

## 基于一种柔性双咪唑和不同双羧基配体构筑的两例镉(II)的配位聚合物

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**摘要:** 在水热条件下合成了 2 个新颖的镉(II)配位聚合物:  $[\text{Cd}_2(\mu_2\text{-H}_2\text{O})(1,5\text{-Bip})(\text{Tpa})_2]_n$  (**1**) 和  $[\text{Cd}(1,5\text{-Bip})(\text{Oba})]_n$  (**2**) ( $\text{H}_2\text{Oba}=4,4'$ -二羧酸二苯甲醚,  $\text{H}_2\text{Tpa}$ =对苯二甲酸,  $1,5\text{-Bip}$ =1,5-二(咪唑基)戊烷)。并通过 X 射线单晶衍射, 粉末 XRD、红外光谱、元素分析以及热重分析对其结构进行表征。单晶解析结果表明: 配位聚合物 **1** 是一个单节点 5 连接( $4^6.6^4$ )拓扑三维空间网络结构, 配位聚合物 **2** 是一个二维的(4,4)网格层状结构。另外, 研究了 2 个配位聚合物在室温下的热稳定和荧光性能。

**关键词:** 水热合成; 配位聚合物; 拓扑; 荧光性质

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## Two Different Cd(II) Coordination Polymers Based on a Flexible Bis(imidazole) and Different Dicarboxylate Co-ligands: Syntheses, Crystal Structures and Properties

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**Abstract:** Two novel Cd(II) coordination polymers,  $[\text{Cd}_2(\mu_2\text{-H}_2\text{O})(1,5\text{-Bip})(\text{Tpa})_2]_n$  (**1**),  $[\text{Cd}(1,5\text{-Bip})(\text{Oba})]_n$  (**2**), where  $1,5\text{-Bip}$ =1,5-bis(imidazole)pentane,  $\text{H}_2\text{Tpa}$ =terephthalic acid,  $\text{H}_2\text{Oba}$ =4,4'-oxybis(benzoic acid), were synthesized under hydrothermal conditions and characterized by single crystal X-ray diffraction, powder XRD, FT-IR, TGA and elemental analysis technique. Single crystal X-ray analysis revealed that complex **1** features a 3D network with a 5-connected ( $4^6.6^4$ ) topology and complex **2** shows a 2D layer with a (4,4) topology. Furthermore, the photoluminescence properties in the solid state at room temperature and thermal behaviors of these complexes were also investigated. CCDC: 1043520, **1**; 1444145, **2**.

**Keywords:** hydrothermal synthesis; coordination polymer; topology; photoluminescence property

## 0 Introduction

Construction of new metal coordination polymers (MCPs) has attracted attention due to their diverse structural topologies and potential applications as functional materials such as gas storage, magnetism, catalysis, and luminescence<sup>[1-5]</sup>. Up to now, the selection

of suitable organic ligands is crucial for constructing extended coordination frameworks, which has been prepared on the basis of carboxylate-type O-donors and amine- or N-donors. Thereinto, di- and polycarboxylic acids are widely used as bridging ligands to construct coordination frameworks with versatile structures<sup>[8]</sup>, such as terephthalic acid( $\text{H}_2\text{Tpa}$ ), 4,4'-

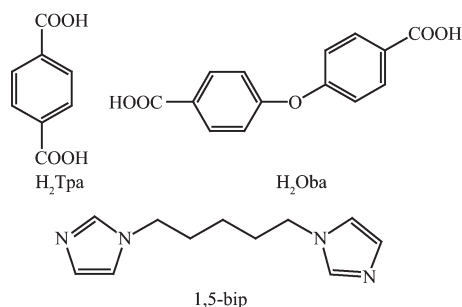
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oxybis(benzoic acid) ( $\text{H}_2\text{Oba}$ )<sup>[9-12]</sup>. Meanwhile, the 1,5-bis(imidazole) pentane(1,5-Bip) bearing alkyl spacers is a good choice of N-donor ligands, in which the flexible nature of spacers allows the ligands to bend and rotate when it coordinates to metal centers<sup>[13-14]</sup>, and it possesses trans and cis conformations which favor the possibility of generating fascinating structures.

