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Synthesis of two luminescent coordination polymers based on self-assembly of Zn(II) with polycarboxylic acids ligands and heteroaromatic N-donor

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Using the principles of molecular self-assembly, two novel zinc complexes {[Zn(phth)(bipy)(H_2O)][Zn(phth)(bipy)]·H_2O}$_n$ (1) and [Zn(1,2,4-btc)(bipy)(H_2O)·2H_2O]$_n$ (2) were obtained by hydrothermal reaction of Zn(CH_3COO)$_2$·2H_2O with phthalic acid (phth), 1,2,4-benzenetricarboxylic acid (1,2,4-btc) and 2,2′-bipyridine (bipy) respectively, and characterized by single-crystal X-ray diffraction. The crystal structures reveal that both complexes form one-dimensional chain structures, and the zinc ions are five-coordinated; there are two types of metal environment in the structure of the complex 1. The photophysical properties have been investigated with fluorescence excitation and emission spectra.
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KEYWORDS: zinc coordination polymer; crystal structure; benzenepolycarboxylic acid; hydrothermal synthesis; luminescence

INTRODUCTION

Transition metal–organic coordination polymers, which are diverse in structure and properties, are currently attracting increasing attention not only owing to their applications in the areas of catalysis, cooperative magnetic behavior, nonlinear optical activity and electrical conductivity, but also because of their interesting topologies. To design metal–organic coordination polymers from transition metals and organic ligands with novel architectures and desired functionalities by use of the principles of crystal engineering has been one of the most challenging subjects in coordination chemistry.[1–12] Hence, the selection or design of a suitable ligand-containing certain features, such as flexibility, versatile binding modes and the ability to form hydrogen bonds, is crucial to the construction of polymeric complexes.[13]

The flexible benzenetricarboxylic acids are good candidates for the construction of novel metal–organic complexes, which show many important advantages over other organic ligands: they have three carboxyl groups that can be completely or partially deprotonated, which produces rich coordination modes; they can act not only as a hydrogen-bond acceptor but also as a hydrogen-bond donor, depending upon the number of deprotonated carboxyl groups; they may also connect with metal ions in different directions due to their rigidity and polycarboxylate groups; and it is easy to form their crystalline complexes, and their metal–organic complexes show highly dimensional structures.[14–34]

In particular, 1,2,4-benzenetricarboxylate is an unsymmetrical benzene polycarboxylate; it can be assembled around metal centers in diverse arrangements owing to the possession of two or more coordination sites with differing donor abilities, resulting in a structure with novel topological features. However, to our knowledge, only a few metal–organic frameworks constructed from 1,2,4-btc have been prepared.[25–34] Therefore, from the standpoint of molecular design, we have attempted to assemble highly dimensional metal–organic complexes using 1,2,4-btc as the bridging ligand.

The benzenetricarboxylic acids can exhibit richer coordination modes in transition metal–organic complexes owing to their rigidity and polycarboxylate groups. Therefore it is easy to form their crystalline complexes, and their metal–organic complexes always show two- or three-dimensional structures.[35–39] In order to obtain one-dimensional complexes, one approach is to introduce terminal ligands such as 2,2′-bipyridine, phen or their derivatives into the carboxylate system, because the terminal

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ligands reduce the available metal–ion binding sites to interdict polymer growth in other directions.[40,41] Many one-dimensional metal–organic polymers have been prepared using mixed ligands of multicarboxylate and 2,2′-bipyridine, phen or their derivatives, in which the interdicting action of 2,2′-bipyridine, phen or their derivatives plays an important role in the formation of the one-dimensional chain.[40,42–49]

In addition, the hydrothermal method is effective for the crystal growth of many coordination polymers. Under hydrothermal conditions, the properties of the reactants and the interactions between organic and inorganic partners are quite different from those under conventional conditions in water. Therefore, various simple precursors and metastable compounds may be produced by hydrothermal reactions, and this facilitates crystal growth from solution.[50–54] Taking account of these, we chose the polycarboxylate ligand and 2,2′-bipyridine as reactants to build one-dimensional architectures by a hydrothermal reaction. Herein, we report the synthesis, structures and properties of two novel one-dimensional zinc complexes with mixed ligands of multicarboxylate phthalic acid (phth), 1,2,4-benzenetricarboxylic acid (1,2,4-btc) and 2,2′-bipy. For these complexes, the coordination number of zinc ions is 5, unlike the usual 4 or 6.

