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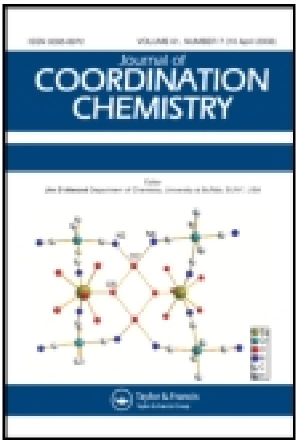

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Syntheses, structures, and luminescence of three 4-connected zinc coordination polymers with bis(1,2,4-triazol-1-yl)propane and benzenebiscarboxylate

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Syntheses, structures, and luminescence of three 4-connected zinc coordination polymers with bis(1,2,4-triazol-1-yl)propane and benzenebiscarboxylate

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Three zinc(II) coordination polymers $\{[Zn(btp)(1,2\text{-}bdc)(H_2O)]\cdot H_2O\}_n$ (**1**), $\{[Zn(btp)(1,3\text{-}bdc)(H_2O)]\cdot 1.5H_2O\}_n$ (**2**), and $\{[Zn(btp)(NO_2\text{-}1,3\text{-}bdc)(H_2O)]\cdot 2H_2O\}_n$ (**3**) were synthesized by 1,3-bis(1,2,4-triazol-1-yl)propane (btp) and bis-carboxylate. Compound **1** is a thick 2-D network; **2** and **3** are undulated 2-D (4,4) networks. In **2** and **3**, two adjacent networks interpenetrate to form a new 2-D double-layer network, which is sustained by hydrogen-bonding interactions. Compounds **1** and **2** reveal blue emission maximum at 351 and 403, respectively, in the solid state at room temperature.

Keywords: Coordination polymer; 2-D network; Zinc complex; 1,3-Bis(1,2,4-triazol-1-yl) propane; Benzenebiscarboxylate

1. Introduction

Interest in crystal engineering of coordination polymer frameworks stems from their potential applications as functional materials for gas storage, separation, microelectronics, nonlinear optics, and catalysis and from their intriguing topologies [1]. Flexible ligands have been used to obtain novel topologies not available from combinations of rigid building blocks. The simplest way to introduce flexibility into a ligand is by incorporating an alkyl chain into the spacer groups [2]. Organic aromatic polycarboxylates, such as 1,2-benzenedicarboxylate (1,2-bdc), 1,3-benzenedicarboxylate (1,3-bdc), 1,4-benzenedicarboxylate (1,4-bdc), 1,3,5-benzenetricarboxylate (btc), and 1,2,4,5-benzenetetracarboxylate (btec), are good building blocks for the construction of coordination polymers and multidimensional supramolecular networks [3, 4].

Our synthetic approach starts by focusing on the construction of new topological frameworks and potential functional materials using flexible ligands by adjusting lengths and flexibilities using 1,2-bis(1,2,4-triazol-1-yl)ethane [5], 1,4-bis(1,2,4-triazol-1-yl)butane [6] and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene [7]. 1,3-Bis(1,2,4-triazol-1-yl)propane (btp) is a long and flexible ligand, which can adopt different conformations

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with respect to the relative orientations of the CH_2 groups [8]. The d^{10} metal coordination polymers have interesting photoluminescent properties [9]. In order to synthesize topological frameworks and potential luminescent materials, in this study, we prepared three zinc(II) coordination polymers $\{[Zn(btp)(1,2\text{-}bdc)(H_2O)] \cdot H_2O\}_n$ (**1**), $\{[Zn(btp)(1,3\text{-}bdc)(H_2O)] \cdot 1.5H_2O\}_n$ (**2**), and $\{[Zn(btp)(NO_2\text{-}1,3\text{-}bdc)(H_2O)] \cdot 2H_2O\}_n$ (**3**) by the reaction of 1,3-bis(1,2,4-triazol-1-yl)propane (btp), $Zn(NO_3)_2$ and 1,2-benzenedicarboxylate (1,2-bdc), 1,3-benzenedicarboxylate (1,3-bdc), 5-nitroisophthalate (NO_2-1,3-bdc). Here we report their syntheses, crystal structures, and luminescent properties.

2. Experimental

2.1. *General procedures*

2.1.1. Materials and general methods. All reagents were of analytical grade and used without purification. 1,3-Bis(1,2,4-triazol-1-yl)propane (btp) was synthesized according to the literature method [8c]. Elemental analyses for C, H, and N were performed on a Perkin Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Luminescence measurements were carried out in the solid state at room temperature and spectra were collected with a Perkin Elmer LS50B spectrofluorimeter.

2.2. *Synthesis of* $\{[Zn(btp)(1,2\text{-}bdc)(H_2O)] \cdot H_2O\}_n$ *(1)*

A solution of H_2-1,2-bdc (0.2 mmol) in 10 mL H_2O was adjusted to pH 6.5 with dilute NaOH solution. Then btp (0.2 mmol) in 10 mL CH_3OH was added. This mixture was added to one side of the "H-shaped" tube and $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol) in 20 mL water was added to the other side of the "H-shaped" tube. Colorless crystals of **1** (yield: 52%) were obtained after 2 weeks at room temperature. Anal. Calcd for $C_{15}H_{18}N_6O_6Zn$ (**1**): C, 40.60; H, 4.09; N, 18.94%. Found: C, 40.49; H, 4.02; N, 18.82. IR data (cm^{-1}): 3250 m, 1657 w, 1604 s, 1545 m, 1531 m, 1483 m, 1404 s, 1373 s, 1281 m, 1209 w, 1136 m, 1088 w, 1007 w, 988 m, 957 w, 909 w, 870 m, 835 w, 773 m, 709 m, 675 s, 632 w, 432 w.

