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### Introduction

The past decades have seen significant growth of interest in the rational design and assembly of coordination polymers (CPs) with predictable structures and desirable properties, because it plays a key role in the exploration of the functional materials with industrial applications.<sup>1</sup> Many efforts have been made to achieve this goal, among which the approach of the appropriate choice of well-designed organic ligands containing modifiable backbones and connectivity information as linkers, together with metal ions or polymetallic clusters (secondary building units) as nodes, has been proved to be an effective route to construct metal-organic frameworks (MOFs) with predictable topologies.<sup>2</sup> In this area, Yaghi and coworkers provide excellent examples where they used different linear dicarboxylate ligands and Zn<sub>4</sub>O clusters to afford a series of IRMOFs with the same structural topology (pcu net) and predetermined cavity size and functionalization.<sup>2a,b</sup> Another

## pH modulated assembly in the mixed-ligand system Cd(II)–dpstc–phen: structural diversity and luminescent properties<sup>†</sup>

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Hydrothermal reaction of cadmium salt, 3,3',4,4'-diphenylsulfonetetracarboxylic acid (H<sub>4</sub>dpstc) and 1,10phenanthroline (phen) under different pH conditions have afforded four novel supramolecular complexes, in which the pH value of the reaction solution plays a crucial structure-directing role. [Cd(H<sub>2</sub>dpstc)(phen)]<sub>n</sub> (**1**) formed in a neutral reaction environment exhibits a 1D infinite chain structure containing partially deprotonated H<sub>2</sub>dpstc<sup>2-</sup> as the H-bond donors and acceptors. Whereas [Cd<sub>2</sub>(dpstc)(phen)<sub>2</sub>]<sub>n</sub>·A.5nH<sub>2</sub>O (**2**), [Cd<sub>2</sub>(dpstc)(phen)<sub>2</sub>]<sub>n</sub>·nH<sub>2</sub>O (**3**) and [Cd<sub>2</sub>(dpstc)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O (**4**) contain fully deprotonated dpstc<sup>4-</sup> ligands due to the alkaline reaction conditions. Complex **2** possesses a unique 2D layered structure with 1D channels. The most striking feature of **2** is that its 2D holed (4,4)-water-net is constructed from hexameric water clusters and two types of dimeric water clusters. Surprisingly, the water net and the metal–organic skeleton are interpenetrated to form a fascinating 3D metal–organic–water supramolecular architecture. A further increase of the pH value leads to another 2D layered framework of **3** containing dumbbell-shaped rings as subunits. Reaction at a strongly alkaline solution leads to a discrete molecule of **4**. Meanwhile solid-state properties such as thermal stability and the photoluminescence properties at room temperature for these complexes have also been systematically investigated.

case is provided by Zhou and coworkers where a series of metal–organic polyhedra were obtained by assembling various V-shaped dicarboxylate ligands as linkers with square four-connected  $[Mo_2(CO_2)_4]$  as nodes.<sup>2e,f,k</sup>

Although some progress has been made in the rational design of MOFs, it is still a great challenge to prepare CPs with predictable structures and valuable properties because many subtle variables, such as temperature, solvent, pH value, and the ratio between metal salts and ligands, have non-ignorable influences on the crystallization processes.<sup>3</sup> Systematic studies on the role of simple variables such as pH value of the reaction solution need to be investigated, although such studies are still relatively rare. To our knowledge, the pH value of the reaction mostly affects the deprotonation extent of ligands and the generation of an OH<sup>-</sup> ligand in aqueous solution.<sup>3b,4</sup> In recent years, some interesting influences of pH value have been discovered, such as its effects on controlling the helicity of helical chains, the morphology of the grown crystals and the in situ formation of ligands.<sup>5</sup> And even in a high pH solution (pH = 9), the CO<sub>2</sub> in air can be captured to generate  $CO_3^{2-}$ anions, as reported by Sun and coworkers.<sup>6</sup> Our interest is to investigate the influence of pH value on the structural diversity of CPs and even on their properties. Our approach is to perform a series of reactions under similar conditions with only one factor varied. In such a case, the diversity in assembly

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and functionality of CPs can be ascribed exclusively to the change of the factor.

In our previous work, we have preliminarily discussed the pH effects on the structures of a series of zinc(II)-4-(4carboxyphenoxy)phthalate complexes.<sup>7</sup> As part of our ongoing interest in understanding the ability of pH value to direct the assembly of metal-organic systems, in this work we investigate the formation of four new cadmium(II) coordination polymers,  $[Cd(H_2dpstc)(phen)]_n$  (1),  $[Cd_2(dpstc)(phen)_2]_n \cdot 4.5nH_2O$  (2),  $[Cd_2(dpstc)(phen)_2]_n \cdot nH_2O$ (3) and  $[Cd_2(dpstc)(phen)_4(H_2O)_2] \cdot 6H_2O$  (4)  $(H_4dpstc = 3,3',4,4'-diphe$ nylsulfonetetracarboxylic acid, phen = 1,10-phenanthroline), under hydrothermal conditions.8 Their structures range from discrete molecules to 2D layered architectures, revealing that the pH value of the reaction plays an essential role in structural control during self-assembly processes.

