# Multifarious Zn<sup>II</sup> and Cd<sup>II</sup> coordination frameworks constructed by a versatile *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene tecton and various benzenedicarboxyl ligands<sup>†</sup>

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A new family of  $Zn^{II}$  and  $Cd^{II}$  coordination complexes **1–8** with a multifunctional building block *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (bpe) have been prepared at ambient conditions in watermethanol solution, by varying the auxiliary benzenedicarboxyl co-ligands from the familiar isophthalic acid (H<sub>2</sub>ip) and terephthalic acid (H<sub>2</sub>tp) to their derivatives 5-hydroxylisophthalic acid (H<sub>2</sub>hip) and tetrabromo-terephthalic acid (H<sub>2</sub>tbta). Single-crystal X-ray diffraction indicates that these complexes display a variety of coordination motifs, from the discrete mononuclear species (**8**) to infinite 1-D (**1** and 7), 2-D (**3**, **5**, and **6**), and 3-D (**2** and **4**) metal–organic networks. Furthermore, extended supramolecular architectures are constructed for these complexes *via* predictable secondary interactions such as hydrogen bonding and aromatic stacking. A comprehensive structural analysis and comparison of **1–8** reveals that their crystalline lattices can be properly regulated by a selection of different metal ions (Zn<sup>II</sup> or Cd<sup>II</sup>) and benzenedicarboxyl co-ligands, as well as the versatile building functionality of the bpe tecton , which can be readily involved in both coordination and secondary interactions. Notably, this work first demonstrates that bpe can also be applied as an angular bridging spacer by using both the 4and 2-pyridyl groups to construct novel Cd<sup>II</sup> coordination frameworks.

# Introduction

Rational design and preparation of coordination polymers with desired network structures and physical or chemical properties is a theme of remarkable concern in recent years.<sup>1,2</sup> As is widely known, the critical factor for the construction of such metal-losupramolecular assemblies is the rational choice of organic building block and metal center.<sup>3,4</sup> Accordingly, the tectonic ligands with suitable functional groups (for example, carboxylate and pyridyl) and molecular backbones are most pivotal in the structural regulation of coordination polymers.<sup>5–7</sup> Notably, coexistent non-coordinating groups of the bridging ligands will also considerably affect the resulting crystalline networks, which have not been sufficiently regarded and well understood so far.<sup>8</sup>

In this context, aromatic dicarboxyl compounds have been extensively explored to design and prepare a variety of intriguing coordination frameworks with promising applications.<sup>9</sup> Such ligands with two carboxyl groups located at different positions of the aromatic backbones may display the distinct spatial effects and deprotonated degrees of carboxyl groups, which results in their diverse binding modes upon metal complexation and, thus, regulates the structural assembly. In addition, these supramolecular tectons can also affect the network structures *via*  noncovalent interactions such as hydrogen bonding and aromatic stacking. However, related dicarboxyl ligands with coordination-unfavored substituents (such as hydroxyl<sup>10</sup> and halogen<sup>11</sup>) have rarely been investigated so far. In this work, two pairs of comparable aromatic dicarboxyl ligands, isophthalic acid (H<sub>2</sub>ip) and 5-hydroxylisophthalic acid (H<sub>2</sub>hip) as well as terephthalic acid (H<sub>2</sub>tp) and tetrabromo-terephthalic acid (H<sub>2</sub>tbta), have been applied in the construction of metallosupramolecular complexes, aiming at demonstrating the influence of the inert groups (–OH and –Br) on coordination assemblies. Theoretically speaking, such substituent groups will change the electron density, steric effect, and hydrogen-bonding capacity of the benzenedicarboxyl building blocks and thus, lead to the formation of distinct coordination complexes.

On the other hand, in comparison with the typical and familiar dipyridyl-type building blocks, trans-1-(2-pyridyl)-2-(4-pyridyl)ethylene (bpe) has seldom been considered<sup>12</sup> as an elongated analogue of 2,4-dipyridyl. Recent research results have revealed that the bpe ligand normally serves as a bifunctional ligand, that is, the 4-pyridyl and 2-pyridyl groups thereof are involved in coordinative and H-bonding interactions, respectively, in the resulting coordination complexes due to their different steric hindrance.12d-12f Moreover, aromatic stacking contacts may also be available from the pyridyl rings. As a result, diverse supramolecular networks can be readily achieved due to the interplay of multiform interactions. In this regard, only two exceptional examples have been known, including a 2-D complex [Ag(b $pe(NO_3)_n^{12b}$  and a 1-D species { $[Cu(bpe)](BF_4)_n^{12c}$  in which bpe acts as a bridging spacer with both types of pyridyl rings being coordination-activated, probably due to the preferable binding ability of the silver(I) and copper(I) ions. Herein, we will

