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# Crystal engineering of mixed-ligand frameworks: Ligand-directed assembly and structural diversity

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# ABSTRACT

Four new coordination networks based on dipyridyl linkages 2,6-(*N*,*N*-di(4-pyridyl)amino)pyridine (dpap) or 1,3-bis(4-pyridyl)propane (bpp) and different dicarboxylates have been synthesized and structurally characterized. Using dpap to react with two different dicarboxylates, maleic acid (H<sub>2</sub>mal) and 4,4'-sulfonyldibenzoate (H<sub>2</sub>sdba), respectively, two different two-dimensional (2D) coordination polymers of Cd(II), [Cd(dpap)(mal)]<sub>n</sub> (**1**) and {[Cd(dpap)(sdba)]  $\cdot$  2H<sub>2</sub>O}<sub>n</sub> (**2**) were obtained. Compound **1** features a 42-membered bimetallic macrocyclic structural motif which is extended by mal groups to form a 2D network. In the case of **2**, two different layers can be achieved depending on the conformation of sdba. The layer has a (8<sup>2</sup>10) net topology with Cd as nodes and dpap, sdba bridges as the connectors. The overall structure of {[Mn(dpap)(sdba)]  $\cdot$  1.5H<sub>2</sub>O}<sub>n</sub> (**3**) similar to that of **2** despite the presence of different metal ions. When dpap was replaced by bp to react with Co(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O, another 1D coordination polymers ([Co(bpp)(H<sub>2</sub>O)<sub>4</sub>]  $\cdot$  sdba]<sub>n</sub>(**4**) was constructed. The 1D chains join sdba to make an overall 3D supramolecular architecture by hydrogen-bonding interactions ( $R_2^4$  (22), $R_2^4$  (12)). The Cd coordination polymers exhibit strong solid-state luminescence emission at room temperature. Thermal stability of these crystal-line materials has been explored by thermogravimetric analysis of mass loss.

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# 1. Introduction

The design and construction of coordination polymers with unique structural motifs and unique chemical and physical properties has attracted extensive interest in supramolecular chemistry and materials chemistry [1-3]. In the past decade, plenty of metal-organic hybrids exhibiting fascinating structures [4] and various properties such as luminescence [5], magnetics [6], sorption [7], ion exchange [8], nonlinear optics [9], high dielectric constants [10] have been synthesized by chemists. In principle, the extended coordination framework solids with desired structural features and/or physicochemical properties greatly depend on the nature of the organic ligands (spacers) and metal ions (nodes). Changes in flexibility, length, symmetry of organic ligands, and metal ions can result in a remarkable class of materials bearing diverse architectures and functions. As a consequence, nowadays, utilizing suitable organic tectons with functional groups that are capable of bridging metal centers to construct such tailored crystalline materials has revealed to be a fast developing field of crystal engineering research [11,12].

In the previous work [13], we reported five isostructural coordination polymers derived from 2,6-(N,N'-di(4-pyridyl)amino)pyridine (dpap) and copper(II) salts. These superstructures were slightly affected by the incorporation of different solvent molecules and anions, concomitant with an increase or decrease in the channel dimensions. To extend the work about dpap, we introduced the dicarboxylic acids as second ligand, which were chosen for their versatile coordination capabilities as well as their sensitive character to acidity in such building blocks [14-16]. Among them, dicarboxylate species with different orientations of the functional groups such as maleic acid (H<sub>2</sub>mal) and fumaric acid (H<sub>2</sub>fum) have been widely used [17]. Then, a typical example of semi-rigid V-shaped dicarboxylate ligand, 4,4'-sulfonyldibenzoate (H<sub>2</sub>sdba) [18] (Scheme 1), also attracts our great interests: (1) as compared with mal, the influence of semi-rigid dicarboxylate ligand sdba on the framework structures may be contrasted to some extent, and the same inorganic counter anions will be introduced to illuminate the effect of dicarboxylate ligand; (2) it also holds dicarboxylate coordination sites that provide a high likelihood for the generation of structures with high dimensions; (3) the deprotonated carboxyl groups generally act as anions organic ligands to complete the metal coordination as well as compensate the charge. Therefore, mal and sdba can provide directional conformation of network structure via dative bonds and also noncovalent





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cooperative forces such as hydrogen bonding and aromatic stacking. Also, another deviation of 4,4'-dipyridine molecule, bpp (1,3bis(4-pyridyl)propane), also attracts our attention because it can assume different conformations that display quite different N-to-N distances [19]. Now, we have concentrated on the construction of mixed-ligand metal–organic frameworks based on the flexible ligands dpap, bpp and dicarboxylates.