### **Experimental section**

#### Materials and methods

All reactants were reagent grade and used as purchased without further purification. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. The FT-IR spectra were performed on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm<sup>-1</sup>. Thermogravimetric analyses were recorded on a NETZSCH STA 449C unit at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. The powder X-ray diffraction (XRD) patterns were collected by a Rigaku DMAX2500 X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). Fluorescent analysis of the complexes was performed on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous (450 W) and pulse xenon lamps.

#### Synthesis of $[Cd(H_2dpstc)(phen)]_n$ (1)

A mixture of CdSO<sub>4</sub>·8/3H<sub>2</sub>O (0.4 mmol, 103 mg), H<sub>4</sub>dpstc (0.1 mmol, 40 mg), phen (0.1 mmol, 20 mg) and H<sub>2</sub>O (5 mL) was placed in a Teflon lined steel autoclave (23 mL). The pH of this mixture solution was about 7.0. The autoclave was sealed, heated to 160 °C and held at the temperature for 72 hours. The autoclave was allowed to cool to 30 °C for 24 h. Brown block-shaped crystals of complex **1** were collected in 88% yield based on phen. Anal. calcd for  $C_{28}O_{10}N_2SH_{16}Cd$  ( $M_r = 684.89$ ): C, 49.10%; H, 2.35%; N, 4.09%. Found: C, 48.96%; H, 2.33%; N, 4.08%. Selected IR data (KBr pellet, cm<sup>-1</sup>): 3256 (m), 3078 (w), 1744 (s), 1704 (s), 1540 (s), 1429 (s), 1387 (s), 1210 (s), 1168 (s), 1094 (m), 1066 (m), 854 (m), 728 (m), 646 (m), 616 (m), 548 (w), 493 (w).

#### Synthesis of $[Cd_2(dpstc)(phen)_2]_n \cdot 4.5 nH_2O(2)$

The preparation of **2** was similar to that of **1** except that the pH value was adjusted to 8.0 by addition of 0.2 M NaOH solution. After cooling to room temperature, colorless lamellar crystals were obtained by filtration in 73% yield based on phen. Anal. calcd for  $C_{40}O_{14.5}N_4SH_{31}Cd_2$  ( $M_r = 1056.55$ ): C, 45.47%; H, 2.96%; N, 5.30%. Found: C, 45.30%; H, 3.02%; N, 5.22%. Selected IR data (KBr pellet, cm<sup>-1</sup>): 3402 (m), 1578 (s), 1388 (s),

1168 (m), 1140 (m), 1092 (w), 846 (m), 760 (m), 728 (m), 670 (m), 624 (w), 488 (w).

#### Synthesis of $[Cd_2(dpstc)(phen)_2]_n \cdot nH_2O(3)$

The preparation of **3** was similar to that of **1** except that the pH value was adjusted to 10.0 by addition of **1** M NaOH solution. After cooling to room temperature, brown block-shaped crystals of complex **3** were obtained by filtration in 70% yield based on phen. Anal. calcd for  $C_{40}O_{11}N_4SH_{24}Cd_2$  ( $M_r = 993.49$ ): C, 48.36%; H, 2.43%; N, 5.64%. Found: C, 48.21%; H, 2.44%; N, 5.59%. Selected IR data (KBr pellet, cm<sup>-1</sup>): 3408 (m), 3058 (w), 1590 (s), 1412 (s), 1330 (m), 1170 (m), 1150 (m), 1094 (m), 1072 (w), 852 (m), 728 (m), 670 (m), 642 (m), 558 (w), 482 (w).

