

3,5-双(4-羧基-苯氧基)苯甲酸与 1,3-双(咪唑基)丙烷构筑的两个 Cd(II) 金属有机骨架材料的合成、结构及荧光性质

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摘要: 以 3,5-双(4-羧基-苯氧基)苯甲酸(H₃BCPBA)、1,3-双(咪唑基)丙烷(bip)与硝酸镉为反应物,在水热、溶剂热条件下以不同的反应温度和不同的降温速率,分别合成出了 2 种金属-有机骨架(MOF)化合物: {[Cd_{1.5}(BCPBA)(bip)]·H₂O·DMF}_n(**1**)和 [Cd_{1.5}(BCPBA)(bip)_{0.5}(H₂O)]_n(**2**)。通过 X 射线单晶衍射(XRD)确定其结构,并用红外光谱(IR)、元素分析、热重(TG)和粉末 X 射线衍射仪(PXRD)等对其进行表征,并测试了 2 种化合物的荧光属性。结构表明化合物 **1** 中 Cd1 原子先与 3 个 BCPBA³⁻配体配位,形成一个一维链结构,2 个相邻的一维链通过 Cd2 原子由羧基氧桥接在一起。然后由含氮配体将一维的双链连结成一个二维的层结构。化合物 **2** 是一个由新颖的篮子型六连结的三核 Cd(II)二级结构单元(SBUs)构筑的二维层结构。

关键词: 3,5-双(4-羧基-苯氧基)苯甲酸; 1,3-双(咪唑基)丙烷; 金属有机骨架材料; 荧光

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Syntheses, Characterizations and Luminescence Properties of Two Cd(II) Metal-Organic Frameworks Based on 3,5-Bis(4-carboxy-phenoxy)benzoic Acid with N-donor Ligand 1,3-Bis(imidazolyl)propane

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Abstract: Two metal-organic frameworks(MOFs), namely, {[Cd_{1.5}(BCPBA)(bip)]·H₂O·DMF}_n(**1**) and [Cd_{1.5}(BCPBA)(bip)_{0.5}(H₂O)]_n(**2**) (H₃BCPBA=3,5-bis(4-carboxy-phenoxy)benzoic acid, bip=1,3-bis(imidazolyl)propane), have been synthesized under hydrothermal/solvothermal conditions with different reaction temperatures and decreasing temperature rates. Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by infrared spectra(IR), elemental analyses, and thermogravimetric analyses(TGA). In compound **1**, the Cd1 cation is coordinated by three BCPBA³⁻ ligands to form a 1D chain, then two adjacent 1D chain are bridged together by carboxylic oxygen and Cd2 atom. Then the bip ligands join all infinite 1D doublechains into a 2D sheets. In compound **2**, trinuclear Cd(II) secondarily building units (SBUs) can be regarded as 6-connected nodes with the BCPBA³⁻ ligands acting as linkers to form a 2D layered network. Photoluminescence properties of **1** and **2** in solid state at room temperature were studied. CCDC: 1052091, **1**; 1052166, **2**.

Keywords: 3,5-bis(4-carboxy-phenoxy)benzoic acid; 1,3-bis(imidazolyl)propane; metal-organic frameworks; luminescence

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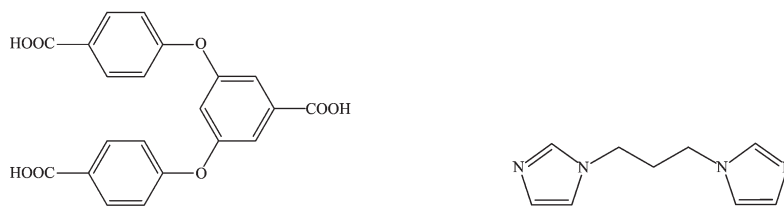
0 Introduction

In recent years, multifunctional metal-organic frameworks (MOFs) have become an attractive prospect^[1]. The major task for synthesizing such functional materials is to choose appropriate ligands (because of their inherent advantages of organic linkers) and inorganic metal cations. Multicarboxylate ligands are often selected as multifunctional organic linkers due to their abundant coordination modes to metal ions, allowing for various structural topologies^[2]. Flexibly N-bridging ligands as auxiliary ligands can freely rotate and adopt a variety of conformations according to the restrictions imposed by the coordination geometry of the metal ions^[3].

