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Synthesis, characterization and properties of series coordination polymers constructed from a biphenyl dicarboxylate and nitrogen-containing mixed ligands

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ABSTRACT

A series of coordination polymers have been prepared by the combination of flexible ligand 1,1′-biphenyl-2,2′-dicarboxylic acid (H_2dpa) and different types of nitrogen-containing ligands, with various metal ions such as Co(II), Zn(II) and Cd(II). The single-crystal structure analyses reveal that the above complexes possess different structure features with the introduction of different nitrogen-containing ligands. When auxiliary linear ligand 4,4′-bipyridine (4,4′-bpy) is introduced, two-dimensional layered complex, $[Co_2(dpa)_2(4,4'\text{-bpy})_2(H_2O)]_n$ (**1**) is formed. Whereas if chelating ligand, 1,10-phenanthroline (1,10′-phen) and 2,2′-bipyridine (2,2′-bpy) are introduced, one-dimensional complex $[Zn(dpa)(1,10'\text{-phen})]_n$ (**2**) and discrete complexes $[Co_2(dpa)_2(2,2'\text{-bpy})_2(H_2O)_2]$ (**3**), $[Co_3(dpa)_3(1,10'\text{-phen})_6(H_2O)_2]$ (**4**), $[Cd(dpa)(1,10'\text{-phen})_2][(H_2dpa)_2(H_2O)_2]$ (**5**) are synthesized. To our interest, **1** and **2** crystallize in homochiral space-group. Furthermore, the magnetic property of complex **1** and the fluorescent properties of complexes **2** and **5** are studied.

1. Introduction

During the past decade, the preparation of coordination polymers with intriguing structures has attracted increasing interests for the sake of potential applications, such as catalysis, magnetic, functional electronic and gas separation [1–6]. Recently, there is an increasing interest in coordination polymers built from flexible bridging ligands [7,8]. Coordination polymers with diverse structures composed of different types of flexible ligands have been reported, particularly those containing O-, N-, or S-donors [9,10]. The biphenyl ligands bearing structural flexibility and conformation freedom are good choice of O-donor ligands, and the flexible nature of spacers allows these ligands to rotate when coordinate to metal centers so as to conform to the coordination geometries of metal ions [11,12]. Significant progress has been achieved in this area; however, the factors that affect the formation of coordination polymers constructed form flexible biphenyl ligands and the exploitation of novel strategies are still comparatively less investigated. Previous investigations including ours indicate that 2,2′-biphenyldicarboxylate (H_2dpa) has a strong capability of affording new coordination polymers for several reasons: (a) it has four potential donor carboxylic oxygen atoms to coordinate to metal ions with different connection modes [13–15], (b) the skew coordination orientation of the carboxylic group, the hindrance between the 2,2′-positioned carboxylic groups, and the nonlinear flexibility around the two benzene groups make it quite a versatile ligand for constructing novel coordination polymers [16–20], and (c) it displays strong reactive ability with d and f block metal ions [21–24].

Recently, studies reveal that coordination polymers constructed by mixed ligands of pyridyl groups and carboxylic groups not only incorporate interesting properties of different functional group but also are more adjustable through changing one of the above two organic ligands [25]. Despite the fact a lot of interesting complexes have been constructed from mixed ligands, the systematic research on this subject is less explored, since the structures are highly influenced by the properties of ligands, coordination preference of metal ions, and some very subtle factors, such as temperature and counter ions [26,27]. In this article, to synthesis new coordination polymers based on mixed ligands as well as enrich the coordination chemistry of H_2dpa, we introduce two types of nitrogen-containing ligands to the metal-dpa system: one is linear 4,4′-bpy, the other is chelating ligand 1,10′-phen or 2,2′-bpy and synthesized a series of coordination polymers exhibit various structural features and rich coordination modes of dpa ligand are obtained.

2. Experimental

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. FT/IR

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spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centaut FTIR spectrophotometer using a KBr pellet. TG analyses were performed on Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Photoluminescence spectra were measuring using a FL-2T2 instrument (SPEX, USA) with 450-W xenon lamp monochromatized by double grating (1200 g/mu).

2.2. Syntheses of complexes **1–5**

2.2.1. [$Co_2(dpa)_2(4,4'\text{-}bpy)_2(H_2O)]_n$ (**1**)

Complex **1** was prepared from the mixture of $Co(OAc)_2{\cdot}2H_2O$ (0.085 g, 0.40 mmol), H_2dpa (0.194 g, 0.80 mmol), 4,4′-bpy (0.125 g, 0.80 mmol) in 8 ml H_2O. The mixture was stirred for 20 min, and pH value was then adjusted to 5 with 1 M NaOH. After transferred to a 23 ml Teflon-lined stainless steel bomb, the mixture was kept at 170 °C under autogenously pressure for 4 days. After cooling the reaction system to room temperature during 24 h, red block crystals of **1**. For complex **1**: yield: 59% (based on Co). *Anal.* Calc. for $C_{48}H_{36}N_4O_{10}Co_2$: C, 60.90; H, 3.83; N, 5.92. Found: C, 60.85; H, 3.89; N, 6.03%. IR: 3314 (s), 3061 (s), 1578 (s), 1435 (s), 1377 (s), 1108 (m), 1046 (w), 1015 (m), 966 (w), 844 (m), 791 (m), 628 (w).

