



# Syntheses, characterization and crystal structure of $d^{10}$ coordination architectures: From 1D to 3D complexes based on mixed ligands

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## ABSTRACT

Three coordination polymers, namely,  $[\text{Zn}_2(\text{ndd})_2(2,2'\text{-bpy})_2 \cdot 2\text{H}_2\text{O}]_n$  (**1**)  $[\text{Cd}(\text{ndd})(2,2'\text{-bpy})]_n$  (**2**), and  $[\text{Cd}(\text{ndd})(1,4\text{-pyb})]_n$  (**3**), where  $\text{H}_2\text{ndd} = 2,2'\text{-(naphthalene-1,5-diylbis(oxy))diacetic acid}$ ,  $1,4\text{-pyb} = 1,4\text{-bis(pyridin-4-ylmethoxy)benzene}$  and  $2,2'\text{-bpy} = 2,2'\text{-bipyridine}$ , have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction analyses, powder X-ray diffraction and thermogravimetric analysis. Compound **1** can be considered as a 1D chain, which is further linked through the strongly multiple  $\pi\text{-}\pi$  interactions into a 3D supramolecular structure. By changing the metal ions, compound **2** is the 2D square structure ( $10.96 \times 15.20 \text{ \AA}$ ) with the  $4^4 \cdot 6^2$  topology. By changing the auxiliary ligand, compound **3** presents a new (4,5)-connected 3D network with the point symbol of  $(4^2 \cdot 6^5 \cdot 8^3)_2 \cdot (6^6)$ . Furthermore, compounds **1–3** show good fluorescence properties in the solid state at room temperature.

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## 1. Introduction

The rational design and synthesis of coordination polymers has undergone tremendous development owing to their potential applications as functional materials, which include magnetism, catalysis, luminescence, and gas sorption as well as their structural diversities and intriguing topologies [1]. In recent years, a number of coordination polymers with various structural types and topological features have been documented [2]. The final structures of complexes can be effectively influenced by multiple factors such as the coordination trend of metal centers, ligands, solvent systems, templates, counteranions, temperature, pH values and so on [3]. Among them, the most important ones are the geometrical and electronic properties of the metal ions and ligands [4]. Thus, the judicious selection of metal ions and organic ligands play an extremely important part in constructing novel 3D-coordination network [5]. To date, a large number of metal carboxylate coordination complexes have been reported [6]. In order to assemble these molecular structures, carboxylate ligands are frequently employed as bridging ligands to construct coordination polymers [7]. Meanwhile, a fairly effective way to construct desirable networks is the introduction of multidentate flexible N-donor ligands [8]. Thus, We explore the  $\text{H}_2\text{ndd}$  ligand ( $2,2'\text{-(naphthalene-1,5-diylbis(oxy))diacetic acid}$ ) to form coordination networks for the following reasons: (i) its flexibility and conformational freedom allow them to meet the coordination environment of the

transition-metal ions owing to the presence of  $\text{-O-CH}_2\text{-}$  group between the phenyl ring and carboxyl moiety; (ii) multidentate carboxylate ligands have proven to be good candidates for building 3D-coordination networks because of their diverse coordination modes as well.

On the other hand, the  $d^{10}$  metal ( $\text{Cu}^I$ ,  $\text{Ag}^I$ ,  $\text{Au}^I$ ,  $\text{Zn}^{II}$ , and  $\text{Cd}^{II}$ ) complexes have attracted considerable attention not only because they exhibit appealing structures but also due to their good luminescence properties [9]. As an interesting search for the coordination networks, we adopt hydrothermal technique and successfully synthesize three coordination polymers from 1D to 3D by changing the metal ions and the auxiliary ligands. Accordingly, our aim is to design and control the structure of crystals by using the different types of metal ions and organic ligands. Herein, we have synthesized the one-dimensional chain  $[\text{Zn}_2(\text{ndd})_2(2,2'\text{-bpy})_2 \cdot 2\text{H}_2\text{O}]_n$  (**1**). By translating the metal ions ( $\text{Cd}^{II}$ ), we have obtained a two-dimensional layer  $[\text{Cd}(\text{ndd})(2,2'\text{-bpy})]_n$  (**2**). By changing the auxiliary ligands, we have acquired a 3D structure  $[\text{Cd}(\text{ndd})(1,4\text{-pyb})]_n$  (**3**).

## 2. Experiment

### 2.1. Materials and physical methods

All reagents and solvents employed were commercially available and used as received without further purification. The ligands  $\text{H}_2\text{ndd}$  and  $1,4\text{-pyb}$  were synthesized readily by the procedure reported in the literature [10]. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets

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in the range 4000–500 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer (Figs. S1–S3). Solid-state luminescent spectra were measured on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 40 to 1000 °C under nitrogen.

