

## 基于一种柔性和角型有机芳香多酸配体的两种 3D 配位聚合物的合成、结构和荧光性

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**摘要:** 通过水热合成的方法制得具有三维超分子结构的 2 种配位聚合物  $\{[\text{Zn}(\text{L})(\text{bpa})_{0.5}(\text{H}_2\text{O})_2] \cdot 2.25\text{H}_2\text{O}\}_n$  (**1**) 和  $\{[\text{Cd}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$  (**2**), 其中,  $\text{H}_3\text{LCl}$  为氯化 5-(4-羟基吡啶基甲基)间苯二甲酸, bpa 为 1,2-二(4-吡啶基)乙烷。这 2 种化合物的结构通过单晶 X 射线衍射、红外光谱(IR)、元素分析、热重分析(TG)等方法进行了表征。结构解析表明: 化合物 **1** 是一种梯型链式结构, 并通过链间氢键作用延伸成了 3D 超分子网络; 化合物 **2** 为含有大量一维隧道空腔的 2D 配位网络。此外, 研究了这 2 种化合物的荧光性质。

**关键词:** 氯化 5-(4-羟基吡啶基甲基)间苯二甲酸; 1,2-二(4-吡啶基)乙烷; 锌; 镉

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## Syntheses, Structures and Photoluminescent Properties of Two 3D Coordination Polymers Based on a Flexible and Angular Organic Aromatic Multi-carboxylate Ligand

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**Abstract:** Two coordination polymers with 3D supramolecular network,  $\{[\text{Zn}(\text{L})(\text{bpa})_{0.5}(\text{H}_2\text{O})_2] \cdot 2.25\text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Cd}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$  (**2**) ( $\text{H}_3\text{LCl}$ =5-(4-hydroxypyridinium-1-ylmethyl) isophthalic acid chloride, bpa=1,2-bis(4-pyridyl)ethane) were hydrothermally synthesized and structurally characterized by X-ray diffraction analyses and further characterized by infrared spectra (IR), elemental analyses, and thermogravimetric (TG) analyses. Compound **1** exhibits a ladder-like chain structure, and such chains are further united together to generate a 3D supramolecular structure through the hydrogen bonding interactions. Compound **2** possesses a 2D coordination network with a 1D channel that run parallel to the coordination layers. Meanwhile, their luminescent properties have also been investigated in detail. CCDC: 908522, **1**; 908526, **2**.

**Keywords:** 5-(4-hydroxypyridinium-1-ylmethyl)isophthalic acid chloride; 1,2-bis(4-pyridyl)ethane; zinc; cadmium

In recent years, the complexes based on organic aromatic carboxylate ligands have become an interesting research area due to their pluridentated and excellent coordinated ability<sup>[1-4]</sup> as well as their charming architectures and potential applications in adsorption, catalysis, and luminescence, and so on<sup>[5-6]</sup>. Among the reported compounds, the coordination

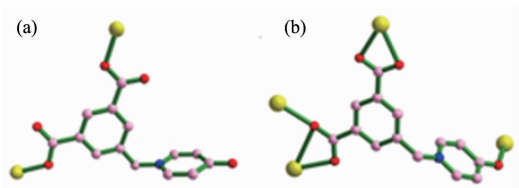
polymers from flexible or angular organic aromatic multi-carboxylate ligands are especially interesting because they can adopt a variety of coordination modes resulting in diverse multidimensional architectures<sup>[7-10]</sup>. Up to now, many aromatic carboxylate ligands with flexible or angular structures have been synthesized and reported. For example, Li et al. have

