

## 由芳香羧酸和 4,4'-二(1-咪唑基)苯砜为配体构筑的 两个配合物的合成、晶体结构及荧光性质

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**摘要:** 通过水热法得到了 2 个配位聚合物  $[\text{Cd}(\text{L})(\text{oba})] \cdot 3.5\text{H}_2\text{O}$  (**1**) 和  $[\text{Cd}(\text{L})_2](p\text{-bdc})$  (**2**) (L=4,4'-二(1-咪唑基)苯砜, H<sub>2</sub>oba=4,4'-联苯醚二甲酸, *p*-H<sub>2</sub>bdc=对苯二甲酸), 对它们进行了元素分析、红外光谱分析, 并利用 X 射线衍射测定了它们的单晶结构。晶体结构分析表明, 配合物 **1** 具有四连接二重穿插的三维网络结构, 其拓扑为  $\{6^5 \cdot 8\}$ 。配合物 **2** 具有四连接的二维结构, 其拓扑为  $\{4^4 \cdot 6^2\}$ 。此外, 在室温下对 2 个配合物进行了荧光分析。

**关键词:** 镉(II)配位聚合物; 咪唑配体; 晶体结构; 荧光性质

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## Syntheses, Crystal Structures and Fluorescence Properties of Two Compounds Constructed by Aromatic Carboxylates and 4,4'-Bis(imidazol-1-yl)-phenyl Sulphone

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**Abstract:** Two coordination polymers, namely  $[\text{Cd}(\text{L})(\text{oba})] \cdot 3.5\text{H}_2\text{O}$  (**1**) and  $[\text{Cd}(\text{L})_2](p\text{-bdc})$  (**2**) have been obtained by the reaction of cadmium nitrate, 4,4'-bis(imidazol-1-yl)-phenyl sulphone (L) with two aromatic carboxylic acids, 4,4'-oxydibenzoic acid (H<sub>2</sub>oba), terephthalic acid (*p*-H<sub>2</sub>bdc). They were characterized by IR, elemental analysis and X-ray diffraction. Compound **1** exhibits 4-connected 2-fold interpenetrating 3D networks with the point symbol of  $\{6^5 \cdot 8\}$ . Compound **2** can be characterized as a 4-connected sql tetragonal planar network with the point symbol of  $\{4^4 \cdot 6^2\}$ . The luminescent properties of two compounds have also been investigated. CCDC: 1451100, **1**; 1451101, **2**.

**Keywords:** Cd(II) coordination polymer; imidazole ligand; crystal structure; photoluminescence

The construction of metal-organic framework (MOFs) has attracted much attention for their intriguing topologies as well as potential application in gas and small molecule storage<sup>[1-2]</sup>, catalysis<sup>[3-4]</sup>, drug

delivery<sup>[5]</sup> and so on. During the attainment of desirable frameworks, many factors can influence the construction progress, for instance, coordination tendency of metal centers, ligand-to-metal ratios, reaction

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temperature, reagents concentration, and so on<sup>[6]</sup>. It is well known that combining different ligands in a complex offers greater tunability of the structural framework than using a single ligand. Hence, a mixed-ligand is undoubtedly a good choice for the construction of new polymeric structures<sup>[7-8]</sup>. Imidazole ligands have been used in the synthesis of remarkable MOFs which possess excellent coordination ability allowing free rotation of the imidazole ring to meet the requirement of coordination geometries of metal ions. Until now, a large number of ingenious MOFs have been synthesized and designed based on imidazole ligands<sup>[9-10]</sup>.

Recently, we have successfully designed and synthesized a new V-shaped imidazole ligand 4,4'-bis(imidazol-1-yl)-phenyl sulphone (L), which may be regarded a semi-flexible ligand. Considering the mixed N-containing ligands and polycarboxylate possessing more tunable factors in the construction of novel MOFs, we carried out the reactions of the ligand L together with different carboxylate ligands and cadmium nitrate.

