

# Different aliphatic dicarboxylates affected assemble of new coordination polymers constructed from flexible–rigid mixed ligands

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## Abstract

In this article, seven coordination polymers:  $[\text{Cd}(\text{C}_5\text{H}_6\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**1**),  $[\text{Zn}(\text{C}_5\text{H}_6\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**2**),  $[\text{Cd}(\text{C}_6\text{H}_8\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**3**),  $\{[\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_4\text{H}_4\text{O}_4) \cdot 4\text{H}_2\text{O}\}_n$  (**4**),  $[\text{Mn}_5(\text{C}_4\text{H}_4\text{O}_4)_4(\text{O})]_n$  (**5**),  $[\text{Cd}(\text{C}_4\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_n$  (**6**) and  $[\text{Zn}(\text{C}_6\text{H}_6\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_n$  (**7**) were synthesized and characterized by single-crystallographic X-ray diffraction. Compounds **1** and **2** are two-dimensional layers connected by glutarate anions and 4,4'-bpy. Unlike compounds **1** and **2**, compound **3** is a two-fold interpenetration network. Compound **4** is a one-dimensional chain-like structure, which is further extended to two-dimensional supramolecular layer structure with hydrogen bond. During the synthesis of compound **4**, to our surprise, we got compound **5**; compound **5** is an interesting three-dimensional network composed of pentanuclear Mn(II) building units and succinate anions. Compound **6** is also a two-dimensional supramolecular layer structure composed of one-dimensional chain-like structure with hydrogen bonds and  $\Pi$ – $\Pi$  interactions. Compound **7** is also a one-dimensional chain-like structure, which is further connected with the same kind of interaction to generate two-dimensional supramolecular layer structure. Furthermore, compounds **1** and **2** both exhibit fluorescent property at room temperature.  
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**Keywords:** Flexible aliphatic ligands; Carbon number affected; Interpenetration; Hydrothermal reaction; Fluorescent property

## 1. Introduction

There has been much research in coordination polymers because of their important applications for the development of new functional materials in molecular selection, ion exchange, electrical conductivity, catalysis, and novel magnetic properties [1–8]. Much effort has been devoted to controllable formation of desirable one-, two-, and three-dimensional coordination polymers with the concept of rational design and crystal engineering. Interest in this area has led to studies of the roles of metal ions (coordination properties), the ligands (functionality and steric and electronic properties), and the anions (size and coordinating ability) in the formed structures [9–14]. The selection of multifunctional organic ligands containing appropriate

coordination sites linked by a spacer with specific positional orientation is especially crucial to the construction of desirable frameworks. It is well known that carboxylate ligands play an important role in coordination chemistry. They usually adopt binding modes as diverse as terminal monodentate, chelating to one metal center, bridging bidentate in a syn–syn, syn–anti, and anti–anti configuration to two metal centers, and bridging tridentate to two metal centers [15–18]. It is noteworthy that rigid dicarboxylates ligand such as 1,4-benzenedicarboxylate; 1,3-benzenedicarboxylate, and 1,2-benzenedicarboxylate, have been widely used in constructing novel metal–organic hybrid complexes [19,20]. However, the saturated aliphatic dicarboxylate such as, succinate, glutarate, and adipate are less used [21–25]. There are at least two intriguing structural features of this kind of ligands. Firstly, different from the rigid dicarboxylate ligands, the saturated aliphatic dicarboxylate ligands exhibit conformational and coordination versatility due to single-bonded carbon chains.

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Secondly, we can control the backbone carbon number of aliphatic dicarboxylate to synthesize some interesting structures [26–31].

Nowadays, coordination polymers constructed from neutral and anionic mixed bridging ligands have attracted chemists' interest not only for this can lead to extended structures and functional properties, but it can also make the assembly process more controllable than a single ligand. The prospect of introducing the second or more organic ligands into a reaction system provides further impetus for research on metal–organic framework [32,33]. It should be pointed out that the different types of mixed ligands can lead to diverse complexes composition [34,35]. We deduce that the species of mixed multifunctional ligands play an important role in crystal structure and have great influence on the properties of the final complexes. Here, to discuss the relationship between different aliphatic dicarboxylates and the final structure constructed by this kind of ligands, as well as enrich this system, three kinds of different aliphatic dicarboxylate were introduced. With the change of the backbone carbon number of aliphatic dicarboxylate, we synthesize seven different coordination polymers:  $[\text{Cd}(\text{C}_5\text{H}_6\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**1**),  $[\text{Zn}(\text{C}_5\text{H}_6\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**2**),  $[\text{Cd}(\text{C}_6\text{H}_8\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]_n$  (**3**),  $\{[\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_4\text{H}_4\text{O}_4) \cdot 4\text{H}_2\text{O}\}_n$  (**4**),  $[\text{Mn}_5(\text{C}_4\text{H}_4\text{O}_4)_4\text{O}]_n$  (**5**),  $[\text{Cd}(\text{C}_4\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_n$  (**6**), and  $[\text{Zn}(\text{C}_6\text{H}_6\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_n$  (**7**).

## 2. Experimental

### 2.1. Materials and methods

All chemicals purchased were of reagent grade and were used without further purification. Elemental analyses (C, N, and H) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. FT/IR spectra were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  on an Alpha Centaur FTIR spectrophotometer using KBr pellet. TG analyses were performed on Perkin-Elmer TGA7 instrument in flowing  $\text{N}_2$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . Photoluminescence spectra were measured using a FL-2T2 instrument (SPEX, USA) with 450 W xenon lamp monochromatized by double grating ( $1200\text{ gr mu}^{-1}$ ). All measurements were performed at room temperature.

### 2.2. Syntheses of compounds 1–7

Compound **1** was prepared from the mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.061 g, 0.20 mmol), glutaric acid (0.053 g, 0.40 mmol), and 4,4'-bpy (0.031 g, 0.20 mmol) in 6 mL of  $\text{H}_2\text{O}$ . The mixture was stirred for 25 min, and pH value was then adjusted to 6 with 1 M NaOH. After stirring for a further 20 min, the mixture was transferred to a 23-mL Teflon-lined stainless steel bomb, and kept at  $150^\circ\text{C}$  under autogenous pressure for 4 days. After cooling the reaction system to room temperature during 24 h, yellow block crystals of **1** were obtained. Yield: 0.048 g, 60% (based on Cd). Elem. anal. calcd.: C, 45.18%; H, 3.51%; N,

7.03%. Found: C, 45.23%; H, 3.62%; N, 7.10%. IR: 3103 (vw), 3063 (w), 3040 (w), 1606 (m), 1574 (m), 1553 (s), 1508 (s), 1449 (m), 1437 (s), 1412 (s), 1338 (m), 1317 (m), 1289 (w), 1244 (w), 1171 (w), 1101 (w), 1066 (m), 1043 (w), 1007 (w), 933 (w), 908 (m), 833 (w), 814 (s), 730 (w), 632 (s), 419 (w).

