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Solvent-induced generation of two cadmium-based metal–organic frameworks from 1, 3, 5-benzenetricarboxylic acid ligand

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A B S T R A C T

Two cadmium-based metal–organic frameworks (MOFs), namely $[Cd_5(BTC)_4(DMAc)_2(H_2O)_2DMF] \cdot 2[H_2N(CH_3)_2] \cdot 4DMAc$ (JUC-133) and $[Cd_3(BTC)_2(DMSO)_4]$ (JUC-134) (JUC = Jilin University, China), based on 1, 3, 5-benzenetricarboxylic acid ligand (H_3BTC) were synthesized by solvent-induced strategy under solvothermal conditions and characterized by single crystal X-ray diffraction, elemental analysis, FT-IR spectroscopy, luminescent spectroscopy, TGA analysis, and powder X-ray diffraction. The ligand is connected to cadmium metals to form different cores with distinctive coordination modes to generate different structures. JUC-133 displays a new three-dimensional (3D) topology with the point symbol $(4 \cdot 6^2)_4(4 \cdot 8^2)_4(4^2 \cdot 6^5 \cdot 8^3)_4(8^6)$ based on $Cd_2(COO)_5$ and $Cd_2(COO)_4$ as secondary building units (SBUs), which is unknown in previously reported MOFs. JUC-134 can be symbolized as a rutile (rtl) topology with the point symbol $(4 \cdot 6^2)_2(4^2 \cdot 6^{10} \cdot 8^3)$ based on $Cd_3(COO)_6$ as SBUs. Furthermore, the luminescent of the ligand H_3BTC and compounds were measured at room temperature. It is worth noting that the solvent could play an important role in the structural assembly process.

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In recent years, metal–organic frameworks (MOFs) [1–4], as a rapidly growing class of organic–inorganic hybrid porous materials, have attracted much attention over the past two decades, not only because their intriguing varieties of architectures, but also because of their potential applications in many fields, such as gas/liquid storage and separation [5–7], sensing materials [8–11], optical devices [12,13], heterogeneous catalysis [14,15] and drug delivery [16,17]. Among these researches, design and construction of new MOFs with diverse structures has always been drawn great attention in recent decades. A lot of synthetic parameters affected their structural assembly process. Up to now, many efforts have been focused on the assembly of organic ligands and inorganic metal clusters to obtain unpredictability architectures and functional materials [18–21]. On the other hand, the structural topology and functionality of MOFs also can be tuned by synthesis conditions such as metal/ligand ratio [22], terminal co-ligands [23], templates [24] and even solvent media [25]. To the best of our knowledge, there are mainly two common methods that affect the structures. Solvents can serve as guest molecules or as terminal co-ligands in the framework to regulate the formation of the frameworks and the coordination geometric configurations. Solvent-directed assembly of MOFs is an effective way to facilitate the design and preparation of new crystalline materials. However, it is also a quite interesting and challenging job to obtain different structures for the same ligand and metal ion in the same synthesis conditions except solvents. Among the reported

researches, it is well known that 1, 3, 5-benezetricarboxylic acid (H_3BTC) is the common and famous tri-connected ligand to be employed to prepare MOF materials with diverse architectures [26–28].

In this work, two different MOFs, namely $[Cd_5(BTC)_4(DMAc)_2(H_2O)_2DMF] \cdot 2[H_2N(CH_3)_2] \cdot 4DMAc$ (JUC-133) and $[Cd_3(BTC)_2(DMSO)_4]$ (JUC-134) (DMF = N,N-Dimethylformamide, DMAc = N,N-Dimethylacetamide, DMSO = dimethyl sulfoxide, and JUC = Jilin University, China), were successfully synthesized under solvothermal conditions and characterized based on H_3BTC. JUC-133 was solvothermal synthesized with a mixture of $Cd(NO_3)_2 \cdot 4H_2O$, H_3BTC, DMAc, DMF and an aqueous $HClO_4$ solution (2 M) sealed into a 20 ml capped vessel and heated at 85 °C for two days. JUC-134 can be synthesized with a mixture of $Cd(NO_3)_2 \cdot 4H_2O$, H_3BTC, DMAc, DMSO and an aqueous $HClO_4$ solution (2 M) sealed into a 20 ml capped vessel and heated at 85 °C for two days [29].

