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Hydrothermal syntheses, structures, and properties of four metal–organic coordination polymers assembled from V-shaped tetracarboxylate ligands and N-donor ancillary ligands

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ABSTRACT

A series of four metal–organic frameworks, namely, $[Cu(sdpa)_{0.5}(2,2'-bpy)]\cdot H_2O$ (1), $[Zn_2(sdpa)(2,2'-bpy)_2(H_2O)_2]\cdot 3H_2O$ (2), $[Zn_2(sdpa)(4,4'-bpy)]\cdot 3H_2O$ (3), $[Cd_2(sdpa)(4,4'-bpy)_{1.5}(H_2O)_2]$ (4), have been hydro(solvo)thermally synthesized through the reaction of 2,3,2',3'-sulfonyldiphthalic acid (H₄sdpa) with divalent copper, zinc and cadmium salts in the presence of ancillary nitrogen ligands (4,4'-bpy = 4,4'-bipyridine, 2,2'-bipy = 2,2'-bipyridine) and structurally characterized by elemental analysis, IR and X-ray diffraction. Both complex 1 and 2 show metal–organic chain structure, and the adjacent chains are further linked by $\pi \cdots \pi$ interactions for 1 and hydrogen bonds and $\pi \cdots \pi$ interactions for 2 to form 3D supramolecular structure. In complex 3, two Zn1 and two Zn2 atoms appear alternately and are bridged by sdpa^{4–} anion ligands to form an infinite Zn-sdpa chain. Such chains are further linked to gether through 4,4'-bpy ligands in four orientations to form a robust 3D metal–organic network. In compound 4, a 3D Cd-sdpa metal–organic network is accomplished through sdpa^{4–} anion ligands, and further stabilized by 4,4'-bpy in six orientations. Their luminescence and thermal analysis have also been investigated.

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1. Introduction

The design and construction of metal–organic frameworks (MOFs) based on various secondary building units (SBUs) which are connected through coordination bonds, supramolecular contacts (hydrogen bonding, $\pi \cdots \pi$ stacking, etc.), or their combination, has been an increasingly active research area [1–8]. The self-assembly of multidentate organic ligands and metal ions has resulted in many coordination polymeric frameworks, whose structures are influenced by the subtle interplay of many factors such as the geometric preference of metal ions, the sizes and shapes of the organic building blocks, templates, and solvent systems [9–18]. Hence, the selection or design of suitable ligands containing certain features like flexibility and versatile binding modes is crucial to the construction of metal–organic coordination polymers.

It is known that multicarboxylate ligands are good candidates for the construction of coordination frameworks with specific structure due to their multicarboxylate groups and various coordination modes, from which a rich variety of one-, two- and threedimensional metal-organic polymeric architectures have been

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constructed [19-32]. According to previous reports, owing to the nonlinear flexibility around etheric oxygen or sulfur atom and twisted conformation of carboxylate groups, it is easy for V-shaped multicarboxylate ligands 2,3,2',3'-oxydiphthalic acid (H₄odpa) [30,31] and 2,3,2',3'-thiaphthalic acid (H₄tdpa) [32,33] ligands to construct helical coordination polymers. The tdpa ligand show dramatic distinction against the odpa ligands: five of the six tdpa complexes are achiral, whereas five odpa complexes are chiral. Results indicate that the small adjustment for the ligand may result large difference for the assembly of metal-organic networks. Considering this, we want to further reinforce rigidity of the ligand by introducing O=S=O group and get more interesting polymeric structures. In particular, the relatively rigid ligands are more useful to produce coordination polymers with active photoluminescent properties when reacting with d^{10} metals such as Zn(II) or Cd(II). On the other hand, the use of auxiliary ligands is also an effective method for the framework formation of coordination polymers owing to the fact that they can satisfy and even mediate the coordination needs of the metal center and consequently generate more meaningful architectures [33-36].

In this study, we investigated four metal coordination polymers assembled from 2,3,2',3'-sulfonyldiphthalic acid (H₄sdpa) ligand in the presence of the "second" ligand 2,2'-bpy or 4,4'-bpy: $[Cu(sdpa)_{0.5}(2,2'-bpy)]\cdot H_2O$ (1), $[Zn_2(sdpa)(2,2'-bpy)_2(H_2O)_2]\cdot 3H_2O$



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(2), $[Zn_2(sdpa)(4,4'-bpy)]\cdot 3H_2O$ (3), and $[Cd_2(sdpa)(4,4'-bpy)_{1.5}-(H_2O)_2]$ (4). The photoluminescent properties of **2**, **3** and **4** compounds were studied as well. To the best of our knowledge, this is the first time to report the metal–organic frameworks constructed from 2,3,2',3'-sulfonyldiphthalic acid.

