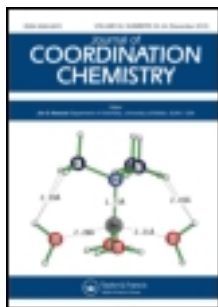


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Syntheses and characterization of four coordination compounds derived from 10,11,12,13-tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene and benzene-dicarboxylic acids

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Syntheses and characterization of four coordination compounds derived from 10,11,12,13-tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene and benzene-dicarboxylic acids

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[Co₂(TTBT)₄(1,2-BDC)₂]_n · 4nH₂O (**1**), [Pb₂(TTBT)₂(1,3-BDC)₂]_n · nTTBT · 2nH₂O (**2**), [Fe(TTBT)(1,4-BDC)(H₂O)]_n (**3**), and [Zn(TTBT)(1,4-BDC)(H₂O)]_n (**4**) have been hydrothermally synthesized by self-assembly of TTBT (TTBT = 10,11,12,13-tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene), benzene-dicarboxylic acid ligands 1,2-H₂BDC, 1,3-H₂BDC or 1,4-H₂BDC (1,2-H₂BDC = 1,2-benzenedicarboxylic acid, 1,3-H₂BDC = 1,3-benzenedicarboxylic acid, 1,4-H₂BDC = 1,4-benzenedicarboxylic acid), and various metal salts. Compound **1** has dinuclear cluster units, four dimeric Co₂ units connected to form a 32-membered ring *via* weak offset π - π interactions, which are further stacked *via* strong π - π interactions to form a 3-D supramolecular framework. Complex **2** contains 2-D layers with rhombohedral grids, which are connected to a 3-D structure by π - π interactions. **3** and **4** feature 1-D infinite chains, which are further extended by strong π - π interactions and O-H...O hydrogen bonds resulting in 3-D supramolecular architectures. The photoluminescent properties of **2** and **4** have also been investigated.

Keywords: 10,11,12,13-Tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene; Benzenedicarboxylic acid; Hydrothermal; Crystal structure

1. Introduction

Design and construction of discrete and polymeric metal-organic frameworks (MOFs) have attracted interest due to intriguing architectures and framework topologies, and also applications in luminescence, magnetism, gas storage, catalysis, etc. [1–4]. Formation of MOFs with desirable supramolecular systems is generally achieved by assembling judiciously selected molecular building blocks [5–7]. A variety of coordination compounds with different structures based on different bridging aromatic

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multicarboxylate ligands, 1,2-benzenedicarboxylic acid (1,2-H₂BDC), 1,3-benzenedicarboxylic acid (1,3-H₂BDC), and 1,4-benzenedicarboxylic acid (1,4-H₂BDC) [8–10], have been synthesized. Benzenedicarboxylic acids (H₂BDC) possess interesting features beneficial to formation of multifold coordination structures owing to diverse coordination modes of carboxylates. Also, 1,10-phenanthroline (phen) and derivatives have been widely used to build supramolecular architectures owing to large conjugated systems that can easily form π - π interactions [11–15]. 10,11,12,13-Tetrahydro-4,5,9,14-tetraazabenzob[b]triphenylene (TTBT) is an important derivative of phen; to the best of our knowledge, coordination compounds constructed by TTBT have rarely been reported [16, 17]. During our preparation of MOFs based on TTBT in combination with aromatic carboxylates, [Co₂(TTBT)₄(1,2-BDC)₂]_n·4nH₂O (**1**), [Pb₂(TTBT)₂(1,3-BDC)₂]_n·nTTBT·2nH₂O (**2**), [Fe(TTBT)(1,4-BDC)(H₂O)]_n (**3**), and [Zn(TTBT)(1,4-BDC)(H₂O)]_n (**4**) were hydrothermally synthesized. Luminescent properties of **2** and **4** are also examined.

2. Experimental

2.1. General materials and methods

TTBT was synthesized by the procedure described previously [18]. Other chemicals were obtained commercially and used without purification. Infrared spectra were recorded from 400 to 4000 cm⁻¹ on a Perkin-Elmer 2400LSII spectrometer using KBr pellets. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 C element analyzer. Luminescent properties of **2** and **4** were measured on a Perkin-Elmer LS55 spectrometer.

2.2. Syntheses of the complexes

2.2.1. [Co₂(TTBT)₄(1,2-BDC)₂]_n·6nH₂O (1**).** A mixture of Co(NO₃)₂·6H₂O (0.0291 g, 0.1 mmol), TTBT (0.0286 g, 0.1 mmol), 1,2-H₂BDC (0.0166 g, 0.1 mmol) and 15 mL of H₂O was stirred for 30 min, and then the pH was adjusted to 6 with 1 mol L⁻¹ NaOH. Subsequently, the mixture was transferred to a 25 mL Teflon-lined stainless steel bomb, kept at 170°C under autogenous pressure for 3 days and cooled to ambient temperature at 5°C h⁻¹. Brown block crystals were obtained by filtration, washed with water and ethanol, and dried in air. Yield: 53% (based on Co). Anal. Calcd for C₈₈H₇₂N₁₆O₁₂Co₂ (%): C, 63.54; H, 4.36; N, 13.47. Found (%): C, 62.23; H, 4.37; N, 13.17. IR (KBr pellet, cm⁻¹): 3412(s), 2938(w), 1603(m), 1558(s), 1439(w), 1399(s), 1376(s), 1309(w), 1217(w), 1083(w), 827(m), 739(s), 650(m).

