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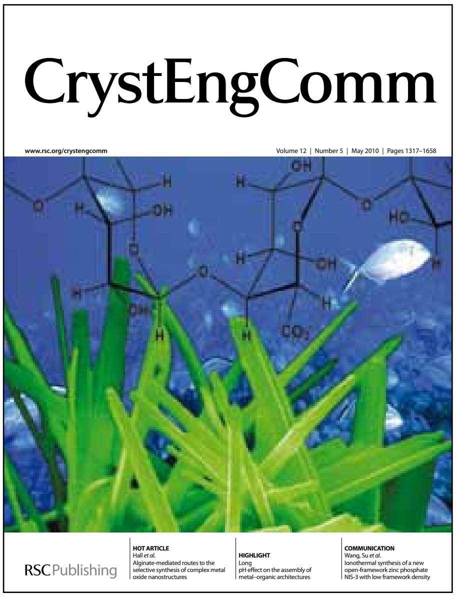

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Diverse topologies of seven d^{10} coordination polymers constructed from a long ligand and different carboxylates

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A long flexible ligand, btd = 1,10-bis(1,2,4-triazol-1-yl)decane, has been prepared. Seven new Zn(II) and Cd(II) coordination polymers based on btd ligand and different carboxylate anions, namely, [Zn(btd)Cl_2] (**1**), [Zn_2(btd)$(L1)_{1.5}$(HL1)]·H_2O (**2**), [Zn(btd)(L2)]·H_2O (**3**), [$Zn_2(btd)_2(HL3)_2$]·$4H_2O$ (**4**), $Zn_2(btd)_2$(L4) (**5**), [Cd(btd)(L2)(H_2O)]·H_2O (**6**) and [$Cd_4(btd)_3(L5)_4$]·H_2O (**7**), where H_2L1 = 1,4-benzenedicarboxylic acid, H_2L2 = 5-hydroxy-1,3-benzenedicarboxylic acid, H_3L3 = 1,3,5-benzenetricarboxylic acid, H_4L4 = 1,2,4,5-benzenetetracarboxylic acid and H_2L5 = 1,3-benzenedicarboxylic acid, have been synthesized under hydrothermal conditions. Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by infrared spectra (IR) and elemental analyses. In **1**, the Zn(II) atoms are bridged by btd ligands to generate an infinite 1D chain, which are arranged in different propagating directions. Compound **2** exhibits an entanglement of 2D → 3D entangled framework with both interpenetration and interdigitation characters, where each sheet is simultaneously interdigitated by two adjacent layers. In compounds **3** and **4**, the undulated (4^4)-sql layers are interpenetrated to each other to result a 2D → 2D interpenetrating network with the carboxylate ligands as arms hanging up both sides of the layer, where the arms of the adjacent non-interpenetrated layers are interdigitated to give a 2D → 2D → 3D framework. Compound **5** shows a 4-connected 3D framework with Schläfli symbol of $6^2 \cdot 8^4$. Compound **6** exhibits a fascinating example of 2D → 2D interdigitation with the **sql** nets using L1 ligands. In compound **7**, the binuclear Cd(II) clusters are linked by L5 anions to construct a Cd-carboxylate chain, and adjacent chains are further extended by btd ligands to generate a 2D net, which are further extended into 3D supramolecular motif through strong π-π stacking. Moreover, elemental analyses, IR spectra, and luminescent properties of these compounds were also studied.

Introduction

Over the past decade, the use of crystal engineering concepts in construction of polymeric metal–organic coordination networks have aroused intense interests because of their potential properties as functional solid material in host-guest chemistry, ion exchange, optical, catalysis, magnetic and electronic devices, many of which exhibit and fascinating structural types and topological features.[1-2] Currently, many chemists have made great contributions to this field, and much effort has been devoted on the control and adjust the topologies of metal–organic coordination polymers.[3-4] Generally, the construction of molecular architectures greatly depends on the coordination geometry of central metal cations, the nature of the anions, structural features of the neutral ligands, pH values and solvents *etc*.[5] Among those mentioned above, the selection of multidentate carboxylate anions are extremely important auxiliary organic ligand because changing the structures of the anions can influence the final frameworks, even for structures containing the same spacer ligand and metal cation.[6]

On the other hand, the structural features of the neutral organic ligands, such as the N-donor ligands as good candidates for the construction of coordination polymers, have aroused a good deal of interests from chemists because of their diversities in coordination modes and conformations.[7] It should be noted that, to date, the triazole-containing N-donor ligands such as 1,2-bis(1,2,4-triazol-1-y1)ethane, 1,3-bis(1,2,4-triazol-1-y1)propane, 1,6-bis(1,2,4-triazol-1-y1)hexane and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene, have been used in the construction of various coordination polymers.[8] However, the coordination polymers constructed by 1,10-bis(1,2,4-triazol-1-yl)decane (btd) ligand have been observed scarcely.[9]

In this work, seven new Zn(II) and Cd(II) coordination polymers based on btd ligand, namely, $[Zn(btd)Cl_2]$ (**1**), $[Zn_2(btd)(L1)_{1.5}(HL1)]\cdot H_2O$ (**2**), $[Zn(btd)(L2)]\cdot H_2O$ (**3**), $[Zn_2(btd)_2(HL3)_2]\cdot 4H_2O$ (**4**), $Zn_2(btd)_2(L4)$ (**5**), $[Cd(btd)(L2)(H_2O)]\cdot H_2O$ (**6**) and $[Cd_4(btd)_3(L5)_4]\cdot H_2O$ (**7**), where H_2L1 = 1,4-benzenedicarboxylic acid, H_2L2 = 5-hydroxy-1,3-benzenedicarboxylic acid, H_3L3 = 1,3,5-benzenetricarboxylic acid, H_4L4 = 1,2,4,5-benzenetetracarboxylic acid and H_2L5 = 1,3-benzenedicarboxylic acid, have been synthesized under hydrothermal conditions. The effects of the carboxylate anions have been elucidated in detail. Further, the photoluminescent properties of the coordination polymers have also been studied.

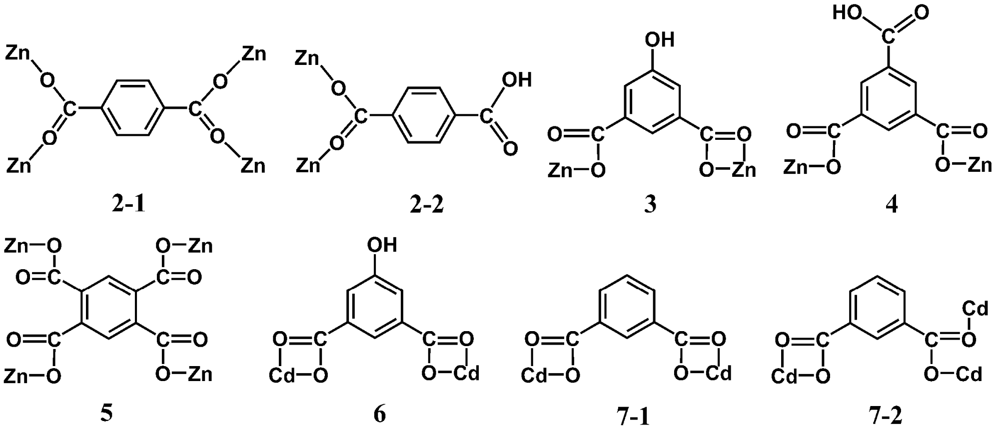


Chart 1. Coordination modes of L1-L5 anions in compounds **2-7.**

Experimental

Materials and methods

The 1,10-bis(1,2,4-triazol-1-yl)decane was synthesized in accordance with the previous report.[9] Other reagents and solvents employed were commercially available and used as received without further purification.

