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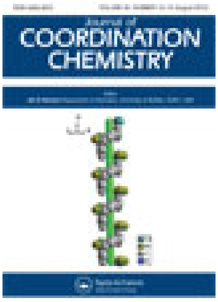

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Syntheses, structures, and properties of four coordination compounds constructed from asymmetric semi-rigid V-shaped multicarboxylate ligand

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Syntheses, structures, and properties of four coordination compounds constructed from asymmetric semi-rigid V-shaped multicarboxylate ligand

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Four new compounds, $[Mn(HL)(phen)_2(H_2O)]$ (**1**), $[Ni(HL)(phen)_2(H_2O)]$ (**2**), $[Zn(HL)(4,4'\text{-bipy})_{1.5}(H_2O)]_n \cdot 2nH_2O$ (**3**) and $[Zn_2(HL)_2(H_2O)_6]$ (**4**), have been synthesized from an asymmetric semi-rigid V-shaped multicarboxylate 4-(4-carboxy-phenoxy)-phthalic acid (H_3L) with 1,10-phenanthroline (phen), or 4,4′-bipyridine (4,4′-bipy) as auxiliary ligands. Single-crystal X-ray diffraction analysis reveals that **1**, **2** and **4** have 0-D structures with 3-D supramolecular frameworks formed by intermolecular hydrogen bonds. Compound **3** shows a 1-D infinite ribbon bridged by 4,4′-bipy, which further forms a 3-D supramolecular architecture by π–π stacking interactions and hydrogen bonds. Thermal stabilities of **1**–**4** and luminescence properties of **3** and **4** have also been investigated.

Keywords: 4-(4-Carboxy-phenoxy)-phthalic acid; Structural analysis; Luminescence

1. Introduction

Design and construction of metal-involved supramolecular architectures have attracted interest, owing to their intriguing structures and applications as functional materials in porosity, catalysis, magnetism, luminescence, non-linear optics and microelectronics [1–10]. To build the supramolecular frameworks, judicious selection of suitable multidentate ligands is a key factor of a successful approach [11–13]. Multi-carboxylate ligands have been employed for preparation of complexes with diverse structures, having versatile coordination and potential as hydrogen bond acceptors and donors in formation of 1-D, 2-D or 3-D frameworks [14, 15]. 4-(4-Carboxy-phenoxy)-phthalic acid (H_3L) is an asymmetric semi-rigid V-shaped multicarboxylate with three carboxylic groups attached at 3-, 4-, and 4′-positions, and the two benzene rings are bridged by an

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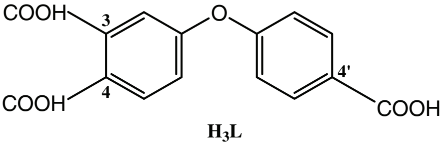

Scheme 1. The molecular structure of H_3L.

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oxygen, resulting in free rotation of the molecule (scheme 1). H_3L can coordinate with metal ions in different ways and extend the structure to higher dimensionality through hydrogen bonds and π–π stacking interactions. Introduction of other N-containing secondary ligands may generate more complicated and interesting compounds with applicable properties. Compared with other V-shaped ligands containing benzimidazole, such as *bis*(*N*-methylbenzimidazol-2-ylmethyl) benzylamine, 2,6-*bis*(2-benzimidazolyl)pyridine, and 1,3-*bis*(1-ethylbenzimidazol-2-yl)-2-thiapropane, as well as 3-(pyridin-3′-yl)-5-(pyridin-2″-yl)-1,2,4-triazole, already used in construction of diverse coordination geometries with transition metal cations [16–19], H_3L is a disparate O-donor V-shaped multicarboxylate worthy of further investigation.

We synthesized supramolecular compounds of H_3L with 1,10-phenanthroline (phen) and 4,4′-bipyridine (4,4′-bipy) as auxiliary ligands, obtaining two mononuclear compounds (**1** and **2**), one binuclear compound (**4**) and one 1-D compound (**3**) under hydrothermal conditions, $[Mn(HL)(phen)_2(H_2O)]$ (**1**), $[Ni(HL)(phen)_2(H_2O)]$ (**2**), $[Zn(HL)(4,4'\text{-bipy})_{1.5}(H_2O)]_n \cdot 2nH_2O$ (**3**) and $[Zn_2(HL)_2(H_2O)_6]$ (**4**). All these compounds possess a 3-D supramolecular structure *via* hydrogen bonds or π–π stacking interactions [20, 21]. Herein, we report their syntheses, crystal structures, thermal stabilities, and the luminescence of **3** and **4**.

