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Effect of organic anions on the self-assembly of Zn(II)-containing coordination polymers based on trigonal N-donor ligands[†]

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A series of coordination polymers, namely, [Zn(2,3'-tmbpt)(o-bdc)(H₂O)] (1), [Zn(2,3'-tmbpt)(m-bdc)] (2), $[Zn(2,3'-tmbpt)(p-bdc)] \cdot H_2O$ (3), $[Zn_2(2,3'-tmbpt)(btc)(OH)] \cdot 0.5H_2O$ (4), $[Zn(2,3'-tmbpt)(btec)_{0.5}] \cdot 2H_2O$ (5), $[Zn(3,3'-tmbpt)(o-bdc)] \cdot H_2O$ (6), $[Zn(3,3'-tmbpt)(m-bdc)(H_2O)] \cdot H_2O$ (7), and $[Zn_2(3,3'-tmbpt)(btc)(OH)(H_2O)]$ (8), where 2,3'-tmbpt = 1-((1H-1,2,4-triazol-1-yl)methyl)-3-(3-pyridyl)-5-(2-pyridyl)-1,2,4-triazole, 3,3'-tmbpt = 1- $((1H-1,2,4-\text{triazol}-1-\text{yl})\text{methyl})-3,5-\text{bis}(3-\text{pyridyl})-1,2,4-\text{triazole}, o-H_2\text{bdc} = 1,2-\text{benzenedicarboxylic}$ acid, m-H₂bdc = 1,3-benzenedicarboxylic acid, p-H₂bdc = 1,4-benzenedicarboxylic acid, H₃btc = 1,3,5-benzenetricarboxylic acid, and H_4 btec = 1,2,4,5-benzenetetracarboxylic acid, have been synthesized under hydrothermal conditions. The structures of 1-8 have been determined by singlecrystal X-ray diffraction analyses and were further characterized by infrared spectroscopy (IR), elemental analyses and powder X-ray diffraction (PXRD) analyses. Compounds 1 and 6 display 1D chain structures. Compound 2 shows a 3D 2-fold interpenetrating $CdSO_4$ framework. Compound 3 reveals a 2D 2-fold interpenetrating square layer (sql) structure. Compound 4 exhibits a 3D 2-fold interpenetrating framework with $(6^3)(6^9 \cdot 8)$ topology. Compound 5 shows a non-interpenetrating 3D framework with $(8^3)(8^5 \cdot 10)$ topology. Compound 7 has a 2D layer structure. Compound 8 displays a 3D 2-fold interpenetrating framework with $(4.6^2)(4^2.6^8.8^5)$ topology. The structural discrepancies of compounds 1-8 imply that the organic anions play an important role in the formation of the resultant structures of the coordination polymers. The luminescent properties of compounds 1-8 have also been investigated.

Introduction

The rational design and assembly of coordination polymers are of current interest due to their fascinating architectures and potential applications in gas storage, luminescence, separation, catalysis, drug delivery, and so on.^{1,2} Up to now, a number of N-donor bridging ligands, such as 4,4'-bipyridine (bpy),³ 1,4-bis(1,2,4-triazol-1-yl)butane (btb),⁴ 1,4-bis(1*H*-1,2,4-triazol-1-ylmethyl)benzene (bbtz),⁵ 2,4,6-tri(pyridyl)-1,3,5-triazine (tptz),⁶ 1,3,5-tris(1,2,4-imidazol-1-ylmethyl)-2,4,6-trimethyl benzene (ttb),⁷ and tetrakis(imidazol-1-ylmethyl)methane (tiym),⁸ have been widely employed to construct coordination polymers with fascinating architectures and interesting properties. Among the various N-donor bridging ligands, trigonal N-donor ligands have been proven to be good candidates for the construction of coordination polymers with versatile topologies and functional

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properties.^{6,7} In our previous work, we have reported a series of fascinating 3D highly connected frameworks based on three structurally related trigonal N-donor ligands 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4'-tmbpt), 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(3-pyridyl)-1,2,4-triazole (3,3'-tmbpt) and 1-((1H-1,2,4-triazol-1-yl)methyl)-3-(3-pyridyl)-5-(4-pyridyl)-1, 2,4-triazole (3,4'-tmbpt).⁹ In these compounds, the tmbpt ligands exhibit merits of both rigid and flexible ligands, and can coordinate with metal ions in diverse coordination modes.⁹

On the other hand, organic anions play an important role in the formation of coordination polymers with fascinating structures. In order to investigate the effects of organic anions on the structures of the compounds based on the tmbpt ligands (2,3'-tmbpt and 3,3'-tmbpt, Scheme 1), five structurally related organic polycarboxylic acids (Scheme 1) were used and a series of Zn(II)-containing coordination polymers, namely, $[Zn(2,3'-\text{tmbpt})(o-bdc)(H_2O)]$ (1), [Zn(2,3'-tmbpt)(m-bdc)] (2), $[Zn(2,3'-\text{tmbpt})(p-bdc)]\cdot\text{H}_2O$ (3), $[Zn_2(2,3'-\text{tmbpt})(btc)(OH)]\cdot0.5\text{H}_2O$ (4), $[Zn(3,3'-\text{tmbpt})(m-bdc)(H_2O)]\cdot1_2O$ (5), $[Zn(3,3'-\text{tmbpt})(o-bdc)]\cdot\text{H}_2O$ (6), $[Zn(3,3'-\text{tmbpt})(m-bdc)(H_2O)]\cdot1_2O$ (7), and $[Zn_2(3,3'-\text{tmbpt})(btc)(OH)(H_2O)]$ (8), where 2,3'-tmbpt = 1-((1*H*-1,2,4-triazol-1yl)methyl)-3-(3-pyridyl)-5-(2-pyridyl)-1,2,4-triazole, 3,3'-tmbpt = 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(3-pyridyl)-1,2,4-triazole,

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Scheme 1 Organic ligands used in this work.