## 2.2. Synthesis of [Zn<sub>2</sub>(nnd)<sub>2</sub>(2,2'-bpy)<sub>2</sub>·2H<sub>2</sub>O]<sub>n</sub> (1)

A mixture of Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.2 mmol, 0.044 g), H<sub>2</sub>nnd (0.2 mmol, 0.055 g), 2,2'-bpy (0.2 mmol, 0.031 g) in H<sub>2</sub>O (14 mL) was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 150 °C for 72 h and then cooled down to room temperature at a rate of 5 °C h<sup>-1</sup>. Colorless crystals of **1** were collected and washed with distilled water and dried in air to give the product; yield, 52.4% (based on Zn<sup>II</sup> salts). Elemental Anal. Calc. for C<sub>48</sub>H<sub>38</sub>N<sub>4</sub>O<sub>14</sub>Zn<sub>2</sub> (1025.65): C, 56.21; H, 3.73; N, 5.46. Found: C, 55.35; H, 3.74; N, 4.83%. IR (KBr pellet, cm<sup>-1</sup>): 3837.44(s), 3732.52(s), 3673.38(s), 3649.04(s), 3613.52(s), 3080.38(m), 1745.99(s), 1591.26(w), 1505.77(m), 1473.72(m), 1442.68(m), 1407.71(w), 1334.67(m), 1318.19(m), 1268.97(w), 1247.17(m), 1212.23(s), 1172.36(s), 1097.79(m), 1071.86(m), 1023.43(m), 973.67(m), 913.32(m), 874.16(s), 768.44(w), 718.58(m), 680.38(m), 632.41(m), 594.49(s), 412.90(s).

## 2.3. Synthesis of [Cd(nnd)(2,2'-bpy)]<sub>n</sub> (2)

Compound **2** was synthesized in an analogous manner to compound **1** except that Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O was replaced by Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.2 mmol, 0.053 g). Colorless crystals of **2** were collected and washed with distilled water and dried in air to give the product; yield, 47.7% (based on Cd<sup>II</sup> salts). Elemental Anal. Calc. for C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Cd (542.82): C, 53.10; H, 3.34; N, 5.16. Found: C, 53.35; H, 2.84; N, 4.83%. IR (KBr pellet, cm<sup>-1</sup>): 3444.41(s), 3057.13(s), 2911.58(s), 1597.87(w), 1573.91(w), 1506.08(w), 1478.92(m), 1409.55(w), 1347.09(w), 1326.43(w), 1274.81(w), 1247.21(w), 1209.28(w), 1168.87(w), 1097.05(w), 1015.13(w),

**Table 1**  
Crystal data and structure refinements for **1–3**.

Complex	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>48</sub> H <sub>38</sub> N <sub>4</sub> O <sub>14</sub> Zn <sub>2</sub>	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> Cd	C <sub>32</sub> H <sub>26</sub> N <sub>2</sub> O <sub>8</sub> Cd
Formula weight	1025.55	542.81	678.96
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>Pna</i> 2(1)	<i>Pbar</i> 1	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	14.207	10.471	19.780
<i>b</i> (Å)	23.962	10.911	18.275
<i>c</i> (Å)	12.772	10.963	7.890
$\alpha$ (°)	90	63.106	90
$\beta$ (°)	90	80.411	101.197
$\gamma$ (°)	90	82.789	90
<i>V</i> (Å <sup>3</sup> )	4348	1099.7	2798
<i>Z</i>	4	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.564	1.639	1.612
$\mu$ (mm <sup>-1</sup> )	1.180	1.037	0.838
<i>F</i> (000)	2096.0	544.0	1376.0
Observed reflection/ unique	21238/7593	6714/4877	16975/6583
<i>R</i> <sub>int</sub>	0.0486	0.0204	0.0611
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	0.994	1.003	1.011
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0360, 0.0701	0.0386, 0.1023	0.0454, 0.0862
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0560, 0.0766	0.0521, 0.1133	0.1178, 0.1283
Flack parameter	0.42		

<sup>a</sup> *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|.

<sup>b</sup> *wR*<sub>2</sub> = [Σ*w*(|*F*<sub>o</sub>|<sup>2</sup> - |*F*<sub>c</sub>|<sup>2</sup>)]/Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>1/2</sup>.

928.76(m), 801.07(w), 779.47(w), 761.67(w), 734.59(w), 713.98(w), 648.09(m), 626.10(w), 586.77(m), 409.99(m).