2. Experimental

2.1. *Reagents and physical measurements*

All reagents and solvents employed were commercially available and used as received. C, H, and N contents were determined by a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany). FT-IR spectra (in KBr pellets) were recorded from 4000–400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10°C min^{-1} from 30 to 900°C. Luminescence spectra for the solid samples were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of 1–4*

2.2.1. Synthesis of $[Mn(HL)(phen)_2(H_2O)]$ (1). A mixture of $MnCl_2 \cdot 4H_2O$ (0.02 mmol, 0.0042 g), phen (0.02 mmol, 0.0042 g), H_3L (0.01 mmol, 0.0030 g), and H_2O (3 mL) was placed in a 25 mL Teflon-lined stainless steel reactor and heated to 130°C for 120 h, then cooled to room temperature at 5°C h^{-1}. Slightly yellow block-shaped crystals suitable for X-ray diffraction were obtained by filtration in 51% yield (based on H_3L ligand). Anal. Calcd for **1** ($C_{39}H_{26}MnN_4O_8$): C, 63.85; H, 3.57; N, 7.64%. Found: C, 63.78; H, 3.62; N, 7.69%. IR (KBr, cm^{-1}): 3425(s), 1593(s), 1423(s), 1228(s), 850(m), 722(m).

2.2.2. Synthesis of [Ni(HL)(phen)$_2$(H$_2$O)] (2). Preparation of **2** was similar to **1** except that $Ni(OAc)_2 \cdot 4H_2O$ (0.02 mmol, 0.0050 g) was used instead of $MnCl_2 \cdot 4H_2O$. Reactants were heated to 150°C for 72 h in a 25 mL Teflon-lined stainless steel reactor, then cooled to room temperature at 2°C h^{-1}. Green block crystals of **2** were collected in 46% yield. Anal. Calcd for **2** ($C_{39}H_{26}Ni\,N_4O_8$): C, 63.53; H, 3.55; N, 7.60%. Found: C, 63.49; H, 3.61; N, 7.65%. IR (KBr, cm^{-1}): 3055(s), 1589(m), 1515(m), 1375(s), 1257(m), 1221(m), 1150(m), 849(m), 725(m).

2.2.3. Synthesis of [Zn(HL)(4,4′-bipy)$_{1.5}$(H$_2$O)]$_n$ • 2nH$_2$O (3). Compound **3** was synthesized in an analogous procedure to **1** using $Zn(OAc)_2 \cdot 2H_2O$ (0.02 mmol, 0.0042 g) and 4,4′-bipy (0.02 mmol, 0.0041 g) instead of $MnCl_2 \cdot 4H_2O$ and phen, giving colorless block X-ray-quality crystals in 60% yield. Anal. Calcd for **3** ($C_{30}H_{26}ZnN_3O_{10}$): C, 55.10; H, 4.01; N, 6.43%. Found: C, 55.01; H, 3.89; N, 6.33%. IR (KBr, cm^{-1}): 3419(s), 1612(s), 1490(m), 1365(s), 1221(s), 822(m).

2.2.4. Synthesis of [Zn$_2$(HL)$_2$(H$_2$O)$_6$] (4). $ZnCl_2$ (0.02 mmol, 0.0027 g) and H_3L (0.02 mmol, 0.0058 g) were dissolved in distilled water (4 mL), then placed in a 25 mL Teflon-lined stainless steel container, and heated to 150°C for 72 h. Upon cooling to room temperature, colorless crystals were collected in 50% yield (based on H_3L ligand). Anal. Calcd for **4** ($C_{30}H_{28}Zn_2O_{20}$): C, 42.93; H, 3.36%. Found: C, 43.08; H, 3.31%. IR (KBr, cm^{-1}): 3417(s), 1614(m), 1536(m), 1392(m), 1227(m), 1042(m), 773(m).

2.3. *Crystallographic data collections and structure determinations*

For **1**–**4**, single-crystal X-ray diffraction analyses were carried out on a Bruker SMART 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collections. Crystallographic data were collected using Mo-Kα radiation at $\lambda = 0.71073$ Å at 296(2) K, and the data reductions were performed using the Bruker SAINT software (SMART and SAINT programs) (Siemens AXS, 1998). Empirical absorption corrections were applied using SADABS (Sheldrick, 2003). The structures were solved by direct methods and refined with full-matrix least-squares on F^2 with SHELXL-97 [22, 23]. All non-hydrogen atoms were located applying difference Fourier synthesis and hydrogen atoms were generated geometrically. Crystal data collections and refinement parameters are summarized in table 1; selected bond lengths and angles are listed in Supplementary material.