College of Chemistry and Life Science, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin, 300387, P. R. China. E-mail: dumiao@public.tpt.tj.cn † Electronic supplementary information (ESI) available: Experimental details, PXRD patterns (Fig. S1), selected bond parameters (Table S1) and possible hydrogen-bonding geometries (Table S2). CCDC reference numbers 737262–737269. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912001g

report the preparation and structural diversity of eight  $Zn^{II}$  and  $Cd^{II}$  complexes based on bpe and the aforementioned aromatic dicarboxyl co-ligands, namely, { $[Zn(bpe)_2(ip)](H_2O)_2$ }<sub>n</sub> (1), { $[Cd_2(bpe)_2(ip)_2(CH_3OH)(H_2O)](H_2O)_4$ }<sub>n</sub> (2), { $[Zn(bpe)_2(hip)](H_2O)_{1,25}$ }<sub>n</sub> (3), { $[Cd_2(bpe)_2(hip)_2(CH_3OH)(H_2O)](H_2O)_4$ }<sub>n</sub> (4), { $[Zn_2(bpe)_2(tp)_2](H_2O)$ }<sub>n</sub> (5), { $[Cd(bpe)(tp)(H_2O)](H_2O)$ }<sub>n</sub> (6), [ $Zn(bpe)_2(tbta)(H_2O)$ ]<sub>n</sub> (7), and [ $Cd(Hbpe)_2(tbta)_2(H_2O)_2$ ]( $H_2tbta$ ) (8). The intrinsic factor for directing the structural construction of the resulting supramolecular frameworks has been established.

## Experimental

#### Materials and general methods

All reagents and solvents were commercially available and used as received. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer. C, H, and N analyses were performed on a CE-440 (Leemanlabs) analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 mA for a Cu-target tube ( $\lambda = 1.5406$  Å). The calculated PXRD patterns were obtained from the single-crystal diffraction data by using the PLATON software.

#### Preparation of the complexes

All complexes were similarly prepared using the following synthetic method and other experimental details and characterization data (IR and microanalysis) were given in the ESI.<sup>†</sup>

General procedure: to a hot CH<sub>3</sub>OH (10 mL) solution of benzenedicarboxyl (0.1 mmol) was added a H<sub>2</sub>O solution (5 mL) of bpe (0.1 mmol) with stirring for *ca*. 10 min. Then, a CH<sub>3</sub>OH (5 mL) solution of  $Zn(NO_3)_2 \cdot 6H_2O$  or  $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 mmol) was added to the above mixture with continuous stirring for *ca*. 30 min. The resulting solution was filtered and left to stand at room temperature. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvents.

#### X-Ray crystallography

Single-crystal X-ray diffraction data for complexes 1-8 were collected on a Bruker Apex II CCD diffractometer with Mo Ka radiation ( $\lambda = 0.71073$  Å) at room temperature. There was no evidence of crystal decay during data collection. In each case, the semiempirical absorption correction was applied (SADABS) and the program SAINT was used for integration of the diffraction profiles.13 All structures were solved by direct methods using the SHELXS program of SHELXTL and refined with SHELXL.<sup>14</sup> The final refinements were performed by fullmatrix least-squares methods with anisotropic thermal parameters for all non-H atoms on  $F^2$ . Notably, both bpe ligands in 1 and 3 as well as one bpe ligand in 5 were treated using a disorder model,<sup>15</sup> in which the pyridyl groups in the two orientations are more or less coincident but with the central -CH=CH- fragment adopting two different locations. In addition, one pyridyl ring in the other bpe ligand in 5 was similarly treated as disorder and notably, multiple structural restraints were applied for all these disorder components. In general, C-bound H atoms were placed geometrically and refined as riding, whereas O- and N-bound H atoms were first

located in difference Fourier syntheses and then fixed at the calculated sites. Isotropic displacement parameters of the hydrogen atoms were derived from their parent atoms. The H atoms of one lattice water molecule (O5) in 1 cannot be properly determined from the difference Fourier maps. In 3, the lattice water molecules of O6, O7, and O8 were assigned to a half or quarter occupancy to obtain the appropriate thermal parameters and their affiliated H atoms were not located. The lattice water molecules of O13 and O14 in 2, O15 and O16 in 4, as well as O9 in 5 are disordered over two or three positions with different partial site-occupancy-factors (see CIF for details),† the H atoms of which were not determined either. Further crystallographic data for 1-8 are listed in Table 1. Selected bond distances and angles are summarized in Table S1 and H-bonding geometries are given in Table S2.†

### **Results and discussion**

#### Synthesis and general characterization

Complexes 1-8 were prepared under similar synthetic conditions, by directly assembling the metal salts with organic ligands in CH<sub>3</sub>OH-H<sub>2</sub>O solution at room temperature. In each case, an equimolar ratio of metal: bpe: dicarboxyl was used for the starting reagents. However, the stoichiometric compositions in the crystalline products are found to be 1 : 2 : 1 for complexes 1, 3, and 7, and 1:2:3 for complex 8. All complexes were characterized by IR, microanalysis, and X-ray single crystal diffraction. In the IR spectra of 1-8, the broad peaks centered at ca. 3400 cm<sup>-1</sup> indicate the O-H characteristic stretching vibrations of water, methanol, hydroxyl, and/or carboxyl. In those of 1-7, the absence of a characteristic absorption band of carboxyl (ca. 1700 cm<sup>-1</sup>) reveals the complete deprotonation of the dicarboxyl ligands. As a result, the antisymmetric and symmetric stretching vibrations of carboxylate appear in the range of 1554-1643 and 1385–1419 cm<sup>-1</sup>, respectively. The IR spectrum of 8 shows strong absorption peaks at 1706, 1628, and 1325 cm<sup>-1</sup> of the carboxyl and carboxylate groups, and a sharp band with medium intensity at 3075 cm<sup>-1</sup> of the protonated pyridyl ring. In addition, the phase purity of bulk crystalline samples for complexes 1-8 was further confirmed by powder X-ray diffraction (PXRD) patterns, which agree well with the calculated ones (see Fig. S1).<sup>†</sup>