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reported a series of metal-organic frameworks based on flexible ligand 4-carboxy-1-(3,5-dicarboxy-benzyl)pyridinium chloride<sup>[11]</sup>; Sun et al. have synthesized a flexible and angular ligands 5-(imidazol-1-ylmethyl) isophthalic acid, and report a series of coordination polymers with novel networks<sup>[12-13]</sup>; Zang et al. have investigated a series of angular carboxylate ligands, 3,5-bis(imidazol-1-ylmethyl) benzoic acid hydrochloride<sup>[14]</sup>, 2, 3, 2', 3'-thiaphthalic acid<sup>[15]</sup>, 1-(pyridin-4-ylthio)benzene-2,4-dioic acid<sup>[16]</sup>. Recently, we have also synthesized a versatile ligand, H<sub>3</sub>LCl (5-(4-hydroxypyridinium-1-ylmethyl) isophthalic acid chloride), and its corresponding coordination polymers have been reported<sup>[17]</sup>. To continue our effort in this area, two coordination polymers, {[Zn(L)(bpa)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>]·2.25H<sub>2</sub>O}<sub>n</sub> (**1**) and {[Cd(L)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub> (**2**), with novel networks from H<sub>2</sub>L ligand have been hydrothermally synthesized and structurally characterized by X-ray diffraction analyses and further characterized by infrared spectra (IR), elemental analyses and thermogravimetric (TG) analyses.



Scheme 1 Coordination mode of the ligand H<sub>3</sub>LCl found in compounds **1** (a) and in **2** (b)

## 1 Experimental

### 1.1 Materials and physical measurement

H<sub>3</sub>LCl was synthesized according to the literature<sup>[17]</sup>, and other starting materials were of reagent quality and obtained from commercial sources without further purification. Elemental analysis for C, H and N was performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4 000 to 400 cm<sup>-1</sup> on a Nicolet NEXUS 470-FTIR spectrometer. Thermal analysis was performed on a SDT 2960 thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C·min<sup>-1</sup> under nitrogen flow. Powder X-ray diffraction (PXRD) for compounds **1** and **2** were measured at 293

K on a Rigaku D/max-3B diffractometer equipped with Cu K $\alpha$  ( $\lambda$ =0.154 06 nm) radiation (45 kV, 200 mA). The crushed single crystalline powder samples were prepared by crushing the crystals and the 2 $\theta$  scanning angle range was from 5° to 50°. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

### 1.2 Synthesis

#### 1.2.1 Synthesis of {[Zn(L)(bpa)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>]·2.25H<sub>2</sub>O}<sub>n</sub> (**1**)

Compound **1** was synthesized hydrothermally in a 25 mL Teflon-lined autoclave by heating a mixture of bpa (0.009 1 g, 0.05 mmol), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.022 g, 0.1 mmol), H<sub>3</sub>LCl (0.015 4 g, 0.05 mmol), and LiOH (0.004 2 g, 0.1 mmol) at 160 °C in 6 mL H<sub>2</sub>O for three days. Colorless block-wise crystals of **1** were obtained in 80% yield based on H<sub>2</sub>L. Anal. Calcd. for C<sub>20</sub>H<sub>23.5</sub>N<sub>2</sub>O<sub>9.25</sub>Zn(%): C 47.54, H 4.69, N 5.54; Found (%): C 47.51, H 4.73, N 5.50. IR (KBr, cm<sup>-1</sup>): 3 388 (m, br), 3 120(m), 1 640(s), 1 620(s), 1 582(s), 1 556 (s), 1 361(s), 1 239(w), 1 226(w), 1 193(m), 1 029(w), 847(w), 774(w), 729(w).

#### 1.2.2 Synthesis of {[Cd(L)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub> (**2**)

A mixture of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.026 g, 0.1 mmol), H<sub>2</sub>L (0.016 8 g, 0.05 mmol), LiOH (0.004 2 g, 0.1 mmol), and H<sub>2</sub>O (6 mL) was placed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for three days. After the mixture was slowly cooled to room temperature, colorless crystals of **2** were obtained in 76% yield based on H<sub>2</sub>L. Anal. Calcd. for C<sub>14</sub>H<sub>15</sub>NO<sub>8</sub>Cd (%): C 38.42, H 3.45, N 3.30; Found(%): C 38.39, H 3.51, N 3.20. IR (KBr, cm<sup>-1</sup>): 3 410 (s, br), 3 045(m), 1 647(s), 1 619(s), 1 563(m), 1 524(s), 1 447(w), 1 340(s), 1 293(w), 1 187(m), 1 049(w), 1 028(w), 856(s), 774(s), 726 (w).