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Table 1. Crystal data and structure refinement details for **1–4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{39}H_{26}Mn\ N_4O_8$	$C_{39}H_{26}Ni\ N_4O_8$	$C_{30}H_{26}ZnN_3O_{10}$	$C_{30}H_{28}Zn_2O_{20}$
Formula weight	733.58	737.33	653.93	839.30
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)				
a	7.5206(9)	7.2970(10)	7.3572(10)	14.3917(18)
b	14.9202(17)	15.130(2)	12.2303(16)	9.5647(13)
c	15.7983(19)	16.172(2)	16.627(2)	11.3578(14)
α	68.911(2)	67.599(2)	91.147(2)	90
β	79.382(2)	79.185(2)	101.314(3)	92.642(2)
γ	85.011(2)	83.975(2)	101.842(2)	90
Volume (Å^3), Z	1625.2(3), 2	1620.3(4), 2	1433.0(3), 2	1561.8(3), 2
Calculated density (g cm^{-3})	1.499	1.511	1.515	1.785
Absorption coefficient (mm^{-1})	0.470	0.663	0.922	1.630
F(000)	754	760	674	856
Crystal size (mm^3)	0.36 × 0.25 × 0.16	0.38 × 0.25 × 0.14	0.37 × 0.26 × 0.15	0.33 × 0.28 × 0.17
θ range for data collection (°)	1.40–25.10	1.46–25.10	1.25–25.10	1.42–25.10
Limiting indices	$-7 \leq h \leq 8$, $-17 \leq k \leq 15$, $-18 \leq l \leq 18$	$-8 \leq h \leq 8$, $-18 \leq k \leq 17$, $-19 \leq l \leq 19$	$-8 \leq h \leq 8$, $-14 \leq k \leq 14$, $-19 \leq l \leq 12$	$-16 \leq h \leq 17$, $-8 \leq k \leq 11$, $-12 \leq l \leq 13$
Reflections collected/unique	8298	8296	7342	7700
Independent reflections	5779 [R(int) = 0.0167]	5776 [R(int) = 0.0191]	5114 [R(int) = 0.0353]	2791 [R(int) = 0.0560]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Max. and min. transmission	0.928 and 0.868	0.911 and 0.820	0.871 and 0.750	0.758 and 0.590
Goodness-of-fit on F^2	1.035	0.812	0.960	0.923
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0375$, $wR_2 = 0.0932$	$R_1 = 0.0392$, $wR_2 = 0.1138$	$R_1 = 0.0586$, $wR_2 = 0.1455$	$R_1 = 0.0439$, $wR_2 = 0.1063$
R indices (all data)	$R_1 = 0.0461$, $wR_2 = 0.1055$	$R_1 = 0.0514$, $wR_2 = 0.1278$	$R_1 = 0.0890$, $wR_2 = 0.1840$	$R_1 = 0.0628$, $wR_2 = 0.1193$

3. Results and discussion

3.1. *Descriptions of the structures*

3.1.1. [Mn(HL)(phen)$_2$(H$_2$O)] (1) and [Ni(HL)(phen)$_2$(H$_2$O)] (2). Molecular structures of isostructural **1** and **2** are elucidated by taking **1** as a typical representative. Compound **1** has a mononuclear motif, crystallizing in the triclinic system with $P\bar{1}$ space group and containing one Mn(II), one HL, two phen, and one coordinated water. As shown in figure 1, Mn(II) is six-coordinate by four nitrogens (N1, N2, N3, and N4) of two chelated phen, one oxygen (O1) of HL, and one oxygen (O3) of coordinated water, resulting in a distorted octahedral coordination geometry. Mn–O bond lengths are 2.1348(17) and 2.1683(19) Å, and the Mn–N bond lengths are 2.240(2)–2.275(2) Å. These data are comparable with those of compounds containing O–Mn–N segments [24]. The dihedral angles between the planes of the two phen rings coordinated with the Mn(II)/Ni(II) ions in **1** and **2** are 84.629(35)° and 83.167(37)°, respectively. And the partly deprotonated carboxylic groups of HL in **1** and **2** are monodentate with only one oxygen (O1) coordinating with Mn(II)/Ni(II) directly; dihedral angles of the two aromatic rings connected by the ether oxygen in **1** and **2** are 78.816(73)° and 83.716(84)°, respectively.