#### Synthesis of [Cd<sub>2</sub>(dpstc)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O (4)

A mixture of CdSO<sub>4</sub>·8/3H<sub>2</sub>O (0.4 mmol, 103 mg), H<sub>4</sub>dpstc (0.1 mmol, 40 mg), phen (0.1 mmol, 20 mg) NaOH (0.75 mmol, 30 mg) and H<sub>2</sub>O (5 mL) was placed in a Teflon lined steel autoclave (23 mL). This mixture solution was strongly alkaline (pH > 12.0). The autoclave was sealed, heated to 160 °C and held at the temperature for 72 hours. The autoclave was allowed to cool to 30 °C for 24 h. Big brown block-shaped crystals of complex **4** (with the dimension about 0.5–1 mm) can be in concomitance with some white powders. After picking out the crystals and washing with water, the yield based on phen is about 21%. Anal. calcd for C<sub>64</sub>O<sub>18</sub>N<sub>8</sub>SH<sub>54</sub>Cd<sub>2</sub> ( $M_r = 1480.01$ ): C, 51.94%; H, 3.67%; N, 7.57%. Found: C, 52.04%; H, 3.65%; N, 7.52%. Selected IR data (KBr pellet, cm<sup>-1</sup>): 3416 (m), 1585 (s), 1435 (s), 1330 (m), 1168 (m), 1093 (m), 1068 (w), 851 (m), 728 (m), 645 (m), 618 (m), 490 (w).

#### X-ray crystallography

All the structural data of complexes 1-4 were collected on a Rigaku Mercury CCD diffractometer equipped with a graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. All of the structures were resolved by the direct method and refined by full-matrix least-squares fitting on  $F^2$  by SHELX-97.9 All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the water molecules and carboxylic groups were found in the electron density map and refined by riding. The other hydrogen atoms were located at geometrically calculated positions and refined by riding. Crystallographic data and structure refinement parameters for complexes 1-4 are summarized in Table 1. Selected bond lengths and bond angles are listed in the ESI<sup>†</sup> (Table S1). More details on the crystallographic studies as well as atomic displacement parameters are given in the ESI<sup>†</sup> as CIF files. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 894377-894380 for complexes 1-4.

#### Result and discussion

The coordination modes of the  $H_4$ dpstc ligand are shown in Scheme 1. The following structure discussion is based on CIF files of complexes 1–4. Final formulas of complexes 1–4 are Paper

Table 1 Crystallographic data for 1-4

Complexes	1	2	3	4
Chemical formula	C28H16CdN2O10S	C40H31Cd2N4O14 5S	$C_{40}H_{24}Cd_2N_4O_{11}S$	C64H54Cd2N8O18S
Formula weight	684.92	1056.55	993.49	1480.01
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a(A)	7.4706(18)	10.905(5)	11.8489(7)	9.885(3)
b (Å)	10.994(2)	13.194(7)	16.7123(6)	14.331(4)
c (Å)	16.357(4)	14.970(8)	18.8636(11)	21.418(7)
α(°)	71.743(7)	110.429(7)	90	85.964(5)
$\beta$ (°)	86.791(7)	95.307(6)	105.170(4)	89.432(6)
γÕ	76.869(7)	91.644(6)	90	86.079(6)
$V(Å^3)$	1242.3(5)	2005.5(17)	3605.2(3)	3019.6(16)
Z	2	2	4	2
T (K)	293(2)	293(2)	293(2)	293(2)
$D_{\rm c}$ (g cm <sup>-3</sup> )	1.831	1.750	1.830	1.628
$\mu (\mathrm{mm}^{-1})$	1.032	1.189	1.310	0.822
F(000)	684	1054	1968	1500
$\theta$ range (°)	2.7-27.5	2.3-27.5	2.2-27.5	2.3-27.5
Collected reflections	13 465	15 581	27 780	22 597
Unique reflections	5660	9042	8229	13 092
Parameters	379	559	523	838
Gof on $F^2$	1.051	1.084	1.077	1.040
$R_1^a (I > 2\sigma(I))$	0.0229	0.0523	0.0394	0.0474
$wR_2^b$ (all data)	0.0544	0.1464	0.0973	0.1438
<sup><i>a</i></sup> $R_1 = \Sigma   F_0  -  F_c   / \Sigma  F_0 .$	$^{b}$ wR <sub>2</sub> = [ $\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2} - F_{c}$	$)^{2}]^{1/2}.$		

further determined by elemental analyses and thermogravimetric studies.

#### Structural description of $[Cd(H_2dpstc)(phen)]_n$ (1)

Complex 1 was hydrothermally synthesized in a neutral reaction environment with pH = 7.0. X-Ray crystallographic analysis reveals that the asymmetric unit of 1 consists of one Cd(II) ion, one partly deprotonated  $H_2dpstc^{2-}$  ligand and one chelating phen ligand as shown in Fig. 1a. The Cd<sup>2+</sup> center is seven-coordinated by two nitrogen atoms of phen ligand and five oxygen atoms from three carboxyl groups belonging to three different  $H_2dpstc^{2-}$  ligands, respectively. Therefore the Cd<sup>2+</sup> center adopts distorted monocapped octahedral coordination geometry. Two Cd<sup>2+</sup> centers aggregate to cadmium binuclear clusters through connections of chelating-bridging carboxyl groups (O3–C8–O4). The  $H_2dpstc^{2-}$  ligands adopt the



Scheme 1 The coordination modes of H<sub>4</sub>dpstc ligands in complexes 1-4

 $\mu_3$ - $\kappa^1$ : $\kappa^2$ : $\kappa^2$  mode (Scheme 1a), linking adjacent cadmium binuclear clusters to form a one-dimensional (1D) chain (Fig. 1b). As shown in Fig. 1c, these chains are decorated with phen ligands at both sides, which are arranged parallel with the centroid distance of 6.702 Å.