The photophysical properties of the complexes have been studied with fluorescence excitation and emission spectra; the results show that complexes **1** and **2** exhibit yellow and blue emission, respectively.

EXPERIMENTAL

Preparation of zinc complexes

$Zn(CH_3COO)_2{\cdot}2H_2O$, phthalic acid and 1,2,4-benzenetricarboxylic acid were purchased from Aldrich and used without further purification. All the other reagents were commercially available and used as received.

Synthesis of {[Zn(phth)(bipy)(H_2O)][Zn(phth)(bipy)]·H_2O}$_n$ (1)

$Zn(CH_3COO)_2{\cdot}2H_2O$ (110 mg, 0.5 mmol), phthalic acid (83.1 mg, 0.5 mmol) and 2,2′-bipyridine (78.1 mg, 0.5 mmol) were mixed in 10 ml deionized water. After stirring for half an hour, the mixture was placed in a 25 ml Teflon-lined reactor and heated at 160 °C in an oven for 4 days. The resulting solution was cooled slowly to room temperature; well-shaped, light, colorless single crystals of the title complex suitable for X-ray four-circle diffraction analysis were obtained. Yield: 63%. Anal. calcd for $C_{36}H_{26}N_4O_{10}Zn_2$: C, 53.64; H, 3.23; N, 6.95%. Found: C, 53.42; H, 3.29; N, 6.85%. IR (KBr pellet, cm^{-1}): 1415 cm^{-1} (υ_{sCOO-}), 1551 cm^{-1} (υ_{asCOO-}).

Syntheses of [Zn(1,2,4-btc)(bipy)(H_2O)·$2H_2O$]$_n$ (2)

$Zn(CH_3COO)_2{\cdot}2H_2O$ (110 mg, 0.5 mmol), 1,2,4-benzenetricarboxylic acid (105.1 mg, 0.5 mmol) and 2,2′-bipyridine (78.1 mg, 0.5 mmol) were mixed in 10 mL deionized water. After stirring for half an hour, the mixture was placed in a 25 ml Teflon-lined reactor and heated at 160 °C in an oven for 4 days. The resulting solution was cooled slowly to room temperature; well-shaped, light, colorless single crystals of the title complex suitable for X-ray four-circle diffraction analysis were obtained. Yield: 63%. Anal. calcd for $C_{19}H_{18}N_2O_9Zn$: C, 47.13; H, 3.72; N, 5.79%; Found: C, 47.01; H, 3.78; N, 5.65%. IR (KBr pellet, cm^{-1}): 1411 cm^{-1} (υ_{sCOO-}), 1546 cm^{-1} (υ_{asCOO-}).

Measurements and apparatus

Elemental analyses (C, H, N) were determined using an Elementar Cario EL elemental analyzer. IR spectra were recorded using a Nicolet Nexus 912 AO446 spectrophotometer (KBr pellet), 4000–400 cm^{-1} region. The luminescence (excitation and emission) spectra for the solid complex samples were determined using a Perkin-Elmer LS-55 spectrophotometer; whole excitation and emission slit widths were 10 and 5 nm, respectively.

Crystal structure determination

Diffraction data for the crystal with dimensions 0.25 × 0.15 × 0.10 mm for complex **1** and 0.15 × 0.10 × 0.08 mm for complex **2** were performed with graphite-monochromated Mo$K\alpha$ radiation (λ 0.71073 Å) on a CCD detector four-circle diffractometer, and were collected by the ω-2θ scan technique. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97.[55,56] Crystallographic data and refinement parameters details for two complexes are listed in Table 1.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-255353 for complex **1** and CCDC-255354 for complex **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (+44) 1223336033; e-mail: deposit@ccdc.cam.ac.ukscomparison].