2. Experiments

2.1. Materials and general methods

All commercially available chemicals are of pure grade and used as received without further purification. Solvents were purified according to the standard methods. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240 elemental analyzer. The FT–IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm⁻¹ on a Bruker VECTOR 22 spectrometer. Thermal analyses were performed on a simultaneous SDT 2960 thermal analyzer from room temperature to 800 °C with a heating rate of 20 °C/min under nitrogen flow. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

2.2. Synthesis of H₄sdpa

2,3,2',3'-tdpa (H₄tdpa) was prepared according to the literature [28–32]. 2,3,2',3'-sdpa (H₄sdpa) was synthesized using an adaptation of a literature [37] procedure. As shown in Charts 1 and 2, 3,2',3'-tdpa (0.6524 g, 2 mmol) and MoO₃ (0.014 g, 0.1 mmol) were dissolved in 10 ml ethanol, and this mixture was added to H₂O₂ (1.2 ml, 10.68 mmol). After 4 h heated at reflux the reaction mixture was clear yellow solution. On cooling of the reaction mixture, the MoO₃ was filtered. The ethanol solution of the H₄sdpa was collected in volume via rotary evaporation. Other reagents and solvents employed were commercially available and used as received without further purification.

2.3. Synthesis of complexes 1-4

2.3.1. Synthesis of [Cu(sdpa)0.5(2,2'-bpy)]·H₂O (1)

Complex **1** was synthesized hydrothermally in a 23 mL Teflonlined autoclave by heating a mixture of Cu(NO₃)₂·3H₂O (0.1 mmol, 24.2 mg), 2,3,2',3'-sdpa (0.05 mmol, 19.7 mg), 2,2'-bipyridine (0.1 mmol, 15.6 mg), and one drop of Et₃N in 10 mL of water at 110 °C for 3 days under autogenous pressure. Then the reaction system was cooled to room temperature with a cooling rate of 5 °C/h. Blue block single crystals were collected (yield: 78% based on Cu). Anal. Calc. for C₃₆H₂₆N₄O₁₂SCu₂ (865.75): C, 49.94; H, 3.03; N, 6.47. Found: C, 49.90; H, 2.98; N, 6.41%. IR (KBr pellet,



Chart 1. Synthesis of H₄sdpa.



Chart 2. Coordination modes of the sdpa⁴⁻ a in 1; b in 2; c in 3; d in 4.

cm⁻¹): 3457(m), 1640(s), 1556(s), 1473(m), 1450(s), 1372(s), 1313(m), 1282(m), 1160(m), 1093(m), 1068(w), 891(m), 847(m), 770(s), 729(m), 633(m), 572(m), 443(w).

2.3.2. Synthesis of $[Zn_2(sdpa)(2,2'-bpy)2(H_2O)_2] \cdot 3H_2O(2)$

Complex **2** can be obtained following the same synthetic procedures as that of **1** except using 0.1 mmol $(29.7 \text{ mg}) \text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ instead of 0.1 mmol Cu(NO₃)₂·3H₂O as the starting material, and the colorless block single crystals were obtained (yield: 80% based on Zn). *Anal.* Calc. for C₃₆H₃₂N₄O₁₅SZn₂ (923.46): C, 46.82; H, 3.49; N, 6.06. Found: C, 46.79; H, 3.41; N, 6.02%. IR (KBr pellet, cm⁻¹): 3404(m), 1656(s), 1597(s), 1578(s), 1445(m), 1376(s), 1314(s), 1160(m), 1147(m), 1095(m), 1061(w), 1027(w), 886(m), 767(s), 743(m), 696(m), 593(w), 463(w).

2.3.3. Synthesis of [Zn₂(sdpa)(4,4'-bpy)]·3H₂O (3)

Similar to the preparation of **2** except using 4,4'-bipyridine (0.1 mmol, 15.6 mg) instead of 2,2'-bipyridine. The resulting colorless block single crystals were collected (yield: 71% based on Zn). *Anal.* Calc. for $C_{52}H_{34}N_4O_{23}S_2Zn_4$ (1408.43): C, 44.34; H, 2.44; N, 3.98. Found: C, 44.31; H, 2.41; N, 3.96%. IR (KBr pellet, cm⁻¹): 3447(m), 1580(s), 1556(m), 1457(m), 1400(s), 1383(m), 1330(m), 1219(s), 1169(m), 1126(w), 1070(m), 896(m), 817(m), 773(m), 702(m), 646(M), 598(m), 461(w).

