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Syntheses, structures, and fluorescence properties of cadmium(II) and zinc(II) complexes based on 1,1′-binaphthalenyl-2,2′-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid

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ABSTRACT

Solvothermal reaction of Cd(II)/Zn(II) salts with 1,1′-binaphthalenyl-2,2′-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4L) ligand results in the formation of five interesting complexes $[Cd_2(L)(phen)_2(H_2O)]\cdot 2H_2O$ (**1**), $[Cd_4(L)_2(phen)_2(H_2O)_7]\cdot CH_3OH\cdot 10H_2O$ (**2**), $\{[Cd_5(L)_2(H_2O)_3(OH)_2]\cdot H_2O\}_n$ (**3**), $[Zn_2(L)(phen)_2(H_2O)]\cdot 2H_2O$ (**4**) and $\{[Zn_2(L)(H_2O)_4]\cdot 2.25H_2O\}_n$ (**5**), where phen = 1,10-phenanthroline. The structure of **1** is dinuclear, and that of **2** is tetranuclear. The structural difference of **1** and **2** indicates a temperature-dependence of the formation of two complexes. **3** Is a 2D polymer with a (6,3) network constructed by a novel asymmetrical pentanuclear Cd clusters with bridging hydroxyl and carboxylate groups as secondary building units, which have never been employed before in the construction of 2D networks. **4** Is a dinuclear compound with a structure similar to that of **1**. Complex **5** exhibits a zigzag chain structure bridged by L^{4-} ligand. A variety of coordination modes of the H_4L ligand were found, some of them are unprecedented for these type of compounds. The fluorescence properties of the compounds were studied, and strong fluorescent emissions were observed.

1. Introduction

The crystal engineering of coordination complexes (CCs) attracts intense attention because controlling the molecular organization in the solid state can lead to the construction of novel materials with desired structure and promising function [1,2]. Despite a number of CCs were obtained by various synthetic strategies [3] such as secondary building units (SBUs), controlling the hydrolysis of the metal ions to construct metal-hydroxy cluster, template-directed, it is still a labyrinth for chemists to design and synthesize a desired architecture in a truly predictable manner because many factors can have an unpredictable impact on the final product structures, such as (a) the coordination geometry preferred by the metal, the counter ion, and functionality, flexibility and symmetry of the ligand; (b) reaction conditions such as solvent, temperature, different kinds of base, pH value of the solution, the ratio of the reactants, and method of crystallization; (c) the non-covalent forces such as hydrogen-bonding, π–π stacking [4–6]. Therefore, considerable elaborate and systematic work is necessary to comprehend aforementioned factors that determine the aggregation fashions of molecular structure in the solid state. Taking into account of the factors mentioned above, we have focused our attention on the reactions of various metal salts with N-containing polycarboxylic acid ligands, and investigated the influences of different bases, different kinds of metal salts and reaction temperature on the structure of the complexes.

Iminodiacetic acid containing a flexible group on the N-atom has attracted much attention and has been extensively used in the preparation of all kinds of functional complexes owing to their numerous coordination sites and flexible connection modes [7,8]. However, the ligands connecting directly a rigid ring on the N-atom of iminodiacetic acid are relatively rarely investigated, especially for the ligands connecting a rigid aromatic ring with four or more flexible CH_2COO^- groups [9,10]. To investigate the influence of the bulky aromatic skeletons of such ligands on the structures and properties of their coordination complexes, we designed and synthesized a new ligand, 1,1′-binaphthalenyl-2,2′-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4L). This ligand exhibits remarkable features such as (a) it contains two iminodiacetic acid units with four carboxylate groups, which would be able to provide a variety of coordination modes by partially or completely deprotonating; (b) it possesses both rigidity and flexibility due to the presence of the naphthyl ring and the C–C single bond at the 1,1′-positions of the binaphthyl framework, and the flexible acetic moiety, which may induce subtle effect on the formation of the complexes under different reaction conditions; (c) the presence of aromatic groups and the carboxylate groups could offer plenty of π–π and hydrogen

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bonding interactions, which will be helpful for the formation of various supramolecular structures.

In this paper, we report the syntheses and characterizations of five cadmium(II) and zinc(II) complexes with H_4L ligand, namely $[Cd_2(L)(phen)_2(H_2O)]\cdot 2H_2O$ (**1**), $[Cd_4(L)_2(phen)_2(H_2O)_7]\cdot CH_3OH\cdot 10H_2O$ (**2**), $\{[Cd_5(L)_2(H_2O)_3(OH)_2]\cdot H_2O\}_n$ (**3**), $[Zn_2(L)(phen)_2(H_2O)]\cdot 2H_2O$ (**4**) and $\{[Zn_2(L)(H_2O)_4]\cdot 2.25H_2O\}_n$ (**5**). These complexes display a variety of structures varying from discrete dinuclear, tetranuclear structure to chain and 2D network. Various coordination modes for the H_4L ligand in the compounds are observed.

2. Experimental

2.1. Materials and measurements

Racemic 1,1′-binaphthalenyl-2,2′-diamine was purchased from Alfa-aesar. Other reagents were commercially available and used as received without further purification. Infrared spectra were recorded as KBr pellets using a Nicolet 360 FT-IR spectrometer. Elemental analyses (C, H and N) were performed on a Vario EL analyser. Thermogravimetric analyses were recorded with a Perkin-Elmer Pyris Diamond TG analyzer at a rate of 10 °C/min from room temperature to 1000 °C under nitrogen atmosphere. The powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max 2200 diffractometer with Cu Kα radiation. Luminescence spectra were recorded on an Edinburgh Analytical Instrument FLS920 Luminescence spectrometer at room temperature.

2.2. Synthesis of 1,1′-binaphthalenyl-2,2′-diamine-N,N,N′,N′-tetraacetic acid (H_4L)

Racemic 1,1′-binaphthalenyl-2,2′-diamine (2.84 g, 10 mmol) was dissolved in freshly distilled acetonitrile (60 mL), then potassium carbonate (13.82 g, 100 mmol) and potassium iodide (1.33 g, 8.0 mmol) were added. The reaction mixture was heated to reflux under nitrogen atmosphere. Then ethyl bromoacetate (8.35 g, 50 mmol) was added dropwise and the reaction mixture was refluxed for 72 h. The mixture was then cooled, diluted with water (200 mL) and extracted with ethyl acetate (3 × 60 mL). The combined organic layer was washed with water (60 mL), dried with $MgSO_4$, and then filtered and evaporated under reduced pressure to remove the solvent. The residue was purified by flash chromatography on silica using ethyl acetate-petroleum ether (v/v 1:6) as eluent to give light yellow solid. (yield 54%): ^1H NMR (500 MHz, DMSO-d_6): 7.86–7.90 (*m*, 4H), 6.90–7.34 (*m*, 8H), 3.68–3.85 (*m*, 16H), 1.02 (*t*, 12H, *J* = 7.1 Hz).

A mixture of above resulted solid product (3.15 g, 5 mmol), ethanol (50 mL) and 2 M aqueous solution of NaOH (8 mL) was refluxed under nitrogen atmosphere for 24 h. The solution was then evaporated to remove most solvent, and then cooled in ice-water, 3 M hydrochloric acid was added until pH 3–4. The crude product was extracted with ethyl acetate (2 × 60 mL). The organic layers were combined and washed with brine (80 mL), dried with Na_2SO_4, and filtered. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography on silica using ethyl acetate as eluent, from which a yellowish solid of H_4L ligand was collected in 76% yield. Mp: 172–173 °C; ^1H NMR (500 MHz, DMSO-d_6) 7.91 (*d*, 2H, *J* = 9.0 Hz), 7.86 (*d*, 2H, *J* = 8.0 Hz), 7.42 (*d*, 2H, *J* = 8.0 Hz), 7.31 (*t*, 2H, *J* = 8.0 Hz); 7.19 (*t*, 2H, *J* = 8.0 Hz); 6.88 (*d*, 2H, *J* = 8.6 Hz); 3.66 (*s*, 8H); ^{13}C NMR (125.77 MHz, DMSO-d_6):172.67, 147.89, 134.27, 130.18, 128.89, 128.38, 126.85, 125.10, 124.47, 124.16, 123.24, 53.13; IR (KBr, cm^{-1}), 3418 (w), 3056 (w), 2929 (m), 1719 (s), 1619 (m), 1594 (m), 1507 (s), 1407 (w), 1375 (w), 1211 (s), 969 (s), 816 (s), 750 (s); *Anal.* Calc. for $C_{28}H_{24}N_2O_8$: C, 65.11; H, 4.68; N, 5.42. Found: C, 65.29; H, 4.53; N, 5.36%.