2.3. *Synthesis of* $\{[Zn(btp)(1,3\text{-}bdc)(H_2O)] \cdot 1.5H_2O\}_n$ *(2)*

The synthetic procedure of **2** was similar to the synthesis of **1**, except that H_2-1,3-bdc (0.20 mmol) was used instead of H_2-1,2-bdc. Colorless crystals of **2** (yield: 61%) were obtained after 2 weeks at room temperature. Anal. Calcd for $C_{15}H_{19}N_6O_{6.5}Zn$ (**2**): C, 39.80; H, 4.23; and N, 18.57%. Found: C, 39.68; H, 4.17; N, 18.52. IR data (cm^{-1}): 3236 m, 1685 m, 1651 m, 1524 s, 1454 m, 1416 w, 1385 m, 1282 m, 1138 m, 987 m, 883 w, 741 w, 667 w.

Table 1. Crystallographic data for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{15}H_{18}N_6O_6Zn$	$C_{15}H_{19}N_6O_{6.5}Zn$	$C_{15}H_{19}N_7O_9Zn$
Formula weight	443.72	452.73	506.74
Temperature (K)	223(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/c	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	22.836(4)	10.0989(6)	10.1193(15)
b	9.3900(13)	10.1872(19)	10.1803(12)
c	18.112(3)	10.7561(16)	10.9269(16)
α	90	80.51(3)	71.717(14)
β	115.826(3)	65.67(2)	81.262(17)
γ	90	68.58(2)	68.148(13)
Volume (Å^3), *Z*	3496.0(10), 8	938.5(2), 2	991.3(2), 2
Calculated density, ρ_{calc} (Mg m^{-3})	1.686	1.602	1.698
Absorption coefficient, μ (mm^{-1})	1.455	1.358	1.306
F(0 0 0)	1824	466	520
Reflections collected	9713	8926	9315
Unique reflections	3962 [*R*(int) = 0.0276]	3392 [*R*(int) = 0.0447]	3568 [*R*(int) = 0.0491]
Parameters	269	268	307
Goodness-of-fit on F^2	1.006	1.077	1.068
R_1 [$I > 2\sigma(I)$]	0.0335	0.0582	0.0631
wR_2 (all data)	0.0857	0.1719	0.1488

2.4. *Synthesis of* $\{[Zn(btp)(NO_2\text{-}ip)(H_2O)]\cdot 2H_2O\}_n$ *(3)*

The synthetic procedure of **3** was similar to the synthesis of **1**, except that H_2–NO_2-1,3-bdc (0.20 mmol) was used instead of H_2-1,2-bdc. Colorless crystals of **3** (yield: 64%) were obtained after 2 weeks at room temperature. Anal. Calcd for $C_{15}H_{19}N_7O_9Zn$ (**3**): C, 35.55; H, 3.78; N, 19.35%. Found: C, 35.49; H, 3.73; N, 19.28. IR data (cm^{-1}): 3263 m, 1608 s, 1569 s, 1532 s, 1451 m, 1382 s, 1344 s, 1282 m, 1210 m, 1137 m, 1081 w, 988 m, 928 w, 896 m, 839 w, 784 m, 732 s, 673 m, 638 m, 480 w.

2.5. *X-ray crystallography*

X-ray crystallography suitable for single crystals of **1**, **2**, and **3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Rigaku Saturn or Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ or 0.71075 Å). Intensities were collected by the ω scan technique and the structures were solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) [10]. Positions of hydrogens of btp and aromatic dicarboxylate were determined with theoretical calculation. Hydrogens of coordination and lattice water molecules were located from successive Fourier syntheses. No appropriate hydrogens of disordered lattice water molecules of **2** were obtained. The parameters of crystal data collection and refinements of **1**, **2**, and **3** are given in table 1. Selected bond lengths and angles are listed in table 2.

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Zn(1)–O(1)	2.4735(15)	Zn(1)–O(2)	2.0660(14)
Zn(1)–O(3A)	2.0266(14)	Zn(1)–N(3)	2.0916(17)
Zn(1)–N(6B)	2.1713(18)	Zn(1)–O(5)	2.1394(16)
O(2)–Zn(1)–O(1)	56.86(5)	O(3A)–Zn(1)–O(1)	150.13(6)
N(3)–Zn(1)–O(1)	88.18(6)	O(3A)–Zn(1)–O(2)	94.22(6)
O(2)–Zn(1)–N(3)	144.40(6)	O(3A)–Zn(1)–N(3)	121.27(6)
N(6B)–Zn(1)–O(1)	96.39(6)	O(2)–Zn(1)–N(6B)	88.87(7)
O(3A)–Zn(1)–N(6B)	89.73(6)	N(3)–Zn(1)–N(6B)	88.64(7)
O(5)–Zn(1)–O(1)	85.27(6)	O(2)–Zn(1)–O(5)	93.92(6)
O(3A)–Zn(1)–O(5)	89.93(6)	N(3)–Zn(1)–O(5)	89.16(6)
O(5)–Zn(1)–N(6B)	177.21(6)		
2			
Zn(1)–O(1)	2.375(4)	Zn(1)–O(2)	2.182(4)
Zn(1)–O(3A)	2.001(3)	Zn(1)–N(3)	2.080(4)
Zn(1)–N(6B)	2.158(4)	Zn(1)–O(5)	2.184(4)
O(2)–Zn(1)–O(1)	56.85(14)	O(3A)–Zn(1)–O(1)	91.22(14)
N(3)–Zn(1)–O(1)	143.74(14)	O(3A)–Zn(1)–O(2)	147.68(16)
N(3)–Zn(1)–O(2)	87.10(15)	O(3A)–Zn(1)–N(3)	124.09(15)
N(6B)–Zn(1)–O(1)	88.64(14)	N(6B)–Zn(1)–O(2)	92.77(15)
O(3A)–Zn(1)–N(6B)	91.17(15)	N(3)–Zn(1)–N(6B)	97.71(15)
O(5)–Zn(1)–O(1)	86.14(15)	O(2)–Zn(1)–O(5)	90.16(16)
O(3A)–Zn(1)–O(5)	82.04(15)	N(3)–Zn(1)–O(5)	90.57(15)
N(6B)–Zn(1)–O(5)	171.34(15)		
3			
Zn(1)–O(1)	2.304(4)	Zn(1)–O(2)	2.253(4)
Zn(1)–O(3A)	2.027(3)	Zn(1)–N(3)	2.124(4)
Zn(1)–N(6B)	2.093(4)	Zn(1)–O(7)	2.134(4)
O(2)–Zn(1)–O(1)	57.51(12)	O(3A)–Zn(1)–O(1)	150.25(14)
N(3)–Zn(1)–O(1)	93.62(14)	O(3A)–Zn(1)–O(2)	93.73(13)
N(3)–Zn(1)–O(2)	86.16(14)	O(3A)–Zn(1)–N(3)	91.59(15)
N(6B)–Zn(1)–O(1)	83.71(14)	N(6B)–Zn(1)–O(2)	141.18(14)
O(3A)–Zn(1)–N(6B)	124.91(15)	N(6B)–Zn(1)–N(3)	95.47(15)
O(7)–Zn(1)–O(1)	87.78(14)	O(7)–Zn(1)–O(2)	88.87(15)
O(3A)–Zn(1)–O(7)	83.88(15)	N(3)–Zn(1)–O(7)	173.05(15)
N(6B)–Zn(1)–O(7)	91.44(15)		