The length of a flexible ligand are always inconsistent in different MOFs. As a result, a large number of interesting frameworks incorporating multicarboxylate ligands and flexible ligands have

been reported recently^[4]. For example, in accord with the subjects, 3,5-bis (4-carboxy-phenoxy)benzoic acid (H_3BCPBA)^[2b,5] and 1,3-bis (imidazolyl)propane (bip)^[6] were investigated for the construction of metal-organic coordination polymers.

In this article, with the aim of understanding the coordination chemistry of this versatile ligand and preparing new materials with interesting structural topologies and physical properties, we only focused our attention on the reactions with different solvents and investigated the influence of reaction temperature and decreased temperature rates on the structure of the resultant complexes. In this paper we describe the syntheses, crystal structures and properties of the MOFs, namely, $\{[Cd_{1.5} (BCPBA)(bip)] \cdot H_2O \cdot DMF\}_n$ (**1**), $[Cd_{1.5} (BCPBA) (bip)_{0.5} (H_2O)]_n$ (**2**). Two compounds have been characterized by X-ray crystallography, IR spectra, TG and elemental analysis in detail.



Scheme 1 Molecular structures of ligands

1 Experimental

1.1 Materials and methods

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. TGA was performed on a Perkin-Elmer TG-7 analyzer heated from 30 to 650 °C under nitrogen. The luminescent properties of these compounds were measured on a HITACHI F-7000 spectrometer. Elemental analyses (C, H, N) were performed with a Perkin-Elmer 240c elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D2 PHASER X-ray diffractometer using $Cu K\alpha$ ($\lambda=0.15418$ nm) at a scan speed of $0.1^\circ \cdot s^{-1}$ in the range of $5^\circ \sim 50^\circ$. IR spectra were obtained from KBr pellets on a Perkin-Elmer

580B IR spectrometer in the $400 \sim 4000$ cm^{-1} region.

1.2 Synthesis of $\{[Cd_{1.5} (BCPBA) (bip)] \cdot H_2O \cdot DMF\}_n$ (**1**)

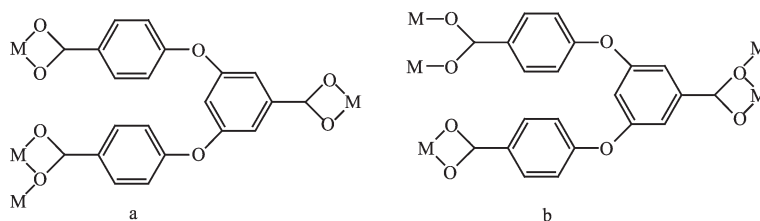
A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0308 g, 0.1 mmol), H_3BCPBA (0.0394 g, 0.1 mmol) and bip (0.0176 g, 0.1 mmol) were added to DMF (8 mL) and H_2O (2 mL), which was placed in a Teflon reactor (20 mL) and heated at 80 °C for 3 days. After gradually cooling to room temperature at a rate of $10^\circ C \cdot h^{-1}$, large quantities of colorless block crystals were obtained and the crystals were filtered off, washed with anhydrous ethyl, and dried under ambient conditions. Yield: 52% based on bip. Anal. Calcd. for $C_{65}H_{61}Cd_3N_9O_{19}$ (%): C, 48.51; H, 3.82; N, 7.83. Found (%): C, 48.43; H, 3.91; N, 7.76 FTIR (KBr, cm^{-1}): 3133 (m), 1665 (s), 1593 (s), 1532 (s),

1 489 (m), 1 362 (s), 1 313(s), 1 279 (s), 1 070 (s), 960 (m), 784 (s), 656(m).