2.3. Synthesis of complexes *1*–*5*

2.3.1. $[Cd_2(L)(phen)_2(H_2O)]\cdot 2H_2O$ (*1*)

A solution of $Cd(NO_3)_2\cdot 4H_2O$ (27.8 mg, 0.09 mmol), H_4L (30.7 mg, 0.06 mmol), phen (11.9 mg, 0.06 mmol), and NaOH (7.2 mg, 0.18 mmol) in CH_3OH/H_2O (1:8, 9 mL) was stirred for 20 min in air, then sealed in a 15 mL Teflon-lined stainless steel vessel and heated at 95 °C for 72 h. The vessel was then taken out from the oven and cooled down naturally at ambient temperature. After cooling to room temperature, colorless block crystals of **1** suitable for X-ray diffraction analysis were obtained in 34% yield (based on Cd). *Anal.* Calc. for $C_{52}H_{42}N_6O_{11}Cd_2$: C, 54.23; H, 3.68; N, 7.30. Found: C, 54.29; H, 3.53; N, 7.12%. IR data (KBr pellet, cm^{-1}): 3415 (s), 1596 (s), 1514 (m), 1405 (m), 1385 (w), 1306 (m), 1193 (w), 1144 (w), 848 (m), 729 (m).

2.3.2. $[Cd_4(L)_2(phen)_2(H_2O)_7]\cdot CH_3OH\cdot 10H_2O$ (*2*)

Similar procedure as that for **1** was performed, except that the reaction temperature was set at 120 °C. Colorless block crystals of **2** were obtained in 26% yield (based on Cd). *Anal.* Calc. for $C_{81}H_{94}N_8O_{34}Cd_4$: C, 44.77; H, 4.36; N, 5.16. Found: C, 44.94; H, 4.46; N, 5.21%. IR data (KBr pellets, cm^{-1}): 3423 (s), 1596 (s), 1514 (w), 1407 (m), 1306 (w), 1193 (w), 848 (w), 746 (w), 727 (w).

2.3.3. $\{[Cd_5(L)_2(H_2O)_3(OH)_2]\cdot H_2O\}_n$ (*3*)

A solution of $Cd(NO_3)_2\cdot 4H_2O$ (27.8 mg, 0.09 mmol) and H_4L (30.7 mg, 0.06 mmol) in H_2O (8 mL) was stirred for 10 min in air, and then placed in Parr Teflon-lined stainless steel vessel (15 mL). After addition of triethylamine (0.1 mL), the vessel was sealed, heated at 120 °C for 96 h, and then taken out from the oven and cooled down naturally at ambient temperature. After cooling to room temperature, colorless block crystals of **3** suitable for X-ray diffraction analysis were obtained in 42% yield (based on Cd). *Anal.* Calc. for $C_{56}H_{50}N_4O_{22}Cd_5$: C, 39.73; H, 2.98; N, 3.31. Found: C, 39.54; H, 2.79; N, 3.12%. IR data (KBr pellet, cm^{-1}): 3437 (s), 1593 (s), 1507(w), 1409 (s), 1310 (m), 1189 (w), 934 (w), 818 (w), 746 (w).

2.3.4. $[Zn_2(L)(phen)_2(H_2O)]\cdot 2H_2O$ (*4*)

A solution of $Zn(NO_3)_2\cdot 4H_2O$ (26.8 mg, 0.09 mmol), H_4L (30.7 mg, 0.06 mmol), phen (11.9 mg, 0.06 mmol), and NaOH (7.2 mg, 0.18 mmol) in CH_3OH/H_2O (1:8, 9 mL) was stirred for 20 min in air, and then sealed in a 15 mL Teflon-lined stainless steel vessel and heated at 90 °C for 72 h. The vessel was then taken out from the oven and cooled down naturally at ambient temperature. After cooling to room temperature, light-yellow block crystals of **4** were obtained in 30% yield (based on Zn). *Anal.* Calc. for $C_{52}H_{42}N_6O_{11}Zn_2$: C, 59.05; H, 4.00; N, 7.94. Found: C, 59.19; H, 4.13; N, 8.06%. IR data (KBr pellet, cm^{-1}): 3421 (s), 1624 (s), 1514 (s), 1424 (w), 1385 (w), 1199 (w), 848 (w), 727 (s).

2.3.5. $\{[Zn_2(L)(H_2O)_4]\cdot 2.25H_2O\}_n$ (*5*)

H_4L (51.6 mg, 0.10 mmol), $Zn(NO_3)_2\cdot 4H_2O$ (29.8 mg, 0.10 mmol), CH_3OH (0.8 mL), 2.7% ammonia solution (0.05 mL), and H_2O (0.30 mL) were placed in a thick Pyrex tube (ca 20 cm long). The tube was frozen using liquid N_2, evacuated under vacuum and flame-sealed. It was then allowed to warm to room temperature and heated at 90 °C for 72 h. The tube was then taken out from the oven and cooled down naturally at ambient temperature. After cooling to room temperature, colorless block crystals of **5** were obtained in 45% yield (based on Zn). *Anal.* Calc. for $C_{28}H_{32.5}N_2O_{14.25}Zn_2$: C, 44.50; H, 4.40; N, 3.71. Found: C, 44.63; H, 4.49; N, 3.62%. IR data (KBr pellet, cm^{-1}): 3395 (s), 1596 (s), 1508 (m), 1409 (s), 1347(w), 1306 (m), 1196 (m), 938 (w), 887 (w), 819 (w), 748 (m).

2.4. X-ray crystallography

Suitable single crystals of **1**–**5** were selected and mounted onto thin glass fibers. Measurements of **2**, **3**, **5** were taken at 185(2) K using a Bruker CCDArea Detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Measurements of **1** and **4** were taken at 153(2) K using a Agilent CrysAlisPro Detector in the same radiation. All the structures were solved by direct methods using the SHELXS-97 program package and refined against F^2 by full-matrix least-squares methods with SHELXL-97 [11] with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined by using a riding model. Hydrogen atoms in water molecules were located from difference Fourier maps and refined by using a riding model. For **2**, restraints were used to maintain chemically sensible bond lengths for the disordered water molecule and a guest methanol molecule. A summary of crystallographic and structural refinement data for **1**–**5** is given in Table 1. Selected bond lengths and bond angles are listed in Table S1. Hydrogen bonds are listed in Table S2.

3. Results and discussion

3.1. Syntheses

Solvothermal reaction of $Cd(NO_3)_2{\cdot}4H_2O$, H_4L and phen in a mixed solvent of CH_3OH and H_2O at 90 °C led to the formation of dinuclear **1**. With the same starting materials as that for **1**, the tetranuclear **2** was obtained at a higher temperature of 120 °C, indicating a temperature-dependence of the formation of **1** and **2**. Complex **3** was obtained by a hydrothermal reaction of $Cd(NO_3)_2$ and H_4L in the presence of Et_3N. The success in the formation of **3** by using the weak base of Et_3N in the reaction may be ascribed to that the base here plays not only the function in the deprotonation of the ligand, but also an important role in directing the construction of cadmium-hydroxy units through controlling the hydrolysis rate of the metal ions. Complex **4** was obtained under the same condition as that of **1** except using $Zn(NO_3)_2{\cdot}4H_2O$ instead of $Cd(NO_3)_2{\cdot}4H_2O$. Different from the reaction system of $Cd(NO_3)_2$, reaction of $Zn(NO_3)_2$ with H_4L did not show a temperature-dependent result. The reaction in a temperature range of 90–125 °C gave only the same product of **4**, which was certified by the IR and PXRD. The similar reaction of $Zn(NO_3)_2$ with H_4L as that for **3** give only unidentified powder samples rather than crystals. However, a modified reaction, carrying in a sealed Pyrex tube with CH_3OH and H_2O as solvent in the presence of ammonia, gave crystals of **5**. The phase purity of all five complexes has been verified by powder X-ray diffraction analysis, in which the patterns of the bulk samples were in agreement with the simulated pattern from the corresponding single crystal data (Fig. S1).