Complex **1** could also be obtained in various yields under the following conditions: (1) $Co(OAc)_2{\cdot}2H_2O$ (0.40 mmol) + H_2dpa (0.80 mmol) + 4,4′-bpy (0.80 mmol) + water (8 ml), 160 °C, 4 days; (2) $Co(OAc)_2{\cdot}2H_2O$ (0.4 mmol) + H_2dpa (0.80 mmol) + 4,4′-bpy (0.80 mmol) + water (8 ml), 180 °C, 4 days. The yields reacted at 180 °C are higher than that reacted at 160 and 170 °C.

2.2.2. [Zn(dpa)(1,10′-phen)]$_n$ (**2**)

The mixture of $Zn(OAc)_2{\cdot}2H_2O$ (0.088 g, 0.40 mmol), H_2dpa (0.194 g, 0.80 mmol), 1,10′-phen (0.144 g, 0.80 mmol), and 6 ml H_2O was stirred for 20 min, and then the pH value was adjusted to 5 with 1 M NaOH. After stirring for another 20 min, the mixture was transferred to a 23 ml Teflon-lined stainless steel bomb and kept at 170 °C under autogenously pressure for 4 days. The reaction system was cooled to room temperature during 24 h. A large amount of colorless block crystals of **2** were obtained. Yield: 46% (based on Zn). *Anal.* Calc. for $C_{26}H_{16}N_2O_4Zn$: C, 64.28; H, 3.32; N, 5.77. Found: C, 64.18; H, 3.46; N, 5.63%. IR: 1573 (s), 1542 (w), 1521 (s), 1455 (w), 1382 (s), 1360 (w), 1130 (m), 1040 (w), 848 (s), 769 (m), 618 (m), 554 (w).

Table 2
Selected bond lengths for complexes **1–5**.

Complex **1**			
Co(1)–O(4)	2.031(2)	Co(2)–O(1)	2.052(2)
Co(1)–O(4)#3	2.031(2)	Co(2)–O(7)	2.067(2)
Co(1)–O(10)	2.083(3)	Co(2)–N(2)#1	2.091(3)
Co(1)–O(10)#3	2.083(3)	Co(2)–O(3)	2.114(2)
Co(1)–N(5)	2.092(4)	Co(2)–N(1)	2.121(3)
Co(1)–N(6)#4	2.137(4)	Co(2)–O(5)	2.151(2)
Co(3)–O(9)#2	2.041(3)	Co(3)–O(6)#2	2.075(2)
Co(3)–O(9)	2.041(3)	Co(3)–N(4)#1	2.092(4)
Co(3)–O(6)	2.075(2)	Co(3)–N(3)	2.113(4)
Complex **2**			
Zn(1)–O(4)	1.959(2)	Zn(1)–O(3)	2.118(3)
Zn(1)–O(2)	2.206(2)	Zn(1)–N(1)	2.113(3)
Zn(1)–N(2)	2.063(2)		
Complex **3**			
Co(1)–O(4)	1.985(2)	Co(1)–O(1)	2.006(2)
Co(1)–O(5)	2.135(2)	Co(1)–N(2)	2.122(2)
Co(1)–N(1)	2.165(2)		
Complex **4**			
Co(1)–O(3)	2.044(3)	Co(2)–O(7)	2.052(3)
Co(1)–O(1)	2.071(2)	Co(2)–O(5)	2.061(2)
Co(1)–N(3)	2.126(3)	Co(2)–N(6)	2.130(3)
Co(1)–N(2)	2.138(3)	Co(2)–N(7)	2.132(3)
Co(1)–N(1)	2.171(4)	Co(2)–N(8)	2.184(3)
Co(1)–N(4)	2.213(3)	Co(2)–N(5)	2.192(3)
Co(3)–O(12)	2.038(3)	Co(3)–N(11)	2.126(3)
Co(3)–O(10)	2.044(2)	Co(3)–N(12)	2.189(3)
Co(3)–N(9)	2.121(3)	Co(3)–N(10)	2.213(4)
Complex **5**			
Cd(1)–O(1)#1	2.292(4)	Cd(1)–O(1)	2.292(4)
Cd(1)–N(1)	2.343(4)	Cd(1)–N(1)#1	2.343(4)
Cd(1)–N(2)	2.389(4)	Cd(1)–N(2)#1	2.389(4)

Symmetry transformations used to generate equivalent atoms for complex **1**: #1 $x, y-1, z$; #2 $-x+1, y, -z+1$; #3 $-x, y, -z$; #4 $x, y+1, z$.
Symmetry transformations used to generate equivalent atoms for complex **5**: #1 $-x+1, y, -z, +3/2$.

This complex could also be obtained in low yields by the solvothermal reactions of Zn salts, H_2dpa, and 1,10′-phen with different molar ratios in 10 ml of ethanol or methanol and other solvent.