## 2.4. Synthesis of [Cd(nnd)(1,4-pyb)]<sub>n</sub> (3)

Compound **3** was synthesized in an analogous manner to compound **2** except that 2,2'-bpy was replaced by 1,4-pyb (0.2 mmol, 0.058 g). Colorless crystals of **3** were collected and washed with distilled water and dried in air to give the product; yield, 47.5% (based on Cd<sup>II</sup> salts). Elemental Anal. Calc. for C<sub>32</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub>Cd (678.97): C, 56.60; H, 3.85; N, 4.13. Found: C, 56.24; H, 3.30; N, 3.94%. IR (KBr pellet, cm<sup>-1</sup>): 3424.20(m), 3079.12(m), 2927.57(m), 1746.93(s), 1620.62(w), 1594.19(w), 1507.74(w), 1411.21(w), 1327.18(w), 1268.91(w), 1246.48(w), 1229.55(w), 1171.30(m), 1097.52(m), 1055.41(m), 1019.32(m), 916.00(m), 875.72(m), 814.34(m), 778.81(m), 731.54(m), 626.65(m), 596.19(m), 485.23(m). The simulated and experimental PXRD patterns of **1–3** are shown in Figs. S4–S6 (in the Supporting information). The simulated and experimental PXRD patterns are in good agreement with each other, indicating the phase purities of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

## 2.5. X-ray crystallography study

Data collection of complexes **1–3** were performed on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at room temperature. All absorption corrections were performed by using the SADABS program. The

**Table 2**  
Selected bond lengths (Å) and angles (°) for complexes **1–3**.

Complex 1			
Zn(2)–N(1)	2.110(4)	Zn(2)–N(2)	2.112(4)
Zn(1)–N(3)	2.125(4)	Zn(1)–N(4)	2.121(4)
Zn(1)–O(1)A	2.156(3)	Zn(1)–O(2)A	2.278(3)
Zn(2)–O(1W)	2.116(3)	Zn(1)–O(2W)	2.093(3)
Zn(2)–O(4)	2.314(3)	Zn(2)–O(5)	2.125(3)
Zn(2)–O(8)	2.057(3)	Zn(1)–O(11)	2.065(3)
O(11)–Zn(1)–O(2W)	92.10(11)	O(11)–Zn(1)–N(4)	111.65(13)
O(2W)–Zn(1)–N(4)	94.59(12)	O(11)–Zn(1)–N(3)	86.58(12)
O(2W)–Zn(1)–N(3)	169.56(13)	N(4)–Zn(1)–N(3)	76.31(15)
O(11)–Zn(1)–O(1)A	149.01(14)	O(2W)–Zn(1)–O(1)A	96.94(12)
N(4)–Zn(1)–O(1)A	149.01(14)	N(3)–Zn(1)–O(1)A	93.51(13)
O(11)–Zn(1)–O(2)A	155.68(11)	O(2W)–Zn(1)–O(2)A	93.80(12)
N(4)–Zn(1)–O(2)A	91.35(13)	N(3)–Zn(1)–O(2)A	91.57(13)
O(1)A–Zn(1)–O(2)A	59.31(12)		
Complex 2			
Cd(1)–O(1)	2.171(3)	Cd(1)–N(2)	2.324(3)
Cd(1)–N(1)	2.342(3)	Cd(1)–O(3)	2.416(3)
Cd(1)–O(4)	2.467(3)	O(1)–Cd(1)–N(2)	139.02(13)
O(1)–Cd(1)–N(1)	105.96(14)	N(2)–Cd(1)–N(1)	71.00(12)
O(1)–Cd(1)–O(3)	101.07(13)	N(2)–Cd(1)–O(3)	108.50(11)
N(1)–Cd(1)–O(3)	135.96(11)	O(1)–Cd(1)–O(4)	134.49(12)
N(2)–Cd(1)–O(4)	86.42(11)	N(1)–Cd(1)–O(4)	83.45(11)
O(3)–Cd(1)–O(4)	53.10(9)		
Complex 3			
Cd(1)–O(7)	2.230(4)	Cd(1)–N(2)A	2.307(4)
Cd(1)–N(1)	2.311(4)	Cd(1)–O(1)	2.374(4)
Cd(1)–O(1)B	2.447(4)	Cd(1)–O(2)B	2.476(4)
O(7)–Cd(1)–N(2)A	102.48(14)	O(7)–Cd(1)–N(1)	83.85(14)
N(2)A–Cd(1)–N(1)	170.20(16)	O(7)–Cd(1)–O(1)	116.73(15)
N(2)A–Cd(1)–O(1)	90.99(14)	N(1)–Cd(1)–O(1)	79.42(14)
O(7)–Cd(1)–O(1)B	111.25(15)	N(2)A–Cd(1)–O(1)B	91.98(13)
N(1)–Cd(1)–O(1)B	92.66(13)	O(1)–Cd(1)–O(1)B	129.96(8)
O(7)–Cd(1)–O(2)B	163.51(15)	N(2)A–Cd(1)–O(2)B	84.62(13)
N(1)–Cd(1)–O(2)B	91.27(13)	O(1)–Cd(1)–O(2)B	77.54(12)
O(1)B–Cd(1)–O(2)B	53.10(12)		

Symmetry codes: A, 1 + *x*, *y*, *z* for **1**; A, 2 - *x*, -*y*, -1 - *z* for **2**; A, -1 + *x*, *y*, -1 + *z*; B, *x*, 0.5 - *y*, -0.5 + *z* for **3**.

crystal structure was solved by direct methods and refined with full-matrix least-squares (SHELXL-97) [11] with atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms of aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. In compound **1**, H atoms of water molecules could not be introduced in the refinement but were included in the structure factor calculation. The detailed crystallographic data and structure refinement parameters are summarized in Table 1. Selected bond lengths and angles for complexes **1–3** are given in Table 2. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data center as Supplementary publication.