Physical measurements. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer, and the FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The powder X-ray diffraction (PXRD) data of the samples was collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu Ka radiation (l = 0.154 nm) and 2h ranging from 5 to 50°.The solid-state emission/excitation spectra of compounds **1–7** were measured on a Perkin-Elmer FLS-920 spectrometer at room temperature.

Synthesis of Zn(btd)Cl$_2$ (1). A mixture of btd (0.057 g, 0.2 mmol), ZnCl$_2$ (0.066 g, 0.2 mmol), and water (10 mL) was placed in a Teflon reactor (18 mL) and heated at 160 ºC for 3 days. Colorless crystals of **1** were obtained with a yield of 66%. Anal. Calcd for $C_{14}H_{24}Cl_2N_6Zn$: C, 40.74; H, 5.86; N, 20.36. Found: C, 40.59; H, 5.95; N, 20.47. IR (cm^{-1}): 3131 (ms), 2925 (s), 2853 (s), 1695 (ms), 1539 (s), 1469 (w), 1456 (w), 1277 (vs), 1211 (ms), 1134 (vs), 999 (vs), 883 (s), 856 (ms), 753 (w), 723 (ms), 673 (vs), 641 (s), 531 (ms), 486 (w).

Synthesis of [Zn_2(btd)$(L1)_{1.5}$(HL1)]·H_2O (2). A mixture of btd (0.057 g, 0.2 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.066 g, 0.3 mmol), H_2L1 (0.048 g, 0.3 mmol), and water (10 mL) was placed in a Teflon reactor (18 mL) and heated at 170 ºC for 3 days. Colorless crystals of **2** were obtained with a yield of 52%. Anal. Calcd for $C_{34}H_{37}N_6O_{11}Zn_2$: C, 48.82; H, 4.46; N, 10.05. Found: C, 48.93; H, 4.38; N, 9.95. IR (cm^{-1}): 3742 (ms), 3420 (ms), 3112 (ms), 2927 (s), 2853 (ms), 1613 (ms), 1552 (vs), 1457 (s), 1373 (vs), 1278 (ms), 1208 (w), 1135 (ms), 985 (w), 936 (w), 885 (w), 772 (ms), 714 (ms), 672 (ms), 424 (ms).

Syntheses of [Zn(btd)(L2)]·H_2O (3), [$Zn_2(btd)_2(HL3)_2$]·$4H_2O$ (4) and $Zn_2(btd)_2$(L4) (5). The preparation of **3-5** were similar to that of **2** except that the H_2L2 (0.055 g, 0.3 mmol) for **3**, H_3L3 (0.042 g, 0.2 mmol) for **4** and H_4L4 (0.038 g, 0.15 mmol) for **5** were used instead of H_2L1 of **2**. Colorless crystals of **3-5** were collected in a 62%, 45%, and 53% yield. Compound **3**. Anal. Anal. Calcd for $C_{22}H_{30}N_6O_6Zn$: C, 48.94; H, 5.60; N, 15.57. Found: C, 48.89; H, 5.73; N, 15.51. Compound **4**. Anal. Calcd for $C_{23}H_{32}N_6O_8Zn$: C, 47.15; H, 5.50; N, 14.34. Found: C, 47.11; H, 5.58; N, 14.20. Compound **5**. Anal. Calcd for $C_{38}H_{50}N_{12}O_8Zn_2$: C, 48.88; H, 5.40; N, 18.00. Found: C, 48.81; H, 5.49; N, 18.12. Compound **3**. IR (cm^{-1}): 3443 (s), 3132 (ms), 2924 (ms), 2853 (ms), 1647 (w), 1554 (vs), 1382 (vs), 1275 m(s), 1218 (ms), 1133 (s), 1005 (ms), 986 (ms), 935 (w), 878 (w), 809 (ms), 783 (s), 731 (s), 673 (ms), 649 (ms), 555 (w), 452 (w). Compound **4**. IR (cm^{-1}): 3448 (s), 3117 (ms), 2923 (s), 2852 (ms), 1708 (s), 1626 (vs), 1576 (s), 1442 (s), 1360 (vs), 1272 (s), 1183 (w), 1130 (ms), 997 (ms), 902 (w), 737 (ms), 672 (ms), 527 (w), 453 (w). Compound **5**. IR (cm^{-1}): 3449 (ms), 3134 (ms), 2927 (ms), 2854(ms), 1553 (vs), 1384 (vs), 1275 (ms), 1276 (ms), 1134 (s), 981 (ms), 935 (w), 884 (ms), 809 (ms), 732 (s), 672 (ms), 454 (w).

Syntheses of [Cd(btd)(L2)(H_2O)]·H_2O (6) and [$Cd_4(btd)_3(L5)_4$]·H_2O (7). A mixture of btd (0.057 g, 0.2 mmol), $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.080 g, 0.3 mmol), H_2L2 (0.054 g, 0.3 mmol), and water (10 mL) was placed in a Teflon reactor (18 mL) and heated at 170 ºC for 3 days. Colorless crystals of **6** were obtained with a yield of 71%. The preparation of **7** was similar to that of **6** except that the H_2L5 (0.048 g, 0.3 mmol) was used instead of H_2L2 in **6**. Colorless crystals of **7** were collected in a 57% yield. Compound **6**. Anal. Calcd for $C_{22}H_{32}N_6O_7Cd$: C, 43.53; H, 5.65; N, 13.85. Found: C, 43.45; H, 5.71; N, 13.77. Compound **7**. Anal. Calcd for $C_{74}H_{90}N_{18}O_{17}Cd_4$: C, 45.50; H, 4.64; N, 12.91. Found: C, 45.66; H, 4.56; N, 13.02. Compound **6**. IR (cm^{-1}): 3439 (ms), 3133 (w), 2926 (ms), 2856(w), 1684 (ms), 1611 (vs), 1552 (vs), 1434 (vs), 1369 (vs), 1279 (s), 1135 (ms), 986 (w), 933 (w), 1001 (w), 879 (w), 733 (s), 672 (ms), 646 (w), 514 (w). Compound **7**. IR (cm^{-1}): 3742 (w), 3384 (s), 3112 (s), 2928 (vs), 2850 (vs), 1687 (ms), 1514 (s), 1464 (ms), 1376 (ms), 1275 (vs), 1221 (ms), 1143 (s), 1018 (ms), 960 (ms), 890 (ms), 735 (ms), 687 (s), 642 (ms), 603 (w), 506 (w).

X-Ray crystallography

Single-crystal X-ray diffraction data for **1–7** were recorded on an Oxford Diffraction Gemini R Ultra diffractometer (Table 1). Diffraction intensities for **1-3**, **6** and **7** were collected on a Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Diffraction data for **4** and **5** were collected on a Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) at 293 K. The structures were solved with the direct method of SHELXS-97[10] and refined with full-matrix least-squares techniques using the SHELXL-97 program[11] within WINGX[12]. Non-hydrogen atoms of **1-7** were refined anisotropically except the atoms C10, C10′, C11, C11′, C12 and C12′ of **5**, C8, C8′, C9, C10, C10′, C11, C11′ and C12 of **6**, and C31 and O1W of **7**. The disordered atoms of **5** (C11, C12, C13) and **6** (C8, C10, C11) were refined isotropically using C atoms split over two sites. The occupancy factor of the lattice water molecule O1W in **7** was reduced to 50% because of their larger thermal parameters. The hydrogen atoms attached to the aqua hydrogen atoms of **3**, **4** and **6** were located from difference Fourier maps and refined with isotropic displacement parameters; the hydrogen atoms associated with the disorder atoms in **5-6** and water molecules in **2** and **7** were not included in the model.