RESULTS AND DISCUSSION

Crystal structure of zinc complexes

The complex **1** {[Zn(phth)(bipy)(H_2O)][Zn(phth)(bipy)]·H_2O}$_n$ crystallizes in the monoclinic system, with space group $P2(1)/n$. X-ray crystallographic analysis shows that complex **1** exhibits a one-dimensional zigzag chain structure, as shown in Fig. 1; there are two crystallographically unique zinc centers in the crystal structure. The Zn(1) center is five-coordinated and displays a distorted trigonal bipyramidal coordination geometry, which is completed by two nitrogen atoms from one chelating bipy ligand with the bond distances between the Zn ion and nitrogen atoms 2.136(11) Å [Zn(1)–N(1)] and 2.197(11) Å [Zn(1)–N(2)], respectively;

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Table 1. Crystal data and structure refinement for complexes **1** and **2**

	Complex **1**	Complex **2**
Empirical formula	$C_{36}H_{26}N_4O_{10}Zn_2$	$C_{19}H_{18}N_2O_9Zn$
Relative molecular weight, M	805.35	483.72
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	$P2(1)/n$	$P-1$
Space group	Monoclinic	Triclinic
Unit dimensions	$a = 11.037(5)$ Å	$a = 7.6176(19)$ Å
	$b = 22.343(10)$ Å	$b = 10.630(3)$ Å
	$c = 14.833(6)$ Å	$c = 12.750(3)$ Å
		$\alpha = 88.969(3)^\circ$
	$\beta = 109.658(7)^\circ$	$\beta = 82.149(3)^\circ$
		$\gamma = 75.600(3)^\circ$
Volume	3444(3) Å^3	990.5(4) Å^3
Z	4	2
Calculated density	1.553 mg/m^3	1.622 mg/m^3
Absorption coefficient	1.458 mm^{-1}	1.297 mm^{-1}
$F(000)$	1640	496
Crystal size	0.25 × 0.15 × 0.10 mm	0.15 × 0.10 × 0.08 mm
Θ range for data collection	1.72–25.01°	1.61–26.01°
Reflections/collected/unique	14 111/6066 [R(int) = 0.1893]	4599/3823 [R(int) = 0.0147]
Completeness to 2Θ = 25.01	99.8%	98.1%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6066/0/469	3823/9/308
Goodness-of-fit on F^2	0.956	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1035$, $wR_2 = 0.02242$	$R_1 = 0.0359$, $wR_2 = 0.0859$
Largest difference peak and hole	1.270 e.Å^{-3} and −1.802 e.Å^{-3}	0.411 e.Å^{-3} and −0.266 e.Å^{-3}

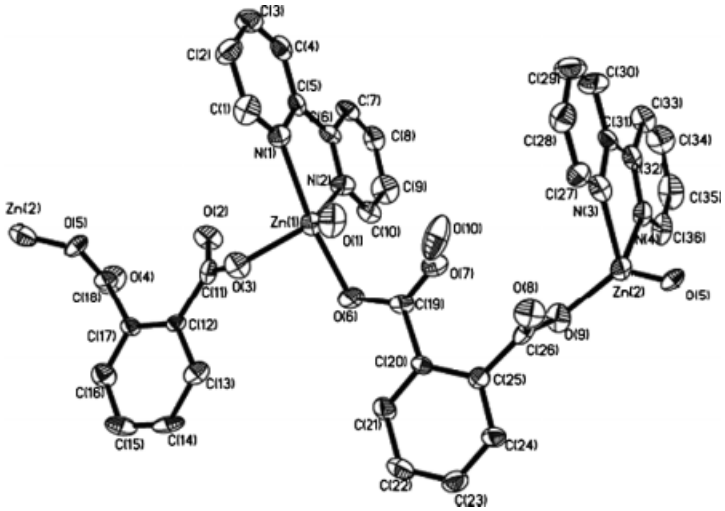

Figure 1. The ORTEP drawing for complex **1** with atom labeling scheme.