2.2.2. [Pb₂(TTBT)₂(1,3-BDC)₂]_n·nTTBT·2nH₂O (2**).** A mixture of Pb(NO₃)₂ (0.0331 g, 0.1 mmol), TTBT (0.0286 g, 0.1 mmol), 1,3-H₂BDC (0.0166 g, 0.1 mmol) and 15 mL of H₂O was stirred for 30 min, and then the pH was adjusted to 6 with 1 mol·L⁻¹ NaOH. Subsequently, the mixture was transferred to a 25 mL Teflon-lined stainless steel bomb, kept at 170°C under autogenous pressure for 3 days and cooled to ambient temperature at 5°C h⁻¹. Pale yellow block crystals were obtained by filtration,

washed with water and ethanol, and dried in air. Yield: 59% (based on Pb). Anal. Calcd for $C_{70}H_{54}N_{12}O_{10}Pb_2$ (%): C, 51.34; H, 3.32; N, 10.26. Found (%): C, 51.30; H, 3.34; N, 10.23. IR (KBr pellet, cm^{-1}): 3442(s), 2931(m), 1663(w), 1598(s), 1543(s), 1428(m), 1378(s), 1214(w), 1081(w), 826(m), 746(s), 714(s), 636(w).

2.2.3. [Fe(TTBT)(1,4-BDC)(H₂O)]_n (3). A mixture of $FeSO_4 \cdot 7H_2O$ (0.0278 g, 0.1 mmol), TTBT (0.0286 g, 0.1 mmol), 1,4-H₂BDC (0.0166 g, 0.1 mmol) and 15 mL of H₂O was stirred for 30 min, and then the pH was adjusted to 6 with 1 mol L⁻¹ NaOH. Subsequently, the mixture was transferred to a 25 mL Teflon-lined stainless steel bomb, kept at 170°C under autogenous pressure for 3 days and cooled to ambient temperature at 5°C h⁻¹. Brown block crystals were obtained by filtration, washed with water and ethanol, and dried in air. Yield: 77% (based on Fe). Anal. Calcd for $C_{26}H_{20}N_4O_5Fe$ (%): C, 59.56; H, 3.84; N, 10.69. Found (%): C, 59.57; H, 3.81; N, 10.67. IR (KBr pellet, cm^{-1}): 3430(s), 2936(s), 1639(m), 1475(w), 1449(s), 1420(s), 1400(s), 1374(s), 1217(m), 1181(w), 1155(w), 1126(w), 1087(w), 877(w), 815(s), 732(s), 585(m).

2.2.4. [Zn(TTBT)(1,4-BDC)(H₂O)]_n (4). Synthesis of **4** followed the similar process for **3** except using $ZnSO_4 \cdot 7H_2O$ instead of $FeSO_4 \cdot 7H_2O$. Yellow block crystals were obtained in 81% yield based on Zn(II). Anal. Calcd for $C_{26}H_{20}N_4O_5Zn$ (%): C, 58.49; H, 3.78; N, 10.49. Found (%): C, 58.47; H, 3.82; N, 10.47. IR (KBr pellet, cm^{-1}): 3435(m), 2933(m), 1715(w), 1571(s), 1520(m), 1398(s), 1378(s), 1220(m), 1128(w), 1085(m), 921(m), 884(m), 751(s), 739(s), 542(s).

2.3. X-ray diffraction determination

Diffraction intensities of **1** and **2**, at 292 k, were collected on a Bruker-AXS Smart CCD diffractometer equipped with a normal-focus, 2.4 kW X-ray source (graphite-monochromated Mo-K α radiation with $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 40 mA with increasing ω (width of 0.3° and exposure time 30 s per frame). Single crystals of **3** and **4** were put on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) at a temperature of 292 k. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXS 97 and SHELXL 97, respectively [19, 20]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for the four complexes are listed in table 1, and selected bond lengths (Å) and angles (°) in table 2.

3. Results and discussion

3.1. Crystal structures of 1–4

The fundamental building unit of **1** is shown in figure 1. Solid **1** features an isolated dinuclear Co^{II} cluster, and the asymmetric unit is composed of one Co^{II}, two TTBT groups, one 1,2-BDC²⁻ and lattice water. Each Co^{II} is bonded to four nitrogen donors