### 1.3 Crystallographic data collection and structure determination

Single-crystal X-ray diffraction data of compounds **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer<sup>[18]</sup> equipped with graphite monochromatized Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) at room temperature using the  $\varphi$ - $\omega$  scan technique. Empirical absorption corrections were applied to the intensities using the SADABS program<sup>[19]</sup>. The struct-

ures were solved with direct methods using the program SHELXS-97<sup>[20]</sup> and refined anisotropically with the program SHELXL-97<sup>[21]</sup> using full matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the coordination water molecules, and ligands were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. The hydrogen atoms of the solvent water

molecules were located from the difference Fourier maps, then restrained at fixed positions and refined isotropically. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data for **1** and **2** are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 908522, **1**; 908526, **2**.

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

Compound	<b>1</b>	<b>2</b>
Formula	C <sub>20</sub> H <sub>23.5</sub> N <sub>2</sub> O <sub>9.25</sub> Zn	C <sub>14</sub> H <sub>15</sub> NO <sub>8</sub> Cd
Formula weight	505.28	437.67
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.969 30(8)	0.738 70(4)
<i>b</i> / nm	1.066 54(9)	1.015 35(4)
<i>c</i> / nm	1.227 35(11)	1.120 03(7)
$\alpha$ / (°)	67.315(8)	70.191(4)
$\beta$ / (°)	78.218(7)	81.994(5)
$\gamma$ / (°)	67.830(8)	76.292(4)
<i>V</i> / nm <sup>3</sup>	1.081 57(18)	0.766 25(7)
<i>Z</i>	1	2
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.552	1.897
<i>F</i> (000)	523	436
Reflection collected	6 391	5 773
Independent reflection	3 811	2 687
<i>R<sub>int</sub></i>	0.058 9	0.024 9
GOF on <i>F</i> <sup>2</sup>	1.057	1.028
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.044 5	0.028 4
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.110 7	0.068 9

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

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

Compound <b>1</b>					
Zn-O(1)	0.195 2(2)	Zn-O(3) <sup>i</sup>	0.196 9(2)	Zn-N(2)	0.205 5(2)
Zn(1)-O(1W)	0.214 2(2)	Zn(1)-O(2W)	0.229 1(2)		
O(1)-Zn(1)-N(2)	133.65(11)	O(1)-Zn-O(3) <sup>i</sup>	125.29(10)	O(1)-Zn(1)-O(1W)	88.55(10)
O(3) <sup>i</sup> -Zn-N(2)	100.60(10)	N(2)-Zn(1)-O(1W)	93.77(10)	O(3) <sup>i</sup> -Zn(1)-O(1W)	95.37(11)
O(3) <sup>i</sup> -Zn(1)-O(2W)	89.56(10)	O(1)-Zn(1)-O(2W)	85.77(10)	O(1W)-Zn(1)-O(2W)	173.98(9)
N(2)-Zn(1)-O(2W)	88.72(10)				
Compound <b>2</b>					
Cd(1)-O(1)	0.232 3(2)	Cd(1)-O(2)	0.239 8(2)	Cd(1)-O(3) <sup>i</sup>	0.274 7(1)
Cd(1)-O(4) <sup>i</sup>	0.228 2(3)	Cd(1)-O(5) <sup>ii</sup>	0.227 6(3)	Cd(1)-O(1W)	0.234 2(3)
Cd(1)-O(3) <sup>iii</sup>	0.227 4(3)				

Continued Table 2

O(3) <sup>i</sup> -Cd(1)-O(4) <sup>i</sup>	50.396(2)	O(5) <sup>ii</sup> -Cd(1)-O(3) <sup>i</sup>	81.625(2)	O(1W)-Cd(1)-O(3) <sup>i</sup>	79.926(2)
O(1)-Cd(1)-O(3) <sup>i</sup>	173.275(3)	O(5) <sup>ii</sup> -Cd(1)-O(3) <sup>iii</sup>	83.16(10)	O(2)-Cd(1)-O(3) <sup>i</sup>	131.347(3)
O(5) <sup>ii</sup> -Cd(1)-O(4) <sup>i</sup>	93.32(10)	O(3) <sup>iii</sup> -Cd(1)-O(4) <sup>i</sup>	131.81(9)	O(1)-Cd(1)-O(3) <sup>iii</sup>	91.73(10)