Results and discussion

Structure of [Zn(btd)Cl$_2$] (1)

Selected bond lengths and angles for compounds **1-7** are listed in Table S1. Compound **1** possesses one crystallographically unique Zn(II) center, two chlorine ions and one btd ligand (Fig. S1a). The Zn(II) center is four-coordinated by two N atoms from two btd ligands [Zn1-N1 = 2.017(2) and Zn1-N6$^{\#1}$ = 2.016(2) Å], and two chlorine ions [Zn1-Cl1 = 2.2145(9) and Zn1-Cl2 = 2.2146(10) Å] in a distorted tetrahedral coordination environment. The adjacent Zn(II) centers are connected by btd ligands to form an infinite 1D polymeric chain, with the Zn···Zn distance separated by btd ligand of 18.37 Å (Fig. S1b). These polymeric chains are arranged on parallel levels in different propagating directions, rotated by 19.38º on passing from one level to the interval one, thus resulting in an AABB sequence (Fig. 1).

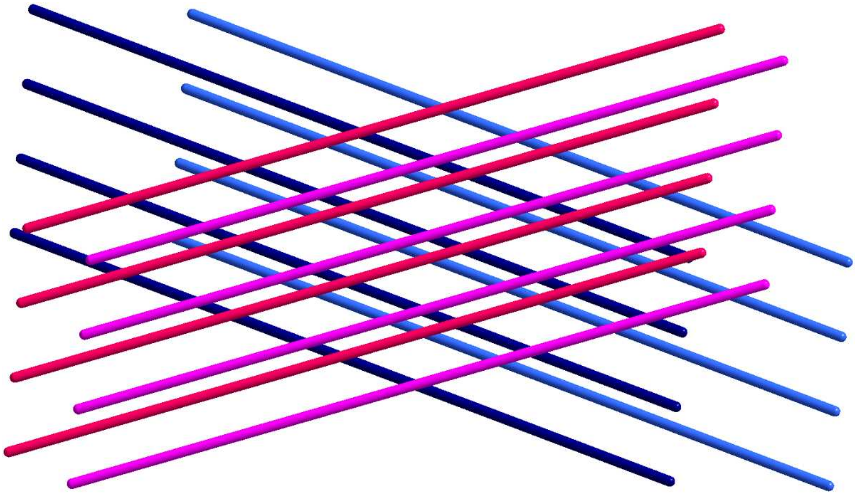
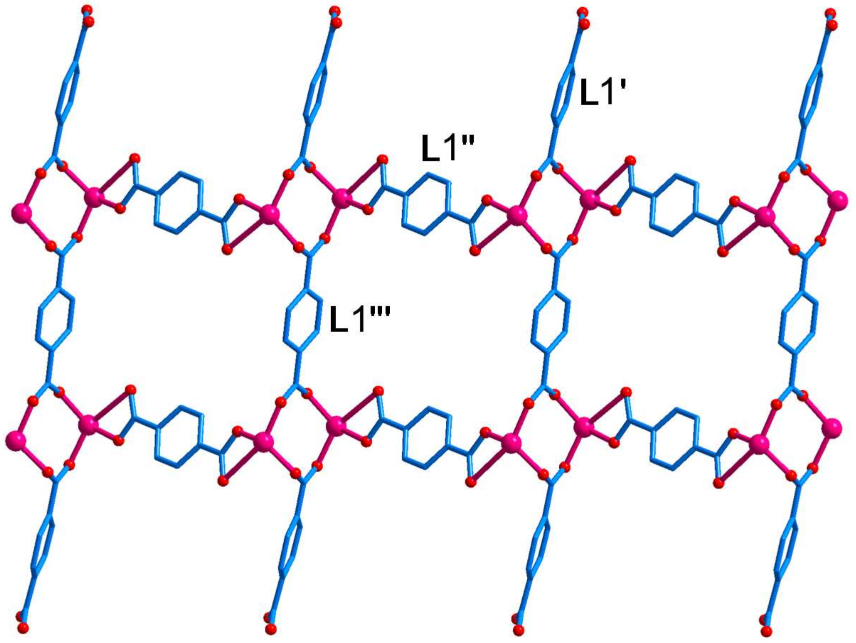


Fig. 1 Rod-packing diagram of the 1D chains spanning two different directions.

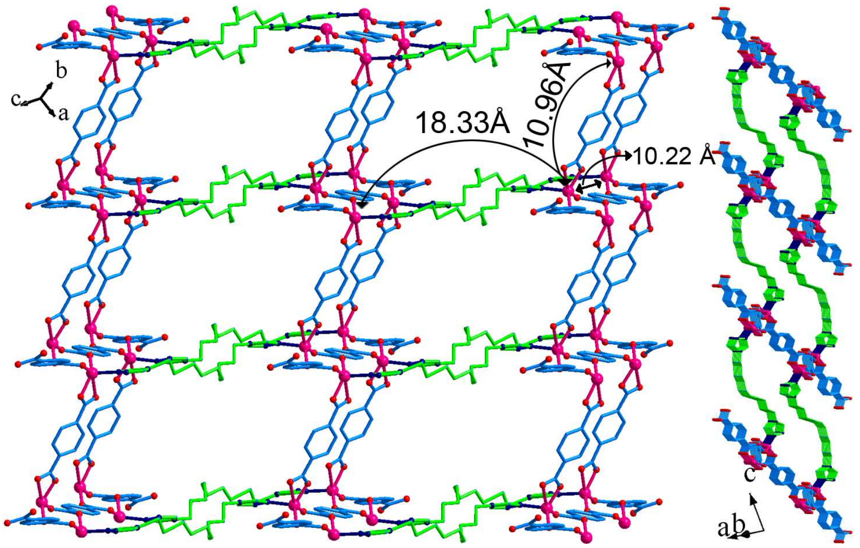
Structure of [Zn$_2$(btd)(L1)$_{1.5}$(HL1)]·H$_2$O (2)

Compound **2** possesses two crystallographically unique Zn(II) centers, three L1 anions (two of them in general positions and one on inversion center), one btd ligand, and one isolated water molecule (Fig. S2a). Both Zn1 and Zn2 centers are four-coordinated by three oxygen atoms from three p-bdc anions [Zn1-O1$^{\#1}$ = 1.991(2), Zn1-O8 = 1.929(2), Zn1-O9$^{\#1}$ = 1.956(2), Zn2-O2 = 1.961(2), Zn2-O5 = 1.934(2), and Zn2-O10 = 1.9534(19) Å], and one nitrogen atom from one btd ligand [Zn1-N6$^{\#2}$ = 2.002(3) and Zn2-N1 = 1.989(3) Å] in distorted tetrahedral geometries.