By intermolecular hydrogen bonds (O–H···O and C–H···O) (table 2) of the carboxylic oxygen atoms between the coordinated water and carbons of HL and phen,

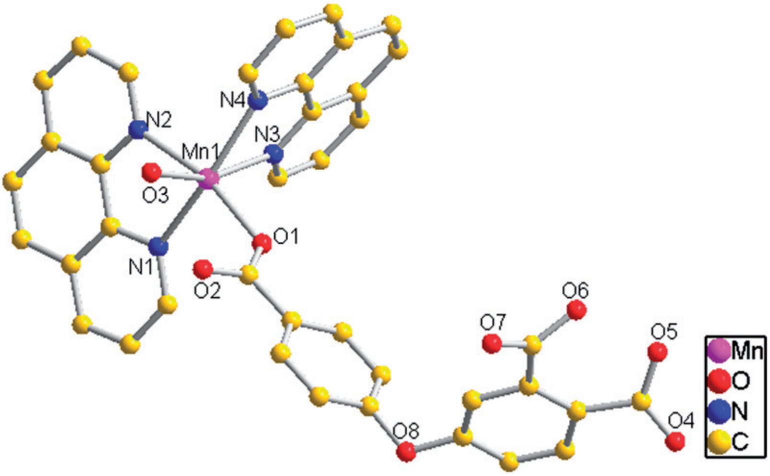

Figure 1. Coordination environment of Mn(II) in **1**. Hydrogen atoms are omitted for clarity.

Table 2. Hydrogen bonding geometry for **1** (in Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(3)–H(3B)···O(4)	0.79(4)	1.91(4)	2.693(3)	168(4)
C(28)–H(28)···O(7)	0.92(2)	2.43(2)	3.211(3)	143(2)
C(82)–H(82)···O(4)	0.95(3)	2.43(3)	3.311 (4)	155(2)
C(84)–H(84)···O(2)	0.96(4)	2.53(3)	3.444(4)	160(3)
C(97)–H(97)···O(6)	0.93	2.49	3.417(5)	171

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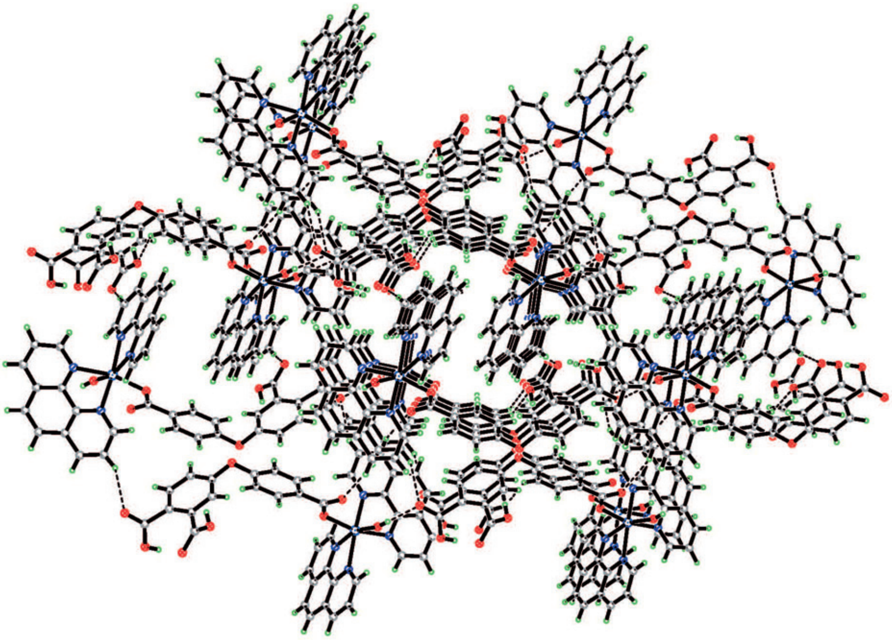

Figure 2. Perspective view of the 3-D supramolecular framework formed by hydrogen bonds along the *a*-axis.

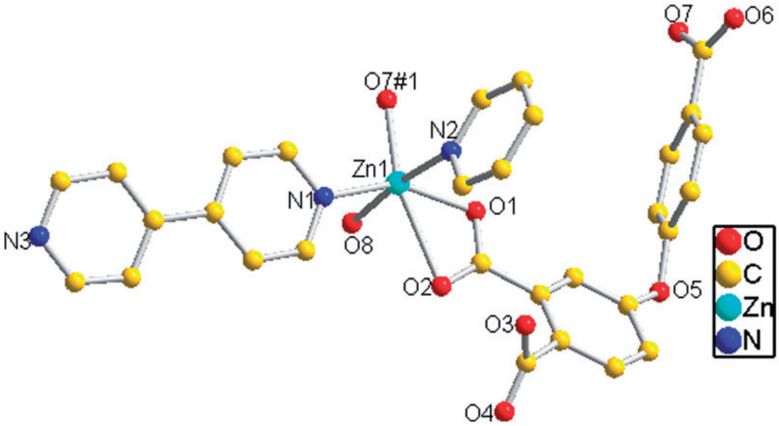

Figure 3. Coordination environment of Zn(II) in **3**. Hydrogen atoms and free waters are omitted for clarity. Symmetry codes: #1 $-x, -y, -z$; #2 $-x+2, -y, -z$.

the contiguous molecules are further integrated into a 3-D supramolecular framework (figure 2).