 $o-H_2bdc = 1,2$ -benzenedicarboxylic acid, $m-H_2bdc = 1,3$ benzenedicarboxylic acid, $p-H_2bdc = 1,4$ -benzenedicarboxylic acid, $H_3btc = 1,3,5$ -benzenetricarboxylic acid, and $H_4btcc =$ 1,2,4,5-benzenetetracarboxylic acid, have been synthesized under hydrothermal conditions. The structures and topological analyses of these compounds, and the influence of the anions on the structures of the coordination polymers have been discussed. The photoluminescent properties of the compounds have also been studied.

Experimental

Materials and methods

The 2,3'-tmbpt and 3,3'-tmbpt ligands were synthesized by the procedures reported previously.⁹ All commercially available chemicals and solvents were of analytical grade and used without further purification. Elemental analyses (C, H and N) were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra of the compounds were measured in the range of 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. The solid-state photoluminescent data were recorded on a Perkin-Elmer FLS-920 spectrometer at room temperature. PXRD measurements were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu-K α radiation ($\lambda = 0.154$ nm) and 2θ varying from 5 to 50°. The experimental PXRD patterns matched well with the corresponding computer-simulated ones (Fig. S1 and S2 in the ESI†).

Synthesis of [Zn(2,3'-tmbpt)(*o***-bdc)(H₂O)] (1). A mixture of Zn(CH₃COO)₂·2H₂O (0.022 g, 0.1 mmol),** *o***-H₂bdc (0.017 g, 0.1 mmol), 2,3'-tmbpt (0.03 g, 0.1 mmol), NaOH (0.008 g, 0.2 mmol) and 8 mL water was sealed in a 15 mL Teflon reactor and heated at 130 °C for 3 days. After cooling to ambient temperature at a rate of 10 °C h⁻¹, colorless crystals of 1 were obtained in 32% yield. Anal. Calcd for C₂₃H₁₈ZnN₈O₅ (M_r = 551.82): C, 50.06; H, 3.29; N, 20.31. Found: C, 49.95; H, 3.22; N, 20.15. IR (cm⁻¹): 3311(w), 3133(w), 3067(w), 3030(w), 1610(m),**

1588(s), 1560(s), 1481(w), 1417(s), 1404(s), 1325(w), 1313(w), 1274(m), 1145(w), 1125(w), 1089(w), 994(w), 889(w), 820(w), 767(w), 717(w), 645(w).

Synthesis of [Zn(2,3'-tmbpt)(m-bdc)] (2). The preparation of **2** was similar to that of **1** except that m-H₂bdc (0.017 g, 0.1 mmol) was used instead of o-H₂bdc. Colorless crystals of **2** were obtained in 37% yield. Anal. Calcd for C₂₃H₁₆ZnN₈O₄ (M_r = 533.81): C, 51.75; H, 3.03; N, 21.00. Found: C, 51.68; H, 3.11; N, 21.11. IR (cm⁻¹): 3384(w), 3153(w), 3078(w), 1610(s), 1589(m), 1565(s), 1460(s), 1389(s), 1355(s), 1284(w), 1199(w), 1143(w), 1122(w), 1100(w), 1049(w), 996(w), 881(w), 831(w), 799(w), 761(w), 743(s), 728(s), 707(w), 670(w).

Synthesis of [Zn(2,3'-tmbpt)(*p***-bdc)]·H₂O (3).** The preparation of **3** was similar to that of **2** except that *p*-H₂bdc (0.017 g, 0.1 mmol) was used instead of *m*-H₂bdc. Colorless crystals of **3** were obtained in 41% yield. Anal. Calcd for $C_{23}H_{18}ZnN_8O_5$ ($M_r = 551.82$): C, 50.06; H, 3.29; N, 20.31. Found: C, 50.18; H, 3.15; N, 20.22. IR (cm⁻¹): 3140(w), 3074(w), 1604(s), 1568(m), 1534(w), 1506(s), 1459(m), 1388(s), 1358(s), 1314(w), 1278(m), 1206(w), 1144(w), 1127(w), 1101(w), 996(m), 954(w), 881(w), 821(w), 798(w), 667(w), 576(w).

Synthesis of $[Zn_2(2,3'-tmbpt)(btc)(OH)] \cdot 0.5H_2O$ (4). The preparation of 4 was similar to that of 3 except that H₃btc (0.014 g, 0.067 mmol) was used instead of *p*-H₂bdc. Colorless crystals of 4 were obtained in 29% yield. Anal. Calcd for C₂₄H₁₇Zn₂N₈O_{7.5} ($M_r = 668.20$): C, 43.14; H, 2.57; N, 16.77. Found: C, 43.21; H, 2.67; N, 16.68. IR (cm⁻¹): 3446(w), 3118(w), 3043(w), 1624(s), 1570(s), 1446(m), 1420(m), 1370(s), 1286(w), 1222(w), 1170(w), 1141(w), 1100(w), 1040(w), 1004(w), 903(w), 808(w), 762(w), 745(w), 721(w), 694(w), 670(w).