Compound **2** was prepared from the mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.059 g, 0.20 mmol); glutaric acid (0.053 g, 0.40 mmol); 4,4'-bpy (0.031 g, 0.20 mmol), and 6 mL of  $\text{H}_2\text{O}$ . The mixture was stirred for 15 min and sealed in a 23-mL Teflon-lined stainless steel bomb. The bomb was kept at  $140^\circ\text{C}$  under autogenous pressure for 4 days. The reaction system was then cooled to room temperature during 24 h; colorless block crystals of **2** were obtained. Yield: 0.040 g, 57% (based on Zn). Elem. anal. calcd.: C, 51.19%; H, 4.00%; N, 7.98%. Found: C, 51.36%; H, 3.92%; N, 7.90%. IR: 3138 (w), 3104 (m), 1549 (s), 1509 (s), 1489 (m), 1439 (s), 1409 (s), 1342 (m), 1321 (m), 1290 (w), 1260 (w), 1240 (w), 1219 (w), 1174 (w), 1154 (w), 1085 (w), 1067 (m), 1007 (w), 935 (w), 907 (w), 818 (s), 732 (s), 632 (s), 589 (w), 576 (w), 536 (w), 470 (w).

Compound **3** was prepared from the mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.061 g, 0.20 mmol); adipate (0.058 g, 0.40 mmol); 4,4'-bpy (0.031 g, 0.20 mmol), and 8 mL of  $\text{H}_2\text{O}$ . The mixture was stirred for 20 min and sealed in a 23-mL Teflon-lined stainless steel bomb. The bomb was kept at  $160^\circ\text{C}$  under autogenous pressure for 4 days. The reaction system was then cooled to room temperature during 24 h; after cooling the reaction system to room temperature during 24 h, yellow block crystals of **3** were obtained. Yield: 0.059 g, 71% (based on Cd). Elem. anal. calcd.: C, 46.54%; H, 3.91%; N, 6.79%. Found: C, 46.66%; H, 3.82%; N, 6.91%. IR: ( $\text{cm}^{-1}$ ): 3434 (m), 3055 (m), 3010 (w), 2952 (m), 2931 (m), 2893 (m), 1587 (s), 1546 (v), 1504 (s), 1461 (m), 1421 (s), 1345 (w), 1324 (m), 1292 (m), 1161 (m), 1154 (m), 856 (s), 827 (m), 728 (s).

Compound **4** was prepared from the mixture of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.049 g, 0.20 mmol); succinic acid (0.047 g, 0.40 mmol); 4,4'-bpy (0.031 g, 0.20 mmol) and 6 mL of  $\text{H}_2\text{O}$ . The mixture was stirred for 25 min and sealed in a 23-mL Teflon-lined stainless steel bomb. The bomb was kept at  $170^\circ\text{C}$  under autogenous pressure for 5 days. The reaction system was then cooled to room temperature during 24 h; yellow block crystals of **4** were obtained. Yield: 0.054 g, 57% (based on Mn). Elem. anal. calcd.: C, 35.64%; H, 5.99%; N, 5.94%. Found: C, 35.48%; H, 6.12%; N, 5.86%. IR ( $\text{cm}^{-1}$ ): 3253 (s), 2974 (s), 2932 (s), 1679 (s), 1610 (s), 1526 (s), 1409 (s), 1384 (s), 1056 (m), 817 (s), 801 (s), 739 (s), 664 (s), 638 (s). During this process, we also got some colorless crystals of compound **5**.

Compound **6** was prepared from the mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.077 g, 0.25 mmol); succinic acid (0.059 g, 0.50 mmol); 2,2'-bpy (0.078 g, 0.50 mmol) and 8 mL of  $\text{H}_2\text{O}$  and then the pH value were adjusted to 5 with 1 M NaOH. The mixture was stirred for 20 min then placed in a Teflon-lined stainless steel bomb and heated to  $160^\circ\text{C}$

Table 1  
Crystal data and structure refinement for complex **1** to complex **7**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>6</b>	<b>7</b>
Empirical formula	C <sub>15</sub> H <sub>14</sub> CdN <sub>2</sub> O <sub>4</sub>	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> Zn	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Cd	C <sub>16</sub> H <sub>16</sub> Mn <sub>5</sub> O <sub>18</sub>	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub> Cd	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub> Zn
Formula weight	398.68	351.65	412.54	770.99	402.67	407.71
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pbcn</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	8.3758	8.0032	8.6378	9.5942	9.2164	22.642
<i>b</i> (Å)	9.7245	9.4809	9.0439	9.6329	15.916	9.0423
<i>c</i> (Å)	10.028	10.404	11.106	12.541	20.147	17.595
$\alpha$ (deg)	107.07	109.67	109.19	90	90	90
$\beta$ (deg)	94.66	93.26	94.88	97.07	90	103.54
$\gamma$ (deg)	106.92	104.53	102.61	90	90	90
Volume (Å <sup>3</sup> )	734.5	710.9	787.9	1150.3	2955.4	3502.2
<i>Z</i>	2	2	2	2	8	8
<i>F</i> (000)	396	360	408	762	1600	1680
<i>R</i> (int)	0.0327	0.0200	0.0363		0.0466	0.0217
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.953	0.933	1.060	1.044	0.920	1.138
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0401 1 <i>wR</i> <sub>2</sub> = 0.1124 24	<i>R</i> <sub>1</sub> = 0.0347 7 <i>wR</i> <sub>2</sub> = 0.1027 27	<i>R</i> <sub>1</sub> = 0.0416 6 <i>wR</i> <sub>2</sub> = 0.1286 86	<i>R</i> <sub>1</sub> = 0.0395 5 <i>wR</i> <sub>2</sub> = 0.1199 99	<i>R</i> <sub>1</sub> = 0.0417 7 <i>wR</i> <sub>2</sub> = 0.098 8	<i>R</i> <sub>1</sub> = 0.0501 1 <i>wR</i> <sub>2</sub> = 0.179 9

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

Table 2  
Selected bond lengths (Å) and angles (deg) for complex **1**

Cd(1)–O(1)	2.275(3)	Cd(1)–O(2)	2.294(3)
Cd(1)–N(2)	2.316(3)	Cd(1)–N(1)	2.324(3)
Cd(1)–O(4)	2.344(3)	Cd(1)–O(3)	2.423(3)
O(1)–Cd(1)–O(2)	127.35(17)	O(1)–Cd(1)–N(2)	87.19(12)
O(2)–Cd(1)–N(2)	95.39(11)	O(1)–Cd(1)–N(1)	85.10(12)
O(2)–Cd(1)–N(1)	88.07(11)	N(2)–Cd(1)–N(1)	172.13(10)
O(1)–Cd(1)–O(4)	94.32(17)	O(2)–Cd(1)–O(4)	137.93(12)
N(2)–Cd(1)–O(4)	91.75(12)	N(1)–Cd(1)–O(4)	90.38(12)
O(1)–Cd(1)–O(3)	147.67(15)	O(2)–Cd(1)–O(3)	84.82(10)
N(2)–Cd(1)–O(3)	86.49(11)	N(1)–Cd(1)–O(3)	100.89(11)
O(4)–Cd(1)–O(3)	54.27(9)		

under autogenous pressure for 4 days. The reaction system was then cooled to room temperature during 24 h. Colorless crystals of **6** were obtained. Yield: 0.064 g, 64% (based on Cd). Elem. anal. calcd.: C, 41.72%; H, 3.50%; N, 6.95%. Found: C, 41.91%; H, 3.41%; N, 6.81%. IR (cm<sup>-1</sup>): 3376 (s), 3112 (w), 1606 (w), 1513 (s), 1482 (w), 1444 (s), 1251 (m), 1219 (m), 1047 (w), 809 (s), 774 (s), 742 (s), 696 (s), 652 (m), 631 (m), 565 (w).