3.2. Description of the crystal structures

*3.2.1. $[M_2(L)(phen)_2(H_2O)]{\cdot}2H_2O$ [M = Cd (**1**), Zn (**4**)]*

X-ray diffraction studies reveal that complexes **1** and **4** exhibit similar dinuclear structure with almost identical framework. Here, the structure of **1** is discussed in detail as a representative. The asymmetric unit of **1** is composed of two Cd atoms, one L^{4-} ligand, two phen ligands, one coordinated water molecule, and two lattice water molecules. As shown in Fig. 1, both Cd atoms in **1** are six-coordinated. The Cd1 atom displays a severely distorted octahedral coordination geometry completed by one carboxylate oxygen atom (O3) from one L^{4-} ligand, four nitrogen atoms (N3, N4, N5, N6) from two phen ligands and one oxygen atom (O9) from one water molecule. The Cd2 atom exhibits a slightly distorted octahedral geometry with N1, O4, O6, O8 atoms from one L^{4-} ligand locating at the basal plane and the N2, O2 atoms from the same L^{4-} ligand at the apices. The coordination bond lengths and angles around the Cd atoms are in the range of 2.1710(18)–2.4937(19) Å and 70.34(7)–168.54(8)°, respectively, as listed in Table S1, which resemble closely to those reported in the literature [12]. Cd1 and Cd2 atoms are bridged by one carboxylate group of the ligand in a *syn-anti* bridging mode to give the dinuclear structure of the complex (Fig. 1). The Cd1···Cd2 distance is of 5.0061(6) Å. The naphthyl rings of the (R_a)-L^{4-} and (S_a)-L^{4-} ligand in **1** subtend a dihedral angle of 82.881(49)° and 82.880(51)°, which is consistent with the reported values in related complexes [13].

The dinuclear $[Cd_2(R_a\text{-}L)(phen)_2(H_2O)]$ and $[Cd_2(S_a\text{-}L)(phen)_2(H_2O)]$ in one unit cell are assembled into a supramolecular dimer via a cyclic $R_4^4(16)$ hydrogen-bonding motif (Fig. S2) formed by

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

Complex	1	2	3	4	5
Formula	$C_{52}H_{42}Cd_2N_6O_{11}$	$C_{81}H_{94}Cd_4N_8O_{34}$	$C_{56}H_{50}Cd_5N_4O_{22}$	$C_{52}H_{42}N_6O_{11}Zn_2$	$C_{28}H_{32.5}N_2O_{14.25}Zn_2$
Formula weight	1152	2173	1693	1058	756
T (K)	153(2)	185(2)	185(2)	153(2)	185(2)
λ (Å)	0.71	0.71	0.71	0.71	0.71
Cryst syst	triclinic	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	*P*2(1)/*c*	$P\bar{1}$	*Pbca*
a (Å)	13.4883(6)	9.663(3)	17.8488(10)	13.3998(4)	10.5254(7)
b (Å)	14.7030(9)	20.744(5)	20.9067(12)	14.4935(5)	14.8582(10)
c (Å)	15.0480(11)	23.176(5)	15.3851(9)	14.5449(5)	38.821(3)
α (°)	62.083(7)	95.562(4)	90	103.285(3)	90
β (°)	74.341(5)	94.179(5)	107.8770(10)	104.830(3)	90
γ (°)	63.374(5)	102.706(5)	90	117.301(4)	90
V ($Å^3$)	2350.5(2)	4489.0(19)	5463.9(5)	2219.47(18)	6071.2(7)
Z	2	2	4	2	8
D_{calc} (g cm^{-3})	1.63	1.61	2.06	1.58	1.65
μ (mm^{-1})	0.98	1.02	2	1.16	1.66
F (000)	1160	2200	3320	1088	3108
Goodness-of-fit (GOF) on F^2	1.05	1.05	1.03	1.05	1.09
R_1 ($I > 2\sigma(I)$)	0.03	0.06	0.02	0.03	0.03
wR_2 ($I > 2\sigma(I)$)	0.07	0.16	0.05	0.08	0.08
R_1 (all data)	0.03	0.09	0.03	0.04	0.04
wR_2 (all data)	0.07	0.17	0.06	0.08	0.08

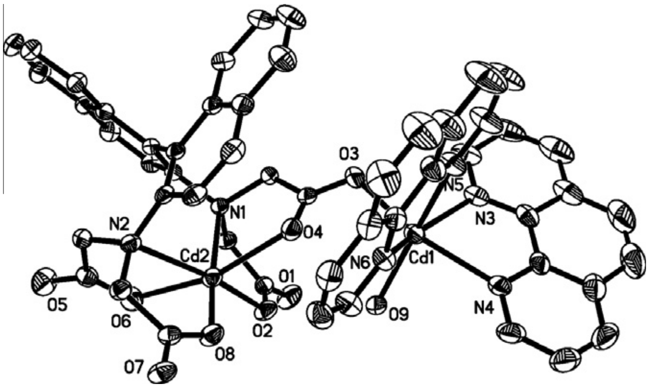

Fig. 1. The coordination environment of Cd(II) in **1** drawn with ellipsoids at the 30% probability level. Hydrogen atoms on carbon atoms are omitted for clarity.

intermolecular hydrogen bonds O9–H9A···O7^D (O9···O7D, 2.694(3) Å, symmetry code D: $-x+1$, $-y+1$, $-z+1$) between one coordinated water molecule (O9) on Cd1 and one oxygen atom (O7) of one carboxylate group, and intramolecular hydrogen bonds O9–H9B···O2 (O9···O2, 2.910(3) Å) between one coordinated water molecule (O9) on Cd1 and one carboxylato oxygen atom (O2). Meanwhile, the neighboring hydrogen-bonded dimers are held together through intermolecular hydrogen bonds O10–H10A···O1^C, O10–H10B···O5^B between guest water molecule and carboxylate oxygen atom to give a hydrogen-bonded chain along the *a* axis (Fig. S3). The adjacent chains are linked further together to form a supramolecular layer through the π–π stacking interactions between the phenyl rings of the phen ligands from the adjacent dimers with a centroid···centroid separation of 3.46 Å (Fig. 2).

3.2.2. [$Cd_4(L)_2(phen)_2(H_2O)_7$]·$CH_3OH$·$10H_2O$ (**2**)

Complex **2** was obtained with a similar procedure as that for **1** except that the reaction temperature was increased to 120 °C. However, **2** displays a different structure from that for **1**, indicating a temperature control for the structures of the complexes **1** and **2**. Complex **2** exhibits a tetranuclear structure with the asymmetric unit containing four Cd centers, two L^{4-} ligands, two phen ligands, seven coordinated water molecules, ten guest water molecules and one non-coordinated methanol molecule. As shown in Fig. 3, the tetranuclear structure shows an arcuate geometry, in which the four cadmium centers are linked by the bridging coordination of the ligand carboxylate groups. The Cd1 and Cd2 atoms are bridged by a carboxylate from one ligand in a μ_2-η^2:η^1 chelating-bridging mode, and the Cd1 and Cd3 atoms are linked by a carboxylate from another ligand in the same mode. However, the Cd3 and Cd4 atoms are bridged by a carboxylate in a μ_2-η^1:η^1 *syn-anti* bridging mode. Four cadmium centers are located in different coordination environments. Cd1 adopts an eight-coordinated polyhedron (Fig. S4) completed by four carboxylate oxygen atoms (O7, O8, O15, O16) from two different L^{4-} ligands, two nitrogen atoms (N5, N6) from one phen ligand, and two coordinated water molecules (O17, O18). Cd2 and Cd3 are both seven-coordinated by two N atoms and four carboxylate O atoms from one L^{4-} ligand, and an O atom from one water molecule in a geometry which may be described as a roughly capped trigonal prism (Fig. S4). The Cd4 center is six-coordinated in a slightly distorted octahedral geometry by two nitrogen atoms (N7, N8) of one phen ligand, three oxygen atoms (O21, O22, O23) of three water molecules, and one oxygen atom (O1) from one carboxylate of the L^{4-} ligand. In **2**, the Cd–O and Cd–N bond distances are in the range of 2.242–2.600 and 2.324–2.605 Å, respectively, which is comparable to the reported values [14]. The naphthyl rings of the L^{4-} ligand subtend a dihedral angle of 72.086(132)° and 75.650(125)°, which is obvious smaller than the value of 82.88° in **1**, indicating that the two naphthyl rings of the ligand can adjust their relative degrees by themselves to meet the requirement for a preferred coordination geometry.

