

金属离子导向的 2,2'-联苯甲酸和 1,4-二(1-苯并咪唑基甲基)苯构筑的配合物的合成、结构和性质

杨玉亭* 屠长征 姚立峰 许丽丽 王君师 尹红菊 汪 帆
(曲靖师范学院化学与环境科学学院, 曲靖 655011)

摘要: 在溶剂热条件下合成并表征了 2 个基于 2,2'-联苯甲酸(H_2dpa)和 1,4-二(1-苯并咪唑基甲基)苯($bbix$)的配位聚合物: $[Cu_2(bbix)(dpa)_2(C_2H_5OH)_2]_n$ (**1**), $\{[Cd(bbix)_{0.5}(dpa)] \cdot 0.5H_2O\}_n$ (**2**)。两者均显示二维结构。**1** 中含有 Cu-dpa 螺旋链, $bbix$ 进而将螺旋链连接形成以 Cu(II)离子为 3-连节点的 6^3 波浪状网格。而在配合物 **2** 中, dpa^{2-} 与 Cd(II)形成四元环和八元环交替连接而成的带状一维链, 并由 $bbix$ 连接得到二维网格。此外, 还研究了 **1** 和 **2** 的热稳定性以及室温下 **2** 的荧光性能。

关键词: 配位聚合物; 晶体结构; 2,2'-联苯甲酸; 1,4-二(1-苯并咪唑基甲基)苯; 荧光

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Metal Ions Tuned Architectures Based on Diphenic Acid and 1,4-Bis(benzimidazol-1-ylmethyl)-benzene: Syntheses, Structures and Properties

YANG Yu-Ting* TU Chang-Zheng YAO Li-Feng XU Li-Li WANG Jun-Shi YIN Hong-Ju WANG Fan
(College of Chemistry and Environmental Science, Qujing Normal University, Qujing, Yunnan 655011, China)

Abstract: Two novel complexes, $[Cu_2(bbix)(dpa)_2(C_2H_5OH)_2]_n$ (**1**) and $\{[Cd(bbix)_{0.5}(dpa)] \cdot 0.5H_2O\}_n$ (**2**) (H_2dpa = diphenic acid, $bbix$ = 1,4-bis(benzimidazol-1-ylmethyl)-benzene), were synthesized and structurally characterized under solvothermal conditions. Both **1** and **2** exhibit two-dimensional (2D) architecture. Complex **1** has 6^3 wave-like layer consisting of Cu-dpa helical chains in which the Cu(II) ions as 3-connecting nodes. While the layer structure of **2** consists of one-dimensional chains containing alternated 4-membered and 8-membered rings. Furthermore, the solid-state properties of thermal stability for all crystalline materials and the fluorescence property of **2** at room temperature have been investigated. CCDC: 1831070, **1**; 1831071, **2**.

Keywords: coordination polymer; crystal structure; diphenic acid; 1,4-bis(benzimidazol-1-ylmethyl)-benzene; fluorescence

0 Introduction

The design and syntheses of coordination polymers (CPs) has become more and more popular in the field of crystal engineering because of the intriguing variety of architectures topologies and potential applications in gas adsorption, magnetism, and luminescence^[1-7]. It

is well known that the synthesis of coordination polymers through self-assembly can be influenced by several factors such as temperatures, pH values, solvents, metal ions, the ligands, cations and/or anions. Until now, although a large number of CPs has been reported, the construction of novel architectures and a systematic research still remain a long-term

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*通信联系人。E-mail: 18288438002@163.com

challenge.