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

Complex	1	2	3	4
Empirical formula	C ₈₈ H ₇₂ N ₁₆ O ₁₂ Co ₂	C ₇₀ H ₅₄ N ₁₂ O ₁₀ Pb ₂	C ₆₄ H ₃₀ N ₄ O ₅ Fe	C ₆₄ H ₃₀ N ₄ O ₅ Zn
Formula weight	1663.48	1637.63	524.31	533.83
Crystal color	Brown	Yellow	Brown	Yellow
Crystal size (mm ³)	0.877 × 0.370 × 0.170	0.400 × 0.310 × 0.192	0.411 × 0.353 × 0.305	0.323 × 0.282 × 0.254
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Fddd	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions (Å, °)				
<i>a</i>	15.494(2)	10.465(2)	10.766(2)	10.599(2)
<i>b</i>	42.157(7)	15.003(3)	14.053(3)	14.094(3)
<i>c</i>	47.986(8)	38.178(8)	14.726(3)	14.824(3)
α	90	90	90	90
β	90	96.371(3)	90.89(3)	92.45(3)
γ	90	90	90	90
Volume (Å ³)	31,344(8)	5958(2)	2227.7(8)	2212.3(8)
<i>Z</i>	16	4	4	4
Temperature (K)	292(2)	292(2)	292(2)	292(2)
Reflections collected	62,069	50,642	20,861	20,814
Reflections unique	7188	11,798	5003	5020
<i>R</i> (int)	0.0778	0.0815	0.0899	0.0387
<i>S</i> on <i>F</i> ²	1.070	1.031	1.022	1.063
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0703	0.0483	0.0507	0.0332
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.2069	0.0950	0.0992	0.0801
<i>R</i> ₁ (all data) ^c	0.1079	0.0984	0.0981	0.0472
<i>wR</i> ₂ (all data) ^b	0.2384	0.1115	0.1130	0.0840

^a $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$.

^b $wR_2 = \sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$.

^c $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$.

Table 2. Selected bond lengths (Å) and angles (°) for 1–4.

Complex 1					
Co1–O1	2.029(3)	Co1A–O2	2.053(3)	Co1–N1	2.206(4)
Co1–N2	2.152(4)	Co1–N5	2.147(4)	Co1–N6	2.134(4)
O1–Co1–N1	95.14(13)	O1–Co1–N6	167.75(13)	O1–Co1–N5	90.50(13)
O1–Co1–O2A	92.83(13)	O2A–Co1–N5	94.30(14)	N2–Co1–N1	76.05(14)
Complex 2					
Pb1–O1	2.536(5)	Pb1–O2	2.7620	Pb1–O3	2.694(5)
Pb1–O4	2.545(5)	Pb1–O5	2.8580	Pb1–N1	2.546(6)
Pb1–N2	2.672(6)	Pb2–O5	2.721(7)	Pb2–O6	2.388(6)
Pb2–O7	2.222(6)	Pb2–N9	2.588(8)	Pb2–N10	2.716(7)
O1–Pb1–O4	81.50(16)	O1–Pb1–N1	79.24(17)	O4–Pb1–N2	120.73(16)
N1–Pb1–N2	62.78(18)	O4–Pb1–O3	49.47(15)	N1–Pb1–O3	76.29(16)
O7–Pb2–O6	88.0(2)	O6–Pb2–N9	74.1(3)	O7–Pb2–N10	71.6(2)
O6–Pb2–O5	50.0(2)	N9–Pb2–N10	61.4(2)	N9–Pb2–O(5)	123.7(2)
Complex 3					
Fe–O1	2.152(2)	Fe–O2	2.329(2)	Fe–O3	2.063(2)
Fe–O1W	2.123(2)	Fe–N1	2.187(3)	Fe–N2	2.176(2)
O1–Fe–O2	59.11(8)	O3–Fe–O1	104.10(8)	O1W–Fe–O1	147.00(9)
O3–Fe–N2	165.82(9)	O1W–Fe–N1	122.29(10)	O3–Fe–O1W	88.13(9)
Complex 4					
Zn–N1	2.1809(16)	Zn–N2	2.1474(18)	Zn–O1	2.0388(16)
Zn–O1W	2.0610(17)	Zn–O3	2.0415(14)		
O1–Zn–O3	101.52(6)	O1–Zn–O1W	139.59(7)	O3–Zn–O1W	89.54(7)
O1–Zn–N2	97.48(7)	O3–Zn–N2	93.42(6)	O1W–Zn–N2	120.76(7)
O1–Zn–N1	87.86(6)	O3–Zn–N1	167.29(6)	O1W–Zn–N1	88.74(7)

Symmetry transformations used to generate equivalent atoms: A: $-x+3, -y+1, -z$.

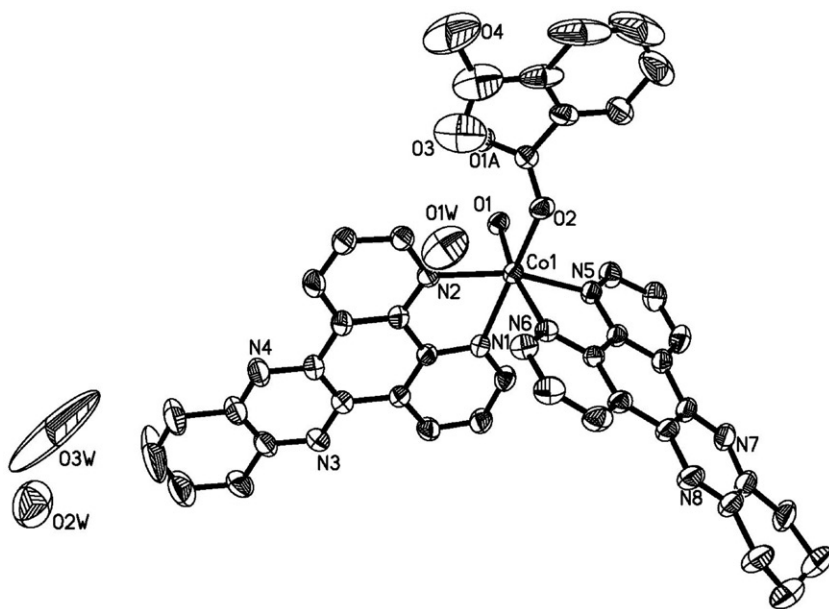
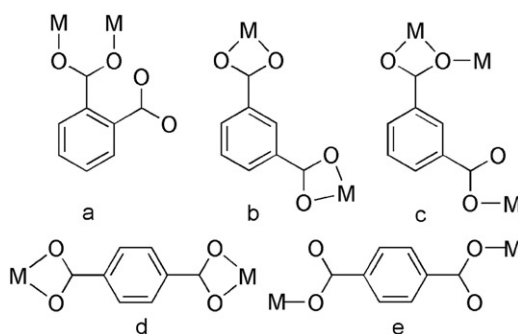