Herein, we report the syntheses, crystal structures, and properties of two new coordination polymers  $\{[\text{Cd}(\text{L})(\text{oba})] \cdot 3.5\text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Cd}(\text{L})_2](p\text{-bdc})\}_n$  (**2**), and the details of their syntheses, structures, and properties were investigated below.

## 1 Experimental

### 1.1 Materials and measurement

All the chemicals except the ligand L were commercially purchased and used without further purification. The ligand L was synthesized according to literature method<sup>[11]</sup>. Elemental analyses of C, H, N were performed on a Elementar Vario MICRO Elemental Analyzer. Fourier transformed Infrared (FT-IR) spectra were obtained on a Bruker Vector 22 FTIR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer under nitrogen with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta$  range of  $5^\circ \sim 50^\circ$  with a scan speed of  $0.2^\circ \cdot \text{s}^{-1}$  on a

Bruker D8 Advance instrument using a Cu  $K\alpha$  radiation ( $\lambda=0.154\ 056\text{ nm}$ ) at room temperature, in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature ( $25\text{ }^\circ\text{C}$ ).

### 1.2 Synthesis of compounds

$\{[\text{Cd}(\text{L})(\text{oba})] \cdot 3.5\text{H}_2\text{O}\}_n$  (**1**): A mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (30.8 mg, 0.1 mmol),  $\text{H}_2\text{oba}$  (25.8 mg, 0.1 mmol) and L (37.2 mg, 0.1 mmol) was dissolved in 5 mL of DMF/ $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:2:2,  $V:V:V$ ). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at  $105\text{ }^\circ\text{C}$  for two days. Colorless block crystals were obtained. The yield of the reaction was ca. 53% based on L. Anal. Calcd. for  $\text{C}_{32}\text{H}_{29}\text{CdN}_4\text{O}_{10.5}\text{S}(\%)$ : C, 49.10; H, 3.71; N, 7.16. Found (%): C, 49.14; H, 3.68; N, 7.20. IR (KBr,  $\text{cm}^{-1}$ ): 3 403 (s), 3 139 (s), 1 606(m), 1 564(m), 1 458(m), 1 401(s), 1 255(w), 1 127(w), 1 046(m), 964(w), 819(w), 780(w), 735(m), 564(w).

$\{[\text{Cd}(\text{L})_2](p\text{-bdc})\}_n$  (**2**): A mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (30.8 mg, 0.1 mmol),  $p\text{-H}_2\text{bdc}$  (16.6 mg, 0.1 mmol) and L (37.2 mg, 0.1 mmol) was dissolved in 5 mL of DMF/ $\text{H}_2\text{O}$  (4:1,  $V/V$ ). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at  $95\text{ }^\circ\text{C}$  for three days. Colorless block crystals were collected. The yield of the reaction was ca. 45% based on L ligand. Anal. Calcd. for  $\text{C}_{44}\text{H}_{32}\text{CdN}_8\text{O}_8\text{S}_2(\%)$ : C, 54.03; H, 3.27; N, 11.46. Found (%): C, 54.09; H, 3.20; N, 11.40. IR (KBr,  $\text{cm}^{-1}$ ): 3 430 (s), 3 091 (s), 1 547(s), 1 478(s), 1 416(m), 1 300(s), 1 256(s), 1 195(m), 1 128 (w), 1 055(s), 956(m), 902(w), 831(s), 735(m), 722(m), 658(m), 545(w), 505(w).

### 1.3 Single crystal X-ray crystallography

Two block single crystals with dimensions of  $0.24\text{ mm} \times 0.20\text{ mm} \times 0.18\text{ mm}$  for **1** and  $0.18\text{ mm} \times 0.16\text{ mm} \times 0.12\text{ mm}$  for **2** were mounted on glass fibers for measurement, respectively. The data collections were carried out on a Bruker Smart Apex II CCD diffraction (Mo  $K\alpha$ ,  $\lambda=0.071\ 03\text{ nm}$ ). The diffraction data were integrated using SAINT program<sup>[12]</sup>, which was also used for the intensity correction for the

Lorentz and polarization effects. Semi-empirical absorption corrections were applied using SADABS program<sup>[13]</sup>. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using SHELXL-97 crystallographic software package<sup>[14]</sup>. The hydrogen atoms except those

of water molecules were generated geometrically and refined isotropically using the riding model. The details of the crystal parameters, data collection, and refinements for the compounds are listed in Table 1, and selected bond lengths and angles are summarized in Table 2.