### 3. Results and discussion

#### 3.1. Description of the crystal structures of **1–3**

##### 3.1.1. Structure of $[Zn_2(ddd)_2(2,2'\text{-bpy})_2\cdot 2H_2O]_n$ (**1**)

The single-crystal X-ray structural analysis reveals that compound **1** crystallizes in the orthorhombic space group  $Pna2_1$  and the asymmetric unit of **1** consists of two  $Zn^{II}$  ions, two *ddd* ligands, two 2,2'-bpy ligands and two lattice water molecules. Each  $Zn^{II}$  ion is coordinated by three carboxylate oxygen atoms of two *ddd* ligands, one oxygen atom of one water molecule and two nitrogen atoms of one 2,2'-bpy ligand to furnish the distorted octahedral coordination geometry, as shown in Fig. 1a. The Zn–O (2.057(3)–2.314(3) Å) and Zn–N (2.110(4)–2.125(4) Å) bond distances are all in the normal ranges [12].

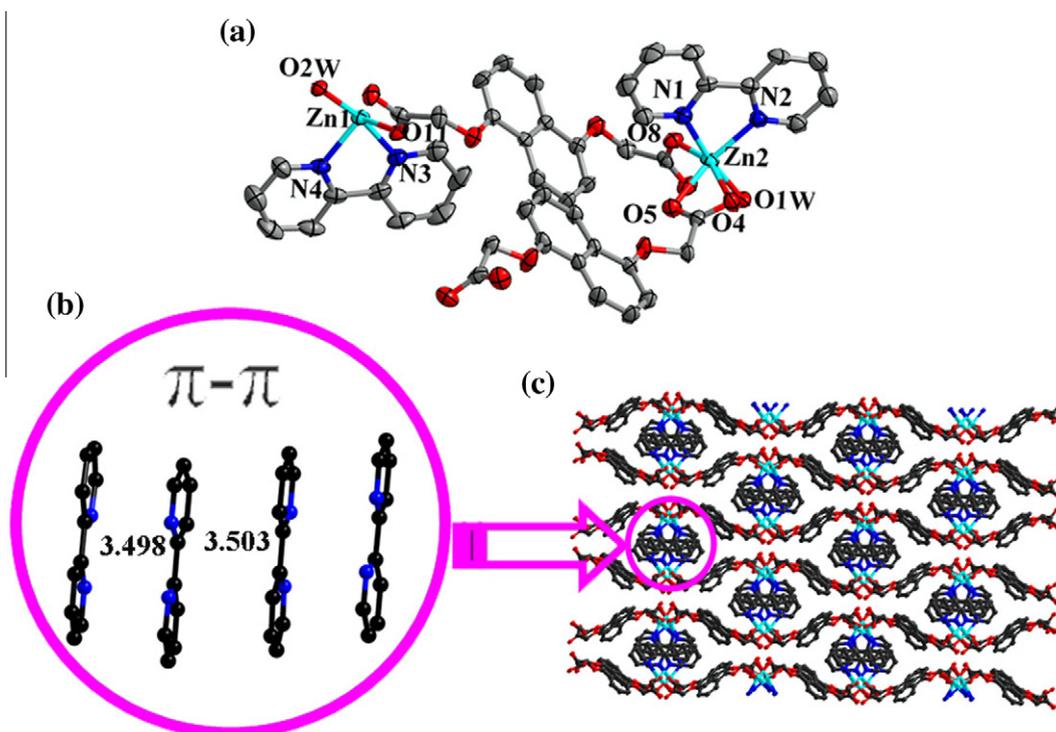
The structure of compound **1** is an infinite zigzag chain constructed by zinc ions and *ddd* ligands, decorated with bidentate 2,2'-bpy ligands. The *ddd* ligand coordinates to metal in a bis-monodentate and bis-bidentate fashion to generate one-dimensional chain (Fig. S7 in the Supporting information). The

adjacent chains possess weak  $\pi$ – $\pi$  interactions, occur between the adjacent 2,2'-bpy ligands (parallel stacking with distances centroid–centroid of 3.498 and 3.503 Å). The ring normal and the vector between the ring centroids form an angle of about 0.5°, as shown in Fig. 1b. Meanwhile, the  $\pi$ – $\pi$  stacking makes the whole structure more stable (Fig. 1c). Remarkably, compound **1** crystallizes in the non-centrosymmetric polar space group  $Pna2_1$  [13]. Accordingly, the molecules must all be oriented in the same direction along the polar [001] directions. This polar packing within the chain and of adjacent chains in the crystal of **1** probably originates from the inter-chain  $\pi$ – $\pi$  interactions [14]. The adjacent chains are further connected through strongly multiple  $\pi$ – $\pi$  interactions to form a layer.