Symmetry transformations used to generate equivalent atoms: A $-x+1/2$, $y+1/2$, $-z+1/2$; B x, $-y+1$, $z-1/2$ for **1**; A $x-1$, y, z; B x, y, $z-1$ for **2**; A x, $y-1$, z; B x, y, $z+1$ for **3**.

3. Results and discussion

The crystal structure of **1** shows a thick 2-D network. Each Zn(II) displays distorted octahedral coordination by four oxygens from two 1,2-bdc and one water molecule and two nitrogens from two btp (figure 1). Each zinc(II) connects four zinc(II)'s through two 1,2-bdc and two btp and is 4-connected. There is one independent 1,2-bdc and one independent btp. One carboxylate (O1O2) of a 1,2-bdc is bidentate chelating. The other carboxylate (O3O4) is monodentate linking zinc(II)'s. Each 1,2-bdc is a two-connected rod bridging two zinc(II)'s to form a $[\mathrm{Zn(1,2\text{-}bdc)}]_n$ zigzag chain along the *b*-direction with Zn $\cdots$ Zn distance of 6.3677(7) Å (figure 2).

The btp exhibits *anti–anti* conformation with dihedral angle between two triazole planes of 68.2(2)°. Each $[\mathrm{Zn(1,2\text{-}bdc)}]_n$ zigzag chain connects two adjacent $[\mathrm{Zn(1,2\text{-}bdc)}]_n$ chains through btp ligands to construct a thick 2-D network along the *a*-direction about 10.3 Å (figures 3 and 4) with Zn $\cdots$ Zn distance of 10.0022(14) Å

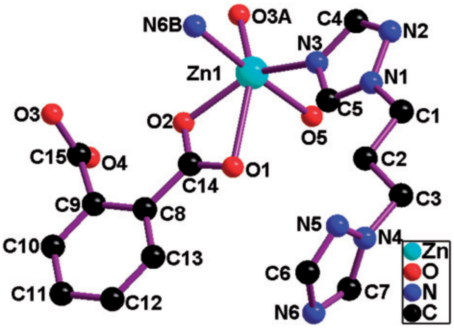


Figure 1. The coordination environment of zinc(II) in **1**.

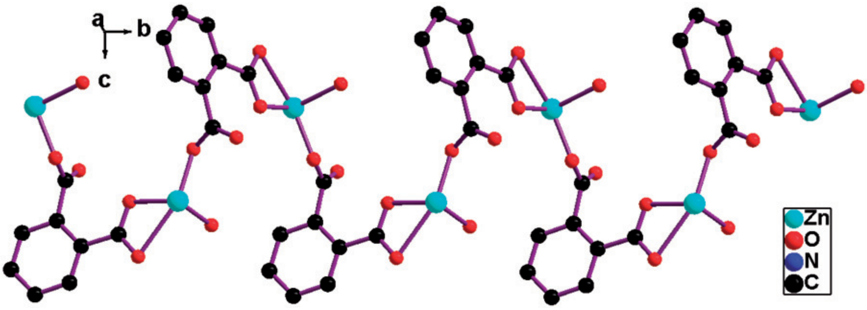


Figure 2. A 1-D zigzag chain $[Zn(1,2\text{-bdc})]_n$ along the *b*-direction in **1**.

through btp bridges. There are hydrogen-bonding interactions between coordination/lattice water and carboxylate oxygens and between coordination and lattice water molecules intra-2-D network (table 3).

Tian and co-workers [8e] synthesized a simple 2-D (4,4) network $\{[Zn(btp)(1,3\text{-bdc})]\cdot 2H_2O\}_n$ by the solvothermal method. $\{[Zn(btp)(1,3\text{-bdc})(H_2O)]\cdot 1.5H_2O\}_n$ (**2**) may be the supramolecular isomer of $\{[Zn(btp)(1,3\text{-bdc})]\cdot 2H_2O\}_n$ [8e] and the main difference is that the former has coordinated water but the latter has no coordinated water.

