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## Cd(II) coordination polymers constructed from flexible disulfide ligand: Solvothermal syntheses, structures and luminescent properties

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#### ABSTRACT

Four novel coordination polymers,  $[Cd(Hdtbb)(dtbb)_{0.5}(DMF)]_n$  (1),  $\{[Cd(dtbb)(2,2'-bpy)(H_2O)]\cdot 2DMA\}_n$  (2),  $\{[Cd_2(dtbb)_2(1,4-bix)_2]\cdot 3DMF\}_n$  (3) and  $[Cd(dtbb)(1,4-btx)]_n$  (4)  $[H_2dtbb = 2,2-dithiobisbenzoic acid, 2,2'-bpy = 2,2'-bipyridine, 1,4-bix = 1,4-bis(imidazol-1-ylmethyl)benzene, 1,4-btx = 1,4-bis(triazol-1-ylmethyl)benzene] have been synthesized and structurally characterized. Complexes 1 and 2 possess one-dimensional (1D) infinite structures. The structures of complexes 3 and 4 exhibit two dimensional (2D) frameworks, which mainly due to the differences in the bridging modes of dtbb<sup>2-</sup> ligand and the effect of the N-donor auxiliary ligands. The infrared spectra, thermogravimetric and luminescent properties were also investigated for these compounds.$ 

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#### 1. Introduction

In the past decades, the realm of crystal engineering has achieved significant success in developing a variety of coordination networks [1-21]. The interest arise not only from their versatile fascinating architectures but also from their promising applications as functional materials [22-24,3,25-30]. Many works have been devoted to the selection or design of suitable ligands containing certain features. Among the reported studies, organic ligands with carboxylate groups are of especial interest because they can adopt a variety of coordination modes and result in diverse multidimensional frameworks [31-38]. To date, a number of rigid ligands, such as benzenedicarboxylate isomers [39-42], 1,3,5benzenetricarboxylate [43-45], 1,2,4,5-benzenetetracarboxylate [46.47] and pyridinedicarboxylate isomers [48-50], have been successfully employed and well documented in the preparation of various carboxylato-containing metal-organic coordination complexes with useful properties. However, there is an unfavorable investigation on the MOFs containing flexible bridging carboxylate ligands [51-55]. Compared with the rigid ligands, the skew and versatile coordination orientation of the flexible bridging ligands is favorable for constructing novel structures [56–59].

Disulfide bridging phenyl carboxylate ligands possess flexibility owing to the presence of -S-S- spacers between the phenyl rings and can adopt various conformations according to geometric requirements when they react with different metal salts, the flexible and multifunctional coordination sites provide a high likelihood for build novel coordination frameworks with high dimensions. Whereas, there have been few reports of studies on flexible disulfide derivatives of carboxylates [60-64]. Considering the points mentioned above, to further explore the coordination characteristics of flexible disulfide bridging aromatic dicarboxylate ligand, we chose 2,2-dithiobisbenzoic acid (H<sub>2</sub>dtbb, Scheme 1(a)) as primary ligand to construct Cd(II) photoluminescent coordination polymers by taking advantage of its multicarboxylate bridging coordination ability together with the flexibility of its C-S-S-C bonds, incorporating the auxiliary ligands 2,2'-bipyridine (2,2'bpy, Scheme 1(b)) for 2, 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix, Scheme 1(c)) for **3**, and 1,4-bis(triazol-1-ylmethyl)benzene (1,4-btx, Scheme 1(d)) for 4. Herein, we report the syntheses, crystal structures and photoluminescent properties of four Cd(II) complexes with these ligands:  $[Cd(Hdtbb)(dtbb)_{0.5}(DMF)]_n$ (1), { $[Cd(dtbb)(2,2'-bpy)(H_2O)] \cdot 2DMA$ }<sub>n</sub> (2), { $[Cd_2(dtbb)_2(1,4$  $bix_{2}$ -3DMF $_{n}$  (**3**) and  $[Cd(dtbb)(1,4-btx)]_{n}$  (**4**).