2.3.4. Synthesis of $[Cd_2(sdpa)(4,4'-bpy)1.5(H_2O)_2]$ (4)

Complex **4** can also be obtained following the same synthetic procedure as that of **3** except using 0.1 mmol (30.8 mg) $Cd(NO_3)_2\cdot 6H_2O$ instead of 0.1 mmol $Zn(NO_3)_2\cdot 6H_2O$, and the colorless block single crystals were obtained (yield: 65% based on Cd). *Anal.* Calc. for $C_{62}H_{50}N_6O_{27}S_2Cd_4$ (1824.80): C, 40.81; H, 2.76; N, 4.60. Found: C, 40.79; H, 2.74; N, 4.55%. IR (KBr pellet, cm⁻¹): 3386(m), 1578(s), 1490(m), 1383(s), 1314(m), 1217(m), 1153(m), 1091(m), 1066(m), 811(m), 780(m), 755(w), 740(w), 686(m), 632(m), 502(w).

2.4. X-ray crystallography

Crystallographic data collections for complexes **1–4** were carried out on a Bruker Smart Apex II CCD with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 296(2) K using the ω -scan technique. The structures were obtained by the direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique which used the SHELXL-97 crystallographic software package [38,39]. The hydrogen atoms of the water molecules except for those of the uncoordinated water molecules were located in a difference Fourier map, and the other hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinements for **1–4** are summarized in Table 1. Selected bond distances and bond angles for **1–4** are listed in Table S1.

3. Results and discussion

3.1. Crystal structures

3.1.1. [Cu(sdpa)_{0.5}(2,2'-bpy)]·H₂O (**1**)

Single-crystal X-ray diffraction analysis reveals that the structure of **1** features a 1D zigzag polymeric coordination chain. As shown in Fig. 1, the sdpa^{4–} anion located at an inversion center and the Cu ion is in a distorted square-pyramid geometry ($\tau = 0.0983$ [40]) coordinated by two nitrogen atoms from the chelating 2,2'-bipyridine ligand and three oxygen atoms from three monodentate carboxylate groups of two sdpa^{4–} anions. Four atoms O3, O5, N1 and N2 comprise the equatorial plane; while another atom O3#1 occupies the axial position.

The sdpa^{4–} anion with trans-conformation is centrosymmetric and the dihedral angle between two phenyl rings is 69.9°. The dihedral angles between the carboxylate groups of sdpa^{4–} and their corresponding phenyl ring are 87.2° (2,2'-COO[–] groups) and 67.8°(3,3'-COO[–] groups), respectively. The 2- and 3-COO[–] groups of the same sdpa^{4–} anion are first connected with one Cu ion in a monodentate coordination mode, and then two O3 atoms of 2-COO[–] groups from two adjacent sdpa^{4–} ligands bridge two Cu ions into a four membered ring to form a binuclear basic building unit.

Table 1

Crystallographic data for compounds 1-4.



Fig. 1. Metal coordination and atom labeling in complex **1** (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. Symmetry codes: $#1 \ 1.5 - x, \ 1.5 - y, \ 2 - z$.

These units are further interlinked by the symmetrically-related sdpa^{4–} ligands to form an infinite zigzag chain (Fig. 2a).

At the same time, owing to the nonlinear flexibility of sdpa^{4–} ligand around O=S=O and twisted carboxylate groups, the interchain $\pi \cdots \pi$ (3.83 Å) stacking interactions of pyridine rings from two neighboring chains are apparent in four orientations to lead a 3D supramolecular structure (Fig. 2b). In addition, the inter-chain C-H= π interactions (C-H···center 2.91 Å) between the pyridine molecules and phenyl rings of sdpa^{4–} ligands from neighboring chains (Fig. S2) make the 3D framework more stable.