and two oxygen atoms from two bridging phth groups with the bond distances between the Zn ion and oxygen atoms 1.993(9) Å [Zn(1)–O(3)] and 2.036(9) Å [Zn(1)–O(6)], respectively; another oxygen atom is from one coordinated water molecule, and the bond distance is longer, 2.069(8) Å [Zn(1)–O(1)]. The bond angle consisting of zinc and the two nitrogen atoms is 76.8(4)° [N(1)–Zn(1)–N(2)]. The Zn(2) center is four-coordinated by two nitrogen atoms and two oxygen atoms, whose coordination geometry can be described as a distorted tetrahedron geometry. Two nitrogen atoms are from one bipy ligand with the bond distances between the zinc ion and nitrogen atoms 2.044(11) Å [Zn(2)–N(3)]

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and 2.080(10) Å [Zn(2)–N(4)], respectively; two oxygen atoms are from two bridging phth ligands with the bond distances between the zinc ion and oxygen atoms 2.001(8) Å [Zn(2)–O(5)] and 1.961(9) Å [Zn(2)–O(9)], respectively. The bond angle consisting of Zn and the two nitrogen atoms is bigger: 79.6(4)° [N(3)–Zn(2)–N(4)]. The selected bond lengths and angles for complexes **1** and **2** are listed in Table 2.

All phth anion are completely protonated; they act as bidentate–bridging ligands towards the zinc central ions. The two zinc centers are interconnected by the bridging phth ligands to form an infinite chain along the *c*-axis, and the chains are further linked by interchain hydrogen bonds with the coordinated H_2O molecules as donors and both coordinated H_2O molecules and oxygen atoms of the carboxylate group act as acceptors; the 2,2′-bipy ligands are on one side of the zigzag chain paralleling each other, as shown in Figs 2 and 3.

The complex **2** $[Zn(1,2,4\text{-btc})(bipy)(H_2O) \cdot 2H_2O]_n$ crystallizes in the triclinic system, with space group $P-1$, which also forms a one-dimensional zigzag chain structure. The 1,2,4-btc anion acts as a bridge–bidentate ligand towards the Zn ions, the benzene rings and the bipy planes on one side of the zigzag chain paralleling each other, respectively. The

Table 2. Selected bond distances (Å) and bond angles (deg) for complexes **1** and **2**

(**1**)		(**2**)	
Zn(1)–O(3)	1.993(9)	Zn(1)–O(7)[a]	1.9964(19)
Zn(1)–O(6)	2.036(9)	Zn(1)–O(2)	2.0192(19)
Zn(1)–O(1)	2.069(8)	Zn(1)–O(1)	2.068(2)
Zn(1)–N(2)	2.136(11)	Zn(1)–N(2)	2.080(2)
Zn(1)–N(1)	2.197(11)	Zn(1)–N(1)	2.137(2)
Zn(2)–O(9)	1.961(9)		
Zn(2)–O(5)[a]	2.001(8)		
Zn(2)–N(3)	2.044(11)		
Zn(2)–N(4)	2.080(10)		
O(3)–Zn(1)–O(6)	88.6(4)	O(7)[a] –Zn(1)–O(2)	93.56(8)
O(3)–Zn(1)–O(1)	100.6(4)	O(7)[a] –Zn(1)–O(1)	100.02(10)
O(6)–Zn(1)–O(1)	93.4(4)	O(2)–Zn(1)–O(1)	90.21(9)
O(3)–Zn(1)–N(2)	123.8(4)	O(7)[a] –Zn(1)–N(2)	130.30(8)
O(6)–Zn(1)–N(2)	96.4(4)	O(2)–Zn(1)–N(2)	94.13(9)
O(1)–Zn(1)–N(2)	134.6(4)	O(1)–Zn(1)–N(2)	128.95(10)
O(3)–Zn(1)–N(1)	99.4(4)	O(7)[a] –Zn(1)–N(1)	103.54(9)
O(6)–Zn(1)–N(1)	171.5(4)	O(2)–Zn(1)–N(1)	162.66(9)
O(1)–Zn(1)–N(1)	88.0(4)	O(1)–Zn(1)–N(1)	84.08(10)
N(2)–Zn(1)–N(1)	76.8(4)	N(2)–Zn(1)–N(1)	77.08(9)
O(9)–Zn(2)–O(5)[a]	114.5(4)		
O(9)–Zn(2)–N(3)	119.6(4)		
O(5)[a] –Zn(2)–N(3)	108.7(4)		
O(9)–Zn(2)–N(4)	109.8(4)		
O(5)[a] –Zn(2)–N(4)	120.6(4)		
N(3)–Zn(2)–N(4)	79.6(4)		