1.3 Synthesis of $[\text{Cd}_{1.5}(\text{BCPBA})(\text{bip})_{0.5}(\text{H}_2\text{O})]_n$ (**2**)

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.030 8 g, 0.1 mmol), H_3BCPBA (0.039 4 g, 0.1 mmol), bip (0.017 6 g, 0.1 mmol) and H_2O (10 mL) was placed in a Teflon reactor (20 mL) and heated at 160 °C for 3 days. After gradually cooling to room temperature at a rate of 20

°C·h⁻¹, large quantities of colorless block crystals were obtained and the crystals were filtered off, washed with ethanol, and dried under ambient conditions. Yield: 61% based on bip. Anal. Calcd. for $\text{C}_{51}\text{H}_{38}\text{Cd}_3\text{N}_4\text{O}_{18}$ (%): C, 45.98; H, 2.88; N, 4.21. Found (%): C, 46.78; H, 2.79; N, 4.15. FTIR (KBr, cm^{-1}): 3 133(m), 1 596 (s), 1 665 (s), 1 592 (s), 1 365 (s), 1 070 (m), 944 (m), 837 (s), 783 (m), 657 (m), 531(m).



Scheme 2 Crystallographically established coordination modes of the carboxylic groups in compounds **1** and **2**

1.4 X-ray crystallography

Single-crystal XRD data for compounds **1** and **2** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromatized $\text{Mo } K\alpha$ radiation ($\lambda = 0.071\ 073$ nm) at 293 (2) K. Absorption corrections were applied using the multiscan technique. All the structures were solved by direct method of SHELXS-97 and refined by the full-matrix least-squares

techniques by using the SHELXL-97^[7] program within WINGX. No-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of the organic ligands were refined as rigid groups. The detailed crystallographic data and structure refinement parameters for **1** and **2** are summarized in Table 1.

CCDC: 1052091, **1**; 1052166, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{65}\text{H}_{61}\text{Cd}_3\text{N}_9\text{O}_{19}$	$\text{C}_{51}\text{H}_{38}\text{Cd}_3\text{N}_4\text{O}_{18}$
Mr	1 609.46	1 332.05
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a / nm	1.657 05(13)	1.068 43(6)
b / nm	1.186 04(9)	1.758 57(10)
c / nm	1.718 67(13)	2.608 96(14)
β / (°)	108.233(2)	100.234 0(10)
V / nm ³	3.208 2(4)	4.824 0(5)
Z	2	4
D_c / ($\text{g} \cdot \text{cm}^{-3}$)	1.663	1.834
μ / mm^{-1}	1.067	1.394
Goodness-of-fit on F^2	1.062	1.102
$R_1, wR_2 [I > 2\sigma(I)]$	0.051 5, 0.132 4	0.032 8, 0.087 8
$R_1, wR_2(\text{all data})$	0.101 0, 0.171 5	0.041 4, 0.099 0