For convenience, the L3 anions containing O1, O5 and O9 are designated L1', L1" and L1'", respectively. Adjacent Zn(II) centers are bridged by L1″ and L1'" anions to form a ladder chain with the protonized L1' anions as arms hanged up two sides of the chain (Fig. 2a). The chains are linked by btd ligands to form a 2D layer with the L1' ligands hanged up two sides of the layer. There are two kinds of windows of the sheet. One kind of window is constructed by four Zn atoms and four L1 anions with the dimensions of *ca*. 10.96 × 10.22 $Å^2$, and another kind of window is constructed by two btd ligands, four L1 ligands and six Zn atoms with the dimensions of *ca*. 18.33 × 10.96 $Å^2$ (Fig. 2b). From a topological viewpoint, the sheet reveals a 5-connected topology, where the Zn atom acts as a 5-connected node, L", L'" and the biim ligand are regarded as linkers. Considering the stoichiometry, the Schläfli symbol of the 2D network can be defined as $4^8 \cdot 6^2$ (Fig. S2b). Further, each sheet is penetrated by another two adjacent nets to result a fascinating 2D → 3D interpenetrating framework. Interestingly, each sheet is simultaneously interdigitated by the arms of adjacent layers located above and below, which consolidates the 3D entanglement (Fig. 2c). As far as we know, so far, only a few examples of 2D → 3D entangled structures have been observed, in which the networks are mainly focused on 4^4 and 6^3 networks.[13] The 2D → 3D entangled frameworks with both interpenetration and interdigitation characters are exceedingly rare.[1h,13c]



(a)



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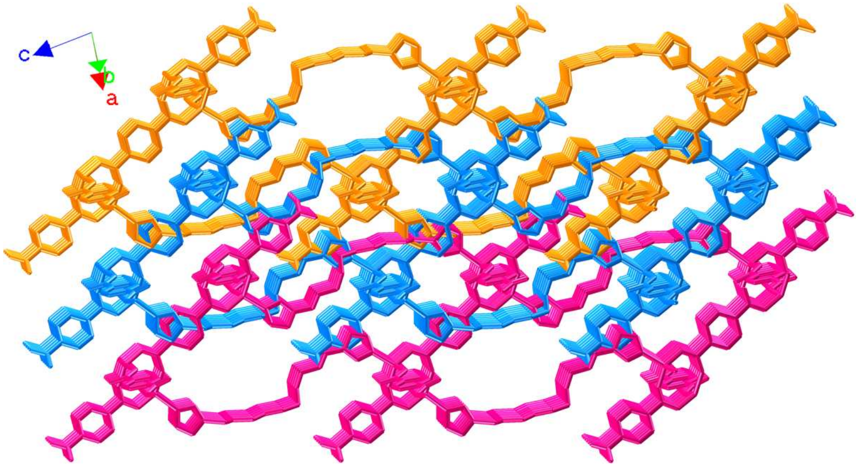


(c)

Fig. 2 (a) The 1D ladder chain of **2**. (b) The 2D layer with windows. (c) The 2D → 3D interpenetrating framework.

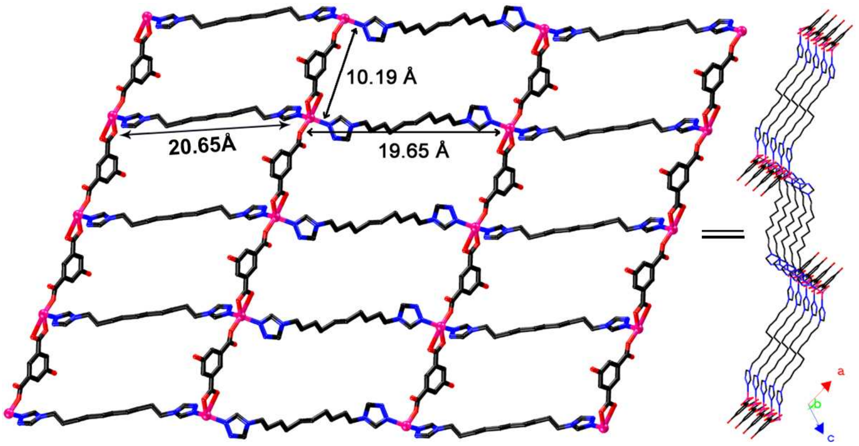
Structures of [Zn(btd)(L2)]·H_2O (3) and [Zn_2(btd)$_2$(HL3)$_2$]·4H_2O (4)

When the p-bdc anion in compound **2** is replaced by 5-OH-bdc ligand, the fascinating structure of **3** is generated.

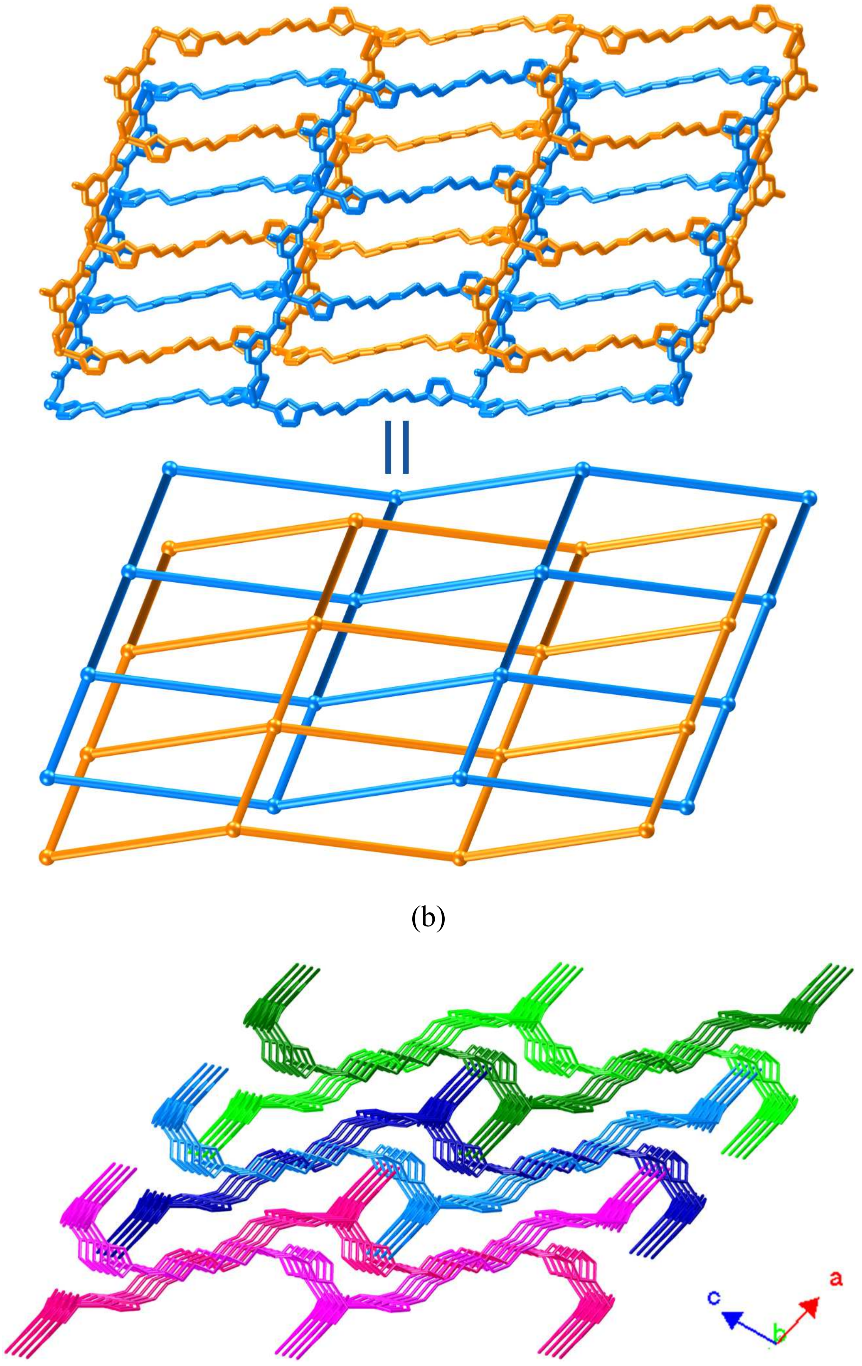
Compound **3** possesses one crystallographically unique Zn(II) center, one unique L2 anion, two halves of two unique btd ligands each lying about independent inversion centers, and one uncoordinated water molecule (Fig. S3). The Zn(II) center is five-coordinated by three oxygen atoms from two L2 anions [Zn1-O1 = 1.9971(17), Zn1-O2 = 2.4760(19), and Zn1-O4$^{\#1}$ = 1.988(3) Å], and two N atoms from two btd ligands [Zn1-N1 = 2.014(2) and Zn1-N4 = 2.014(2) Å] in a distorted square-pyramidal coordination geometry. The adjacent Zn(II) centers are bridged by btd ligands to give a Zn-btd-Zn chain, which is further linked by L2 ligands in the monodentate and didentate modes to give a 2D layer (Fig. 3a). It is noteworthy that there are two kinds of large windows of $Zn_2(L2)_2(btd)_2$ in the resulting layer, which are composed of two Zn(II) atoms, two L2 anions and two btd ligands with the dimensions of 10.19 ×19.65 Å^2 and 10.19 × 20.65 Å^2 (based on the Zn···Zn distance) respectively (Fig. 3a). From a topological perspective, the Zn(II) atoms can be viewed as 4-connected nodes, the btd and L2 ligands are considered as a linker, and this 2D layer can be described as a undulated (4^4)-sql net with the L2 anions arranging on different directions relative to the layer.