The structure of **2** is an undulated 2-D (4,4) network. Each Zn(II) displays distorted octahedral coordination, by four oxygens from two 1,3-bdc and one water and two nitrogens from two btp (figure 5). There are one independent 1,3-bdc and one independent btp. One carboxylate (O1O2) of 1,3-bdc is bidentate chelating joining zinc(II)'s. The other carboxylate (O3O4) is monodentate linking zinc(II)'s. Each node (Zn1) of the 2-D network is surrounded by four nodes (Zn1) which are bridged by btp and 1,3-bdc ligands (figure 6). The btp exhibits *anti–gauche* conformation with the dihedral angle between two triazole planes of 62.9(2)°. Four Zn1(II)'s, two btp, and two 1,3-bdc form a $[Zn_4(btp)_2(1,3\text{-bdc})_2]$ unit with Zn ··· Zn distances 10.756(2) and 10.099(2) Å for bridging btp and 1,3-bdc.

The 1,3-bdc groups of two adjacent sheets project into voids of the adjacent sheet (figure 7). Hydrogen bonds between coordinated water and carboxylate oxygens of

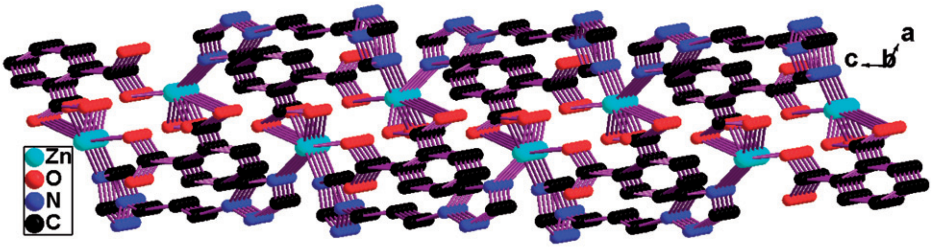


Figure 3. A thick 2-D network in **1**.

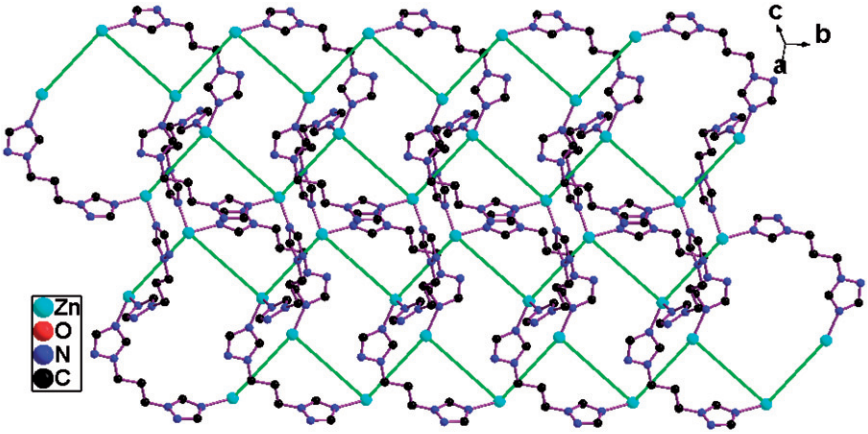


Figure 4. Side schematic of the thick 2-D network in **1**. The representation of 1,2-bdc is simplified by a bright stick.

Table 3. Hydrogen bonds for **1**–**3** (Å and °).

D–H $\cdots$ A	d(D–H)	d(H $\cdots$ A)	d(D $\cdots$ A)	$\angle$(DHA)
1				
O(5)–H(1W) $\cdots$ O(6)	0.79(3)	1.94(3)	2.731(2)	173(3)
O(5)–H(2W) $\cdots$ O(1)$^{\text{i}}$	0.83(3)	1.94(3)	2.761(2)	171(3)
O(6)–H(3W) $\cdots$ O(4)$^{\text{ii}}$	0.76(3)	2.24(3)	2.978(3)	163(3)
O(6)–H(3W) $\cdots$ O(2)$^{\text{ii}}$	0.76(3)	2.65(3)	3.080(2)	118(3)
O(6)–H(4W) $\cdots$ O(3)$^{\text{iii}}$	0.80(3)	1.94(3)	2.740(2)	174(3)
2				
O(5)–H(1W) $\cdots$ O(6)$^{\text{iv}}$	0.92(4)	2.04(4)	2.922(4)	161(5)
O(5)–H(2W) $\cdots$ O(2)$^{\text{v}}$	0.91(4)	1.88(3)	2.752(5)	160(5)
3				
O(7)–H(1W) $\cdots$ O(1)$^{\text{vi}}$	0.83(2)	1.87(2)	2.699(5)	171(6)
O(7)–H(2W) $\cdots$ O(8)$^{\text{vi}}$	0.83(2)	2.07(3)	2.854(6)	157(6)
O(8)–H(3W) $\cdots$ O(4)	0.90(2)	1.92(3)	2.783(6)	160(7)
O(8)–H(4W) $\cdots$ O(9)	0.88(2)	2.20(6)	2.873(6)	132(6)
O(9)–H(5W) $\cdots$ O(5)$^{\text{vii}}$	0.91(2)	2.24(4)	3.057(7)	149(6)
O(9)–H(5W) $\cdots$ O(6)$^{\text{vii}}$	0.91(2)	2.41(4)	3.245(6)	152(7)

Symmetry transformations used to generate equivalent atoms: $^{\text{i}}$ $-x+1/2, -y+3/2, -z+1$; $^{\text{ii}}$ $-x+1/2, y+1/2, -z+1/2$; $^{\text{iii}}$ $x, y+1, z$ for **1**; $^{\text{iv}}$ $x-1, y, z$; $^{\text{v}}$ $-x, -y+1, -z+1$ for **2**; $^{\text{vi}}$ $-x+1, -y+2, -z+1$; $^{\text{vii}}$ $x-1, y, z+1$ for **3**.

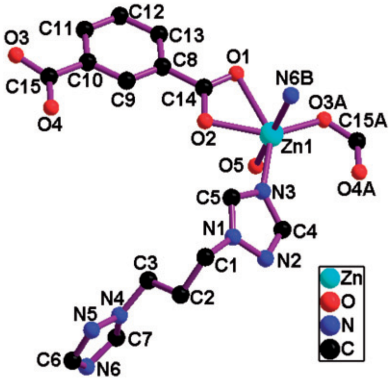


Figure 5. The coordination environment of zinc(II) in **2**.