2.2.3. [$Co_2(dpa)_2(2,2'\text{-}bpy)_2(H_2O)_2$] (**3**)

Complex **3** was prepared from the mixture of $Co(OAc)_2{\cdot}2H_2O$ (0.085 g, 0.40 mmol), H_2dpa (0.194 g, 0.80 mmol), 2,2′-bpy

Table 1
Crystal data and structure refinement for complexes **1–5.**

	1	**2**	**3**	**4**	**5**
Formula	$C_{48}H_{36}Co_2N_4O_{10}$	$C_{26}H_{16}N_2O_4Zn$	$C_{48}H_{36}Co_2N_4O_{10}$	$C_{114}H_{76}Co_3N_{12}O_{14}$	$C_{66}H_{48}CdN_4O_{14}$
FW	946.67	485.78	946.67	2014.66	1233.48
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$C2$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$C2/c$
a (Å)	22.540(5)	9.4909(19)	11.015(2)	16.738(3)	32.628(7)
b (Å)	11.301(2)	11.601(2)	9.5133(19)	18.302(4)	9.998(2)
c (Å)	18.824(4)	18.547(4)	20.765(4)	18.349(4)	18.122(4)
α (°)	90	90	90	113.89(3)	90
β (°)	119.84(3)	90	104.57(3)	102.96(3)	107.11(3)
γ (°)	90	90	90	108.34(3)	90
V (Å^3)	4159.1(15)	2042.1(7)	2106.0(7)	4459.6(15)	5650(2)
Z	4	4	2	2	4
ρ_{calcd} (g/cm^3)	1.512	1.580	1.493	1.500	1.450
Data/restraints/parameters	7040/5/596	3577/0/298	3625/2/280	15498/4/1290	4944/2/375
R_{int}	0.0357	0.0482	0.0487	0.0309	0.0415
S	0.864	0.920	1.030	1.179	1.149
R_1 [$I > 2\sigma(I)$]	0.0323	0.0321	0.0448	0.0532	0.0677
wR_2 [$I > 2\sigma(I)$]	0.0764	0.0821	0.1352	0.1604	0.2027
Flack × parameter	0.036(10)	0.034(18)			

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

(0.125 g, 0.80 mmol), and 8 ml H_2O, was stirred for 20 min, and then the pH value was adjusted to 4 with 1 M NaOH. After stirring for another 20 min, the mixture was transferred to a 23 ml Teflon-lined stainless steel bomb and kept at 180 °C under autogenously pressure for 4 days. The reaction system was cooled to room temperature during 24 h. A large amount of red block crystals of **3** were obtained. Yield: 52% (based on Co). *Anal.* Calc. for $C_{48}H_{36}N_4O_{10}Co_2$: C, 60.90; H, 3.83; N, 5.92. Found: C, 61.02; H, 3.86; N, 5.99%. IR: 3269 (s), 3118 (s), 1571 (s), 1465 (m), 1378 (s), 1286 (w), 1138 (m), 1040 (w), 947 (w), 861 (s), 769 (m), 608 (m), 563 (w).

Complex **3** could also be obtained in low yields (<20%) by the hydrothermal reactions of $Co(OAc)_2·2H_2O$, H_2dpa and 2,2′-bpy with lower the starting pH value.

2.2.4. [$Co_3(dpa)_3(1,10'\text{-phen})_6(H_2O)_2$] (**4**)

Complex **4** was prepared from a mixture of $Co(OAc)_2·2H_2O$ (0.085 g, 0.40 mmol), H_2dpa (0.194 g, 0.80 mmol), 1,10′-phen (0.144 g, 0.80 mmol) and 8 ml H_2O. The mixture was stirred for 15 min and sealed in a 23 ml Teflon-lined stainless steel bomb. The bomb was kept at 165 °C under autogenously pressure for 3 days. The reaction system was then cooled to room temperature during 24 h, and red block crystals of **4** were obtained. Yield: 54% (based on Co). *Anal.* Calc. for $C_{114}H_{76}N_{12}O_{14}Co_3$: C, 67.96; H, 3.80; N, 8.34. Found: C, 67.86; H, 3.91; N, 8.29%. IR: 3256 (s), 3094 (s), 1541 (s), 1345 (s), 1268 (w), 1179 (m), 977 (w), 825 (m), 784 (m), 708 (w), 677 (w), 561 (w).

This complex could also be obtained in various yields with the following different molar ratios in 8 ml of water. (1) $Co(OAc)_2·2H_2O/H_2dpa$/1,10′-phen 1:2:1, (2) $Co(OAc)_2·2H_2O/H_2dpa$/1,10′-phen 2:2:1, (3) $Co(OAc)_2·2H_2O/H_2dpa$/1,10′-phen 1:2:4, and (4) $Co(OAc)_2·2H_2O/H_2dpa$/1,10′-phen 1:4:4.

2.2.5. [$Cd(dpa)(1,10'\text{-phen})_2$][$(H_2dpa)_2(H_2O)_2$] (**5**)

Complex **5** was prepared from a mixture of $Cd(OAc)_2·2H_2O$ (0.107 g, 0.40 mmol), H_2dpa (0.194 g, 0.80 mmol), 2,2′-bpy (0.125 g, 0.80 mmol) and 8 ml H_2O. The mixture was stirred for 15 min and sealed in a 23 ml Teflon-lined stainless steel bomb. The bomb was kept at 150 °C under autogenously pressure for 3 days. The reaction system was then cooled to room temperature during 24 h, and yellow block crystals of **5** were obtained. Yield: 60% (based on Cd). *Anal.* Calc. for $C_{66}H_{48}N_4O_{14}Cd$: C, 64.26; H, 3.92; N, 4.54. Found: C, 64.33; H, 3.86; N, 4.48%. IR: 3239 (s),