## 2. Experimental

## 2.1. Materials and methods

The ligand 1,4-bix and 1,4-btx were synthesized according to literatures [65,66]. All other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses for C, H, and N were carried out



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**Scheme 1.** Chemical structures of H<sub>2</sub>dtbb (a) and auxiliary ligand 2,2'-bpy (b), 1,4-bix (c) and 1,4-btx (d).

using a Perkin–Elmer 240 elemental analyzer. The IR spectra were obtained as KBr pellets on a Bruker VECTOR 22 spectrometer in the 4000–400 cm<sup>-1</sup> region. Thermogravimetric analyses were performed on a TGAV5.1A Dupont 2100 instrument from room temperature to 600 or 800 °C with a heating rate of 10 °C min<sup>-1</sup> in nitrogen environment. Luminescence spectra for the solid samples were recorded using a Hitachi 850 fluorescence spectrophotometer.

#### 2.2. Synthesis of the complexes

#### 2.2.1. $[Cd(Hdtbb)(dtbb)_{0.5}(DMF)]_n$ (1)

A mixture of CdCO<sub>3</sub> (0.03 g, 0.20 mmol), H<sub>2</sub>dtbb (0.09 g, 0.30 mmol), DMF (2 ml), H<sub>2</sub>O (1 ml) and NaOH (0.1 mol/L, 2 ml), was placed in a 25 ml Teflon-lined stainless steel vessel, which was sealed and heated at 80 °C for 2d. After the mixture had been slowly cooled to room temperature, yellow plate crystals of **1** were obtained with 65% yield on cadmium basis. Elemental analysis, *Anal.* Calc. for C<sub>24</sub>H<sub>20</sub>CdNO<sub>7</sub>S<sub>3</sub> (Mr. 643.03): C, 44.83; H, 3.14; N,

Table 1

Crystal data and structure refinements for compounds 1-4.

2.18. Found: C, 44.76; H, 3.21; N, 2.14%. IR data (KBr pellet, *v*[cm<sup>-1</sup>]): 3420(m), 2941(w), 2489(w), 1664(s), 1575(m), 1374(s), 1229(m), 1134(w), 1032(w), 932(w), 833(w), 725(m).

## 2.2.2. {[ $Cd(dtbb)(2,2'-bpy)(H_2O)$ ]·2DMA}<sub>n</sub> (**2**)

A mixture of CdO (0.02 g, 0.20 mmol), H<sub>2</sub>dtbb (0.06 g, 0.20 mmol), 2,2'-bpy (0.02 g, 0.10 mmol), DMA (3 ml), H<sub>2</sub>O (2 ml) was sealed in a 25 ml Teflon-lined stainless steel vessel and heated at 80 °C for 2d. After the mixture had been slowly cooled to room temperature over 24 h, yellow block crystals of **2** were obtained with 56% yield on cadmium basis. Elemental analysis, *Aanl.* Calc. for  $C_{32}H_{36}CdN_4O_7S_2$  (Mr. 765.17): C, 50.23; H, 4.74; N, 7.32. Found: C, 50.27; H, 4.71; N, 7.28%. IR data (KBr pellet,  $\nu$ [cm<sup>-1</sup>]): 3438(m), 2923(m), 1588(s), 1544(s), 1374(s), 1248(s), 1008(m), 839(w), 744(m), 634(m).

#### 2.2.3. { $[Cd_2(dtbb)_2(1,4-bix)_2] \cdot 3DMF$ }<sub>n</sub> (**3**)

A mixture of CdO (0.03 g, 0.20 mmol), H<sub>2</sub>dtbb (0.09 g, 0.30 mmol), 1,4-bix (0.03 g, 0.10 mmol), DMF (5 ml) was sealed in a 25 ml Teflon-lined stainless steel vessel and heated at 80 °C for 48 h, and then cooled to room temperature over 1d. Yellow block crystals of **3** suitable for X-ray diffraction were obtained with 75% yield on cadmium basis. Elemental analysis, *Anal.* Calc. for C<sub>65</sub>H<sub>63</sub>Cd<sub>2</sub>N<sub>11</sub>O<sub>11</sub>S<sub>4</sub> (Mr. 1527.30): C, 51.12; H, 4.16; N, 10.09. Found: C, 51.20; H, 4.13; N, 10.12%. IR data (KBr pellet,  $\nu$ [cm<sup>-1</sup>]): 3445(m), 2815(w), 2513(w), 1683(s), 1621(s), 1367(m), 1254(s), 1115(m), 1041(w), 913(w), 801(w), 732(m), 669(w), 536(w).