#### 2. Experimental

#### 2.1. Materials and physical measurements

The ligand dpap was prepared as we reported before [13]. All reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra on KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer in the range 4000–400 cm<sup>-1</sup>. Elemental analyses were determined with a Perkin–Elmer model 240C instrument. Thermal analyses were performed on a NETZSCH STA 449C microanalyzer with a heating rate of 10 °C min<sup>-1</sup> under air atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer.

#### 2.2. synthesis of $[Cd(dpap)(mal)]_n$ (1)

Complex **1** was obtained by the reaction of  $Cd(NO_3)_2 \cdot 4H_2O$ , dpap,  $H_2$ mal and NaOH in molar ratio of 1:1:1:2 mixed with 15 mL of aqua-methanol (water/methanol = 1:1 (v/v)) under hydrothermal conditions (at 150 °C for 6 days and cooled to room temperature with a 5 °C h<sup>-1</sup> rate). The colorless block crystals were washed with water and ethanol, and dried in air. Yield: 52% (based on Cd).  $C_{19}H_{15}CdN_5O_4$  (489.76): *Anal.* Calc. C, 46.59; H, 3.09; N, 14.30. Found: C, 46.48; H, 3.01; N, 14.41%.

# 2.3. synthesis of $\{[Cd(dpap)(sdba)] \cdot 2H_2O\}_n$ (2)

The synthesis methods of **2** are similar to that of **1** except for H<sub>2</sub>sdba instead of H<sub>2</sub>mal. Yield: 43% (based on Cd).  $C_{29}H_{25}CdN_5O_8S$  (715.98): *Anal.* Calc. C, 48.53; H, 3.51; N, 9.76. Found: C, 48.48; H, 3.41; N, 9.65%.

# 2.4. synthesis of $\{[Mn(dpap)(sdba)] \cdot 1.5H_2O\}_n$ (3)

The synthesis methods of **3** are similar to that of **2** expect for  $Mn(AcO)_2 \cdot 4H_2O$  as a substitute for  $Cd(NO_3)_2 \cdot 4H_2O$ . Yield: 36 %

(based on Cd). C<sub>29</sub>H<sub>24</sub>MnN<sub>5</sub>O<sub>7.50</sub>S (649.51): *Anal.* Calc. C, 53.62; H, 3.72; N, 10.78. Found: C, 53.50; H, 3.61; N, 10.81%.

# 2.5. synthesis of $\{[Co(bpp)(H_2O)_4] \cdot sdba\}_n$ (4)

A methanol solution (5 mL) of bpp (0.1 mmol, 0.020 g) was added to a methanol solution (5 mL) of  $Co(NO_3)_2 \cdot 6H_2O$  (0.1 mmol, 0.029 g). An aqueous solution (5 mL) of  $Na_2$ sdba (0.1 mmol, 0.035 g) was then added dropwise to give a transparent solution. After six days, pink block crystals of **4** were obtained as a single phase, as confirmed by XRPD. Compound **4** can also be obtained by hydrothermal conditions following the same methods of **1–3**.  $C_{27}H_{30}CoN_2O_{10}S$  (633.52): *Anal.* Calc. C, 51.18; H, 4.78; N, 4.42. Found: C, 51.25; H, 4.71; N, 4.31%.

#### 2.6. Crystal structure determination

Diffraction experiments for **1–4** were carried out with  $MoK_{\alpha}$  radiation using a BRUKER SMART APEXCCD diffractometer at 293(2) K. A summary of the crystallography data and structure refinement is given in Table 1, and selected bond lengths and an-