Table 2 Selected bond lengths(nm) and angles(°) for compounds 1 and 2

Compound 1					
N2-Cd1	0.225 9(5)	N3-Cd2	0.216 7(5)	O1-Cd1	0.246 6(5)
O2-Cd1	0.229 0(4)	O5-Cd1 ⁱⁱ	0.244 9(5)	O6-Cd1 ⁱⁱ	0.243 0(4)
O7-Cd1 ⁱⁱⁱ	0.228 2(4)	O8-Cd2	0.231 4(4)	O8-Cd1 ⁱⁱⁱ	0.259 4(4)
Cd1-O7 ^{iv}	0.228 2(4)	Cd1-O6 ^v	0.243 0(4)	Cd1-O5 ^v	0.244 9(5)
Cd1-O8 ^{iv}	0.259 4(4)	Cd2-N3 ^{vi}	0.216 7(5)	Cd2-O8 ^{vi}	0.231 4(4)
O1-C5-Cd1	64.9(3)	O2-C5-Cd1	56.8(3)	C6-C5-Cd1	168.9(4)
C4-N2-Cd1	125.9(4)	C3-N2-Cd1	127.7(5)	C26-N3-Cd2	124.1(4)
C28-N3-Cd2	127.8(4)	C5-O1-Cd1	88.0(4)	C5-O2-Cd1	95.8(4)
C18-O5-Cd1 ⁱⁱ	91.3(4)	C18-O6-Cd1 ⁱⁱ	92.9(3)	C25-O7-Cd1 ⁱⁱⁱ	100.7(4)
C25-O8-Cd2	131.2(3)	C25-O8-Cd1 ⁱⁱⁱ	85.4(3)	Cd2-O8-Cd1 ⁱⁱⁱ	108.71(15)
N2-Cd1-O7 ^{iv}	86.59(17)	N2-Cd1-O2	134.25(17)	O7 ^{iv} -Cd1-O2	122.02(17)
N2-Cd1-O6 ^v	84.60(17)	O7 ^{iv} -Cd1-O6 ^v	148.09(15)	O2-Cd1-O6 ^v	84.97(16)
N2-Cd1-O5 ^v	95.97(19)	O7 ^{iv} -Cd1-O5 ^v	97.96(15)	O2-Cd1-O5 ^v	112.19(18)
O6 ^v -Cd1-O5 ^v	52.79(13)	N2-Cd1-O1	84.55(19)	O7 ^{iv} -Cd1-O1	108.02(17)
O2-Cd1-O1	54.42(17)	O6 ^v -Cd1-O1	101.59(15)	O5 ^v -Cd1-O1	153.99(16)
N(2)-Cd(1)-O(8) ^{iv}	134.77(15)	O7 ^{iv} -Cd1-O8 ^{iv}	52.67(14)	O2-Cd1-O8 ^{iv}	88.65(14)
O6 ^v -Cd1-O8 ^{iv}	118.45(13)	O5 ^v -Cd1-O8 ^{iv}	74.34(14)	O1-Cd1-O8 ^{iv}	122.86(16)
N2-Cd1-C5	109.0(2)	O7 ^{iv} -Cd1-C5	119.91(18)	O2-Cd1-C5	27.38(19)
O6 ^v -Cd1-C5	91.93(16)	O5 ^v -Cd1-C5	134.87(19)	O1-Cd1-C5	27.16(19)
O8 ^{iv} -Cd1-C5	108.44(17)	N3-Cd2-N3 ^{vi}	145.9(3)	N3-Cd2-O8	92.77(16)
N3 ^{vi} -Cd2-O8	112.04(17)	N3-Cd2-O8 ^{vi}	112.04(17)	N3 ^{vi} -Cd2-O8 ^{vi}	92.77(17)
O8-Cd2-O8 ^{vi}	87.6(2)				
Compound 2					
N1-Cd2	0.222 9(3)	O3-C5	0.139 2(4)	O8-Cd1	0.227 4(2)
O7-Cd2	0.220 3(2)	O9-Cd2	0.246 2(3)	O5-Cd2 ^{vi}	0.225 3(3)
O6-Cd2 ^v	0.245 2(3)	O6-Cd2 ^{vi}	0.256 4(3)	O1-Cd1 ^{vii}	0.245 7(3)
O2-Cd1 ^{vii}	0.229 4(3)				
C21-O8-Cd1	143.5(2)	C21-O7-Cd2	104.9(2)	Cd2-O9-H1WA	122(4)
O8-Cd1-O8 ⁱ	138.27(14)	O8-Cd1-O2 ⁱⁱ	90.02(10)	O8 ⁱ -Cd1-O2 ⁱⁱ	89.16(10)
O8-Cd1-O2 ⁱⁱⁱ	89.16(10)	O8 ⁱ -Cd1-O2 ⁱⁱⁱ	90.02(10)	O2 ⁱⁱ -Cd1-O2 ⁱⁱⁱ	177.69(14)
O8-Cd1-O1 ⁱⁱ	113.10(10)	O8 ⁱ -Cd1-O1 ⁱⁱ	99.99(9)	O2 ⁱⁱ -Cd1-O1 ⁱⁱ	54.51(9)
O2 ⁱⁱⁱ -Cd1-O1 ⁱⁱ	127.78(9)	O8-Cd1-O1 ⁱⁱⁱ	99.99(9)	O8 ⁱ -Cd1-O1 ⁱⁱⁱ	113.10(10)
O2 ⁱⁱ -Cd1-O1 ⁱⁱⁱ	127.78(9)	O2 ⁱⁱⁱ -Cd1-O1 ⁱⁱⁱ	54.51(9)	O1 ⁱⁱ -Cd1-O1 ⁱⁱⁱ	74.78(12)
O8-Cd1-C1 ⁱⁱ	103.74(9)	O8 ⁱ -Cd1-C1 ⁱⁱ	93.86(9)	O2 ⁱⁱ -Cd1-C1 ⁱⁱ	27.00(10)
O2 ⁱⁱⁱ -Cd1-C1 ⁱⁱ	155.27(11)	O1 ⁱⁱ -Cd1-C1 ⁱⁱ	27.56(10)	O1 ⁱⁱⁱ -Cd1-C1 ⁱⁱ	101.91(10)