Interestingly, one arcuate [$Cd_4(R_a\text{-}L)_2(phen)_2(H_2O)_7$] unit and one arcuate [$Cd_4(S_a\text{-}L)_2(phen)_2(H_2O)_7$] unit in **2** are linked into a supramolecular dimer (Fig. S5) with an elliptic motif in the head-to-end fashion by intermolecular hydrogen bond O21–H21C···O13^D (O···O: 2.695(9) Å, symmetry code D: $-x+2$, $-y+1$, $-z$) and O22–H22B···O14^D (O···O: 2.842(9) Å) between the coordinated water molecule (O21 and O22) on Cd4 and carboxylato oxygen atom (O13 and O14) of the ligand. The supramolecular dimer displays an elliptic cavity with a long axis

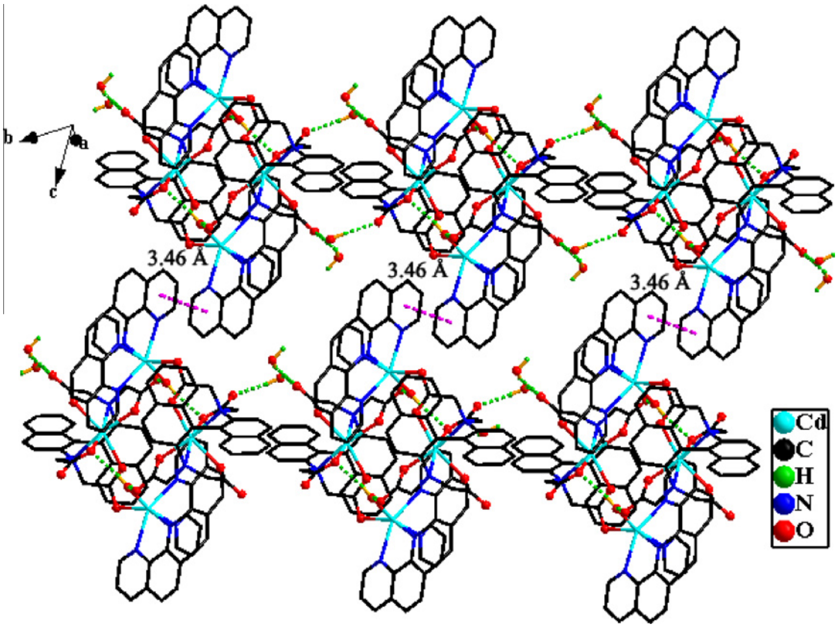

Fig. 2. The supramolecular layer in **1** constructed by π–π stacking interactions between the two adjacent chains in the *ab* plane. Hydrogen bonds and π–π stacking are indicated by dashed lines.

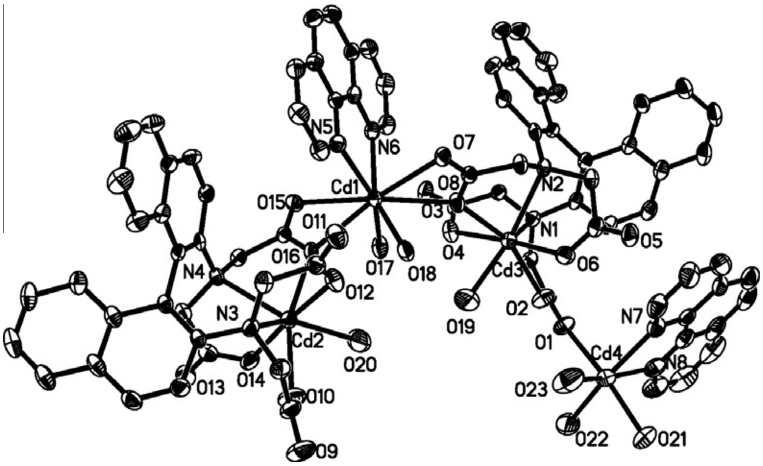

Fig. 3. The tetranuclear structure of **2** drawn with ellipsoids at the 30% probability level. Solvent molecules and hydrogen atoms on carbon atoms are omitted for clarity.

of 15.52 Å and a short axis of 11.04 Å. The guest water molecules and one disordered methanol molecule exist in the cavity via a number of hydrogen bond interactions, such as O22–H22A···O29 and O17–H17A···O27 hydrogen bonds between guest water molecules and coordinated water molecules; O29–H292···O26 and O27–H27C···O25 hydrogen bonds between different guest water molecules; and weak O35–H35A···O26 hydrogen bond between coordinated water molecule and guest methanol molecule (Table S2). The intramolecular hydrogen bond interactions between coordinated water molecules and carboxylate oxygen atoms of the ligand (O18–H18B···O12 and O17–H17B···O4) are also observed in the supramolecular dimer. The neighbor elliptic supramolecular dimers are further linked into a supramolecular layer in the *bc* plane by π–π interactions among the phen molecules with the values of the centroid···centroid separation of 3.67 and 3.96 Å, respectively (Fig. 4). Furthermore, the supramolecular layers are stacked along *a* direction by hydrogen bond interactions between coordinated water and guest water molecules (O18–H18A···O25^{A}, O19–H19A···O32^{A}, O20–H20B···O34^{B}); between different guest water molecules (O25–H25F···O32); and between guest water molecules and carboxylato oxygen atoms of the ligand (O27–H27D···O11^{E}, O26–H26B···O5^{E}, O32–H321···O6^{E}) to give a final 3D supramolecular framework structure (Fig. S6).

3.2.3. $\{[Cd_5(L)_2(H_2O)_3(OH)_2]\cdot H_2O\}_n$ (**3**)

The structure of **3** is a two-dimensional polymer constructed from novel pentanuclear cadmium cluster units $[Cd_5(\mu_2\text{-}OH)(\mu_3\text{-}OH)(\mu_2\text{-}RCOO)(\mu_3\text{-}RCOO)_3]$. To our best knowledge, only a few cadmium carboxylate MOFs [15–17] are constructed by high nuclearity cluster (>4 Cd^{2+} ions) as secondary building units (SBUs). Such asymmetrical pentanuclear cluster containing μ_2-OH, μ_3-OH and carboxylic bridges with different bridging mode used for the construction 2D network has never been presented before. In the pentanuclear unit (Fig. S7), Cd1 is connected to another four Cd centers by three μ_3-carboxylate groups and two

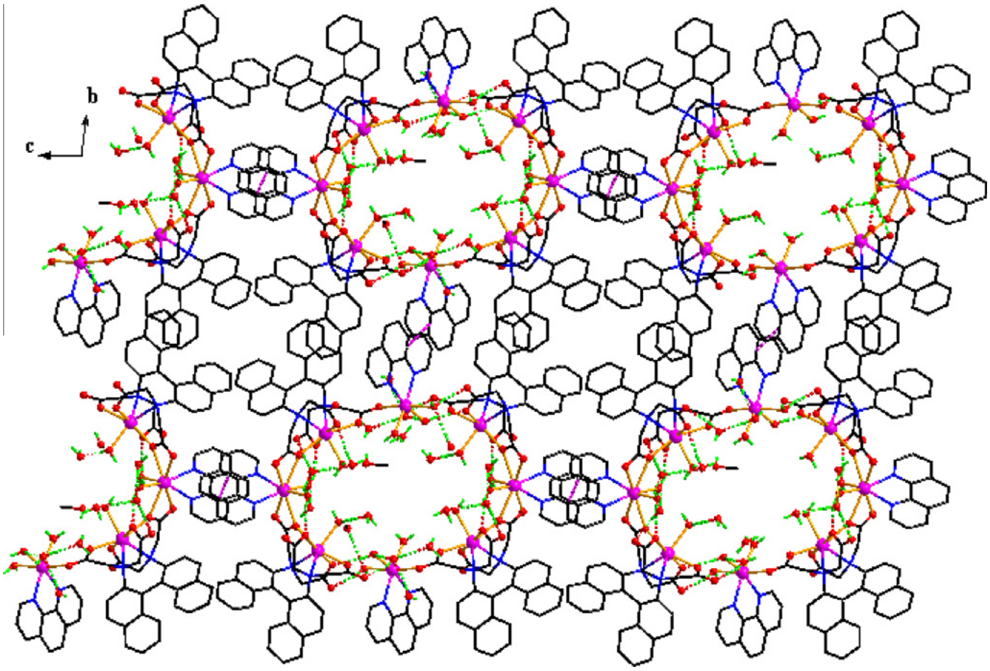

Fig. 4. View of the 2D supramolecular network of **2**. Part hydrogen atoms are omitted for clarity. Hydrogen bonds and π–π stacking are indicated by dashed lines.