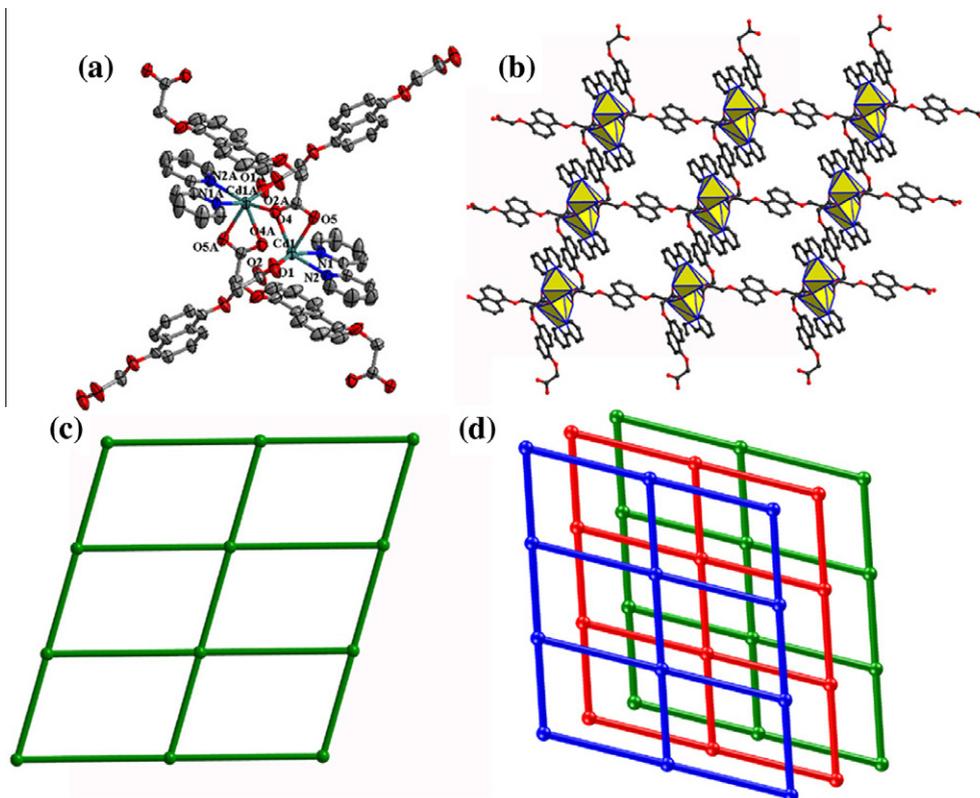
##### 3.1.2. Structure of $[Cd(ddd)(2,2'\text{-bpy})]_n$ (**2**)

Compound **2** was obtained by changing the metal ions and it shows a 2D square structure with dimension of  $10.963 \times 15.202$  Å (the distance of adjacent dinuclear units) that is built from dinuclear  $Cd_2$  units. The crystal structure of **2** contains one  $Cd^{II}$  atom, one *ddd* ligand and one 2,2'-bpy ligand in the asymmetric unit. Each  $Cd^{II}$  ion is coordinated by four carboxylate oxygen atoms (Cd–O 2.172(3)–2.416(3) Å) of two *ddd* ligands and two nitrogen atoms (Cd–N 2.324(3)–2.342(3) Å) of one 2,2'-bpy ligand to complete the distorted octahedral coordination geometry. As shown in Fig. 2a, the Cd–O and Cd–N bond distances are all in the normal ranges [15]. Two crystallographically equivalent  $Cd^{II}$  atoms are bridged by two  $\mu_2$ -carboxylates oxygen giving a shaped SBU  $[Cd_2(CO_2)_4N_2]$  in which the Cd···Cd distance is 3.9446(12) Å.