Multidentate N or O donor ligands have been employed extensively as organic spacers in the construction of extended structures^[8-14]. Among the family of multidentate O-donor ligands, diphenic acid (H_2dpa) is a flexible ligand in which the carboxyl groups may not be coplanar to the phenyl ring because of steric hindrance in the coordination process^[15-26]. It is apt to generate helical chains with different transitional metals^[18-21]. However, the investigation of H_2dpa has been far less common in the construction of Cps, which does not readily fit into a predictable template due to their structural flexibility and conformational freedom. As for the N-donor ligands, bimidazole-containing ligands have proven to be good candidates for the construction of new CPs for their diverse coordination modes. Among them, the 1,4-bis(benzimidazol-1-ylmethyl)-benzene (bix) group has strong coordination ability and the $\pi \cdots \pi$ interactions between their aromatic rings are of benefit for the stabilizations of the Cps as well^[27-29]. As a derivative of bix, the semi-rigid bbix synthon incorporating two bulky benzene rings, which will enhance the donated electrons ability and make it exhibit stronger collaborative coordination ability with organic carboxylate ligands^[30-35]. However, the two bulky benzene rings also will cause steric crowding on central metal atoms^[33]. Whether the bbix ligand can satisfy the coordination needs of the central metal atoms and consequently generate more robust and intricate networks? Thus, it is significant to research Cps based on bbix and organic aromatic polycarboxylate ligands. Considering aforementioned facts, herein we extended our previous work to assemble Cu(II)/Cd(II) coordination polymers with bbix and H_2dpa ligands, $[Cu_2(bbix)(dpa)_2(C_2H_5OH)_2]_n$ (**1**) and $\{[Cd(bbix)_{0.5}(dpa)] \cdot 0.5H_2O\}_n$ (**2**), to comparatively study the role in the self-assembly and the structural diversity played by the metal ions. Both **1** and **2** were synthesized under hydrothermal conditions and characterized by elemental analysis (EA), infrared (IR), X-ray crystallography, and thermogravimetric analysis (TGA). The fluorescence property of complex **2** was also studied.

1 Experimental

1.1 Materials and measurements

All commercially available chemicals were of reagent grade and were used as received without further purification. The ligand 1,4-bis(benzimidazol-1-ylmethyl)-benzene (bbix) was synthesized by literature procedure^[36]. Acetonitrile, toluene and diethyl ether were pre-dried with activated molecular sieves and heated at reux over the appropriate drying agents under argon. The infrared spectra were performed on a Varian FT-IR 640 spectrometer with KBr pellets in the $400 \sim 4\,000\text{ cm}^{-1}$ region. Elemental analyses were measured on a Perkin-Elmer 2400 elemental analyzer (C, H and N). Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/MAX-III C powder diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\,18\text{ nm}$) in the 2θ range of $5^\circ \sim 30^\circ$ in which the X-ray tube was operated at 40 kV and 40 mA. Thermogravimetric analyses (TGA) were taken on a Pyris Diamond TG/DTA instrument in flowing N_2 with a heating rate of $5\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

1.2 Preparation of complex 1

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.5 mmol, 0.12 g), bbix (0.25 mmol, 0.09 g) H_2dpa (0.5 mmol, 0.11 g), distilled water (3 mL) and ethanol (95%, 3 mL) was placed in a Teflon-lined stainless steel vessel. The pH value was adjusted to 7 by addition of NaOH solution ($0.5\text{ mol} \cdot \text{L}^{-1}$). The mixture was sealed and heated at $160\text{ }^\circ\text{C}$ for 3 days, and cooled to room temperature at a rate of $5\text{ }^\circ\text{C} \cdot \text{h}^{-1}$. Green block-shaped crystals were filtered off and dried in air. Yield: 51% (based on Cu). Elemental analysis Calcd. for $C_{54}H_{46}Cu_2N_4O_{10}$ (%): C 62.48, H 4.47, N 5.40. Found(%): C 62.35, H 4.36, N 5.28. IR (KBr, cm^{-1}): 3 107(m), 2 795(m), 1 629(s), 1 573(s), 1 507(m), 1 448(m), 1 420(m), 1 389(s), 1 264(m), 1 049(m), 870(s), 748(s).