#### Crystal structures of complexes 1-8

{[Zn(bpe)<sub>2</sub>(ip)](H<sub>2</sub>O)<sub>2</sub>}<sub>n</sub> (1). In the structure of 1, each Zn<sup>II</sup> ion is surrounded by four carboxylate oxygen atoms from three ip ligands and two pyridyl nitrogen donors from a pair of bpe ligands (see Fig. 1a), and the local coordination geometry of Zn<sup>II</sup> can be described as a distorted octahedron. For each ip ligand, the two carboxylate groups adopt the  $\eta$ -O,O' (chelating) and  $\mu$ -O,O'<sub>syn</sub> (bridging) coordination modes, and are inclined to the attached phenyl plane with dihedral angles of 15.6(2) and 1.6(2)°, respectively, which deviate from each other by 16.5(2)° from coplanarity. In this way, the Zn<sup>II</sup> centers are connected by the ip dianions (behaving as  $\mu_3$ -linkers) to form a 1-D array along [100] with the familiar dimeric [Zn<sub>2</sub>( $\mu$ -COO<sup>-</sup>)<sub>2</sub>] nodes (see Fig. 1b), within which the adjacent Zn···Zn distance is 4.295(1) Å. A side view from the [010] direction reveals that the unidentate bpe ligands are located at both sides of each [Zn(ip)]<sub>n</sub> array and the