Synthesis of $[Zn(2,3'-tmbpt)(btec)_{0.5}] \cdot 2H_2O$ (5). The preparation of 5 was similar to that of 4 except that H₄btec (0.013 g, 0.05 mmol) was used instead of H₃btc. Colorless crystals of **5** were obtained in 22% yield. Anal. Calcd for $C_{20}H_{17}ZnN_8O_6$ ($M_r = 530.79$): C, 45.25; H, 3.23; N, 21.12. Found: C, 45.40; H, 3.27; N, 21.01. IR (cm⁻¹): 3481(w), 3138(w), 3033(w), 1617(s), 1571(s), 1558(s), 1485(w), 1423(s), 1347(s), 1320(s), 1271(m), 1201(w), 1118(w), 1011(w), 991(w), 937(w), 894(w), 868(w), 804(w), 747(w), 671(w), 567(w).

Synthesis of [Zn(3,3'-tmbpt)(*o***-bdc)]·H₂O (6). The preparation of 6** was similar to that of **1** except that 3,3'-tmbpt (0.03 g, 0.1 mmol) was used instead of 2,3'-tmbpt. Colorless crystals of **6** were obtained in 35% yield. Anal. Calcd for $C_{23}H_{18}ZnN_8O_5$ (M_r = 551.82): C, 50.06; H, 3.29; N, 20.31. Found: C, 50.16; H, 3.14; N, 20.22. IR (cm⁻¹): 3503(w), 3138(w), 3034(w), 1617(s), 1557(s), 1423(s), 1341(m), 1320(m), 1291(w), 1271(w), 1201(w), 1118(w), 1089(w), 1011(w), 991(w), 937(w), 868(w), 823(w), 766(w), 747(w), 670(w).

Synthesis of [Zn(3,3'-tmbpt)(m-bdc)(H₂O)]·H₂O (7). The preparation of 7 was similar to that of 6 except that m-H₂bdc (0.017 g, 0.1 mmol) was used instead of o-H₂bdc. Colorless crystals of 7 were obtained in 41% yield. Anal. Calcd for C₂₃H₂₀ZnN₈O₆ (M_r = 569.84): C, 48.48; H, 3.54; N, 19.67. Found: C, 48.59; H, 3.47; N, 19.39. IR (cm⁻¹): 3384(m), 1614(s), 1559(s), 1481(w), 1442(m), 1416(s), 1376(s), 1272(w), 1199(w), 1151(w), 1127(w), 1075(w), 1012(w), 986(w), 953(w), 816(w), 784(w), 748(m), 725(w), 699(w), 670(w), 641(w).

Synthesis of [**Zn**₂(**3**,3'-**tmbpt**)(**bt**c)(**OH**)(**H**₂**O**)] (**8**). The preparation of **8** was similar to that of **7** except that H₃btc (0.014 g, 0.067 mmol) was used instead of *m*-H₂bdc. Colorless crystals of **8** were obtained in 38% yield. Anal. Calcd for C₂₄H₁₈Zn₂N₈O₈ (M_r = 677.20): C, 42.56; H, 2.68; N, 16.55. Found: C, 42.42; H, 2.55; N, 16.44. IR (cm⁻¹): 3442(w), 3144(w), 3087(w), 1618(s), 1567(s), 1458(w), 1435(m), 1411(m), 1369(s), 1286(w), 1163(w), 1137(w), 1096(w), 1029(w), 989(w), 885(w), 820(w), 810(w), 722(w), 704(w), 669(w), 634(w).

Table 1 Crystal data and structure refinements for compounds 1-8

X-Ray crystallography

Single-crystal X-ray diffraction data were collected on an Oxford Diffraction Gemini R Ultra diffractometer with graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were performed using a multi-scan technique. The structures of compounds 1-8 were solved by the Direct Method of SHELXS-97^{10a} and refined by full-matrix least-squares techniques employing the SHELXL-97 program.^{10b} Non-hydrogen atoms of compounds 1-8 were refined with anisotropic temperature parameters. The hydrogen atoms attached to the carbon atoms were generated geometrically and were refined using a riding model with d(C-H) = 0.93 Å, $U_{iso} =$ $1.2U_{eq}(C)$ for aromatic and d(C-H) = 0.97 Å, $U_{iso} = 1.2U_{eq}(C)$ for CH₂ atoms. The hydrogen atoms of water molecules and hydroxyl group were located from difference Fourier maps and were refined as riding atoms with d(O-H) = 0.811-0.857 Å and $U_{\rm iso} = 1.5 U_{\rm eq}(O)$. In 4, the hydrogen atoms of O1W and hydroxyl group (O7) were not included in the model. The detailed crystallographic data and structure refinement parameters for 1-8 are listed in Table 1. Selected bond distances and angles for the compounds are given in the Tables S1-S8[†]. The topologies of the compounds were analyzed by the OLEX program.11

Results and discussion

In this work, two trigonal N-donor ligands (2,3'-tmbpt and 3,3'-tmbpt) and five structurally related aromatic carboxylates anions were used to investigate the effect of the organic anions on the final structures of the compounds. The numbers and positions of the carboxylate groups in the five organic anions are different. Compounds 1–5 are based on Zn(II) ions, 2,3'-tmbpt ligands and distinct aromatic carboxylate anions (*o*-bdc, *m*-bdc, *p*-bdc, btc and btec). However, compounds 6–8 are based on Zn(II) ions, 3,3'-tmbpt ligands and different aromatic carboxylate anions (*o*-bdc, *m*-bdc, ylate anions (*o*-bdc, *m*-bdc and btc).