Figure 1. The coordination environment of Co(II) ion in complex 1 with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. Symmetry code: A: $1-x, 1-y, -z$.



Scheme 1. Coordination modes of benzene-dicarboxylic acid ligands in complexes **1–4**.

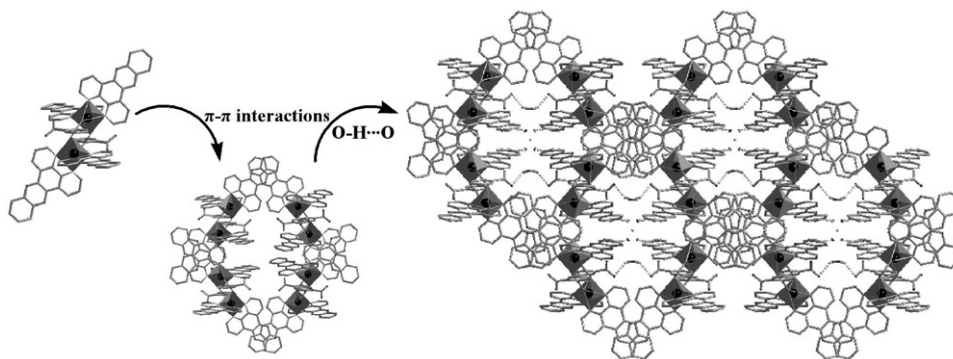


Figure 2. Polyhedral representation of dimeric Co_2 unit, 32-membered ring *via* offset π - π interactions and $\text{O-H}\cdots\text{O}$ supramolecular framework of **1**.

(N1, N2, N5, N6) of two TTBT and two oxygen atoms (O1, O2) from two 1,2-BDC²⁻ ligands in distorted octahedral coordination. In this complex, only one carboxyl of 1,2-BDC²⁻ coordinates bidentate to two adjacent Co^{II} centers (scheme 1a), whereas the other carboxyl remains free. Coordination of 1,2-BDC²⁻ is different from the reported modes in $[\text{Cd}(\text{o-bdc})(\text{bth})_{0.5}(\text{H}_2\text{O})]_n$ [21] and $\{[\text{Zn}(\text{btp})(1,2\text{-bdc})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ [22]. The four dimeric Co_2 units connect to form a 32-membered ring *via* weak offset π - π interactions between TTBT ligands (with average distance of 3.76 Å), with eight Co^{II} ions, sixteen TTBT ligands, and eight 1,2-BDC²⁻. All 32-membered rings stack with each other to form a 3-D framework by π - π interactions between TTBT ligands (figure 2). Intermolecular $\text{O-H}\cdots\text{O}$ hydrogen bonds appear in **1** [$\text{O1W-H1WA}\cdots\text{O2W}$, 2.006 Å, 134.87°, symmetry code = $-x + 7/4, y, -z - 1/4$], contributing to the stability of annular and supramolecular structure.

As depicted in figure 3, the asymmetric unit of **2** contains two crystallographically inequivalent Pb^{II} ions, two TTBT, two 1,3-BDC²⁻, one lattice TTBT and two free waters. Pb1 is seven-coordinate, supplied by two nitrogen atoms (N1, N2) from one bidentate TTBT and five oxygen atoms (O1, O2, O3, O4, and O5) from three 1,3-BDC²⁻, two coordinated with center metal by weak interaction. Pb2 adopts a distorted tetragonal-bipyramidal geometry with two nitrogen atoms (N9 and N10) from one

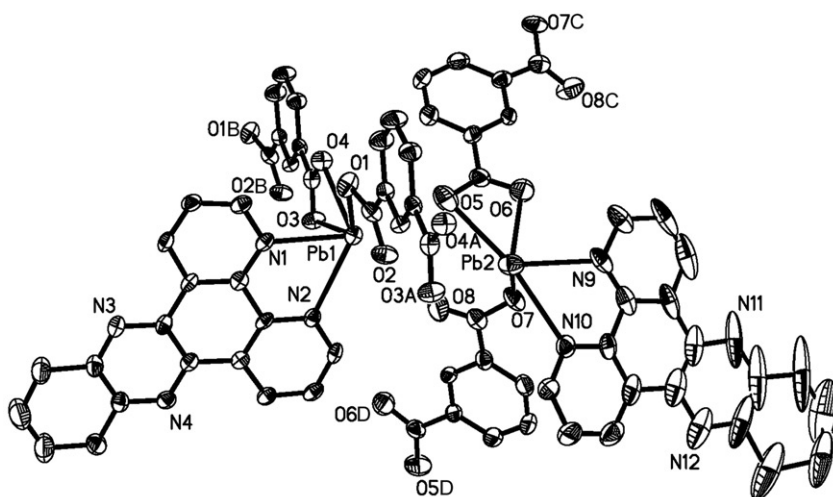


Figure 3. The coordination environment of Pb(II) ion in complex **2** with 30% thermal ellipsoids, all hydrogen atoms, free TTBT ligand, and free water molecules are omitted for clarity. Symmetry code: A: $1+x, y, z$; B: $-1+x, y, z$; C: $1-x, -1/2+y, 1/2-z$; D: $1-x, 1/2+y, 1/2-z$.