Table 1 Crystallography dat	and structural ref	inement summary for	complexes 1–8					
	1	2	3	4	5	6	7	8
Chemical formula Formula weight Crystal size/mm Crystal size/mm Crystal system Space group a/A	$\begin{array}{l} C_{32}H_{28}N_4O_6Zn\\ 629.95\\ 0.45\times0.34\times0.2\\ Triclinic\\ P\bar{1}\\ 10.241(3)\\ 10.241(3)\\ 10.241(3)\\ 10.241(3)\\ 10.241(3)\\ 10.241(3)\\ 10.359(3)\\ 10.359(3)\\ 96.187(3)\\ 10.359(3)\\ 96.187(3)\\ 11.449\\ 0.0128\\ 0.000\\ 652\\ 7913/5067\\ 534\\ 0.0158\\ 0.0158\\ 0.0128\\ 0.0128\\ 0.01379, 0.11131\\ 1.117\end{array}$	$\begin{array}{c} C_{41}H_{42}N_{4}O_{14}Cd_{2}\\ 1039.59\\ 10.24\times0.22\times0.18\\ Monoclinic\\ P2_{1}/c\\ 14.965(2)\\ 17.256(2)\\ 90\\ 111.517(2)\\ 90\\ 111.517(2)\\ 90\\ 111.517(2)\\ 90\\ 111.577(2)\\ 90\\ 237927803\\ 559\\ 1.029\\ 2080\\ 237927803\\ 559\\ 1.003$	$\begin{split} & \text{C}_{32}\text{H}_{26.5}\text{N}\text{A}_{06.25}\text{Zm}\\ & \textbf{632.44}\\ & \textbf{0.25}\times\textbf{0.20}\times\textbf{0.14}\\ & \text{Monoclinic}\\ & \text{P}_{21}/c\\ & \textbf{14.975(1)}\\ & \textbf{11.6808(8)}\\ & \textbf{20.019(1)}\\ & \textbf{90}\\ & \textbf{11.6808(8)}\\ & \textbf{20.019(1)}\\ & \textbf{90}\\ & \textbf{10.8.963(1)}\\ & \textbf{90}\\ & \textbf{10.8.963(1)}\\ & \textbf{90}\\ & \textbf{10.8.963(1)}\\ & \textbf{90}\\ & \textbf{10.7570/5832}\\ & \textbf{564}\\ & \textbf{0.03556}\\ & \textbf{0.03556}\\ & \textbf{0.03556}\\ & \textbf{0.0593}, \textbf{0.1927}\\ & \textbf{1.082}\\ & \textbf{10.82\\} \\ & \textbf{10.82\\} \end{split}$	$\begin{array}{c} C_{41}H_{42}N_4O_{16}Cd_2\\ 1071.59\\ 0.24\times 0.20\times 0.18\\ Monoclinic\\ P2/\ellc\\ 14.8550(7)\\ 18.3497(9)\\ 17.3074(8)\\ 90\\ 109.786(1)\\ 90\\ 109.786(1)\\ 90\\ 109.786(1)\\ 90\\ 109.786(1)\\ 1.032\\ 2160\\ 0.0223\\ 0.022$	$\begin{array}{c} C_{40}H_{30}N_{4}O_{9}Zn_{2}\\ 841.42\\ 0.24 \times 0.20 \times 0.16\\ Triclinic\\ P\overline{l}\\ 10.182(2)\\ 12.374(2)\\ 12.374(2)\\ 12.374(2)\\ 12.374(2)\\ 10.486(2)\\ 90.654(2)\\ 10.486(2)\\ 103.408(2)\\ 103.408(2)\\ 103.408(2)\\ 10.466(519\\ 2\\ 1.495\\ 1.345\\ 860\\ 10146(6519\\ 297\\ 0.0162\\ 0.0386, 0.1089\\ 1.108\end{array}$	$\begin{array}{c} C_{20}H_{18}N_2O_6Cd\\ 494.76\\ 0.24\times 0.23\times 0.17\\ Monoclinic\\ C2/c\\ C2/c\\ 17.603(3)\\ 17.603(3)\\ 17.603(3)\\ 12.788(2)\\ 90\\ 10.597(2)\\ 90\\ 10.597(2)\\ 90\\ 10.11\\ 1984\\ 1.011\\ 1984\\ 1.011\\ 1984\\ 1.011\\ 1984\\ 0.0399\\ 0.1072\\ 1.069\\ 1.017\\ 1.069\\ 1.072\\ 1.069\\ 1.072\\ 1.069\\ 1.072\\ 1.069\\ 1.017\\ 1.069\\ 1.072\\ 1.069\\ 1.072\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.069\\ 1.017\\ 1.008\\ 1$	$\begin{array}{c} C_{32}H_{22}Br_4N_4O_5Zn\\ 927.55\\ 0.20\times 6.114\times 0.12\\ Monoclinic\\ P2/n\\ 11.949(1)\\ 11.949(1)\\ 11.949(2)\\ 90\\ 90\\ 91.4482(2)\\ 90\\ 91.4482(2)\\ 90\\ 91.866(2)\\ 90\\ 3181.8(6)\\ 90\\ 3181.8(6)\\ 1.936\\ 5.844\\ 1.936\\ 5.844\\ 1.936\\ 0.0293\\ 0.0361, 0.0864\\ 1.024\\ 1.024\end{array}$	$\begin{array}{c} C_{48}H_{28}Br_{12}N_4O_{14}Cd\\ 1956.06\\ 0.24 \times 0.20 \times 0.18\\ Monoclinic\\ P2/n\\ 9.1883(4)\\ 13.9263(7)\\ 21.925(1)\\ 90\\ 97\\ 21.925(1)\\ 90\\ 97\\ 21.925(1)\\ 90\\ 97\\ 21.3263(7)\\ 22.334\\ 90\\ 00\\ 378\\ 1388/4876\\ 358\\ 0.0910\\ 1.011\\ 1.011\end{array}$
(c) Fig. 1 Crystal structure of 1. (a) A local view showing the coordination environment of $Zn^{II}$ (symmetry codes: $A = -x + 1, -y + 1, -z + 1$ ; $B = x$ -1, y, z). (b) 1-D [Zn(ip)] <sub>n</sub> coordination array. (c) Packing diagram of the 1-D coordination motifs showing aromatic stacking (purple dashed lines) and hydrogen bonding (red dashed lines) interactions.	48 48 48	13138138138	24-184-184-4 84-184-184-4			(a)		

resulting 1-D patterns adopt an interdigitated stacking fashion, which facilitates the formation of aromatic stacking interactions between the adjacent bpe ligands (see Fig. 1c). The centroid-to-centroid distance and the dihedral angle between the pyridyl rings are 3.511(1) Å and  $15.0(2)^{\circ}$ , respectively. In addition, the lattice water molecules encased therein are hydrogen bonded (O6–H6A···O5) to each other and there also exists an O6–H6B···N4 H-bonding between one lattice water molecule and the 2-pyridyl ring of bpe (see Fig. 1c and Table S2† for details). Secondary interactions between the lattice water molecule of O5 and 2-pyridyl/carboxylate are also observed (O5···N2<sup>*i*</sup> = 2.895(9) Å and O5···O1<sup>*ii*</sup> = 2.825(4) Å; i = -x, -y + 1, -z and ii = x, y + 1, z).