Considering all these above-mentioned points and our previous work<sup>[15-17]</sup>, we selected the flexible 1,5-Bip ligand and  $\text{H}_2\text{Tpa}$ ,  $\text{H}_2\text{Oba}$  ligands as an interesting candidate to construct two novel MCPs,  $[\text{Cd}_2(\mu_2\text{-H}_2\text{O})(1,5\text{-Bip})(\text{Tpa})_2]_n$  (**1**) and  $[\text{Cd}(1,5\text{-Bip})(\text{Oba})]_n$  (**2**) ( $\text{H}_2\text{Tpa}$  = terephthalic acid,  $\text{H}_2\text{Oba}$  = 4,4'-oxybis (benzoic acid) and 1,5-Bip = 1,5-bis(imidazole)pentane) (Scheme 1).



Scheme 1 Structures of the organic ligands

The single crystal structures and photoluminescence properties of **1** and **2** have been investigated.

## 1 Experimental

### 1.1 Materials and physical measurements

All reagents used in the syntheses were purchased from Beijing Labmaterial Technology Development Co., Ltd. Elemental analyses for carbon, hydrogen, and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra ( $4\,000\sim 400\text{ cm}^{-1}$ ) were recorded by using KBr pellet on an Avatar 360 E.S.P. IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda=0.154\,056\text{ nm}$ ). Thermogravimetric analysis (TGA) was performed on a TA-SDT Q600 thermal analyzer under  $\text{N}_2$  atmosphere with a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  in the range of  $30\sim 800\text{ }^\circ\text{C}$ . The luminescent spectra for polycrystalline samples were measured at room temperature on a Perkin Elmer LS 55 fluores-

cence spectrometer with a xenon arc lamp as the light source.

### 1.2 Synthesis of complex

#### 1.2.1 Synthesis of $[\text{Cd}_2(\mu_2\text{-H}_2\text{O})(1,5\text{-Bip})(\text{Tpa})_2]_n$ (**1**)

A mixture of  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (0.2 mmol, 58.2 mg), 1,5-Bip (0.20 mmol, 40.8 mg), NaOH (0.2 mmol, 8 mg),  $\text{H}_2\text{Tpa}$  (0.2 mmol, 31.5 mg) and 8 mL  $\text{H}_2\text{O}$  were placed in a 25 mL Teflon-lined stainless steel container, which was heated to  $150\text{ }^\circ\text{C}$  for 3 days, and then cooled to room temperature over 24 hours. Colorless block crystals of **1** were collected. Yield: 43% based on Cadmium. Elemental analysis(%): Calcd. for  $\text{C}_{27}\text{H}_{28}\text{Cd}_2\text{N}_4\text{O}_{10}$ : C 40.84, H 3.52, N 7.06; Found: C 40.53, H 3.72, N 7.81. IR ( $\text{cm}^{-1}$ ): 3 440 (s), 3 125(w), 2 918(w), 1 615(s), 1 557(m), 1 500(w), 1 420(m), 1 352 (m), 1 270(w), 1 153(w), 1 091(w), 997(w) and 721(m).

#### 1.2.2 Synthesis of $[\text{Cd}(1,5\text{-Bip})(\text{Oba})]_n$ (**2**)

The synthetic procedure of **2** was similar to that for **1**, except that  $\text{H}_2\text{Tpa}$  (0.2 mmol) was used instead of  $\text{H}_2\text{Oba}$ . Colorless block crystals of **2** were collected. Yield: 67% based on Cadmium. Elemental analysis(%): Calcd. for  $\text{C}_{25}\text{H}_{24}\text{CdN}_4\text{O}_5$ : C 52.37, H 4.19, N 9.78; Found: C 52.53, H 4.72, N 9.81. IR ( $\text{cm}^{-1}$ ): 3 416(w), 3 119(m), 2 944(m), 2 885(w), 1 611(s), 1 564(s), 1 512 (s), 1 375(s), 1 274(m), 1 026(m) and 832(m).