	1	2	3	4	5	6	7	8
Formula	$C_{23}H_{18}$ N ₈ O ₅ Zn	$C_{23}H_{16}$ N ₈ O ₄ Zn	$C_{23}H_{18}$ N ₈ O ₅ Zn	$C_{24}H_{17}$ N ₈ O _{7 5} Zn ₂	C ₂₀ H ₁₇ N ₈ O ₆ Zn	$C_{23}H_{18}$ N ₈ O ₅ Zn	$C_{23}H_{20}$ N ₈ O ₆ Zn	$C_{24}H_{18}$ N ₈ O ₈ Zn ₂
Formula weight	551.82	533.81	551.82	668.20	530.79	551.82	569.84	677.20
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	C2/c	$P\overline{1}$	C2/c	$P2_1/c$	$P\overline{1}$	$P2_1/n$	C2/c
aĺÅ	8.9771(6)	22.1231(10)	10.8170(5)	25.9785(7)	11.8534(5)	9.7186(5)	9.8552(3)	25.5723(13)
b/Å	11.0283(7)	12.5698(4)	11.0298(7)	10.1939(2)	15.0975(5)	11.4928(6)	23.1468(8)	10.2646(3)
c/Å	12.0901(6)	18.1222(7)	11.3773(6)	19.4052(5)	12.5650(5)	11.6881(6)	10.2245(4)	20.2916(9)
α (°)	74.718(5)	90	114.656(6)	90	90	63.618(5)	90	90
β(°)	85.000(5)	109.511(5)	104.715(4)	101.070(3)	111.268(5)	80.197(5)	98.033(3)	112.618(6)
γÕ	81.608(6)	90	95.911(5)	90	90	81.893(4)	90	90
V/Å ³	1140.77(12)	4750.1(3)	1159.00(11)	5043.3(2)	2095.45(14)	1149.29(10)	2309.49(14)	4916.7(4)
Ζ	2	8	2	8	4	2	4	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.607	1.493	1.581	1.760	1.682	1.595	1.639	1.830
F(000)	564	2176	564	2696	2168	564	1168	2736
Reflections (collected/unique)	7062/4154	9070/4340	7289/4214	9907/4610	7768/3822	7529/4189	9048/4215	8998/4493
R _{int}	0.0353	0.0310	0.0308	0.0263	0.0295	0.0497	0.0412	0.0455
Goodness-of-fit (GOF) on F^2	1.057	1.026	1.036	1.026	1.041	1.016	1.015	1.010
$R_1^{a}[I > 2\sigma(I)]$	0.0418	0.0360	0.0469	0.0432	0.0414	0.0565	0.0474	0.0443
$wR_2^{b}[I > 2\sigma(I)]$	0.0838	0.0745	0.1096	0.1039	0.1053	0.1093	0.0804	0.0777
${}^{a}R_{1} = \sum F_{o} - F_{c} \sum F_{o} . \ {}^{b}wR_{2} = \sum w(F_{o} ^{2} - F_{c} ^{2}) \sum w(F_{o}^{-2})^{2} ^{1/2}.$								

Compound 1 displays a 1D chain structure. The asymmetric unit of 1 consists of one Zn(II) ion, one 2,3'-tmbpt ligand, one *o*-bdc anion and one coordinated water molecule. As shown in Fig. 1a, each Zn(II) ion is five-coordinated in a distorted trigonal bipyramid coordination geometry, defined by two nitrogen atoms from two individual 2,3'-tmbpt ligands [Zn1–N1 = 2.091(2) and Zn1–N7^{#2} = 2.215(2) Å] and three oxygen atoms from two distinct *o*-bdc anions and one coordinated water molecule [Zn1–O1 = 1.988(2), Zn1–O3^{#1} = 1.999(2) and Zn1– O1W = 2.179(2) Å]. Each 2,3'-tmbpt ligand acts as a bidentate ligand with the free 2-position pyridyl group. A pair of 2,3'-tmbpt ligands link two Zn(II) ions to form a closed loop. The two carboxylate groups of the *o*-bdc anions in a μ_1 - η^1 : η^0 coordination mode (mode I in Scheme S1, ESI†) further connect the neighboring loops in pairs to generate a 1D chain (Fig. 1b).

Moreover, there are intermolecular O–H···O hydrogen-bonding interactions between water molecules and the carboxylate oxygen atoms (Table S1b†). The chains of **1** are extended by the hydrogen-bonding interactions to generate a 2D supramolecular layer (Fig. S3 in ESI†).

Structure of [Zn(2,3'-tmbpt)(m-bdc)] (2)

Compound **2** shows a 3D 2-fold interpenetrating framework with CdSO₄ topology. The asymmetric unit of **2** contains one Zn(II) ion, one 2,3'-tmbpt ligand and one *m*-bdc anion. As shown in Fig. 2a, each Zn(II) ion is four-coordinated by two nitrogen atoms from two different 2,3'-tmbpt ligands (Zn1–N1 = 2.042(2) and Zn1–N8^{#2} = 2.044(2) Å) and two oxygen atoms from two individual *m*-bdc anions (Zn1–O1 = 1.984(2) and Zn1–O4^{#1} = 1.942(2) Å) in a tetrahedral coordination geometry. Each 2,3'-tmbpt ligand behaves as a bidentate ligand with the free 2-position pyridyl group. In this way, the 2,3'-tmbpt ligands link the Zn(II) ions to form a wave like chain (Fig. 2b). The two carboxylate groups of the *m*-bdc anion adopt a μ^1 - η^1 : η^0 coordination mode (mode II in Scheme S1, ESI†). In this way,



Fig. 1 (a) ORTEP view of **1** showing the local coordination environment of Zn(II) ion with hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ${}^{\#1} - x + 1, -y + 1, -z; {}^{\#2} - x, -y, -z + 1$. (b) View of the 1D chain of **1**.



