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# An interdigitated 3D framework with 5-connected BN topology

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### ARTICLE INFO

## ABSTRACT

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Keywords: Coordination polymer Interdigitated framework BN topology 4,4'-(hexafluoroisopropylidene)bis (benzoic acid) A flexible coordination polymer **1** with interdigitated structure has been synthesized from 4.4'-(hexafluoroisopropylidene)bis(benzoic acid) ligand and  $Cd^{2+}$  salt, whose 3D interdigitated framework displays novel 5-connected BN topology involving both covalent and strong hydrogen bonds. The luminescent properties of **1** are discussed.

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Considerable effort has been devoted to the synthesis and characterization of metal-organic coordination polymers as functional materials because of their potential applications and fascinating topologies [1,2]. Currently, the topological analysis of coordination polymers has been a topical research area not only for the importance of simplifying complicated structures but also for the instructive role in the rational design of predicted functional materials [3,4]. To date, a large number of coordination polymers with topologies related to classical inorganic structures, such as SrSi<sub>2</sub>, diamond, quartz, NbO, CdSO<sub>4</sub>,  $\alpha$ -Po, CsCl, C<sub>3</sub>N<sub>4</sub>, Pt<sub>3</sub>O<sub>4</sub>, PtS, CaF<sub>2</sub> and zeolite-like nets [4,5], have been obtained via the use of crystal engineering concepts of node, net and vertex symbols. However, the rational design and controlled syntheses of novel coordination frameworks with unusual topologies are still challenging topics. For example, the 5-connected coordination networks, especially 5-connected BN net, are relatively rare [6-12]. The 5-connected BN (or bnn) net may be described as cross-linked (6,3) honeycomb network based on the trigonal bipyramidal node with the Schläfli symbol 4<sup>6</sup>. 6<sup>4</sup>.

On the other hand, the construction of flexible and dynamic porous coordination polymers has attracted growing research interest because of their potential applications in separation, sensor and switching materials [13]. The flexible frameworks can reversibly change their structures and properties in response to external stimuli, such as guest adsorption, pressure, and temperature. As known, the interdigitated porous frameworks constructed from two-dimensional (2D) layers display tunable flexibility associated with layer-layer weak interactions, including H-bonds,  $\pi$ -electron stacking and van der

Waals interactions [14–22]. Recently, Kitagawa's group reported a series of interdigitated structures with selective guest sorption and gas separation, and their pore size and shape can be tuned by varying the V-shaped dicarboxylate ligands [18–22]. Herein we report a new flexible coordination polymer with interdigitated motif of 2D layer by exploring the V-shaped ligand, 4,4'-(hexafluoroisopropylidene)-bis-(benzoic acid) (H<sub>2</sub>hfipbb) [23–25]. The compound, [Cd(hfipbb)(H<sub>2</sub>O) (H<sub>2</sub>hfipbb)]<sub>n</sub> (1), displays an interesting 5-connected BN topology involving both covalent and strong hydrogen bonds.

The colorless crystals of **1** were hydrothermally synthesized in 64% yield by reacting CdCl<sub>2</sub>· 2.5H<sub>2</sub>O with H<sub>2</sub>hfipbb ligand at 170 °C for 3 days [26]. The structure of **1** was identified by satisfactory elemental analysis. IR and single crystal X-ray diffraction [27]. The phase purity of the crystalline sample of **1** was characterized by powder X-ray diffraction (Fig. S1). The asymmetric unit of **1** contains one  $Cd^{2+}$  cations, one H<sub>2</sub>O molecule, one deprotonated hfipbb ligand and one protonated H<sub>2</sub>hfipbb ligand. As shown in Fig. 1, each Cd<sup>2+</sup> cation exhibits distorted pentangular-bipyramidal configuration and is seven-coordinated by five oxygen atoms from deprotonated hfipbb ligands, one oxygen atom from protonated H<sub>2</sub>hfipbb ligand, and one oxygen atom from water molecule. The Cd—O bond distances present a broad region in range from 2.226 Å to 2.676 Å, in which the longest bond length is axial Cd (1)—O(5) from protonated H<sub>2</sub>hfipbb ligand. Two carboxylate groups of deprotonated hfipbb adopt chelate and chelate-bridging coordination modes, respectively, and the dihedral angle between two benzene rings is 116.3°. The protonated H<sub>2</sub>hfipbb ligand adopts weak coordination bond by only use of one oxygen atom, and others act as donor or acceptor of hydrogen bonds. The dihedral angle between two benzene rings of protonated H<sub>2</sub>hfipbb is 75.1°. The extended structure of 1 exhibits 2D framework constructed by Cd<sup>2+</sup> cations and deprotonated hfipbb ligands with coordination bonds. The protonated

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**Fig. 1.** View of the coordination sphere in **1** with 50% ellipsoid probability. The hydrogen bonds are indicated with dashed line. (symmetry codes. a: x - 1, y, z; b: x - 1, 1/2 - y, z - 1/2; m: 1 + x, y, z; n: 1 + x, 1/2 - y, 1/2 + z; i: x, 1/2 - y, z - 1/2; j: 1 - x, -y, 2 - z).