1.3 Preparation of complex 2

Complex **2** was synthesized in a similar way to **1**, except that $Cu(NO_3)_2 \cdot 3H_2O$ was replaced by $Cd(NO_3)_2 \cdot 4H_2O$ (0.5 mmol, 0.15 g). Colorless block-shaped

crystals were filtered off and dried in air. Yield: 57% (based on Cd). Elemental analysis Calcd. for $C_{25}H_{16}CdN_2O_{4.5}$: C 56.78, H 3.05, N 5.30. Found(%): C 56.96, H 3.41, N 5.22. IR (KBr, cm^{-1}): 3 430 (m), 2 990(m), 1 605(s), 1 560(s), 1 512(m), 1 381(m), 1 295(m), 1 193 (s), 863(m), 837(s), 810(s).

1.4 X-ray crystallography and structure determination

The well-shaped single crystals of **1** and **2** were selected for X-ray diffraction study. The intensity data were collected on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo $K\alpha$

($\lambda = 0.071\ 073\ nm$) radiation. Multiscan absorption corrections were applied with the SADABS program^[37]. The structures were solved by direct method using SHELXS program of the SHELXTL-97 package and refined by full-matrix least-squares fitting on F^2 by SHELXL-97^[38-39]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of organic ligands were located geometrically. The crystal data and structure refinement parameters for **1** and **2** are summarized in Table 1. Selected bond distances and angles are listed in Table 2 and 3.

CCDC: 1831070, **1**; 1831071, **2**.

Table 1 Crystallographic data for **1** and **2**

| | 1 | 2 |
|-----------------------------------------------------|---------------------------------------|--------------------------------------|
| Formula | $C_{54}H_{46}Cu_2N_4O_{10}$ | $C_{25}H_{16}CdN_2O_{4.5}$ |
| Formula weight | 1 038.03 | 528.80 |
| T / K | 293(2) | 293(2) |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | $C2/c$ |
| a / nm | 1.255 7(3) | 1.524 0(3) |
| b / nm | 1.752 9(4) | 2.512 9(5) |
| c / nm | 2.097 5(4) | 1.211 3(2) |
| $\beta / (^\circ)$ | | 113.31(3) |
| V / nm^3 | 4.616 8(16) | 4.260 2(14) |
| Z | 4 | 8 |
| $D_c / (g \cdot cm^{-3})$ | 1.493 | 1.649 |
| $F(000)$ | 2 144 | 2 112 |
| θ range / $(^\circ)$ | 3.00~27.48 | 3.05~27.48 |
| Limiting indices (h, k, l) | -16~-14, -22~-22, -27~-26 | -19~-19, -32~-32, -15~-15 |
| Reflection collected, unique | 43 885, 10 569 ($R_{int}=0.077\ 1$) | 20 630, 4 862 ($R_{int}=0.091\ 5$) |
| Flack parameter | 0.004(9) | |
| GOF on F^2 | 0.964 | 1.037 |
| $R_1, wR_2 [I > 2\sigma(I)]^*$ | 0.041 8, 0.081 3 | 0.043 8, 0.098 9 |
| R_1, wR_2 (all data) | 0.069 4, 0.087 9 | 0.059 9, 0.106 3 |
| Largest diff. peak and hole / ($e \cdot nm^{-3}$) | 273 and -322 | 554 and -1 210 |

$$^* R_1 = \sum ||F_o| - |F_c|| / |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) for complex **1**

| | | | | | |
|-------------------|------------|-------------------|------------|-----------------|------------|
| Cu(1)-O(5)#2 | 0.209 6(2) | Cu(1)-O(6)#2 | 0.196 8(2) | O(5)-Cu(1)#1 | 0.209 6(2) |
| O(6)-Cu(1)#1 | 0.196 8(2) | Cu(1)-O(8) | 0.191 3(2) | Cu(1)-O(9) | 0.221 0(3) |
| Cu(1)-N(4) | 0.197 2(3) | Cu(2)-O(1) | 0.198 8(2) | Cu(2)-O(4)#3 | 0.191 9(2) |
| Cu(2)-O(2) | 0.208 1(2) | O(4)-Cu(2)#4 | 0.191 9(2) | Cu(2)-O(10) | 0.222 7(3) |
| Cu(2)-N(1) | 0.196 7(3) | | | | |
| O(8)-Cu(1)-O(6)#2 | 164.47(9) | O(6)#2-Cu(1)-N(4) | 94.04(10) | O(8)-Cu(1)-N(4) | 100.77(10) |

