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Short communication

Two anionic metal-organic frameworks with tunable luminescent properties induced by cations

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ABSTRACT

Two three-dimensional (3-D) MOFs, $[(C_2H_5)_4N]_3[H_3O]_2[Cd_6Br(H_2-DHBDC)_8(DMF)_4]$ (**1**; H₄-DHBDC = 2,5-dihydroxy-1,4-benzenedicarboxylic acid, DMF = N,N-dimethylformamide) and $[(CH_3)_2NH_2]_2[Cd_3(H_2-DHBDC)_4(DMF)_2] \cdot 2DMF$ (**2**), are prepared from the self-assembly reactions between Cd(CH₃COO)₂ and H₄-DHBDC, respectively. Both anionic frameworks consist of linear trinuclear Cd units (e.g., **1**: [Cd₃BrO₂(CO₂)₇] and [Cd₃O₂(CO₂)₈]; **2**: [Cd₃O₂(CO₂)₈]) linked by the H₂-DHBDC ligands. The photoluminescent properties of compound **1** are tunable through cation-exchange with different metal ions. The results demonstrated an effective ion-exchange approach toward the functional modification of MOF materials.

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1. Introduction

In the last decade, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) built from metal ions or metal clusters with multifunctional organic ligands have received considerable attention, owing to their potential applications in separations, heterogeneous catalysis, drug delivery, nonlinear optics, and luminescence etc [1]. The ability to tune the luminescent emission of materials in a simple fashion is of great interest in the light-emitting diodes [2], nonlinear optical (NLO) materials [3], bio-imaging agents [4], and other photon emitting devices. Several effective methods can be applied to fabricate this aim: (i) incorporation of fluorescent ligands or luminescent metal nodes in the core structure [5], (ii) alteration of the shape and size of the framework [6], (iii) guest inclusion [7], or (iv) external stimulus [8]. Such phenomena have been observed in lanthanide-based MOFs or MOFs containing lanthanide cations as guests [9]. However, the metal cations-dependent photoluminescent emission is rarely known for MOFs.

In this work, we report two three-dimensional (3-D) MOFs, $[(C_2H_5)_4N]_3[H_3O]_2[Cd_6Br(H_2-DHBDC)_8(DMF)_4]$ (**1**; H₄-DHBDC = 2, 5-dihydroxy-1,4-benzenedicarboxylic acid, DMF = N, N-dimethylformamide) and $[(CH_3)_2NH_2]_2[Cd_3(H_2-DHBDC)_4(DMF)_2] \cdot 2DMF$ (**2**), which are prepared from the self-assembly reactions between Cd(CH₃COO)₂ and

H₄-DHBDC, respectively. Both anionic frameworks consist of linear trinuclear Cd units (e.g., **1**: [Cd₃BrO₂(CO₂)₇] and [Cd₃O₂(CO₂)₈]; **2**: [Cd₃O₂(CO₂)₈]) linked by the H₂-DHBDC ligands. Although several MOFs based on this H₄-DHBDC ligand have been reported [10], the anionic framework type like compounds **1** and **2** reported here is truly novel.

2. Experimental section

Synthesis of **1**: a mixture of Cd(NO₃)₂ (0.0573 g, 0.24 mmol), H₄-DHBDC (0.0568 g, 0.30 mmol), tetraethylammonium bromide (0.0395 g, 0.19 mmol), 4 ml mixture of N,N-dimethylformamide (DMF) and ethanol (1:1) was stirred to give a colorless turbid solution. The mixture was heated at 100 °C for 2 days, and then cooled to room temperature. The reddish-block crystals were filtered off and dried in air. IR (solid KBr pellet v/cm⁻¹): 3068 w, 1647 s, 1515 s, 1450 s, 1328 s, 1263 s, 1104 m, 805 s, 552 m.

Synthesis of **2**: a mixture of Cd(NO₃)₂ (0.052 g, 0.22 mmol), H₄-DHBDC (0.065 g, 0.35 mmol), 4 ml mixture of N, N-dimethylformamide (DMF) and ethanol (1:1) was stirred to give a colorless turbid solution. The mixture was heated at 100 °C for 2 days, and then cooled to room temperature. The yellow-rod crystals were filtered off and dried in air. IR (solid KBr pellet v/cm⁻¹): 1648 s, 1522 s, 1441 s, 1323 m, 1261 m, 1106 w, 800 m, 539 m. The phase purity for each compound was identified by powder X-ray diffraction.