CCDC: 1451100, **1**; 1451101, **2**.

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

Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>32</sub> H <sub>29</sub> CdN <sub>4</sub> O <sub>10</sub> S	C <sub>44</sub> H <sub>32</sub> CdN <sub>8</sub> O <sub>8</sub> S <sub>2</sub>
Formula weight	782.00	977.30
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$F222$
$a$ / nm	2.440 41(16)	1.189 0(3)
$b$ / nm	1.783 71(11)	1.189 1(3)
$c$ / nm	1.416 63(9)	2.832 3(11)
$\beta$ / (°)	91.986 0(10)	
$V$ / nm <sup>3</sup>	6.162 9(7)	4.005(2)
$Z$	8	4
$D_c$ / (g·cm <sup>-3</sup> )	1.550	1.621
$\mu$ / mm <sup>-1</sup>	0.831	0.718
$F(000)$	2 896	1 984
$\theta_{\min}$ , $\theta_{\max}$ / (°)	1.41, 27.48	1.44, 27.70
Goodness of fit on $F^2$	1.059	1.041
Reflections collected	20 500	6 795
Independent reflections ( $R_{\text{int}}$ )	7 071 (0.022 0)	2 327 (0.047 8)
$R_1$ , $wR_2$ [ $I > 2\sigma(I)$ ]	0.026 9, 0.068 9	0.035 3, 0.084 5
$R_1$ , $wR_2$ (all data)	0.034 1, 0.071 7	0.037 8, 0.086 1
$(\Delta\rho)_{\max}$ , $(\Delta\rho)_{\min}$ / (e·nm <sup>-3</sup> )	449, -279	540, -411

**Table 2** Selected bond distances (nm) and bond angles (°) of compounds **1** and **2**

Compound <b>1</b>					
Cd(1)-N(1)	0.224 1(2)	Cd(1)-O(3)	0.249 5(2)	Cd(1)-O(4)	0.228 1(2)
Cd(1)-O(1)#1	0.264 0(2)	Cd(1)-O(2)#1	0.220 5(2)	Cd(1)-N(4)#2	0.226 9(2)
O(2)#1-Cd(1)-N(1)	130.54(6)	O(2)#1-Cd(1)-N(4)#2	108.10(6)	N(1)-Cd(1)-N(4)	96.03(6)
O(2)#1-Cd(1)-O(4)	104.26(6)	N(1)-Cd(1)-O(4)	90.48(6)	N(4)#2-Cd(1)-O(4)#1	130.21(6)
O(2)#1-Cd(1)-O(3)	103.88(6)	N(1)-Cd(1)-O(3)	122.41(6)	N(4)#2-Cd(1)-O(3)	81.25(6)
O(4)-Cd(1)-O(3)	54.61(6)	O(2)#1-Cd(1)-O(1)#1	53.16(6)	N(1)-Cd(1)-O(1)#1	87.26(6)
N(4)#2-Cd(1)-O(1)#1	86.58(6)	O(4)-Cd(1)-O(1)#1	143.13(6)	O(3)-Cd(1)-O(1)#1	148.79(6)
Compound <b>2</b>					
Cd(1)-N(1)	0.235 3(2)	Cd(1)-N(1)#1	0.235 3(2)	Cd(1)-N(1)#2	0.235 3(2)
Cd(1)-N(1)#3	0.235 3(2)				
N(1)#1-Cd(1)-N(1)#3	162.90(11)	N(1)#2-Cd(1)-N(1)#3	94.70(12)	N(1)#1-Cd(1)-N(1)#2	87.84(12)
N(1)#1-Cd(1)-N(1)	94.70(12)	N(1)#3-Cd(1)-N(1)	87.84(12)	N(1)#2-Cd(1)-N(1)	162.90(11)