Continued Table 2

O8-Cd1-C1 ⁱⁱⁱ	93.86(9)	O8 ⁱ -Cd1-C1 ⁱⁱⁱ	103.74(9)	O2 ⁱⁱ -Cd1-C1 ⁱⁱⁱ	155.27(11)
O(2) ⁱⁱⁱ -Cd(1)-C(1) ⁱⁱⁱ	27.00(10)	O(1) ⁱⁱ -Cd(1)-C(1) ⁱⁱⁱ	101.91(10)	O1 ⁱⁱⁱ -Cd1-C1 ⁱⁱⁱ	27.56(10)
C(1) ⁱⁱ -Cd(1)-C(1) ⁱⁱⁱ	129.31(16)	O(7)-Cd(2)-N(1)	110.62(10)	O7-Cd2-O5 ^{iv}	123.31(11)
N(1)-Cd(2)-O(5) ^{iv}	118.85(11)	O(7)-Cd(2)-O(6) ^v	87.38(10)	N(1)-Cd(2)-O(6) ^v	82.52(10)
O5 ^{iv} -Cd2-O6 ^v	123.57(9)	O7-Cd2-O9	86.13(13)	N1-Cd2-O(9)	88.34(11)
O5 ^{iv} -Cd2-O9	70.06(11)	O6 ^v -Cd2-O9	166.15(10)	O7-Cd2-O6 ^{iv}	136.08(10)
N1-Cd2-O6 ^{iv}	104.43(10)	O5 ^{iv} -Cd2-O6 ^{iv}	53.19(9)	O6 ^v -Cd2-O6 ^{iv}	71.58(9)
O9-Cd2-O6 ^{iv}	121.06(11)	O7-Cd2-C11 ^{iv}	136.44(10)	N1-Cd2-C11 ^{iv}	112.94(10)
O5 ^{iv} -Cd2-C11 ^{iv}	26.51(10)	O6 ^v -Cd2-C11 ^{iv}	97.99(9)	O9-Cd2-C11 ^{iv}	95.15(11)
O6 ^{iv} -Cd2-C11 ^{iv}	26.74(9)	O6-C11-Cd2 ^{vi}	68.06(18)	O5-C11-Cd2 ^{vi}	53.69(16)
C10-C11-Cd2 ^{vi}	169.3(2)	C11-O5-Cd ^{vi}	99.8(2)	C11-O6-Cd2 ^v	162.5(2)
C11-O6-Cd2 ^{vi}	85.2(2)	Cd2 ^v -O6-Cd2 ^{vi}	103.29(8)	C1-O1-Cd1 ^{vii}	88.1(2)
O2-C1-Cd1 ^{vii}	56.89(18)	O1-C1-Cd1 ^{vii}	64.37(18)	C2-C1-Cd1 ^{vii}	173.8(2)
C1-O2-Cd1 ^{vii}	96.1(2)				

Symmetry codes: ⁱ $-x+1, -y, -z+3$; ⁱⁱ $x+1/2, -y, z+1/2$; ⁱⁱⁱ $x+1, y, z+1$; ^{iv} $x-1, y, z-1$; ^v $x-1/2, -y, z-1/2$; ^{vi} $-x+5/2, y, -z+7/2$ for **1**; ⁱ $-x-1, y, -z+1/2$; ⁱⁱ $-x, y, -z+1/2$; ⁱⁱⁱ $x-1, y, z$; ^{iv} $x-1/2, -y+1/2, z-1/2$; ^v $-x-1/2, -y+1/2, -z+1$; ^{vi} $x+1/2, -y+1/2, z+1/2$; ^{vii} $x+1, y, z$ for **2**