3.1.2. [Zn₂(sdpa)(2,2'-bpy)₂(H2O)₂]·3H₂O (**2**)

Single-crystal X-ray diffraction analysis reveals that compound **2** presents a double zipper chain. The asymmetric unit of **2** contains two crystallographically nonequivalent Zn^{II} ions, one $sdpa^{4-}$ anion, one 2,2'-bipyridine molecule, two coordinated water molecules and three solvent water molecules (Fig. 3). The Zn1 ion is in a distorted square-pyramid geometry ($\tau = 0.1115$ [40]) coordinated by two nitrogen atoms from one chelating 2,2'-bipyridine ligand, two oxygen atoms from monodentate 2- and 2'-COO⁻ groups of

	1	2	3	4
Empirical formula	C36H26N4O12Cu2S	C ₃₆ H ₃₂ N ₄ O ₁₅ Zn ₂ S	C ₅₂ H ₃₄ N ₄ O ₂₃ Zn ₄ S ₂	C62H50N6O27Cd4S2
Formula weight	865.75	923.46	1408.43	1824.80
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	C2/c	ΡĪ	$P2_1/c$	$P2_1/c$
a (Å)	15.282(5)	10.626(2)	11.098(2)	10.232(2)
b (Å)	11.841(4)	13.991(3)	21.441(4)	13.410(3)
c (Å)	21.799(9)	14.941(3)	11.773(2)	22.890(5)
α (°)	90	109.22(3)	90	90
β (°)	113.728(1)	101.95(3)	94.43(3)	100.39(3)
γ (°)	90	109.76(3)	90	90
$V(Å^3)$	3611(2)	1842.9(1)	2793.1(1)	3089.4(1)
Ζ	4	2	2	2
T (K)	296(2)	296(2)	296(2)	296(2)
$D_{\text{calc}} (\text{g cm}^{-3})$	1.592	1.664	1.675	1.962
F(0 0 0)	1760	944	1420	1808
θ range (°)	2.25-25.00	2.10-25.00	1.84-25.00	2.02-25.00
Reflections collected	10035	21107	31575	34423
Independent reflections	3538	6331	4881	5362
Independent reflections (R_{int})	0.0358	0.0423	0.0741	0.0402
Goodness-of-fit (GOF) on F ²	1.036	1.056	1.186	1.1013
$R_1^a (I > 2\sigma(I))$	0.0327	0.0370	0.0649	0.0363
$wR_2^{b}(I > 2\sigma(I))$	0.0930	0.0833	0.1477	0.0977
Largest difference in peak and hole (e $Å^{-3}$)	0.814 and -0.353	0.469 and -0.387	0.954 and -0.381	0.585 and -0.698

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

^b $wR^2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)_2\right]^{1/2}.$



Fig. 2. (a) Cu-sdpa Chain in 1. 2,2'-bpy ligands are partial omitted for clarity. (b) 3D supramolecular structure for 1. Cu atoms are marked as blue.



Fig. 3. Metal coordination and atom labeling in complex **2** (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. Symmetry codes: #1 x, -1 + y, z.

sdpa^{4–} ligand, another oxygen atom from the coordinated water. The Zn₂ ion is in a distorted trigonal bipyramid geometry ($\tau = 0.4723$ [40]) coordinated by O10 from 3'-COO⁻ group of sdpa^{4–} anion, O6#1 from 3-COO⁻ group of neighboring sdpa^{4–} ligand, O2W from the coordinated water, N3 and N4 from another chelating 2,2'-bipyridine molecule.

As to sdpa^{4–} anion ligand, the dihedral angle between two phenyl rings is 74.1°, the bond angle $\angle C_1SC_7$ is 107.3° and the four COO⁻ groups (2-, 3-, 2'-, 3'-carboxylate groups) make dihedral angles of 54.9°, 76.9°, 83.8°, and 79.4° with the corresponding linked benzene rings, respectively. The four carboxylate groups of sdpa⁴⁻ are all monocoordinated, in which the 2- and 2'-COO⁻ groups from the same sdpa⁴⁻ ligand bind Zn1 atom into a 10-membered ring, While the 3- and 3'-COO⁻ groups from two neighboring sdpa⁴⁻ ligands connect Zn2 atoms to form an infinite chain running along the *b* axis, and two adjacent chains are face-to-face packed into a double slide fastener chain (Fig. 4a) connected by two kinds of $\pi \cdots \pi$ stacking interactions between the 2,2'-bipyridine, as show in Fig. 4a. The centroid-to-centroid distances are 3.615 Å for type A and 3.559 Å for type B, respectively. The double chains are further linked into 2D undulating layers through another kind of weak $\pi \cdots \pi$ stacking interaction along the *c* axis happening between adjacent sdpa^{4–} ligands from neighboring double chains with a edge-to-centroid distance of 4.022 Å, as shown in Fig. 4b.

