

Substituent effect on the assembly of coordination polymers containing isophthalic acid and its derivatives†

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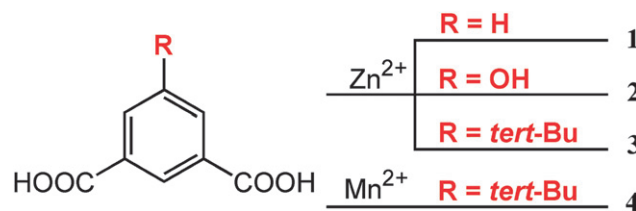
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Four coordination polymers $[\text{Zn}_4(\text{H}_2\text{O})(\text{ip})_4(\text{py})_6]_n$ **1**, $\{[\text{Zn}_2(\text{hip})_2(\text{py})_4]_2 \cdot (\text{py})\}_n$ **2**, $[\text{Zn}(\text{tbip})(\text{py})_2]_n$ **3** and $[\text{Mn}(\text{tbip})(\text{py})_2]_n$ **4** (H_2ip = isophthalic acid, H_2hip = 5-hydroxyisophthalic acid, H_2tbip = 5-*tert*-butylisophthalic acid, py = pyridine), have been hydrothermally synthesized and characterized. The photoluminescent properties of **1–3** have also been investigated. For **1–3**, as substituents change from H, OH to *tert*-butyl, the coordination numbers of Zn^{2+} ions decrease, and the dimensionalities of the structures of **1–3** decrease from 2D (4,4) net, 1D double stranded chain to 1D chain. For **3** and **4**, as Mn^{2+} tends to have a higher coordination number as compared to Zn^{2+} , the structure of **4** is a 2D (4,4) net while the structure of **3** is a 1D chain. The substituents on isophthalic acid influence the coordination environments of metal ions and the coordination modes of the carboxyls, and thus determine the structures of the coordination polymers. The coordination behavior of metal ions also affects the formation of the structures.

1. Introduction

The crystal engineering of coordination polymers (CPs) has attracted great interest within inorganic chemistry in recent years. Many efforts have been made to control the structures of CPs as their properties and potential applications are determined by their structures.^{1–6} A better understanding of the factors that control the structures is a prerequisite for improving the ability to rationally design and synthesize CPs functional materials. Organic ligands are easily modified with different substituents, and as a result their coordination modes can be influenced by the substituents. This strategy is crucial in controlling the structures and tuning the properties of CPs.^{7–11} A lot of CPs containing isophthalic acid^{12–28} or its derivatives,^{29–45} with or without nitrogen heteroaromatic ligands, have been reported recently. However, systematic studies on the influence of the substituents on the structures of CPs are rare.^{8–11} As a part of our ongoing research of the influence on the assembly of CPs,^{46–49} we selected 5-substituted isophthalic acids as ligands, and pyridine as an ancillary ligand, to react with metal ions in this study. Herein we would like to report the hydrothermal syntheses and structures of four CPs: $[\text{Zn}_4(\text{H}_2\text{O})(\text{ip})_4(\text{py})_6]_n$ **1**, $\{[\text{Zn}_2(\text{hip})_2(\text{py})_4]_2 \cdot (\text{py})\}_n$ **2**, $[\text{Zn}(\text{tbip})(\text{py})_2]_n$ **3** and $[\text{Mn}(\text{tbip})(\text{py})_2]_n$ **4**. (H_2ip = isophthalic acid, H_2hip = 5-hydroxyisophthalic acid, H_2tbip = 5-*tert*-butylisophthalic acid, py = pyridine) (Scheme 1).



Scheme 1

2. Experimental

2.1. Materials and methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 740 FTIR Spectrometer at the range of 4000–400 cm^{-1} . Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescent properties were measured on a Hitachi F-4500 Fluorescence Spectrophotometer. X-Ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with $\text{Cu K}\alpha$ radiation.

2.2. Syntheses

2.2.1. $[\text{Zn}_4(\text{H}_2\text{O})(\text{ip})_4(\text{py})_6]_n$ **1.** A suspension of isophthalic acid (H_2ip , 0.166 g, 1.00 mmol) in H_2O (12 ml) was slowly added to pyridine until the pH of the solution was adjusted to 7, then $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.296 g, 1.00 mmol) was added. The mixture was placed in a 20 ml Teflon-lined vessel, heated to 170 °C at the rate of 0.2 °C min^{-1} , and kept at 170 °C for 3 d, then slowly cooled down to room temperature at a rate of 0.1 °C min^{-1} . Colorless platelet crystals (0.103 g, yield 29.2%) were separated by filtration, washed with deionized water and dried in air. Elemental analysis: $\text{C}_{62}\text{H}_{48}\text{N}_6\text{O}_{17}\text{Zn}_4$, found (calc.) C 52.64 (52.79), H 3.39 (3.43), N 5.89 (5.96)%. FTIR (KBr, cm^{-1}):

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† Electronic supplementary information (ESI) available: Selected bond lengths and angles, X-ray powder diffraction patterns and IR spectra of the compounds. CCDC reference numbers 725966, 715534, 725967 and 725968 for **1**, **2**, **3** and **4**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907142c

3428 (m), 1642 (vs), 1606 (s), 1562 (m), 1453 (s), 1397(vs), 1042 (m), 697 (s), 641 (m).