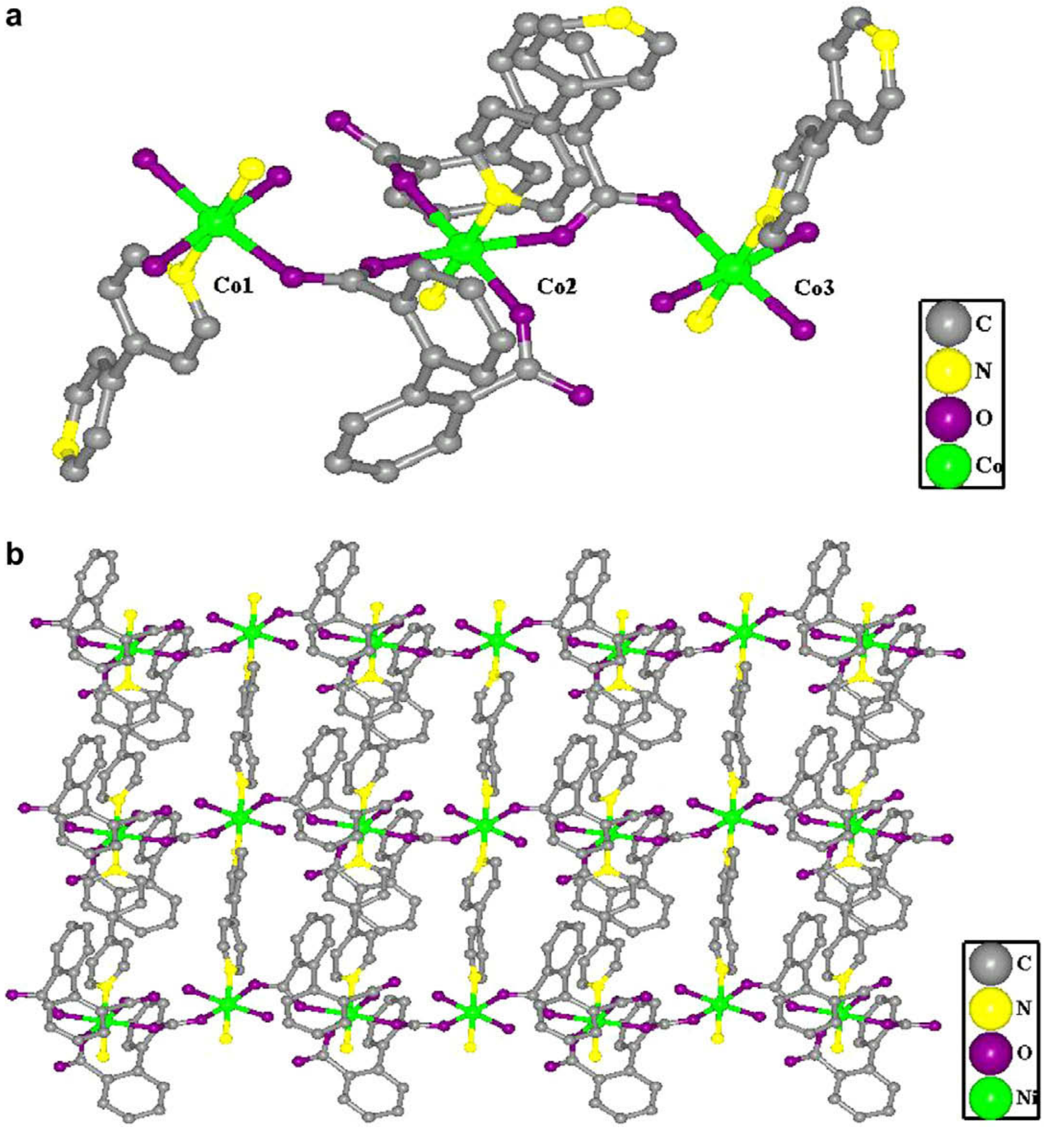

Fig. 1. (a) The fundamental unit of complex **1**. (b) The two-dimensional layer structure of complex **1**.

3109 (s), 1551 (s), 1358 (s), 1336(s), 1288 (w), 1184 (m), 972 (w), 827 (m), 783 (w), 712 (w), 677 (w), 563 (w).

Complex **5** could also be obtained in about the same yields by the hydrothermal if we use other based adjusting the pH value, such as pyridine, KOH.

2.3. X-ray crystallography

Single-crystals of complexes **1**–**5** were glued on glass fibers, respectively. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and IP technique. Empirical absorption correction was applied. The structures were solved by the direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL 97 crystallographic software package [28,29]. 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 are listed in Table 2.

3. Result and discussion

3.1. Crystal structure of complexes *1*–*5*

According to single-crystal X-ray diffraction, complex **1** possesses a fundamental unit which consists of three crystallographic distinct Co atoms, two 4,4′-bpy ligands, three dpa