Continued Table 2

| | | | | | |
|-------------------|-----------|---------------------|-----------|-------------------|------------|
| O(8)-Cu(1)-O(5)#2 | 100.02(9) | O(6)#2-Cu(1)-O(5)#2 | 64.45(8) | N(4)-Cu(1)-O(5)#2 | 153.33(10) |
| O(8)-Cu(1)-O(9) | 90.11(12) | O(6)#2-Cu(1)-O(9) | 91.47(11) | N(4)-Cu(1)-O(9) | 101.66(13) |
| O(5)#2-Cu(1)-O(9) | 94.82(11) | O(4)#3-Cu(2)-N(1) | 99.79(10) | O(4)#3-Cu(2)-O(1) | 165.05(9) |
| N(1)-Cu(2)-O(1) | 94.96(10) | O(4)#3-Cu(2)-O(2) | 101.05(9) | N(1)-Cu(2)-O(2) | 151.02(10) |
| O(1)-Cu(2)-O(2) | 64.29(8) | O(4)#3-Cu(2)-O(10) | 89.44(10) | N(1)-Cu(2)-O(10) | 105.83(11) |
| O(1)-Cu(2)-O(10) | 88.83(9) | O(2)-Cu(2)-O(10) | 94.31(10) | | |

Symmetry codes: #1: $x-1/2, -y+1/2, -z$; #2: $x+1/2, -y+1/2, -z$; #3: $x+1/2, -y+3/2, -z$; #4: $x-1/2, -y+3/2, -z$.

Table 3 Selected bond lengths (nm) and bond angles ($^{\circ}$) for complex 2

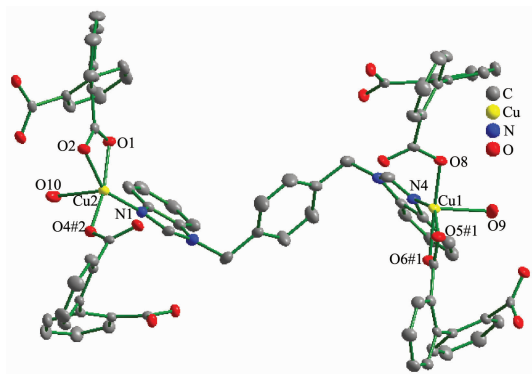
| | | | | | |
|---------------------|------------|---------------------|------------|-------------------|------------|
| Cd(1)-O(4) | 0.223 1(2) | Cd(1)-O(3)#3 | 0.223 1(3) | Cd(1)-O(2)#1 | 0.229 8(3) |
| Cd(1)-O(1)#1 | 0.239 6(3) | O(1)-Cd(1)#1 | 0.239 6(3) | O(2)-Cd(1)#1 | 0.229 8(3) |
| O(3)-Cd(1)#3 | 0.223 1(3) | Cd(1)-N(1) | 0.224 3(3) | | |
| O(4)-Cd(1)-O(3)#3 | 98.31(9) | O(4)-Cd(1)-N(1) | 112.46(10) | O(3)#3-Cd(1)-N(1) | 92.11(11) |
| O(4)-Cd(1)-O(2)#1 | 94.15(9) | O(3)#3-Cd(1)-O(2)#1 | 122.58(11) | N(1)-Cd(1)-O(2)#1 | 133.08(11) |
| O(4)-Cd(1)-O(1)#1 | 147.79(9) | O(3)#3-Cd(1)-O(1)#1 | 91.65(10) | N(1)-Cd(1)-O(1)#1 | 97.58(11) |
| O(2)#1-Cd(1)-O(1)#1 | 55.31(9) | | | | |

Symmetry codes: #1: $-x, -y, -z+1$; #2: $-x+1, -y, -z+2$; #3: $-x, y, -z+1/2$.