Some interesting supramolecular contacts are observed in the solid-state structure of **1**. Besides strong intermolecular hydrogen bonds between the carboxyl oxygen atoms of  $H_2$ dpstc<sup>2-</sup> ligands in the neighboring chains (O6···O4<sup>*i*</sup> = 2.585 (2) Å and O8···O5<sup>*ii*</sup> = 2.726 (2) Å, *i* = 1 - *x*, 1 - *y*, 2 *z*, *ii* = -*x*, -*y*, 2 - *z*), obvious  $\pi$ - $\pi$  stacking interactions provided by the nearly parallel aromatic rings belonging to the adjacent phen ligands (the centroid distances range from 3.4618 to 3.8070 Å) (Table S2, ESI,† Fig. 1e) link together the 1D chains into a three-dimensional (3D) supramolecular framework (Fig. 1d).

#### Structural description of $[Cd_2(dpstc)(phen)_2]_n \cdot 4.5 nH_2O(2)$

Compared to **1**, complex **2** was obtained by adjusting pH value of the same reaction mixture to 8.0. Complex **2** crystallizes in the triclinic space group  $P\bar{1}$ , and its structure features a twodimensional layered framework with 1D channels. As shown in Fig. 2a, the asymmetric unit contains two Cd(II) ions, one dpstc<sup>4-</sup> ligand, two phen ligands and four and a half lattice water molecules. Each Cd(II) ion adopts distorted octahedral coordination geometry, completed by two nitrogen atoms of chelating phen ligand and the other four carboxyl oxygen atoms from three different dpstc<sup>4-</sup> ligands. In complex **2**, the carboxyl groups of ligand dpstc<sup>4-</sup> are all deprotonated, which can be classified into two types. One type of carboxyl groups (O3–C3–O4, O5–C9–O6 and O7–C11–O8) coordinates to two Cd(II) ions through *syn–anti* bidentate mode, and the other



**Fig. 1** (a) The coordination environments of Cd(II) atoms in complex 1 (hydrogen atoms are omitted for clarity). Symmetry transformations used to generate equivalent atoms: A = x - 1, y, z, B = 1 - x, -y, 1 - z. (b) The 1D chain of **1** in *ac* plane (phen ligands are omitted for clarity). (c) The 1D chain of **1**, viewed along the [1 0 0] direction. (d) The 3D supramolecular framework of complex **1** viewed along the [1 0 0] direction (violet dashed lines represent the hydrogen bonds between the carboxyl groups). (e) The illustration of  $\pi$ - $\pi$  interactions in complex **1**.

carboxyl group (O1-C1-O2) serves as a bridge to connect two Cd(II) ions by µ-O2 atom. The Cd1 and Cd2 centers are connected by these two types of carboxyl groups to form an infinite Cd(II)-carboxylate chain (Fig. S1a, ESI<sup>†</sup>). As depicted in Fig. 2c, the 1D chains are further bridged by dpstc<sup>4-</sup> ligands to fabricate a 2D layered network. The bridging dpstc<sup>4-</sup> ligands between the adjacent chains are arranged alternately and the vertices (-SO<sub>2</sub> groups) of neighboring V-shaped ligands are directed in opposite orientations (Fig. 2b and S1b, ESI<sup>†</sup>). Therefore, 1D channels with approximately square windows in the 2D layer are generated from the alternant arrangement of the V-shaped ligands. The lattice water molecules are filled in the channels (Fig. 2b). Similar to 1, there are strong  $\pi$ - $\pi$ interactions between the nearly parallel phen ligands in complex 2 (Fig. 2e, Table S2, ESI<sup>†</sup>) with the distances between planes of phen from 3.408 to 3.536 Å. The 2D layers in 2 are stacked in AAAA fashion to a 3D supramolecular assembly which is stabilized by these intense supramolecular interactions (Fig. 2d).

