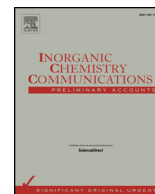




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Short communication

Synthesis, structure and luminescence property of a cadmium-organic framework based on 6-connected paddle-wheel building units and btc ligands

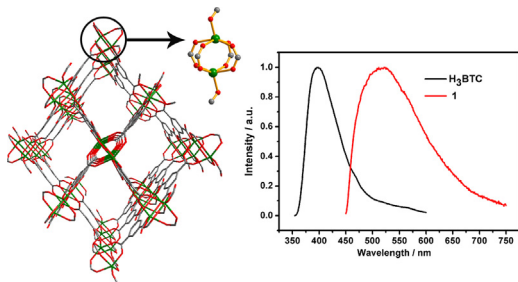
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GRAPHICAL ABSTRACT

A three dimensional (3D) cadmium-organic framework consisting of 6-connected paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ building units and 3-connected H_3BTC ligands and shows excellent solid-state photoluminescent emission property.



ARTICLE INFO

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ABSTRACT

A novel three-dimensional cadmium-organic framework $[(\text{Me}_2\text{NH}_2)\text{Cd}(\text{BTC})(\text{DMA})]\cdot\text{H}_2\text{O}$ (**1**) (H_3BTC = benzene-1,3,5-tricarboxylate, DMA = *N,N*-dimethylacetamide) has been obtained through the assemble of paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ units as 6-connected nodes and H_3BTC ligands under solvothermal reaction condition. Topological analysis indicates that the whole framework structure of **1** possesses a non-interpenetrating 3,6-connected *rtl* topology. Moreover, **1** shows an emission maximum peak at 520 nm upon excitation at 420 nm in the solid-state at room temperature, which is remarkable red-shift compare with that of free ligand.

Metal-organic Frameworks (MOFs), constructed from adjustable organic ligands and metal ions/clusters as secondary building units (SBUs), have gained significant interest as one of the most promising materials due to their intriguing structural diversities, unique properties and potential applications in gas storage and separation, heterogeneous catalysis, luminescent sensor and so on [1–5]. Great efforts

have been made on the systematic design and synthesis of MOFs. The family of polycarboxylate ligands have been widely employed and investigated for their predictable bridging and coordination fashions [6]. Specially, the benzene-1,3,5-tricarboxylate (H_3BTC) as 3-connected linker is the most commonly used in the synthesis of various functional and aesthetically elegant polyhedron-MOFs, such as HKUST-1, CPM-4

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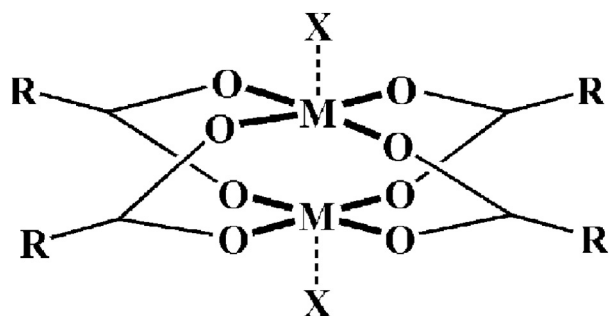
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Scheme 1. The coordination geometry of paddle-wheel $[M_2(\text{COO})_4]$ SBUs: M = metal ion; R = bicarboxylate ligand and X = solvent or pyridyl ligand.

and InOF-14 [7–10]. On the other hand, it has been found that the dinuclear $[M_2(\text{COO})_4]$ (M = Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , etc.) clusters as the classical paddle-wheel SBUs can construct MOFs with wonderful architectures and interesting properties [11–15]. Until now, the paddle-wheel SBUs have emerged as a common 4-connected node, while the axial coordination sites are occupied by the solvent molecules (Scheme 1). Therefore, the combination of paddle-wheel $[M_2(\text{COO})_4]$ SBUs and tridentate H_3BTC ligands can usually afford a (3,4)-connected network. For example, HKUST-1 or $\text{Cu}_3(\text{BTC})_2$ is a representative (3,4)-connected MOFs built from 4-connected paddle-wheel SBUs and 3-connected H_3BTC ligands [7,16]. Moreover, the coordination solvent molecules of paddle-wheel SBUs can be replaced by pyridyl ligands to form 6-connected nodes in highly connected porous MOFs [17,18]. Alternatively, the assembly of the single ligands and 6-connected paddle-wheel SBUs is considered as another available approach. However, studies focusing on the construction and properties of MOFs based on paddle-wheel SBUs as 6-connected nodes and H_3BTC ligands are seldom documented so far. In this study, we choose the paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ SBUs and H_3BTC ligands as the building blocks for the construction of a novel 3D cadmium-organic framework, which possesses a noninterpenetrating 3,6-connected *rtl* topology.

The solvothermal reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and H_3BTC ligands with a 1:1 molar ratio in a DMA/ CH_3OH (DMA = *N,N*-dimethylacetamide) mixed solution (4:1, 5 mL) for 5 days successfully obtained needle shaped crystals of $[(\text{Me}_2\text{NH}_2)\text{Cd}(\text{BTC})(\text{DMA})] \cdot \text{H}_2\text{O}$ (**1**) when the acetic acid (HAc) was added in [19]. The crystalline phase purity of the bulk sample for **1** has been characterized using powder X-ray diffraction (PXRD) (Fig. S3). The good agreement between the experimental PXRD pattern with the simulated one from single crystal data indicates the phase purity of **1**. The thermal stability of **1** has been investigated under nitrogen stream from 30 to 1000 °C. And the thermogravimetric analysis (TGA) of **1** shows that the removal of solvent molecules occurs at the temperature of 30–350 °C (calcd. 32.12%; found 32.02%), and then there is a relatively steady plateau from 350 to 400 °C. Subsequently, the host framework starts to decompose until 650 °C (Fig. S4).