2.2.2. $\{[\text{Zn}_2(\text{hip})_2(\text{py})_4]_2 \cdot (\text{py})\}_n$ 2. A suspension of 5-hydroxyisophthalic acid (H_2hip , 0.091 g, 0.50 mmol) in H_2O (10 ml) and pyridine (0.50 ml) was slowly added with NaOH aqueous solution (2 mol L^{-1}) until the pH of the solution was adjusted to 7, then $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 g, 0.50 mmol) was added. The mixture was treated as that with **1** and yellow platelet crystals (0.065 g, yield 31%) were obtained. Elemental analysis: $\text{C}_{77}\text{H}_{61}\text{N}_9\text{O}_{20}\text{Zn}_4$, found (calc.) C 54.60 (54.58), H 3.63 (3.67), N 7.52 (7.44). FTIR (KBr, cm^{-1}): 3259(s), 1560 (vs), 1368 (vs), 785 (m), 695 (m).

2.2.3. $[\text{Zn}(\text{tbip})(\text{py})_2]_n$ 3. The synthetic procedure for **3** is the same as that for **2** except that 5-*tert*-butylisophthalic acid (H_2tbip , 0.111 g, 0.50 mmol) was used instead of H_2hip , colorless platelet crystals (0.065 g, yield 29%) were obtained. Elemental analysis: $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Zn}$, found (calc.) C 58.75 (59.54), H 5.04 (5.00), N 6.18 (6.31). FTIR (KBr, cm^{-1}): 3435 (s), 2961(m), 1622 (vs), 1575 (vs), 1369 (vs), 781 (w), 725 (w).

2.2.4. $[\text{Mn}(\text{tbip})(\text{py})_2]_n$ 4. The synthetic procedure for **4** is the same as that for **3** except that 50% $\text{Mn}(\text{NO}_3)_2$ aqueous solution (0.50 ml, 4.3 mmol) was used instead of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, brown platelet crystals (0.146 g, yield 66% based on H_2tbip) were obtained. Elemental analysis: $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Mn}$, found (calc.) C 59.87 (60.97), H 5.05 (5.12), N 6.52 (6.46). FTIR (KBr, cm^{-1}):

3436 (s), 2961(m), 1566 (vs), 1443 (s), 1376 (vs), 1046 (w), 785 (m), 723 (w).

2.3. X-Ray crystallography

Data collection for **1–4** was performed on an Oxford, Gemini S Ultra CCD diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption correction and data reduction were carried out by using the program CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.5. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXS and SHELXL program.⁵⁰ The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Crystal data are summarized in Table 1.

3. Results and discussion

3.1. Structure descriptions

3.1.1. $[\text{Zn}_4(\text{H}_2\text{O})(\text{ip})_4(\text{py})_6]_n$ 1. Single-crystal X-ray diffraction analysis reveals that there are two Zn^{2+} ions, two ip^{2-} (isophthalate), three py and half H_2O in the asymmetric unit of **1**. Zn1 is in a square pyramidal coordination environment, connected to four oxygen atoms from ip^{2-} and one nitrogen atom from py at the axial position. Each pair of Zn1 ions are bridged by four carboxyl groups to form a paddle-wheel SBU. The two Zn1 ions in the SBU are related by an inversion center located at