A single-crystal X-ray diffraction analysis [30] reveals that JUC-133 crystallizes in the triclinic space group $P - 1$ and shows a 3D coordination framework. In the asymmetric unit, there are five Cd(II), four BTC^{3-} ligands, one terminal coordinated DMF molecule, two terminal coordinated DMAc molecules, two terminal coordinated water molecules, four guest DMAc molecules and two guest $H_2N(CH_3)_2$ molecules (Fig. S1). There are three kinds of SBUs in the framework (Fig. 1a, b). The Cd4 exhibits a distorted paddle-wheel SBU, which is bound with four carboxylates from four different ligands and two terminal coordinated DMAc molecules (Cd–O = 2.183–2.279 Å). Cd2 and Cd5 adopt the same geometries and Cd2 is selected to discuss the structure in detail. Cd2 is bound with six

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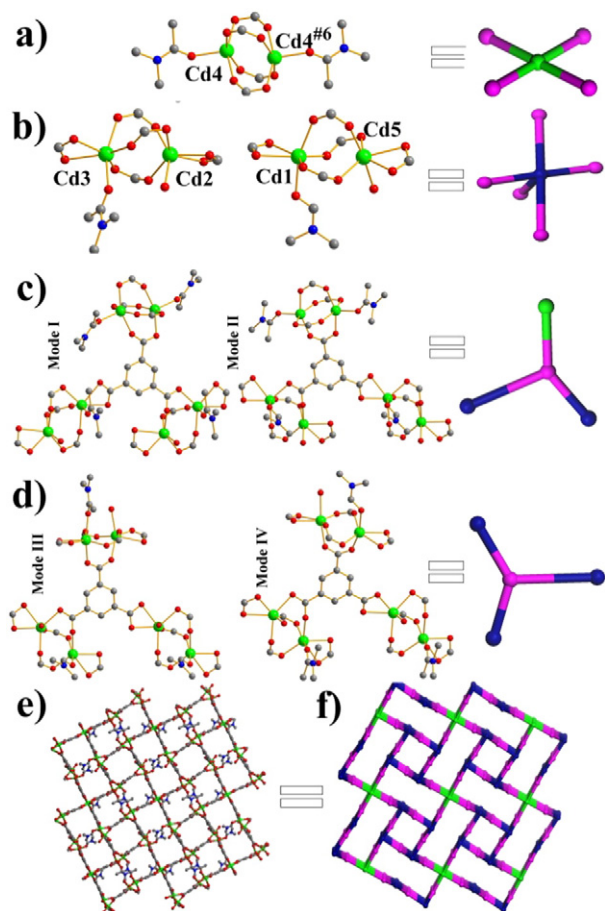*E-mail addresses:* djs3043@126.com (J. Du), fxsun@jlu.edu.cn (F. Sun).

Fig. 1. (a, b) Coordination environments of Cd(II) (symmetry code: #6 − x + 1, −y, −z + 1). Cd$_2$(COO)$_4$ SBUs and Cd$_2$(COO)$_5$ SBUs viewed as a 4-connected node and 5-connected node, respectively; (c, d) four coordination modes in JUC-133 and each BTC$^{3−}$ ligand viewed as a 3-connected node; (e) view of the 3D framework along the a-axis; (the hydrogen atoms are omitted for clarity and C, gray; O, red; N, blue; Cd, green) (f) simplified network of the 3D coordination framework along the a-axis with the point symbol $(4·6^2)_4(4·8^2)_4(4^2·6^5·8^3)_4(8^6)$.

oxygen atoms from four carboxyl groups of four diverse ligands and one terminal H$_2$O to form a distorted octahedral geometry (Cd–O = 2.230–2.491 Å). The Cd1 is bound with six oxygen atoms, which

come from four different carboxyl groups and one terminal DMF molecule. In addition, the Cd3 is also connected to six oxygen atoms, corresponding five oxygen atoms from ligands and one oxygen atom from a coordinated DMAc molecule. It should be noted that BTC$^{3−}$ ligands exhibit four coordination modes. As shown in Fig. 1c, the ligand is linked with two Cd$_2$(COO)$_5$ SBUs and one Cd$_2$(COO)$_4$ SBU in mode I and mode II. On the other hand, each ligand is connected to three Cd$_2$(COO)$_5$ SBUs (Fig. 1d) in modes III and IV. The Cd$_2$(COO)$_5$ and Cd$_2$(COO)$_4$ SBUs are further linked with the BTC$^{3−}$ ligands to form a 3D framework (Fig. 1e). From the topologic point of view, the Cd$_2$(COO)$_5$ and Cd$_2$(COO)$_4$ SBUs can be regarded as 5-connected node and 4-connected node, respectively. The BTC$^{3−}$ ligands can be simplified for 3-connected linkers. Notably, the resulting 3D network can be symbolized as a new type of topology with the point symbol $(4·6^2)_4(4·8^2)_4(4^2·6^5·8^3)_4(8^6)$, which is unknown in previously reported MOFs (Fig. 1f).