### 1.3 Determination of crystal structures

Single crystal data of **1** ( $0.26\text{ mm}\times 0.21\text{ mm}\times 0.17\text{ mm}$ ) or **2** ( $0.23\text{ mm}\times 0.18\text{ mm}\times 0.14\text{ mm}$ ) were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda=0.071\,073\text{ nm}$ ) by using the  $\varphi\text{-}\omega$  scan mode at room temperature. Absorption corrections based on multi-scan were obtained using the SADABS program<sup>[18]</sup>. All the structures were solved with direct methods and refined with a full-matrix least-squares on  $F^2$  using SHELX 97<sup>[19-20]</sup>. Hydrogens were located by geometric calculations, and their positions and thermal parameters were fixed during the structure refinement. Crystallographic data and experimental details of structural analyses for complexes **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles of **1** and **2** are given in Table 2.

CCDC: 1043520, **1**; 1444145, **2**.

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

Complex	1	2
Chemical formula	C <sub>27</sub> H <sub>28</sub> Cd <sub>2</sub> N <sub>4</sub> O <sub>10</sub>	C <sub>25</sub> H <sub>24</sub> CdN <sub>4</sub> O <sub>5</sub>
Formula weight	793.33	572.88
Temperature / K	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>C2/c</i>
<i>a</i> / nm	2.241 5(3)	1.335 93(9)
<i>b</i> / nm	0.586 51(6)	1.539 19(11)
<i>c</i> / nm	2.130 2(3)	1.271 21(7)
$\beta$ / (°)		112.267(7)
<i>V</i> / nm <sup>3</sup>	2.800 5(6)	2.419 0(3)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.882	1.573
<i>F</i> (000)	1 576	1 160
Reflection collected	6 921	4 429
Independent reflection	2 453	2 092
Observed reflection ( <i>I</i> >2 $\sigma$ ( <i>I</i> ))	1 891	1 712
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>	Full-matrix least squares on <i>F</i> <sup>2</sup>
Numbers parameters	203	261
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.030	1.022
Final <i>R</i> indices ( <i>I</i> >2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> =0.035 2, <i>wR</i> <sub>2</sub> =0.074 2	<i>R</i> <sub>1</sub> =0.110 7, <i>wR</i> <sub>2</sub> =0.229 1
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.051 4, <i>wR</i> <sub>2</sub> =0.079 0	<i>R</i> <sub>1</sub> =0.129 1, <i>wR</i> <sub>2</sub> =0.236 8
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub> / (e·nm <sup>-3</sup> )	873, -963	1 066, -1 575

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

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

1					
Cd(1)-N(1)	0.225 4(4)	Cd(1)-O(2)	0.229 3(3)	Cd(1)A-N(1) <sup>i</sup>	0.225 4(4)
Cd(1)A-O(2)A	0.229 3(3)	Cd(1)-O(3)	0.227 6(3)	Cd(1)-O(1)	0.248 0(3)
Cd(1)A-O(3) <sup>i</sup>	0.227 6(3)	Cd(1)A-O(1)A	0.247 3(3)	Cd(1)-O(1)W	0.240 9(3)
Cd(1)-O(4)	0.247 3(3)	Cd(1)-O(1)W <sup>ii</sup>	0.244 1(3)	Cd(1)A-O(4)A	0.247 3(3)
N(1)-Cd(1)-O(3)	102.93(12)	O(3)-Cd(1)-O(1)W <sup>ii</sup>	83.90(12)	N(1)-Cd(1)-O(2)	87.28(12)
O(1)WB-Cd(1)-O(1)W	86.14(6)	O(2)-Cd(1)-O(3)	163.25(11)	O(4)-Cd(1)-O(1)W	137.44(11)
N(1)-Cd(1)-O(1)W	95.22(12)	O(4)-Cd(1)-O(1)W <sup>ii</sup>	88.33(10)	O(3)-Cd(1)-O(1)W	82.35(12)
N(1)-Cd(1)-O(1)	88.09(12)	O(2)-Cd(1)-O(1)W	83.53(11)	O(3)-Cd(1)-O(1)	137.46(10)
O(2)-Cd(1)-O(1)	54.90(9)	O(1)-Cd(1)-O(1)W	138.15(11)	O(4)-Cd(1)-O(1)	83.35(9)
O(1)-Cd(1)-O(1)W <sup>ii</sup>	86.44(10)	N(1)-Cd(1)-O(1)W <sup>ii</sup>	173.16(13)		
2					
Cd(1)-N(1)	0.199 4(8)	Cd(1)-N(1)B	0.199 4(8)	Cd(1)-O(2)	0.190 7(8)
Cd(1)-O(2)B	0.190 7(8)				
O(2)-Cd(1)-O(2) <sup>ii</sup>	112.9(7)	N(1)B-Cd(1)-O(2) <sup>ii</sup>	114.5(4)	N(1)-Cd(1)-O(2)	114.5(4)
N(1)B-Cd(1)-O(2)	104.0(4)	N(1)-Cd(1)-O(2) <sup>ii</sup>	104.0(4)	N(1)-Cd(1)-N(1) <sup>ii</sup>	107.2(5)