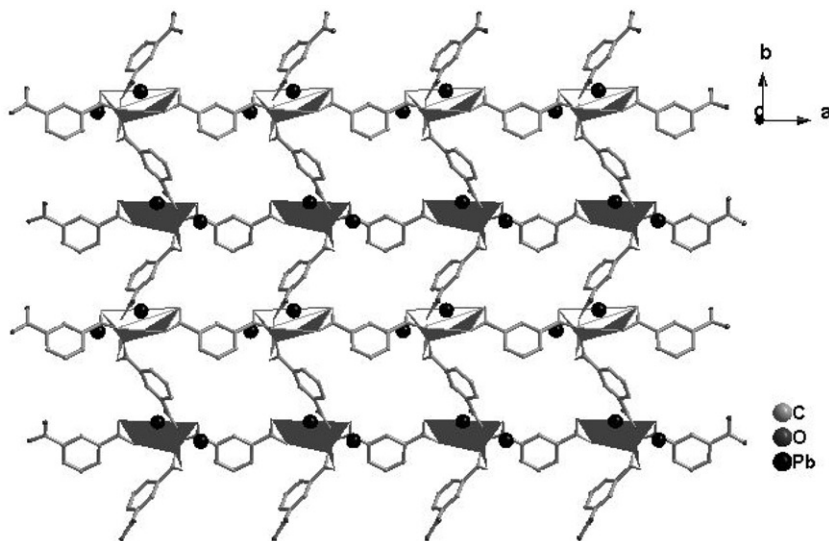


Figure 4. Polyhedral views of 2-D layers of **2**.

TTBT and three oxygen atoms (O5, O6, and O7) from two 1,3-BDC²⁻ ligands, and an electron lone pair [23]. The 1,3-BDC²⁻ ligands adopt b or c coordination modes in **2** (scheme 1), bis-chelating (this coordination mode is the same as in $\{[\text{Cd}_2(\text{btrm})(\text{ip})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ [24]) and chelating/bridging-monodentate. Coordination of 1,3-BDC²⁻ in **2** is different from $[\text{Zn}(\text{m-bdc})(\text{bth})]_n$ [21] and $\{[\text{Zn}(\text{btp})(1,3\text{-bdc})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}\}_n$ [22]. Compound **2** generates a 2-D network

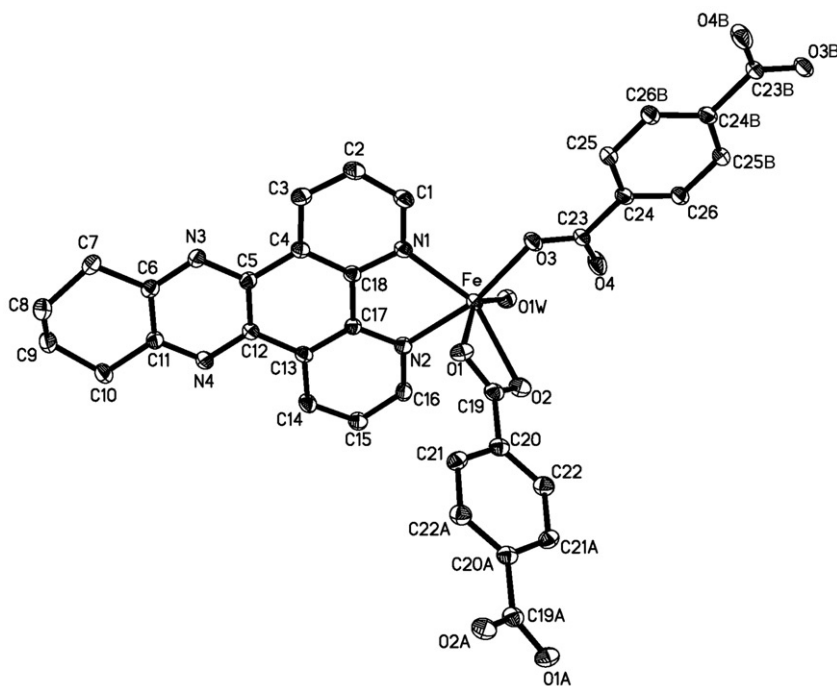


Figure 5. The coordination environment of Fe(II) ion in complex **3** with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. Symmetry code: A: $1-x, 1-y, 1-z$; B: $2-x, -y, 1-z$.

along the *ab* plane (figure 4) with unique rhombohedral grids (size *ca* $10.47 \times 10.32 \text{ \AA}^2$), similar with $[\text{Co}_2(\text{H}_2\text{O})(\text{TATP})_2(\text{oba})_2]_n \cdot 2n\text{H}_2\text{O}$ and $[\text{Ni}_2(\text{H}_2\text{O})(\text{TATP})_2(\text{oba})_2]_n \cdot 2n\text{H}_2\text{O}$ [25]. Free and coordinating TTBT have face-to-face or offset π - π interactions (*ca* 3.60 \AA and 3.54 \AA) to generate an interesting 3-D supramolecular motif. Finally, O-H \cdots N hydrogen bonds involving water O1W and N7 of the free TTBT acceptors [O1W-H1WA \cdots N(7), 2.529 \AA , 158.74°] complete the structure of **2**.