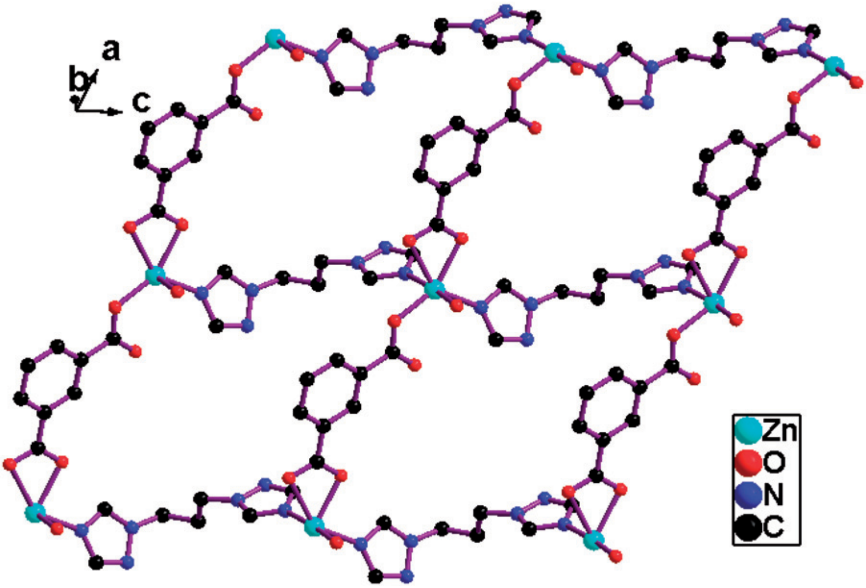


Figure 6. 2-D (4,4) network in **2**.

1,3-bdc intra-sheet (O(5)$\cdots$O(2) $(-x,-y+1,-z+1)$ 2.752(5) Å) sustain the double-layer unit (table 3).

The structure of **3** is an undulated 2-D (4,4) network. Each Zn(II) displays distorted octahedral coordination with four oxygens from two NO_2-1,3-bdc and one water and two nitrogens from two btp (figure 8). There are one independent NO_2-1,3-bdc and one independent btp. One carboxylate (O1O2) of NO_2-bdc has bidentate chelating coordination joining zinc(II)'s. The other carboxylate (O3O4) is monodentate linking zinc(II)'s. Each node (Zn1) of the 2-D network is surrounded by four nodes (Zn1) which are bridged by btp and NO_2-1,3-bdc ligands (figure 9). The btp exhibits *anti–gauche* conformation with the dihedral angle between two triazole planes of 63.3(2)°.

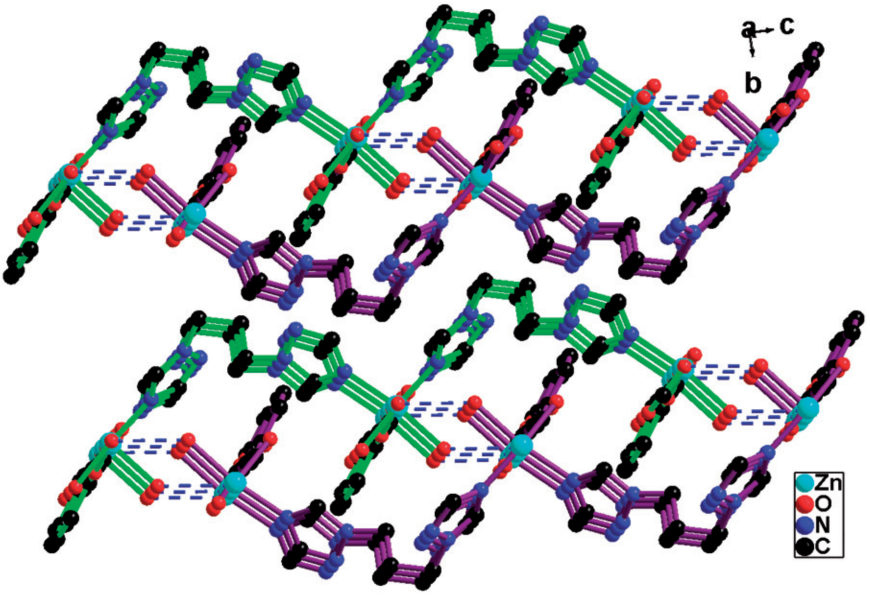
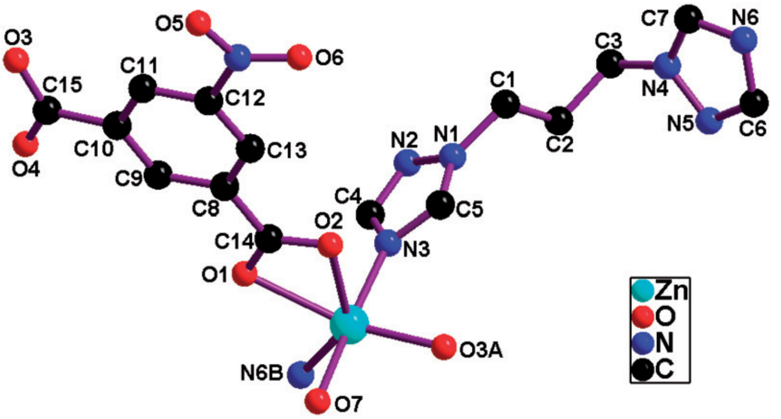