## 2.2.4. $[Cd(dtbb)(1,4-btx)]_n$ (4)

A mixture of CdO (0.04 g, 0.30 mmol),  $H_2$ dtbb(0.09 g, 0.30 mmol), 1,4-btx (0.02 g, 0.10 mmol), DMF (2 ml) ,  $H_2$ O (3 ml) was heated at 80 °C for 2d in a sealed Teflon-lined stainless steel vessel (25 ml) under autogenous pressure. Slow cooling of the reaction mixture to room temperature gave yellow block crystals with 56% yield on cadmium basis. Elemental analysis, *Anal.* Calc. for  $C_{26}H_{20}$ CdN<sub>6</sub>O<sub>4</sub>S<sub>2</sub> (Mr. 657.00): C, 47.53; H, 3.07; N, 12.79. Found: C, 47.23; H, 3.22; N, 12.2%. IR data (KBr pellet, v[cm<sup>-1</sup>]): 3398(m), 3103(m), 1587(s), 1533(s), 1380(s), 1272(s), 1133(m), 966(m), 861(m), 752(m).

5				
	1	2	3	4
Empirical formula	C24H20CdNO7S3	C32H36CdN4O7 S2	$C_{65}H_{63}Cd_2N_{11}O_{11}S_4$	C26H20CdN6O4 S2
Formula mass	642.99	765.17	1527.30	657.00
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	$P2_1/c$	C2/c	ΡĪ
a (Å)	30.351(3)	11.803(6)	31.263(3)	10.7370(17)
b (Å)	8.8251(8)	26.668(14)	12.0748(10)	11.2552(17)
<i>c</i> (Å)	21.869(2)	10.907(6)	18.9417(16)	11.7481(18)
α (°)	90	90	90	73.996(2)
β(°)	122.0180(10)	107.330(7)	105.9230(10)	88.977(2)
γ(°)	90	90	90	76.188(2)
Ζ	8	4	4	2
$V(Å^3)$	4966.5(8)	3277(3)	6876.0(10)	1323.5(4)
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.720	1.551	1.474	1.649
$\mu (\mathrm{mm}^{-1})$	1.178	0.847	0.806	1.028
F(0 0 0)	2584	1568	3116	660
Crystal size (mm)	$0.40 \times 0.30 \times 0.10$	$0.38 \times 0.20 \times 0.18$	$0.34 \times 0.25 \times 0.20$	$0.34 \times 0.28 \times 0.20$
$\theta$ Range (°)	1.58-27.65	2.10-25.50	1.82-25.00°	1.81-27.60
Reflections collected	21084	23978	24355	11599
Unique reflections	$5776[R_{int} = 0.0212]$	$6069 [R_{int} = 0.075]$	$6056 [R_{int} = 0.0375]$	5970 $[R_{int} = 0.0309]$
Data/restraints/parameters	5776/0/328	6069/0/427	6056/83/409	5970/0/352
Goodness-of-fit (GOF) on $F^2$	1.049	1.072	1.118	1.121
$R_1, wR_2 [I > 2\sigma(I)]$	0.0218, 0.0619	0.0471, 0.1176	0.0411, 0.1119	0.0421, 0.1109
$R_1$ , $wR_2$ (all data)	0.0219, 0.0678	0.0621, 0.1260	0.0660, 0.1250	0.0691, 0.1600
Largest difference in peak and hole (e Å <sup><math>-3</math></sup> )	0.344 and -0.288	1.24 and -1.01	0.923 and -0.745	0.644 and -1.185

 $R_1 = \Sigma ||F_0| - |F_c| / \Sigma |F_0|, \ wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2)| / \Sigma |w(F_0^2)^2|^{1/2}.$ 

Table 2
Selected bond lengths (Å) and angles (°) for complexes $\bm{1}^a, \bm{2}^b, \bm{3}^c$ and $\bm{4}^d.$