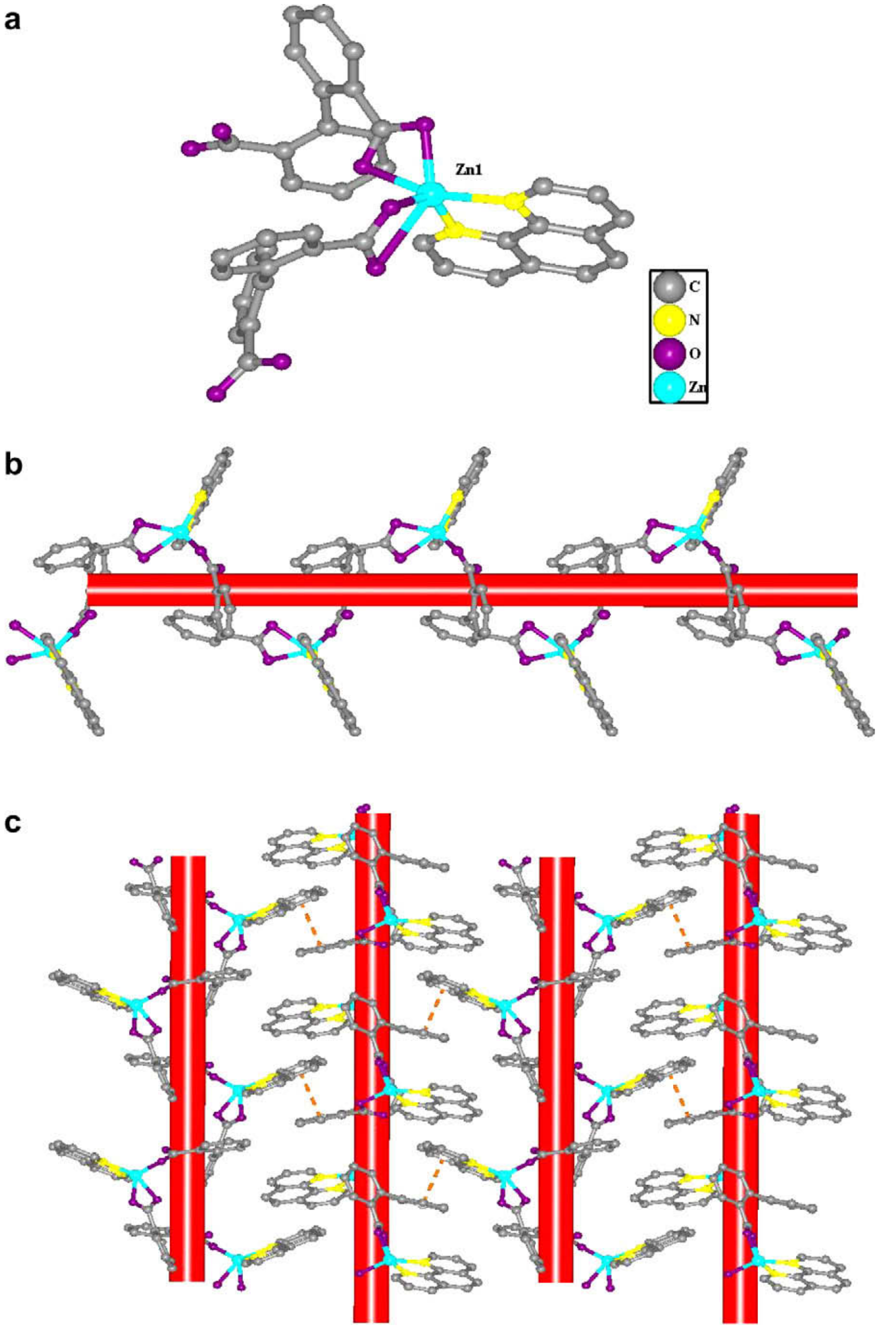

Fig. 2. (a) The fundamental unit of complex **2**. (b) One-dimensional helical chain structure of complex **2**. (c) Two-dimensional supramolecular layer network of complex **2**.

ligands and one water molecule as shown in Fig. 1a. Co1 connects with two oxygen atoms from two dpa ligands, two nitrogen atoms from different 4,4′-bpy ligands, the other two coordination sites is occupied by water. The Co–O bond distances are 2.031 and 2.083 Å, Co–N bond distance is 2.138 Å. This results a distorted octahedral coordination mode. Unlike Co1, Co2 connects four carboxylic oxygen atoms from two dpa ligands, two nitrogen atoms from two 4,4-bpy ligands. The Co–O bond distances range from 2.052 to 2.151 Å, the average Co–N bond distance is 2.106 Å, and the O–Co–O bond angles are 78.39–176.18°. Co3 adopts the same kind of coordination mode with Co1, but with different bond lengths and bond angles. The two carboxylic groups in dpa ligand adopt two kinds of connection mode, one is monodentate, the other is bridging. All the dpa ligands adopt right-handed coordination mode, connects the adjacent Co atoms together and form one-dimensional right-handed (*P*) helix. The right-handed (*P*) helixes are linked together with 4,4-bpy ligands and form two-dimensional homochiral layer structure as shown in Fig. 1b. To our interest, complex **1** crystallizes in a chiral space group. To our knowledge, although some complexes with helical structures had been synthesized from dpa ligands, homochiral complexes had never been synthesized from dpa ligand [15]. Therefore, complex **1** is the first homochiral complex constructed by dpa ligand.