3.1.2. $[Zn(HL)(4,4'\text{-bipy})_{1.5}(H_2O)]_n \cdot 2nH_2O$ (3). Compound **3** crystallizes in the space group $P\bar{1}$ and the asymmetric unit contains one Zn(II), one HL, one and half 4,4′-bipy, one coordinated water, and two solvent water molecules. As shown in figure 3, Zn(II) is six-coordinate with a distorted octahedral geometry formed by two nitrogen atoms (N1 and N2) of one and half 4,4′-bipy, two oxygen atoms (O1 and O2) from one bidentate chelating carboxylate of HL, one oxygen (O7#1) from monodentate coordinated carboxylate of HL, and one oxygen (O8) of coordinated water. Zn–N bond lengths are 2.069(4) and 2.156(4) Å, and Zn–O bonds are 1.995(4)–2.521(4) Å. These bond distances correspond with those reported for compounds containing Zn–N and Zn–O bonds [25]. Dihedral angle of the two aromatic rings connected by ether O5 of HL ligand is 82.659(17)°.

As can be seen in figure 4(a), dimers of **3** are linked by 4,4′-bipy, leading to a 1-D infinite ribbon, further packed into a 2-D structure *via* intermolecular π–π stacking interactions between 4,4′-bipy ligands of adjacent chains (figure 4b). The centroid-to-centroid distance between two parallel pyridine rings of 4,4′-bipy in the neighboring chains is 3.6895(3) Å and the dihedral angle between the planes of two rings is 0.478(106)°. The most significant feature of **3** is that adjacent chains recognize each other to generate a stable 3-D supramolecular architecture *via* several kinds of hydrogen bonding interactions (O–H···O, O–H···N, and C–H···O) (table 3), as shown in figure 4(c).

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3.1.3. [$Zn_2(HL)_2(H_2O)_6$] (4). Compound **4** belongs to the $P2_1/c$ space group, which exists as a dimer consisting of two Zn(II) ions, two HL, and six coordinated waters. As seen in figure 5, the overall molecule is a centrosymmetric binuclear structure, each Zn(II) displaying a distorted octahedral geometry coordinated by six oxygen atoms, in which three come from two monodentate carboxylates of HL, and the others are from coordinated water. The Zn–O bond lengths are 2.051(3)–2.162(3) Å, consistent with those reported for compounds containing Zn–O bonds [26]. Dihedral angle of the two aromatic rings connected by ether O8 of HL is 70.069(13)°. In the dimer, two Zn(II) ions are further connected by two carboxylic groups of HL forming an octagon.

Significant hydrogen bonding interactions (O–H···O and C–H···O) (table 4) of the carboxylate oxygen atoms between the coordinated water as well as carbon are also observed in **4**, by which the neighboring molecules are further packed into a 3-D supramolecular network (figure 6).

3.2. *Demonstrations of the final products*

Structures of coordination compounds depend on various factors. For **1** and **2**, from steric hindrance, the aryl carboxylic group attached at 4′-position of H_3L coordinates with Mn(II)/Ni(II). Ether of H_3L is an electron donating group that makes less electron density of carbon located in the meta-position of benzene according to the conjugative effect. Consequently, the aryl carboxylic group attached at 3-position is more easily deprotonated for decrease of its pK_a, whereas, this effect has an opposite influence on carbon located para of benzene ring that makes the pK_a of aryl carboxylic group attached at 4-position increase and leaves the undissociated proton in **1** and **2**. This phenomenon is reflected in **3** where aryl carboxylic groups attached at 4′- and 3-positions coordinate with Zn(II) compared with carboxylic group attached at 4-position. Compound **4** was obtained without auxiliary ligands, displaying a binuclear motif that contains two Zn(II) ions in the structural unit; to satisfy their high