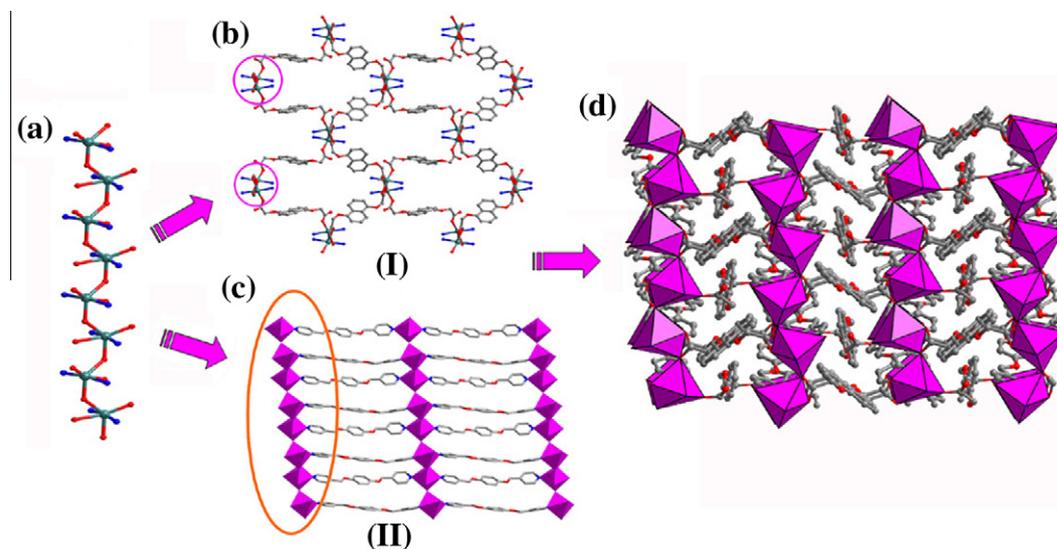
In compound **2**, the *ddd* ligand can be considered as a linear linker. All Cd atoms are connected by carboxyl groups and pyridyl-N atoms of 2,2'-bpy ligands, thus forming novel shape of framework  $\{Cd_4O_{36}C_{42}N_8\}$ , as illustrated in Fig. 2b. Meanwhile, each dinuclear units can be considered as a node, each node is attached to four *ddd* ligands and two 2,2'-bpy ligands, which can be considered as



**Fig. 1.** (a) Coordination environment of  $Zn^{II}$  in **1** with the ellipsoids drawn at the 30% probability level and hydrogen atoms were omitted for clarity (symmetry transformations used to generate equivalent atoms: A,  $1+x, y, z$ ). (b) The compound **1** is packed by the  $\pi$ – $\pi$  interactions along the axis. (c) Schematic view of the 3D supramolecular structure.



**Fig. 2.** (a) Coordination environment of  $\text{Cd}^{\text{II}}$  atom in **1** with the ellipsoids drawn at the 30% probability level and hydrogen atoms were omitted for clarity (symmetry transformations used to generate equivalent atoms: A,  $2 - x, -y, 1 - z$ ). (b) Ball-and-stick and schematic representation of the (4,4) nets in the structure of **2**. (c) Schematic view of the 4-connected net of **2** with  $(4^4.6^2)$  topology. (d) The packing mode of 2D nets in **2**.



**Fig. 3.** (a) View of the 1D chain. (b and c) View of the 2D layer structure of compound **3**. (d) Schematic representation of the 3D-coordination network.

a 4-connected node; While, each *ndd* ligand can be seen as a linear linker between two nodes. Thus, a distorted 2D network sustained by 4-connected nodes is then yielded, as illustrated in Fig. 2c. The 2D nets are packing in *-aaa-* mode as show in Fig. 2d. Each window shows dimension of  $10.963 \times 15.202 \text{ \AA}^2$  for each side: Each window shows dimension of  $10.963 \times 15.202 \text{ \AA}^2$  for each side:  $\pi$ - $\pi$  stacking interactions exist between pyridine and aromatic rings from adjacent layers. The ring normal and the vector between the ring centroids form an angle of about  $8.431^\circ$  up to centroid-

centroid distances of  $3.791 \text{ \AA}$  [16]. Significant  $\pi$ - $\pi$  and C-H $\cdots\pi$  (edge-to-face separation  $3.428$  and  $3.576 \text{ \AA}$ ) supramolecular interactions between the aromatic rings contained in this structure stabilize the structure adopted.

### 3.1.3. Structure of $[\text{Cd}(\text{ndd})(1,4\text{-pyb})]_n$ (**3**)

Compound **3**, obtained by changing the auxiliary ligands, is a 3D-coordination network. The single-crystal X-ray structural analysis reveals that compound **3** crystallizes in the monoclinic space

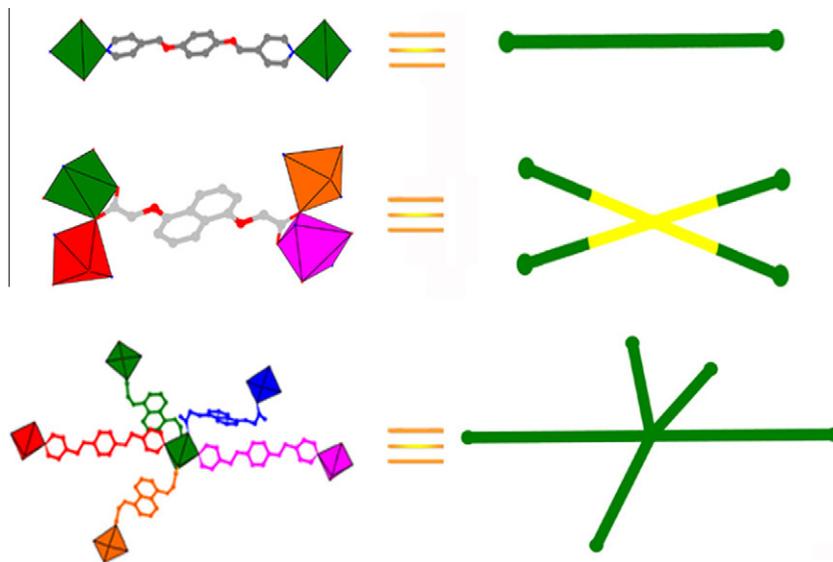


Fig. 4. Ball-and-stick and polyhedral representations of the 1,4-pyb line linker, 4-connected ndd ligand and 5-connected mononuclear cadmium.