More interestingly, two such layers are interpenetrated to each other in a face to face fashion to result a 2D → 2D interpenetrating network (Fig. 3b). The most fascinating structural feature of **3** is the L2 ligands as arms interpenetrating to adjacent layers to give a 2D → 2D → 3D interdigitated framework (Fig. 3c).

Compounds **3** and **4** are isomorphous. The coordination environment of **4** is shown in Fig. S4. There are small differences between **3** and **4**. The Zn(II) atom in **4** is four-coordinated in a distorted tetrahedral coordination geometries, while the Zn(II) atom in **3** is five-coordinated in a distorted square-pyramidal coordination geometry.



(a)



(b)

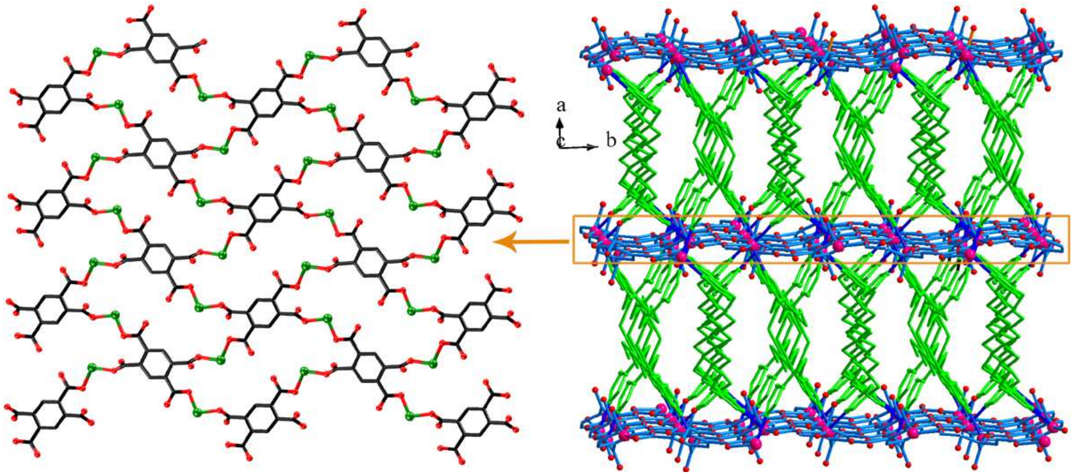
(c)

Fig. 3 (a) The 2D layer of **3** with two kinds of windows. (b) The 2D → 2D interpenetrating network and the 4-connected topology of **3**. (c) The 2D → 2D → 3D interdigitated framework.

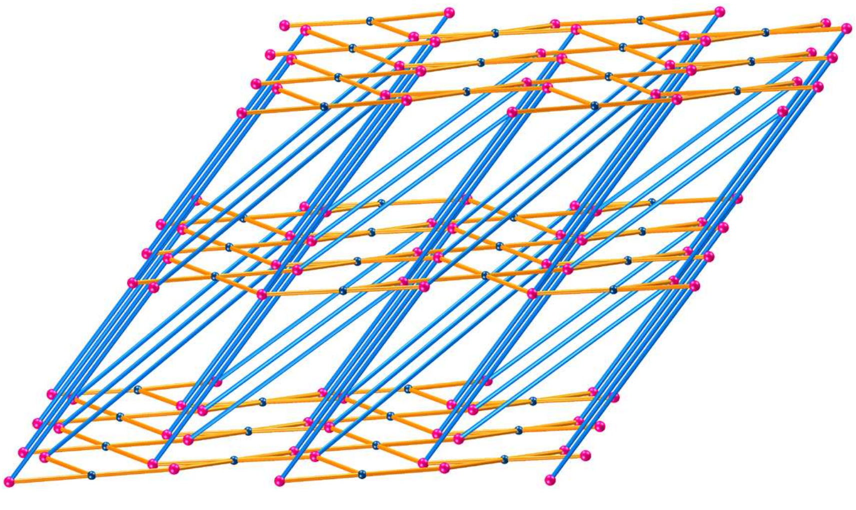
Structure of $Zn_2(btd)_2(L4)$ (5)

Compound **5** possesses one crystallographically unique Zn(II) center, two half btd ligands and half of one L4 anion (Fig. S5). The Zn1 center is four-coordinated by two oxygen atoms from two L4 anions [Zn1-O1 = 1.940(3) and Zn1-O3$^{\#1}$ = 1.968(4) Å], and two nitrogen atoms from two btd ligands [Zn1-N3 = 2.013(5) and Zn1-N4 = 2.034(6) Å] in a distorted tetrahedral geometry. Adjacent Zn(II) centers are linked by L4 anions in tetra-monodentate fashions to generate Zn-carboxylate layers, which are further extended by btd ligands to give a 3D framework (Fig. 4a).

Topologically, the L4 ligand can be considered as 4-connected node, and the Zn1 atom can also be regarded as 4-connected node. Thus, the overall structure of **5** is a unique 4-connected net with Schläfli symbol of $6^2{\cdot}8^4$ (Fig. 4b).