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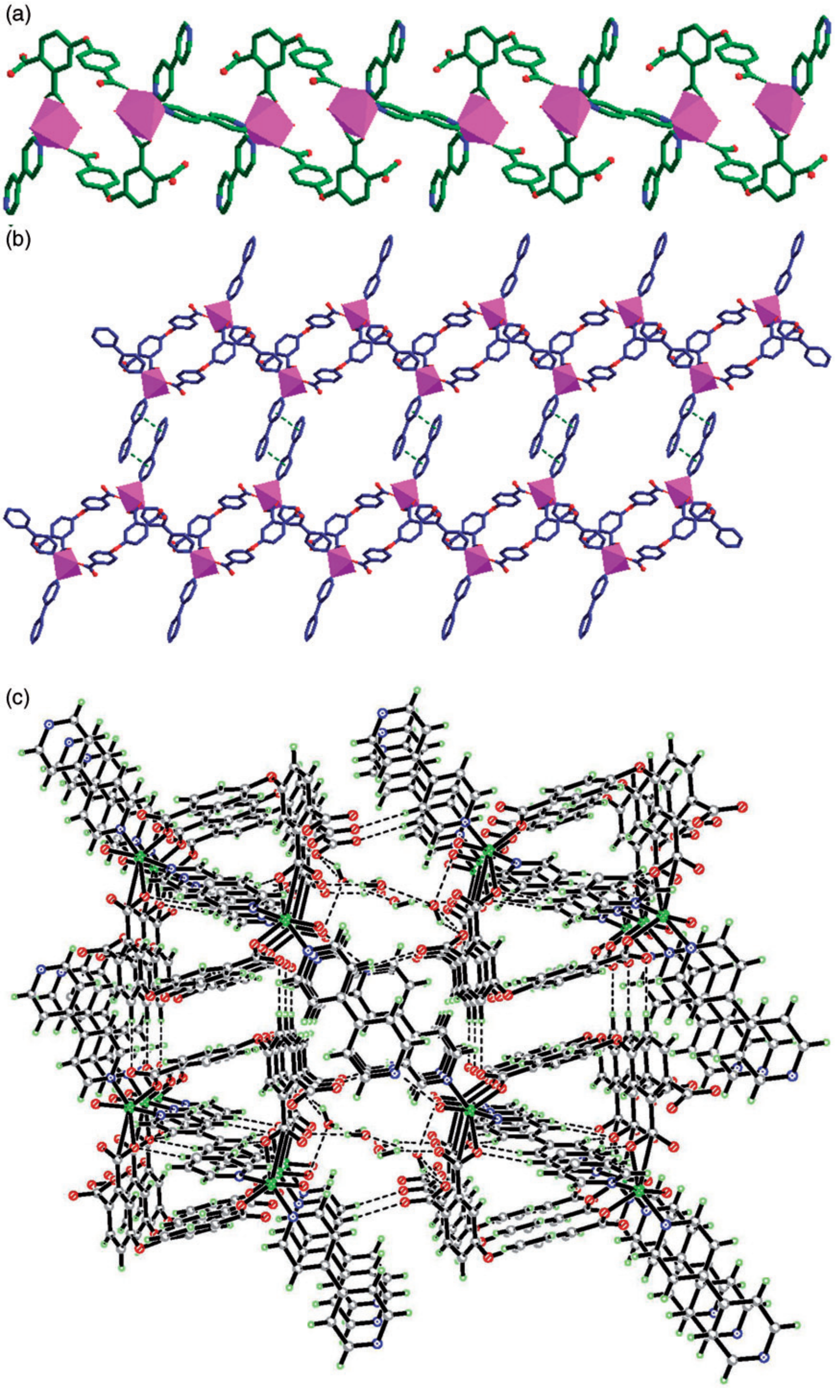

Figure 4. (a) 1-D infinite ribbon of **3** along the *c*-axis. Hydrogen atoms and water molecules are omitted for clarity. (b) View of the 2-D layer extended in the *ab* plane formed by π–π stacking interactions. (c) 3-D supramolecular architecture of **3** viewed along the *a*-axis.

Table 3. Hydrogen bonding geometry for **3** (in Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(3)–H(3)···O(10)	0.83(6)	1.79(5)	2.622(8)	178(6)
O(8)–H(8A)···N(3)	0.75(7)	2.06(6)	2.790(7)	168(6)
O(9)–H(9A)···O(4)	0.85	2.35	3.130(9)	153
O(9)–H(9B)···O(2)	0.85	2.06	2.841(6)	152
O(10)–H(10A)···O(9)	0.77(8)	2.00(8)	2.769(8)	177(11)
O(10)–H(10B)···O(8)	0.88(8)	1.99(9)	2.834(6)	158(8)
C(2)–H(2)···O(4)	0.93	2.48	3.342(7)	154
C(14)–H(14)···O(6)	0.93	2.45	3.370(6)	173
C(27)–H(27)···O(1)	0.93	2.39	3.299(7)	166
C(29)–H(29)···O(1)	0.93	2.49	3.407(6)	169