The most attractive feature for **2** is the hydrogen-bonding two-dimensional water sheets. As depicted in Fig. 3a, the water network consists of three types of water clusters including a hexamer of twofold O11, O14 and O15 atoms, a dimer of two O12 atoms and another dimer of two O13 water molecules. Each hexamer serves as a four-connected node linking two dimers of O12 atoms along the crystallographic *c* axis and two

dimers of O13 atoms along the crystallographic a axis through hydrogen-bonds. All of the dimeric water clusters act as bridges to connect the adjacent hexamers. Therefore, a (4,4)net containing the fused hexamers and dimers is formed through abundant hydrogen-bonding interactions in the ac plane (Fig. 3c). In addition, the water sheets stack along the a axis forming one-dimensional rectangular channels with the windows of effective dimensions 7.3  $\times$  12.2 Å, taking into account the van der Waals radii of the oxygen atoms (Fig. 4). This 32-menbered water rectangle contains four hexamers as the vertices and four dimers including two dimers of O12 atoms and two dimers of O13 atoms as the edges (Fig. 3b). The information of the hydrogen-bonding interactions in 2 is listed in Table 2, and the average O…O separation of 2.81 Å among the water molecules in the layer is between the corresponding value of 2.76 Å in ice I<sub>h</sub> and 2.85 Å in liquid water.<sup>10</sup> Interestingly, the 2D holed water network is interpenetrated with the metal-organic skeleton, where the dpstc<sup>4-</sup> ligands pass through the holes of water sheet while the water chains composed of hexamers and dimers of two O12 atoms are filled in the channels of 2D metal-organic skeleton (Fig. 4 and S3a, ESI<sup>†</sup>). The planes of the water polymers and the metal-organic layered frameworks meet each other at an angle of 86.57° (Fig. S2, ESI<sup>†</sup>). There is a unique class of connection between both polymers. Two carboxyl oxygen atoms of each dpstc<sup>4-</sup> ligand are hydrogen-bonded to the water network (O6…O11 = 2.821(8)



**Fig. 2** (a) The coordination environments of Cd(II) atoms in complex 2 (hydrogen atoms are omitted for clarity). Symmetry transformations used to generate equivalent atoms: A = -x, -y, 1 - z, B = x, y - 1, z, C = -x, 1 - y, 2 - z. (b) The 2D layer with 1D channels in **2**, water molecules are filled in the channels, viewed along the [0 0 1] direction. (c) The 2D layer of **2** in the *bc* plane (phen ligands are omitted for clarity). (d) The 3D supramolecular framework of complex **2** viewed along the [0 0 1] direction. (e) The illustration of  $\pi$ - $\pi$  interactions in complex **2**.

Å, O1…O12 = 2.75(1) Å) (Fig. S3b, ESI†). Consequently, the overall structure of **2** can be considered as a fascinating 3D metal–organic–water supramolecular architecture (Fig. 4 and S2, ESI†). To our knowledge, the examples of the interlocked structures between water networks and metal–organic frameworks are still limited.<sup>11</sup>

#### Structural description of $[Cd_2(dpstc)(phen)_2]_n \cdot nH_2O(3)$

When the pH value of the reaction mixture was adjusted to 10.0, a two-dimensional layered structure of **3** was obtained. Single-crystal X-ray analysis has revealed that **3** crystallizes in a  $P2_1/n$  space group. As shown in Fig. 5a, there are two crystallographically independent cadmium atoms, one dpstc<sup>4–</sup> ligand, two phen molecules and one free water molecule in an asymmetric unit. Two Cd(II) ions are both six-coordinated with

four carboxyl oxygen atoms and two nitrogen atoms of chelating phen ligand but located in different coordination environments, where Cd1 is surrounded by a distorted octahedra and Cd2 is in a triangular prism. The two types of Cd(II) centers aggregate to cadmium binuclear clusters through sharing the vertex of O6 atoms. As illustrated in Fig. 5b, every four binuclear units are linked by four dpstc<sup>4-</sup> ligands resulting in a dumbbell-shaped ring. Each fully deprotonated dpstc<sup>4-</sup> ligand in **3** adopts  $\mu_5$ - $\kappa^1$ : $\kappa^2$ : $\kappa^2$ : $\kappa^2$  mode (Scheme 1c) to connect five Cd(II) ions which belong to three different cadmium binuclear clusters. The two phthalic groups (named phthalic group A and B) of the dpstc<sup>4-</sup> ligand exhibit different connectivity. Phthalic group A binds to one binuclear unit, whereas phthalic group B bridges two binuclear clusters. As depicted in Fig. 5c, the dumbbell-



Fig. 3 (a) A perspective view of the hexameric water cluster and two types of dimeric water clusters in complex 2. (b) Large  $(H_2O)_{32}$  water rectangle in the water layer. (c) The 2D water net in 2 containing large windows in the *ac* plane.

shaped rings, acting as the subunits, assemble into a 2D herringbone-like net by connecting the binuclear units of neighboring rings through the phthalic groups B. In addition, the phen ligands are decorated in and out of the plane of the 2D layer of **3**.