Symmetry codes: <sup>i</sup>  $x+1, y, z$  for **1**; <sup>i</sup>  $x, 1+y, z$ ; <sup>ii</sup>  $2-x, 1-y, 1-z$ ; <sup>iii</sup>  $3-x, 1-y, -z$  for **2**.

## 2 Results and discussion

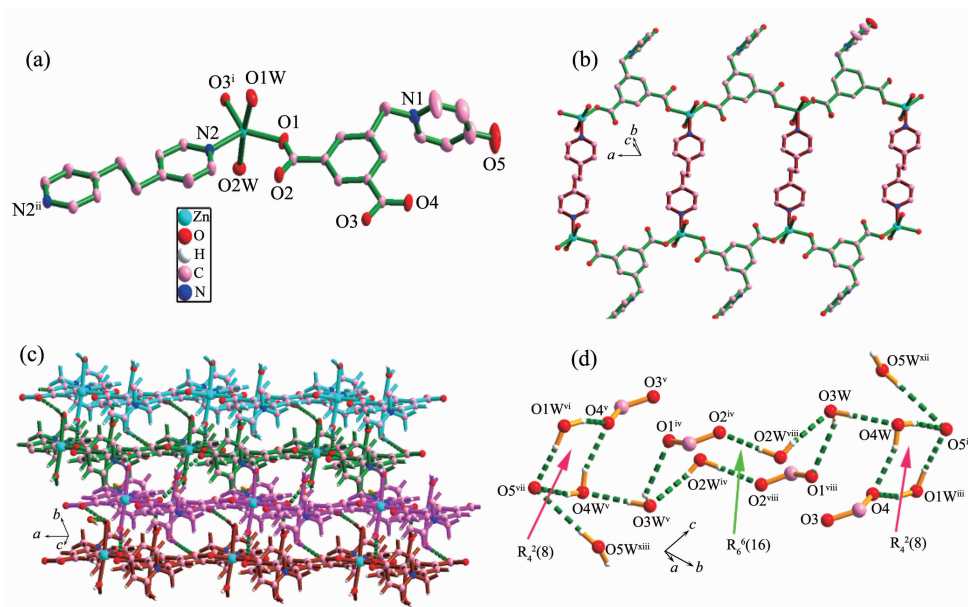
### 2.1 Crystal structure of $\{[\text{Zn}(\text{L})(\text{bpa})_{0.5}(\text{H}_2\text{O})_2] \cdot 2.25\text{H}_2\text{O}\}_n$ (**1**)

The compound **1** crystallizes in the monoclinic system with space group  $P\bar{1}$ . Its asymmetric unit consists of one Zn(II) center, half of a bpa ligand, one  $\text{L}^{2-}$  anion, two coordinated water molecules, and three free water molecules with the total site occupancies of 2.25 (Fig.1a). The Zn(II) center is five-coordinated by two carboxylic oxygen atoms (O1, O4<sup>i</sup>) from two different  $\text{L}^{2-}$  ligands, two oxygen atoms (O1W, O2W) from two water molecules and one nitrogen atom (N2) from one bpa ligand. The coordination geometry of Zn1 atom is a distorted trigonal bipyramidal with two water oxygen atoms (O1W and O2W) at the axial position (Fig.1a). The Zn1-O bond lengths range from 0.195 2(2) to