 $\{ [Cd_2(bpe)_2(ip)_2(CH_3OH)(H_2O)](H_2O)_4 \}_n$ (2). Structural analysis of complex 2 indicates an unexpected 3-D coordination network, in which the fundamental building unit contains two types of Cd<sup>II</sup> centers as well as the bridging bpe and ip ligands. As depicted in Fig. 2a, the octahedral sphere of Cd1 is provided by two pyridyl nitrogen donors of bpe, three carboxylate oxygen atoms of two ip dianions, and one methanol. However, Cd2 adopts a distorted pentagonal-dipyramidal geometry, in which a pair of chelated carboxylate groups of ip and one water ligand are located at the equatorial plane and two pyridyl nitrogen atoms of bpe occupy the axial sites with the N1-Cd2-N3 angle of 161.3(1)°. Notably, in this structure, the 2-pyridyl group of bpe never remains coordination inert but interacts with Cd<sup>II</sup>. As a result, both independent bpe ligands serve as the angular spacers to link the Cd<sup>II</sup> ions with the Cd···X···Cd (X is the center of each 2-pyridyl ring) angles of 66.5(1) and 67.0(1)°. Also, the two types of ip ligands act as the spacers but show different coordination modes. One of the ip ligands with two  $\eta$ -O,O' chelating carboxylate groups connects the adjacent Cd2 ions, forming a zigzag chain motif with  $Cd \cdots Cd$  separation of 9.675(1) A. However, the other ip spacer bridges the Cd1 centers with n-O,O' and monodentate modes of the two carboxylates, leading to the generation of a  $2_1$  helical array along [010], with a helical pitch of 18.433(2) Å that is equal to the length of the b axis (see Fig. 2b). In this way, these zigzag chains and helices are interconnected by bpe, resulting in a 3-D achiral coordination net due to the alternate arrangement of the P and M helices. From the viewpoint of network topology, both Cd1 and Cd2 centers can be considered as equivalent 4-connected nodes and all organic ligands serve as two-connecting spacers. As a result, the Cd<sup>II</sup> nodes are extended by bpe and ip to constitute a familiar 3-D diamond (dia)<sup>16</sup> coordination framework (see Fig. 2c). In addition, the lattice water molecules are hydrogen bonded to this 3-D network (O10-H10B···O13 and O12-H12A···O1) and also to each other (O11-H11B····O13), besides the intralayer O10-H10A····O4 interactions (see Fig. 2d and Table S2).†

 $\{[Zn(bpe)_2(hip)](H_2O)_{1.25}\}_n$  (3). Although the introduction of an electron-donating –OH group on the phenyl group of ip normally defines the inert nature of coordination behavior, it does exert significant influence on the resulting coordination motif. In contrast to the 1-D  $[Zn(ip)]_n$  array in 1, complex 3 shows a 2-D  $[Zn(hip)]_n$  layer. In the asymmetric unit of 3 (see Fig. 3a), each Zn<sup>II</sup> ion is surrounded by three carboxylate oxygen atoms from different hip ligands and two 4-pyridyl nitrogen



(d)

**Fig. 2** Crystal structure of **2**. (a) A local view showing the coordination environments of Cd<sup>II</sup> ions (symmetry codes: A = -x + 1, y + 1/2, -z + 3/2; B = -x, y + 1/2, -z + 1/2; C = x - 1, -y + 1/2, z - 1/2). (b) A perspective view of the 3-D coordination framework (each bpe is represented by a blue rod for clarity), highlighting a 2<sub>1</sub> helical array of [Cd(ip)]<sub>n</sub> and its side view in the space-filling model. (c) Schematic representation of the 3-D diamond (**dia**) network (Cd1 and Cd2 are indicated by orange and green balls, and the bpe and ip linkers are simplified as blue and red rods, respectively). (d) A perspective view of the 3-D supramolecular architecture (each bpe is represented by a blue rod for clarity), highlighting a 2-D hydrogen-bonding layer therein.



**Fig. 3** Crystal structure of **3**. (a) A local view showing the coordination environment of  $Zn^{II}$  (symmetry codes: A = -x, y + 1/2, -z + 1/2; B = -x, -y + 2, -z + 1). (b) 2-D [Zn(hip)]<sub>n</sub> coordination layer. (c) Interdigitated stacking fashion of the layered networks.

donors from a pair of unidentate bpe, displaying a distorted trigonal-bipyramidal geometry ( $\tau = 0.68$ ).<sup>17</sup> Each hip is linked to three Zn<sup>II</sup> centers by using the  $\mu$ -O, $O'_{syn}$  and monodentate carboxylate groups, affording a 2-D coordination layer with dimeric [Zn<sub>2</sub>( $\mu$ -COO<sup>-</sup>)<sub>2</sub>] subunits (see Fig. 3b). This pattern can be topologically considered as a 4.8<sup>2</sup> (fes) network<sup>16</sup> with both

Zn<sup>II</sup> and hip acting as the 3-connected nodes. Furthermore, the bpe ligands are nearly perpendicular to the propagation orientation of such parallel layers to facilitate an interdigitated stacking mode (see Fig. 3c). Unexpectedly, no significant interlayer aromatic stacking interaction is found in this case. There exists intralayer O5–H5…O3 bonding between the hydroxyl and carboxylate groups as well as secondary interactions between the uncoordinated 2-pyridyl rings and lattice water molecules (N2…O8<sup>*i*</sup> = 2.696(4) Å and N4…O6 = 2.865(3) Å; *i* = -x, y + 1/2, -z + 1/2).

 ${[Cd_2(bpe)_2(hip)_2(CH_3OH)(H_2O)](H_2O)_4}_n$  (4). Contrary to the significant structural discrepancy of 1 and 3, complex 4 is isostructural to 2 and also forms a 3-D coordination framework with diamond (dia) topology. Although adding the hydroxyl group makes no direct impact on the coordination motif, different hydrogen-bonding interactions are found in the structure of 4. As depicted in Fig. 4, besides the lattice/coordinated water molecules and carboxylates, the hydroxyl groups of hip are also involved in H-bonding interactions by acting as both H-bonding donors (O5–H5…O14 and O10–H10…O13) and acceptors (O13–H13B…O5).