What interests us is that the channels of adjacent layers are occupied by the remaining water molecules, which are associated by strong O-H···O hydrogen bonds into cyclic centrosymmetric hexamers to result in a (H₂O)₆ cluster that adopts a plane conformation (Fig. 4c) different from the aforetime report [41]. The hydrogen bond lengths (Å) and angles (°) are listed in Table S2. The average O...O distance is 2.731 Å. There is a variation in the $0 \cdots 0 \cdots 0$ angles, with an average of 119.9° ($\angle O_{4W}O_{3W}O_{5W\#1}$ = 130.6°, $\angle O_{4W}O_{5W}O_{3W\#1} = 112.3^\circ$, $\angle O_{5W}O_{4W}O_{3W} = 116.8^\circ$), which deviates considerably from the corresponding value of 109.3° in hexagonal ice [42]. The solvent $(H_2O)_6$ cluster from two asymmetric unit of neighboring chains fills in the interspace of adjacent chains to form rich hydrogen-bonds of inter- and intra-chains (Fig. 4c). In addition, the hydrogen-bonds exist not only among the solvent $(H_2O)_6$ cluster but also between $(H_2O)_6$ cluster and coordinated water O2W, O6, O8 from the carboxylate groups of sdpa⁴⁻ ligand, and O2 from sulphone (Fig. 4c). Adjacent layers are interconnected by hydrogen bonds to form a 3D supramolecular structure as shaded in purple, as shown in Fig. 4d. This supramolecular association of water molecules in tapes is presumably



Fig. 4. (a) The slide fastener structure in **2**. (b) Slide fastener structures are further linked together through another kind of $\pi \cdots \pi$ interactions to form a 2D supramolecular structure. (c) Representation of the cyclic water hexamers found in the channels of **2** and self-assembly of the water hexamers into extended structure. (d) 3D supramolecular network in **2**.

enforced by the shape of the host's channels, whose relatively narrow openings result in the formation of more stable clusters. In conclusion, the packing structure of **2** shows a three-dimensional supramolecular network via rich hydrogen bonds and $\pi \cdots \pi$ stacking interactions.

3.1.3. [Zn₂(sdpa)(4,4'-bpy)]·3H₂O (**3**)

When a space extending 4,4'-bpy ligand was used as an bridging auxiliary linkage, compound **3** displays a 3D coordination network consisting of tetranuclear zinc SBU chains and 4,4'-bpy bridge ligands. As illustrated in Fig. 5, the asymmetric unit of **3** contains two independent Zn^{II} ions, one sdpa⁴⁻ anion, one 4,4'bipyridine (bpy) molecule, and three solvent water molecules. The Zn1 ion is in a distorted octahedral geometry coordinated by N1 from the bridging 4,4'-bipyridine ligand, O3, O5 from 2- to 3-COO⁻ groups of sdpa⁴⁻ ligand, O3#1, O4#1 and O7#1 from 2- to 2'-COO⁻ groups of another sdpa⁴⁻ ligand. The Zn2 ion is in a tetrahedral geometry coordinating to O6, O9#1, and O8#2 from 2-, 3'-, to 2'-COO⁻ groups of three different sdpa⁴⁻ ligands, N2#3 from another bridging 4,4'-bipyridine ligand.

The 2,3,2',3'-sdpa employs a twisted conformation with the bond angle around S1 is 105.2°, and the dihedral angle between the two phenyl rings is 89°. The dihedral angles between the 2-,



Fig. 5. Metal coordination and atom labeling in complex **3** (thermal ellipsoids at 50% probability level). Hydrogen atoms and the solvent water molecules are omitted for clarity. Symmetry codes: #1 1 - x, -0.5 + y, 1.5 - z; #2 1 + x, y, z; #3 2 - x, -0.5 + y, 1.5 - z.

3-, 2'- and 3'-carboxylate groups and their corresponding phenyl rings are 84.3°, 10.8°, 82.6° and 20.5°, respectively. It is worth noting that the sdpa⁴⁻ ligand adopts a octadentate coordination mode: the 2-COO⁻ group adopts a chelate/bridge tridentate coordination mode connecting two Zn1 ions, the 2'- and 3-COO⁻ groups adopt bridge bidentate coordination modes connecting Zn1 and Zn2 ions, whereas the 3'-COO⁻ group is monocoordinated to Zn2.