0.229 1(2) nm, and the Zn1-N bond distance is 0.205 5(2) nm. The  $\text{L}^{2-}$  anion bridges two Zn(II) atoms with both two carboxylic groups in  $\mu_2\text{-}\eta^1:\eta^1$  modes (Scheme 1a). In this way,  $\text{L}^{2-}$  anions link neighboring Zn1 atoms to yield an infinite 1D  $(\text{Zn-L})_n$  chain. Such  $(\text{Zn-L})_n$  chains are further bridged by bpa molecules into an infinite 1D ladder-like chain (Fig.1b). Such chains are further united together by numerous hydrogen bonds involving the coordinated waters, lattice waters and carboxyl oxygen atoms to generate a 3D supramolecular architecture (Fig.1c). According to graph set analysis nomenclature<sup>[22]</sup>, the hydrogen motifs within the water cluster can be assigned to be  $R_4^2(8)$  and  $R_6^6(16)$ , respectively (Fig.1d, Table 3).

### 2.2 Crystal structure of $\{[\text{Cd}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ (**2**)

Compound **2** crystallizes in the triclinic space group  $P\bar{1}$ . The asymmetric unit contains one Cd(II)

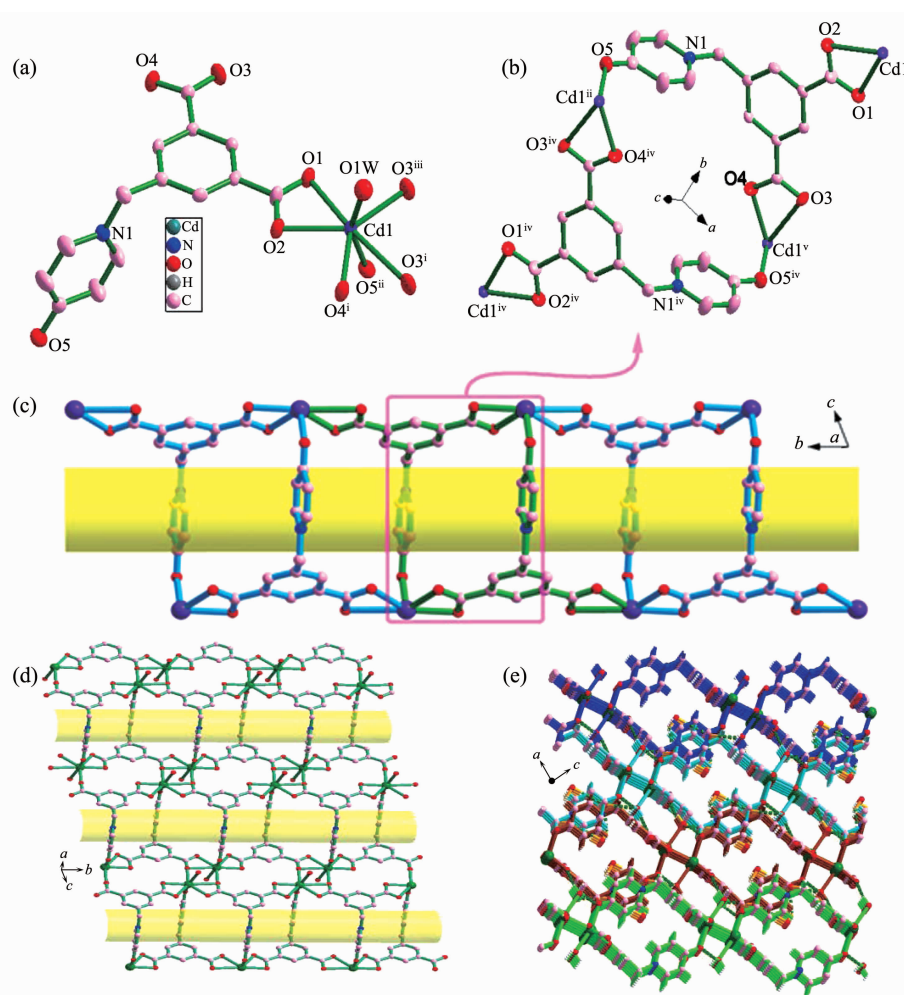


Hydrogen atoms and the solvent water molecule are omitted for clarity in (a); Symmetry codes: <sup>i</sup>  $1+x, y, z$ ; <sup>ii</sup>  $3-x, -y, -z$ ; <sup>iii</sup>  $1-x, 1-y, 1-z$ ; <sup>iv</sup>  $1-x, -y, 1-z$ ; <sup>v</sup>  $-x, -y, 1-z$ ; <sup>vi</sup>  $-1+x, -1+y, z$ ; <sup>vii</sup>  $x, -1+y, -1+z$ ; <sup>viii</sup>  $-1+x, y, z$ ; <sup>ix</sup>  $-x, 1-y, 2-z$ ; <sup>x</sup>  $2-x, -y, 1-z$ ; <sup>xi</sup>  $1+x, y, -1+z$ ; <sup>xii</sup>  $-x, 1-y, 1-z$ ; <sup>xiii</sup>  $x, -1+y, z$

Fig.1 (a) Metal coordination and atom labeling in compound **1** with thermal ellipsoids at 50% probability level; (b) 1D ladder-like chain; (c) View of 3D supramolecular framework of **1** via hydrogen bonds (the dashed lines represent the hydrogen bonds); (d) Hydrogen bonds in compound **1**