For **3**, Fe^{II} is coordinated by two nitrogen atoms from one TTBT, four oxygen atoms from two different 1,4-BDC²⁻ and one water (figure 5). The Fe-N1 and Fe-N2 distances are $2.187(3) \text{ \AA}$ and $2.176(2) \text{ \AA}$, respectively. Fe-O distances are $2.063(2)$ – $2.329(2) \text{ \AA}$. The coordination geometry of Fe^{II} can be described as trigonal prismatic. Carboxyl groups of 1,4-BDC²⁻ in **3** exhibit different coordination modes, one is two carboxylates of 1,4-BDC²⁻ chelated two Fe^{II} and the other is each carboxylate of 1,4-BDC²⁻ bonded to one Fe^{II} (scheme 1d, 1e). Coordination of 1,4-BDC²⁻ is different from reported modes in $[\text{Cd}_3(\text{MeHbiim})_2(1,4\text{-BDC})_3]_n$ [26]. Fe^{II} ions are bridged by 1,4-BDC²⁻ into 1-D infinite single-strand zigzag chains (figure 6) viewed along the *b*-axis. Additionally, the zigzag chains are extended into 2-D sheets by hydrogen bonds between hydrogen from coordinated water and oxygen [O2, O4] of carboxyl groups [O1W-H1WA \cdots O2, 2.787 \AA , 168.63° , symmetry code = $-x, -y + 1, -z + 1$, and O1W-H1WB \cdots O4, 2.569 \AA , 162.26°]. These 2-D layers are stacked to generate a 3-D supramolecular network through π - π interactions between parallel TTBT and 1,4-BDC²⁻ (the shortest centroid-to-centroid distance being 3.61 \AA).

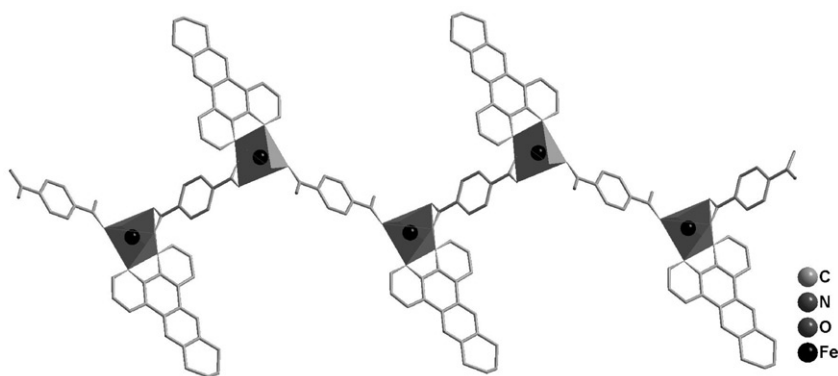
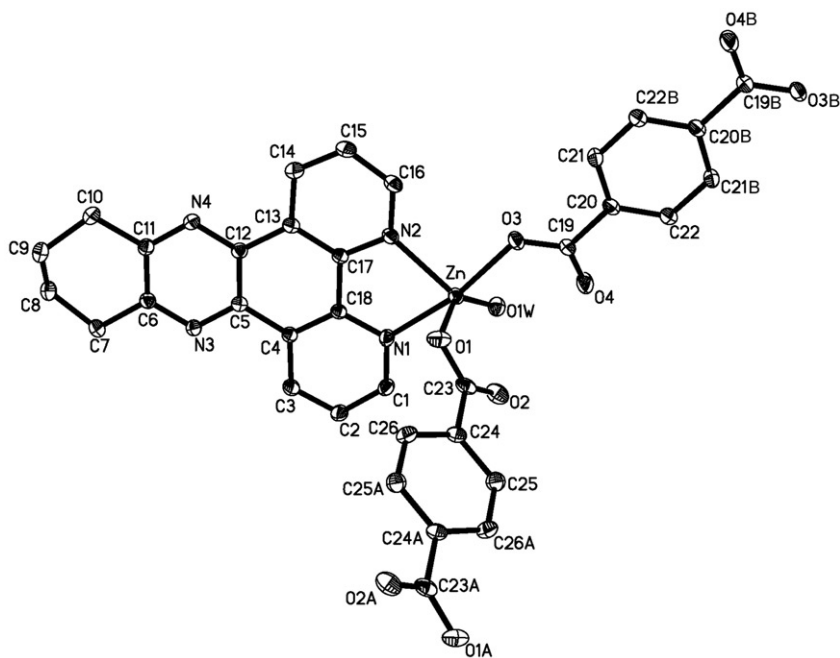


Figure 6. Structure of the 1-D chain in 3.

Figure 7. The coordination environment of Zn(II) ion in complex 4 with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. Symmetry code: A: $2-x, 1-y, 1-z$; B: $1-x, 2-y, 1-z$.