Symmetry transformations used to generate equivalent atoms: for complex **1**, [a] $x, y, z+1$; for complex **2**, [a] $x+1, y, z$.

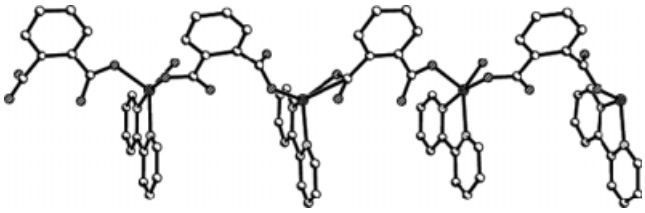

Figure 2. The one-dimensional chain drawing for complex **1**.

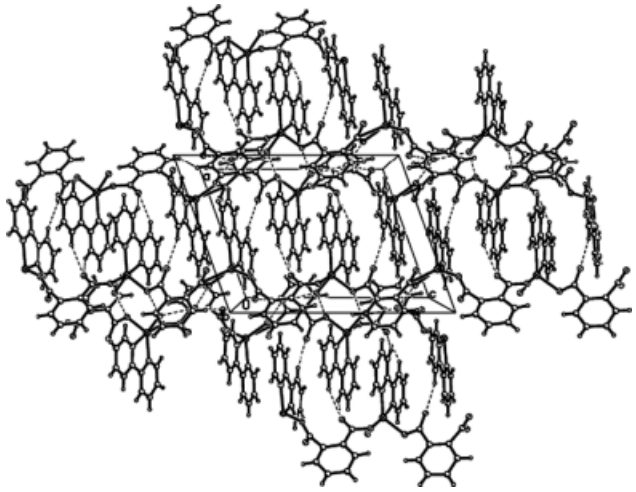

Figure 3. The packing unit cell diagram for complex **1**.

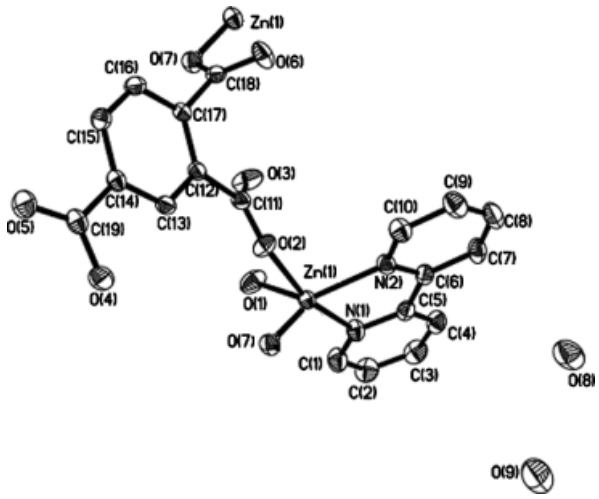

Figure 4. The ORTEP drawing for complex **2** with atom labeling scheme.

least asymmetric unit of the complex consists of one central metal ion Zn(II), one bridging 1,2,4-btc ligand, one chelating bipy ligand, one coordinated water molecule and two lattice water molecules, as shown in Fig. 4. Each Zn(II) ion is five-coordinated by two nitrogen atoms from the bipy ligand and three oxygen atoms from the 1,2,4-btc ligand, whose