(a)

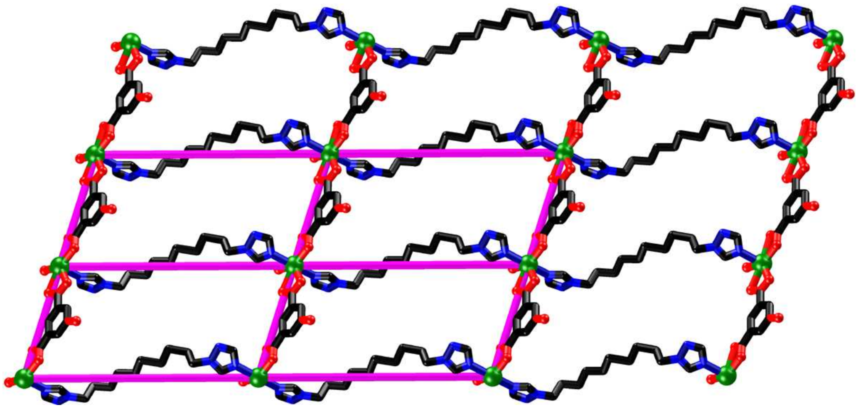


(b)

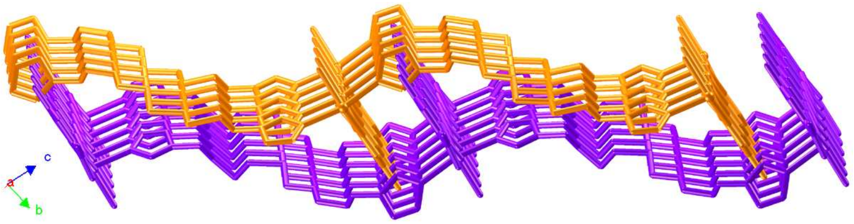
Fig. 4 (a) The Zn-carboxylate layer (left) and 3D framework (right) in **5**. (b) Schematic illustration of the topology of **5**.

Structure of [Cd(btd)(L2)(H_2O)]·H_2O (6)

Compound **6** possesses one crystallographically unique Cd(II) center, one btd ligand, one L2 anion and two water molecules (Fig. S6). The Cd1 center is seven-coordinated by five oxygen atoms from two L1 anions [Cd1-O1 = 2.336(2), Cd1-O2 = 2.491(2), Cd1-O3$^{\#2}$ = 2.591(2) and Cd1-O4$^{\#2}$ = 2.313(2) Å] and one water molecule [Cd1-O1W = 2.319(2) Å], and two nitrogen atoms from two btd ligands [Cd1-N1 = 2.287(3) and Cd1-N6$^{\#1}$ = 2.300(3) Å] in a distorted pentagonal-bipyramidal geometry. Adjacent Cd(II) centers are linked by L1 anions in bis-bidentate bridging fashions to generate Cd-carboxylate chains, which are further extended by btd ligands to give a 2D **sql** net (Fig. 5a). Notably, the **sql** net has large square windows with dimensions of 19.947 × 10.149 Å, which may offer a good chance to form a polydigitated network. Indeed, in **6**, an example of 2D → 2D interdigitation is observed, where each layer is digitated directly by one adjacent **sql** net with L1 anions (Fig. 5b).



(a)



(b)

Fig. 5 (a) The 2D layer in **6**. (b) The 2D → 2D interdigitation of **6**.

Structure of [Cd_4(btd)$_3$(L5)$_4$]·H_2O 7

Compound **7** possesses two crystallographically unique Cd(II) centers, one and a half btd ligands, two L5 anions and half of a water molecule (Fig. S7a). The Cd1 center is seven-coordinated by six oxygen atoms from four L5 anions [Cd1-O2 = 2.296(4), Cd1-O5 = 2.675(3), Cd1-O6 = 2.272(3), Cd1-O5$^{\#2}$ = 2.406(4), Cd1-O7$^{\#1}$ = 2.545(3) and Cd1-O8$^{\#1}$ = 2.306(4) Å], and one nitrogen atom from one btd ligand [Cd1-N1 = 2.266(5) Å] in a distorted pentagonal-bipyramidal geometry. The Cd2 center is six-coordinated and exhibits a twist tetragonal-bipyramidal geometry, which is surrounded by four oxygen atoms from two L5 anions [Cd2-O1 = 2.225(4), Cd2-O3$^{\#1}$ = 2.349(3), Cd2-O4$^{\#1}$ = 2.421(4) and Cd2-O7$^{\#1}$ = 2.359(4) Å], and two nitrogen atoms from two btd ligands [Cd2-N4 = 2.320(5) and Cd2-N9$^{\#3}$ = 2.302(6) Å]. These two Cd(II) centers (Cd1, Cd2) are bridged to construct a binuclear metal cluster. Moreover, the binuclear metal clusters are linked by L5 anions to construct a Cd-carboxylate chain (Fig. 6a). Adjacent chains are further extended by btd ligands to generate a 2D net with a thickness of *ca*. 12.07 Å (Fig. 6b). Furthermore, there exists extensive offset strong π-π interaction between benzene rings of adjacent 2D layers with average centroid-centroid and slippage distance of 3.67 and 1.49 Å, respectively. Consequently, the 2D sheets are extended into 3D superamolecular motif through strong π-π stacking (Fig. 7b).

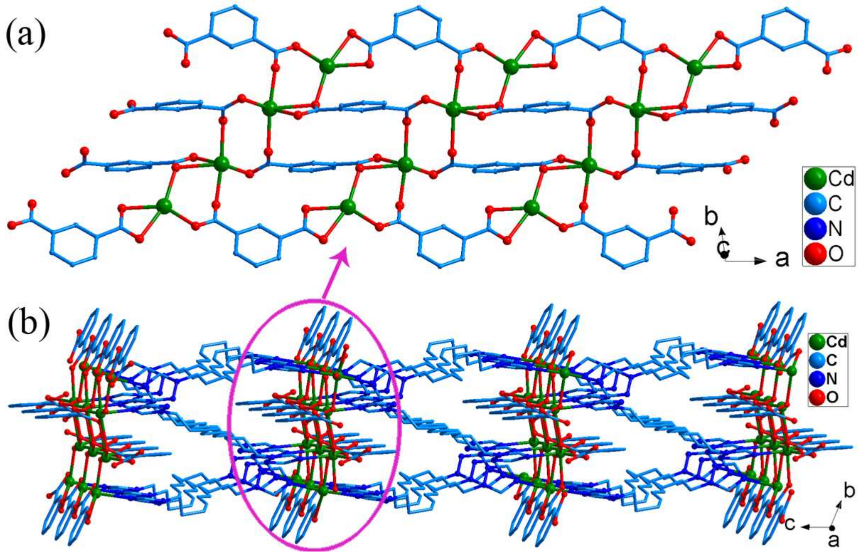


Fig. 6 (a) The Cd-carboxylate chain in **7**. (b) The 2D layer of **7**.