#### Structural description of [Cd<sub>2</sub>(dpstc)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O (4)

Complex 4 crystallizes in the triclinic space group  $P\overline{1}$ . The discrete Cd(II) complex within 4 is a neutral binuclear



**Fig. 4** Partial structure of **2** exhibits the interpenetration between the metal– organic network and the water 2D polymers, viewed along the [0 1 0] direction. One of the 2D metal–organic networks is highlighted in light blue, 2D water layers are represented in space-filling mode.

molecule with two  $Cd^{2+}$  ions, one  $\mu$ -bridging fully deprotonated dpstc<sup>4-</sup> ligand, four chelating phen ligands, two aqua ligands and six lattice water molecules in its asymmetry unit (Fig. 6a). Both  $Cd^{2+}$  ions lie in similar octahedral { $N_4O_2$ } environments. All of the nitrogen atoms come from two chelating phen ligands and the other two oxygen atoms are from a monodentate carboxyl group of dpstc<sup>4-</sup> ligands and one coordinated water molecule, respectively. Although all of the carboxyl groups of the dpstc<sup>4-</sup> ligand are deprotonated, only 3- and 3'-carboxyl groups coordinate to the Cd(II) ions in the *syn*-coordination mode (Scheme 1d). Therefore, the dpstc<sup>4-</sup> ligand can be viewed as a bridge to aggregate the two Cd(II) centers to a binuclear molecule and the distance between the two Cd<sup>2+</sup> ions is 10.329(3) Å.

Table 2 Selected hydrogen-bond lengths (Å) and angles (°) for $2^a$							
	D-H	Н…Ч	D…Y	D-H···A			
O11-H11A…O6	0.93	1.97	2.824(9)	152.2			
O11-H11B…O15	0.93	2.04	2.96(3)	174.3			
O12-H12A…O1	0.86	2.17	2.760(12)	125.7			
O12-H12B····O12 <sup>i</sup>	0.94	2.28	2.96(2)	129.0			
O13-H13A…O13 <sup>ii</sup>	0.86	2.26	2.64(3)	106.8			
O13-H13B…O14	0.88	1.99	2.81(2)	155.4			
O14-H14A…O11	0.90	2.02	2.705(16)	132.2			
O15-H15A…O12	0.90	1.97	2.84(3)	163.1			
015–H15B…O14 <sup>iii</sup>	0.88	1.83	2.63(3)	149.0			

<sup>*a*</sup> Symmetry codes: (i) -x, 1 - y, 1 - z; (ii) -1 - x, 1 - y, 2 - z; (iii) -x, 1 - y, 2 - z.



**Fig. 5** (a) The coordination environments of Cd(II) atoms in complex 3 (hydrogen atoms are omitted for clarity). Symmetry transformations used to generate equivalent atoms: A = 1/2 - x, 1/2 + y, 1/2 - z, B = -x, 1 - y, -z. (b) A dumbbell-shaped ring in **3**. (c) The two-dimensional net of complex **3** (phen ligands are omitted for clarity). (d) The 2D layer of **3**, viewed along the [0 1 0] direction.

Some interesting supramolecular contacts are observed in the solid-state structure of **4**. In this complex, half of the carboxyl groups of the dpstc<sup>4–</sup> ligands remain uncoordinated; therefore, they can act as excellent hydrogen bond acceptors. As shown in Fig. S4, ESI,<sup>†</sup> abundant and strong hydrogen bonding interactions can be found among carboxyl groups, lattice water molecules and aqua ligands which hold together the discrete binuclear coordination molecules into a 3D supramolecular structure (Fig. 6c, Table S4, ESI<sup>†</sup>). Furthermore, the 3D supramolecule is stabilized by  $\pi$ - $\pi$ stacking interactions between almost parallel phen ligands and the C-H··· $\pi$  interactions (or so called edge-to-face aromatic interactions) between nearly perpendicular phen aromatic rings (Fig. S6b, Tables S2 and S3, ESI<sup>†</sup>).

## The effects of pH value of the reaction on the final structures of the complexes

As the pH value is the only difference in the syntheses of complexes **1–4**, it is clear that the assembly process of this type of crystalline products is pH-dependent. By comparison of complexes **1–4**, the changes in pH value of the initial solution can lead to different protonated extent and therefore the connectivity of the polycarboxylate ligands. At a neutral reaction condition (pH = 7), complex **1** was isolated, where the H<sub>4</sub>dpstc ligands are partially deprotonated to H<sub>2</sub>dpstc<sup>2–</sup> anions which include both protonated phthalic groups and