Symmetry codes: <sup>i</sup> 1-*x*, *y*, 0.5-*z*; <sup>ii</sup> 0.5-*x*, *y*-0.5, 0.5-*z* for **1**; <sup>ii</sup> 1-*x*, *y*, 1.5-*z* for **2**

## 2 Results and discussion

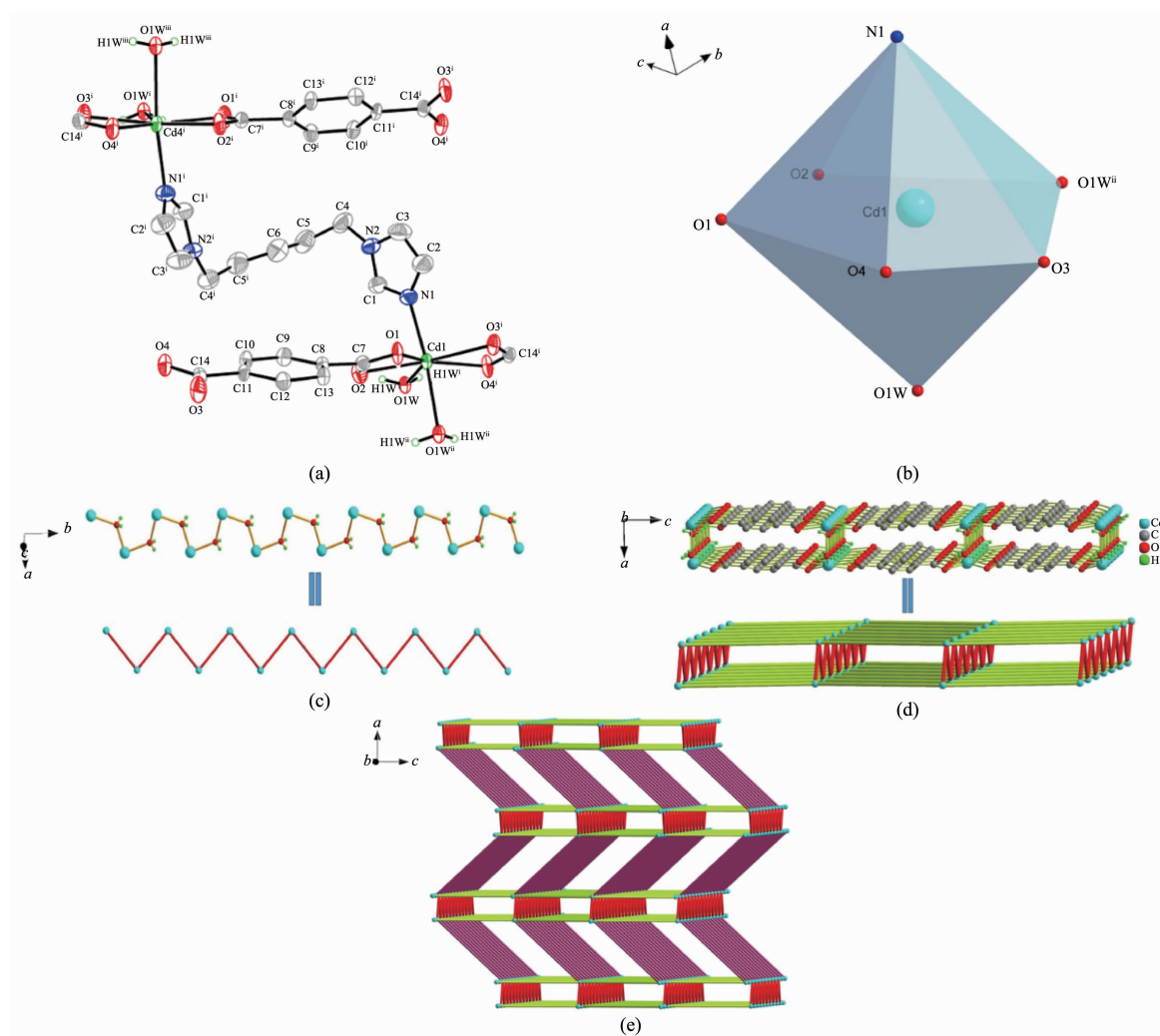
### 2.1 Description of the structures

#### 2.1.1 $[\text{Cd}_2(\mu_2\text{-H}_2\text{O})_2(1,5\text{-Bip})(\text{Tpa}^2)_2]_n$ (**1**)

Single X-ray diffraction study revealed that the asymmetric unit of **1** contains two Cd(II) cations, two  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule, two  $\text{Tpa}^{2-}$  anions and one 1,5-Bip ligand (Fig.1a). As shown in Fig.1b, the two crystallographic symmetric Cd(II) ions have the same distorted decahedral coordination geometry, which are seven-coordinated by four carboxylate oxygen atoms from two  $\text{Tpa}^{2-}$  ligands, one nitrogen atom of

1,5-Bip ligand and two  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule. A  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule connected two adjacent Cd(II) ions to form a 1D zigzag chain (Fig.1c), and  $\text{Tpa}^{2-}$  anions as a  $\mu_2$ -bridge connect the abovementioned 1D zigzag chain to form a 2D layer, as depicted in Fig.1d. Then, neighboring 