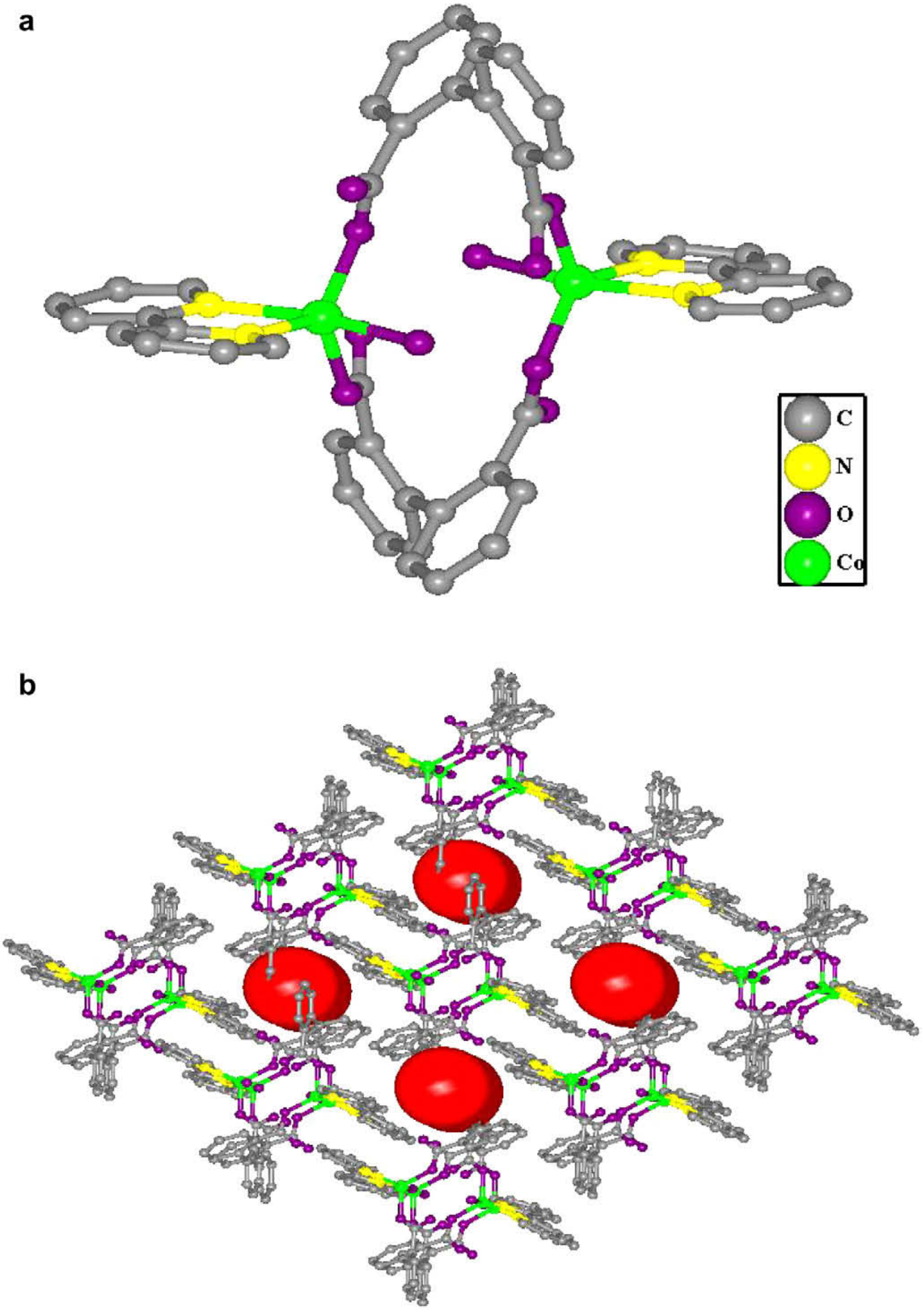

Fig. 3. (a) The fundamental unit of complex **3**. (b) Three-dimensional supramolecular network of the complex **3**.

Single-crystal X-ray diffraction analysis reveals that complex **2** exhibits a one-dimensional chiral helical chain like structure. In the fundamental unit, there exists only one crystallographic independent Zn atom, which adopts tetrahedral-pyramidal coordination mode as shown in Fig. 2a. It connects with three oxygen atoms from two dpa ligands with Zn–O bond distances ranging from 1.959 to 2.206 Å, and the O–Zn–O bond angles range from 60.82° to 104.38°. Two nitrogen atoms from 1,10′-phen occupy the other two coordination sites with the average Zn–N bond distance of 2.088 Å. The two carboxylic groups from dpa ligands connect Zn atoms together and form homochiral one-dimensional right-handed (*P*) helix as shown in Fig. 2b, which results the chirality in this complex. These one-dimensional chains are further extended into two-dimensional sheets through the π–π interactions from the phenyl rings of the 1,10′-phen and dpa ligands. The distances of the adjacent phenyls range from 3.43 to 3.57 Å as shown in Fig. 2c.

In homochiral complexes **1** and **2**, the screw of carboxylate groups resulted in the formation of the helical chain, and then the homochiral information can be effectively transferred through the oxygen atoms, which lead to the whole chirality of the two complexes.

For complex **3**, there also exists only one crystallographic independent Co atom, which adopts square pyramidal coordination mode as shown in Fig. 3a. The Co atom connects with two oxygen atoms from two dpa ligands with average Co–O bond distance 1.99 Å, two nitrogen atoms from 2,2′-bpy ligand, and the last coordination site is occupied by one aqua ligand. With such kind of connection mode, two Co atoms, two dpa ligands, and two 2,2′-bpy ligands form a large ring. With the π–π interactions between 2,2′-bpy and dpa ligands, these rings are further extended to two-dimensional layers. With the same kind of weak interactions, two-dimensional layers are further connected to form three-dimensional supramolecular network as shown in Fig. 3b. The distances of the adjacent phenyl rings range from 3.47 to 3.56 Å.