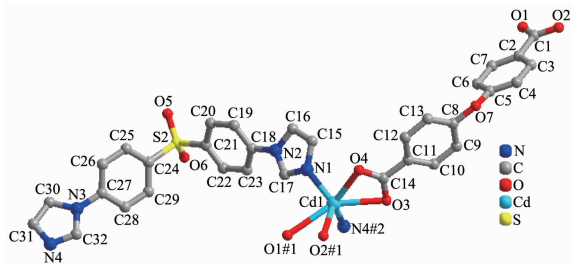
Symmetry codes: #1:  $x-1/2, y-1/2, z$ ; #2:  $x+1/2, -y+1/2, z+1/2$  for **1**; #1:  $1-x, y, 2-z$ ; #2:  $x, 1-y, 2-z$ ; #3:  $1-x, 1-y, z$  for **2**.

## 2 Results and discussion

### 2.1 Structures description

#### 2.1.1 Crystal structure analysis of $\{[\text{Cd}(\text{L})(\text{oba})] \cdot 3.5\text{H}_2\text{O}\}_n$ (**1**)

Single-crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic crystal system of  $C2/c$  space group. As shown in Fig.1, the asymmetric unit contains one Cd(II) cation, one L ligand, one deprotonated 4,4'-oxydibenzoic acid and three point five water molecules, which was removed by the SQUEEZE routine in PLATON<sup>[15]</sup>. Each Cd(II) atom is surrounded by four O atoms from two different carboxylate groups of two  $\text{oba}^{2-}$  ligands and two nitrogen atoms from two different L ligands. The Cd-O/N bond distances fall in the normal range found in other Cd compounds<sup>[16-17]</sup>. The  $\text{oba}^{2-}$  anions link Cd(II) cations to form one infinite 1D linear chain with an  $\text{Cd} \cdots \text{Cd}$  distance of 1.511 4 nm and  $\text{Cd} \cdots \text{Cd} \cdots \text{Cd}$  angle of  $180.00^\circ$ . Similarly, the neighboring Cd(II) cations are linked by L ligands via Cd-N bonds, affording a not-so-common *meso*-helical motif, a special type of helical chain where right- and left-handed helices are formed in equal amounts within a single helical chain (Fig.2). Finally, these two kinds of 1D chains are cross-linked by sharing the Cd(II) cations into a three-dimensional network (Fig.3). Cd(II) can be regarded as a network node, and each node connects to four adjacent ones. Thus the 3D coordination polymer lattice for **1** can be characterized as a 4-connected cds network with the point symbol of  $\{6^5 \cdot 8\}$ . The potential voids are large enough to be filled via mutual interpenetration of an independent equivalent framework, generating a 2-fold interpenetration 3D architecture (Fig.4).



All hydrogen atoms were omitted for clarity; Symmetry codes: #1:  $x-1/2, y-1/2, z$ ; #2:  $x+1/2, -y+1/2, z+1/2$

Fig.1 Coordination environment of the Cd(II) cation in **1**

trating 3D architecture (Fig.4).

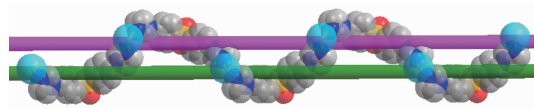


Fig.2 View of the infinite *meso*-helical chain formed by L ligands linked through Cd ions