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Crystal data for **1**: $C_{93}H_{102}Cd_6BrN_6O_{59}$, $M_w=3002.12$, monoclinic, $a=22.9880(4)$ Å, $b=33.9844(6)$ Å, $c=18.1708(3)$ Å, $\beta=106.213(2)^\circ$, $V=13,631.1(4)$ Å³, $T=293(2)$ K, space group $C2/m$, $Z=4$, 12,207 reflections measured, 10,861 independent reflections ($R_{int}=0.0257$). The final R_1 value was 0.0700 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1951 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.047. Crystal data for **2**: $C_{48}H_{52}Cd_3N_6O_{32}$, $M_w=1562.19$, monoclinic, $a=18.3148(5)$ Å, $b=9.4506(3)$ Å, $c=19.0993(5)$ Å, $\beta=106.091(3)^\circ$, $V=3176.30(16)$ Å³, $T=293(2)$ K, space group $P2_1/c$, $Z=2$, 5592 reflections measured, 4817 independent reflections ($R_{int}=0.0600$). The final R_1 value was 0.0624 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1619 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.033. The contribution of the disordered solvent molecules in **1** was subtracted from the reflection data by the SQUEEZE method as implanted in PLATON program.

3. Results and discussion

It is interesting that compounds **1** and **2** crystallize in monoclinic crystal system but with different space groups (**1**: $C2/m$; **2**: $P2_1/c$). In the structure of **1**, the asymmetric unit contains one and four half Cd(II) ion, one and half $(C_2H_5)_4N^+$, two and four half H_2 -DHBDC²⁻ ligand, half Br⁻, one H_3O^+ cation, and one coordinated DMF molecule. The configuration of Cd centers can be classified as two groups in terms of their coordination atoms: (1) Cd1, Cd2, and Cd5 are six-coordinated, Cd1 and Cd5 are coordinated by five oxygen atoms and one bromine atoms, while Cd3 are coordinated by six oxygen atoms and located in slightly distorted octahedral coordination environments; (2) both Cd3 and Cd4 are coordinated by seven carboxylate oxygen atoms and located in a deviated pentagonal bipyramidal environment. The Cd2 center has space-group-imposed $2/m$ symmetry. The cadmium

centers as well as their symmetry-related atoms to form two different trinuclear Cd units, $[Cd_3BrO_2(CO_2)_7]$ and $[Cd_3O_2(CO_2)_8]$ (Fig. 1a). Three cadmium centers in each unit are located in the same line, and the distance between the adjacent Cd atoms in $[Cd_3O_2(CO_2)_8]$ is 3.7734(3) Å. The $[Cd_3BrO_2(CO_2)_7]$ unit is formed through the Br atom substitute the corresponding carboxylate group of $[Cd_3O_2(CO_2)_8]$, and the distances between the adjacent Cd atoms are 3.7291(9) Å and 3.9273(9) Å, respectively.

The $[Cd_3BrO_2(CO_2)_7]$ and $[Cd_3O_2(CO_2)_8]$ units in compound **1** are further connected to adjacent units through the H_2 -DHBDC²⁻ ligands, which lead to the formation of a 3D anionic framework with channels along the a -axis (Fig. 1b). These channels are partly filled with $(C_2H_5)_4N^+$ cations and formed void of 3153.6 Å³, which is 23.1% of the unit cell volume. From the topological point of view, the $[Cd_3BrO_2(CO_2)_7]$ and $[Cd_3O_2(CO_2)_8]$ units can be simplified as 7- and 8-connected nodes, respectively, and the H_2 -DHBDC²⁻ ligands act as linkers. The whole framework of **1** can be topologically represented as a (7, 8)-connected net with point symbol of $(3^4.4^{10}.5^6.6)(3^5.4^{13}.5^9.6)$ (Fig. 1d).