Based on these connection modes, each pair of Zn1 ions are bridged by O3, O3#1 atoms of 2-COO⁻ groups from two face-toface sdpa⁴⁻ ligands to form a four membered ring $\{Zn1_2O_2\}$ unit, such rings are further associated together through Zn2 ions to form an infinite Zn-sdpa chain (Fig. 6a and b), in which Zn1 and Zn2 atom pairs appear alternately. Each Zn-sdpa chain is further connected to the other four Zn-sdpa chains through 4,4'-bipvridine ligands along four orientations to form a 3D network structure (Fig. 6c and Fig. S3). A better understanding of this complicated structure can be achieved via topological considerations [43-45]. If the sdpa⁴⁻ ligand is considered as a three-connected node (connecting to two bimetallic units $[Zn2_2(CO_2)_2]$ and one bimetallic unit $[Zn1_2(CO_2)_2]$)?the bimetallic unit $[Zn1_2(CO_2)_2]$ as a sixconnected node (connectiong four 4,4'-bipyridine and two sdpa⁴⁻), the bimetallic unit $[Zn2_2(CO_2)_2]$ as an eight-connected node (connecting four sdpa⁴⁻ and four 4,4'-bipyridine), the structure of 3 can be described as a (3,6,8)-connected network with a Schläfli symbol of $(4^3)_2(4^5 \cdot 6^{10})(4^6 \cdot 6^{18} \cdot 8^4)$ topology.

3.1.4. $[Cd_2(sdpa)(4,4'-bpy)_{1.5}(H_2O)_2] \cdot 2H_2O$ (4)

Single-crystal X-ray diffraction analysis reveals that compound 4 exhibits a 3D coordination network consisting of tetranuclear cadmium unit chains interlinked through sdpa^{4–} and 4,4'-bpy ligands. The asymmetric unit of **4** contains one sdpa⁴⁻ anion ligand, two independent Cd^{II} ions, one and a half bpy molecules, as well as two coordinated water molecules (Fig. 7). Cd1 is in an octahedron geometry coordinating to O4, O5 from 2- and 3-COO⁻ groups of sdpa4- ligand, 08#1 ,09#1 from 2'- to 3'-COO- groups of the neighboring sdpa^{4–} anion ligand, and N1, N2#4 from two different bicoordinated bpy molecules. Four O atoms comprise the equatorial plane, while N1 and N2 occupy the axial positions. Cd2 is in a distorted octahedron geometry coordinating to O3 from 2-COOgroup of sdpa^{4–} ligand, O6#2 from 3-COO[–] group of the neighboring sdpa⁴⁻ ligand, O10#3 from 3'-COO⁻ group of another neighboring sdpa^{4–} ligand, N3 from the third bicoordinated bpy molecule, O1W and O2W from two coordinated water molecules. Four atoms O3, N3, O1W and O2W comprise the equatorial plane, while O6#2 and O10#3 occupy the axial positions. As to sdpa⁴⁻ anion ligand, the dihedral angle between the two phenyl rings is 87.7° and the bond angle $\angle C_1S_1C_7$ is 104.9°. The dihedral angles between the 2-, 3-, 2'- and 3'-carboxylate groups and their corresponding phenyl rings are 20.2°, 7.9°, 89.1° and 45.7°, respectively. The 2-, 3- and 3'-COO⁻ groups of sdpa⁴⁻ adopt bridge bidentate coordination modes connecting Cd1 and Cd2 ions, whereas the 2'-COO⁻ group is monocoordinated to Cd1.



Fig. 6. (a) Zn-Sdpa chain in **3.** Hydrogen atoms and water molecules are omitted for clarity. (b) Chain structure with Zn shown as polyhedra. Irrespective atoms are omitted for clarity. (c) Zn-Sdpa chains are linked together through 4.4'-bpy ligands (marked as blue rods) to form a 3D metal-organic network. (d) Schematic presentations of a (3,6,8)-connected network with a Schläfli symbol of $(4^3)_2(4^5.6^{10})(4^6.6^{18}.8^4)$ topology: pink, purple and blue represent bimetallic unit $[Zn1_2(CO_2)_2]$, bimetallic units $[Zn2_2(CO_2)_2]$ and sdpa⁴⁻ ligand, respectively.