1					
Cd1-02	2.1796(14)	Cd1-07	2.2418(15)	Cd1-01#1	2.2539(14)
Cd1-06	2.2945(15)	Cd1-05	2.4676(13)	Cd1-03#2	2.5022(14)
02-Cd1-07	113.14(5)	O2-Cd1-O1#1	105.68(5)	07-Cd1-01#1	87.25(6)
02-Cd1-06	143.28(5)	07-Cd1-06	91.71(6)	01#1-Cd1-06	101.95(5)
02-Cd1-05	102.82(5)	07-Cd1-05	143.83(5)	01#1-Cd1-05	86.75(5)
06-Cd1-05	54.96(5)	02-Cd1-03#2	78,45(5)	07-Cd1-03#2	82.33(6)
01#1-Cd1-O3#2	169.58(5)	06-Cd1-O3#2	78.67(5)	05-Cd1-03#2	101.80(5)
2					
Z Cd1-01	2.309(3)	Cd1-03#1	2.332(3)	Cd1-N2	2.347(3)
Cd1-N1	2.354(3)	Cd1-05	2.379(3)	Cd1-02	2.456(3)
Cd1-O4#1	2.555(3)		,		
01-Cd1-O3#1	98.12(12)	01-Cd1-N2	140.25(11)	O3#1-Cd1-N2	87.60(12)
01-Cd1-N1	146.41(11)	O3#1-Cd1-N1	96.78(11)	N2-Cd1-N1	70.19(11)
01-Cd1-05	81.91(13)	O3#1-Cd1-O5	177.39(11)	N2-Cd1-O5	94.04(12)
N1-Cd1-O5	81.89(12)	01-Cd1-O2	55.26(9)	O3#1-Cd1-O2	95.56(10)
N2-Cd1-O2	85.10(10)	N1-Cd1-O2	151.76(10)	05-Cd1-02	86.61(11)
01-Cd1-O4#1	84.71(9)	O3#1-Cd1-O4#1	53.69(9)	N2-Cd1-O4#1	127.72(10)
N1-Cd1-O4#1	80.21(11)	O5-Cd1-O4#1	123.77(11)	O2-Cd1-O4#1	127.11(10)
3					
Cd1–N1	2.227(3)	Cd1-02	2.442(3)	Cd1-N3	2.262(3)
Cd1-03#1	2.265(3)	Cd1-O4#1	2.522(3)	Cd1-01	2.313(3)
N1-Cd1-N3	101.07(13)	O3#1-Cd1-O1	100.28(11)	N1-Cd1-O4#1	87.54(11)
N1-Cd1-O3#1	134.85(12)	N1-Cd1-O2	95.85(13)	N3-Cd1-O4#1	133.30(12)
N3-Cd1-O3#1	92.11(12)	N3-Cd1-O2	81.76(12)	O3#1-Cd1-O4#1	54.06(10)
N1-Cd1-O1	102.07(12)	O3#1-Cd1-O2	128.91(12)	01-Cd1-04#1	89.20(11)
N3-Cd1-O1	131.98(13)	01-Cd1-02	54.52(11)	O2-Cd1-O4#1	143.52(11)
4					
Cd1-01#1	2.232(4)	Cd1-03	2.349(3)	Cd1-N1	2.291(4)
Cd1-02#2	2.333(3)	Cd1-04	2.374(4)	Cd1-N6#3	2.382(4)
01#1-Cd1-N1	112.75(16)	01#1-Cd1-02#2	99.95(15)	N1-Cd1-O2#2	83.17(15)
01#1-Cd1-O3	94.37(14)	N1-Cd1-O3	151.52(16)	02#2-Cd1-O3	83.75(13)
01#1-Cd1-O4	146.11(14)	N1-Cd1-O4	99.92(16)	02#2-Cd1-O4	92.39(15)
03-Cd1-O4	55.53(13)	O4-Cd)-N6#3	86.05(16)	O1#1-Cd1-N6#3	83.25(15)
N1-Cd1-N6#3	93.58(16)	O2#2-Cd1-N6#3	176.12(15)	O3-Cd1-N6#3	98.25(15)
	• •				. ,

<sup>a</sup> Symmetry codes: #1 - x + 2, -y + 2, -z #2 x, -y + 2, z - 1/2 #3 x, -y + 2, z + 1/2 #4 - x + 2, y, -z - 1/2.