group  $P2(1)/c$  and the asymmetric unit of **3** consists of one  $\text{Cd}^{\text{II}}$  ion, one ndd ligand and one 1,4-pyb ligand. Each  $\text{Cd}^{\text{II}}$  ion is coordinated by four oxygen atoms from three ndd ligands and two N sites from two 1,4-pyb ligands to furnish the distorted octahedral coordination geometry, as shown in Fig. S8 (in the Supporting information). The Cd–O (2.230(4)–2.476(4) Å) and Cd–N (2.307(4)–2.311(4) Å) bond distances are all in the normal ranges [15]. In compound **3**, the two carboxylate groups of  $\text{H}_2\text{ndd}$  exhibit the two types of coordination modes, one is bis(monodentate) coordination mode and the other is tridentate coordination mode (Fig. S9 in the Supporting information). Apart from the bis(monodentate), such a tridentate bridge mode is a key factor for the formation of the multinuclear cluster.

In order to interpret the whole network clearly, the structure of **3** could be described as  $-\text{Cd}-\text{O}-\text{Cd}-$  chain (Fig. 3a), which is constructed by bridging  $\mu_2$ -carboxylate oxygens and Cd ions. In addition, the adjacent chains were connected to build a 2D layer structure with the Cd...Cd distance of 4.362 Å. In the network, there are the two types of building blocks (Fig. 3b and c): one is formed to shape of framework  $[\text{Cd}_5\text{O}_{36}\text{C}_{34}]$  (Fig. S10 in the Supporting information), which is constructed by the ndd ligands and  $\text{Cd}^{\text{II}}$  ions; the other is constructed to shape of framework  $[\text{Cd}_4\text{O}_{18}\text{C}_{36}\text{N}_8]$  (Fig. S11 in the Supporting information), which is constructed by the 1,4-pyb ligands and  $\text{Cd}^{\text{II}}$  ions. Finally, the adjacent layers were linked by the ndd ligands to lead to a complicated 3D network (Fig. 3d).

The construction of the topological network and the topological analysis of the structure were performed using OLEX along with TOPOS program [17]. The mononuclear cadmium is treated as a single node. The ndd ligand is considered as the 4-connected node owing to the ndd ligand connects four cadmium atoms. Meanwhile, each 1,4-pyb ligand is considered as the line linker and each cadmium atom is considered as a 5-connected node (Fig. 4), the overall structure of complex **3** is an extended neutral 3D (4,5)-connected network with the point symbol of  $(4^2\cdot 6^5\cdot 8^3)_2\cdot (6^6)$  (Fig. 5).

According to present literature, the one known example of a (1D  $\rightarrow$  3D) chain is the compound  $[\text{Zn}(\text{L})(\text{phen})(\text{H}_2\text{O})_n]$  (L = 2,2'-(naphthalene-1,5-diylbis(oxy))diacetic acid, Phen = 1,10-phenanthroline) reported by us very recently [18]. Differing from the compound **1** is auxiliary ligands (2,2'-bpy is changed to Phen). A few crystal structures have been observed for the compound **2**

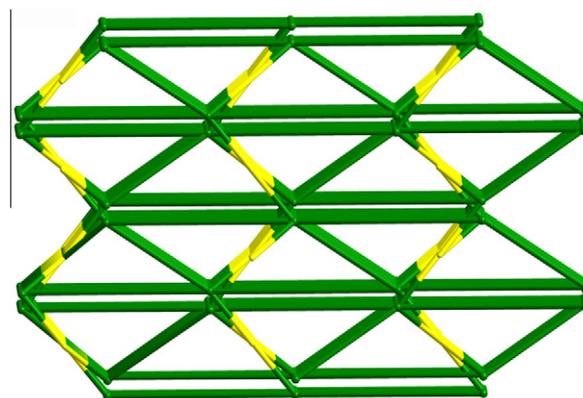


Fig. 5. Schematic representation of the (4,5)-connected network with point symbol of  $(4^2\cdot 6^5\cdot 8^3)_2\cdot (6^6)$ .

[19]. As far as we know, the only one example of the 3D-coordination network is the complex  $[\text{Cd}_2(\text{btec})(\text{btb})_3(\text{H}_2\text{O})_{10}(\text{btb} = 1,4\text{-bis}(1,2,4\text{-triazol-1-yl})\text{butane}, \text{btec} = 1,2,4,5\text{-benzenetetracarboxylate})$  [20]. The different of this compound is that compound **3** exhibits  $-\text{Cd}-\text{O}-\text{Cd}-$  chain.