2D layers constructed by Cd(II) ions,  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule and  $\text{Tpa}^{2-}$  anion were further connected by 1,5-Bip ligands to give a novel 3D framework with 1D channels whose internal dimension is *ca.* 1.177 02 nm $\times$ 1.119 67 nm along *b* axis (Fig.1e).

From the topological perspective<sup>[21]</sup>, the Cd(II)



Some hydrogen atoms are omitted for clarity in (a); Symmetry codes: <sup>i</sup> 1-*x*, *y*, 0.5-*z*; <sup>ii</sup> 0.5-*x*, *y*-0.5, *z*; <sup>iii</sup> 1-*x*, *y*-0.5, 0.5-*z*;  
Green pillar:  $\text{Tpa}^{2-}$  ligands; Purple pillar: 1,5-Bip ligands; Red pillar:  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule in (e)

Fig.1 (a) Structure of complex **1** with thermal ellipsoid at 50% probability levels; (b) View of distorted coordination geometry of Cd(II) ion; (c) View of a 1D zigzag chain constructed by Cd(II) ions and  $\text{H}_2\text{O}$  molecule; (d) View of a 2D layer constructed by Cd(II) ions,  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  and  $\text{Tpa}^{2-}$  anions; (e) View of 3D uninodal 5-connected net of (4<sup>6</sup>. 6<sup>6</sup>) topology in complex **1**