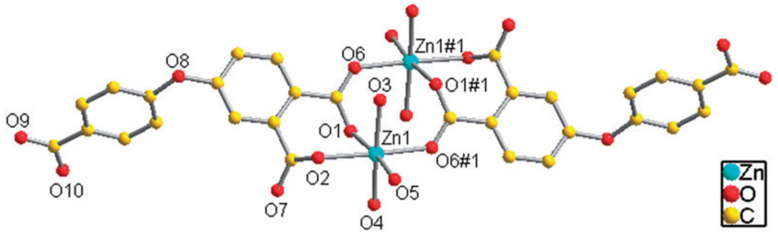

Figure 5. Coordination environment of Zn(II) in **4**. Hydrogen atoms are omitted for clarity. Symmetry codes: #1 $-x$, $-y+1$, $-z+1$.

Table 4. Hydrogen bonding geometry for **4** (in Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(3)–H(1)···O(7)	0.76(6)	2.02(6)	2.779(4)	170(7)
O(5)–H(3)···O(9)	0.82	1.93	2.747(5)	171
O(5)–H(4)···O(1)	0.81(6)	2.09(6)	2.849(4)	156(6)
O(5)–H(4)···O(4)	0.81(6)	2.60(6)	3.158(4)	128(5)
O(4)–H(7)···O(2)	0.76(6)	2.12(6)	2.835(4)	157(6)
O(4)–H(9)···O(9)	0.82	2.16	2.864(5)	144
O(4)–H(9)···O(3)	0.82	2.52	2.911(4)	118
O(10)–H(15)···O(7)	0.82	1.76	2.579(4)	175
C(14)–H(14)···O(8)	0.93	2.48	3.137(6)	128

coordination numbers as well as stability of the final product, the aryl carboxylic groups attached at 3- and 4-positions of H_3L coordinate with the two Zn(II) ions.

3.3. *IR spectroscopy*

In the IR spectrum (Supplementary material) of the asymmetric semi-rigid V-shaped ligand (curve a), the absorption at 1675 cm^{-1} is ascribed to asymmetric stretching

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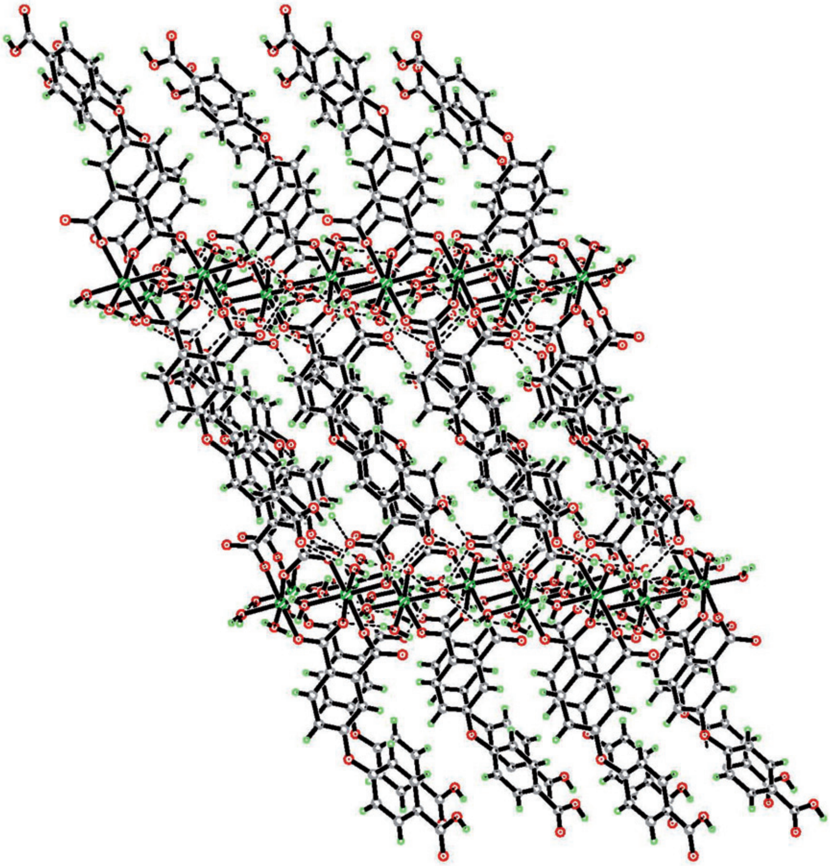

Figure 6. Packing of **4** along the *b*-axis.

vibration of uncoordinated carboxylic groups, which red-shifts to 1593, 1589, 1612, and 1614 cm^{-1} in spectra of **1**–**4** (curves b–e), respectively. This is attributed to formation of M(II)–O (M = Mn, Ni, and Zn) coordination bond of carboxylic oxygen in the ligand.