2 Results and discussion

2.1 Structure description of 1

The crystal structure determination reveals that compound **1** crystallizes in a monoclinic space group $P2_1/n$. The asymmetric unit contains one and half Cd(II) cation, one bip ligand, one deprotonated BCPBA³⁻ ligand, one uncoordinated DMF and one H₂O molecule, which are omitted for clarity (Fig.1a). The hydrogen atoms of OW1 were not located. In the asymmetric unit, the Cd1 cation is seven-coordinated by six oxygen atoms belonging to three separated BCPBA³⁻ ligands as well as one nitrogen atom from bip ligands. While the other Cd2 cation is bimonodentate coordinated by two carboxylic O atoms from two BCPBA³⁻ ligands and two nitrogen atoms from two bip ligands to form a distorted tetrahedron geometry (Fig.1a). In an asymmetric unit, three carboxylate groups of the BCPBA³⁻ ligands take the different coordination modes, other two carboxylate groups take the same coordination modes. They all take a chelating in bidentate mode to bridge Cd center while the other carboxylate group adopts a μ_3 -

chelating-bidentate tridentate mode (Scheme 2a). The bond lengths of Cd-O bond distance vary in the range of 0.228 4(4)~0.246 7(5) nm and the Cd-N bond distance is 0.216 6(5)~0.226 1(5) nm. All the distances and bond angles are within the normal range (Table 2).

The Cd1 cation is coordinated by three carboxylic O atoms from three BCPBA³⁻ ligands to form a 1D chain (Fig.1b). Then two adjacent 1D chain are bridged together by carboxylic oxygen and Cd2 atom (Fig.1c,d). Then the N ligands join all infinite 1D double chains into a 2D sheets (Fig.1e). The sheets are stacked fashion and form a 3D framework.

2.2 Structure description of 2

The crystal structure determination reveals that compound **2** crystallizes in a monoclinic space group $C2/c$. The asymmetric unit contains one and half Cd(II) cation, a half of bip ligand and one deprotonated BCPBA³⁻ ligand and one coordinated H₂O molecule. In the asymmetric unit, the Cd1 cation is coordinated by six carboxylic O atoms from four BCPBA³⁻ ligands forming a distorted octahedron environment. While the Cd2 cation exists in a distorted octahedron geometry, being ligated by five oxygen atoms from four BCPBA³⁻

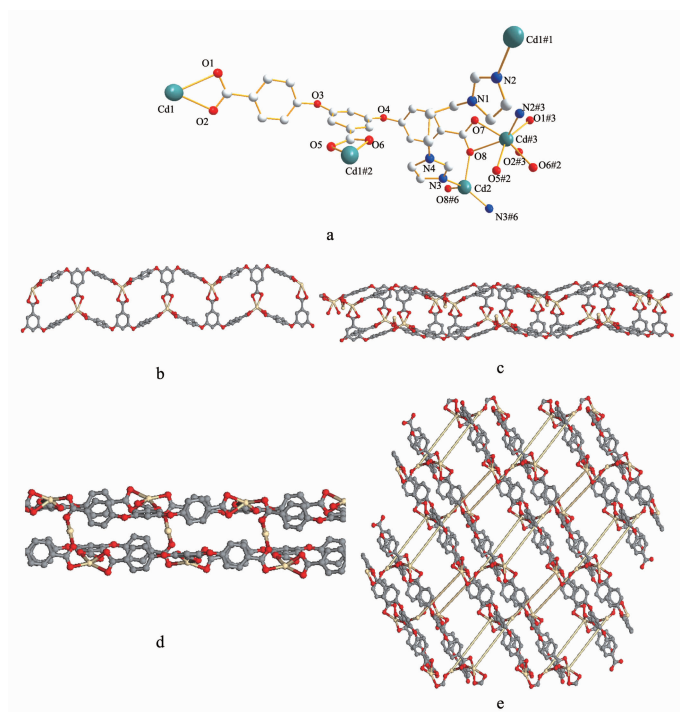


Fig.1 (a) Coordination environment of the Cd(II) ions in compound **1**; (b) View of 1D chain; (c,d) View of double chain; (e) A schematic view of the 2D sheet

ligands and one H₂O molecule and one nitrogen atom from one bip ligand(Fig.2a).