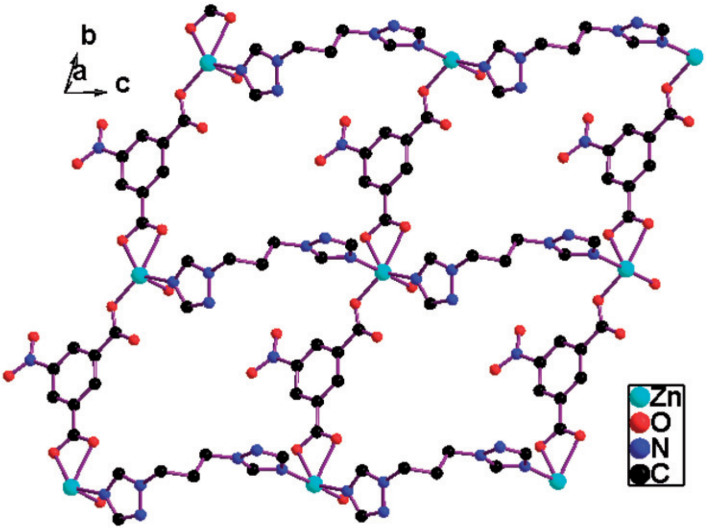
Figure 7. Two double layers sustained by O–H ··· O hydrogen-bonding interactions in **2**.

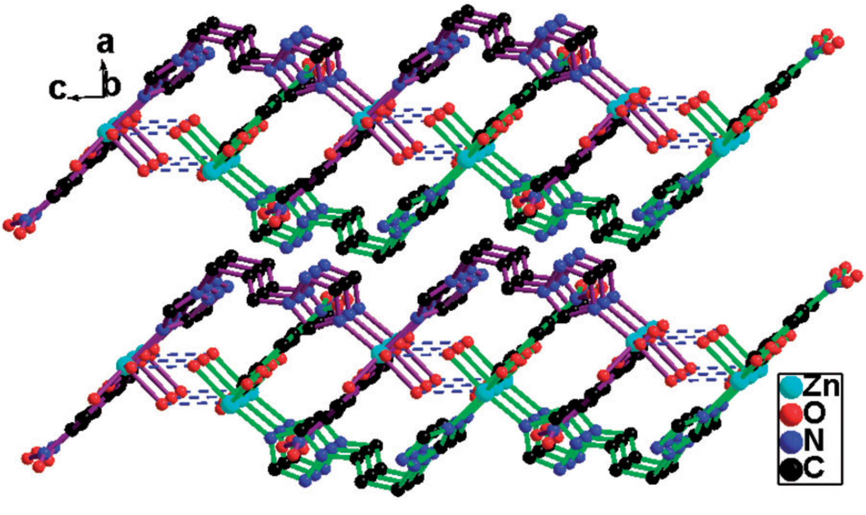


Four Zn1(II)'s, two btp, and two NO_2-1,3-bdc form a $[Zn_4(btp)_2(NO_2\text{-1,3-bdc})_2]$ unit with Zn ··· Zn distances 10.927(2) and 10.181(2) Å for bridging btp and NO_2-1,3-bdc.

Hydrogen-bonding interactions between coordinated water and carboxylate oxygen of 1,3-bdc intra-sheets (O(7) ··· O(1) $(-x+1,\ -y+2,\ -z+1)$ 2.699(5) Å) sustain the interpenetrating double-layers (figure 10). The hydrogen-bonding interactions between lattice water and carboxylate or nitro-oxygens construct the 3-D hydrogen-bonding network (table 3).

For comparison, some Zn/polycarboxylate complexes (1,2-bdc = 1,2-benzenedicarboxylate, 1,3-bdc = 1,3-benzenedicarboxylate, 1,4-bdc = 1,4-benzenedicarboxylate,





btc = 1,3,5-benzenetricarboxylate, btec = 1,2,4,5-benzenetetracarboxylate, and hip = 5-hydroxyisophthalate) are summarized. Tian and co-workers [8e] also synthesized two zinc coordination polymers, $\{[Zn(btp)(hip)]\cdot 2H_2O\}_n$ and $\{[Zn_{1.5}(btp)(btc)(H_2O)]\cdot H_2O\}_n$. The former is a 2-D infinite layer framework, and the resulting 2-D structure is interconnected by hydrogen bond and π–π interactions giving a 3-D supramolecular architecture. The latter exhibits a 2-D framework with three nonequivalent points, $\{5\cdot 6^2\}\{5^2\cdot 6\}\{5^4\cdot 8^2\}$. $\{[Zn(btp)(1,4\text{-bdc})]\text{-}[Zn(btp)(1,4\text{-bdc})_{0.5}Cl]\cdot H_2O\}_n$ represents a new type of entanglement that only half loops of 2-D networks

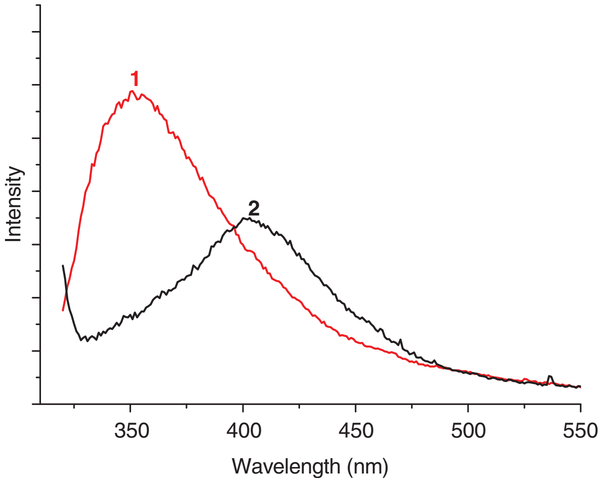


Figure 11. Solid-state emissions of **1** and **2**.