The single crystal X-ray diffraction reveals that JUC-134 crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of JUC-134 contains one Cd1, a half Cd2, one unique BTC$^{3−}$ ligand and two coordinated DMSO molecules (Fig. S2, Supporting information). As shown in Fig. 2a, the crystallographically independent two Cd(II) centers (Cd1 and Cd2) are linked by carboxylate and DMSO in the sequence of Cd1–Cd2–Cd1 to form a trinuclear Cd$_3$(COO)$_6$ SBU. The Cd1 is bound with six oxygen atoms, originating from one chelating and two bridging carboxylates of three diverse ligands, and two coordinated DMSO molecules (Cd–O = 2.217–2.397 Å). Each Cd2 is also bound with six oxygen atoms from four bridging carboxylates of different ligands and two coordinated DMSO molecules to form a distorted octahedral geometry (Cd–O = 2.213–2.420 Å). As shown in Fig. 2b, each BTC$^{3−}$ ligand is connected to three [Cd$_3$(COO)$_6$] SBUs. They are further linked with each other to form a 3D framework (Fig. 2c). From the topologic point of view, Cd$_3$(COO)$_6$ SBUs and BTC$^{3−}$ ligands can be regarded as 6-connected and 3-connected linkers, respectively. The resulting network could be regarded as a 3D network with the point symbol $(4·6^2)_2(4^2·6^{10}·8^3)$, which belongs to rutile (rtl) topology (Fig. 2d) [31,32].

The Powder X-ray diffraction (PXRD) of JUC-133 and JUC-134 were executed to confirm the phase purity of their bulk crystalline materials. As shown in Fig. 3, the experimental patterns of as-synthesized samples exhibited good agreement with those simulated from the single-crystal structures, verifying that the as-synthesized samples have been successfully obtained. From the thermogravimetric analyses (Fig. 4), JUC-133 showed a slow weight loss of 33.67% before 400 °C, corresponding to the loss of
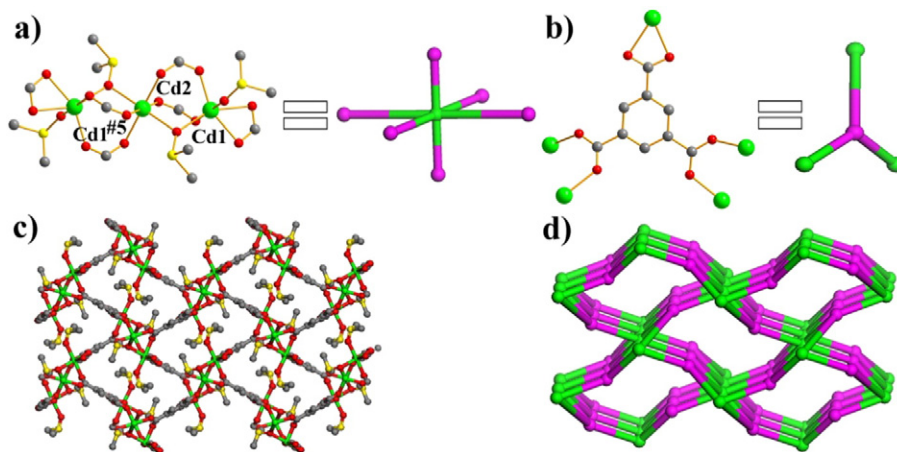

Fig. 2. (a) Coordination environments of Cd(II) and Cd$_2$(COO)$_6$ SBUs viewed as a 6-connected node (symmetry code: #5 − x, −y, −z); (b) the BTC$^{3−}$ ligand coordinated to three Cd$_2$(COO)$_6$ SBUs and viewed as a 3-connected linker; (c) the 3D coordination framework along the a-axis; (the hydrogen atoms are omitted for clarity and C, gray; O, red; S, yellow; Cd, green) (d) simplified network of the 3D coordination framework along the a-axis with the point symbol $(4·6^2)_2(4^2·6^{10}·8^3)$.