 $\{[Zn_2(bpe)_2(tp)_2](H_2O)\}_n$  (5). In the structure of complex 5, there are two crystallographically independent Zn<sup>II</sup> ions in the asymmetric unit with similar tetrahedral geometries, both of which are coordinated by three oxygen atoms of three carboxvlate groups and one pyridyl nitrogen donor of bpe (see Fig. 5a). In addition, the distances of Zn1…O2 and Zn2…O3A are 2.771(4) and 2.665(4) Å, respectively, revealing the presence of weak contacts. As shown in Fig. 5b, the tp ligands display two types of bridging fashions *via* a pair of monodentate or  $\mu$ -O,O'<sub>svn</sub> carboxylates, which extend the  $Zn^{II}$  centers to constitute a 2-D coordination layer along the *ab* plane. From a topology viewpoint, such a 2-D layer can be regarded as a (3,4)-connected network with a Schläfli symbol of  $(4.6^2)_2(4^2.6^2.8^2)$ , in which each 3-connecting  $Zn^{II}$  ion is linked to two 4-connecting tp ligands and one Zn<sup>II</sup> center via the 2-connecting tp spacer. Such a 2-D pattern is considerably undulated with large rhombic grids of 10.940(1)  $\times$  10.182(2) Å<sup>2</sup> (measured by the inner Zn…Zn distances), which is further decorated with the unidentate bpe ligands at both sides



Fig. 4 A perspective view showing the hydrogen-bonding interactions in 4.



(a)



**(b)** 



**Fig. 5** Crystal structure of **5**. (a) A local view showing the coordination environments of  $Zn^{II}$  ions (symmetry codes: A = x + 1, *y*, *z*; B = x, *y* - 1, *z*). (b) 2-D [Zn(tp)]<sub>*n*</sub> coordination layer. (c) 3-D packing diagram showing the interlayer aromatic stacking interactions (purple dashed lines), in which the phenyl groups of the tp linkers are simplified as rods. (d) A schematic representation of the 2-fold interpenetrating 3-D framework.

with extended lengths of ca. 9.3 Å (measured by the terminal N···· C distances). As a result, the prominent bpe branches penetrate into the cavities of two adjacent layers to construct a 3-D poly-threading architecture with finite components. Moreover, aromatic stacking interactions are observed between the opposite

bpe arms coming from the adjacent layers (see Fig. 5c). The centroid-to-centroid distances between the pyridyl rings are 3.666(1) and 3.873(1) Å, respectively, and the dihedral angles between them are 7.7(2) and  $10.9(2)^{\circ}$ . If such secondary interactions are further considered, the Zn<sup>II</sup> centers also act as the

4-connected nodes and thus, a 2-fold interpenetrating 3-D framework is formed (see Fig. 5d), in which each single net shows a binodal moganite (**mog**) topology with a Schläfli symbol of

 $(4.6^4.8)_2(4^2.6^2.8^2)$ .<sup>16</sup> In addition, secondary interactions are found between the disorder lattice water molecule and 2-pyridyl/ carboxylate (O9...O2<sup>*i*</sup> = 2.774(3) Å, O9'...N2<sup>*ii*</sup> = 3.332(2) Å, and



(b)



**Fig. 6** Crystal structure of **6**. (a) A local view showing the coordination environment of Cd<sup>II</sup> (symmetry codes: A = x + 1/2, -y + 1/2, z + 1/2; B = -x + 1/2, y + 1/2, -z + 3/2). (b) A perspective view of the 2-D coordination layer, highlighting the left- and right-handed helical arrays by purple and green rods, respectively. (c) 3-D supramolecular network showing the interlayer hydrogen-bonding interactions (red dashed lines). (d) Packing diagram in a space-filling model showing the 1-D channels along [001].

 $O9'' \cdots O2^i = 2.846(3)$  Å; i = -x + 1, -y + 2, -z + 2 and ii = -x + 1, -y + 1, -z + 1).

 $\{[Cd(bpe)(tp)(H_2O)](H_2O)\}_n$  (6). As for the Cd<sup>II</sup> complex 6, a layered coordination network is constructed by the mixed spacers of bpe and tp. In this case, each Cd<sup>II</sup> ion is bound to two pyridyl nitrogen atoms of bpe and five oxygen donors of two chelated carboxylate groups from tp and one water ligand (see Fig. 6a). Thus, the coordination sphere (CdN<sub>2</sub>O<sub>5</sub>) around Cd<sup>II</sup> can be considered as a distorted pentagonal bipyramid with N1 and O5 occupying the axial sites. As shown in Fig. 6b, the bpe spacers bridge the Cd<sup>II</sup> centers to afford 1-D [Cd(bpe)]<sub>n</sub> motifs with 21 helicity along the [010] direction, in which the helical pitch is equal to the length of the b axis. The neighboring helical arrays with opposite chirality are further connected by the tp spacers to generate a 2-D coordination layer, in which the adjacent Cd…Cd distances separated by bpe and tp ligands are 9.550(2) and 11.328(2) Å, respectively. The staggered stacking fashion of these 2-D layers facilitates the interlayer O5-H5B...