deprotonated phthalic motifs. Nevertheless, at the alkaline condition (the higher pH value of 8, 10 and more than 12), all of the products of complexes 2-4 own completely deprotonated ligand dpstc4-. To understand how pH controls the extent of deprotonation, we estimate the acidity of each carboxylic group on the H<sub>4</sub>dpstc. By considering the electronwithdrawing and electron-donating effects of the substituent groups (sulphone group and carboxylic group itself), the 4-carboxylic group seems to be the most acidic, and the 4'-carboxylic group is the second most one, and then the 3and 3'-carboxylic groups are relatively weaker. To confirm this deduction, the MarvinSketch software<sup>12</sup> is used to calculate the  $pK_a$  values of carboxylic groups through some approximate treatments. And if the ligand is viewed as a monoprotic acid, the p $K_a$  value of 4-COOH (p $K_a = 2.55$ ) is smaller than that of 3-COOH ( $pK_a = 2.75$ , and two phthalic groups are equally). Further considering the ligand as a diacid, we suppose that the 4-COOH is deprotonated to evaluate the  $pK_a$  values of the remaining three carboxylic groups, respectively. The result tells us that the  $pK_a$  value of 4'-COOH shows slightly smaller than that of 3'-COOH, and the  $pK_a$  value of 3-COOH is significantly larger than those of former ones. From comparing the  $pK_a$  values of these carboxylic groups, obviously, 4-COOH is the most acidic and the 4'-COOH may be the second most. The description of the deduction, the model used to calculate  $pK_a$  values and the detailed result of the



**Fig. 6** (a) The coordination environments of Cd(II) atoms in complex **4** (hydrogen atoms are omitted for clarity). (b) Illustration of supramolecular interactions in **4** (cyan dashed lines represent the  $\pi$ - $\pi$  stacking interactions and violet dashed lines represent the C-H··· $\pi$  interactions). (c) The 3D stacking mode of dinuclear molecules in **4**, viewed along the [1 0 0] direction.

calculation can be seen in ESI.† In addition, we calculated the distribution of partial and fully deprotonated ligand species in aqueous solution with various pH values (Fig. S7 and S8, ESI<sup>†</sup>). In complex 1, the deprotonated phthalic groups serve as bridges to ligate the metal ions to 1D chains, and the protonated ones act as the hydrogen bond donors and acceptors to extend the 1D chains to a 3D supramolecule structures. As depicted in Fig. S7 and S8, ESI,† this type of deprotonated ligands can hardly be generated, because the 3-COOH exhibits weaker acidity than the both 3'- and 4'-COOH. This phenomenon may be caused by some other factors in the crystallization process. One probable reason we guessed is that the coordination of 3- and 4-COOH to metal ions might trend to congregate the metal ions to clusters, which make the system more stable. And from Fig. S7, ESI,† we can see that at a higher pH value than 8.0, the ligand exists in aqueous solution as the form of dpstc<sup>4-</sup> completely, which is in accord with the situation of complexes 2-4. Because of the different deprotonated extent, the connectivity of the ligand may be different. In complex 1, the partially deprotonated  $H_2$ dpstc<sup>2-</sup> ligand only connects three Cd(II) ions leading to a relatively low dimensional structure. And in structures of 2 and 3, the  $dpstc^{4-}$  ligands manifest various coordination abilities (linking six and five cadmium ions per ligand respectively).

Therefore, two higher dimensional and more complicated 2D networks including one 2D layered architecture with 1D channels and a 2D herringbone-like network are formed, respectively. When we further elevate the pH value of reaction solution (strongly alkaline), a new structure of 4 was obtained, where the dpstc<sup>4-</sup> ligands are fully deprotonated. However, the discrete molecule 4 shows a low dimensional structure. This is probably because the metal salt converts to the precipitate of M(OH)<sub>2</sub> when meeting a strongly alkaline solution. This assumption can be confirmed by the PXRD pattern of the precipitate of reaction, which matches the  $\beta$ -Cd(OH)<sub>2</sub> (ref. 13) well (Fig. S9, ESI<sup>†</sup>). Because the precipitates of metal hydroxide are hard to participate in self-assembly process, increasing the pH value may reduce the concentration of the metal ion which coincides with the low product yield. Meanwhile, because of the satisfactory water-solubility of phen at high temperature, the high pH value of the reaction solution will result in a high ratio of phen vs. metal ion. As a result, more phen ligands chelate to the metal centers (two phen per Cd(II) center in 4 and one phen per Cd(II) center in 1–3). The increase of the steric hindrance and the decrease of the coordination sites on  $Cd^{2+}$  ions confine the dpstc<sup>4-</sup> ligands coordinating to metal centers in a low connectivity mode and finally lead to a simple 0D molecular structure of 4.

Paper



Fig. 7 TGA curves for complexes 1-4.

The above-mentioned results show that the reaction pH value has an important influence on the structures of the assembly process since it determines the deprotonation extent and then indirectly influences the connectivity of the polycarboxylate ligand. And in the extreme alkaline pH value, the decrease of concentration of the metal ion derived from generation of precipitate of metal hydroxide must also be taken into account in the assembly process.