Fig. 2 (a) ORTEP view of **2** showing the local coordination environment of Zn(II) ion with hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ^{#1} x, -y, z - 1/2; ^{#2} x - 1/2, y - 1/2, z. (b) View of the 1D chain constructed by Zn(II) ions and 2,3'-tmbpt ligands. (c) View of the 3D framework of **2**. (d) View of the 3D 2-fold interpenetrating framework of **2**.

the neighboring chains are further linked by the *m*-bdc anions to yield a 3D framework (Fig. 2c).

Topologically, if the Zn(II) ions can be considered as 4-connected nodes, and the 2,3'-tmbpt ligands and the *m*-bdc anions are viewed as linkers, the 3D framework of **2** can be simplified as a 4-connected net with $(6^{5} \cdot 8) \text{ CdSO}_{4}$ -type topology. Two identical nets interpenetrate each other, giving rise to a 2-fold interpenetrating framework (Fig. 2d).

Structure of [Zn(2,3'-tmbpt)(p-bdc)]·H₂O (3)

Compound 3 exhibits a 2D 2-fold interpenetrating structure. The asymmetric unit of 3 contains one Zn(II) ion, one 2,3'-tmbpt ligand, one *p*-bdc anion and one lattice water molecule. As shown in Fig. 3a, each Zn(II) ion is four-coordinated in a tetrahedral coordination geometry, completed by two nitrogen atoms from two distinct 2,3'-tmbpt ligands (Zn1-N1 = 2.026(3)) and $Zn1-N7^{\#1} = 2.059(3)$ Å) and two oxygen atoms from two different p-bdc anions (Zn1-O1 = 1.954(3) and Zn1-O3 = 1.941(2) Å). Each 2,3'-tmbpt ligand acts as a bidentate ligand with the free 2-position pyridyl group. The 2,3'-tmbpt ligands bridge the Zn(II) ions to form a 1D chain. The two carboxylate groups of the *p*-bdc anion adopt a μ_1 - η^1 : η^0 coordination mode (mode III in Scheme S1, ESI[†]). In this manner, the neighboring chains are then linked by the *p*-bdc anions to yield a wave like layer (Fig. 3b). Further, two networks interlock each other to generate a 2D 2-fold interpenetrating network (Fig. 3c). In addition, there is intramolecular hydrogen-bonding interaction between O1W and O2 of the carboxylate group, which further stabilizes the layer of **3** (Fig. S4 and Table S3b[†]).

Topologically, if the Zn(II) ions are regarded as 4-connected nodes, and the 2,3'-tmbpt ligands and the *p*-bdc anions are simplified as linkers, the layer can be described as a 2D sql network with $(4^{4} \cdot 6^{2})$ topology.

Structure of [Zn₂(2,3'-tmbpt)(btc)(OH)]·0.5H₂O (4)

Compound 4 has a 3D 2-fold interpenetrating framework with $(6^3)(6^9 \cdot 8)$ topology. The asymmetric unit of 4 consists of two Zn(II) ions, one 2,3'-tmbpt ligand, one btc anion, one hydroxyl group, and half a lattice water molecule. As shown in Fig. 4a, Zn1 and Zn2 show similar tetrahedral coordination geometries, completed by one nitrogen atom from one 2,3'-tmbpt ligand $(Zn1-N1 = 2.018(3) \text{ and } Zn2-N7^{\#3} = 2.070(3) \text{ Å})$ and three oxygen atoms from two different btc anions and one hydroxyl group (Zn1–O7 = 1.925(3), Zn1–O3^{#1} = 1.959(2), Zn1–O6^{#2} = 2.017(3), Zn2–O1 = 1.925(3), Zn2–O7 = 1.920(3) and Zn2–O5^{#2} = 1.928(3) Å). Zn1 and Zn2 ions are held together by the hydroxyl group to form a binuclear unit [Zn₂O]. The carboxylate groups of the btc anion in μ_1 - η^1 : η^0 and μ_2 - η^1 : η^1 coordination modes (mode IV in Scheme S1, ESI[†]) further connect the binuclear units to generate a 2D layer (Fig. 4b). Each 2,3'-tmbpt ligand, as a bidentate ligand with the free 2-position pyridyl group, links the neighboring layers to yield a 3D framework (Fig. 4c). Two identical nets interpenetrate each other to form a 2-fold interpenetrating framework. There are O-H...O hydrogen-bonding interactions between the lattice water molecule and the carboxylate oxygen atoms, which consolidate the whole 2-fold interpenetrating framework (Fig. S5 and Table S4b[†]).

Topologically, if the binuclear units $[Zn_2O]$ are considered as 5-connected nodes, the btc anions are viewed as 3-connected nodes, and the 2,3'-tmbpt ligands are regarded as linkers, the 3D framework can be simplified as a (3,5)-connected framework with $(6^3)(6^9 \cdot 8)$ topology (Fig. 4d).

Structure of [Zn(2,3'-tmbpt)(btec)_{0.5}]·2H₂O (5)

Compound 5 shows a 3D (3,4)-connected framework with $(8^3)(8^5 \cdot 10)$ topology. The asymmetric unit of 5 contains one



Fig. 3 (a) ORTEP view of **3** showing the local coordination environment of Zn(II) ion with hydrogen atoms and lattice water molecules omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ${}^{\#1}x$, y + 1, z + 1; ${}^{\#2} - x + 1$, -y + 1, -z; ${}^{\#3} - x + 1$, -y, -z + 1. (b) View of the 2D layer formed by Zn(II) ions, 2,3'-tmbpt ligands and *p*-bdc anions. (c) View of the 2-fold interpenetrating sql network.