OH^- groups with the μ_2-OH (O17) group bridging Cd1 and Cd3, the μ_3-OH (O18) group linking Cd1, Cd4 and Cd5 atoms, and the three μ_3-carboxylate groups connecting Cd1–Cd2–Cd3, Cd1–Cd2–Cd5, and Cd1–Cd3–Cd4, respectively. In addition, Cd2 is further linked to Cd4 by a η^2-oxygen atom (O12) of the other carboxylate group. The nonbonding Cd···Cd distances are 3.5313(3)–5.7477(4) Å. The five cadmium centers are in different coordination environment (Fig. 5). Cd1 is six-coordinated by four carboxylate oxygen atoms O4, O8, O10 and $O5^A$ (symmetry code A: x, $-y + 3/2$, $z - 1/2$) from three different L^{4-} ligands and two hydroxyl oxygen atoms (O17, O18) in a severely distorted octahedral coordination environment with the twist angle θ of 22.18° (30° for standard octahedral [18]). Cd2 is seven-coordinated by four carboxylate oxygen atoms (O2, O4, O6, O8) and two nitrogen atoms (N1, N2) from one L^{4-} ligand and one carboxylate oxygen atom (O12) from the other L^{4-} ligand in a capped distorted trigonal prismatic coordination environment. Cd3 is also seven-coordinated by four carboxylate oxygen aotms from three different L^{4-} ligands and one hydroxyl oxygen atom (O17) and two oxygen atoms of two water molecules (O19, O20), but in a distorted pentagonal-bipyramidal coordination environment. The equatorial atoms (O3, O9, O13B, O14B, O19) deviate slightly from the pentagonal plane, the maximum deviation from the mean equatorial plane being 0.135 Å at O(13B). The range of the equatorial chelating angles is 51.76(7)–79.58(7)°, some of them are far from the value of 72° for the ideal pentagonal bipyramid polyhedron. Cd4 is seven-coordinated by four carboxylate oxygen atoms (O12, O14, O16, O10) and two nitrogen atoms (N3, N4) from one L^{4-} ligand, one μ_3-OH oxygen atom (O18) in a capped distorted trigonal prism coordination environment. The Cd4–N4 bond (2.774 Å) is significantly longer than the other bonds (2.224–2.605 Å) around Cd4 (Table S1). The coordination polyhedron around Cd5 center formed by four carboxylate oxygen atoms (O2A, O6A, O7, O11A) from two L^{4-} ligands, one hydroxyl oxygen atom (O18) and one oxygen atom of coordinated water molecule (O21) could be defined as a slightly distorted octahedral with the twist angle θ of 27.1°. In **3**, the Cd–O and Cd–N bond distances are in the range of 2.177–2.658 and 2.450–2.774 Å, respectively. The naphthyl rings of the L^{4-} ligand containing C10, C11 and C38, C39 atom subtend a dihedral angle of 70.964(42)° and 73.817(60)°, respectively.

The 2D structure of **3** is constructed via the connection of the pentanuclear Cd(II) cluster units by the bridging of the carboxylate groups of the ligand. Every pentanuclear Cd(II) cluster unit in the compound is connected to other three ones (Fig. S8). The pentanuclear Cd(II) unit (marked with purple color) which we take as reference is linked to its neighboring pentanuclear Cd(II) unit (marked with turquiose color) via two symmetry related Cd atoms (Cd3 and Cd3B) by the bridging of two carboxylate groups in μ_2-η^1:η^2 chelating-bridging mode. From Fig. S8b, we can see that the referenced purple pentanuclear Cd(II) unit connects to another neighboring pentanuclear Cd(II) unit (marked with orange color) by the bridging of three carboxylate groups, in which two carboxylate groups act in μ_3-η^1:η^2 bridging mode and one in μ_2-η^2:η^0 mode. In the same connecting mode, the referenced purple pentanuclear Cd(II) unit is linked to the third neighboring pentanuclear Cd(II) unit (marked with green color, Fig. S8c). As a whole, the connection of the referenced purple pentanuclear Cd(II) unit to its three neighboring pentanuclear Cd(II) units is shown in Fig. S8d. Topologically, if the pentanuclear Cd(II) SBUs are viewed as nodes, the 2D structure of **3** can be described as a (6,3)-connected network with the Schläfli symbol 6^3, as shown in Fig. 6. To the best of our knowledge, it is the first 2D (6,3) network based on cadmium cluster SBUs built from ligands containing *N*,*N*-diacetic acid units.

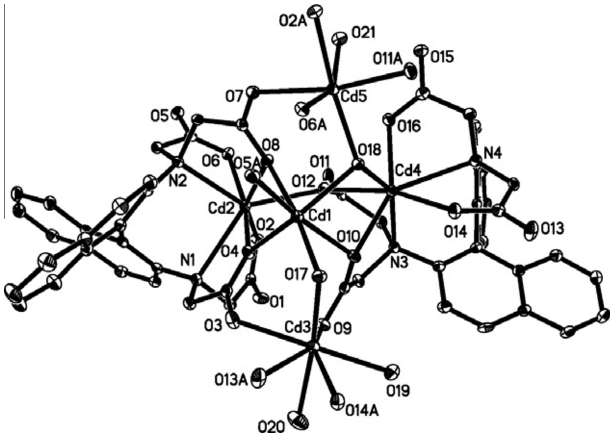

Fig. 5. The coordination environment of Cd(II) in **3** drawn with ellipsoids at the 30% probability level. Hydrogen atoms on carbon atoms are omitted for clarity. Symmetry codes: (A) x, $-y + 3/2$, $z - 1/2$; (B) $-x + 1$, $-y + 2$, $-z + 1$.

3.2.4. *{[$Zn_2(L)(H_2O)_4$]·2.25H_2O}$_n$ (5)*

Complex **5** is a 1D coordination polymer consisting of dinuclear Zn(II) unit [$Zn_2(L^{4-})(H_2O)_4$]. As shown in Fig. 7, two Zn atoms in the dinuclear Zn(II) unit are in different coordination environments. The Zn1 atom is six-coordinated in a distorted octahedral geometry. The best equatorial plane is defined by the O1, O3, O6, N2 atoms from one L^{4-} ligand, and the metal deviated by 0.076 Å toward O7 from the mean plane. The axial positions are occupied by a nitrogen atom (N1) and an oxygen atom (O7) from the same L^{4-} ligand. The Zn2 center is coordinated by four oxygen atoms (O9, O10, O11, O12) from four water molecules and two oxygen atoms ($O4^A$, O8) from two carboxylates of the ligand in a slightly distorted octahedral geometry. The Zn1 and Zn2 atoms are bridged by a carboxylate of the ligand in a μ_2-η^1:η^1 *trans–trans* bridging mode with a Zn1···Zn2 separation of 5.9622(5) Å. The neighboring dinuclear Zn(II) units are linked by a carboxylate group of the ligand in a μ_2-η^1:η^1 *syn-trans* bridging mode with a Zn(II)···Zn(II) distance of 5.1730(5) Å, which results in the formation of a chain along the *b* axis (Fig. 8). A number of hydrogen bonds between coordinated water molecules and guest water molecules (O9–H9B···O13, O11–H11B···$O13^A$, O12–H12B···$O14^E$) and between coordinated water molecules and carboxylato oxygen atom (O9–H9A···$O2^C$, O10–H10A···$O1^C$, O11–H11A···$O3^A$), and so on (Table S2) are observed, which resulted in the formation of 2D network (Fig. S9).

The Zn–N and Zn–O bond lengths in **5** are in the range of 2.243(2)–2.285(2) and 2.0264(19)–2.177(2) Å, respectively, which are comparable to those reported in the literatures [19]. The naphthyl rings of the L^{4-} ligand subtend a dihedral angle of 78.626(53)°.