#### Thermal analyses

To investigate the thermal stability of these complexes, the thermogravimetric analysis (TGA) experiments are carried out in the temperature range of 30–900 °C under a flow of nitrogen with heating rate of 10 °C min<sup>-1</sup> (Fig. 7). There is no obvious weight loss before 250 °C for complex **1** and then it decomposes rapidly on further heating. A total loss of 7.82% is observed for **2** in the temperature range of 30–120 °C, which can be attributed to the loss of lattice water molecules (calcd 7.67%), and the decomposition of the residue is observed at about 300 °C. For complex **3**, the weigh loss in the range of 30–

220 °C corresponds to the departure of one lattice water molecule (calculated: 1.81%, found: 1.90%) and then the framework undergoes decomposition after 280 °C. As to **4**, a weight loss of 9.39% is observed in the temperature range of 30–145 °C, which corresponds to the release of six lattice water molecules and two coordinated aqua molecules (calcd 9.76%), and then the framework is found to decompose at about 200 °C.

#### Photoluminescence properties

Metal-organic coordination polymers, especially those containing d<sup>10</sup> metal ions, exhibit excellent photoluminescence properties and have potential on the field of light emitting devices, chemical or biological sensors and so on.<sup>14</sup> As a series of d<sup>10</sup> metal-organic hybrid coordination polymers, the solid state emission spectra of complexes 1-4 together with the ligands H<sub>4</sub>dpstc and phen have been investigated at room temperature (Fig. 8). The free ligand H<sub>4</sub>dpstc displays photoluminescence with emission maximum at 434 nm upon excitation at 365 nm, and the free phen ligand shows tricenters emission with three split peaks centered at 380 nm, 415 nm and 440 nm ( $\lambda_{ex}$  = 350 nm), respectively. It can be presumed that these bands originated from the  $\pi \rightarrow \pi^*$  or  $n \rightarrow$  $\pi^*$  transitions. The emission spectra of complexes 1-4 are shown in Fig. 8b. Excitation at 330 nm leads to an intense blue fluorescent emission with maximum and shoulder bands at 431 and 450 nm for 1, which possibly originates from the intraligand transitions of H2dpstc2- and phen ligands, respectively. Irradiation of complex 2 at 350 nm results in a blue fluorescent emission band at 436 nm, which closely matches to those of the fluorophore ligand H<sub>4</sub>dpstc indicating the metal-perturbed intraligand charge transfer. While complex 3 shows intense UV/violet luminescent emissions under UV irradiation, and its solid state emission spectrum contains two peaks at 370 and 390 nm and a weak shoulder bands 413 nm ( $\lambda_{ex}$  = 330 nm), respectively. In comparison to the metal free ligand phen, these bands of 3 can be assigned to intraligand  $(\pi \rightarrow \pi^*)$  fluorescent emissions (Table S2, ESI<sup>†</sup>). The



Fig. 8 Emission spectra of (a) ligand H<sub>4</sub>dpstc, phen and (b) complexes 1-4 in the solid state at room temperature

spectrum of complex **4** shows a broad emission band centered at 458 nm, which can probably be assigned to the intraligand  $(\pi-\pi^*)$  fluorescent emission of both dpstc<sup>4-</sup> and phen. Compared to the free ligands (H<sub>4</sub>dpstc and phen), the emission spectra of complexes **1**, **2** and **4** show slight redshifts. It may tentatively be ascribed to the strong  $\pi$ -stacking interactions in these solid-state compounds (Table S2, ESI<sup>†</sup>), which are expected to play an essential role in decreasing the HOMO-LUMO gaps.<sup>15</sup> The slight blue-shift observed in the emission spectrum of **3** may due to the weaker  $\pi$ -stacking interaction in **3** than that in the crystalline phen ligand.

### Conclusions

The dependence of simple variables such as the reaction pH value under hydrothermal conditions has been investigated during the preparation of Cd-dpstc/phen mixed ligands systems. The structural variation of the four compounds from 0D binuclear molecule to 1D chain and two types of 2D layers indicates that the pH value has great influence on the structures of the products. Through comparison of the structures of 1-4, we have found that the effect of the pH value can modulate the structures of complexes through affecting the deprotonation extent and then the connectivity of the polycarboxylate ligands as well as the existent states of the metal ions in the reaction solution. At the same time, we have also investigated the thermal stability and the luminescent properties of these compounds, and discovered that the properties can be adjusted indirectly by pH value through their influence on the structures. It is believed that the initiatory researches of this work will provide a valuable approach for the construction of other coordination polymers with diverse structures under different reaction conditions.

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