Table 1 Crystal data for **1–4**^a

Compound	1	2	3	4
Empirical formula	$\text{C}_{62}\text{H}_{48}\text{N}_6\text{O}_{17}\text{Zn}_4$	$\text{C}_{77}\text{H}_{61}\text{N}_9\text{O}_{20}\text{Zn}_4$	$\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Zn}$	$\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Mn}$
Formula weight	1410.54	1693.83	443.79	433.36
Crystal size (mm)	$0.20 \times 0.20 \times 0.10$	$0.40 \times 0.38 \times 0.12$	$0.36 \times 0.25 \times 0.22$	$0.50 \times 0.39 \times 0.30$
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P-1$	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	18.1879(6)	9.9814(3)	7.4965(2)	9.8673(3)
$b/\text{\AA}$	10.6838(3)	11.9312(3)	15.5495(4)	15.6848(4)
$c/\text{\AA}$	31.7400(1)	16.8666(6)	18.1063(4)	13.2389(3)
$\alpha/^\circ$	90	107.263(3)	90	90
$\beta/^\circ$	102.899(4)	95.397(3)	98.516(2)	95.342(2)
$\gamma/^\circ$	90	99.704(2)	90	90
$V/\text{\AA}^3$	6011.9(3)	1868.43(10)	2087.32(9)	2040.04(9)
T/K	295(2) K	173(2)	173(2)	223(2)
$Z, D_{\text{calcd}}/\text{Mg m}^{-3}$	4, 1.558	1, 1.505	4, 1.412	4, 1.411
$F(000)$	2872	866	920	900
μ/mm^{-1}	1.654	1.348	1.207	0.678
$h_{\text{min}}/h_{\text{max}}$	−23/24	−13/13	−9/9	−11/12
$k_{\text{min}}/k_{\text{max}}$	−14/14	−15/16	−21/20	−12/21
$l_{\text{min}}/l_{\text{max}}$	−40/43	−22/22	−23/23	−17/17
Ref. collected/unique	19334/6995	17585/8638	12829/4874	12046/4736
R_{int}	0.0494	0.0253	0.0310	0.0241
Parameters	406	523	265	281
Max./min. transmissions	0.8521/0.7333	0.8550/0.6146	0.7772/0.6706	0.8226/0.7281
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$ $wR_2 = 0.1011$	$R_1 = 0.0274$ $wR_2 = 0.0636$	$R_1 = 0.0303$ $wR_2 = 0.0676$	$R_1 = 0.0395$ $wR_2 = 0.1051$
R indices (all data)	$R_1 = 0.1176$ $wR_2 = 0.1471$	$R_1 = 0.0439$ $wR_2 = 0.0668$	$R_1 = 0.0563$ $wR_2 = 0.0726$	$R_1 = 0.0600$ $wR_2 = 0.1125$
Goodness-of-fit on F^2	0.997	0.952	0.926	1.073
Max/min, $\Delta\rho/e \text{ \AA}^{-3}$	0.449/−0.708	0.361/−0.404	0.368/−0.346	0.609/−0.478
Completeness/%	99.4	99.2	99.5	98.7

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^{1/2}$.

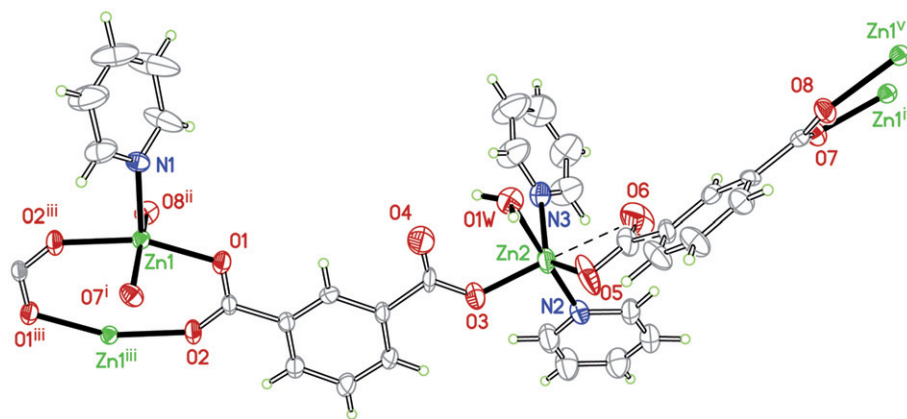


Fig. 1 Coordination geometry in **1** with the thermal ellipsoids at 30% probability level. Symmetry codes: ⁱ $-x, y + 1, -z + 3/2$; ⁱⁱ $x, -y + 1, z + 1/2$; ⁱⁱⁱ $-x, -y + 2, -z + 2$; ^{iv} $-x, y - 1, -z + 3/2$; ^v $x, -y + 1, z - 1/2$.

any of the corners or C-centers of the unit cell. Zn2 is in a distorted tetrahedral geometry, coordinated by two oxygen atoms from ip^{2-} and two nitrogen atoms from py, in addition to two long and weak coordination bonds (Zn2–O1W = 2.440(6), Zn2–O6 = 2.493(6) Å). (Fig. 1, Table 2) In the structure of **1**, SBU acts as a four connecting node, and results in the formation of the 2D