Zn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.051 g, 0.20 mmol); adipate (0.073 g, 0.50 mmol); 1,10-phen (0.090 g, 0.50 mmol) was dissolved in 6 mL water, then pH value was adjusted to 5 by 1 M NaOH. The mixture was stirred in air for 20 min and then transferred to a 23-mL Teflon reactor and kept at 170 °C for 5 days under autogenous pressure; compound **7** was obtained. Yield: 0.058 g, 71% (based on Zn). Elem. anal. calcd.: C, 53.00%; H, 4.45%; N, 6.87%. Found: C, 52.91%; H, 4.41%; N, 6.81%. IR spectrum (cm<sup>-1</sup>): 3412

Table 3  
Selected bond lengths (Å) and angles (deg) for complex **2**

Zn(1)–O(4)#1	2.0223(16)	Zn(1)–O(2)	2.0309(17)
Zn(1)–O(3)	2.0313(16)	Zn(1)–N(1)	2.1722(19)
Zn(1)–N(2)	2.1892(19)		
O(4)#1–Zn(1)–O(2)	137.30(8)	O(4)#1–Zn(1)–O(3)	126.03(8)
O(2)–Zn(1)–O(3)	96.30(8)	O(4)#1–Zn(1)–N(1)	92.04(7)
O(2)–Zn(1)–N(1)	92.45(8)	O(3)–Zn(1)–N(1)	91.15(7)
O(4)#1–Zn(1)–N(2)	87.37(7)	O(2)–Zn(1)–N(2)	89.90(8)
O(3)–Zn(1)–N(2)	86.90(7)	N(1)–Zn(1)–N(2)	177.10(6)

Symmetry transformations used to generate equivalent atoms: (#1)  $-x, -y, -z$ .

Table 4  
Selected bond lengths (Å) and angles (deg) for complex **3**

Cd(1)–O(3)#1	2.264(9)	Cd(1)–O(2)	2.333(6)
Cd(1)–N(2)	2.339(5)	Cd(1)–O(4)	2.359(7)
Cd(1)–N(1)#2	2.375(5)	Cd(1)–O(3)	2.442(10)
Cd(1)–O(1)	2.383(5)		
O(3)#1–Cd(1)–O(2)	160.3(3)	O(3)#1–Cd(1)–N(2)	84.3(3)
O(2)–Cd(1)–N(2)	92.9(2)	O(3)#1–Cd(1)–O(4)	114.8(3)
N(1)#2–Cd(1)–O(1)	86.3(2)	O(3)–Cd(1)–O(1)	167.5(2)
O(4)–Cd(1)–O(1)	139.3(3)	N(2)–Cd(1)–O(1)	91.3(2)
O(2)–Cd(1)–O(1)	54.8(2)	O(3)#1–Cd(1)–O(1)	105.7(3)
N(1)#2–Cd(1)–O(3)	104.1(3)	N(2)–Cd(1)–O(4)	96.3(2)
N(2)–Cd(1)–O(3)	77.8(3)	O(4)–Cd(1)–O(3)	49.6(3)
O(3)#1–Cd(1)–O(3)	67.5(4)	O(2)–Cd(1)–O(3)	131.0(2)
N(2)–Cd(1)–N(1)#2	174.90(16)	O(4)–Cd(1)–N(1)#2	88.5(2)
O(3)#1–Cd(1)–N(1)#2	92.1(3)	O(2)–Cd(1)–N(1)#2	89.4(2)
O(2)–Cd(1)–O(4)	84.8(2)		

Symmetry transformations used to generate equivalent atoms: (#1)  $-x, -y, -z$ ; (#2)  $x, y+1, z+1$ .

(s), 3061 (w), 2951 (w), 1624 (w), 1585 (s), 1516 (s), 1460 (s), 1408 (s), 1296 (m), 1142 (m), 861 (s), 731 (s).

### 2.3. X-ray crystallography study

Crystallographic data for compounds **1–7** were all collected at 298 K with a Rigaku R-axis Rapid IP diffractometer using graphite monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) and IP technique. The structure

Table 5  
Bond lengths (Å) and angles (deg) for **5**

Mn(1)–O(1)#1	2.091(2)	Mn(2)–O(9)	2.1236(18)
Mn(1)–O(7)#4	2.0913(19)	Mn(2)–O(9)#3	2.1236(18)
Mn(1)–O(3)#5	2.2124(18)	Mn(2)–O(4)	2.1320(18)
Mn(1)–O(5)#3	2.3513(19)	Mn(2)–O(4)#3	2.1320(18)
Mn(1)–O(9)	2.1376(16)	Mn(2)–O(6)#3	2.2518(18)
Mn(1)–O(4)	2.2886(18)	Mn(2)–O(6)	2.2518(18)
Mn(3)–O(9)	2.0931(16)	Mn(3)–O(3)#3	2.5095(19)
Mn(3)–O(8)	2.116(2)	Mn(3)–Mn(2)	3.2264(7)
Mn(3)–O(2)#1	2.124(2)	Mn(2)–Mn(1)	3.2213(7)
Mn(3)–O(5)#2	2.1918(19)	Mn(2)–Mn(1)#3	3.2213(7)
Mn(3)–O(6)	2.2397(19)	Mn(2)–Mn(3)#3	3.2264(7)
O(9)–Mn(3)–O(8)	167.80(8)	O(5)#2–Mn(3)–Mn(2)	126.86(5)
O(9)–Mn(3)–O(2)#1	96.01(7)	O(6)–Mn(3)–Mn(2)	44.23(5)
O(8)–Mn(3)–O(2)#1	95.62(8)	O(3)#3–Mn(3)–Mn(2)	72.77(4)
O(9)–Mn(3)–O(5)#2	93.30(7)	O(9)–Mn(2)–O(9)#3	180.0
O(8)–Mn(3)–O(5)#2	87.59(7)	O(9)–Mn(2)–O(4)	84.08(7)
O(2)#1–Mn(3)–O(5)#2	103.35(8)	O(9)#3–Mn(2)–O(4)	95.92(7)
O(9)–Mn(3)–O(6)	82.79(7)	O(9)–Mn(2)–O(4)#3	95.92(7)
O(8)–Mn(3)–O(6)	93.02(7)	O(9)#3–Mn(2)–O(4)#3	84.08(7)
O(2)#1–Mn(3)–O(6)	92.58(9)	O(4)–Mn(2)–O(4)#3	180.0
O(5)#2–Mn(3)–O(6)	163.93(7)	O(9)–Mn(2)–O(6)#3	98.17(6)
O(9)–Mn(3)–O(3)#3	81.04(6)	O(9)#3–Mn(2)–O(6)#3	81.83(6)
O(8)–Mn(3)–O(3)#3	87.39(7)	O(4)–Mn(2)–O(6)#3	82.60(8)
O(2)#1–Mn(3)–O(3)#3	176.91(7)	O(4)#3–Mn(2)–O(6)#3	97.40(8)
O(5)#2–Mn(3)–O(3)#3	76.01(7)	O(9)–Mn(2)–O(6)	81.83(6)
O(6)–Mn(3)–O(3)#3	87.97(7)	O(6)–Mn(2)–Mn(1)	99.39(5)
O(9)–Mn(3)–Mn(2)	40.43(5)	O(9)–Mn(2)–Mn(1)#3	138.95(4)
O(8)–Mn(3)–Mn(2)	131.76(6)	O(9)#3–Mn(2)–Mn(1)#3	41.05(4)
O(2)#1–Mn(3)–Mn(2)	105.57(6)	O(4)–Mn(2)–Mn(1)#3	134.83(5)
O(9)#3–Mn(2)–O(6)	98.17(6)	O(4)#3–Mn(2)–Mn(1)#3	45.17(5)
O(4)#3–Mn(2)–O(6)	82.60(8)	O(6)–Mn(2)–Mn(1)#3	80.61(5)