In an asymmetric unit, the wholly deprotonated BCPBA³⁻ anion adopts different coordination modes to

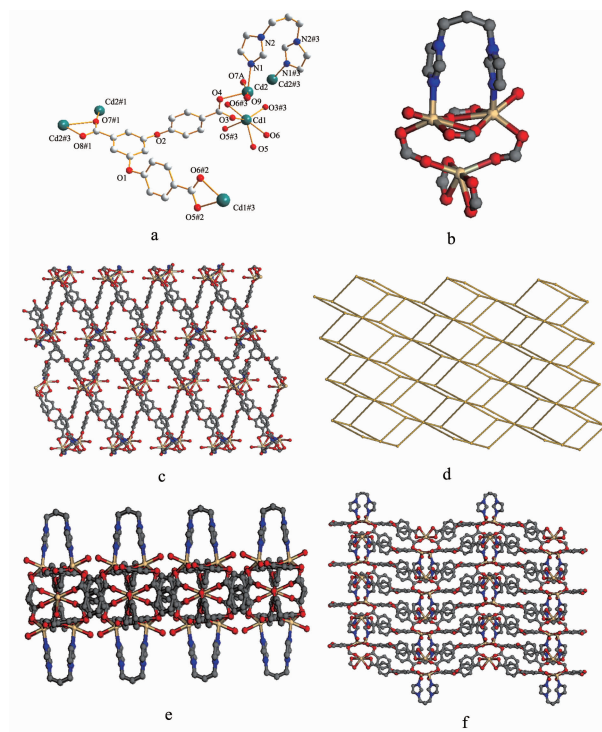


Fig.2 (a) Coordination environment of the Cd(II) ions in compound **2**; (b) Trinuclear Cd(II) SBUs; (d) Simplified topological consideration of the 2D sheet;(c, e, f) A schematic view of the 2D sheet

bridge Cd centers (Scheme 2b). The bond lengths of Cd-O bond distance vary in the range of 0.220 3(2)~0.256 4(3) nm and the Cd-N bond distance is 0.222 9(3) nm. All the distances and bond angles are within the normal range (Table 2). In this compound, the BCPBA³⁻ ligands bridge three Cd(one Cd1 and two Cd2) centers to form [Cd₃(CO₂)₆] clusters (Cd1-Cd2 0.401 3 nm; Cd2-Cd2 0.393 4 nm). Then, the two Cd2 atom are connected by the bip ligand to form a baskets clusters which can be compared with the structures reported previously(Fig.2b)^[8].

The trinuclear Cd(II) SBUs can be regarded as 6-connected nodes with the BCPBA³⁻ ligands acting as linkers to form a 2D layered network (Fig.2c,d). The sheets are stacked fashion and form a 3D framework.

2.3 Thermal analysis

The thermal stabilities of compounds **1** and **2** were investigated by thermogravimetric analyses(TGA) (Fig.3). The experiments were performed on samples consisting of numerous single crystals of **1** or **2** under nitrogen atmosphere with a heating rate of 10 °C · min⁻¹. The compound **1** showed a slow weight loss form 30 to 255 °C, corresponding to the exclusion of uncoordinated DMF and H₂O molecules. The destruction of the framework occurred at *ca.* 300 °C. The remaining weight might correspond to the formation of CdO (Obsd. 24.91%, Calcd. 23.94%). The Compound **2** showed a slow weight loss form 30 to 300 °C, corresponding to the loss of coordinated H₂O molecules. Then its framework began to destruct at *ca.* 400 °C, and finally the stoichiometric amount of CdO formed as residue (Obsd. 29.00%, Calcd.