 Table 1

 Crystal data and structure refinements for 1–4

Complex	1	2	3	4
Empirical formula	$C_{19}H_{15}CdN_5O_4$	C <sub>29</sub> H <sub>25</sub> CdN <sub>5</sub> O <sub>8</sub> S	$C_{29}H_{24}MnN_5O_{7.5}S$	C <sub>27</sub> H <sub>30</sub> CoN <sub>2</sub> O <sub>10</sub> S
Formula mass	489.76	716.01	649.51	633.52
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/c	C2/c	P2(1)/n
a (Å)	8.0741(9)	22.3808(2)	22.213(8)	6.2948(4)
b (Å)	8.7580(10)	14.9314(1)	14.269(5)	25.7829(2)
c (Å)	25.713(3)	20.4597(2)	19.978(7)	16.9050(1)
β(°)	90.733(2)	114.4980(10)	112.402(7)	96.7530(1)
V (Å <sup>3</sup> )	1818.1(4)	6221.6(8)	5854(4)	2724.6(3)
Ζ	4	8	8	4
$D_{\rm calc}~({\rm g~cm^{-3}})$	1.789	1.529	1.474	1.544
$\mu$ (mm <sup>-1</sup> )	1.240	0.825	0.580	0.769
F [000]	976	2896	2672	1316
Data/ restraints/ parameters	3235/0/263	10988/48/793	5783/0/393	4858/8/403
Goodness-of- fit on F <sup>2</sup>	1.003	0.997	1.023	1.033
$R_1 [I > 2\sigma(I)]^a$	0.0520	0.0495	0.0689	0.0316
$wR_2$ (all data)	0.1178	0.1291	0.0974	0.0802

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c| / \sum |F_0|$ ;  $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$ .

Table 2
Selected bond lengths [Å] and angles [°] for $14$

Complex 1			
Cd(1)-N(2)	2.231(6)	Cd(1) = O(2)	2.301(5)
Cd(1) - N(1)	2.242(5)	Cd(1) - O(1)	2.473(5)
Cd(1) = O(3) # 1	2.237(5)	Cd(1) - O(4) # 1	2.638(5)
N(2)-Cd(1)-N(1)	128.3(2)	N(2)-Cd(1)-O(4)#1	88.91(2)
N(1)-Cd(1)-O(3)#1	108.6(2)	N(1) - Cd(1) - O(2)	105 6(2)
O(3) #1 - Cd(1) - O(2)	88.00(2)	N(1) - Cd(1) - O(1)	87.83(2)
O(3)#1-Cd(1)-O(4)#1	52.70(2)	O(2)-Cd(1)-O(1)	54.08(2)
Complex <b>2</b>			
Cd(1) - N(1)	2.216(4)	Cd(1)-N(10)	2.262(4)
Cd(1) - O(7)	2.283(3)	Cd(1) - O(1)	2.342(4)
Cd(1) - O(2)	2.411(4)	Cd(1)-O(8)	2.500(4)
Cd(2) - N(6)	2.254(4)	Cd(2) - N(5)	2.279(4)
Cd(2)-O(11)#1	2.304(4)	Cd(2) = O(5)#2	2.320(4)
Cd(2)-O(6)#2	2.405(4)	Cd(2)-O(12)#1	2.444(4)
N(1)-Cd(1)-N(10)	100.16(2)	N(1) - Cd(1) - O(1)	106.75(2)
O(7) - Cd(1) - O(2)	86.47(1)	O(1) - Cd(1) - O(2)	54.91(1)
N(1)-Cd(1)-O(8)	98.83(2)	O(7)-Cd(1)-O(8)	54.25(1)
N(6)-Cd(2)-N(5)	93.21(2)	N(6)-Cd(2)-O(5)#2	106.48(2)
N(5)-Cd(2)-O(6)#2	98.29(1)	O(5)#2-Cd(2)-O(6)#2	55.37(1)
N(5)-Cd(2)-O(11)#1	96.82(2)	O(11)#1-Cd(2)-O(12)#1	55.06(1)
Complex <b>3</b>			
Mn(1)-N(4)#1	2.043(8)	Mn(1)-O(2)	2.071(6)
Mn(1) - N(1)	2.076(7)	Mn(1)-O(5)#2	2.113(6)
Mn(1)-O(6)#2	2.273(6)	Mn(1)-O(1)	2.343(6)
N(4)#1-Mn(1)-O(2)	101.06(3)	N(4)#1-Mn(1)-N(1)	99.2(3)
N(1)-Mn(1)-O(5)#2	104.3(3)	O(5)#2-Mn(1)-O(6)#2	60.8(2)
O(2)-Mn(1)-O(1)	59.5(2)	O(6)#2-Mn(1)-O(1)	82.3(2)
Complex <b>4</b>			
Co(1)-O(2)	2.0943(2)	Co(1)-O(3)	2.0984(2
Co(1) - N(2)	2.1143(2)	Co(1)-O(1)	2.1179(2
Co(1) - N(1)	2.1203(2)	Co(1)-O(4)	2.1495(2
O(3)-Co(1)-N(2)	88.25(7)	O(2)-Co(1)-O(1)	85.03(7)
O(2)-Co(1)-N(1)	88.73(7)	O(3)-Co(1)-O(4)	86.03(7)
N(1)-Co(1)-O(4)	89.03(7)	N(2)-Co(1)-O(1)	88.86(7)