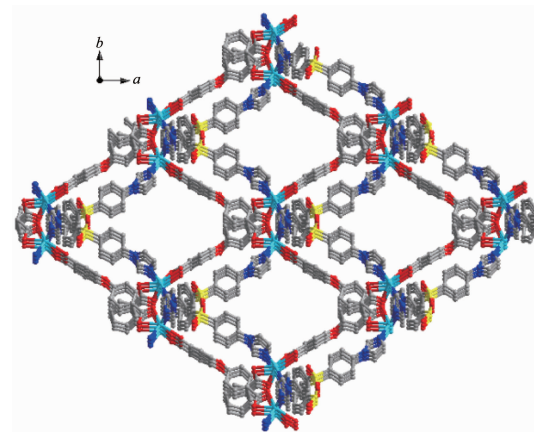


Fig.3 Schematic view of the 3D network of **1** along the  $c$  axis

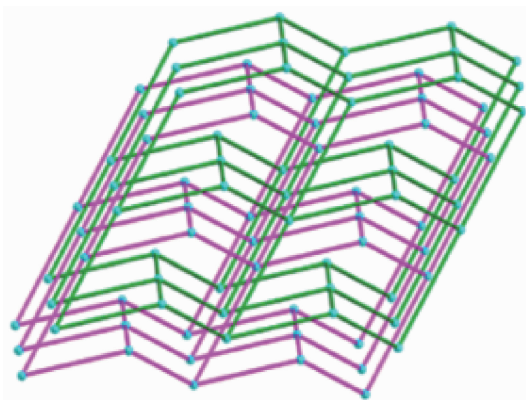
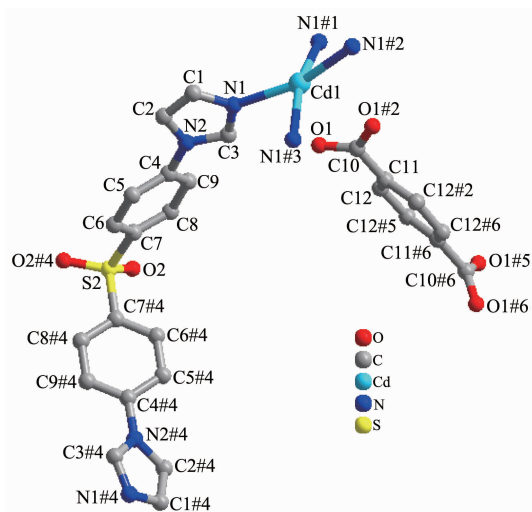


Fig.4 Two-fold interpenetrating 3D cds-type topology of **1**

#### 2.1.2 Crystal structure analysis of $\{[\text{Cd}(\text{L})_2](p\text{-bdc})\}_n$ (**2**)

Single-crystal X-ray structural analysis reveals that **2** crystallizes in orthorhombic crystal system of the  $F222$  space group. The asymmetric unit contains one Cd(II) cation, two L ligands, one singly deprotonated  $p\text{-bdc}^{2-}$  anion in free form. The coordination environment around the Cd(II) cation is exhibited in Fig.5. Each Cd(II) is coordinated by four N donors from four L ligands with a slightly distorted square-planar geometry, which have rarely reported for Cd(II) coordination polymers. The Cd-N distances are 0.235 3(3) nm, and the N-Cd-N angles range from  $87.84(14)^\circ$  to

162.90(13)°. These are similar to values found in other Cd(II) compounds. As shown in Fig.6, each Cd(II) atoms are linked by L ligands to produce a 2D layer. Topological analysis reveals that each Cd(II) center can be regarded as the four-connected nodes and L ligands as linkers. Thus, the 2D layer can be regarded as a 4-connected sql network with the point symbol of



All hydrogen atoms were omitted for clarity; Symmetry codes: #1: 1-x, y, 2-z; #2: x, 1-y, 2-z; #3: 1-x, 1-y, z; #4: 3/2-x, y, 3/2-z; #5: 2-x, y, 2-z; #6: 2-x, 1-y, z

Fig.5 Coordination environment of the Cd(II) cation in **2**

{4<sup>4</sup>·6<sup>2</sup>} (Fig.7).