center, one  $L^{2-}$  anion, one coordinated water molecule, and two lattice water molecules. The Cd1 is seven-coordinated in a pentagonal bipyramidal geometry. As shown in Fig.2a, five carboxylate oxygen atoms (O1, O2, O3<sup>i</sup>, O4<sup>i</sup>, and O3<sup>iii</sup>) from three distinct  $L^{2-}$  anions form the equatorial plane; O5<sup>ii</sup> (HO- $L^2$ ) and O1W (H<sub>2</sub>O) occupy the axial positions. The bond length of Cd1-O is in the range of 0.227 4(3)~0.239 8(2) nm. Each  $L^{2-}$  ligand bridges four crystallographically identical Cd1 ions with one of the carboxylate groups in a  $\mu_2-\eta^1:\eta^1$  mode, while the other in a  $\mu_3-\eta^1:\eta^2$  coordination mode and the hydroxyl group in monodentate coordination mode (Scheme 1b). Thus,

two cadmium ions are first linked by two  $L^{2-}$  anions via the carboxylate groups and monodentate hydroxyl group to generate a  $[Cd_2(L)_2]$  metallamacrocycle with the Cd-Cd distance being 1.129 1 nm (Fig.2b). Each metallamacrocycle links two distinct metallamacrocycle together to form the tube (Fig.2c). The carboxylate groups in  $\mu_3-\eta^1:\eta^2$  coordination mode further participate in the coordination with Cd1 ions of the tube. Thus, the tubes are connected together to give rise to a 2D layer with tubular channels (Fig.2d). Furthermore, the 2D layers are further extended into 3D supramolecular architecture via hydrogen-bonding interactions (Fig.2e, Table 3).



Thermal ellipsoids at 50% probability level in (a) and (b); Hydrogen atoms and the solvent water molecule are omitted for clarity; Symmetry codes: <sup>i</sup>  $x, 1+y, z$ ; <sup>ii</sup>  $2-x, 1-y, 1-z$ ; <sup>iii</sup>  $3-x, 1-y, -z$ ; <sup>iv</sup>  $2-x, -y, 1-z$ ; <sup>v</sup>  $x, -1+y, z$ ; <sup>vi</sup>  $1+x, 1+y, -1+z$ ; <sup>vii</sup>  $2-x, 2-y, -z$ ;

<sup>viii</sup>  $1-x, -y, 1-z$ ; <sup>ix</sup>  $2-x, 1-y, -z$

Fig.2 (a) Metal coordination and atom labeling in compound **2**; (b) Dinuclear metallamacrocycle unit; (c) Side view of the tubular structure; (d) Tubular channels perpendicular to the  $ab$  plane of **2**; (e) Three dimensional supramolecular structure of **2**