Symmetry codes: **1**: #1 -*x* + 1/2, *y* - 1/2, -*z* + 1/2. **2**: #1 -*x*, *y* - 1/2, -*z* + 1/2; #2 -*x* + 1, *y* + 1/2, -*z* + 1/2. **3**: #1 -*x* + 2, *y*, -*z* + 3/2; #2 *x* + 1/2, *y* + 1/2, *z*.

gles of four complexes are listed in Table 2. All structures were solved by direct methods and refined with the full-matrix least-squares technique on  $F^2$  using the SHELXS-97 [20] and SHELXL-97

[21] program. All non-hydrogen atoms present were anisotropically refined. All hydrogen atoms of water were located in successive different Fourier Maps and the other hydrogen atoms were treated as riding method.

#### 3. Results and discussion

### 3.1. Description of the structures

#### 3.1.1. $[Cd(dpap)(mal)]_n$ (1)

The structure of compound **1** crystallizes in the Monoclinic form with P2(1)/n space group, and the coordination geometry around cadmium(II) center is a distorted octahedron, the equatorial plane of which comprises four oxygen atoms from two chelating carboxylate groups of different mal anions; nitrogen atoms from two different dpap ligands occupy the remaining apical coordination sites, as shown in Fig. 1. The Cd–O = 2.237(5)–2.638(5) Å and Cd– N = 2.231(6) - 2.242(5) Å, which are consistent with the values reported for Cd-carboxylate and Cd-pyridyl complexes [22]. The Cd(II) octahedra are connected to each other to form an infinite wave-like 1D chain that consists of a 42-membered bimetallic macrocycle-containing building block (Fig. 1). In each elliptical ring, the Cd(II) ··· Cd(II) contact is around 9.3 Å, which is shorter than the corresponding lengths found in similar framework complex such as  $[Cd(L_1)_2(NO_3)](L_1 = 2,5-bis(4-(1H-1,2,4-triazol-yl$ methyl)phenyl)-1,3,4-oxadiazole) [23]. It is noteworthy that two adjacent macrocycles are not coplanar, and the centroid-centroid separation is 13.90 Å and the dihedral is about 40.35°, respectively. Therefore, such macrocycles are extended by mal groups to a 2D corrugated network ((Fig. S1)). Interestingly, Cd(II) ions are bridged by mal groups to generate two hetero-chiral helical chains (Fig. 2a). which are alternately arranged in *bc* plane. Adjacent Cd-mal hetero-chiral helices are interconnected through the dpap ligands. As shown in Fig. 2b, the left-handed and right-handed metal-mal helical chains with a pitch of 8.758 Å run along crystallographic 21 screw axis. A more revealing description from the viewpoint of network topology is that the adjacent Cd<sup>II</sup> nodes are extended along the (011) plane via mal and Cd(II) connectors to form a 2D (6,3) network (Fig. S2).



3.1.2. {[Cd(dpap)(sdba)] · 2H<sub>2</sub>O}<sub>n</sub> (**2**), {[Mn(dpap)(sdba)] · 1.5H<sub>2</sub>O}<sub>n</sub> (**3**)

The structures of **2** and **3** are similar, except the different free water molecules and space group. So, only the structure of compound **2** will be discussed in detail. The X-ray crystallographic study shows that **2** crystallizes in the space group P2(1)/c and the asymmetric unit of **2** contains two distinct Cd centers (Fig. 3). Cd(1) atom is coordinated to two N atoms of pyridine unit from different dpap (Cd(1)–N, 2.216(4)–2.262(4) Å) and four additional positions are occupied by O atoms from two carboxylate groups (Cd(1)–O, 2.342(4)–2.500(4) Å). Therefore, the local coordination geometry around Cd(1) can also be regarded as a distorted octahe-