<sup>b</sup> Symmetry codes: #1 x + 1, y, z #2 x - 1, y, z.

<sup>c</sup> Symmetry codes: #1 x, y + 1, z #2 x, y - 1, z #3 -x + 1, -y + 2, -z + 2 #4 -x + 3/2, -y + 1/2, -z + 2 #5 -x + 1, y, -z + 3/2.

<sup>d</sup> Symmetry codes: #1 x, y, z - 1 #2 -x + 2, -y, -z + 2 #3 -x + 2, -y + 1, -z #4 x, y, z + 1.

## 2.3. X-ray crystallography

Single crystal X-ray diffraction analyses of **1–4** were carried out on a Bruker SMART APEX II CCD diffractometer with graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296(2) K. Empirical absorption corrections were applied by using the sADABS program [67]. The structures were solved by direct methods and refined by the full matrix least-squares based on  $F^2$  using SHELXTL programe package [68]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms except for those of water molecules were generated geometrically and refined using a riding model. Crystal data and details of the structure determination for complexes **1–4** are listed in Table 1. Selected bond lengths and angles are given in Table 2.

## 3. Results and discussion

## 3.1. Crystal structure of complex 1

The crystallographic analysis reveals that **1** is a one dimensional chain coordination polymer. Complex **1** crystallizes in the monoclinic system, C2/c space group. The asymmetric unit of **1** contains one crystallographically nonequivalent Cd(II) ion (Cd1), one Hdtbb<sup>-</sup> ligand, half dtbb<sup>2-</sup> ligand and one DMF molecule. Cd1 is six-coordinated by three oxygen atoms from two carboxylic groups of two dtbb<sup>2-</sup> ligands, two oxygen atoms from two carboxylic groups of two Hdtbb<sup>-</sup> ligands and one oxygen atom from DMF molecule, exhibiting the distorted octahedral geometry (Fig. 1a).

The six Cd–O distances range from 2.1796(14) to 2.5022(14) Å. The dtbb<sup>2-</sup> ligand adopts  $\mu_4$ - $\eta^1$ : $\eta^1$ : $\eta^1$ : $\eta^1$  coordination mode, and two carboxylate groups of ligand link to two Cd(II) ions in the bidentate bridging mode, while the partly deprotonated Hdtbb<sup>-</sup> anion employs  $\mu_2 - \eta^1 : \eta^1 : \eta^1$  coordination mode and two carboxylate groups coordinate to two Cd(II) ions in the bidentate chelate and monodentate modes, respectively. The two aromatic rings of Hdtbb<sup>-</sup> ligands form dihedral angle and torsion angle (C3/S1/ S1#4/C3#4) of 72.53(67)° and 89.63(92)°, the dihedral angle between the two phenyl rings of dtbb<sup>2-</sup> ligands and torsion angle (C14/S2/S3/C21) are 82.40(76)° and 88.42(99)°. Two Cd1 atoms are joined by carboxylate groups of two dtbb<sup>2-</sup> ligands construct a dimeric unit with Cd-Cd distance to be 3.654 Å. These dimeric units are further organized into an infinite one dimensional chain through bidentate bridging mode dtbb<sup>2-</sup> ligands (Fig. 1b). While the other Hdtbb<sup>-</sup> anion connects this chain forming a one-dimensional triple chain structure (Fig. 1c). The O-H-O hydrogen bondings (04...06, 2.626(2)Å) stabilize the 1D chain structure. Further, such chains showing a parallel arrangement are connected by interchains C-H-O H-bonds between phenyl rings and carboxylic groups (Table S1, supporting information), forming a 3-D supramolecular network (Fig. S1).

## 3.2. Crystal structure of complex 2

X-ray crystallographic analysis reveals that **2** crystallizes in a monoclinic space group P21/c and there are one Cd(II) ion (Cd1), one dtbb<sup>2–</sup> ligand, one 2,2'-bpy ligand, one H<sub>2</sub>O molecule and



**Fig. 1.** (a) Molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity. Symmetry code: #1 - x + 2, -y + 2, -z #2 x, -y + 2, z - 1/2 #3 x, -y + 2, z + 1/2 #4 - x + 2, y, -z - 1/2. (b) A view of the 1D chain in **1**. (c) A view of the 1D triple chain structure along the *b*-axis in **1**. DMF molecules are omitted for clarity.