are polythreading by 1-D chains containing alternating rings and rod [8f]. $\{[Zn(btp)(1,4\text{-}bdc)]\cdot CH_3OH\cdot 2H_2O\}_n$ has a special 2-D (6,3) network, with six Zn(II)'s at six corners and four 1,4-bdc and two double btp at six edges [8f]. In $[Zn_2(4,4'\text{-}bipy)(1,4\text{-}bdc)(HCOO)_2]_n$ (4,4′-bipy = 4,4-bipyridine), both 1,4-bdc and 4,4′-bipy link Zn(II)'s alternatively, resulting in a zigzag chain; the chains are joined by formates to form a 2-D network [4a]. $\{[Zn_2(bim)_4]btec)]\cdot DMF$ (bim = benzimidazole) presents 1-D linear ribbons extended by btec [4b]. $\{[Zn(bim)(btc)]\cdot Htea\}_n$ (tea = triethylamine) consists of an anionic $[Zn(bim)(btc)]_n$ 2-D layer and a cationic triethylamine [4b]. $[Zn(bim)_2(1,4\text{-}bdc)]_n$ possesses a 1-D zigzag chain bridged by 1,4-bdc [4b]. $\{[Zn(1,3\text{-}bdc)(phen)]_2\}_n$, $[Zn(1,2\text{-}bdc)(phen)(H_2O)]_n$, and $[Zn(1,4\text{-}bdc)(phen)(H_2O)]_n$ (phen = 1,10-phenanthroline) form 1-D zigzag chain, 1-D ladder and 1-D helical chain, respectively [4c]. $[Zn(1,2\text{-}bdc)(bth)_{0.5}(H_2O)]_n$ and $[Zn(1,3\text{-}bdc)(bth)]_n$ (bth = 1,6-bis(triazol-1-yl)hexane) show a (3,4)-connected $(6^3)(6^5\cdot 8)$ 3-D network and a 2-D (4,4) network, respectively [4d]. $[Zn_2(bte)_2(1,2\text{-}bdc)_2]\cdot(H_2O)_4$ forms a 2-D network through helical chains linking $Zn_2(1,2\text{-}bdc)_2$ 14-membered rings [5d]; $[Zn(bte)(1,4\text{-}bdc)]\cdot(H_2O)_2$ constructs a 2-D rhombic network through 1,4-bdc ligands linking $Zn_2(bte)_2$ 18-membered rings [5d].

The solid-state luminescence spectra of **1** and **2** at room temperature are determined (figure 11). Free btp molecule in the solid state displays a weak emission band at 397 nm when excited at 340 nm. Compound **1** exhibits strong luminescence maximum at 351 nm upon excitation at 320 nm. Compound **2** exhibits strong luminescence maximum at 403 nm upon excitation at 340 nm. The emission of **1** can be attributed to ligand-to-metal charge-transfer [9, 11]. Luminescence spectra of **2** may be assigned to intraligand π–π* transition [8e, 9, 11]. However, no obvious luminescence of **3** is observed.

4. Conclusion

Self-assembly of the flexible ligand 1,3-bis(1,2,4-triazol-1-yl)propane (btp) and bis-carboxylate gives three 2-D network zinc(II) coordination polymers. Compound **1** is a thick 2-D network, while **2** and **3** are undulated 2-D (4,4) networks. The 1,3-bdc or NO_2-1,3-bdc groups of two adjacent sheets project into the voids of the adjacent sheet and hydrogen bonds sustain the double-layer unit in **2** and **3**. The dicarboxylates 1,2-bdc, 1,3-bdc, and NO_2-1,3-bdc exhibit similar tridentate coordination as 2-connected nodes bridging two zinc(II)'s. The structural difference between **1**, **2**, and **3** is mainly caused by the different positions of carboxylate groups and the high flexibility of btp (the *anti–anti* conformation in **1**, the *anti–gauche* conformation in **2** and **3**). Compounds **1** and **2** reveal blue emission maxima at 351 and 403 nm, respectively, in the solid state at room temperature. Compounds **1** and **2** may be candidates for potential photoactive materials.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference numbers CCDC-799946, 799947, and 799948.

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References

[1] (a) S.R. Batten, R. Robson. *Angew. Chem. Int. Ed.*, **37**, 1460 (1998); (b) S.R. Batten. *CrystEngComm*, **3**, 67 (2001); (c) L. Carlucci, G. Ciani, D.M. Proserpio. *CrystEngComm*, **5**, 269 (2003); (d) X.H. Bu, M.L. Tong, H.C. Chang, S. Kitagawa, S.R. Batten. *Angew. Chem. Int. Ed.*, **43**, 192 (2004); (e) T.C. Stamatatos, S.J. Teat, W. Wernsdorfer, G. Christou. *Angew. Chem. Int. Ed.*, **48**, 521 (2009); (f) D.Y. Wu, O. Sato, Y. Einaga, C.Y. Duan. *Angew. Chem. Int. Ed.*, **48**, 1475 (2009).

[2] (a) T.L. Hennigar, D.C. Macquarrie, P. Losier, R.D. Rogers, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **36**, 972 (1997); (b) L. Carlucci, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato, *Angew. Chem. Int. Ed.*, **39**, 1506 (2000); (c) G.A.V. Albada, R.C. Guijt, J.G. Haasnoot, M. Lutz, A.L. Spek, J. Reedijk. *Eur. J. Inorg. Chem.*, 121 (2000); (d) Q.H. Zhao, H.F. Li, X.F. Wang, Z.D. Chen. *New J. Chem.*, **26**, 1709 (2002); (e) L.M. Zhu, H.L. Wang, D.Y. Yuan, B.L. Li, H.Y. Li. *J. Coord. Chem.*, **63**, 2307 (2010).