Table 2 Selected bond lengths (Å) and angles (°) for **1**^a

Zn1–O1	2.035(3)	Zn2–O3	1.977(4)
Zn1–O2 ⁱⁱⁱ	2.084(3)	Zn2–O5	1.989(5)
Zn1–O7 ⁱ	2.019(3)	Zn2–N2	2.091(4)
Zn1–O8 ⁱⁱ	2.033(3)	Zn2–N3	2.070(4)
Zn1–N1	2.044(4)	Zn2–O1W	2.440(6)
O7 ⁱ –Zn1–O1	89.43(14)	O1–Zn1–O2 ⁱⁱⁱ	158.82(13)
O1–Zn1–O8 ⁱⁱ	87.11(13)	O3–Zn2–O5	112.98(17)
O7 ⁱ –Zn1–O2 ⁱⁱⁱ	86.93(14)	O3–Zn2–N2	93.34(16)
O8 ⁱⁱ –Zn1–O2 ⁱⁱⁱ	88.65(14)	O3–Zn2–N3	105.92(17)
O1–Zn1–N1	108.88(15)	O5–Zn2–N2	104.93(19)
O7 ⁱ –Zn1–N1	104.18(14)	O5–Zn2–N3	133.12(19)
O8 ⁱⁱ –Zn1–N1	97.08(14)	N3–Zn2–N2	97.69(18)
N1–Zn1–O2 ⁱⁱⁱ	92.23(15)		

^a Symmetry codes: ⁱ $-x, y + 1, -z + 3/2$; ⁱⁱ $x, -y + 1, z + 1/2$; ⁱⁱⁱ $-x, -y + 2, -z + 2$.

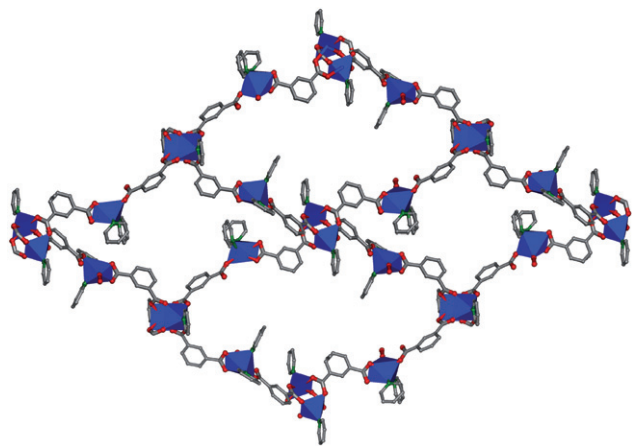


Fig. 2 View of the 2D (4,4) net structure in **1**. Hydrogen atoms are omitted for clarity.

Table 3 Hydrogen-bond geometries for **1** and **2** (Å and °)^a

D–H...A	<i>d</i> (D...A)	∠DHA
1		
O1W–H1A...O4	2.459(8)	149
O1W–H1A...O3	3.081(7)	138
O1W–H1B...O4 ⁱⁱ	2.848(7)	139
2		
O5–H5A...O9 ^{iv}	2.704(2)	180
O10–H10B...O4 ^v	2.655(2)	172

^a Symmetry codes for **1**: ⁱ $-x, y + 1, -z + 3/2$; ⁱⁱ $x, -y + 1, z + 1/2$; ⁱⁱⁱ $-x, -y + 2, -z + 2$; ^{iv} $-x, y - 1, -z + 3/2$; ^v $x, -y + 1, z - 1/2$; for **2**: ⁱ $x - 1, y, z$; ⁱⁱ $x + 1, y, z$; ⁱⁱⁱ $-x + 2, -y + 1, -z$; ^{iv} $x - 1, y + 1, z$; ^v $x + 1, y - 1, z$.

(4,4) net parallel to the *bc* plane. (Fig. 2) The edges of the (4,4) net are 19.131 and 19.388 Å, with two connecting Zn2 ions lying in the middle of the edges. The (4,4) nets pack along the *a* axis with py protruding into the cavities of the crystal structure. The coordinated water molecules form intra- and intermolecular hydrogen bonds to carboxyl oxygen atoms. (Table 3).

3.1.2. {[Zn₂(hip)₂(py)₄]₂·(py)}_n **2.** In the structure of **2**, there are two Zn²⁺ ions, two hip²⁻ (5-hydroxyisophthalate), four coordinated py and half solvent py in the asymmetric unit. The unit cell of **2** contains two asymmetric units related by an inversion center. The solvent pyridine molecules are disordered over two positions and restraints have been applied in the refinement. The Zn²⁺ ions lie in triangle bipyramidal coordination environments, coordinated by three oxygen atoms from three hip²⁻ ligands in the plane, and two nitrogen atoms from py at the apexes. The two carboxyls of hip²⁻ adopt different coordination modes, one is bidentate bridging mode, and the other is monodentate. (Fig. 3) The moieties in **2** are connected by coordination bonds, hydrogen bonds and π – π interactions to form the crystal structure: firstly, pairs of zinc ions are bridged by pairs of carboxyls to form an eight-member-ring dinuclear SBUs,^{9–11} then the SBU expands along the *a* axis to form a 1D double stranded chain; secondly, the chain is connected to adjacent chains along the *b* axis to form hydrogen bonded layers by the intermolecular O–H...O_{carboxylate} hydrogen-bond; (Fig. 4,