**Fig. 2.** (a) Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and free DMA molecules are omitted for clarity. Symmetry code : #1 x + 1, y, z #2 x - 1, y, z. (b) A view of the 1D chain structure in **2**.

two free DMA molecules in the asymmetric unit. The Cd(II) ion is seven-coordinated by four oxygen atoms from two carboxylic groups of two different dtbb<sup>2-</sup> ligands, two nitrogen atoms from one 2,2'-bpy molecule and one O atom from water molecule in a pentagonal bipyramid geometry (Fig. 2a). The five Cd-O distances range from 2.309(3) to 2.555(3) Å and the Cd–N bond lengths are 2.354(3) Å and 2.347(3) Å. The dtbb<sup>2-</sup> ligand is tetradentate, two carboxyl groups adopt bidentate chelating fashions. The pair of phenyl rings of dtbb<sup>2-</sup> employs a bended conformation, and the dihedral angle between the two phenyl rings and torsion angle (C7/S2/S1/C8) are 77.56 (11)° and 93.07(19)°. The Cd centers are linked together by the bis-chelating dtbb<sup>2-</sup> ligands to form a 1D chain (Fig. 2b). The 2,2'-bpy molecule coordinate to a Cd center in chelate mode. Interestingly, the DMA molecules is hydrogen bonded to coordinated H<sub>2</sub>O molecules and 2,2'-bpy phenyl rings. leading to the formation of a 3D supramolecular network (Table S1. Fig. S2).

## 3.3. Crystal structure of complex 3

Utilizing the bridging N,N'-donor ligand 1,4-bix, instead of the chelating ligand 2,2'-bipy, the 2D complex **3** is obtained. Complex **3** crystallizes in *C*2/*c* space group and the asymmetric unit contains one crystallographically nonequivalent Cd(II) ion (Cd1), one dtbb<sup>2-</sup> ligand, two half 1,4-bix molecules, one and a half DMF molecules (Fig. 3a). Each Cd(II) ion is coordinated by four oxygen atoms from two carboxylic groups of two different dtbb<sup>2-</sup> ligands and two

nitrogen atoms from two 1,4-bix molecules, resulting in a slightly distorted octahedral geometry. The four Cd-O distances fall in the range of 2.262(3)-2.522(3) Å and the Cd-N bond lengths are 2.227(3) Å and 2.262(3) Å. Each  $dtbb^{2-}$  anion links two Cd(II) ions with its two carboxylate groups in bidentate chelating modes. The pair of phenyl rings of the ligand employs a bended conformation, the dihedral angle between the two phenyl rings and torsion angle (C7/S1/S2/C8) are 79.76(16)° and 88.65(20)°. Two crystallographically independent 1,4-bix ligands adopting trans conformations connect Cd1 atoms, alternately, to form a rare one dimensional meso-helical chain with a pitch of 23.925 Å (Fig. 3b), which are further extended by the dtbb<sup>2-</sup> ligands to afford a 2D 4-connected staircase-like net (Fig. 3c and d). The adjacent 2D structure are linked together through both  $C_{phenyl}\text{-}H\text{--}O_{carboxylic}$  and  $C_{imidazol}\text{--}$ H...O<sub>carboxylic</sub> hydrogen bonds (Table S1) to afford a 3D supramolecular network (Fig. S3).

#### 3.4. Crystal structure of complex 4

Compound **4** crystallizes in the triclinic system,  $P\bar{1}$  space group. It contains one crystallographically Cd(II) ion (Cd1), one dtbb<sup>2–</sup> ligand and one 1,4-btx ligand in the asymmetric unit. The coordination geometry for the six-coordinate Cd1 atom can be described as a distorted octahedral geometry (Fig. 4a). The Cd1 atom is coordinated by four oxygen atoms from three different dtbb<sup>2–</sup> ligands and two nitrogen atoms from two 1,4-btx molecules. The Cd–O distances range from 2.232(4) to 2.374(4) Å and the Cd–N bond