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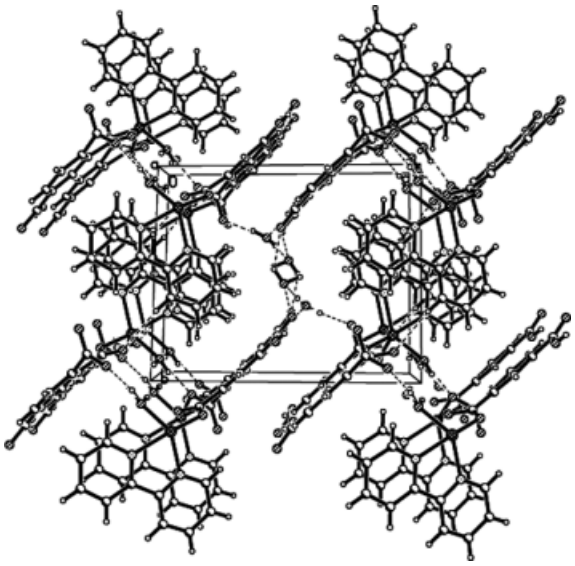

Figure 5. The packing unit cell diagram for complex **2**.

coordination geometry can also be described as a distorted trigonal bipyramidal coordination geometry. The bond distances between the Zn ion and the two nitrogen atoms are 2.137(2) Å [Zn(1)–N(1)] and 2.080(2) Å [Zn(1)–N(2)], respectively; the bond angle consisting of Zn and these is 77.08(9)° [N(1)–Zn(1)–N(2)]. The bond distances between the Zn ion and oxygen atoms are 2.068(2) Å [Zn(1)–O(1)], 2.0192(19) Å [Zn(1)–O(2)] and 1.9964(19) Å [Zn(1)–O(7)], respectively.

Figure 5 shows the packing view of a unit cell for complex **2**. The existence of the two additional lattice water molecules causes more hydrogen bonding than complex **3**; there exist five types of O–H···O intermolecular hydrogen bonds: one is O–H···O intermolecular hydrogen bonding between the oxygen atoms of the lattice water molecules, the bond angle of which is 112(7)° [O(9)–H(9B)···O(8)^{c}]; the second is O–H···O intermolecular hydrogen bonding between the oxygen atoms of the lattice water molecules and the oxygen atoms of the uncoordinated carboxyls, the bond angle of which is 136(5)° [O(9)–H(9B)···O(5)^{d}]; the third is O–H···O intermolecular hydrogen bonding between the oxygen atoms of the coordinated water molecules and the coordinated oxygen atoms of the bridging carboxyls, the bond angle of which is 167(4)° [O(1)–H(1B)···O(7)^{e}]; the fourth is O–H···O intermolecular hydrogen bonding between the oxygen atoms of the lattice water molecules and the uncoordinated oxygen atoms of the bridging carboxyls, the bond angle of which is 174(4)° [O(8)–H(8A)···O(6)^{f}]; the last one is O–H···O intermolecular hydrogen bonding between the oxygen atoms of the uncoordinated carboxyls and the oxygen atoms of the lattice water molecules, the bond angle of which is 176(4)° [O(4)–H(4A)···O(8)^{g}]. Besides these O–H···O intermolecular hydrogen bonds, there also exist two types of O–H···O intramolecular hydrogen bonds: one is O–H···O intramolecular hydrogen bonding between the oxygen atoms of the lattice water molecules, the bond angle of which is 171(3)° [O(8)–H(8B)···O(9)]; another is O–H···O intramolecular hydrogen bonding between the oxygen atoms of the coordinated water molecules and the uncoordinated oxygen atoms of the bridging carboxyls, the band angle of which is 134(3)° [O(1)–H(1A)···O(3)]. The interchain hydrogen bonds are in an alternate fashion, and consolidate the stacked arrangement, leading to a three-dimensional supramolecular architecture. These hydrogen bonds link up the complex units, which results in a three-dimensional network. The detailed data of hydrogen bonding for complex **2** are shown in Table 3.