Effect of anions on the frameworks

In this work, the simultaneous use of the flexible btd ligand, inorganic and multidentate carboxylate anions yields a series of 1D, 2D and 3D frameworks. The L1-L5 anions exhibit a variety of coordination modes (Chart 1) and play a crucial role in the formation of the final structures. Further, the structural features of the carboxylate ligands such as the carboxylate number and the substituted group are the underlying reason for the structural differences of the complexes **2-7**. Compound **1** containing inorganic chlorine ion displays a 1D chain, while the structures of compounds **2-7** show 2D and 3D frameworks related to the carboxylate anions strongly. When the inorganic anion in **1** is replaced by L1-L4 anions in **2-5** respectively, the 1D structure is substituted for 3D frameworks. Although compounds **2-5** show 3D structures, the differences exist among these compounds. For compound **2**, the 2D layers constructing of Zn(II) centers, 1,4-benzenedicarboxylate anions (L1) and btd ligands are interpenetrated each other to form an interesting entanglement of 2D → 3D framework, where each sheet is simultaneously interdigitated by two adjacent layers. Interestingly, when the 1,3,5-benzenetricarboxylate anion (L3) was employed in **4**, the structure changed greatly. In compound **4**, the 2D layers constructing of Zn(II) centers, 1,3,5-benzenetricarboxylate anions (L3) and btd ligands are interpenetrated each other to generate 2D → 2D interpenetrating networks, which are further interdigitated by the lateral arms of the adjacent sheets to give a 2D → 2D → 3D entangled framework. In addition, when the 1,2,4,5-benzenetetracarboxylate anion (L4) was used in the synthesis of compound **5**, the 3D 4-connected $6^2{\cdot}8^4$ framework was obtained. From the structures of compounds **2**, **4** and **5**, we can see that the structural differences are mainly determined by the number of the carboxylate groups. It should be pointed out that, although 5-hydroxy-1,3-benzenedicarboxylate anion (L2) and 1,3,5-benzenetricarboxylate anion (L3) are dicarboxylate and tricarboxylate anions respectively, one protonized carboxylate group of L3 anion is the main reason for the formation of isomorphous **3** and **4**.

The structural discrepancy caused by the differences of the carboxylate anions can also be found in compounds **6** and **7**. Although compounds **6** and **7** were synthesized under similar conditions, their structures are very different. For compound **6**, adjacent Cd(II) centers are linked by 5-hydroxy-1,3-benzenedicarboxylate anion (L2) anions and btd ligands to give 2D **sql** layers, where two 2D sheets are further interdigitated each other to generate a unique 2D→2D polydigitated network. However, for compound **7**, the binuclear Cd(II) metal cluster are linked by 1,3-benzenedicarboxylate anions (L5) to construct a Cd-carboxylate chain, which are further extended by btd ligands to generate a 2D net. Furthermore, the 2D sheets are extended into 3D superamolecular motif through strong π-π interactions. Obviously, the different substituted groups of L2 and L5 carboxylate anions are the major reason for the structural differences between the complexes **6** and **7**.

In addition, the central metals also have a remarkable effect on the formation of the frameworks. The varieties in coordination numbers and atomic radius of the central metal atoms play important roles in the final structures. Since the radius of Cd(II) ion is larger than the Zn(II) ion, the coordination numbers of Cd(II) in **6** (6 and 7) is larger than the Zn(II) ion in **3** (5). Thus, the structural discrepancies between **3** and **6** may be attributed to the differences in the steric hindrance of the metal ions.

Comparisions of the bis(1,2,4-triazole) ligands on the frameworks

Up to now, many bis(triazole) ligands have been used to construct the coordination polymers, such as bis(1,2,4-triazol-1-yl)-ethan, -propane, -butane，and –hexane, etc.[8] In this study, the long flexible 1,10-bis(1,2,4-triazol-1-yl)decane ligand was selected to build the ultimate structures. From the structure descriptions of **1-7** and reported compounds, we can see that the additional –CH_2– groups of the long flexible bridging bis(1,2,4-triazol-1-yl)decane ligand plays important roles in the formation of the final structures. Compared the compounds $[Zn_3(L3)_2(btp)_2(H_2O)_2]\cdot 2H_2O$ (**8**) (btp = 1,3-bis(1,2,4-triazol-1-yl)propane)[8d] and **4**, the trinodal (3,3,4)-connected $(5.6^2)(5^2.6)(5^4.8^2)$ layers of **8** penetrate each other in parallel interpenetrating modes to give a 2D → 2D entangled network while the compound **4** shows 2D → 2D → 3D framework with the 4^4 layers. Although the compounds **5**, $[Zn_2(bte)(L4)(H_2O)_4]\cdot 2H_2O$ (**9**) and $[Zn_2(btp)_2(L4)]\cdot 10H_2O$ (**10**) (bte = 1,2-bis(1,2,4-triazol-1-yl)ethane)[8e] contain the same 1,2,4,5-benzenetetracarboxylate anions, the structures of the compounds are completely different. Compound **5** shows a 4-connected 3D framework with Schläfli symbol of $6^2\cdot 8^4$. In **9**, the bte ligands connect the 2D $[Zn_2(L4)]_n$ networks to generate an (3,4)-connected 3D network with Schläfli symbol being $(6\cdot 10^2)(6^2\cdot 10^4)$. In **10**, each btp ligand links two $[Zn_2(L4)]_n$ 1D belts to form a (4,4)-connected 2D sheet, which is interpenetrated by the btp ligands of two adjacent identical layers to form a 3D supramolecular network. Further, the structural differences caused by the –CH_2– spacers between the two triazole rings of the bis(triazole) ligands are also supported by compounds **6** and $[Cd(btp)(L2)(H_2O)]\cdot 3H_2O$ (**11**), and **7** and $[Cd(btp)(L5)(H2O)]\cdot 2.5H_2O$ (**12**).[8g]

As described above, the additional –CH_2– group will increase the length of the btd ligand and decrease stericindrances when the btd ligand coordinated with the metal atoms. Therefore, the –CH_2– spacers between the two triazole rings of the bis(triazole) ligands are the main factors that led to their complex structure differences.

Luminescent properties

Luminescent properties of d^{10} complexes have attracted intense interest of chemists due to their potential applications in chemical sensors, photochemistry and electroluminescent display.[14] The solid-state photoluminescent properties of free ligands and compounds **1-7** have been investigated at ambient temperature (Fig. 7). The wavelengths of the emission maximums and excitation are listed in Table 2.

The photoluminescent spectrum of the btd ligand has been investigated and shows the emission maxima at 410 nm (λ_{ex} = 353 nm). The emissions of H_2L1, H_2L2, H_3L3, H_4L4 and H_2L5 are observed at 390 nm (λ_{ex} = 350 nm), 392 nm (λ_{ex} = 343 nm), 330 nm (λ_{ex} = 448 nm), 430 nm (λ_{ex} = 356 nm) and 390 nm (λ_{ex} = 350 nm), respectively. The emissions for these free ligands can be assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the intraligands as previously reported.[15]

On complexation of these ligands with Zn(II) or Cd(II), the emission peaks occur at 406 nm (λ_{ex} = 327 nm) for **1**, 446 nm (λ_{ex} = 335 nm) for **2**, 495 nm (λ_{ex} = 338 nm) for **3**, 423 nm (λ_{ex} = 323 nm) for **4**, 450 nm (λ_{ex} = 325 nm) for **5**, 455 nm (λ_{ex} = 347 nm) for **6**, 408 nm (λ_{ex} = 324 nm) for **7**. The main emission bands of **1** and **7** are located at similar positions, which are similar to those of the free btd ligand. Thus, the emissions of compounds **1** and **7** are probably assigned to the btd intraligand fluorescence. The emission peak of **4** is similar to that of H_3L3 ligand, and the result indicates that the luminescence of **4** can be attributed to the L3-based emission. Compounds **2**, **3**, **5** and **6** show significantly red-shifted emissions relative to the bands shown by the free btd and corresponding carboxylic acid ligands (Table2). These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature since Zn^{2+} or Cd^{2+} ions are difficult to oxidize or to reduce due to its d^{10} configuration.[16] This result indicates that the photoluminescence of **2**, **3**, **5** and **6** may be attributed to a mixture characteristics of intraligand and ligand-to-ligand charge transition (LLCT), as reported for other Zn(II) or Cd(II) complexes with N-donor ligands.[15c, 16] Further, the deprotonation or replaced by metal ions of the carboxylate ligands can also decrease the $n\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ gap of the carboxylate ligands, resulting in the red-shift of the emission peaks.