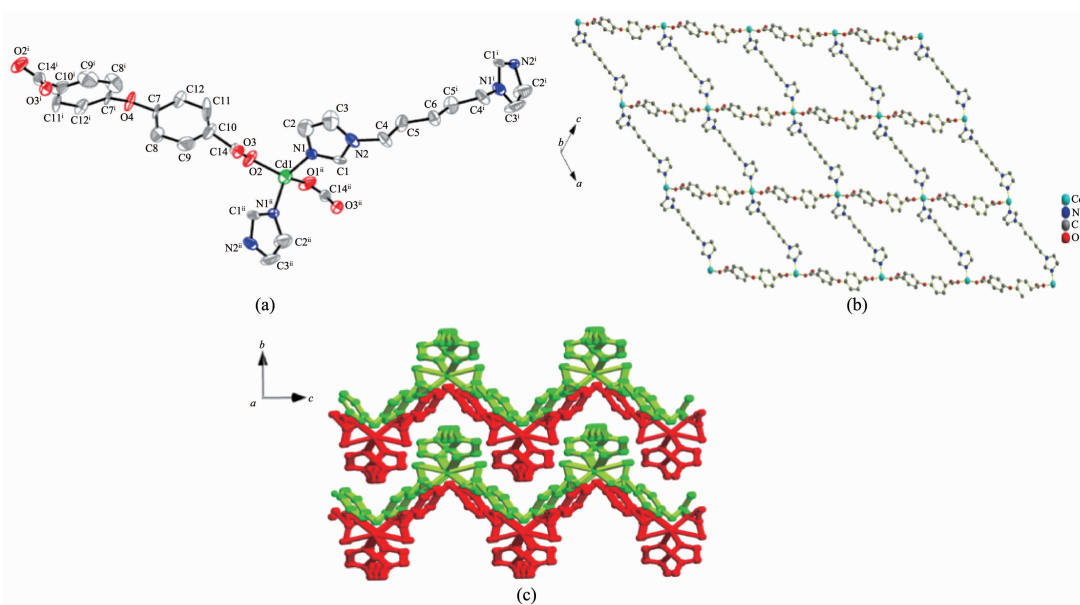
ions can be considered as a 5-connected uninodal node, the 1,5-Bip,  $\text{Tpa}^{2-}$  ligands and  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule as a  $\mu_2$ -bridged linker with a Schlfli symbol of  $(4^6.6^4)$ .

### 2.1.2 $[\text{Cd}(1,5\text{-Bip})(\text{Oba})]_n$ (**2**)

Single-crystal X-ray diffraction analysis showed that complex **2** exhibits a 2D (4,4) grid structure. The asymmetric unit contains one Cd (II) ion on the inversion center, one 1,5-Bip ligand and one  $\text{Oba}^{2-}$  anion. As depicted in Fig.2a, the Cd(II) ion is in a  $\text{CdN}_2\text{O}_2$  tetrahedral geometry, completed by two N atoms from two 1,5-Bip ligands, two O atoms from two  $\text{Oba}^{2-}$  anions (Cd-O 0.190 7 nm, Cd-N 0.199 5 nm). The bond angles for Cd are in the range of  $103.98^\circ \sim$

$114.49^\circ$ . The Bip and  $\text{Oba}^{2-}$  ligands adopt a bidentate bridging mode to extend the Cd (II) atoms to the resulting 2D (4,4) sql network (Fig.2b) incorporating a  $[\text{Cd}_4(1,5\text{-Bip})_2(\text{Oba})_2]$  window of  $1.453\ 8\ \text{nm} \times 1.335\ 9\ \text{nm}$  based on the Cd $\cdots$ Cd distances.

Although the interpenetration often occurs in  $4^4$ -sql networks with large windows<sup>[22-23]</sup>, no interpenetration between adjacent sheets is observed in **2**, which may be due to the occupancy of the part of the twisting of flexible 1,5-Bip and  $\text{Oba}^{2-}$  ligands. The adjacent 2D sheet are packed into the resultant 3D supramolecular framework (Fig.2c) by  $\text{C}_{\text{Bip}}\text{-H}\cdots\text{O}_{\text{Oba}}$  (0.264 5 nm) and  $\text{C}_{\text{Bip}}\text{-H}\cdots\text{C}_{\text{Oba}}$  (0.269 7 nm) hydrogen bonds.