Table 3 Geometrical parameters of hydrogen bonds in compounds 1~2

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
Compound 1				
O(1W)-H(1WA)···O(5) <sup>vi</sup>	0.085 6	0.183 1	0.267 7	169.72
O(1W)-H(1WB)···O(4) <sup>iii</sup>	0.086 6	0.213 7	0.289 0	144.98
O(2W)-H(2WA)···O(2) <sup>x</sup>	0.085 1	0.188 0	0.272 9	175.72
O(2W)-H(2WB)···O(3W) <sup>i</sup>	0.072 1	0.215 6	0.282 5	154.77
O(3W)-H(3WA)···O(4w)	0.085 8	0.194 8	0.280 6	178.94
O(3W)-H(3WB)···O(1) <sup>viii</sup>	0.085 0	0.233 4	0.292 3	126.69
O(4W)-H(4WA)···O(4)	0.085 0	0.199 1	0.280 5	160.05
O(4W)-H(4WB)···O(5) <sup>ix</sup>	0.072 0	0.207 5	0.275 8	158.52
Compound 2				
O(1W)-H(1WA)···O(1) <sup>vii</sup>	0.083 2	0.227 6	0.298 9	143.85
O(1W)-H(1WB)···O(5) <sup>vi</sup>	0.089 7	0.203 8	0.284 8	149.66
O(2W)-H(2WA)···N(1)	0.082 2	0.242 3	0.319 0	155.83
O(2W)-H(2WC)···O(1W) <sup>ix</sup>	0.085 0	0.212 9	0.298 0	179.94
O(3W)-H(2WA)···O(2W)	0.085 0	0.234 0	0.318 8	175.81
O(3W)-H(2WC)···O(2W) <sup>viii</sup>	0.080 1	0.213 9	0.281 3	141.94

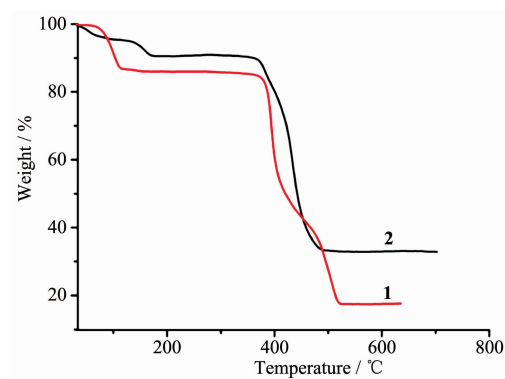
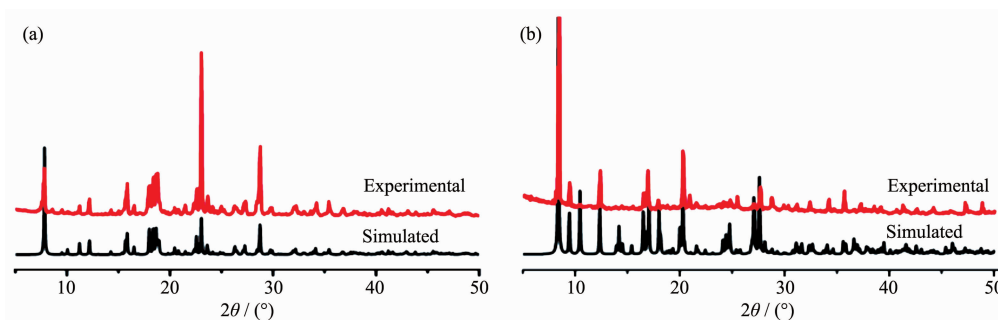
Symmetry codes: <sup>i</sup> 1+x, y, z; <sup>iii</sup> 1-x, 1-y, 1-z; <sup>viii</sup> -1+x, y, z; <sup>ix</sup> -x, 1-y, 2-z; <sup>x</sup> 2-x, -y, 1-z; <sup>vi</sup> 1+x, y, -1+z for **1**; <sup>vi</sup> 1+x, 1+y, -1+z;

<sup>vii</sup> 2-x, 2-y, -z; <sup>viii</sup> 1-x, -y, 1-z; <sup>ix</sup> 2-x, 1-y, -z for **2**.