3.3. *Coordination modes of the H_4L ligand*

The H_4L ligand contains two aminodicarboxylic acid groups with ten coordination atoms. All carboxylate groups of H_4L in the five complexes are found to be completely deprotonated and involved in coordination. Total six coordination modes for the carboxylates in L^{4-} anion were observed in five complexes, that is μ_1-η^1:η^0 monodentate mode, μ_2-η^1:η^1 *syn-anti* bridging mode, μ_2-η^1:η^1 *trans–trans* bridging mode, μ_2-η^1:η^2 chelating-bridging mode, μ_2-η^2:η^0 bidentate bridging mode and μ_3-η^1:η^2 tridentate bridging mode. Both two N atoms of the L^{4-} ligand coordinate to metal ion in chelating mode in all cases. As a whole, the L^{4-} ligand exhibits a variety of coordination fashions due to various coordination modes of carboxylates. Six distinct kinds of coordination fashions for the L^{4-} ligands have been found in complexes **1–5**,

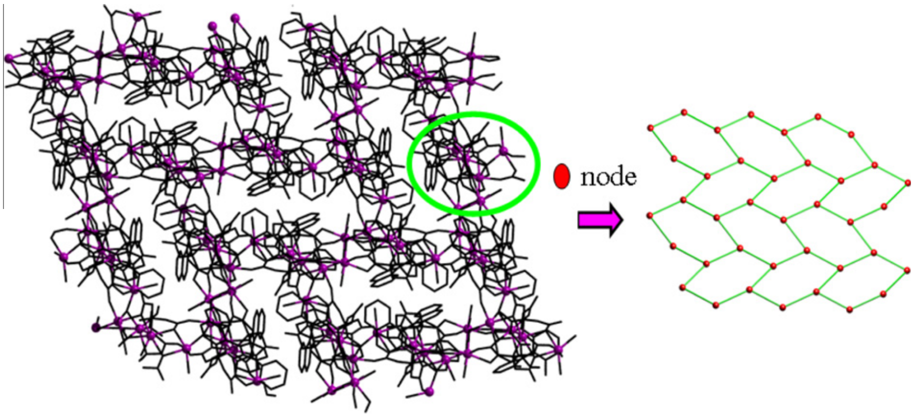

Fig. 6. View of the 2D framework of **3** constructed by pentanuclear cadmium SBUs and simplified (6,3)-connected network with pentanuclear Cd(II) core as a node.

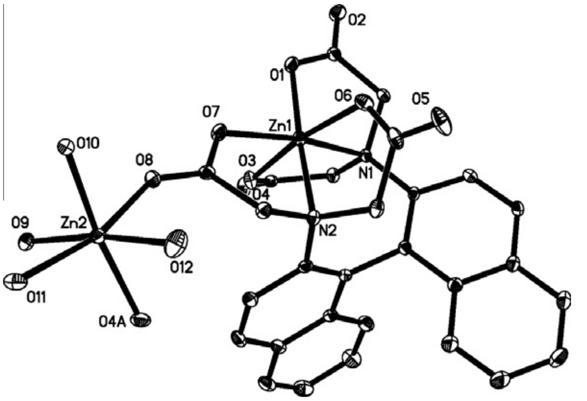

Fig. 7. The dinuclear Zn(II) unit in **5** drawn with ellipsoids at the 30% probability level. Symmetry codes: (A) $-x + 1/2$, $y - 1/2$, z; (B) $-x + 1/2$, $y + 1/2$, z.

as shown in Fig. 9. In complexes **1** and **4**, the L^{4-} anion acts as a heptadentate ligand in a μ_2-bridging fashion with one of the four carboxylate groups in a μ_2-η^1:η^1 *syn-anti* bridging mode, and the other three in μ_1-η^1:η^0 monodentate modes (Fig. 9a). In complex **2**, one L^{4-} anion acts as heptadentate ligand in a μ_2-bridging fashion with one of the four carboxylate groups in a μ_2-η^2:η^1 chelating-bridging mode, and the other three in μ_1-η^1:η^0 monodentate modes (Fig. 9b). The other L^{4-} anion in **2** acts as octadentate ligand in a μ_3-bridging mode with one of the four carboxylate groups in a μ_2-η^1:η^1 *syn-anti* bridging mode, one in a μ_2-η^2:η^1 chelating-bridging mode, and the other two in μ_1-η^1:η^0 monodentate mode (Fig. 9c). In complex **3**, all L^{4-} anions act as nonadentate ligand. One L^{4-} anion coordinates in μ_6-bridging fashion with one of the four carboxylate groups in a μ_1-η^1:η^0 monodentate mode, one in μ_2-η^1:η^2 chelating-bridging mode and the other two in μ_3-η^1:η^2 bridging modes (Fig. 9d). The other L^{4-} anion coordinates in μ_6-bridging fashion with one of the four carboxylate groups in a μ_2-η^2:η^0 bridging mode and the other three in μ_3-η^1:η^2 bridging modes (Fig. 9e). In complex **5**, the L^{4-} anions act as a octadentate ligand in a μ_3-bridging fashion with one of the four carboxylate groups in μ_2-η^1:η^1 *trans–trans* bridging mode, one in μ_2-η^1:η^1 *syn-anti* bridging mode, and the other two in μ_1-η^1:η^0 monodentate mode (Fig. 9f). To the best of our knowledge, four coordination modes (Fig. 9b–e) have never been observed in other metal complexes with aminopolycarboxylic acids ligand. The diversity of the coordination mode of the H_4L ligand may be ascribed to its characteristics with both rigidity and flexibility.

*3.4. Thermal stability of the complexes **1–5***

The thermal behaviors of complexes **1**–**5** were studied by thermogravimetric analysis (TGA) under a N_2 atmosphere (Fig. S10). Compound **1** lost its water molecules in the range of 28–106 °C, the weight loss of 5.0% corresponding to the loss of guest water and one coordinated water molecule per formula unit (calc. 4.7%). The dehydration process is followed by a plateau of stability from 106 to 329 °C, and then the compound decomposes rapidly with a two-step weight loss. The TGA curve of **2** shows a weight loss from room temperature to 198 °C, corresponding to the loss of guest molecules and seven coordinated water molecules (observed 14.8%, calculated 15.6%). The dehydrated solid shows no weight loss until 263 °C. Further heating leads to the final decomposition of the compound **2**. For the TG curve of **3**, the first weight loss of 4.2% in the temperature range of 99–211 °C corresponds to the loss of guest H_2O and three coordinated H_2O molecules (calc.

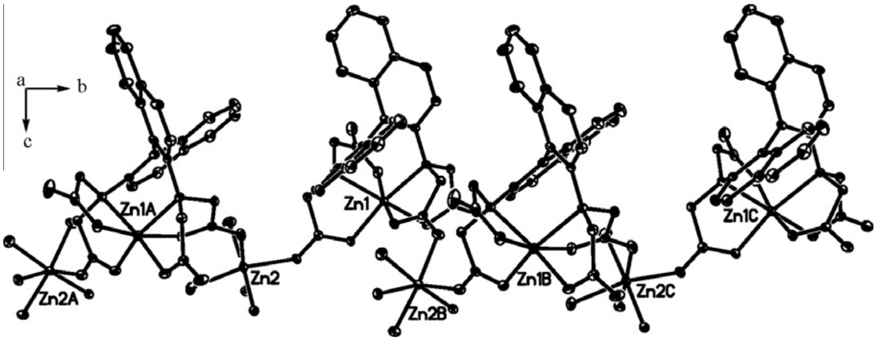

Fig. 8. Zigzag chain structure of **5** along the *b* axis drawn with ellipsoids at the 30% probability level. Symmetry codes: (A) $0.5 - x$, $y - 0.5$, z; (B) $0.5 - x$, $0.5 + y$, z.

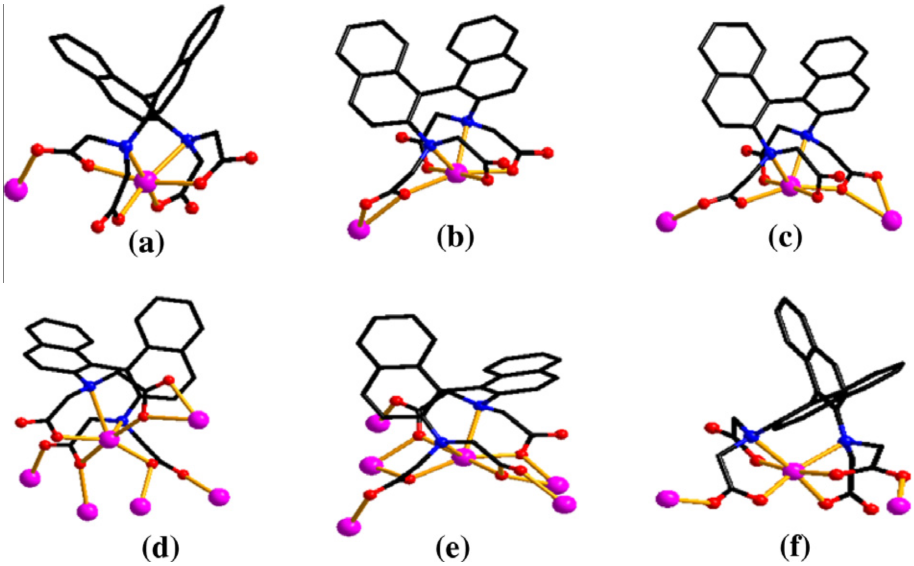

Fig. 9. Coordination modes of L^{4-} in complexes **1**–**5** (a in **1** and **4**, b and c in **2**, d and e in **3**, f in **5**).