Symmetry transformations used to generate equivalent atoms: (#1)  $-x+2, -y+1, -z+1$ ; (#2)  $x, -y+1/2, z-1/2$ ; (#3)  $-x+1, -y+1, -z+1$ .

Table 6  
Selected bond lengths (Å) and angles (deg) for complex **6**

Cd(1)–O(5)	2.314(3)	Cd(1)–O(2)	2.333(3)
Cd(1)–O(4)	2.360(3)	Cd(1)–N(1)	2.366(3)
Cd(1)–N(2)	2.381(3)	Cd(1)–O(3)	2.392(3)
Cd(1)–O(1)	2.403(4)		
O(5)–Cd(1)–O(2)	106.53(13)	O(5)–Cd(1)–O(4)	81.81(11)
O(2)–Cd(1)–O(4)	137.19(10)	O(4)–Cd(1)–N(2)	88.06(12)
O(5)–Cd(1)–N(1)	92.52(12)	N(1)–Cd(1)–N(2)	69.77(10)
O(2)–Cd(1)–N(1)	128.68(11)	O(5)–Cd(1)–O(3)	99.04(11)
O(4)–Cd(1)–N(1)	91.69(9)	O(2)–Cd(1)–O(3)	82.10(9)
O(5)–Cd(1)–N(2)	159.38(12)	O(4)–Cd(1)–O(3)	55.11(8)
O(2)–Cd(1)–N(2)	93.12(12)	N(1)–Cd(1)–O(3)	142.21(9)
O(5)–Cd(1)–O(1)	79.84(11)	N(2)–Cd(1)–O(3)	89.64(10)
O(2)–Cd(1)–O(1)	54.58(10)	N(2)–Cd(1)–O(1)	107.69(12)
O(4)–Cd(1)–O(1)	160.98(13)	O(3)–Cd(1)–O(1)	133.20(9)
N(1)–Cd(1)–O(1)	84.15(10)		

Table 7  
Selected bond lengths (Å) and angles (deg) for complex **7**

Zn(1)–O(1)	2.174(3)	Zn(1)–O(2)	2.224(3)
Zn(1)–O(3)	2.054(3)	Zn(1)–N(1)	2.116(3)
Zn(1)–N(2)	2.185(3)	Zn(1)–O(5)	2.080(3)
N(2)–Zn(1)–O(3)	171.06(12)	N(2)–Zn(1)–O(5)	87.29(13)
O(3)–Zn(1)–O(5)	91.55(12)	N(1)–Zn(1)–O(1)	161.20(10)
N(2)–Zn(1)–N(1)	77.45(11)	N(2)–Zn(1)–O(2)	95.36(10)
O(3)–Zn(1)–N(1)	94.05(11)	O(3)–Zn(1)–O(2)	89.47(10)
O(5)–Zn(1)–N(1)	100.10(11)	O(5)–Zn(1)–O(2)	154.81(11)
N(2)–Zn(1)–O(1)	93.08(11)	N(1)–Zn(1)–O(2)	104.93(10)
O(3)–Zn(1)–O(1)	95.86(11)	O(1)–Zn(1)–O(2)	59.32(9)
O(5)–Zn(1)–O(1)	95.56(10)		

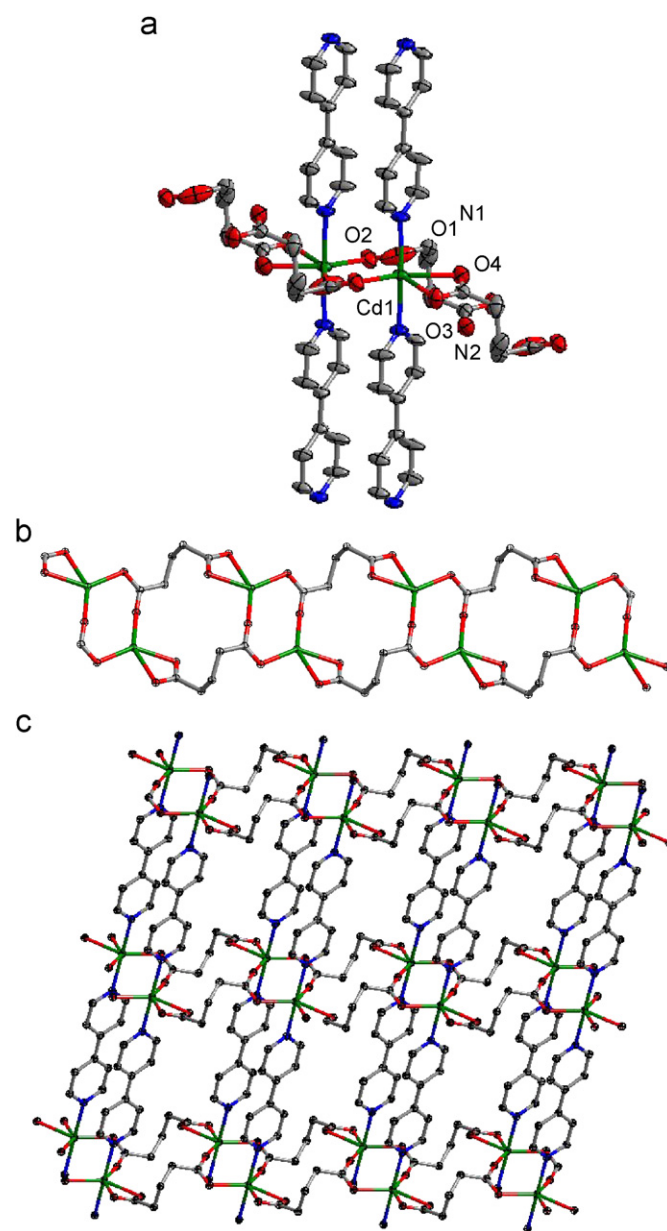


Fig. 1. (a) The coordination environment of Cd(II) in compound **1**. (b) The one-dimensional chains composed by Cd and glutarate acid. (c) The two-dimensional layer composed by 4,4'-bpy of compound **1**.

was solved by the direct method and refined by the full-matrix least-squares method on  $F^2$  using the SHELXTL 97 crystallographic software package [37,38]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogen atoms were placed in

geometrically calculated positions; oxygen-bound hydrogen atoms were located in the difference Fourier maps and kept in that position. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Tables 2–7.