Compound **1** crystallizes in monoclinic system, $P2_1/c$ space group, which is illuminated by the single crystal diffraction analysis [20]. The asymmetric unit of **1** is made up of one Cd(II) cation, one BTC^{3-} anion ligand, one free DMA molecule, and one Me_2NH_2^+ cation which is from in situ decomposition of the DMA solvent molecules, thus the total charge of **1** is neutral (Fig. S1). The Cd(II) ion is five-coordinated by five O atoms from five different BTC^{3-} ligands in distorted square pyramidal coordination geometry. The Cd–O distances range from 2.206(3) to 2.295(3) Å, which are comparable with those reported in the literature [21–23]. For BTC^{3-} ligand, two carboxylate groups are separately coordinated by four Cd(II) ions in $\mu_2\text{-}\eta^1\text{:}\eta^1$ bidentate coordination mode, while the other carboxylate group connects to one Cd(II) ion in $\mu_2\text{-}\eta^1\text{:}\eta^0$ monodentate fashion (Fig. 1a). Meanwhile, two neighboring Cd(II) ions are linked by four bridging carboxylate groups to form a typical paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ SBU with the Cd...Cd distance of 3.3234(6) Å, while the axial positions are occupied by two O atoms from another two

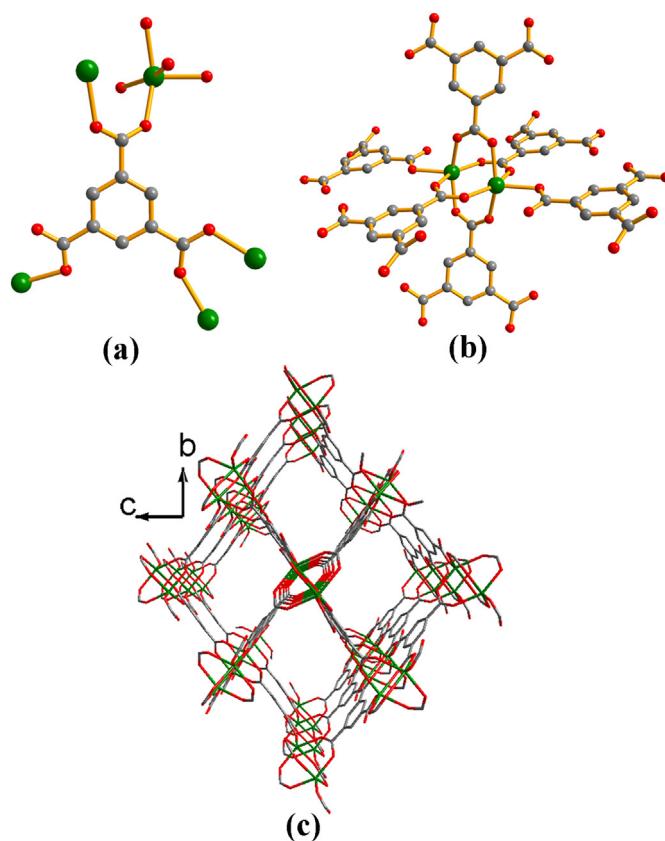


Fig. 1. (a) The coordination environment of Cd(II) ions and BTC^{3-} ligands in **1**. (b) The paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ SBUs in **1**. (c) The 3D structure of **1** as viewed along the *a*-axis. Colour code: C, gray; N, blue; O, red; Cd, green. The guest molecules and hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

BTC^{3-} ligands (Fig. 1b). However, there are 4-connected paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ SBUs in the reported Cd-BTC compounds [22,24]. It is worthwhile to note that although paddle-wheel $[M_2(\text{COO})_4]$ SBUs as 6-connected are often found in MOFs, their combination with the single ligands has not been reported so far. Interestingly, each $[\text{Cd}_2(\text{COO})_4]$ SBU is linked to six neighboring SBUs through six BTC^{3-} ligands to generate a three dimensional (3D) framework structure with square channels occupied by solvent molecules and Me_2NH_2^+ cations along the *a* axis (Fig. 1c). Topologically speaking, the host framework of **1** can be symbolized as a noninterpenetrating 3,6-connected rutilite (*rtl*) net with $(4.6^2)_2(4^2.6^{10}.8^3)$ by treating the $[\text{Cd}_2(\text{COO})_4]$ SBUs and BTC^{3-} ligands as 6- and 3-connected nodes, respectively (Fig. 2).

Considering the excellent photoluminescent properties of MOFs containing d^{10} transition-metal ions, the solid-state luminescent properties of compound **1** and free H_3BTC ligand were investigated at room temperature (Fig. 3). The luminescent spectrum of H_3BTC ligand shows that it has the main emission peak at 396 nm under 334 nm excitation, which may be attributed to the $\pi^*\text{-n}$ transition [25]. In contrast to the H_3BTC ligand, compound **1** displays remarkable red-shift with an emission maximum peak at 520 nm upon excitation at 420 nm. The emission of compound **1** is obvious shift compared with that of the free ligand, therefore, it can be assigned to the ligand-to-metal charge transfer (LMCT) [26].

In summary, we have successfully synthesized a novel 3D cadmium-organic framework consisting of 6-connected paddle-wheel $[\text{Cd}_2(\text{COO})_4]$ SBUs and 3-connected H_3BTC ligands, which exhibits a noninterpenetrating 3,6-connected *rtl* topology. **1** represents the first example of the combination of the single ligands and 6-connected

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