3.4. *Thermal analysis*

TGA analyses of **1**–**4** were studied from 30 to 900°C under nitrogen (Supplementary material). Compound **1** shows one distinct thermal decomposition stage from 51 to 83°C corresponding to the weight loss of coordinated H_2O (lost weight is 2.34%, calculated value is 2.46%). The skeleton of **1** begins to collapse at 205°C. For **2**, the TGA curve shows two main weight loss steps. The first at 210 and completed at 285°C represents the release of coordinated H_2O (lost weight is 2.37%, calculated value is 2.44%). The second step loses two phen ligands between 285°C and 800°C (lost weight is 54.68%, calculated value is 53.77%). TGA curve of **3** also exhibits two main weight losses. The first at 55°C and completed at 125°C corresponds to release of three H_2O (lost weight is 2.83%, calculated value is 2.75%). The second step loses one 4,4′-bipy

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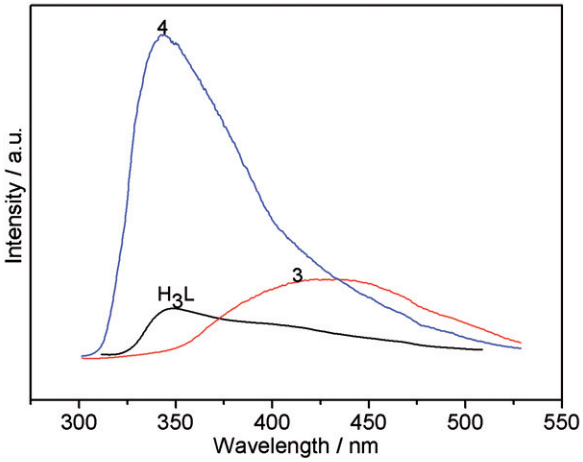

Figure 7. Solid-state emission spectra of H_3L, **3** and **4** recorded at room temperature.

and HL ligands between 125°C and 510°C (lost weight is 75.31%, calculated value is 74.92%). For **4**, the TGA curve displays one main weight loss from 40°C to 232°C, owing to release of six H_2O (lost weight is 12.88%, calculated value is 12.99%). The residual composition of **4** begins to decompose at 232°C.

3.5. *Luminescence properties*

Taking into account the excellent luminescent properties of d^{10} metal complexes, luminescence spectra of free H_3L, **3** and **4** in the solid state at room temperature were investigated. Free H_3L exhibits one very weak emission band at *ca* 349 nm upon excitation at 280 nm. **3** and **4** exhibit emission peaks at *ca* 428 and 344 nm at the same excitation condition, respectively, (figure 7). In comparison with free ligand, **3** shows a red-shift emission of *ca* 79 nm, which could be assigned to ligand-to-metal-charge-transfer, probably due to the increase of conjugated system from cooperation of HL and 4,4′-bipy [27–30]. Compound **4** exhibits a strong emission peak at *ca* 344 nm, very close to the emission band of free ligand H_3L (344 nm), suggesting that this may be ascribed to the intraligand transition [31–33]. By comparing the emission spectra of **4** and ligand, we conclude that the enhancement of luminescence in **4** may be attributed to rigidity, which favors energy transfer and reduces the loss of energy by radiationless decay [34–36]. Therefore, **4** may be an excellent candidate for luminescent materials.

4. Conclusions

Four mono- or binuclear coordination compounds were synthesized under hydrothermal conditions using an unusual V-shaped multicarboxylate ligand 4-(4-carboxy-phenoxy)-phthalic acid (H_3L) in the presence of phen and 4,4′-bipy. In these compounds, the carboxylate of partly deprotonated HL are hydrogen bond donors/acceptors with water or carbons to generate 3-D supramolecular architectures. Dihedral angles of the two aromatic rings connected by the ether oxygen of HL in **1**–**4** are 78.816(73)°, 83.716(84)°, 82.659(17)°, and 70.069(13)°, respectively. Further systematic work focused on the structures and properties of a series of coordination compounds constructed by H_3L is in progress.

Supplementary material

CCDC 868906–868909 for **1**–**4** contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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