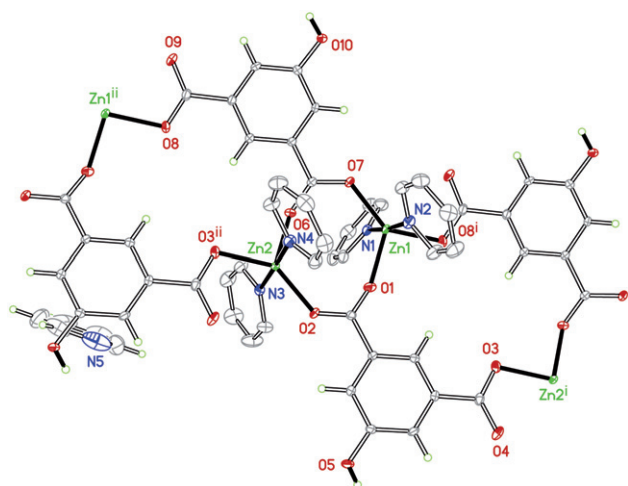


Fig. 3 The coordination geometry in **2** with the thermal ellipsoids at 30% probability level. Hydrogen atoms on coordinated pyridine molecules are omitted for clarity. Symmetry codes: ⁱ $x - 1, y, z$; ⁱⁱ $x + 1, y, z$.

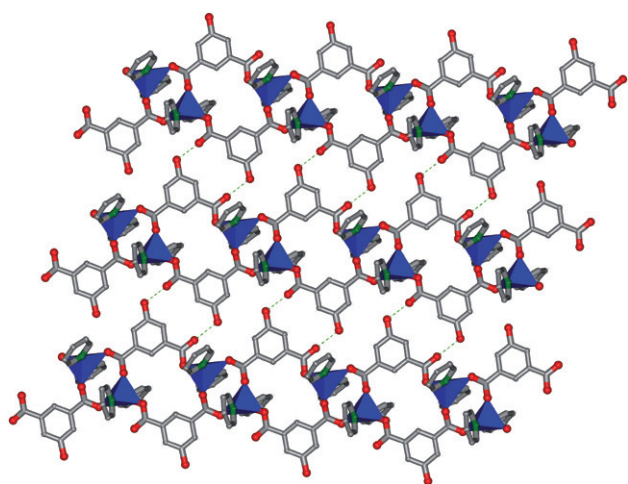


Fig. 4 View of the layer formed by 1D double stranded chains in **2**. Hydrogen bonds are indicated with dashed line. Hydrogen atoms and guest pyridine molecules are omitted for clarity.

Table 3) and finally, adjacent layers extend to form the supramolecular network along the c axis through π - π interactions between the pyridine rings of adjacent layers. There are also pyridine guest molecules included in the voids of the structure through C-H \cdots π weak interactions. In **2**, hydrogen-bonds and π - π interactions play an important role in the formation of the crystal structure.

3.1.3. [Zn(tbip)(py)₂]_n 3. In the asymmetric unit of **3**, there are one Zn²⁺ ion, one tbip²⁻ (5-*tert*-butylisophthalate) and two py ligands. The Zn²⁺ is in a distorted tetrahedral geometry, coordinated by two monodentate carboxyl groups of two tbip²⁻ and two nitrogen atoms from py. (Fig. 5) The Zn²⁺ ions are connected by tbip²⁻ to form a 1D chain along the [101] direction, (Fig. 6) which is further linked by inter-chain π - π interactions between py rings from adjacent chains to form the crystal structure. The offset face-to-face π - π distances between the aromatic rings are about 3.936 and 4.060 Å.

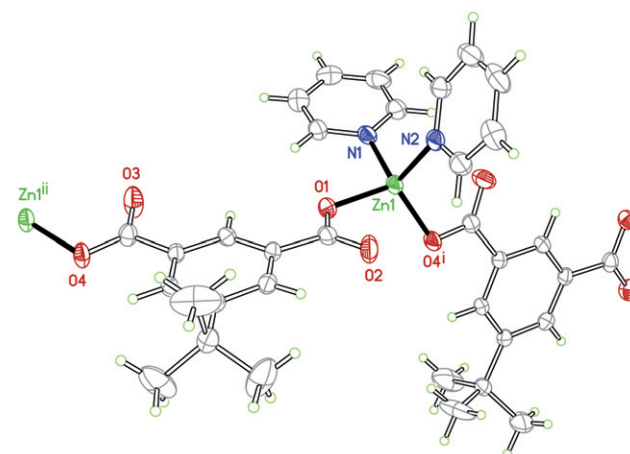


Fig. 5 The coordination geometry in **3** with the thermal ellipsoids at 50% probability level. Symmetry code: ⁱ $x - 1/2, -y + 3/2, z - 1/2$; ⁱⁱ $x + 1/2, -y + 3/2, z + 1/2$.