The asymmetric unit of complex **4** contains three Co atoms. Co1 connects with two carboxylic oxygen atoms from one dpa ligand four nitrogen atoms from two 1,10′-phen ligands, the Co–O bond distances are 2.045 and 2.071 Å, the Co–N bond distances are in

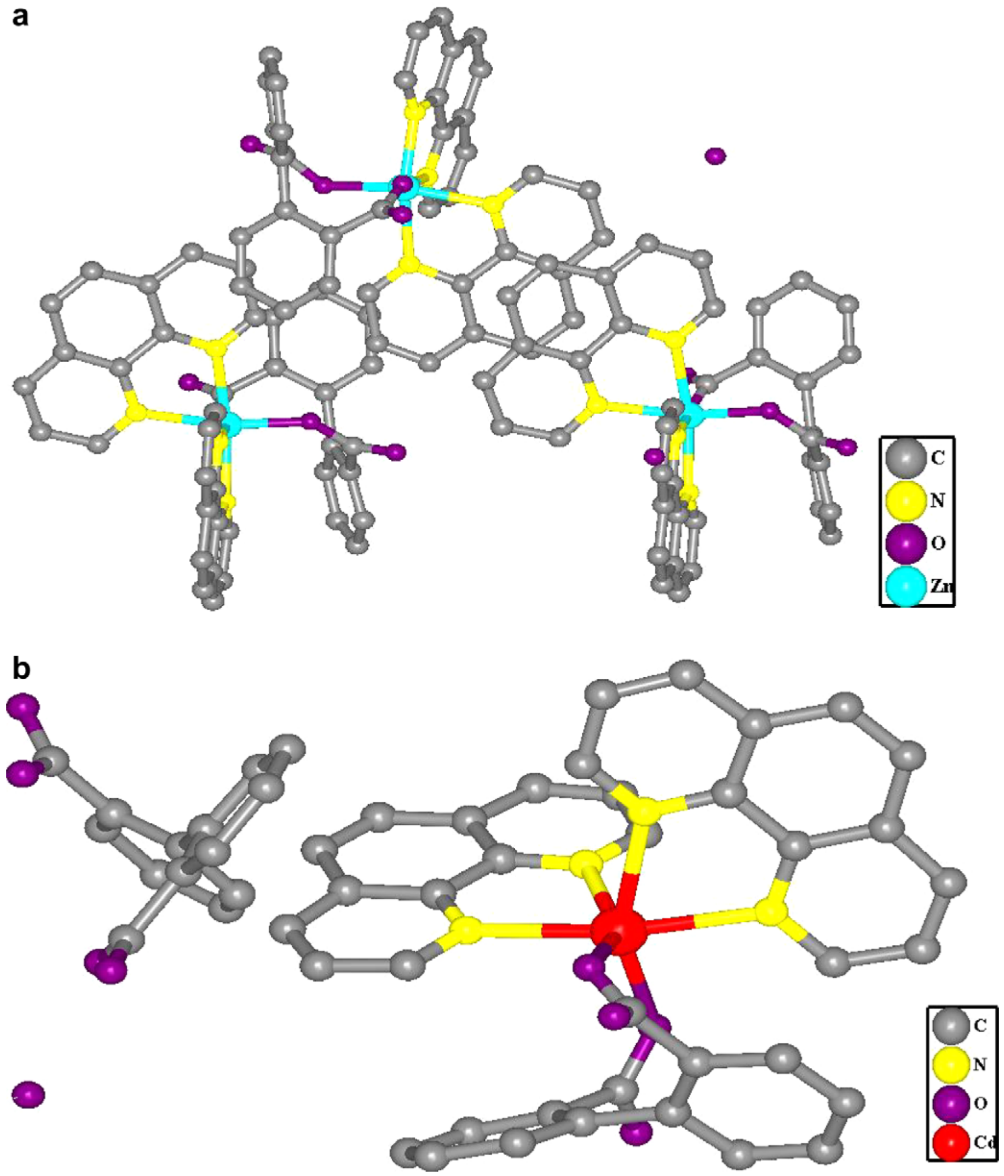

Fig. 4. (a) The fundamental unit of complex **4**. (b) The fundamental unit of complex **5**.

the range of 2.126 and 2.214 Å. This results a discrete unit of [Co(dpa)(1,10′-phen)$_2$], in which Co1 adopts distorted octahedral coordination mode. Co2 and Co3 adopt the same kind of coordination mode with Co1, but with different bond lengths and bond angles as shown in Fig. 4a. To our interests, these three kind of [Co(dpa)(1,10′-phen)$_2$] units exhibit two kind of configuration, Co1 and Co2 adopt Δ configuration, while Co3 uses Λ mode.

Like complex **4**, complex **5** also exhibits discrete structural feature. There exist only one crystallographic independent Cd atom in the fundamental unit. Cd1 adopts two carboxylic oxygen atoms from dpa ligand, four nitrogen atoms from two 1,10′-phen ligands. The Cd–O bond distance is 2.239 Å, Cd–N bond distances are 2.343 and 2.389 Å, respectively, which results a distorted octahedron coordination mode. Besides the [Cd(dpa)(1,10′-phen)$_2$] unit, there exist a free H$_2$dpa and water molecule in the fundamental unit as shown in Fig. 4b.