Some hydrogen atoms are omitted for clarity in (a); Symmetry codes: <sup>i</sup>  $-x, y, 0.5-z$ ; <sup>ii</sup>  $1-x, y, 1.5-z$

Fig.2 (a) Structure of complex **2** with thermal ellipsoid at 40% probability levels; (b) 2D (4,4) grid structure of **2** along *b* axis; (c) Packing of 2D nets in the crystal with an -ABAB- fashion

## 2.2 FT-IR spectra and X-ray diffraction

As shown in Fig.3, The strong band at  $3\ 440\ \text{cm}^{-1}$  for **1** may be attributed to the stretching vibration of  $\mu_2$ -coordinated  $\text{H}_2\text{O}$  molecule. The strong absorptions at  $1\ 615, 1\ 420\ \text{cm}^{-1}$  for **1**, and  $1\ 611, 1\ 512\ \text{cm}^{-1}$  for **2**, respectively, are characteristic of asymmetric and symmetric stretching bands of carboxylate groups ( $\text{COO}^-$ ), and the difference in the value between them is less than  $200\ \text{cm}^{-1}$ , which indicates that the carboxylate groups behave as the chelate coordination modes<sup>[24]</sup>.

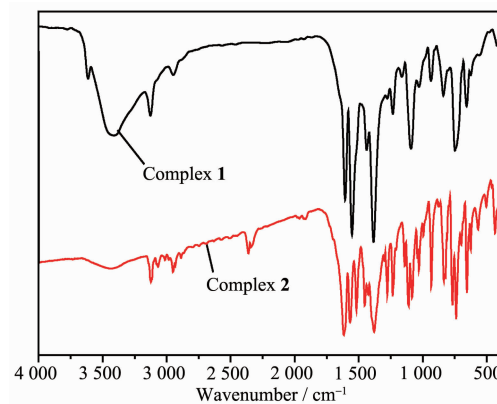


Fig.3 IR spectra of complexes **1** and **2**

The phase purities of complexes **1** and **2** were confirmed by powder X-ray diffraction measurements. As shown in Fig.4, the experimental patterns of **1** and **2** are consistent with the simulated ones based on the single crystal X-ray diffraction data.

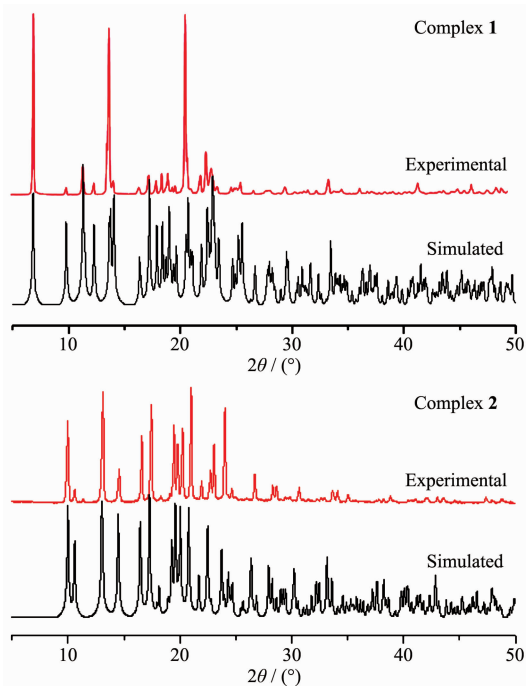


Fig.4 Powder XRD patterns of complexes **1** and **2**

### 2.3 Thermal behaviors

To have insight into the changes occurring during heat treatment of the prepared complexes, thermal gravimetric analysis (TGA) of the sample were carried out from 30 to 800 °C at a heating rate of 10 °C · min<sup>-1</sup>. The TGA curve of **1** displays a weight loss of 4.2% (Calcd. 4.5%) from room temperature to 250 °C, which corresponds to complete loss of two  $\mu_2$ -coordinated water molecule per unit cell. Its framework is stable up to 380 °C and then the framework begins to collapse,