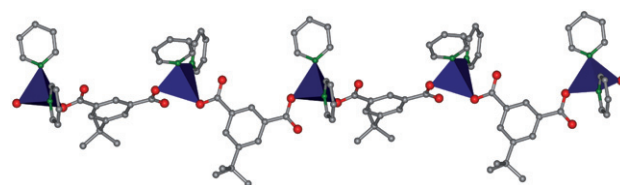


Fig. 6 View of the 1D chain in **3**. Hydrogen atoms are omitted for clarity.

3.1.4. [Mn(tbip)(py)₂]_n 4. In the structure of **4**, there are one Mn²⁺, one tbip²⁻ and two py in the asymmetric unit. The coordination environment of Mn²⁺ can be described as a distorted octahedron formed by four carboxyl oxygen atoms from three different tbip²⁻ in the plane and two nitrogen atoms from two different py molecules at the apexes. (Fig. 7, Table 4) One of the two py molecules is disordered over two positions and restraints have been applied in the refinement. The two carboxyls of

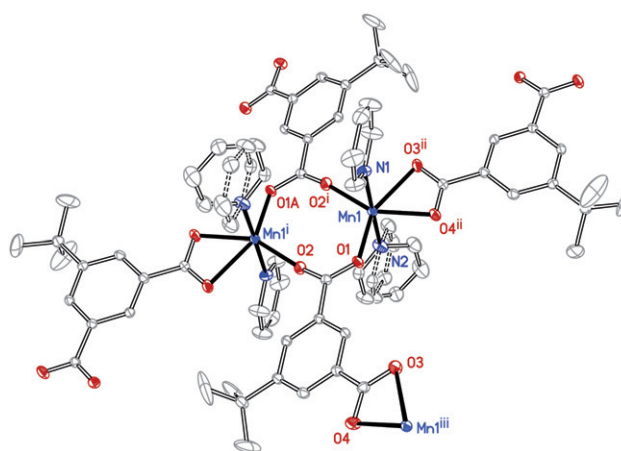


Fig. 7 The coordination geometry in **4** with the thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: ⁱ $-x + 1, -y, -z + 1$; ⁱⁱ $x - 1/2, -y + 1/2, z + 1/2$; ⁱⁱⁱ $x + 1/2, -y + 1/2, z - 1/2$.

Table 4 Selected bond lengths (Å) and angles (°) for **4**^a

Mn1–O1	2.1420(14)	Mn1–O4 ⁱⁱ	2.1859(16)
Mn1–O2 ⁱ	2.0968(15)	Mn1–N1	2.294(2)
Mn1–O3 ⁱⁱ	2.4052(15)	Mn1–N2	2.281(2)
O1–Mn1–O4 ⁱⁱ	94.93(5)	O1–Mn1–N1	89.33(6)
O4 ⁱⁱ –Mn1–O3 ⁱⁱ	57.00(5)	O2 ⁱ –Mn1–N1	88.53(7)
O2 ⁱ –Mn1–O3 ⁱⁱ	92.96(6)	N1–Mn1–O3 ⁱⁱ	88.62(7)
O2 ⁱ –Mn1–O1	115.08(6)	O4 ⁱⁱ –Mn1–N1	90.79(7)
O1–Mn1–O3 ⁱⁱ	151.82(5)	O1–Mn1–N2	93.44(6)
O2 ⁱ –Mn1–O4 ⁱⁱ	149.96(6)	O2 ⁱ –Mn1–N2	89.78(8)
N2–Mn1–N1	177.17(7)	N2–Mn1–O3 ⁱⁱ	89.20(7)

^a Symmetry codes: ⁱ $-x + 1, -y, -z + 1$; ⁱⁱ $x - 1/2, -y + 1/2, z + 1/2$.

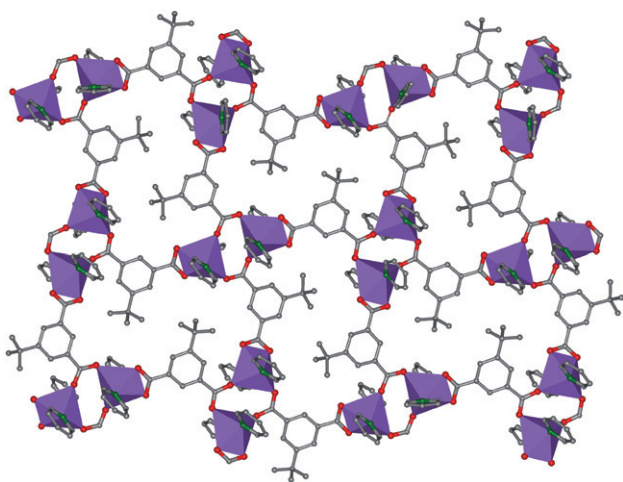


Fig. 8 View of the 2D (4,4) net structure in **4**. Hydrogen atoms are omitted for clarity.