Fig. 7. Molecular structures of **4** showing the geometry of the Cd^{2+} ions and the coordination modes of the carboxylate groups. Hydrogen atoms and the solvent water molecules are omitted for clarity. Symmetry codes: #1 2 - *x*, 0.5 + *y*, 0.5 - *z*; #2 2 - *x*, -*y*, 1 - *z*; #3 1 - *x*, 0.5 + *y*, 0.5 - *z*; #4 *x*, 0.5 - *y*, 0.5 + *z*.

Based on these connection modes, each Cd1 and Cd2 ion appear alternately and connected through 2-, 3- and 3'-COO⁻ groups from three different sdpa⁴⁻ ligands (Fig. 8a) to form a tetranuclear cadmium Unit{Cd1₂Cd2₂C4O₈} (Fig. 8b). The Units are interlinked through sdpa^{4–} ligands to form an infinite tetranuclear basic Cd-sdpa chain, and such Cd-sdpa chains are interlinked through sdpa^{4–} anion ligands in four orientations to form a 3D network structure which are further strengthened by 4,4'-bpy ligands in six orientations (*Fig.* S4 and Fig. 8c). If the sdpa^{4–} are considered as five-connected node (connecting to two Cd1 cations and three Cd2 cations), and Cd1 cations as four-connected node (connecting two sdpa^{4–} and two 4,4'-bpy), Cd2 also as four-connected node (connecting three sdpa^{4–} and one 4,4'-bpy), the structure of **4** can be described as a (4,4,5)-connected network with a Schläfli symbol of (4.5³.7²)(4.5⁵.6.8²)(5².6².7.8) topology.

3.2. Discussions

According to the above structural description of the four coordination polymers, there are four different coordination modes of the 2,3,2',3'-sdpa⁴⁻ ligand. In **1**, the sdpa⁴⁻ anion with *trans*-conformation is centrosymmetric and adopts μ_4 -bridging mode with four carboxylate group to coordinate four Cu atoms with μ_4 : $\eta^1\eta^1\eta^2\eta^2$ coordination modes (Chart 2a), while in the case of **2**, sdpa⁴⁻ adopts a μ_4 -bridging mode with each of the four carboxylate groups in a same monodentate mode (μ_4 : $\eta^1\eta^1\eta^1\eta^1\eta^1$) as show in Chart 2b. The sdpa⁴⁻ ligand in **3** also adopts a μ_4 -bridging fashion with four carboxylate groups to coordinate to four Zn atoms with μ_4 : $\eta^1\eta^1\eta^2\eta^2$ coordination mode (Chart 2c), whereas in **4**, each sdpa⁴⁻ ligand adopts μ_5 -bridging fashion with four carboxylate group to coordinate four Cu atoms with μ_5 : $\eta^1\eta^2\eta^2\eta^2$



Fig. 8. (a) The unit in **4**. Cd is shown as polyhedron. (b) Units linked together via sdpa⁴⁻ anion ligands to form a chain structure. (c) A view of Cd-sdpa 3D metal-organic network. (d) (4,4,5)-connected network with a Schläfli symbol of (4.5³·7²)(4.5⁵·6·8²)(5²·6²·7·8) topology: sdpa (blue), Cd1 (green), Cd2 (bottle green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mode (Chart 2d). Furthermore, the steric hindrance of the 2,2'-bpy molecule may contribute to the simple bridging fashion of the sdpa^{4–} ligand, whereas rigid rod-like 4,4'-bpy acts as a pillar connector to make sdpa^{4–} adopt relatively complicated coordination modes.

As V-shaped multicarboxylate ligands, the rigidity of the ligand is known to be essential for the polymeric structure, which is similar to H₄tdpa and H₄odpa ligands. The tdpa ligand behave much like the odpa ligand since the nonlinear flexibility around etheric oxygen or sulfur atom and twisted conformation of carboxylate groups which make it easy to form helical structure, whereas sdpa ligand lost its flexibility owing to the O=S=O which make it not suitable for the construction of helixes. The sdpa ligands show dramatic distinction against the tdpa and odpa ligands: six of the seven tdpa complexes and five of the six odpa complexes contain helical structures, whereas all four sdpa complexes have no helix. which proved that the flexibility is the crucial factor in the formation of the helical architecture. These interesting results suggest that there exist some fundamental differences between sdpa and tdpa, odpa that are covered up by their seeming analogy and thus need further exploration.