4.3%). The dehydrated solid shows no weight loss until 296 °C. Further heating leads to the final collapse of the framework of the compound. For complex **4**, there is a 4.7% weight loss in the temperature range 29–108 °C, which is attributed to the loss of one coordinated and two guest water molecules (calculated 5.1%). The compound began to decompose at above 176 °C with a sharp weight loss. Compound **5** showed a weight loss from room temperature to 203 °C, corresponding to the release of guest and coordinated water molecules (observed weight loss 14.0%, calculated 14.9%). Further heating leads to the final collapse of the skeleton of the compound by the decomposition of the ligand.

3.5. Fluorescence properties

The luminescent properties of complexes with d^{10} metal centers are of great interest for their potential applications in photochemistry, chemical sensors, and electroluminescent display [5e,20]. Therefore, the luminescence properties of **1**–**5**, as well as the free H_4L ligand and phen ligand, were investigated in the solid state at room temperature. As shown in Fig. 10, intense emission bands were observed at 428 nm (λ_{ex} = 363 nm) for the H_4L ligand, 415 and 436 nm (λ_{ex} = 370 nm) for the phen ligand, 500 nm (λ_{ex} = 366 nm) for **1**, 403 nm (λ_{ex} = 356 nm) for **3**, 520 nm (λ_{ex} = 360 nm) for **4**, and 389 nm (λ_{ex} = 346 nm) for **5**, respectively. Since the Cd^{2+} and Zn^{2+} ions are difficult to be oxidized or reduced due to their d^{10} configuration, the emissions of their compounds cannot be attributed to either a metal-to-ligand charge transfer (MLCT) or a ligand-to-metal charge transfer (LMCT) [21]. For complexes **3** and **5**, they can probably be assigned to the intraligand charge transfer due to their resemblance to the emission of the H_4L ligand. The emissive blue-shifts relative to the free H_4L ligand probably originate from the coordination interactions between the metal atom and the ligand [22]. Conversely, for complex **1** and **4**, obvious red shifts compared with the emission spectra of the H_4L ligand and phen ligand have been observed. A possible explanation is that the cooperative association of coordination interactions as well as hydrogen bonds and π–π packing interactions compared with those of other related complexes [19,23]. It is noteworthy that there is no emission observed for complex **2** for excitation wavelengths between 250 and 400 nm, which is a sharp contrast to the complex of **1**. Although more detailed theoretical and spectroscopic studies may be necessary for better understanding of the luminescent mechanism, the strong fluorescence emissions of those complexes make them potentially useful photoactive materials.

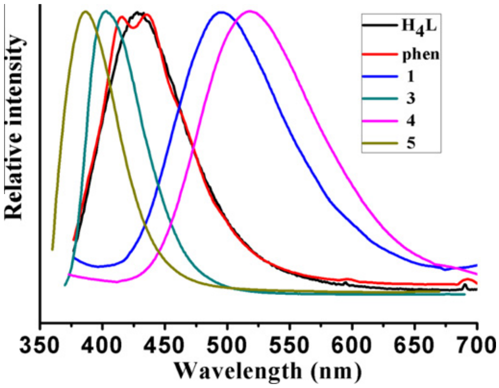

Fig. 10. The emission spectra of H_4L, phen and the complexes **1**, **3**, **4**, **5** in the solid state at room temperature.

4. Conclusion

In summary, five new Zn(II)/Cd(II) complexes with a new polycarboxylic acid ligand, 1,1′-binaphthalenyl-2,2′-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4L), have been synthesized and structurally characterized. The five complexes are found to display various architectures from 0D to 2D, and the ligands in the compounds are found to show a variety of coordination modes. The diversity of the coordination mode of the ligand may be ascribed to its characteristics with both rigidity and flexibility. A wealth of coordination mode for the ligand results in the structural diversity of the complexes, which implies the significance of the rational design and selection of the ligand in the construction of the complexes with novel structure. In the work, two temperature-dependent coordination compounds of **1** and **2** were obtained. These two complexes are found to display total different fluorescence properties, in which complex **1** shows a strong fluorescence emission, while complex **2** shows no signal. Such a phenomenon is of interesting for the study of the structure–property relationship, although more investigations are needed for understanding the essential reason for this difference. Further elaborate studies on the synthesis and properties of the metal complexes with this H_4L ligand are in progress.

Acknowledgements

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Appendix A. Supplementary material

CCDC 874703-874707 contain the supplementary crystallographic data for complexes **1**–**5**, respectively. These data can be obtained free of charge via 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.10.042.

References

[1] (a) D. Sun, Z.H. Wei, C.F. Yang, D.F. Wang, N. Zhang, R.B. Huang, L.S. Zheng, CrystEngComm 13 (2011) 1591;
(b) S. Kitagawa, R. Kitaura, S.I. Noro, Angew. Chem., Int. Ed. 43 (2004) 2334;
(c) M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.

[2] (a) M. Ikeda, Y. Tanaka, T. Hasegawa, Y. Furusho, E. Yashima, J. Am. Chem. Soc. 128 (2006) 6806;
(b) H.C. Chen, H.L. Hu, Z.K. Chan, C.W. Yeh, H.W. Jia, C.P. Wu, J.D. Chen, J.C. Wang, Cryst. Growth Des. 7 (2007) 698;
(c) M. Fujita, K. Ogura, Coord. Chem. Rev. 148 (1996) 249.

[3] (a) S. Chitsaz, D. Fenske, O. Fuhr, Angew. Chem., Int. Ed. 45 (2006) 8055;
(b) E.J. Kang, S.Y. Lee, H. Lee, S.S. Lee, Inorg. Chem. 49 (2010) 7510.

[4] (a) I. Stoll, R. Brodbeck, B. Neumann, H.G. Stammler, J. Mattay, CrystEngComm 11 (2009) 306;
(b) I. Stoll, R. Brockhinke, A. Brockhinke, M. Bottchert, T. Koop, H.G. Stammler, B. Neumann, A. Niemeyer, A. Hutten, J. Mattay, Chem. Mater. 22 (2010) 4749;
(c) J. Fielden, D.L. Long, A.M.Z. Slawin, P. Kögerler, L. Cronin, Inorg. Chem. 46 (2007) 9090;
(d) H. Furukawa, J. Kim, N.W. Ockwig, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 130 (2008) 11650;
(e) R. Custelcean, Chem. Soc. Rev. 39 (2010) 3675;
(f) X.L. Tang, W. Dou, J.A. Zhou, G.L. Zhang, W.S. Liu, L.Z. Yang, Y.L. Shao, CrystEngComm 13 (2011) 2890;
(g) D. Zhao, D.J. Timmons, D.Q. Yuan, H.C. Zhou, Acc. Chem. Res. 44 (2011) 123.

[5] (a) Y. Chen, H.X. Li, D. Liu, L.L. Liu, N.Y. Li, H.Y. Ye, Y. Zhang, J.P. Lang, Cryst. Growth Des. 8 (2008) 3810;
(b) J. Heo, Y.M. Jeon, C.A. Mirkin, J. Am. Chem. Soc. 129 (2007) 7712;
(c) W.H. Zhang, Y.L. Song, Y. Zhang, J.P. Lang, Cryst. Growth Des. 8 (2008) 253;
(d) L.S. Long, CrystEngComm 12 (2010) 1354;
(e) Q. Chu, G.X. Liu, T.A. Okamura, Y.Q. Huang, W.Y. Sun, N. Ueyama, Polyhedron 27 (2008) 812;
(f) C.W. Yeh, T.R. Chen, J.D. Chen, J.C. Wang, Cryst. Growth Des. 9 (2009) 2595;
(g) P.X. Yin, J. Zhang, Zh.J. Li, Y.Y. Qin, J.K. Cheng, L. Zhang, Q.P. Lin, Y.G. Yao, Cryst. Growth Des. 9 (2009) 4884.