### 3. Results and discussion

#### 3.1. Crystal structure of compounds 1–7

The single-crystal X-ray structural analysis shows that the structure of compound 1 is a unique two-dimensional network based on binuclear Cd block with mixed glutarate anion and 4,4'-bpy and the fundamental unit is shown in Fig. 1a. There is one crystallographically independent Cd center in the fundamental unit. The Cd(1) center coordinates to two oxygen atoms (O3, O4) of one chelating carboxylate group and two oxygen atoms (O1, O2) from two different bridging carboxylate groups, two nitrogen atoms (Cd(1)–N(1) = 2.324 Å, Cd(1)–N(2) = 2.317 Å) of different 4,4'-bpy ligands. The Cd–O bond distances are in the range of 2.275–2.424 Å and the O–Cd(1)–O bond angles vary from 54.27° to 147.67°. Therefore, Cd center displays distorted octahedral coordination geometry. Such two  $\{CdN_2O_4\}$  octahedral are connected together to form a binuclear Cd building unit via the edge-sharing mode. In addition, two carboxylate groups of the glutarate anion exhibit two kinds of coordination modes with Cd centers. That is, one carboxylate group uses the bridging mode and connects two Cd centers, while the other exhibits chelating mode to link with one Cd center. Thus, four glutarate anion connect with two Cd centers by covalent bonds to form one-dimensional ladder-like chains parallel with the  $a$ -axis as shown in Fig. 1b. The most interesting structure feature of compound 1 is that such two adjacent one-dimensional chains are interconnected by 4,4'-bpy ligands each other to form a two-dimensional double layer structure as shown in Fig. 1c. Compound 2 is isostructural with compound 1. However, small difference lies in the bond angles and bond lengths.

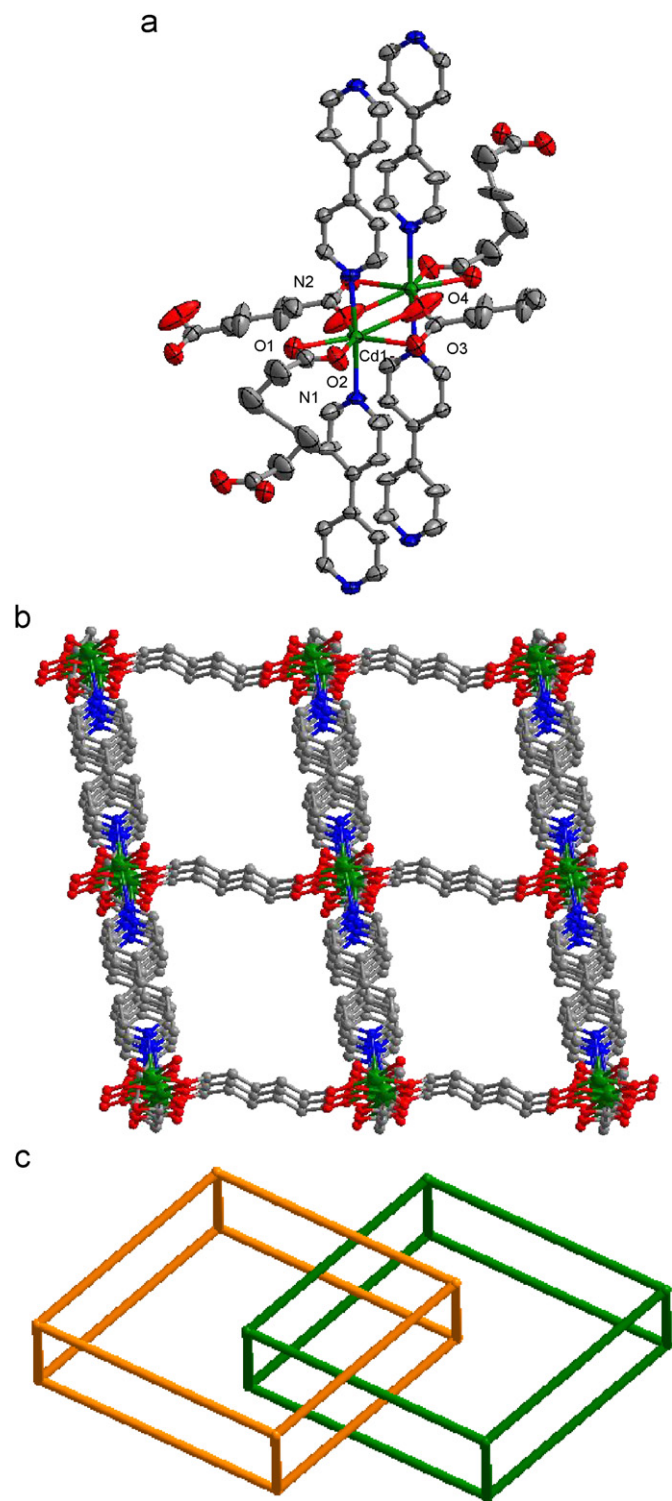


Fig. 2. (a) The coordination environment of Cd(II) in compound 2. (b) The three-dimensional network composed by 4,4'-bpy of compound 2. (c) The three-dimensional two-fold interpenetration network of 2.

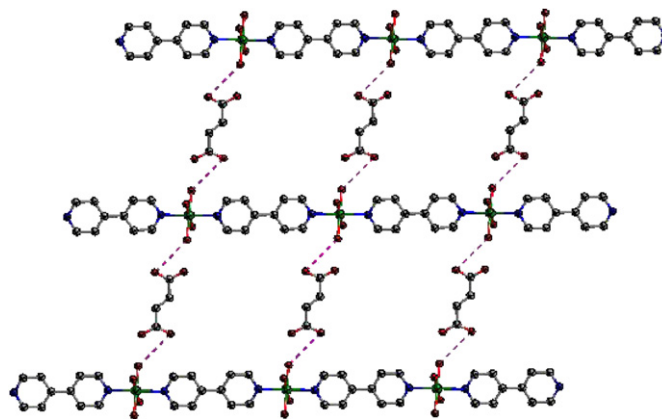


Fig. 3. The two-dimensional layer constructed by hydrogen bond of 4.