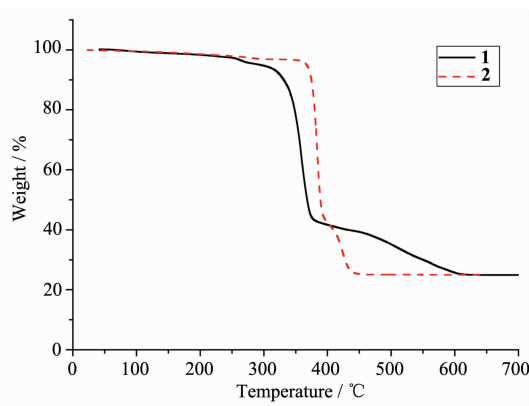


Fig.3 TGA curves of compounds **1** and **2**

28.92%).

2.4 Photoluminescence properties

The luminescent properties of the compounds **1**, **2**, H₃BCPBA and bip were investigated separately in the solid state at room temperature, as shown in Fig.4. The excitation maxima for H₃BCPBA and bip are at 370 and 345 nm, and the maxima emission of spectra are at 424 and 440 nm (shoulder peak). The emission peaks were at 424 nm for compound **1** (λ_{ex} =360 nm), while compound **2** shows a red-shift in emission at λ_{em} =438 nm when λ_{ex} =343 nm, which may be assigned to ligand to metal charge transfer (LMCT)^[9].

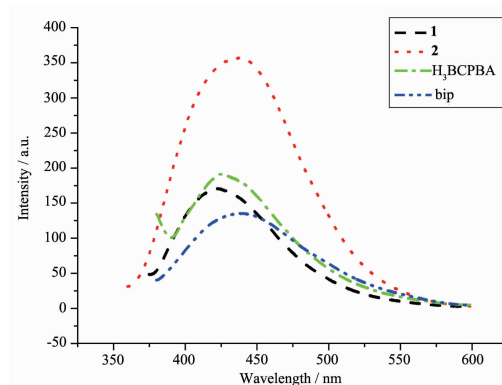


Fig.4 Solid-state emission spectra of compounds **1**, **2**, H₃BCPBA and bip at room temperature

2.5 XRD analysis

To confirm the phase purity and to examine the crystallinity of bulk samples, the X-ray powder diffraction patterns of the compounds were recorded. As shown in Fig.5, the peak positions of simulated and experimental patterns are in good agreement with each other, demonstrating the phase purity of the product. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

3 Conclusions

In this study, two metal-organic frameworks have been synthesized successfully under hydrothermal conditions with different solvents, temperatures and decreasing temperature rates by using the flexible carboxylic acid and the N-donor ligands as auxiliary ligands. Their structural differences indicates that the solvothermal conditions have remarkable influence on

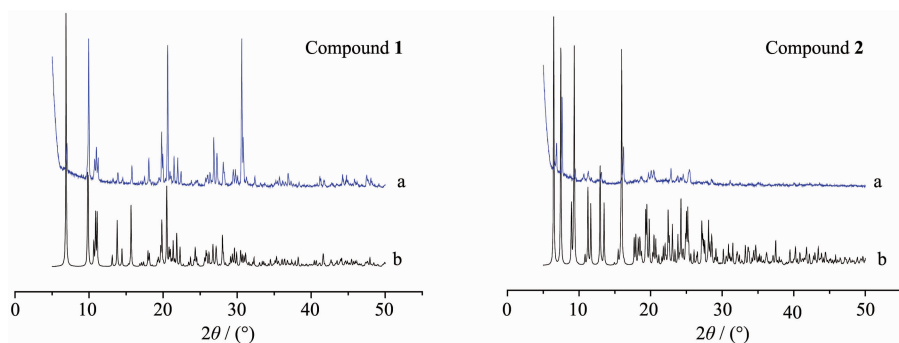


Fig.5 Experimental(a) and simulated(b) XRD patterns of compound 1 and 2

the resultant topologies. The results also show that the flexible carboxylic acid are good candidates for the construction of high dimensional MOFs.

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