Comparison with zinc analogs

To prepare metal–organic coordination polymers, the phthalic acid ligands may possess many possible coordination modes. As previously reported, modes 1a, 2a, 3a, 4a, 5a and 6a were found in Zn phthalate polymers (Fig. 6). In the H-bonded bridging Zn–phth–bipy complex [(2,2′-bipy)$_2$Zn(phth)H(phth)Zn(2,2′-bipy)$_2$](Hphth)(H_2phth)·2H_2O, the coordinated phths show bidentate chelating coordination mode (6a);[57] in the one-dimensional structure of complex [Zn(phth)(2,2′-bipy)(H_2O)]$_n$, each phth anion acts as a tridentate bridging-chelating group to link two metal atoms (3a);[58] however, for complex **1**, the phth anion is coordinated to zinc ions as a bidentate bridging ligand

Table 3. Hydrogen bonds (Å) for complex **2**

D–H...A	d (D–H)	d(H...A)	d(D...A)	d (DHA)
O(8)–H(8B)...O(9)	0.847(10)	1.837(13)	2.677(5)	171(3)
O(9)–H(9B)...O(8)^{c}	0.855(10)	2.64(8)	3.068(5)	112(7)
O(9)–H(9B)...O(5)^{d}	0.855(10)	2.28(4)	2.959(4)	136(5)
O(1)–H(1B)...O(7)^{e}	0.843(10)	1.875(13)	2.703(3)	167(4)
O(1)–H(1A)...O(3)	0.840(10)	2.11(3)	2.763(3)	134(3)
O(8)–H(8A)...O(6)^{f}	0.854(10)	1.839(12)	2.689(3)	174(4)
O(4)–H(4A)...O(8)^{g}	0.69(4)	1.83(4)	2.519(3)	176(4)

For symmetry transformations used to generate equivalent atoms: for complex **2**, ^{c} $-x+1, -y+1, -z+1$, ^{d} $-x+1, -y, -z+1$, ^{e} $-x, -y, -z$; ^{f} $-x, -y+1, -z+1$; ^{g} $x, y-1, z$.

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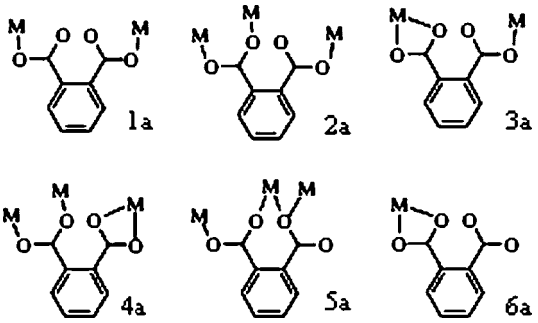

Figure 6. The coordination modes of phthalate ligand in Zn complexes.

(1a). In the above-mentioned two complexes, zinc ions are six-coordinated, and there exists only one metal coordination environment in the molecular structure; in complex **1**, zinc ions are four- or five-coordinated, and there are two types of zinc ions in the structure. The distinction of Zn(1) and Zn(2) is that the lattice water molecule is not coordinated to Zn(2), which is peculiar in zinc complexes as the difference between central ions is always caused by the coordination behaviors of organic ligands.

A majority of benzenetricarboxylate complexes were synthesized under neutral or alkaline (pH > 7) conditions by the hydrothermal method, which causes benzenetricarboxylates such as 1,3,5-btc and 1,2,4-btc to always be completely deprotonated and their metal–organic complexes show highly dimensional structures (two or three dimensions).[35–39] In our work, the pH of the reaction solution was not adjusted, and the reaction was under a mild-acid conditions (pH = 4–7). The resulting crystals show that 1,2,4-btc is biprotonated, two carboxylic groups are coordinated to zinc centers while another is uncoordinated. Therefore, in order to investigate the coordination behaviours, 1,2,4-btc can be considered as a derivative of phthalic acid. In contrast to $[Zn(phth)(2,2'\text{-bipy})(H_2O)]_n$ and complex **1**, there is one crystallographically unique zinc center in the structure of complex **2** and Zn ions are five-coordinated;