The single-crystal analysis reveals that compound **3** is an interesting three-dimensional interpenetrating network. There is only one crystallographic independent Cd atom in the fundamental unit as shown in Fig. 2a. The Cd(1) atom is coordinated with four oxygen atoms, two from a chelating carboxylate group, and another two from two

different bridging carboxylate groups. The Cd–O bond distances are in the range of 2.264–2.442 Å, and the O–Cd–O bond angles range from 54.8° to 160.3°. Such two Cd atoms are linked by two bridging carboxylate groups and form a binuclear Cd unit. A binuclear Cd unit connects with four adipate ions to form a (4,4)-lattice two-dimensional layer with cavities  $13.477 \times 11.059$  Å and such layer are extended to form a three-dimensional network by 4,4'-bpy ligand as shown in Fig. 2b. Two such three-

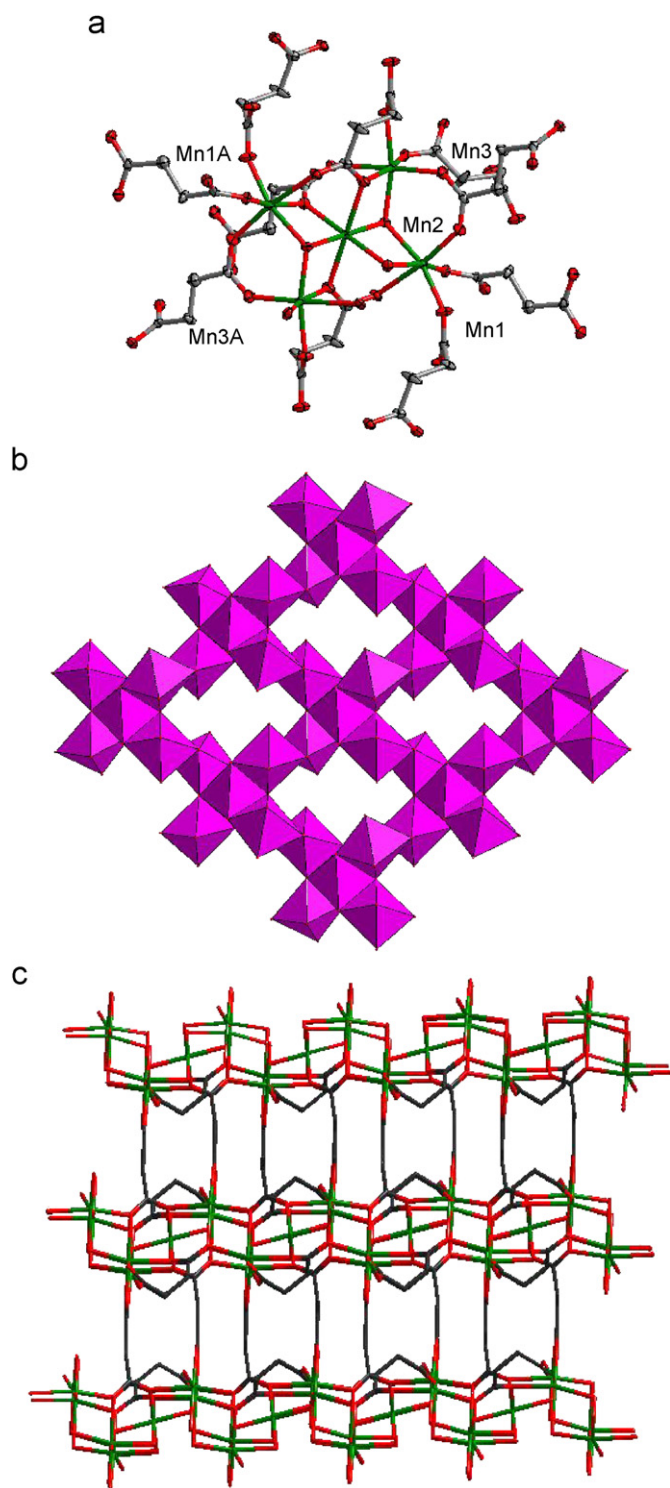


Fig. 4. (a) The coordination environment of Mn(II) in compound **5**. (b) The two-dimensional layer structure in compound **5**. (c) The three-dimensional of compound **5**.

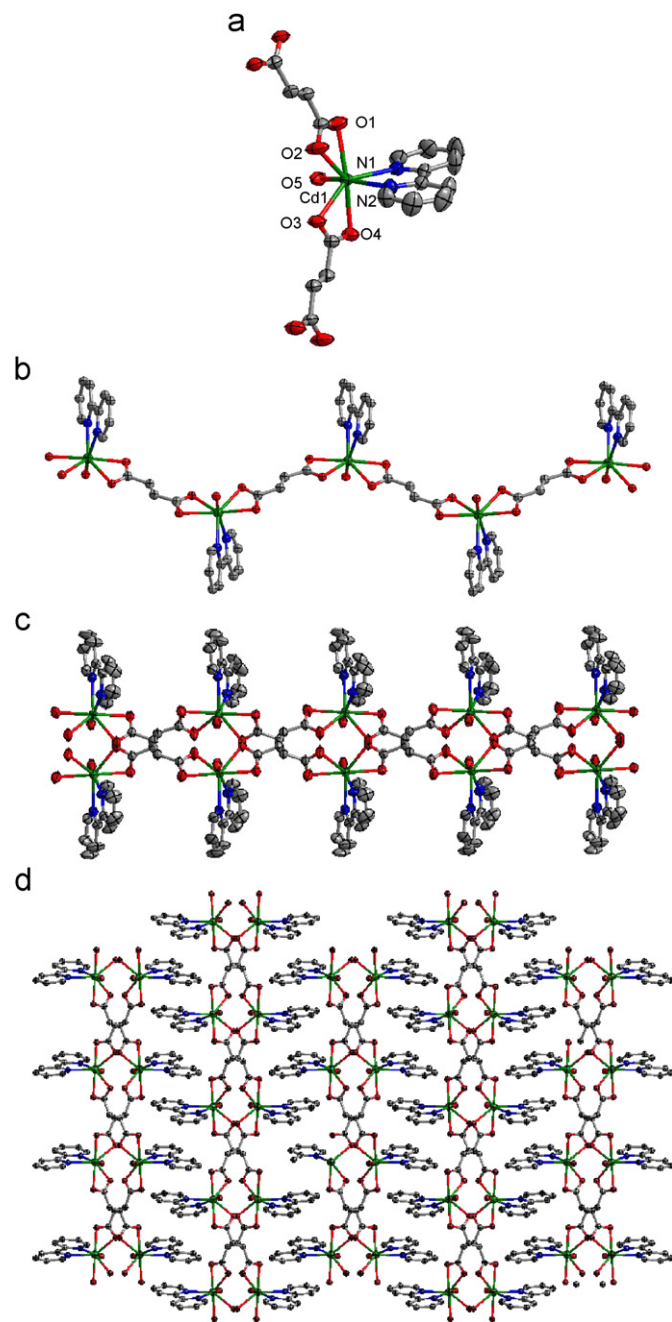


Fig. 5. (a) The coordination environment of Cd(II) in compound **6**. (b) The one-dimensional chain-like structure of compound **6**. (c) The double chain-like structure of compound **6**. (d) The two-dimensional layer structure composed of  $\pi$ - $\pi$  interaction.

dimensional networks together form an interesting two-fold interpenetrating structure as is shown in Fig. 2c.