Zn(II) ion, one 2,3'-tmbpt ligand, one btec anion, and two lattice water molecules. As shown in Fig. 5a, each Zn(II) ion is fourcoordinated by two nitrogen atoms from two individual 2,4'-tmbpt ligands (Zn1–N1 = 2.040(3) and Zn1–N8^{#2} = 2.050(3) Å) and two oxygen atoms from two distinct btec anions (Zn1–O1 = 1.931(2) and Zn1–O3^{#1} = 1.959(2) Å) in a tetrahedral coordination geometry. The carboxylate groups of the btec anion in a μ_1 - η^1 : η^0 coordination mode (mode V in Scheme S1, ESI†) links the Zn(II) ions to form a layer (Fig. 5b). Each





Fig. 4 (a) ORTEP view of **4** showing the local coordination environments of Zn(II) ions with hydrogen atoms and lattice water molecules omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ^{#1} x, -y, z + 1/2; ^{#2} x, -y + 1, z + 1/2; ^{#3} x - 1/2, y + 1/2, z. (b) View of the layer formed by Zn(II) ions, hydroxyl groups and btc anions. (c) View of the 3D framework of **4**. (d) View of the 3D 2-fold interpenetrating framework of **4** with (6³)(6⁹·8) topology.

Fig. 5 (a) ORTEP view of **5** showing the local coordination environment of Zn(II) ion with hydrogen atoms and lattice water molecules omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ${}^{\#1}x, -y + 1/2, z - 1/2; {}^{\#2}-x + 1, -y, -z; {}^{\#3}-x + 2, -y + 1, -z.$ (b) View of the layer formed by Zn(II) ions and btec anions. (c) View of the 3D framework of **5**. (d) Schematic view of the 3D (3,4)-connected framework of **5** with (8³)(8⁵.10) topology.

2,3'-tmbpt ligand acts as a bidentate ligand with the free 2-position pyridyl group. In this way, the 2,3'-tmbpt ligands further connected the layers in pairs to generate a 3D framework (Fig. 5c). Furthermore, there are O–H···O hydrogen-bonding interactions between the lattice water molecules and the carboxy-late oxygen atoms, which stabilize the whole 3D framework of **5** (Fig. S6 and Table S5b†).

Topologically, if the Zn(II) ions are regarded as 3-connected nodes, the btec anions are considered as 4-connected nodes, and the 2,3'-tmbpt ligands are viewed as linkers, the 3D framework of **5** can be described as a (3,4)-connected framework with $(8^3)(8^5 \cdot 10)$ topology (Fig. 5d).

Structure of $[Zn(3,3'-tmbpt)(o-bdc)] \cdot H_2O$ (6)

Compound 6 exhibits a 1D chain structure. The asymmetric unit of 6 consists of one Zn(II) ion, one 3,3'-tmbpt ligand, one o-bdc anion and one lattice water molecule. As shown in Fig. 6a, each Zn(II) ion is four-coordinated by two nitrogen atoms from two distinct 3,3'-tmbpt ligands (Zn1-N1 = 2.050(3) and Zn1-N8^{#2} = 2.116(3) Å) and two oxygen atoms from two different o-bdc anions (Zn1–O2 = 1.956(3) and Zn1–O3^{#1} = 1.959(3) Å). Each 3.3'-tmbpt ligand acts as a bidentate ligand with the free peripheral triazolyl group. A pair of 3,3'-tmbpt ligands link two Zn(II) ions to generate a closed loop. The two carboxylate groups of the *o*-bdc anion adopt a μ_1 - η^1 : η^0 coordination mode (mode I in Scheme S1, ESI[†]). In this way, neighboring loops are further linked by the o-bdc anions into a 1D chain (Fig. 6b). Moreover, there are intramolecular O-H···O and O-H···N hydrogenbonding interactions, which further consolidate the 1D chain (Fig. S7 and Table S6b in ESI[†]).

Structure of [Zn(3,3'-tmbpt)(m-bdc)(H₂O)]·H₂O (7)

Compound 7 has a 2D layer structure. The asymmetric unit of 7 consists of one Zn(II) ion, one 3,3'-tmbpt ligand, one *m*-bdc anion and two water molecules. As shown in Fig. 7a, each Zn(II)



Fig. 6 (a) ORTEP view of **6** showing the local coordination environment of Zn(II) ion with hydrogen atoms and lattice water molecules omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ${}^{\#1}-x+1, -y, -z$; ${}^{\#2}-x+2, -y+1, -z-1$. (b) View of the 1D chain of **6**.



Fig. 7 (a) ORTEP view of 7 showing the local coordination environment of Zn(II) ion with hydrogen atoms and lattice water molecules omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ^{#1} x, y, z + 1; ^{#2} x - 1/2, -y + 1/2, z + 1/2. (b) View of the *meso*helix chain constructed by Zn(II) ions, 3,3'-tmbpt ligands and *m*-bdc anions. (c) View of the 2D layer of 7.

ion is five-coordinated by two nitrogen atoms from two different 3.3'-tmbpt ligands (Zn1–N1 = 2.157(2) and Zn1–N8^{#2} = 2.217(3) Å) and three oxygen atoms from two individual m-bdc anions and one water molecule (Zn1–O2 = 2.042(2), Zn1–O4^{#1} = 2.057(2) and Zn1–O1W = 2.082(2) Å) in a trigonal bipyramid coordination geometry. Each 3,3'-tmbpt ligand serves as a bidentate ligand with one of the free 3-position pyridyl group. In this way, the 3,3'-tmbpt ligands bridge the Zn(II) ions to form a single-stranded meso-helical chain (Fig. 7b). Notably, the mesohelix chain, having alternating right and left turns of the strand, is not a helical structure, because the strand contains inversion centers and does not have chirality.¹² The two carboxylate groups of the *m*-bdc anion adopt a μ_1 - η^1 : η^0 coordination mode (mode II in Scheme S1, ESI[†]). In this fashion, adjacent chains are further bridged by the *m*-bdc anions to form a layer (Fig. 7c). In addition, there are intermolecular O-H···O and O-H···N hydrogen-bonding interactions, which led the layers to a 3D supramolecular architecture (Fig. S8 in ESI[†]).