### 2.3 Thermal analyses and PXRD analyses

Thermal gravimetric analysis (TGA) was used to characterize the thermal stability of compounds, and the TGA of compounds **1~2** were carried out in nitrogen atmosphere (Fig.3). For compound **1**, the weight loss of 14.99% from 30 to 117 °C is assigned to the loss of two coordinated and 2.25 lattice water molecules (Calcd. 15.15%). There is no further weight loss from 117 to 362 °C. After 362 °C, the organic components start to decompose. In the TG curve of compound **2**, the weight loss in the range of 30~209 °C (Obsd. 11.53%, Calcd. 12.35%) can be attributed to the removal of two lattice and one coordinated water molecules. The further weight losses represented the decomposition of the compound **2**.

The synthesized products of **1~2** have been characterized by powder X-ray diffraction (PXRD). As shown in Fig.4, the experimental PXRD patterns correspond well with the results simulated from the

Fig.3 TG curves for compounds **1** and **2**Fig.4 Simulated and experimental PXRD patterns for compounds **1** (a) and **2** (b)

single crystal data, indicating the high purity of the synthesized samples and single phases of compounds **1**~**2**.

## 2.4 Photochemical properties

The solid-state photo-luminescent properties of the free  $H_3LCl$  ligand, coordination polymers **1** and **2** have been investigated in the solid state at room temperature. The emission spectra of these compounds are shown in Fig.5. An intense band is observed at 412 nm ( $\lambda_{ex}$ =317 nm) for  $H_2L$ . Compared to the  $H_3LCl$  ligand, compound **1** results in red shift of 13 nm (425 nm,  $\lambda_{ex}$ =364 nm). The shift of the emission maximum between **1** and  $H_3LCl$  is considered to mainly originate from the influence of the coordination of the ligand to metal atom<sup>[23-24]</sup>. The compound **2** has same emission peak of 412 nm ( $\lambda_{ex}$ =315 nm) with the free  $H_2L$ , which indicates that it may originate from metal-perturbed intraligand charge transfers<sup>[25-27]</sup>.

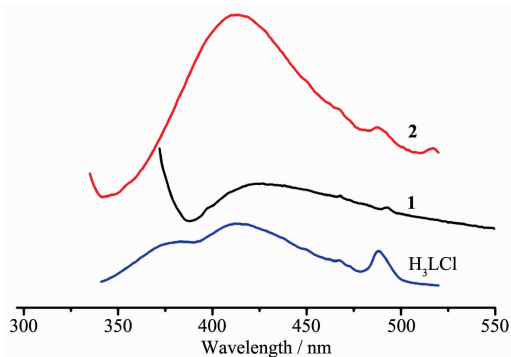


Fig.5 Solid-state emission spectra of free  $H_2L$  and compounds **1** and **2** at room temperature

## 3 Conclusions

We have reported the syntheses, crystal structures and properties of two coordination polymers,  $\{[Zn(L)(bpa)_{0.5}(H_2O)_2] \cdot 2.25H_2O\}_n$  (**1**) and  $\{[Cd(L)(H_2O)] \cdot 2H_2O\}_n$  (**2**) with different structure derived from 5-(4-hydroxypyridinium-1-ylmethyl) isophthalic acid chloride ligand. Both compound **1** and **2** have a 3D supramolecular architecture extended by hydrogen-bonding interactions, but the 3D network of compound **1** is constructed by an infinite 1D ladder-like chain, and that of compound **2** is formed by a 2D layer structure with tubular channels. In addition, the coordination modes of carboxylate groups in two compounds are

different:  $\mu_2-\eta^1:\eta^1$  mode for compound **1**,  $\mu_3-\eta^1:\eta^2$  mode for **2**. Compared to the compounds based on the present ligand and reported in the literature<sup>[17]</sup>, they have not only different structure, but also different coordination modes, which indicate that  $H_3LCl$  ligand is a favorable and fashionable building block for compounds with abundant structural features and useful properties. Subsequent studies will focus on the structures and properties of the novel functional coordination polymers constructed by the present ligand with a wide range of rare earth metals. Further investigations on this domain are underway.

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