The single-crystal X-ray structural analysis shows that the structure of compound **4** is an interesting one-dimensional chain-like structure composed of Mn(II) and 4,4'-bpy. Such one-dimensional chains are connected by succinate ligands with hydrogen bond to form two-dimensional layer structure as shown in Fig. 3. To our knowledge, compound **4** had been synthesized at room temperature, here; we synthesized it at hydrothermal condition [22]. Unlike compound **4**, compound **5** is a three-dimensional network composed of succinate ligands and Mn(II) ions. There exist three crystallographic independent Mn(II) ions in this compound. Mn(1) adopts distorted octahedral coordination mode and connects with six oxygen atoms, the Mn(1)–O distance is in the range of 2.091–2.351 Å. Mn(2) and Mn(3) adopt the same kind of

coordination mode, but with different bond lengths and bond angles. To our interest, one Mn(2) ion connects with two Mn(2) ions and two Mn(3) ions with  $\mu_3$ -oxygen atoms to form an interesting pentanuclear Mn(II) cluster as shown in Fig. 4a. Bridging succinate anion and oxygen atoms connect such pentanuclear Mn(II) clusters to form a two-dimensional layer structure as shown in Fig. 4b. At last, such two-dimensional layers are connected by succinate ligands to form three-dimensional network as shown in Fig. 4c.

The single crystal structural analysis shows that the structure of compound **6** is an interesting one-dimensional framework. There is only one Cd(II) ion in the fundamental unit as shown in Fig. 5a. Cd(II) connects with four oxygen atoms from two succinate anions, the succinate acid ligand adopt chelating coordination mode and the Cd(II)–O bond angles range from 2.333 to 2.403 Å. At the

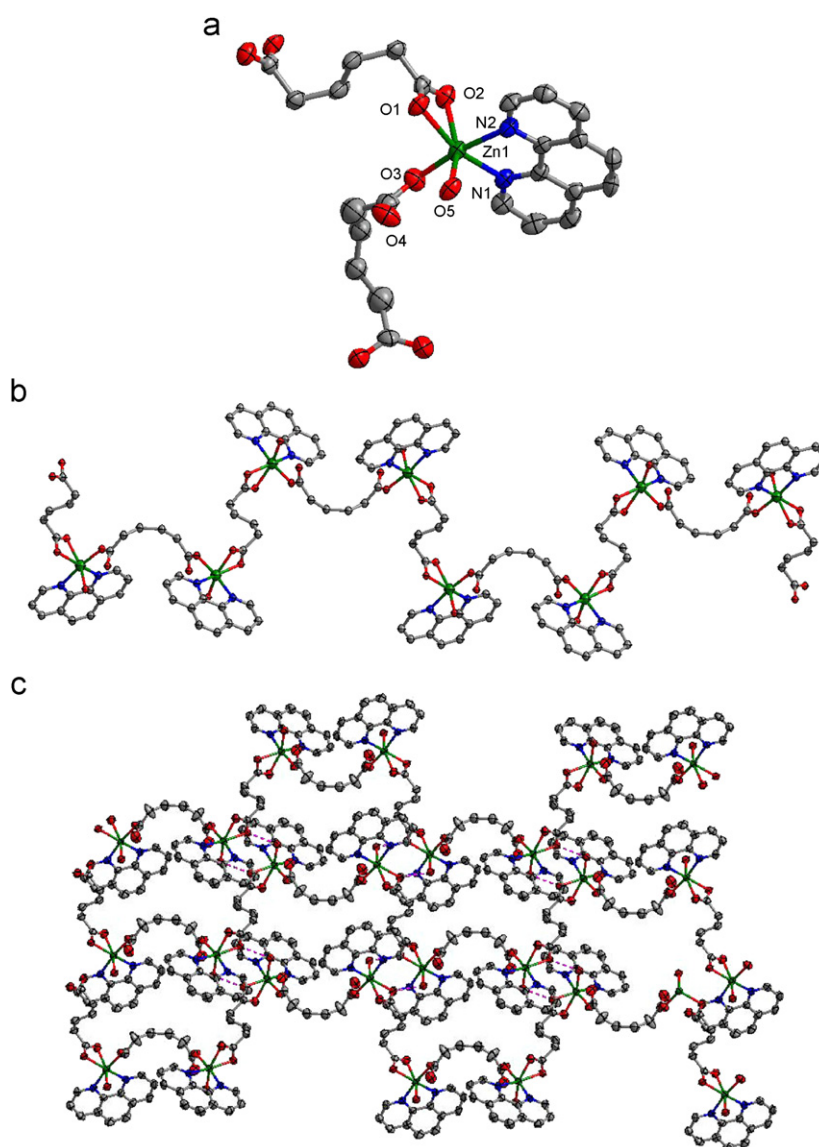


Fig. 6. (a) The coordination environment of the Zn(II) of compound **7**. (b) The one-dimensional chain-like structure of compound **7**. (c) The two-dimensional layer structure composed by hydrogen bond.

same time, Cd(II) connects with chelating 2,2'-bpy ligands, with average Cd(II)–O distance 2.373 Å and the other coordination site is occupied by water molecular. Such Cd(II) is linked by succinate acid ligand and forms a one-dimensional chain-like structure along the *b*-axis as shown in Fig. 5b. Such two chains are connected by hydrogen bonds to form double chain-like structures as shown in Fig. 5c. The  $\pi$ – $\pi$  interaction links these double chains together to form two-dimensional layer as shown in Fig. 5d.

Compound 7 is also a two-dimensional supramolecular network composed of one-dimensional chains. The fundamental unit is shown in Fig. 6a, there is only one crystallographic independent Zn(II) ion in the structure, and it adopts distorted octahedral coordination mode and connected with three oxygen atoms, two come from a chelating carboxylate group and the other from a monodentate carboxylate group, two nitrogen atoms from a 1,10-phen molecular, the other coordination site is occupied by a water molecular. The Zn–O distance range from 2.054 to 2.224 Å, and the O–Zn–O bond angles are in the range of 59.32–154.81°. That is to say, the adipic acid ligand in this compound adopt two kinds of coordination modes. One is bis-chelating and the other is bis-monodentate. The Zn(II) ions are connected by these two kinds of adipate anions to form one-dimensional chain-like structure along [101] axis as shown in Fig. 6b. Two adjacent chains are connected by hydrogen bond to form two-dimensional supramolecular network as shown in Fig. 6c.

Although the above seven compounds exhibit different network topology and dimensionality, this can be seen affected by the different aliphatic dicarboxylate with

different backbone carbon numbers. In the case of succinate ( $n = 4$ ), the metal ions are connected by 4,4'-bpy and form a one-dimensional chain-like structure. When glutarate ( $n = 5$ ) is used, a two-dimensional layer structure is formed; we can attribute this to the increase of chain length brought by the increase of the aliphatic dicarboxylate backbone carbon number. At last, adipic ligand ( $n = 6$ ) is employed and a two-dimensional network is generated. This is because of the large cavity built by adipic ligand in this system. Compared with previous research [23] and from the above result, we can conclude the increase of the carbon number lead to the change of the flexibility of the backbone, which further influence the final products as shown in Table 8.

Besides effect of organic ligand, the role of reaction conditions is also very important, the factors, such as pH value and molar ratio are also very important. Subtle difference of pH value has significant effect on the structure of the complex formed.