2 Results and discussion

2.1 Structural description of 1

The results of single crystal X-ray analysis shows that complex **1** crystallizes in orthorhombic $P2_12_12_1$ space group. There are one crystallographically independent Cu(II) ion, one dpa^{2-} anion, half bbix ligand, and one $\text{C}_2\text{H}_5\text{OH}$ molecule in the asymmetric unit of **1**. As shown in Fig.1, both Cu1 and Cu2 ions are five-coordinated with the similar distorted square-based pyramidal geometry ($\tau=0.18$ for Cu1, $\tau=0.23$ for Cu2)^[40].

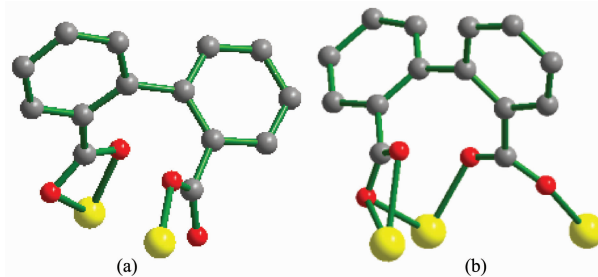


Atoms are drawn at the 30% probability level; Symmetry codes: #1: $-0.5+x, 1.5-y, 1-z$; #2: $0.5+x, 2.5-y, 1-z$; Hydrogen atoms and lattice water molecule are omitted for clarity

Fig.1 View of the local coordination environment for Cu(II) ions in **1**

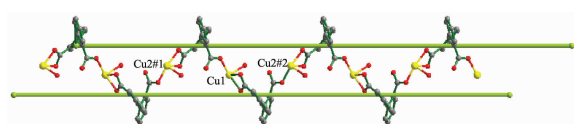
All the Cu(II) ions are coordinated by three oxygen atoms from different carboxyl groups, one oxygen atom from the coordinated ethanol molecule and one nitrogen atom from a bridging bbix ligand. The bond lengths of Cu-O are in the range of 0.191 3(2) nm to 0.222 7(3) nm, and those of Cu-N bond are 0.197 2(3) and 0.196 7(3) nm, which are typical values for Cu-N and Cu-O coordination distances.

Each dpa^{2-} bridges two central Cu(II) atoms through $\mu_1-\eta^1:\eta^0$ (monodentate) and $\mu_1-\eta^1:\eta^1$ (chelation) carboxylate groups (Scheme 1a). The dihedral angle between two phenyl rings in dpa^{2-} is 55.53° , and the carboxylate groups are out of the plane of correspondingly linking phenyl rings with the dihedral angles between them being 29.43° and 55.52° . A dramatic twisting is observed between two carboxylate



Scheme 1 Coordination modes of dpa^{2-} ligands in complexes **1** and **2**

groups in dpa^{2-} anion with the dihedral angle being 38.37° . The combination of these twists results in the formation of Cu-dpa helical chain (Fig.2). The Cu1 bridged by dpa^{2-} and the distance of helical pitch within the chain is 1.255 70 nm, which is larger than those in helical complexes $[\text{M}(\text{dpa})(\text{H}_2\text{O})_4]_n$ ($\text{M}=\text{Co}(\text{II}), \text{Ni}(\text{II})$)^[16-17], $[\text{Cu}_2(\text{dpp})_2(\text{H}_2\text{O})_2(\text{dpa})_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}]_n$ ($\text{dpp}=1,3\text{-di}(4\text{-pyridyl})\text{propane}$)^[19], indicating that the introduction of bbix has certain effect on the helical framework. While the bbix ligand displays two different $\text{N}_{\text{donor}} \cdots \text{N}-\text{C}_{\text{sp}^3} \cdots \text{C}_{\text{sp}^3}$ torsion angle values of 69.83° and 96.54° ,