Structure of [Zn₂(3,3'-tmbpt)(btc)(OH)(H₂O)] (8)

Compound 8 displays a 3D 2-fold interpenetrating framework. The asymmetric unit of 8 contains two Zn(II) ions, one 3,3'-tmbpt ligand, one btc anion, one hydroxyl group and one coordinated water molecule. As shown in Fig. 8a, both Zn1 and Zn2 are five-coordinated in trigonal bipyramid coordination geometries, but their coordination environments are entirely different. Zn1 is coordinated by two nitrogen atoms from two different 3,3'-tmbpt ligands (Zn1-N1 = 2.100(4) and Zn1-N7^{#3} = 2.167(4) Å) and three oxygen atoms from two btc anions and one hydroxyl group (Zn1–O1 = 2.056(3), Zn1–O4^{#2} = 2.095(2), $Zn1-O7^{\#1} = 1.954(2)$ Å). Zn2 is coordinated by one nitrogen atom from one 3,3'-tmbpt ligand (Zn2–N8^{#5} = 2.280(4) Å) and four oxygen atoms from two individual btc anions, one hydroxyl group and one water molecule (Zn2–O5 = 1.939(3), Zn2–O7 = 1.913(2), $Zn2-O3^{\#4} = 1.977(3)$ and Zn2-O1W = 2.288(3) Å). Zn1 and Zn2 ions are held together by one hydroxyl group to form a binuclear unit [Zn₂O]. Each 3,3'-tmbpt ligand, as a tridentate ligand, links the binuclear units to generate a 1D chain (Fig. 8b). The carboxylate groups of the btc anion adopt μ_1 - η^1 : η^0 and μ_2 - η^1 : η^1 coordination modes, respectively (mode IV in Scheme S1, ESI[†]). In this manner, neighboring chains are further joined together by the btc anions to yield a 3D framework (Fig. 8c). Topologically, if the binuclear units [Zn₂O] are considered as 6-connected nodes, and the btc anions and the 3,3'-tmbpt ligands are viewed as 3-connected nodes, the 3D framework can be simplified as a (3,6)-connected framework with $(4 \cdot 6^2)(4^2 \cdot 6^8 \cdot 8^5)$ topology. Two identical (3,6)-connected nets interlock each other, giving rise to a 3D 2-fold interpenetrating framework (Fig. 8d).

Effect of the organic anions on the structures of the compounds

It is well known that the organic anions play an important role in determining the final structures of the compounds. By varying the anions under similar synthetic conditions eight related Zn(II) compounds with different structures were successfully synthesized. The roles played by the carboxylate anions in compounds **1–8** can be explained in terms of their differences in the positions and numbers of the carboxylate groups.



Fig. 8 (a) ORTEP view of **8** showing the local coordination environments of Zn(II) ions with hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: ^{#1} x, -y, z - 1/2; ^{#2} x, y + 1, z; ^{#3} x + 1/2, -y + 1/2, z + 1/2; ^{#4} x, -y - 1, z + 1/2; ^{#5} x + 1/2, -y - 1/2, z + 1/2; (b) View of the chain formed by Zn(II) ions, hydroxyl groups and 3,3'-tmbpt ligands. (c) View of the 3D framework of **8**. (d) Schematic view of the 2-fold interpenetrating framework of **8**.

Compounds $[Zn(2,3'-tmbpt)(o-bdc)(H_2O)]$ (1), [Zn(2,3'-tmbpt)(m-bdc)] (2), and $[Zn(2,3'-tmbpt)(p-bdc)]\cdot H_2O$ (3), as well as $[Zn(3,3'-tmbpt)(o-bdc)]\cdot H_2O$ (6) and [Zn(3,3'-tmbpt)(m-bdc) (H₂O)]·H₂O (7), show the effect of the positions of the carboxylate groups on the structures. Take compounds 1–3 for example. Although the *o*-bdc, *m*-bdc and *p*-bdc anions serve as dicarboxylate anions with the rigid benzene ring spacers, the positions and



Fig. 9 Solid-state excitation (blue) and emission (black) spectra of 2,3'-tmbpt and compounds 1–5 at room temperature.

angles of the two carboxylate groups are entirely different. In the o-bdc and m-bdc anions, the two carboxylate groups are located in the 1,2- and 1,3-positions with the angles of 60° and 120° , respectively, whereas in the *p*-bdc anion, the two carboxylate groups are in the 1,4-positions with the angle of 180°. The different angles between the two carboxylate groups in o-bdc, *m*-bdc and *p*-bdc anions led to their coordination with the Zn(II) ions in different directions, which further results in different Zn(II)-carboxylate motifs in 1–3. In 1, a pair of o-bdc anions link two Zn(II) ions to generate a closed loop. Neighboring loops are further extended by the 2,3'-tmbpt ligands into a chain. In 2, each *m*-bdc anion bridges two Zn(II) ions to form slightly undulated chains, which are further linked by the 2,3'-tmbpt ligands into a 3D 2-fold interpenetrating framework. However, in 3, each p-bdc anion bridges two Zn(II) ions to form highly undulated chains, which are further connected by the 2,3'-tmbpt ligands to form a 2D 2-fold interpenetrating network. It is clear that the position discrimination of the carboxylate groups leads to the structural difference of compounds 1–3.

