-layer structure (Fig. 1c). Of particular interest, tetra- and octa-nuclear Cd-trz loops can be observed in the 2D layers (A and B in Fig. 1b). Each centrosymmetric tetra-nuclear Cd-trz loop is thus surrounded by four octa-nuclear Cd-trz loops via edge sharing. There are four octa-nuclear Cd-trz loops and four tetra-nuclear Cd-trz loops around each octa-nuclear Cd-trz loop in alternating arrangement. To obtain a clear observation of extension of dicarboxylate pillars, we connected the symmetric centers of seven

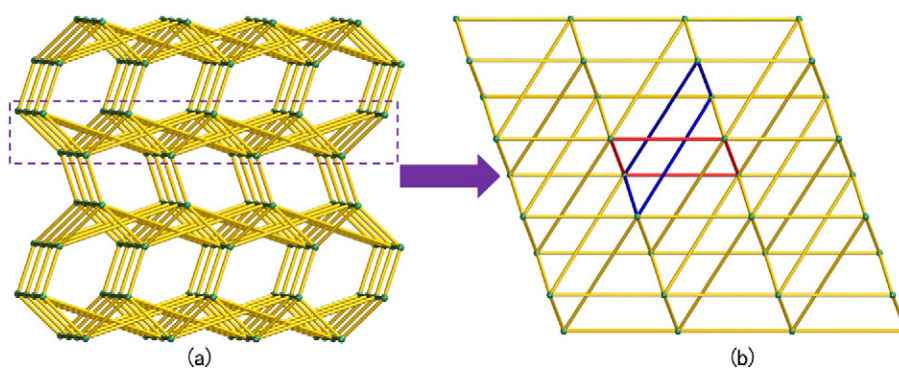


Fig. 2. (a) Topological representation of **1** showing the $\{4^{14}-5-6^6\}$ topology and (b) the highlighted self-penetrating shortest circuits. The trinuclear cadmium clusters are represented by balls.

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