Symmetry codes: #1: $-0.5+x, 0.5-y, -z$; #2: $0.5+x, 0.5-y, -z$

Fig.2 View of the left- and right-handed helices chains in **1**

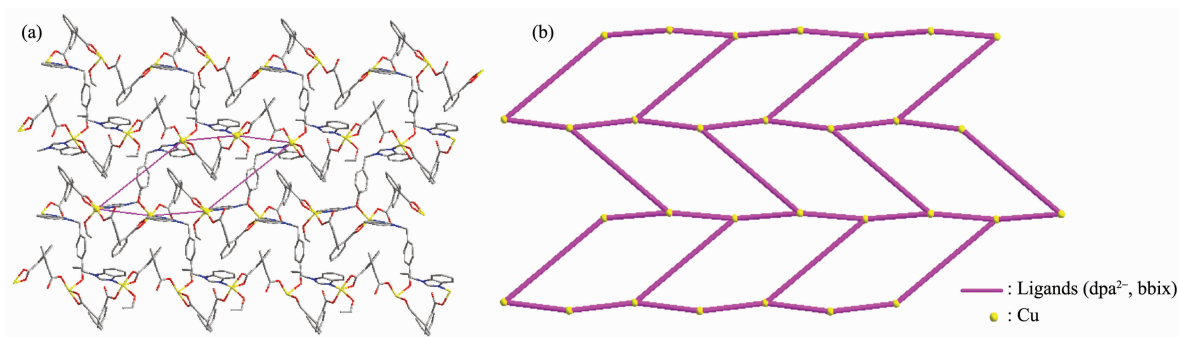


Fig.3 (a) View of 2D layered structure in **1**; (b) Schematic representation of the 6^3 framework

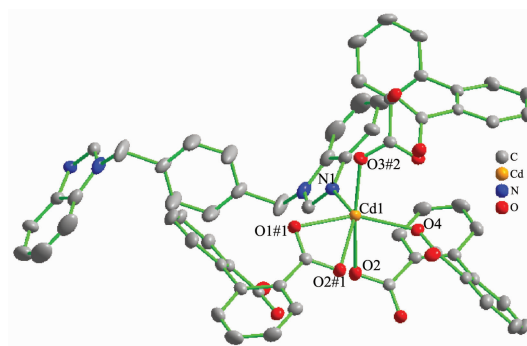
2.2 Structural description of **2**

When Cu(II) ion in **1** was replaced by Cd(II) ion, which has different coordination geometry and larger radius, complex **2** was synthesized in the same reaction condition. Complex **2** crystallizes in triclinic system, space $P\bar{1}$ group, and exhibits 2D structure. The asymmetric unit of **2** consists of one Cd(II) ion, one dpa^{2-} ligand, half bbix ligand, and half lattice water molecule. As shown in Fig.4, the Cd(II) ion is hexacoordinated by one nitrogen atom from flexible bbix ligand and five carboxylate oxygen atoms from three different dpa^{2-} to finish a distorted octahedral coordination geometry. The bond distances of Cd-O in **2** fall in the range of 0.223 1(2)~0.239 6(3) nm, and the Cd-N length is 0.224 3(3) nm, all of which are comp-

and dihedral angles between benzimidazole and phenyl rings are 80.62° and 85.94° .

The bridging ligand bbix adopts bis-monodentate coordination mode, and displays *trans*-conformation, the $\text{Cu} \cdots \text{Cu}$ distance across bbix ligands is 1.255 6 nm. The above-mentioned helical chains are connected by bbix ligands to form a 2D wave-like layer consisting of the hexagonal meshes with the size of $0.636\ 0\ \text{nm} \times 0.638\ 5\ \text{nm} \times 1.255\ 6\ \text{nm}$ (Fig.3a). The distance between adjacent layers is 1.033 21 nm. From topological point of view, the Cu(II) atoms can be regarded as nodes, dpa^{2-} and bbix ligands as connectors, so the 2D layer can be simplified to a 3-connected 6^3 net (Fig.3b). The structure characteristics of **1** are similar to the complex reported by Wang et al.^[19]. However, there are no significant supramolecular interactions such as H-bonds and $\pi\text{-}\pi$ interactions are observed between 6^3 layers.