In the structure of **2**, the asymmetric unit contains one and half Cd(II) ion, one $(CH_3)_2NH_2^+$, one coordinated DMF molecule, and one guest DMF molecule. The Cd1 center is coordinated by seven oxygen atoms from four different H_2 -DHBDC²⁻ ligands and one DMF molecule, and the Cd2 center is coordinated by six oxygen atoms from six different ligands. The Cd2 center has space-group-imposed symmetric center. There also exist $[Cd_3O_2(CO_2)_8]$ unit which is much similar to that of **1**, and the adjacent Cd...Cd distance is 3.7749(2) Å. In the structures of **1** and **2**, the H_2 -DHBDC²⁻ ligand have three coordination modes. The first $(k^2)-(k^2)-\mu_2$ -mode is that two carboxylate groups of the ligand chelated to two Cd centers, respectively. The second $(k^1-k^1)-(k^1-k^1)-\mu_4$ -mode is that each carboxylate group in a H_2 -DHBDC²⁻ ligand bridges two Cd

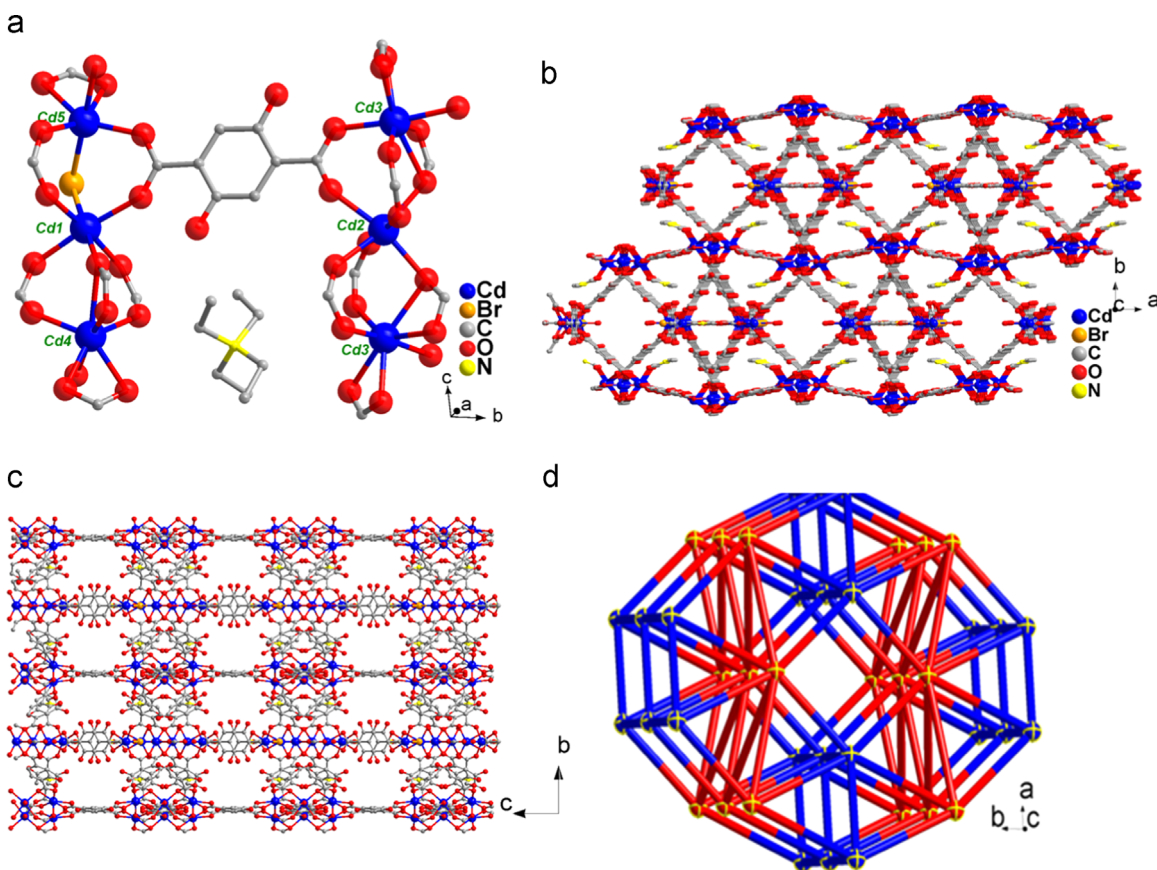


Fig. 1. (a) The coordination environment in compound **1**; (b) (c) the 3D framework of **1** along the c and a -axis; (d) the (7, 8)-connected topology of **1**.

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