Results also revealed that the secondary ligands play an important role in determining the structural diversity in MOFs: 2,2'bipyridine ligands chelate metal cations which makes it difficult to form three-dimensional structure, such as in **1** and **2**, whereas in **3** and **4**, the rigid rod-like 4,4'-bpy makes it easy to form three-dimensional architecture.

3.3. IR spectral analyses

In the IR spectrum of complexes **1** and **2**, the characteristic bands observed at around 1650 cm^{-1} are attributed to the protonated carboxylic groups, indicating the incomplete deprotonation H₄sdpa. Strong absorption bands between 1350 and 1600 cm⁻¹ in the IR spectra of complexes **1–4** can be assigned to the coordinated carboxylate groups. The sulfones characteristic bands are measured at around 1310, 1160, 1080 cm⁻¹ [37]. All this agrees well with the result of X-ray single-crystal analyse.

3.4. Thermal properties and photoluminescence properties

Thermal analyses for 1-4 were carried out from room temperature to 800 °C under a nitrogen atmosphere (see Fig. S1 for TGA curves). The TGA curve of 1 shows that the first weight loss of 2.41% appeared between 80 and 150 °C corresponds to the loss of the coordinated water molecule (calculated, 2.07%), and then the network was decomposed quickly at 209 °C, resulting in the residue. Comparably, compound **2** is dehydrated, with the weight loss of 9.52% between 42.5 to 170 °C also corresponding to the loss of three lattice water molecules per formula unit (calculated, 9.76%), and the framework collapsed in the temperature range of 250–530 °C resulting in the residue. For **3**, the first weight loss of 4.10% indicates that the water molecules (calculated, 3.83%) lost in the range of 34-229 °C. A gradual weight loss from 395 °C indicates the structure was decomposed. The TGA curve of **4** shows that the weight loss of 3.72% appeared between 40 and 200 °C corresponds to the loss of two coordinated water molecules per formula unit (calculated, 3.94%), and the framework collapsed in the temperature range of 200–500 °C.

Taking into account the excellent luminescent properties of d^{10} metal–organic polymers, the luminescent properties of compound **2–4** were investigated in the solid-state at room temperature. As shown in Fig. 9, complexes **2–4** exhibit photoluminescence with an emission maximum at ca. 395, 395, and 397 nm upon excitation at 362 nm, respectively. These emissions can probably be assigned to the intraligand $(\pi - \pi^*)$ fluorescent emission because similar



Fig. 9. Fluorescence emission spectrum of the complexes 2, 3, 4.

emission is observed at 396 nm for the free 2,3,2',3'-sdpa ligand [46–48]. By comparing the emission spectra of **2–4** and ligand, we can conclude that the enhancement of luminescence in **2–4** may be attributed to the ligation of ligand to the metal center, which effectively increases the rigidity and reduces the loss of energy by radiationless decay [49–51]. Comparably, the complexes from 2,3,2',3'-tdpa exhibit intense blue fluorescence emission bands at ca. 429~492 nm [32]. The shifts of emission spectrum are due to the differences of ligand. The ligand 2,3,2',3'-sdpa is more rigid than 2,3,2',3'-tdpa, and this phenomena reduces the loss of energy by radiationless decay so as to make the Anti-Stoke's shift.

4. Conclusion

In this paper, a series of four MOFs constructed from 2,3,2',3'sdpa have been hydrothermally synthesized and structurally characterized. Different structures of compounds **1–4** indicate that the new aromatic tetracarboxylic acid anion ligand sdpa^{4–} has the ability of adjusting its coordination configuration and mode in different reaction systems. The results also revealed that the secondary ligands play an important role in determining the structural diversity in MOFs: 2,2'-bipyridine ligands chelate metal cations ligand which make it difficult to form three-dimensional structure, such as in **1** and **2**, whereas in **3** and **4**, the rigid rod-like 4,4'-bpy behave good space extending and make it easy to form threedimensional architecture.

In conclusion, the 2,3,2',3'-sdpa ligand could be used as a versatile ligand to construct novel MOFs by appropriate choice of coligands and metal-centers. Subsequent works will be focused on the construction of new interesting coordination polymers by reacting 2,3,2',3'-sdpa and other assistant N-donor ligands with more metal ions.

5. Supplementary data

CCDC 777761–777764 contain the supplementary crystallographic data for complexes **1–4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.07.013.

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