As shown in figure 7, Zn^{II} is coordinated by two nitrogen atoms from one TTBT, three oxygen atoms from two $1,4\text{-BDC}^{2-}$ and one water in 4. The Zn–N1 and Zn–N2 distances are 2.1809(16) Å and 2.1474(18) Å, respectively. Zn–O distances are 2.0388(16)–2.0610(17) Å. The coordination geometry of Zn^{II} can be described as a distorted pyramid. In 4, every $1,4\text{-BDC}^{2-}$ bridges two neighboring Zn^{II} ions in bis-monodentate mode (scheme 1e), generating 1-D infinite single zigzag chains (figure 8) viewed along the *b*-axis. The zigzag chains are extended into 2-D sheets by hydrogen bonds between hydrogen from coordinated water and oxygen [O2, O4] of carboxyl

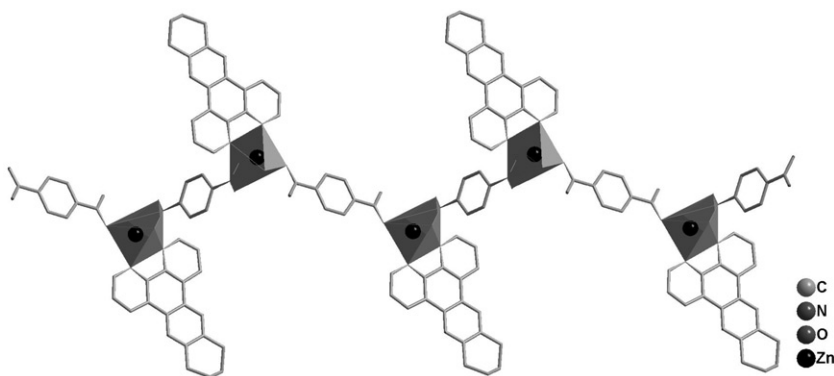


Figure 8. The 1-D zigzag polymeric chain of **4**.

groups [O1W–H1WB···O2, 2.740 Å, 174.58°, symmetry code = $-x + 1, -y + 1, -z + 1$, and O1W–H1WA···O4, 2.571 Å, 160.80°]. There exist π – π interactions between TTBT and 1,4-BDC²⁻ of neighboring chains (the shortest centroid-to-centroid distance being 3.62 Å), connecting the 2-D layers by π – π interactions to form a 3-D supramolecular network.

The effects of the aromatic acid on **1–4** have been clearly demonstrated by X-ray single-crystal diffraction. Through varying organic acid linkers under similar synthetic conditions, four related complexes were isolated and exhibit some differences in their architectures. Complex **1** exhibits a dinuclear cluster unit. Complex **2** contains a 2-D network with unique rhombohedral grids, in which 1,3-BDC²⁻ ligands connect the dinuclear or trinuclear Pb(II) units into layers. Complexes **3** and **4** are 1-D wavy chains, with TTBT attached to two sides of the chain. In contrast with **3** and **4**, variation of the binding of the carboxylates have been observed through selecting metal centers with dissimilar coordination preferences. The results show that the coordination mode of 1,4-H₂BDC is changeable when assembling to a given metal center under similar synthetic conditions, attributed to metal-controlled assembly; the metal plays a crucial and steering role in the binding of carboxylate.

3.2. Luminescent properties

Luminescent compounds are of interest because of applications in display devices, solar-energy conversion and chemical sensors [27–29]. The photoluminescent (PL) properties of **2** and **4** were studied in the solid state at room temperature. As indicated in figure 9, the maximum emission wavelength occurs at 612 nm for **2** and 526 nm for **4** upon excitation at 365 nm. To understand these emission bands, luminescent properties of free 1,3-H₂BDC, 1,4-H₂BDC, and TTBT were analyzed, showing they exhibit strongest emission peaks at 382 nm, 378 nm [16], and 549 nm [17], respectively. On complexation of the ligands with Pb²⁺, the emission was not observable. Emission of **2** could originate from a metal-centered transition involving the s and p metal orbitals, as proposed by Vogler *et al.* [30]. Comparing the PL spectra of **4** and free ligands, the

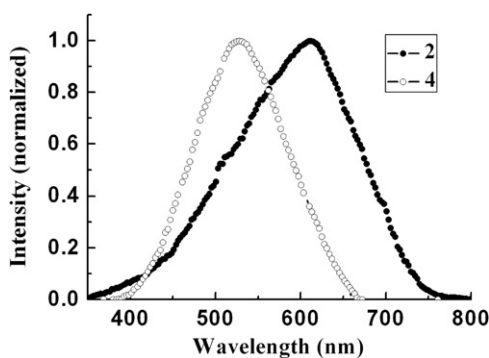


Figure 9. Normalized PL spectra of **2** and **4** under excitation with 365 nm UV light.

emission spectrum of **4** is similar to that of TTBT, attributable to intraligand fluorescent emissions of TTBT [15].

4. Conclusions

Four coordination compounds have been prepared by using TTBT and 1,2-H₂BDC, 1,3-H₂BDC, or 1,4-H₂BDC with metallic salts under hydrothermal conditions. The results indicate that introduction of different metal ions and benzenedicarboxylates with various coordination modes may be a key for controlling formation and dimension of the resulting structures. Weak interactions, such as π - π stacking and O-H...O (or O-H...N) interactions, connect 0-D cluster unit, 1-D chains or 2-D layers to generate 3-D supramolecular networks. Strong luminescence of **2** and **4** may make them excellent candidates for photoactive materials. Further studies on analogous functional solids are underway in our laboratory.