**Fig. 3.** (a) Molecular structure of **3.** Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and free DMF molecules are omitted for clarity. Symmetry code: #1 x, y + 1, z #2 x, y - 1, z #3 - x + 1, -y + 2, -z + 2 #4 - x + 3/2, -y + 1/2, -z + 2 #5 - x + 1, y, -z + 3/2. (b) 1D meso-helical chain along the *a*-axis in **3.** (c) Perspective view of the 2D structure in **3.** (Hydrogen atoms are omitted for clarity). (d) Schematic representation of 2D (4,4)-connected structure of complex **3** (dtbb<sup>2-</sup> ligands are show as yellow linkers and 1,4-bix ligands are show as purple links). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** (a) Molecular structure of **4.** Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity. Symmetry code: #1 x, y, z - 1 #2 -x + 2, -y, -z + 2 #3 -x + 2, -y + 1, -z #4 x, y, z + 1. (b) 1D double chain along the *b*-axis in **4.** (c) Perspective view of the 2D structure in **4.** (Hydrogen atoms are omitted for clarity). (d) The 2D 4<sup>4</sup>-sql layer formed in compound 4 (blue spheres represent the bisnuclear Cd(II) units, two dtbb<sup>2-</sup> ligands are show as blue linkers and two 1,4-btx ligands are show as purple links). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lengths are 2.291(4) Å and 2.382(4) Å. The two carboxylate groups of dtbb<sup>2-</sup> ligand adopt different coordination modes, namely bidentate bridging and chelating bidentate. The two aromatic rings of dtbb<sup>2-</sup> ligands form dihedral angle and torsion angle (C18/S1/ S2/C19) of 84.80(22)° and 90.09(25)°. Cd1 atoms are connected by two carboxylate groups of two dtbb<sup>2-</sup> ligands construct a dimeric unit with Cd–Cd distance to be 4.407 Å. Each Cd(II) dimeric unit connects with the other two neighboring ones by the dtbb<sup>2–</sup> ligands leading to an infinite one dimensional double chain (Fig. 4b). The cis-1,4-btx ligands linking one dimensional double chain further generate an infinite 2D framework (Fig. 4c). Binuclear Cd(II) units as 4-connected joints are bridged by two kinds of 2connected struts: dtbb<sup>2-</sup> and 1,4-btx ligand, so the 2D net can be simplified to be a 4<sup>4</sup>-sql net (Fig. 4d). The adjacent 2D nets pack to form the supramolecular network through intersheets C-H-O H-bonds (Table S1), C-H $\cdots$  $\pi_{triazol}$  and C-H $\cdots$  $\pi_{phenyl}$  interactions (Table S2, Fig. S4).

# 3.5. The coordination modes of the multi-carboxylate $dtbb^{2-}$ ligands and effect of N-donor ligands

It is known that multi-carboxylate ligands are good candidates for the construction of supramolecular frameworks with specific structure due to their varied coordination modes. According to the above structural descriptions of our example compounds, four kinds of coordination modes for the dtbb<sup>2–</sup> ligand are found as shown in Scheme 2. In complexes **1–4**, all the carboxylate groups of dtbb<sup>2–</sup> employ monodentate, bidentate chelating and bidentate bridging coordination modes. In **1**, two carboxylate groups of dtbb<sup>2–</sup> ligand both adopt  $\mu_2$ - $\eta^1$ : $\eta^1$  bridging mode links to two Cd(II) ions, while those of another Hdbb<sup>–</sup> ligand coordinate to



**Scheme 2.** The coordination modes of Hdtbb<sup>-</sup> and dtbb<sup>2-</sup> ligands observed within compounds **1–4**.

two Cd(II) ions in  $\mu_1 - \eta^{1:} \eta^0$  and  $\mu_1 - \eta^{1:} \eta^1$  modes (Scheme 2a and b). Two carboxylate groups in **2** and **3** both show chelating mode ( $\mu_1 - \eta^{1:} \eta^1$ ) (Scheme 2c). Two carboxylate groups of dtbb<sup>2-</sup> ligand coordinated to Cd(II) ions in  $\mu_1 - \eta^{1:} \eta^1$  and  $\mu_2 - \eta^{1:} \eta^1$ modes in the complex **4** (Scheme 2d). The results described above show that the bridging fashions of the dtbb<sup>2-</sup> ligand play an important role in the construction of supramolecular frameworks. In addition, the conformation of dtbb<sup>2-</sup> ligands impacts on the structures of coordination polymers. The S–S bond lengths, the C–S–S–C torsion angles, and the dihedral angle between two phenyl rings in dtbb<sup>2-</sup> ligands are listed in Table S3. The considerably larger dihedral angles, torsion angles and thus less repulsion between the two benzoate groups are believed to partially contribute to their thermodynamically and kinetically favored formation.