### 3.2. The thermal and photoluminescent properties of **1–3**

The photoluminescent properties of **1–3** and the free ligand  $\text{H}_2\text{ndd}$  were examined in the solid state at room temperature. As shown in Fig. 6, the main emission peak of  $\text{H}_2\text{ndd}$  is at 474 nm ( $\lambda_{\text{ex}} = 363$  nm). Compound **1** shows the emission maxima at 457 nm ( $\lambda_{\text{ex}} = 388$  nm). While, compound **2** shows the emission maxima at 498 nm ( $\lambda_{\text{ex}} = 336$  nm). Compound **3** shows the emission maxima at 450 nm ( $\lambda_{\text{ex}} = 370$  nm). In comparison with that of the free ligand, the maximum emission wavelengths of compounds **1** and **3** exhibit slight blue-shift, which is probably due to intraligand charge transitions. On the contrary, compound **2** shows slight red-shift, which might be attributed to intraligand charge transitions [21].

The TGA of compounds **1–3** have been investigated in order to characterize the three compounds more fully in terms of their thermal stability, as shown in Fig. 7. For compound **1**, the weight loss

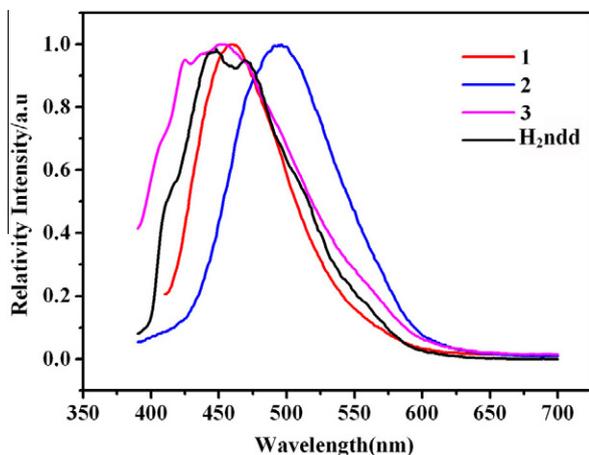


Fig. 6. Emission spectra of compounds **1–3** and H<sub>2</sub>ndd in the solid state at room temperature.

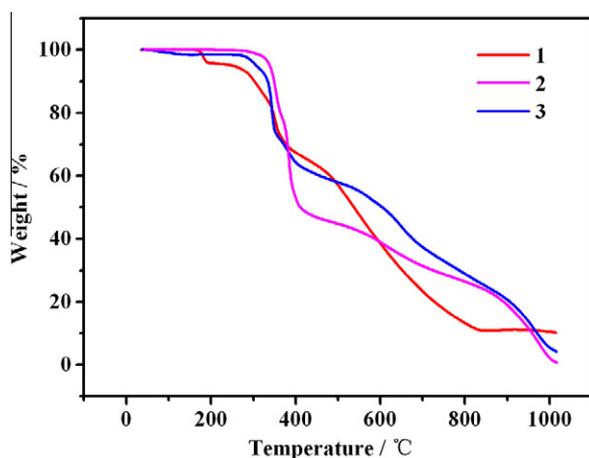


Fig. 7. The TGA curves of **1–3**.

corresponding to the release of a lattice water molecule is observed (obsd 3.51%, calcd 4.08%). The dehydrated complex is stable up to 319 °C. The frameworks collapsed in the temperature range of 319–823 °C. The remaining weight corresponds to the formation of ZnO (obsd 10.37%, calcd 15.80%). The TGA study of compound **2** shows no weight loss from room temperature to 336 °C, suggesting that the frameworks are thermally stable. Above 336 °C, a rapid weight loss is observed which is attributed to the burning of the organic ligands. The TGA study of compound **3** shows no weight loss from room temperature to 330 °C. Above 330 °C, a rapid weight loss is observed which is attributed to the burning of the organic ligands.

#### 4. Conclusions

In summary, we have synthesized and characterized three new coordination polymers by using 2,2'-(naphthalene-1,5-diylbis(oxy))diacetic acid, 2,2'-bipyridine and 1,4-bis(pyridin-4-ylmethoxy)benzene ligands. Compound **1** is a 1D chain, which is constructed to a 3D supramolecule structure by the strong  $\pi$ – $\pi$  interactions. By changing the metal ions, we have obtained a 2D layer with the 4<sup>4</sup>.6<sup>2</sup> topology. Meanwhile, by changing the auxiliary ligands, we have acquired a 3D-coordination network. Moreover, compounds **1–3** show good fluorescence properties in the solid state at room temperature.

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#### Appendix A. Supplementary material

CCDC 860060–860062 contain the supplementary crystallographic data for compounds **1–3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2012.05.037>.

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