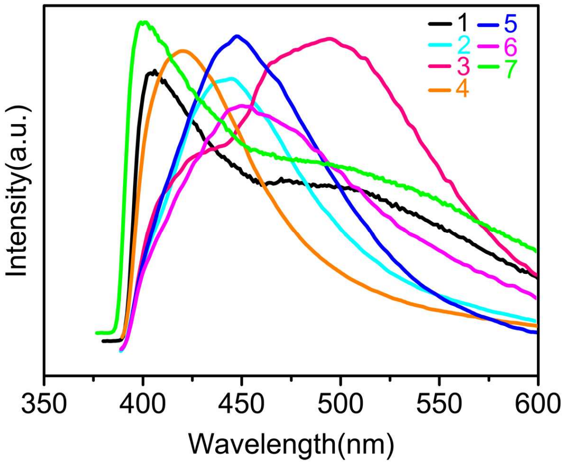


Fig. 7 Solid-state photoluminescent spectra of **1-7** at room temperature.

Conclusion

In conclusion, a series of new coordination complexes based on btd and different carboxylate ligands, have been synthesized and characterized by single-crystal X-ray diffraction analyses. These compounds exhibit diverse fascinating architectures from 1D chain to 3D entangled frameworks depending on anions and metal centers variations. The entangled modes observed in **2-4** and **6** are interesting in the metal–organic interpenetrating frameworks. The synthetic strategy presents an example for the construction of high dimensional entangled frameworks using longer organic ligand.

Acknowledgments

We thank the National Natural Science Foundation of China (grant no. 21371098), the National Key Technologies R&D Program of China (2011BAE06B04), the Natural Science Foundation of Jiangsu Province (no. BK20131314), and the Fundamental Research Fund for the Central Universities (KYZ201323).

† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, structure description of **4**, Fig. S1-7 for compounds **1-7**, selected bond lengths and angles of the compounds **1-7**, the simulated and experimental PXRD patterns for the compounds. CCDC reference numbers 961127-961133.

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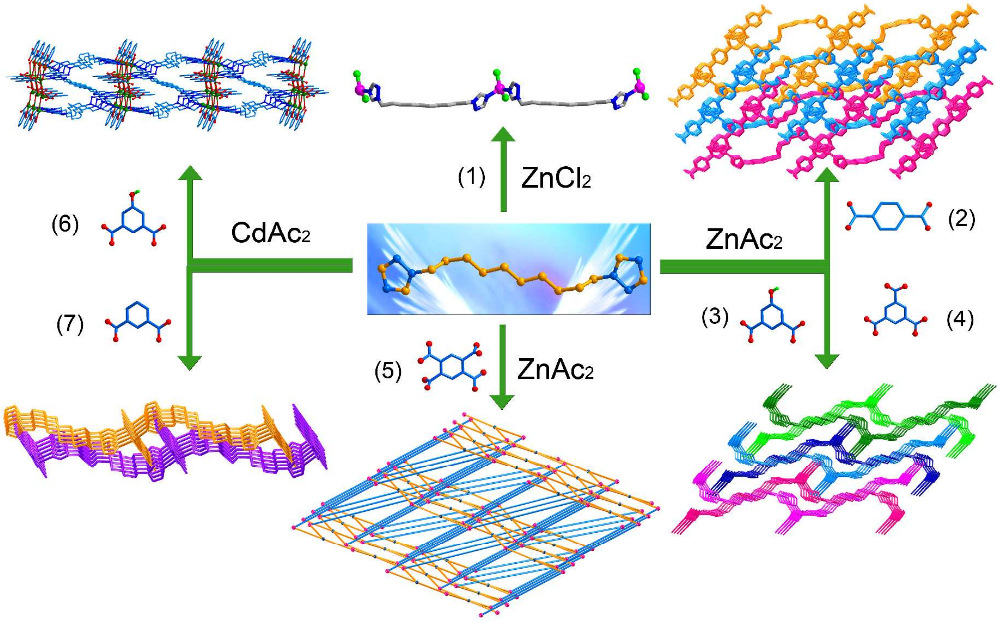
Table 1 Crystal data and structure refinements for compounds **1-7**.

	1	**2**	**3**	**4**
Empirical formula	$C_{14}H_{24}Cl_2N_6Zn$	$C_{34}H_{37}N_6O_{11}Zn_2$	$C_{22}H_{30}N_6O_6Zn$	$C_{23}H_{32}N_6O_8Zn$
Fw	412.66	836.44	539.89	585.92
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1	P-1
a [Å]	17.429(3)	7.9316(4)	10.0880(4)	10.142(2)
b [Å]	5.8100(10)	11.5548(3)	10.1850(4)	11.524(2)
c [Å]	25.244(5)	20.3743(10)	15.0410(7)	11.819(2)
α [^{0}]	90	87.909(3)	109.498(4)	85.816(15)
β [^{0}]	130.35(1)	80.351(4)	92.338(4)	88.121(17)
γ [^{0}]	90	75.405(3)	117.693(7)	77.469(17)
V [Å^3]	1948.1(6)	1781.41(13)	115.87(9)	1344.7(5)
Z	4	2	2	2
R_{int}	0.0414	0.0303	0.0176	0.1419
R1 [I>2σ(I)]	0.0317	0.0379	0.0400	0.0731
wR2 (all data)	0.0373	0.0824	0.1125	0.1969

	5	**6**	**7**
Empirical formula	$C_{38}H_{50}N_{12}O_8Zn_2$	$C_{22}H_{32}N_6O_7Cd$	$C_{74}H_{90}N_{18}O_{17}Cd_4$
Fw	933.64	604.94	1953.24
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	P-1	P-1
a [Å]	30.249(3)	10.1490(7)	10.1865(10)
b [Å]	9.1097(3)	10.4230(7)	13.716(2)
c [Å]	18.2763(13)	14.5960(10)	15.936(2)
α [^{0}]	90	75.494(6)	111.617(13)
β [^{0}]	122.814(11)	81.455(6)	93.704(9)
γ [^{0}]	90	66.286(7)	95.474(10)
V [Å^3]	4232.6(5)	1366.58(16)	2048.6(5)
Z	4	2	1
R_{int}	0.0905	0.0202	0.0473
R1 [I>2σ(I)]	0.0722	0.0367	0.0393
wR2 (all data)	0.1908	0.0980	0.0735

Table 2 The wavelengths of the emission maximums and excitation (nm) for compounds **1-7** and free Ligands.

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
λ_{em}	406	446	495	423	450	455	408
λ_{ex}	327	335	338	323	325	347	324
Ligand	H_2L1	H_2L2	H_3L3	H_4L4	H_2L5	btd	
λ_{em}	390	392	430	416	390	410	
λ_{ex}	350	343	330	356	350	353	



Seven d^{10} coordination complexes exhibiting diverse architectures from 1D chain to 3D entangled frameworks based on long flexible 1,10-bis(1,2,4-triazol-1-yl)decane and different carboxylate anions have been synthesized and characterized by single-crystal X-ray diffraction analyses, where their luminescent properties were studied in detail.