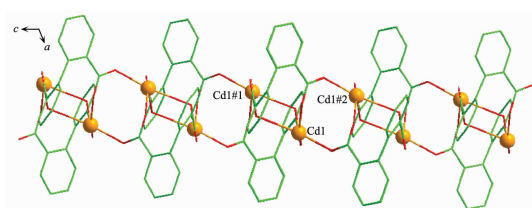
able to those documented values in the previous literature^[14-15,29].



Hydrogen atoms and lattice water molecule are omitted for clarity; Atoms are drawn at the 30% probability level; Symmetry codes: #1: $-x, -y, 1-z$; #2: $-x, y, 0.5-z$

Fig.4 View of the local coordination environment for Cd(II) ions in **2**

The carboxylate groups of dpa^{2-} bridge three Cd(II) centers through uncommon $\mu_3:\eta^1, \eta^2, \eta^1, \eta^1$ coordination mode, which is never reported in the literature (Scheme 1b). The carboxylate groups are out of the plane of correspondingly linking phenyl rings with the dihedral angles between them being 1.83° and 37.94° , respectively. A more obvious twisting between two phenyl rings in dpa^{2-} is observed with the dihedral angle between them being 62.39° . The combination of these twisting allows dpa^{2-} to link Cd(II) centers into a one-dimensional chain containing alternated 4-membered and 8-membered ($-\text{Cd}-\text{O}-\text{C}-\text{O}-$) rings (Fig.5).



Symmetry codes: #1: $-x, -y, 1-z$; #2: $-x, y, 0.5-z$

Fig.5 View of one-dimensional chain formed by dpa^{2-} and Cd(II) atoms in **2**

Similar to **1**, the bridging ligand bbix adopts bis-monodentate coordination mode, and displays *trans*-conformation with a $\text{N}_{\text{donor}} \cdots \text{N}-\text{C}_{\text{sp}^3} \cdots \text{C}_{\text{sp}^3}$ torsion angle value of 95.95° , and dihedral angles between two benzimidazole and phenyl rings are very closely (76.94° and 76.72°). The $\text{Cd} \cdots \text{Cd}$ distance across bbix ligands is 1.4814 nm , which is slightly longer than $\text{Cu} \cdots \text{Cu}$ distance in **1**. Aforementioned chains are connected by bbix ligands to form a 2D wave-like layer (Fig.6).

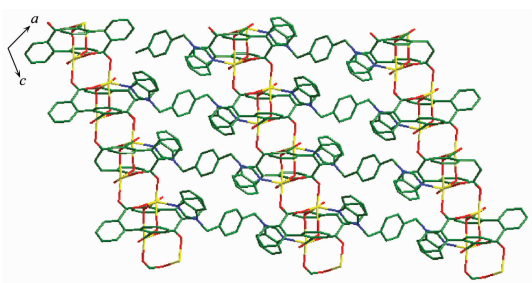


Fig.6 View of two-dimensional layered structure in **2**

2.3 Thermogravimetric analysis and PXRD

Thermogravimetric analysis (TGA) was carried out to study the thermal behavior of the frameworks.

The experiments were performed on samples consisting of numerous single crystals of each complex under a N_2 atmosphere with a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$ (Fig. 7). For complex **1**, the TGA curve showed the loss of coordinated ethanol molecules between 95 and 275°C (Calcd. 8.9% , Obsd. 8.9%). After that, the further weight losses are attributed to the decomposition of **1**. The first weight loss in complex **2** occurred before 90°C , implying removal of the free water molecule (Calcd. 1.7% , Obsd. 1.8%). So, the framework is stable up to 307°C , at which point the removal of organic ligands can ensure.