### 3.2. Thermo gravimetric analyses

The thermal stability of compounds 1–7 has been determined on powder samples in the nitrogen atmosphere by thermo gravimetric analysis (TGA). For compound 1, the weight loss of 71.79% from 322 to 501 °C displays the loss of glutaric acid and 4,4'-bpy ligands (calculated: 71.74%). For compound 2, TGA exhibits one-weight losses: from 330 to 478 °C is also attributed to the loss of glutaric acid and 4,4'-bpy ligands about 81.26% (calculated 81.33%). Like the above two compounds, compound 3 also exhibits one weight loss about 72.81% from 330 to 540 °C, corresponds to the removal of adipate acid and 4,4'-bpy

Table 8  
Some compounds composed from different aliphatic ligands

Compounds	Dimension	<i>N</i> (the number of backbone carbon)	The rigid bidentate nitrogen ligand	Reference
[Cd(mal)(pyz) <sub>0.5</sub> (H <sub>2</sub> O)]	3	3	Pyrazine	[22]
[Cd <sub>2</sub> (suc) <sub>2</sub> (pyz)(H <sub>2</sub> O) <sub>2</sub> ]	3	4	Pyrazine	[22]
[Cu(suc)(bipy)(H <sub>2</sub> O) <sub>2</sub> ] · 2H <sub>2</sub> O	3	4	4,4'-bpy	[24]
[Zn(suc)(bipy)]	1	4	4,4'-bpy	[24]
[Co(bipy)(H <sub>2</sub> O) <sub>4</sub> ] [suc] · 4H <sub>2</sub> O	1	4	4,4'-bpy	[22]
[Mn(bipy)(H <sub>2</sub> O) <sub>4</sub> ] [suc] · 4H <sub>2</sub> O	1	4	4,4'-bpy	[22]
[Ni(bipy)(H <sub>2</sub> O) <sub>4</sub> ] [suc] · 4H <sub>2</sub> O	1	4	4,4'-bpy	[23]
[Mn(bipy)(H <sub>2</sub> O)(suc)] · 0.5bpy	3	4	4,4'-bpy	[23]
[Mn(bipy)(glut)]	2	5	4,4'-bpy	[23]
[Zn(bipy)(glut)]	2	5	4,4'-bpy	This article
[Cd(bipy)(glut)]	2	5	4,4'-bpy	This article
[Mn(bipy)(adip)]	2	6	4,4'-bpy	[23]
[Cd(bipy)(adip)]	3	6	4,4'-bpy	This article
[Mn <sub>3</sub> (glut) <sub>3</sub> (H <sub>2</sub> O)]	3	5	None	[21]
[Mn <sub>5</sub> (suc) <sub>4</sub> (O)]	3	4	None	This article
[Cd(suc)(bipy)(H <sub>2</sub> O)]	1	4	2,2'-bpy	This article
[Zn(adip)(1,10'-phen)(H <sub>2</sub> O)]	1	6	1,10-phen	This article

Note: mal, malonate; suc, succinate dianion; glut, glutarate dianion; adip, adipate dianion; pyz, pyrazine; 1,10-phen, 1,10-phenanthroline; bipy, 2,2'-bpy or 4,4'-bpy.



ligand (calculated: 72.72%). For compound **6**, TGA exhibits two weight losses: one (4.55%) from 141 to 178 °C is attributed to the loss of coordinated water (calculated: 4.47%). Another weight loss (67.61%), from 374 to 471 °C, corresponds to the removal of 2,2'-bpy and succinate ligand (calculated: 67.55%). For compound **7**, the first weight loss of 4.57% (calculated: 4.41%) represents the loss of water molecular, and the next weight loss represents the loss of 79.26% (calculated: 79.49%), which can be attributed to the loss of adipate acid and 1,10-phen ligand.

### 3.3. Fluorescent property

The photoluminescence spectrum of compounds **1** and **2** in the solid state at room temperature are shown in Fig. 7.

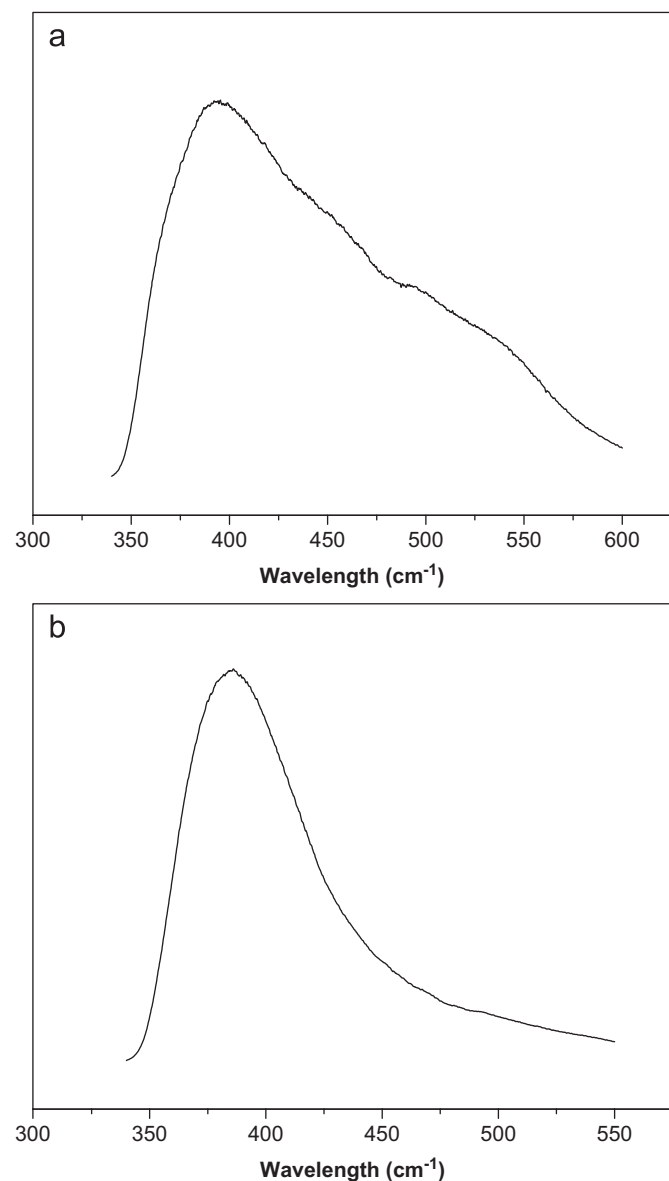


Fig. 7. (a) The emission spectrum of compound **1**. (b) The emission spectrum of compound **2**.

It can be observed that compound **1** exhibits intense photoluminescence with an emission maximum at ca. 389 nm upon excitation at 318 nm. According to the previous reports, this emission band could be assigned to the emission of ligand-to-metal charge transfer (LMCT) [36]. Unlike compound **1**, compound **2** exhibit emission at ca. 396 nm upon excitation at 320 nm.

## 4. Conclusion

In this paper, we successfully combined the merits of saturated aliphatic dicarboxylate and 3d metal units and synthesized seven coordination polymers. Compared the structures of these compounds, we found the introduction of flexible aliphatic dicarboxylate with different carbon atom numbers may have significant effect on the formation and dimension of the resulting structure. The successful preparation of the seven different compounds provides a valuable approach for the construction of other coordination polymers with different structures via the introduction of ligands. Furthermore, the fluorescent properties of compounds **1** and **2** are studied.

## Acknowledgment

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## Appendix A. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 608218–608220 and 630682–630685 for compound **1–3** and **4–7**. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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