H<sub>2</sub>hfipbb ligands act as up-and-down arms of 2D layer through both weak coordination bond (Cd(1)—O(5) of 2.676 Å) and strong intralayer hydrogen bonds (O(6)—H(1)·O(1) with 2.596 Å and 170°).

To clearly analyze the whole 3D topology structure of 1, the 2D coordination framework is shown in Fig. 2a. This 2D framework without H<sub>2</sub>hfipbb arms can be simplified as a (4,4) grid topology considering Cd atom as 4-connected node, hfipbb ligand and Cd–O–Cd chain as linear linkers, respectively. The strong intra-layer hydrogen bond is present between coordinated H<sub>2</sub>O molecule and carboxylate oxygen atom with O(9)—H(3)·O(2i) of 2.699 Å (symmetry code: i x, 1/2 - y, z - 1/2). Furthermore, the (4,4) grids are mutually interdigitated to create a stable 3D assembled framework by strong inter-layer hydrogen bonds, as shown in Fig. 3a. Interestingly, there are two kinds of inter-layer hydrogen bonds (Figs. 2b and 1), one is O(7)—H(2)·O(5j) of 2.717 Å (symmetry code: j 1 - x, -y, 2 - z) between protonated H<sub>2</sub>hfipbb and deprotonated hfipbb ligand, the other is O(9)—H(4)·O(8j) of 2.785 Å

between coordinated H<sub>2</sub>O molecule and protonated H<sub>2</sub>hfipbb ligand. This interdigitated motif with inter-layer hydrogen bonds results in a dimmer ring of two protonated H<sub>2</sub>hfipbb from two layers, which can serve as a linear linker in layer-to-layer (Fig. 2b). Therefore, the whole 3D interdigitated framework can be simplified as a novel 5-connected  $4^{6}$ .  $6^{4}$  net with BN topology (Fig. 3b). In contrast to the extensive investigations on 3-, 4-, 6-, 8-connected 3D coordination networks [4], there have been only a few on 5-connected BN topology [6–12]. To the best of our knowledge, the compound 1 is the first example of 3D interdigitated coordination network with interesting 5-connected BN topology involving both covalent and strong hydrogen bonds. Moreover, it should be pointed out that the structure of **1** may be flexible and candidate as dynamic framework for separation application due to its interdigitated architecture. The total potential solvent accessible volume is 124.0 Å<sup>3</sup>, as calculated by *PLATON*[28], which indicates the microporous feature of 1.



Fig. 2. (a) 2D (4,4) grid network and schematic representation of 1; (b) view of H-bonds modes of layer-to-layer, which act as linear linkers.



Fig. 3. (a) 3D interdigitated framework of 1 assembled with H-bonds; (b) schematic representation of 5-connected BN topology.

Taking into account the excellent luminescent properties of d<sup>10</sup> metal complexes, the preliminary photoluminescent property of **1** has been investigated in the solid state at room temperature. It gave strong emission peak maximum at 500 nm under 352 nm light excitation (Fig. S2). It has been reported that the organic H<sub>2</sub>hfipbb ligand has emission band centered at 383 nm ( $\lambda_{ex}$  = 342 nm) [29]. Therefore, the emission bands for **1** are tentatively attributed to the ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) [29–32]. These observations indicate that **1** may be candidate as potential photoactive materials. On the other hand, thermogravimetric analysis (TGA) of **1** was performed at a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub> atmosphere. The result shows that the weight loss in the range of 150–180 °C corresponds to the loss of coordinated water molecules, and the removal of the organic components occurs at 270 °C (Fig. S3).

In conclusion, a novel Cd(II)-organic coordination polymer has been synthesized from the V-shaped ligand 4,4'-(hexafluoroisopropylidene)bis-(benzoic acid). Compound **1** is a 3D interdigitated coordination network from 2D layer and exhibits interesting 5-connected BN topology involving both covalent and strong hydrogen bonds. The successful isolation of this solid material not only affords new coordination polymer with interesting topology structure but also helps us to further understand the flexible interdigitated motif.

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#### Appendix A. Supplementary material

X-ray crystallographic file in CIF format and powder X-ray diffraction for complex 1. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.04.019.

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1601(m), 1529(s), 1398(s), 1248(s), 1210(w), 1167(s), 1027(m), 982(s), 938(s), 859(m), 772(s), 726(s), 667(s), 540(w).

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