3.2. Thermo gravimetric analyses

In order to examine the thermal stabilities of the five complexes, thermal gravimetric (TG) analyses were carried out. Complex **1** exhibits two steps of weight losses. The first weight loss about 1.86% occurs in the range of 110–153 °C, corresponding to the removal of water (calcd. 1.90%). The second weight loss is about 83.73% from 271 to 439 °C, assigned to the loss of organic ligands (calcd. 83.75%). The curve of complex **2** also exhibits one-step weight loss in the range 262–430 °C (86.42%), corresponding to the loss of organic ligands (calcd. 86.54%). Like complex **1**, complex **3** shows two steps weight losses; the weight loss about 3.71% from 109 to 163 °C represents the loss of water (calcd. 3.80%). The second weight loss about 69.85% from 304 to 420 °C represents the loss of organic ligands (calcd. 83.75%). Complex **4** also displays two steps weight loss, the first weight loss about 1.66% from 71 to 112 °C shows the release of water, and the second about 89.48% from 343 to 427 °C exhibits the loss of organic ligands. These are in agreement with the calculated values (1.79% and 89.44%). The TG curve of complex **5** shows that chemical decomposition starts at 81 °C and ends at 460 °C with the weight loss of 3.01% and 87.79% are equivalent to the loss of water and organic molecules (calcd. 2.92% and 87.94%).

3.3. Fluorescent property

The photoluminescence properties of complex **2** and complex **5** in the solid state at room temperature are shown in Fig. 5. It can be observed that complexes **2** and **5** exhibit photoluminescence with emission maximum at ca. 387 and 381 nm upon excitation at 325 and 337 nm. According to the previous reports [30], these emission bands could be assigned to the emission of ligand-to-metal charge transfer (LMCT).

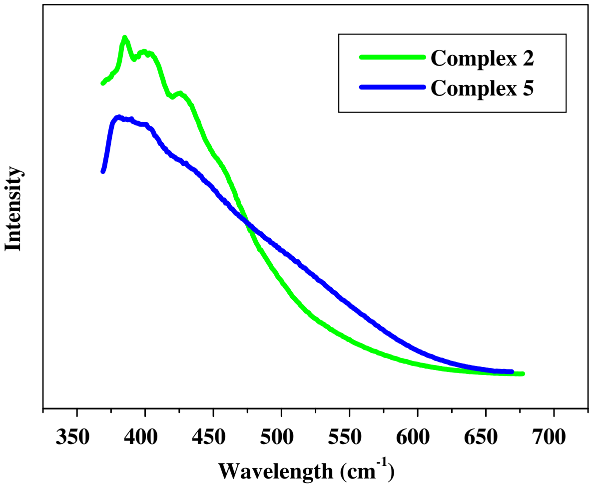

Fig. 5. The fluorescent spectra of complexes **2** and **5**.

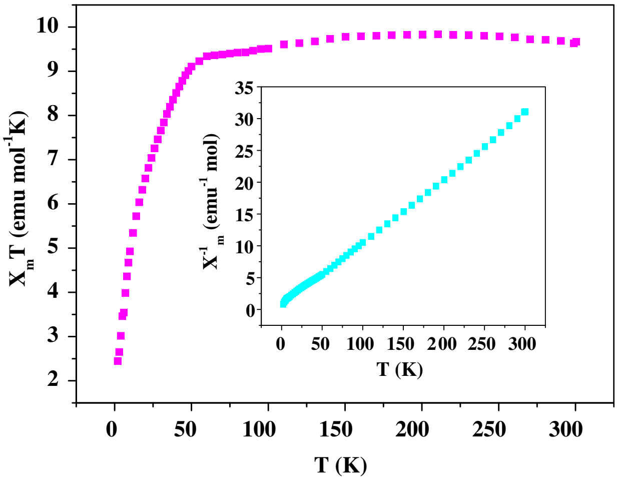

Fig. 6. The magnetic property of complex **1**.

3.4. Magnetic property

The temperature dependence of the magnetic susceptibility for complex **1** was investigated in the temperature range from 1.99 to 300 K under a magnetic field of 1000 G. The variation of $\chi_M T$ and χ_M^{-1} with T for complex **1** is shown in Fig. 6. At 300 K, the $\chi_M T$ is 9.67 cm^3 K mol^{-1}. As temperature is lowered, the $\chi_M T$ value decreases continuously to a value of 2.45 cm^3 K mol^{-1} at 2 K. Such a behavior of $\chi_M T$ curve indicates a mainly antiferromagnetic interaction in **1**. The variation of the χ_M with temperature follows the Curie–Weiss equation because of the linear relationship between χ_M^{-1} and T. The Curie constant and Weiss temperature are found to be 10.11 cm^3 K mol^{-1} and −8.03 K. The negative Weiss temperature further indicates the antiferromagnetic interactions between Co(II) ions [31–33].

4. Conclusions

Here, we synthesized five new coordination polymers generated from mixed ligand systems of H$_2$dpa and various nitrogen-containing ligands under hydrothermal condition. Among the complexes we synthesized, complex **1** exhibits two-dimensional layer structure, complex **2** exhibits one-dimensional chain like structure, complexes **3**–**5** shows discrete structures, complexes **1** and **2** crystallized in homochiral spacegroup. Our findings will enrich the coordination chemistry and crystal engineering study of dpa and mixed ligands. We studied the magnetic property of complex **1** and the fluorescent properties of complexes **2** and **5**. Furthermore, this work prompts us to synthesize more complexes from flexible organic ligands.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.09.025.

CCDC 701330, 701331, 710384, 710385 and 710386 contain the supplementary crystallographic data for complexes **1**, **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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