Compounds $[Zn_2(2,3'-tmbpt)(btc)(OH)] \cdot 0.5H_2O$ (4) and $[Zn(2,3'-tmbpt)(btcc)_{0.5}] \cdot 2H_2O$ (5) exhibit the effect of the number of the carboxylate groups on the resultant structures. Compared with btc, the btec anion has an extra carboxylate group. Usually, the additional carboxylate group can increase the connection number of the ligand, which further results in different structure motifs. In 4, each btc anion, as a 3-connected node, links the Zn(II) ions to generate a planar layer, whereas, in 5, each btec anion, as a 4-connected node, bridges the Zn(II) ions to yield a wave-like layer. The layers in 4 are further linked by the 2,3'-tmbpt ligands to form a 3D 2-fold interpenetrating framework, whereas, in 5, the layers are further connected by the 2,3'-tmbpt ligands to furnish a 3D non-interpenetrating framework. Obviously, the numbers of the carboxylate group show an important influence on the structures of the compounds.



Fig. 10 Solid-state excitation (blue) and emission (black) spectra of 3,3'-tmbpt and compounds 6-8 at room temperature.

IR spectra

The bands in the range of 3030–3503 cm⁻¹ are assigned to the OH stretching modes of the water molecules for the complexes.^{13a} The asymmetric and symmetric stretching vibrations of carboxylate groups are observed in the ranges of 1506–1624 and 1313–1485 cm⁻¹, respectively.^{13a-c} The absence of the characteristic bands at around 1700 cm⁻¹ in the compounds indicates the complete deprotonation of the carboxylic groups upon reaction with Zn(II) ions.^{13a-c} The peaks observed from 1201 to 1286 cm⁻¹ are assigned to the triazole ring vibration.^{13d}

Luminescent properties. Coordination polymers with d^{10} metals display interesting luminescent properties.¹⁴ The luminescent properties of the free organic ligands and compounds **1–8** have been investigated in the solid state at room temperature (Fig. 9 and 10).

The free 2,3'-tmbpt, 3,3'-tmbpt, *o*-H₂bdc, *m*-H₂bdc, *p*-H₂bdc, H₃btc and H₄btc show emission bands centered at 542 nm, 421/537 nm, 375 nm,^{15a} 390 nm,^{15b} 393 nm,^{15c} 395 nm^{15d} and 380 nm,^{15e} respectively. The ligand emission peaks may be attributed to the π *–*n* or π *– π transition as previously reported.¹⁶ Compounds **1–5** show emission bands at 410 nm (λ_{ex} = 340 nm), 407 nm (λ_{ex} = 337 nm), 417 nm (λ_{ex} = 344 nm), 428 nm (λ_{ex} = 334 nm) and 410 nm (λ_{ex} = 331 nm), respectively. These emissions are probably due to the intraligand charge transitions of the corresponding anions, since similar emission peaks are observed for the organic polycarboxylic acids.¹⁷ The small red shifts with respect to the anions may be assigned to the coordination of carboxylate groups to the Zn(II) ions.¹⁸ The emission bands of compounds **6–8** are at 402/524 nm (λ_{ex} =

342 nm), 412/526 nm (λ_{ex} = 342 nm) and 425/524 nm (λ_{ex} = 335 nm), respectively. These emissions should originate from the 3,3'-tmbpt ligand, because similar peaks also appear for the free 3,3'-tmbpt ligand.¹⁹

The luminescence decay curves of **1–8** at room temperature (Figs. S9 and S10 in ESI[†]) fit well into a double-exponential function as $I = A + B1 \times \exp(-t/\tau_1) + B2 \times \exp(-t/\tau_2)$. The emission decay lifetimes are $\tau_1 = 3.94$ ns (59.85%) and $\tau_2 = 16.54$ ns (40.15%) ($\chi^2 = 1.024$) for **1**, $\tau_1 = 2.81$ ns (28.52%) and $\tau_2 = 11.61$ ns (71.48%) ($\chi^2 = 1.000$) for **2**, $\tau_1 = 4.02$ ns (39.80%) and $\tau_2 = 14.19$ ns (60.20%) ($\chi^2 = 1.027$) for **3**, $\tau_1 = 7.90$ ns (35.42%) and $\tau_2 = 25.09$ ns (64.58%) ($\chi^2 = 1.173$) for **4**, $\tau_1 = 2.34$ ns (75.25%) and $\tau_2 = 8.45$ ns (24.75%) ($\chi^2 = 1.006$) for **5**, $\tau_1 = 1.39$ ns (76.85%) and $\tau_2 = 7.92$ ns (23.15%) ($\chi^2 = 1.006$) for **7**, and $\tau_1 = 2.73$ ns (80.51%) and $\tau_2 = 9.47$ ns (19.49%) ($\chi^2 = 1.000$) for **8**. The luminescence lifetimes of **1–8** are much shorter than the ones from a triplet state (>10⁻³ s), so the emissions should arise from the singlet state.²⁰

Conclusions

In summary, eight Zn(II)-containing coordination polymers based on polycarboxylates and trigonal N-donor ligands have been synthesized under hydrothermal conditions. These compounds display various structure variations from 1D to 3D. The diverse structures of the compounds reveal that the numbers and positions of the carboxylate groups play important roles in the formation of the final structures. The photoluminescent spectra indicate that compounds **1–8** may be good candidates for optical materials.

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