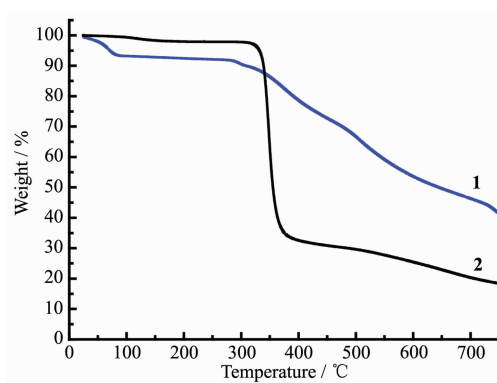
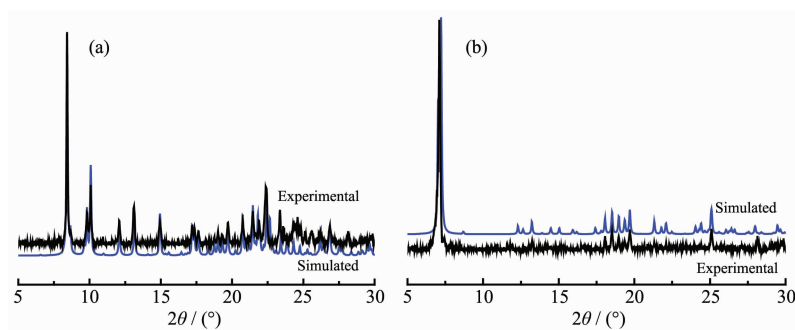


Fig.7 TGA curves of complexes **1** and **2**

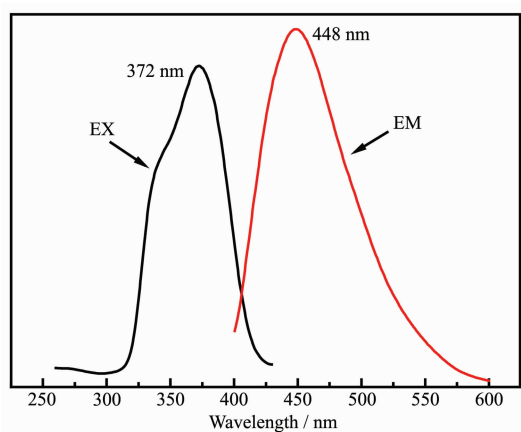
The purities and crystallinities of the bulk samples for complexes **1** and **2** were checked by powder X-ray diffraction (PXRD). The measured PXRD patterns very closely matched the simulated patterns generated from the results of single-crystal diffraction data of **1** and **2** (Fig.8), indicative of pure products. The observed differences in intensity could be due to preferred orientation of the powder samples.

2.4 Photoluminescence properties

Coordination polymers with d^{10} metal centers and conjugated organic linkers are promising candidates for photoactive materials with potential applications such as chemical sensors and photochemistry. Hence, the solid state fluorescence properties of Cd(II) -complex **2** was investigated at room temperature. As shown in Fig.9, complex **2** shows the emission maximum at 448 nm ($\lambda_{\text{ex}}=372 \text{ nm}$). It is known that free dpa^{2-} and bbix ligands display a photoluminescent emission at 415 and 376 nm , respectively^[31,41]. In contrast to the free ligands, the emission maxima of **3**

Fig.8 PXRD patterns of **1** and **2**

is red-shifted, which may be assigned as the metal-to-ligand charge transfer^[42-43].

Fig.9 Solid-state fluorescent spectrum of **2** at room temperature

3 Conclusions

In conclusion, we have described construction of two new coordination polymers of Cu(II) and Cd(II) ions using diphenic acid (H_2dpa) and 1,4-bis(benzimidazol-1-ylmethyl)-benzene (bbix) as ligands under hydrothermal conditions. Complex **1** exhibits a two-dimensional 6^3 wave-like network structure, which consists of Cu-dpa helical chains. The dimensions of the hexagonal meshes with the size of $0.636\ 0\ nm \times 0.638\ 5\ nm \times 1.255\ 6\ nm$. Differently, the layer architecture of **2** consists of one-dimensional chain containing alternated 4-membered and 8-membered (-Cd-O-C-O-) rings. Meanwhile, the dpa^{2-} ligand displays different coordination modes in the two complexes. The successful synthesis of **1** and **2** further enriches crystal engineering methods that can provide new perspectives for design and fabrication of different networks, and such results also reveal that the kinds of metal ions have a

great influence on the final structures. Furthermore, solidstate emission characteristic of **2** presents new vistas for materials design.

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