tbip^{2-} belong to two different coordination modes, one is bidentate bridging mode, and the other is chelate. Pairs of Mn^{2+} ions are also bridged by pairs of carboxyls to form eight-member-ring dinuclear SBUs^{9–11} connected to four tbip^{2-} bridging ligands. Although the SBU looks quite similar to that in **2**, it is a real four-connecting node and results in the formation of a 2D (4,4) net in (101) plane. (Fig. 8) The difference in the SBU in **2** and **4** may be caused by the steric hindrance of the bulky *tert*-butyl on tbip^{2-} and the six-coordination ability of the Mn^{2+} ion. The adjacent 2D nets pack along the *b* axis to form a supramolecular network through π – π interactions between the pyridine rings from adjacent layers.

3.2. Syntheses

X-Ray powder diffraction measurements (ESI[†]) and elemental analyses show that the pure phases of **1–4** have been obtained by hydrothermal syntheses. The formation of the products is not sensitive to synthetic conditions. For example, in the syntheses under 120–210 °C hydrothermal conditions, the same pure product of **1** is always obtained verified by X-ray powder diffraction patterns of the products. The results verify that the structures of the four CPs are determined by the substituents of isophthalic acid and its derivatives.

3.3. Discussion

When we consider the structures of the zinc CPs **1–3** assembled with different isophthalate derivatives, we find that there is a clear relationship between the coordination numbers (CN) of metal ions and the dimensionalities of the structures. The average CN of Zn^{2+} ions in these three complexes decrease from 5.5 in **1** (including the two long coordination bonds to Zn2) to 5 in **2**, and then to 4 in **3**, the dimensionalities of these structures decrease from 2D layer to 1D double stranded chain, and then to 1D chain, correspondingly. It seems reasonable to conclude that this tendency is caused by the substituents on isophthalate derivatives—the volumes of the substituents increase markedly from H, OH to *tert*-butyl in ip^{2-} , hip^{2-} and tbip^{2-} , respectively, and the steric hindrance prevents the Zn^{2+} ion from having high CN when coordinated to tbip^{2-} . It is noteworthy that the substituent effect may be enhanced by the bulky ancillary ligand, namely, pyridine.

When we compare **3** and **4** with the same ratio of M : tbip^{2-} : py in their formula, the structure of **3** is 1D (CN = 4 for Zn^{2+} ion) while **4** is 2D (CN = 6 for Mn^{2+} ion). The ligands are the same, but the Mn^{2+} ion in **4** has an ability to adopt a six-coordination mode as compared to the Zn^{2+} ion which usually adopts four, five or six CN. The coordination behavior of the metal ions plays a crucial role in this case.

Both **2** and **4** are assembled with almost the same eight-member-ring dinuclear SBUs commonly seen in isophthalate CPs,^{9–11} but they have definitely different structures. In the structure of **2**, the hip^{2-} possesses a hydrogen bond forming group, the hydroxyl. The SBU in **2** act as a two-connecting node to allow the hydroxyls on hip^{2-} pointing outward to form hydrogen bonds with oxygen atoms from adjacent double stranded chains. (Fig. 3, 4 and Table 3) In the SBU of **4**, the four tbip^{2-} ligands with bulky hydrophobic *tert*-butyls try to separate from each other and result in the formation of the 2D (4,4) net. (Fig. 8) This time the difference in the properties of the substituents in **2** and **4** determines the structures. The different coordination behavior of Zn^{2+} and Mn^{2+} may also affect the assemblies of **2** and **4**.

3.4. IR spectra

The IR spectra of carboxylate complexes can provide useful information to distinguish the coordination modes of the carboxyl groups.⁵¹ The solid state IR spectra of **1–4** (ESI[†]) show no band in the region 1690–1730 cm^{-1} , indicating complete deprotonation of the carboxyl groups. For **1**, very strong $\nu_{\text{as}}(\text{COO}^-)$ bands appear at 1606 and 1642 cm^{-1} , and $\nu_{\text{s}}(\text{COO}^-)$ band at 1397 cm^{-1} , $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-) = 245$ and 209 cm^{-1} show that the carboxyls in **1** adopt monodentate and bidentate bridging modes. For **2**, $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ bands are at 1560 and 1368 cm^{-1} , and $\Delta\nu = 192$ cm^{-1} confirms that one of the carboxyls adopts bidentate bridging mode. For **3**, $\Delta\nu = 253$ cm^{-1} (1622–1369 cm^{-1}) indicates that the coordinate modes of the two carboxyls are monodentate. For **4**, $\Delta\nu = 190$ cm^{-1} (1566–1376 cm^{-1}) also confirms that one of the carboxyls adopts bidentate mode under the conditions employed. The IR spectra also show characteristic peaks at 3259 cm^{-1} for a phenol hydroxyl group engaged in hydrogen

bonding in **2**,⁵² and at 2961 cm⁻¹ for CH₃ groups in **3** and **4**. The above results are consistent with the X-ray diffraction studies.