O2 interactions, which extend the 2-D layers to form a 3-D supramolecular architecture (see Fig. 6c). There also exists O5–H5A····O6 H-bonding between the lattice and coordination water molecules. Notably, 1-D channels are found along the [001] direction (see Fig. 6d) in which the lattice water molecules are located and even now, the total solvent-accessible voids of this 3-D crystalline lattice are 779.8 Å<sup>3</sup>, corresponding to 18.1% of the unit-cell volume as calculated using the PLATON program.<sup>18</sup>

 $[Zn(bpe)_2(tbta)(H_2O)]_n$  (7). As a Br-substituted derivative of tp, the tbta ligand may display different binding fashions due to the steric effect of the substituents. The Zn<sup>II</sup> ion in 7 is primarily five-coordinated by three oxygen donors of two monodentate carboxylates from tbta and one water ligand as well as a pair of pyridyl nitrogen atoms of bpe (see Fig. 7a). The coordination geometry of Zn<sup>II</sup> is significantly distorted with a  $\tau$  parameter of 0.42.<sup>17</sup> Additionally, the Zn1...O4A distance of 2.656(3) Å reveals a weak interaction. As for tbta, the carboxylate groups



**Fig. 7** Crystal structure of 7. (a) A local view showing the coordination environment of  $Zn^{II}$  (symmetry codes: A = x - 1/2, -y + 1/2, z + 1/2). (b) View of the 1-D fishbone-like coordination motif. (c) A perspective view of the 2-D layer constructed by interchain hydrogen bonds (red dashed lines), in which the bpe ligands are omitted for clarity. (d) Packing diagram showing hydrogen-bonding and aromatic stacking interactions (indicated as red and green dashed lines, respectively).

deviate from the Br<sub>4</sub>-substituted phenyl plane with dihedral angles of 85.3(3) and 83.6(4)°, adopting a monodentate coordination mode. Thus, the Zn<sup>II</sup> ions are linked by the tbta dianionic bridges and decorated with bpe terminals to produce a 1-D fishbone-like zigzag motif along the  $[10\overline{1}]$  direction, with the adjacent Zn…Zn separation of 11.124(1) Å (see Fig. 7b).









**Fig. 8** Crystal structure of **8**. (a) View of the molecular structure consisting of a mononuclear coordination unit and an uncoordinated H<sub>2</sub>tbta molecule (symmetry codes: A = -x, -y, 2 - z). The hydrogen atoms on the pyridyl nitrogen (H2A) and the carboxyl (H5A) are also shown. (b) A perspective view of the 2-D layer *via* intermolecular hydrogen bonds (red dashed lines). (c) 3-D supramolecular network *via* hydrogen bonds (green dashed lines) between the 2-D layers and lattice H<sub>2</sub>tbta molecules.

Interestingly, the adjacent 1-D arrays are linked by O5–H5A··· O4 bonds between the water ligands and carboxylates to afford a 2-D layer (see Fig. 7c). These 2-D patterns are overlapped and further extended by O5–H5B···N2 H-bonding between the water ligands and bpe tectons to construct a 3-D supramolecular architecture, in which aromatic stacking interactions are found between the 2-pyridyl groups of bpe and phenyl rings of tbta (dihedral angles = 2.8(2) and  $6.6(1)^{\circ}$ ; centroid-to-centroid distances = 3.866(1) and 3.988(1) Å), as shown in Fig. 7d.

 $[Cd(Hbpe)_2(tbta)_2(H_2O)_2](H_2tbta)$  (8). The structure of 8 indicates a discrete complex, which is composed of a centrosymmetric mononuclear unit [Cd(Hbpe)<sub>2</sub>(tbta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and an uncoordinated H<sub>2</sub>tbta molecule that lies about an inversion center (see Fig. 8a). Notably, the bpe ligand is protonated in this structure. Three pairs of Hbpe, tbta, and water ligands surround the Cd<sup>II</sup> ion in a *trans*-fashion to constitute a distorted octahedral geometry. As expected, the carboxylate (for tbta) and carboxyl (for H<sub>2</sub>tbta) groups deviate from the central aromatic ring due to the steric effect of -Br, with dihedral angles of 82.1(2)/85.6(2) and 87.1(3)°, respectively. Intramolecular O7-H7B···O1 bonds are found within the mononuclear units, which are further assembled into a 2-D supramolecular layer along the bc plane via O7-H7A...O4 interactions between the aqua ligands and carboxylates (see Fig. 8b). Moreover, the lattice H<sub>2</sub>tbta molecules are hydrogen bonded to such 2-D layers via N2-H2...O6 and O5-H5A...O3 H-bonding, resulting in a 3-D supramolecular network (see Fig. 8c).