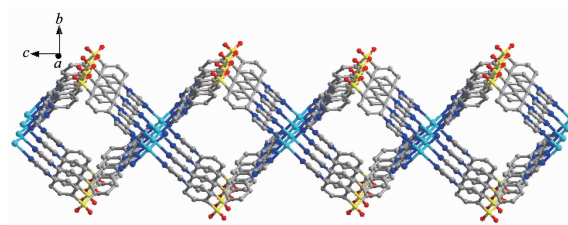


Fig.6 2D network of **2** along the *a* axis

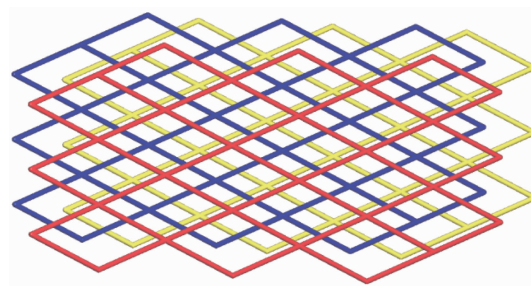


Fig.7 Schematic view of sql topology of **2**

## 2.2 Thermal stability and powder X-ray diffraction (PXRD)

Powder X-ray diffraction analysis (PXRD) experiments were carried out for **1** and **2** at room temperature to characterize their purity. As shown in Fig.8, the measured peak positions closely match the simulated peak positions, indicative of pure products.

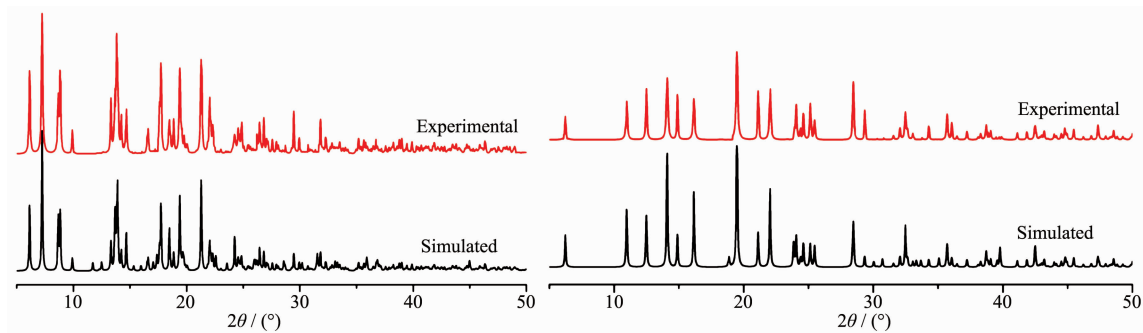


Fig.8 PXRD patterns of compounds **1** (left) and **2** (right)

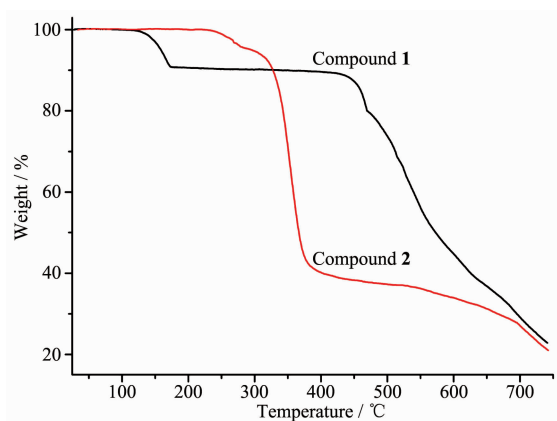
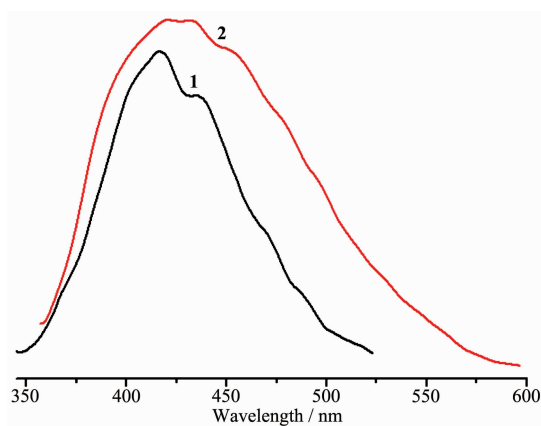
To examine the thermal stabilities of compounds **1** and **2**, their thermal decomposition behavior was investigated from 20 to 750 °C under nitrogen atmosphere (Fig.9). The TGA curve of compound **1** indicate that there is a weight loss of approximate 8.24% between 130 and 160 °C, corresponding to the loss of release of lattice water molecule (Calcd. 8.06%), and the framework collapses at 430 °C. The TGA study of compound **2** indicates no obvious weight loss from 20 to 240 °C, suggesting that the frameworks

are thermally stable.