Supplementary material

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 804492, 804493, 804495, and 804494 for **1-4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk; Fax: 44-1223-336-033; <http://www.ccdc.cam.ac.uk>).

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References

- [1] X.Y. Yu, J. Lu, J.H. Yu, X. Zhang, J.Q. Xu, T.G. Wang. *Z. Anorg. Allg. Chem.*, **633**, 490 (2007).
- [2] M.Y. Wu, D.Q. Yuan, Y.G. Huang, W. Wei, Q. Gao, F.L. Jiang, M.C. Hong. *Cryst. Growth Des.*, **7**, 1146 (2007).
- [3] B. Kesanli, Y. Cui, M.R. Smith, E.W. Bittner, B.C. Bockrath, W.B. Lin. *Angew. Chem., Int. Ed.*, **44**, 72 (2005).
- [4] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994).
- [5] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Science*, **423**, 705 (2003).
- [6] D. Tanaka, S. Kitagawa. *Chem. Mater.*, **20**, 922 (2008).
- [7] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem.*, **116**, 2388 (2004).
- [8] Y.H. Wan, L.P. Zhang, L.P. Jin, S. Gao, Z. Lu. *Inorg. Chem.*, **42**, 4985 (2003).
- [9] X.J. Gu, D.F. Xue. *Cryst. Growth Des.*, **6**, 2551 (2006).
- [10] X.D. Guo, G.S. Zhu, F.X. Sun, Z.Y. Li, X.J. Zhao, X.T. Li, H.C. Wang, S.L. Qiu. *Inorg. Chem.*, **45**, 2581 (2006).
- [11] G. Marinescu, M. Andruh, M. Julve, F. Lloret, R. Llusar, S. Uriel, J. Vaissermann. *Cryst. Growth Des.*, **5**, 261 (2005).
- [12] Y.J. Qi, Y.H. Wang, C.W. Hu, M.H. Cao, L. Mao, E. Wang. *Inorg. Chem.*, **42**, 8519 (2003).
- [13] G.B. Che, C.B. Liu, B. Liu, Q.W. Wang, Z.L. Xu. *CrystEngComm*, **10**, 184 (2008).
- [14] J. Yang, J.F. Ma, Y.Y. Liu, J.C. Ma, S.R. Batten. *Inorg. Chem.*, **46**, 6542 (2007).
- [15] X.Y. Li, C.B. Liu, G.B. Che, X.C. Wang, C.X. Li, Y.S. Yan, Q.F. Guan. *Inorg. Chim. Acta*, **363**, 1359 (2010).
- [16] G.B. Che, J. Wang, B. Liu, X.Y. Li, C.B. Liu. *J. Coord. Chem.*, **62**, 302 (2009).
- [17] G.B. Che, J. Wang, C.B. Liu, X.Y. Li, B. Liu, J. Sun, Y. Liu, L. Lu. *Inorg. Chim. Acta*, **362**, 2756 (2009).
- [18] G.B. Che, W.L. Li, Z.G. Kong, Z.S. Su, B. Chu, B. Li, Z.Q. Zhang, Z.Z. Hu, H.J. Chi. *Synth. Commun.*, **36**, 2519 (2006).
- [19] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
- [20] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
- [21] P. Zhang, D.-S. Li, J. Zhao, Y.-P. Wu, C. Li, K. Zou, J.Y. Lu. *J. Coord. Chem.*, **64**, 2329 (2011).
- [22] J. Wang, X. Qian, Y.-F. Cui, B.-L. Li, H.-Y. Li. *J. Coord. Chem.*, **64**, 2878 (2011).
- [23] J. Yang, G.D. Li, J.J. Cao, Q. Yue, G.H. Li, J.S. Chen. *Chem. Eur. J.*, **13**, 3248 (2007).
- [24] L. Tian, L. Yan, S.-Y. Liu. *J. Coord. Chem.*, **64**, 2945 (2011).
- [25] Z.B. Han, X.N. Cheng, X.M. Chen. *Cryst. Growth Des.*, **5**, 695 (2005).
- [26] L.-N. Yang, Y.-X. Zhi, J.-H. Hei, J. Li, F.-X. Zhang, S.-Y. Gao. *J. Coord. Chem.*, **64**, 2912 (2011).
- [27] G.B. Che, Z.S. Su, W.L. Li, B. Chu, M.T. Li, Z.Z. Hu, Z.Q. Zhang. *Appl. Phys. Lett.*, **89**, 103511-1 (2006).
- [28] Z.L. Xu, C.H. Xu, Q.W. Wang, W.L. Jiang, C.B. Liu, L.H. Liu, M. Liu, W.L. Li, G.B. Che, F.N. Shi. *Synth. Met.*, **160**, 2260 (2010).
- [29] L.F. Shi, B. Li, S.Z. Lv, D.X. Zhu, W.L. Li. *Appl. Organomet. Chem.*, **23**, 379 (2009).
- [30] A. Vogler, A. Paukner, H. Kunkely. *Coord. Chem. Rev.*, **33**, 227 (1980).