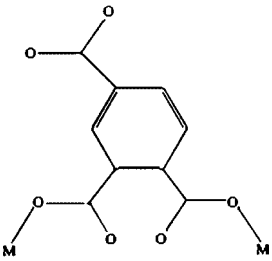

Figure 7. The coordination modes of 1,2,4-btc in complex **2**.

1,2,4-btc shows a bidentate bridging coordination mode which is comparable with phth lidand (1a), as shown in Fig. 7.

Photophysical properties of zinc carboxylate complexes

Complex **2** exhibits intense blue photoluminescence upon the radiation of UV light in the solid state at room temperature [Fig. 8(a)]. The excitation spectrum of solid complex **2** under an emission wavelength 447 nm possesses one main peak at 325 nm. The emission spectrum of complex **2** mainly exhibits a broad band ranging from 400 to 500 nm, and the maximum emission wavelengths are at 450 nm. While the emission spectrum of free 1,2,4-btc molecules shows one emission at 327 nm, indicating that 1,2,4-btc ligand has no emission in the visible region, when bound to a zinc center blue luminescence is observed. The lower energy band is assigned to ligand-to-metal charge transfer (LMCT), and the observed luminescence of the complex is attributed to the coordinated 1,2,4-btc ligand.[59] In addition, the free bipy molecule exhibits a weak luminescence at 503 nm in the solid state at room temperature, there also existing the intraligand charge transfer bond.[60] Similarly, The excitation spectrum of complex **1** under 450 nm shows five main peaks, 239, 257, 295, 320 and 393 nm; the emission spectrum of complex **1** mainly ranges from 530 to 700 nm and the emission spectrum shows one emission peak under excitation at 393 nm with the maximum emission wavelength at 568 nm; the emission spectrum of the free phth

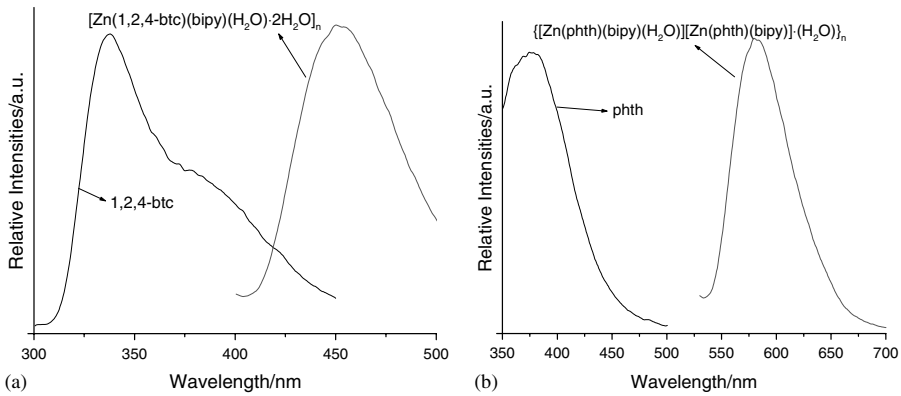

Figure 8. Luminescent emission spectra of Zn complexes.

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molecule shows one emission at 375 nm [Fig. (8b)]. Since hydrothermal products are usually stable and insoluble in common solvents arising from their polymeric structures, both complexes may be potential candidates for photoactive materials.

CONCLUSIONS

We have successfully assembled phthalic acid, 1,2,4-benzenetricarboxylic acid and Zn with 2,2′-bipyridine into two novel one-dimensional chain polymeric complexes by the hydrothermal method. The coordination number of the zinc ions in these complexes is 5, unlike the usual 4 or 6. The fluorescence excitation and emission spectra studies reveal that complexes **1** and **2** exhibit yellow and blue emissions, respectively.

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