3.5. Photoluminescence

Many CPs assembled with *d*¹⁰ metal centers have been investigated for photoluminescent properties and for potential applications as fluorescence-emitting materials owing to their higher thermal stability and the ability to be adjusted by metal coordination.^{53–59} The photoluminescent properties of the free ligands H₂ip, H₂hip, H₂tbip and **1–3** have been measured in the solid state at room temperature. (Fig. 9) The free ligands H₂ip, H₂hbdc and H₂tbip display luminescence with emission maxima at 358 nm ($\lambda_{\text{ex}} = 330$ nm), 362 nm ($\lambda_{\text{ex}} = 320$ nm) and 320 nm ($\lambda_{\text{ex}} = 290$ nm), respectively. It can be presumed that these peaks should be assigned to the $\pi^* \rightarrow n$ transitions in the benzene ring of the isophthalate ligands.^{53–56} Intense emissions are observed at 375 nm ($\lambda_{\text{ex}} = 320$ nm) for **1**, 470 nm ($\lambda_{\text{ex}} = 380$ nm) for **2** and 320 nm ($\lambda_{\text{ex}} = 290$ nm) for **3**, respectively. The luminescent

emissions of **1** and **2** can be assigned to ligand-to-metal charge transfer (LMCT).^{53–57} The fluorescence intensity of **3** is much stronger than that of H₂tbip, and the emission wavelength is the same (320 nm), indicating that the stronger fluorescence of **3** can probably be assigned to intraligand fluorescent emission enhanced by the coordination of the Zn²⁺ ion to the ligand.^{58,59}

4. Conclusions

Four coordination polymers, [Zn₄(H₂O)(ip)₄(py)₆]_n **1**, {[Zn₂(hip)₂(py)₄]₂·(py)}_n **2**, [Zn(tbip)(py)₂]_n **3** and [Mn(tbip)(py)₂]_n **4** have been synthesized with isophthalic acid, 5-hydroxyisophthalic acid and 5-*tert*-butylisophthalic acid. As substituents change from H, OH to *tert*-butyl, the coordination numbers of Zn²⁺ ions decrease from 5.5, 5 to 4, and the dimensionalities of the structures of **1–3** decrease from 2D (4,4) net, 1D double stranded chain to 1D chain, correspondingly. The results show that by changing the substituents on isophthalic acids, it is possible to control the structures of the coordination polymers. The coordination behavior of the metal ions also affects the structures. Metal ions tending to have a higher coordination number are more likely to form a structure with higher dimensionality. Mn²⁺ tends to have a higher coordination number compared to Zn²⁺, in this case, the structure of **4** is a 2D layer while the structure of **3** is a 1D chain.

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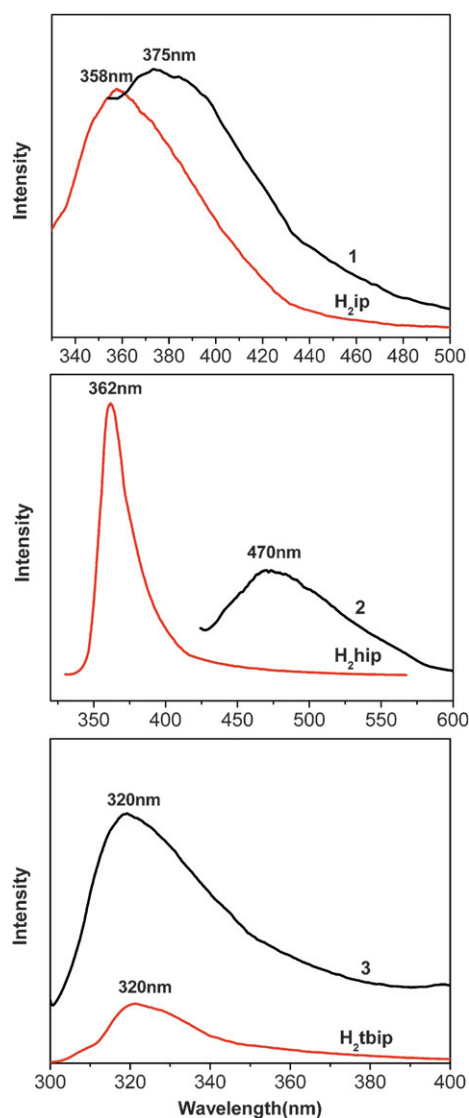


Fig. 9 Photoluminescent properties of **1–3**.

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