A comparison of the crystal structures of **1–4** clearly indicates that the auxiliary N-donor ligands also have a significant influence on structural assembly of coordination architectures. When no auxiliary ligand or rigid chelating 2,2'-bpy is introduced, the expected low-dimensional species **1**(1D) and **2** (1D) are obtained. However, when the semi-rigid bridging ligands 1,4-bix or 1,4-btx are introduced into the systems, the resulting complexes **3** and **4** show 2D coordination frameworks.

#### 3.6. Thermal properties

To examine the thermal stability of compounds 1-4, thermal gravimetric (TG) analyses were carried out (Fig. S5). Complex 1 gives a gradual weight loss of 11.24% in the range of 25-296 °C, which corresponds to the loss of the DMF molecule (calculated 11.36%). The framework starts to decompose at 296 °C. For complex 2, the weight loss between 95 and 218 °C corresponds to the release of isolated DMA and coordinated H<sub>2</sub>O molecules (calcd 25.12%, obsd 25.55%), followed by losing the 2,2'-bpy molecules between 297 and 345 °C (calcd 20.41%, obsd 20.96%), and then began to decompose upon further heating. For **3**, the first weight loss of 13.86% (calcd 14.16%) in the range of 96-271 °C reveals the exclusion of DMF molecule and immediately followed by the structure decomposition. In the case of 4, the 2D framework was stable up to 261 °C, then a sharp weight loss occurs from 261 to 365 °C(46.06%), and is attributed to the loss of the coordinated dtbb<sup>2-</sup> ligands (46.48%).

## 3.7. Photoluminescent Properties

The solid-state emission spectra of the free  $H_2$ dtsa ligand and complexes **1–4** were measured at room temperature (Fig. 5). The



Fig. 5. Fluorescent emission spectra for solid H<sub>2</sub>dtbb and compounds 1-4 at 298 K.

main emission peak of H<sub>2</sub>dtbb is at 465 nm ( $\lambda_{ex} = 389$  nm), which may be attributed to  $\pi^* \rightarrow \pi$  transition. The compounds **1–4** show emissions at about 455 nm ( $\lambda_{ex} = 396$  nm), 468 nm ( $\lambda_{ex} = 395$  nm), 453 nm ( $\lambda_{ex} = 403$  nm) and 452 nm ( $\lambda_{ex} = 385$  nm), respectively. It should be pointed out that the emissions of compounds **1–4** are neither metal-to-ligand charge transfer (MLCT) nor ligand-tometal charge transfer (LMCT) in nature since the Cd<sup>2+</sup> ions are difficult to oxidize or to reduce due to their d<sup>10</sup> configuration, which are mainly based on the luminescence of ligands. They can probably be assigned to the intraligand  $\pi^* \rightarrow \pi$  transitions of dtbb<sup>2-</sup> ligand. Different intensity emission bands of **1–4** are probably due to the variation of the metal ions and the coordination environment around them because the photoluminescence behavior is closely associated with the metal ions and the ligands coordinated around them [69,70].

## 4. Conclusion

In summary, four novel Cd(II) coordination polymers have been synthesized based on 2,2-dithiobisbenzoic acid and different auxiliary N-donor ligands, which display various 1D and 2D topological networks. Our research results not only demonstrate that the coordination modes and conformations of the flexible dtbb<sup>2–</sup> ligand have a significant influence on the final supramolecular architectures of complexes **1–4**, but also illustrate that the structural diversity in MOFs that can be achieved by adjustments of the auxiliary ligands in the present system. In addition, the photoluminescence investigation shows that all the coordination polymers **1–4** appear potentially applied as new luminescent materials.

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#### Appendix A. Supplementary material

CCDC 798109, 798110, 798111 and 798112 contain the supplementary crystallographic data for complexes **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011. 06.020.

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