[3] (a) X. Zhu, J.W. Zhao, B.L. Li, Y. Song, Y.M. Zhang, Y. Zhang. *Inorg. Chem.*, **49**, 1266 (2010); (b) L.Y. Wang, Y. Yang, K. Liu, B.L. Liu, Y. Zhang. *Cryst. Growth Des.*, **8**, 3902 (2008); (c) F.P. Huang, J.L. Tian, W. Gu, X. Liu, S.P. Yan, D.Z. Liao, P. Cheng. *Cryst. Growth Des.*, **10**, 1145 (2010); (d) J.D. Lin, X.F. Long, P. Lin, S.W. Du. *Cryst. Growth Des.*, **10**, 146 (2010); (e) F. Luo, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **9**, 1066 (2009); (f) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi. *Nature*, **402**, 276 (1999); (g) X.G. Liu, L.Y. Wang, X. Zhu, B.L. Li, Y. Zhang. *Cryst. Growth Des.*, **9**, 3997 (2009); (h) O.M. Yaghi, G.M. Li, H.L. Li. *Nature*, **378**, 703 (1995); (i) F. Luo, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **8**, 176 (2008); (j) O. Fabelo, J. Pasan, F. Llored, M. Julve, C. Ruiz-Perez. *Inorg. Chem.*, **47**, 3568 (2008); (k) C. Gao, S. Liu, L. Xie, C. Sun, J. Cao, Y. Ren, D. Feng, Z. Su. *CrystEngComm*, **11**, 177 (2009); (l) Y. Yang, Y.F. Feng, N. Liang, B.L. Li, Y. Zhang. *J. Coord. Chem.*, **62**, 3819 (2009).

[4] (a) D. Feng, S.X. Liu, P. Sun, F.J. Ma, W. Zhang. *J. Coord. Chem.*, **63**, 1737 (2010); (b) H. Chang, M. Fu, X.J. Zhao, E.C. Yang. *J. Coord. Chem.*, **63**, 3551 (2010); (c) X.M. Lu, Y.Y. Chen, P.Z. Li, Y.G. Bi, C. Yu, X.D. Shi, Z.X. Chi. *J. Coord. Chem.*, **63**, 3923 (2010); (d) P. Zhang, D.S. Li, J. Zhao, Y.P. Wu, C. Li, K. Zou, J.Y. Lu. *J. Coord. Chem.*, **64**, 2329 (2011).

[5] (a) X.Y. Wang, B.L. Li, X. Zhu, S. Gao. *Eur. J. Inorg. Chem.*, 3277 (2005); (b) X. Zhu, H.Y. Ge, Y.M. Zhang, B.L. Li, Y. Zhang. *Polyhedron*, **25**, 1875 (2006); (c) B.L. Li, X. Zhu, J.H. Zhou, Y.F. Peng, Y. Zhang. *Polyhedron*, **23**, 3133 (2004); (d) J.H. Zhou, X. Zhu, Y.N. Zhang, Y. Zhang, B.L. Li. *Inorg. Chem. Commun.*, **7**, 949 (2004); (e) B.L. Li, B.Z. Li, X. Zhu, X.H. Lu, Y. Zhang. *J. Coord. Chem.*, **57**, 1361 (2004).

[6] (a) L.Y. Wang, Y. Yang, K. Liu, B.L. Li, Y. Zhang. *Cryst. Growth Des.*, **8**, 3902 (2008); (b) X.G. Liu, L.Y. Wang, X. Zhu, B.L. Li, Y. Zhang. *Cryst. Growth Des.*, **9**, 3997 (2009); (c) X. Zhu, X.G. Liu, B.L. Li, Y. Zhang. *CrystEngComm*, **11**, 997 (2009).

[7] (a) B.L. Li, Y.F. Peng, B.Z. Li, Y. Zhang. *Chem. Commun.*, 2333 (2005); (b) Y.F. Peng, H.Y. Ge, B.Z. Li, B.L. Li, Y. Zhang. *Cryst. Growth Des.*, **6**, 994 (2006).

[8] (a) G. Yin, Y.P. Zhang, B.L. Li, Y. Zhang. *J. Mol. Struct.*, **837**, 263 (2007); (b) X. Zhu, K. Lu, Y. Yang, B.L. Li, Y. Zhang. *J. Coord. Chem.*, **62**, 2358 (2009); (c) G.A.V. Albada, R.C. Guijt, J.G. Haasnoot, M. Lutz, A.L. Spek, J. Reedijk. *Eur. J. Inorg. Chem.*, 121 (2000); (d) Q.H. Zhao, H.F. Li, X.F. Wang, Z.D. Chen. *New J. Chem.*, **26**, 1709 (2002); (e) L. Tian, N. Yang, G.Y. Zhao. *Inorg. Chem. Commun.*, **13**, 1497 (2010); (f) J. Wang, X. Zhu, Y.F. Cui, B.L. Li, H.Y. Li. *CrystEngComm*, **13**, 3342 (2011).

[9] (a) L. Wang, M. Yang, G.H. Li, Z. Shi, S.H. Feng. *Inorg. Chem.*, **45**, 2474 (2006); (b) S.R. Li, L. Xu, *Inorg. Chem.*, **44**, 3731 (2005); (c) J. Lu, K. Zhao, Q.R. Fang, J.Q. Xu, J.H. Yu, X. Zhang, H.Y. Bie, T.G. Wang. *Cryst. Growth Des.*, **5**, 1091 (2005); (d) R. Sun, Y.Z. Li, J.F. Bai, Y. Pan. *Cryst. Growth Des.*, **7**, 890 (2007).

[10] G.M. Sheldrick. *SHELX-97*, University of Göttingen, Germany (1997).

[11] (a) W. Chen, J.Y. Wang, C. Chen, Q. Yue, H.M. Yuan, J.S. Chen, S.N. Wang. *Inorg. Chem.*, **42**, 944 (2003); (b) Y.F. Zhou, Y.J. Zhao, D.F. Sun, J.B. Weng, R. Cao, M.C. Hong. *Polyhedron*, **22**, 1231 (2003); (c) J.P. Collin, I.M. Dixon, J.P. Sauvage, J.A.G. Williams, F. Barigelletti, L. Flamigni. *J. Am. Chem. Soc.*, **121**, 5009 (1999).