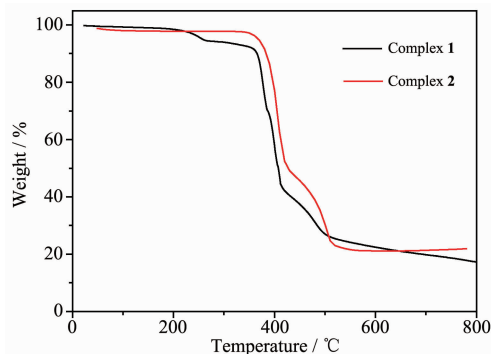


Fig.5 TGA curves for complexes **1** and **2**

accompanied by the release of Bip and Tpa<sup>2-</sup> ligands. After decomposition, the final residues is 17.3% , which can be attribute to CdO (Calcd. 16.2%). For **2**, the framework is stable up to 360 °C and then the framework begins to collapse, accompanying the release of coordinated Bip and Oba<sup>2-</sup> ligands, the final residues of **2** is 21.9% corresponding to CdO (Calcd. 22.4%).

### 2.4 Fluorescent properties

MCPs with  $d^{10}$  metal centers have many potential applications such as in chemical sensors, photochemistry, and electroluminescent display<sup>[25-27]</sup>. Therefore, in the present work, the photoluminescent properties of 1,5-Bip and complexes **1** and **2** have been investigated in the solid state at room temperature. The photoluminescence spectra of 1,5-Bip ligand and complexes **1** and **2** are shown in Fig.5. The free ligand Bip displays photoluminescence with emission maximum at 405 nm ( $\lambda_{ex}$ =322 nm.). It can be presumed that this peak originate from the  $\pi^*$ - $\pi$  transition. While the emission of dicarboxylate belongs to  $\pi^*$ - $n$  transitions which is very weak compared to that of the  $\pi^*$ - $\pi$  transition of the Bip, so the dicarboxylates almost have no contribution to the fluorescent emission of as-synthesized complexes<sup>[28]</sup>. Upon an excitation band at 322 nm, intense emissions are observed at 427 nm for **1** and 432 nm for **2**, respectively. In comparison to the free Bip ligands, the emission maximums of complexes **1** and **2** have changed and show blue or red shifts. This inequality in emission behavior may be a combination of several factors together, such as

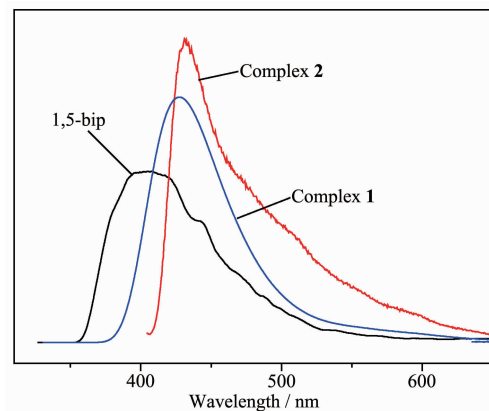


Fig.6 Fluorescent emission spectra of complexes **1**, **2** and 1,5-Bip ligand in solid state at room temperature

different dicarboxylate co-ligand, coordinated water molecule, and the role of structural complexity and framework robustness cannot be ignored. Meanwhile, the Cd(II) ion is difficult to oxidize or to reduce due to the  $d^{10}$  configuration, so the emission of this compound is neither MLCT nor LMCT in nature. As a result, the emission can be assigned to intraligand transitions.

### 3 Conclusions

In conclusion, we presented two novel Cd(II) coordination polymers constructed from dicarboxylate and bis (imidazole) mixed ligands. Complex **1** is a 3D framework with a 5-connected ( $4^6.6^4$ ) topology. Complex **2** shows a 2D layer with a (4,4) topology. In addition, photoluminescence of complexes **1** and **2** were studied in the solid state at room temperature. Further experiments exploring the structural effects of the spacer length of bis(imidazole) ligands on coordination polymers, and any resulting changes in physicochemical properties, are underway in our laboratory.

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