#### Significant opinions on the structural assembly of 1-8

Structural variety is obviously observed for this series of mixedligand  $Zn^{II}$  and  $Cd^{II}$  complexes that are prepared under similar conditions (for example, from the discrete mononuclear motif to infinite 1-D, 2-D, and 3-D coordination networks), which can be temporarily ascribed to the choice of metal ions and benzenedicarboxyl ligands. A detailed comparison of the structural features for these complexes is listed in Table 2.

With the exception of that in 8, the benzenedicarboxyl ligand is generally doubly deprotonated and the carboxylate group may show monodentate, chelating, and bridging coordination modes, respectively. As a result, the benzenedicarboxylate tectons can serve as 2- or 3-connecting bridges in these complexes, connecting the metal centers to generate the 1-D double chain (for 1), helix (for 2 and 4), 2-D 4.8<sup>2</sup> (fes) network (for 3), 2-D  $(4.6^2)_2(4^2.6^2.8^2)$  layer (for 5), and 1-D zigzag array (for 6 and 7). As stated above, one of the main goals of this research is to demonstrate the influence of the substituent group of benzenedicarboxyl on directing the structural assemblies. Above all, both the -OH and -Br substituent groups are normally inactive in metal coordination, and as an electron-donating or -withdrawing group, will affect the electronic density of the aromatic ligands. Of further importance, the hydroxyl is a reliable H-bonding donor, whereas the bromo group has a significant spatial effect to make the carboxylate groups deviating from the central aromatic plane, which will make a profound impact on the resulting coordination motifs or the extended supramolecular networks. In this work, such substituent effect can be clearly revealed by a structural comparison of the related complexes (for instance,

 Table 2
 A comparison of the structural features for complexes 1–8

Complex	Co-ligand	Binding of bpe	Coordination motif	H-bonding	Aromatic stacking
1 (Zn <sup>II</sup> )	H <sub>2</sub> ip	4-pyridyl	1-D double chain	O…N/O	4-pyridyl/2-pyridyl
2 (Cd <sup>II</sup> )	H <sub>2</sub> ip	2-/4-pyridyl	3-D diamond network	00	
$3(Zn^{II})$	$H_2hip$	4-pyridyl	2-D 4.8 <sup>2</sup> network	O…O/N	
4 (Cd <sup>II</sup> )	$H_2hip$	2-/4-pyridyl	3-D diamond network	00	
5 (Zn <sup>II</sup> )	H <sub>2</sub> tp	4-pyridyl	2-D $(4.6^2)_2(4^2.6^2.8^2)$ layer	O…O/N	4-pyridyl/2-pyridyl
6 (Cd <sup>II</sup> )	H <sub>2</sub> tp	2-/4-pyridyl	2-D 4 <sup>4</sup> network	00	
7 (Zn <sup>II</sup> )	H <sub>2</sub> tbta	4-pyridyl	1-D fishbone-like chain	O…N/O	2-pyridyl/phenyl
8 (Cd <sup>II</sup> )	$H_2^{t}$ tbta	4-pyridyl	monomeric molecule	N/O…O	

complexes 1 vs. 3, 5 vs. 7, and 6 vs. 8). Notably, although complexes 2 and 4 show similar 3-D diamond coordination frameworks, the structural discrepancy of the local hydrogenbonding pattern is also observed due to the presence of a hydroxyl in 4.

A more attractive finding resides in the versatile function of bpe in the construction of these supramolecular architectures. In previous studies it has been well suggested that the bifunctional building block bpe usually tends to display the end-capping terminal coordination mode by using only the 4-pyridyl group and further provides the feasible utilization of the secondary interactions by 2-pyridyl.<sup>12d-12f</sup> This feature is also broadly observed for the complexes presented in this work (see Table 2). Remarkably, in the Cd<sup>II</sup> complexes **2**, **4**, and **6**, the bpe tecton unexpectedly shows the ability to serve as an angular spacer to connect the Cd<sup>II</sup> centers, resulting in 1-D zigzag or helical arrays. This unusual observation reveals the new functionality of bpe in constructing the coordination supramolecular architectures.

#### **Conclusions and perspective**

This work presents a series of new Zn<sup>II</sup> and Cd<sup>II</sup> supramolecular complexes generated from the mixed-ligand systems of trans-1-(2-pyridyl)-2-(4-pyridyl)ethylene (bpe) and two pairs of related benzenedicarboxyl compounds under similar synthetic conditions. Apparently, the network structures of these complexes largely depend on the choice of dicarboxyl tectons and metal ions. Further analysis at a molecular level indicates the significant substituent effect of the dicarboxyl ligands and the versatile functionality of the bpe building block, which can offer a rational structural construction of the resulting coordination motifs and further 3-D supramolecular stacking of the crystalline lattices, via interplay of the coordination bonds and secondary interactions such as hydrogen bonding and aromatic stacking. Interestingly, the bridging role of bpe is first demonstrated in the Cd<sup>II</sup> complexes, which normally leads to the formation of higherdimensional coordination networks. These fascinating results prompt us to further develop the metallosupramolecular systems based on bpe and other co-ligands, which will promise new insights into the crystal engineering of such network-based crystalline materials.

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