[6] (a) I.A. Gural'skiy, D. Escudero, A. Frontera, P.V. Solntsev, E.B. Rusanov, A.N. Chernega, H. Krautscheid, K.V. Domasevitch, Dalton Trans. (2009) 2856;
(b) B.L. Schottel, H.T. Chifotides, M. Shatruk, A. Chouai, L.M. Pérez, J. Bacsa, K.R. Dunbar, J. Am. Chem. Soc. 128 (2006) 5895;
(c) X.L. Wang, C. Qin, E.B. Wang, Cryst. Growth Des. 6 (2006) 439.

[7] (a) J.X. Ma, X.F. Huang, Y. Song, X.Q. Song, W.S. Liu, Inorg. Chem. 48 (2009) 6326;
(b) S. Duval, S. Floquet, C.S. Jégat, J. Marrot, R.N. Biboum, B. Keita, L. Nadjo, M. Haouas, F. Taulelle, E. Cadot, J. Am. Chem. Soc. 132 (2010) 2069;
(c) C. Gunanathan, Y.D. Posner, D. Milstein, Cryst. Growth Des. 10 (2010) 4235.

[8] (a) M.A. Camargo, A. Neves, B. Szpoganicz, A.J. Bortoluzzi, F.L. Fischer, H. Terenzi, E.E. Castellano, Inorg. Chem. 49 (2010) 3057;
(b) Z.G. Gu, S.C. Sevov, Inorg. Chem. 48 (2009) 8066.

[9] (a) B.Q. Ma, S. Gao, O. Bai, H.L. Sun, G.X. Xu, Dalton Trans. (2000) 1003;
(b) A. Brausam, J. Maigut, R. Meier, P.A. Szilágyi, H.J. Buschmann, W. Massa, Z. Homonnay, R.V. Eldik, Inorg. Chem. 48 (2009) 7864;
(c) M. Murugesu, C.E. Anson, A.K. Powell, Chem. Commun. (2002) 1054;
(d) M. Murugesu, P. King, R. Clérac, C.E. Anson, A.K. Powell, Chem. Commun. (2004) 740;
(e) Y.J. Zhang, B.Q. Ma, S. Gao, J.R. Li, Q.D. Liu, G.H. Wen, X.X. Zhang, Dalton Trans. (2000) 2249;
(f) L.S. Cai, Y. Han, H. Mahmoud, W.G. Xie, B.M. Segal, Inorg. Chem. Commun. 1 (1998) 71;
(g) S. Zhan, S.H. Feng, Y. Sun, J. Hua, Inorg. Chem. 40 (2001) 5312;
(h) M. Murugesu, R. Clérac, C.E. Anson, A.K. Powell, J. Phys. Chem. Solids 65 (2004) 667;
(i) O. Sengupta, B. Gole, P.S. Mukherjee, Inorg. Chim. Acta 363 (2010) 3093.

[10] (a) Q.L. Zhu, T.L. Sheng, R.B. Fu, S.M. Hu, J.S. Chen, S.C. Xiang, C.J. Shen, X.T. Wu, Cryst. Growth Des. 9 (2009) 5128;
(b) J.Y. Xu, B. Zhao, H.D. Bian, W. Gu, S.P. Yan, P. Cheng, D.Z. Liao, P.W. Shen, Cryst. Growth Des. 7 (2007) 1044;
(c) M. Stylianou, C. Drouza, Z. Viskadourakis, J. Giapintzakis, A.D. Keramidas, Dalton Trans. (2008) 6188;
(d) P. Thuéry, Cryst. Growth Des. 11 (2011) 347;
(e) C.A. González, M. Hernández-Padilla, S. Dominguez, A. Mederos, F. Brito, J.M. Arrieta, Polyhedron 16 (1997) 2925;
(f) J. Sanchiz, S. Domínguez, A. Mederos, F. Brito, J.M. Arrieta, Inorg. Chem. 36 (1997) 4108;
(g) N. Nakasuka, S. Azuma, M. Tanaka, Acta Crystallogr., Sect. C. 42 (1986) 1736;
(h) J. Sanchiz, P. Esparza, S. Domínguez, A. Mederos, D. Saysell, A. Sánchez, R. Ruano, J.M. Arrieta, Dalton Trans. (2001) 1559;
(i) A. Mederos, P. Gili, S. Domínguez, A. Benitez, M.S. Palacios, M. Hernández-Padilla, P. Martin-Zarza, M.L. Rodríguez, C.R. Pérez, F.J. Lahoz, L.A. Oro, F. Brito, J.M. Arrieta, M. Vlassi, G. Germain, Dalton Trans. (1990) 1477.

[11] (a) G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997; (b) G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[12] Y.Q. Xu, D.Q. Yuan, B.L. Wu, L. Han, M.Y. Wu, F.L. Jiang, M.C. Hong, Cryst. Growth Des. 6 (2006) 1168.

[13] S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong, Inorg. Chem. 43 (2004) 830.

[14] X.Y. Lu, J.W. Ye, W. Li, W. Gong, L.J. Yang, Y. Lin, G.L. Ning, CrystEngComm 14 (2012) 1337.

[15] (a) P.D. Frischmann, G.A. Facey, P.Y. Ghi, A.J. Gallant, D.L. Bryce, F. Lelj, M.J. MacLachlan, J. Am. Chem. Soc. 132 (2010) 3893;
(b) X.L. Wang, C. Qin, Y.Q. Lan, K.Z. Shao, Z.M. Su, E.B. Wang, Chem. Commun. (2009) 410;
(c) D.R. Xiao, R. Yuan, Y.Q. Chai, E.B. Wang, Eur. J. Inorg. Chem. (2008) 2610;
(d) Q.R. Fang, G.S. Zhu, Z. Jin, M. Xue, X. Wei, D.J. Wang, S.L. Qiu, Angew. Chem., Int. Ed. 45 (2006) 6126.

[16] (a) H. Chun, D. Kim, D.N. Dybtsev, K. Kim, Angew. Chem., Int. Ed. 43 (2004) 971;
(b) X.L. Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu, Angew. Chem., Int. Ed. 43 (2004) 5036;
(c) J. Tao, X. Yin, Z.B. Wei, R.B. Huang, L.S. Zheng, Eur. J. Inorg. Chem. (2004) 125.

[17] D.C. Zhong, M. Meng, J. Zhu, G.Y. Yang, T.B. Lu, Chem. Commun. 46 (2010) 4354.

[18] (a) K. Wieghardt, U. Bossek, P. Chanduri, W. Herrmann, B.C. Menke, J. Weiss, Inorg. Chem. 21 (1982) 4308;
(b) M.J. Van der Merwe, J.C.A. Boeyens, R.D. Hancock, Inorg. Chem. 24 (1985) 1208;
(c) A. Bevilacqua, R.I. Gelb, W.B. Hebard, L.J. Zompa, Inorg. Chem. 26 (1987) 2699;
(d) W.P. Cacheris, S.K. Nickle, A.D. Sherry, Inorg. Chem. 26 (1987) 958.

[19] X.X. Zhou, H.C. Fang, Y.Y. Ge, Z.Y. Zhou, Z.G. Gu, X. Gong, G. Zhao, Q.G. Zhan, R.H. Zeng, Y.P. Cai, Cryst. Growth Des. 10 (2010) 4014.

[20] H.Y. Bai, J.F. Ma, J. Yang, L.P. Zhang, J.C. Ma, Y.Y. Liu, Cryst. Growth Des. 10 (2010) 1946.

[21] L.Y. Xin, G.Z. Liu, X.L. Li, L.Y. Wang, Cryst. Growth Des. 12 (2012) 147.

[22] L.L. Wen, Y.Z. Li, Z.D. Lu, J.G. Lin, C.Y. Duan, Q.J. Meng, Cryst. Growth Des. 6 (2006) 530.

[23] L.N. Li, J.H. Luo, S.Y. Wang, Z.H. Sun, T.L. Chen, M.C. Hong, Cryst. Growth Des. 11 (2011) 3744.