## 2.3 Photoluminescence properties

The solid-state luminescent properties of compounds **1** and **2** have been investigated at room temperature under the same conditions. The emission spectra of the compounds are depicted in Fig.10. It can be seen that the emission bands of compounds were observed at 416 nm ( $\lambda_{\text{ex}}=342$  nm) for **1** and 432 nm ( $\lambda_{\text{ex}}=350$  nm) for **2**, respectively. The enhancement in the fluorescence intensity is realized compared with



Fig.9 TGA curves of compounds **1** and **2**Fig.10 Solid-state photoluminescent spectra for **1** and **2**

the free L, H<sub>2</sub>oba and *p*-H<sub>2</sub>bdc ligands, which have almost no fluorescence properties. The enhancement of luminescence in *d*<sup>10</sup> compounds may be attributed to the ligation of the metal center to the ligands. The coordination effect increases the rigidity of the ligands and thus reduces the loss of energy through a radiationless pathway<sup>[18]</sup>.

### 3 Conclusions

In summary, we have successfully synthesized two new coordination polymers, which were constructed from a simple “V-shaped” ligand in the presence of co-ligands and Cd ions under hydrothermal conditions. The ancillary ligands play a

significant role in the structure of the final products. Additionally, compounds **1** and **2** display strong fluorescence and better thermal stability.

### References:

- [1] Lin Z J, Huang Y B, Liu T F, et al. *Inorg. Chem.*, **2013**,**52**: 3127-3132
- [2] Li P, He Y, Guang J, et al. *J. Am. Chem. Soc.*, **2014**,**136**: 547-549
- [3] Zhu Y, Wang Y M, Zhao S Y, et al. *Inorg. Chem.*, **2014**,**53**: 7692-73699
- [4] Wang L H, Zeng Y, Shen A G, et al. *Chem. Commun.*, **2015**, **51**:2052-2055
- [5] He C B, Lu K D, Liu D M, et al. *J. Am. Chem. Soc.*, **2014**, **136**:5181-5184
- [6] Zhang C L, Qin L, Shi Z Q, et al. *Dalton Trans.*, **2015**,**44**: 4238-4245
- [7] Qin L, Zheng M X, Guo Z J, et al. *Chem. Commun.*, **2015**, **51**:2447-2449
- [8] Zheng M X, Gao X J, Zhang C L, et al. *Dalton Trans.*, **2015**, **44**:4751-4758
- [9] Wang T, Zhang C L, Ju Z M, et al. *Dalton Trans.*, **2015**,**44**: 6926-6935
- [10] Li X J, Yu Z J, Guan T N, et al. *Cryst. Growth Des.*, **2015**, **15**:278-290
- [11] Hu J S, Shang Y J, Yao X Q, et al. *Cryst. Growth Des.*, **2010**,**10**:4135-4142
- [12] SMART and SAINT, Siemens Analytical X-ray Instrument Inc., Madison, WI, **1996**.
- [13] Sheldrick G M. SADABS, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.
- [14] Sheldrick G M. SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [15] Spek A L. *Acta Crystallogr. A*, **1990**,**A46**:194-201
- [16] Yi F Y, Li J P, Wu D, et al. *Chem. Eur. J.*, **2015**,**1**:1-9
- [17] Wu Y L, Yang G P, Zhou X, et al. *Dalton Trans.*, **2015**,**44**: 10385-10391
- [18] Wang Z J, Qin L, Zhang X, et al. *Cryst. Growth Des.*, **2015**, **15**:1303-1310