dron with N<sub>2</sub>O<sub>4</sub> donor set. Cd(2) has a similar coordination geometry with N<sub>2</sub>O<sub>4</sub> binding set, but with longer distance of Cd(2)–N (2.254(4)–2.279(4) Å) and shorter distance of Cd(2)–O (2.304(4)–2.444(4) Å). The position of two dpap is different from those of **1**, the dihedral angle between two dpap ligands are nearly 75.5° and the Cd(II)  $\cdots$  Cd(II) contact is 7.9 Å. Depending on the conformation of sdba, two different layers (A and B) can be achieved. As shown in Fig. 4a, in layer A, the V-shaped sdba are arranged in a transverse pattern while in layer B these are arranged in a vertical manner. Dpap ligands link two layers and protrude from the sheets. Each layer is formed by parallel arrangement of metal–organic chains (Fig. 4b). Such a regular crossing coordination fashion



**Fig. 2.** (a) A view of 2D network structure of **1** with hetero-chiral helical chains alternately arranged in *bc* plane, emphasizing the right (yellow) and left (green)-handed helix chains. (b) The left (M) is a left-handed helical chain and the right (P) is a right-handed helical chain with 2<sub>1</sub> screw axis.

is still rare in the system of multi-carboxylate, and it plays an important role in the formation of a bilayer structure [24]. Rather, the bilayers are parallel and stacked without interpenetrating with 3-connected ( $8^210$ ) metal nets (Fig. S3), which is analogous to that of [Cu(Mtta)]<sub>n</sub> (Mtta = 5-methyl tetrazolate) [25], but different from that of {[Ph<sub>3</sub>PCH<sub>2</sub>Ph] [Cd(tp) · Cl] · 2H<sub>2</sub>O}<sub>n</sub> (tp = terphthalate) [26], which contains 2-fold interpenetration of the 3D ( $8^210$ ) network. Of further interest, the bilayer arrays of **2** display a unique structural feature of butterfly network, which propagated along [011] direction (Fig. 5).

Complex **3** crystallizes in the monoclinic system, C2/c space group and the coordination environment around Mn(II) ion is shown in Fig. S4 along with atom numbering scheme.

#### 3.1.3. {[ $Co(bpp)(H_2O)_4$ ] · sdba}<sub>n</sub> (4)

Compound 4 consists of the cationic 1-D helix chains  $\{[Co(bpp)(H_2O)_4]\}_n^{n+}$  and  $sdba^{2-}$  anions. As shown in Fig. 6a, the Co(II) center exhibits a slightly distorted octahedral geometry, with two N donor atoms from different bpp ligands composing the apical position and four water molecules completing the six-coordinated sphere at the equatorial plane. All coordinated bonds are also within the normal range [27]. Each bpp ligand with TG conformation [28] connect two Co(1) ions, forming a left-handed helical chain along the *b* axis. As shown in Fig. 6b, the chain is generated by a 2<sub>1</sub> axis with a pitch of 25.8 Å. Furthermore, the coordinated O2, O3 atoms act as the donors of O2-H2B ··· O6, O2-H2C ··· O9, and O3-H3C ··· O7, O3-H3B ··· O8 interactions, linking the sdba from adjacent chains. As a consequence, these 1D chains are extended to a 2D network along the bc plane, and two new hydrogen-bonding patterns marked as C  $[R_2^4 (22)]$ , D $[R_2^4 (12)]$  come into being [29] (Fig. 6c). In addition, these 2D coordination layers are interlinked via another two hydrogen-bonding interactions (04-H4B ··· O8, O1–H1B ··· O10) to finally produce a 3D supramolecular architecture (see Fig. S5).

When  $H_2$ sdba was replaced by  $H_2$ fum, we obtained {[Co(bp-p)<sub>2</sub>( $H_2O$ )<sub>2</sub>] · fum · 8 $H_2O$ }<sub>n</sub> (**5**), which has been reported by us before [30]. The compound **5** also has a 1D polymeric chain ([Co(bp-p)<sub>2</sub>( $H_2O$ )<sub>2</sub>]<sup>2+</sup>) and free fumaric dianion. An unprecedented 2D (6,3) net topology of hydrogen-bonded water layers results from free water molecules through templating with fum. The free water molecules of sdba<sup>2-</sup> and fum<sup>2-</sup> may be attributed to the much greater flexibility of bpp compared to that of the dpap ligand, as well as ions effect. Comparison of polymers **1** and **2**, containing the same metal salt and dpap ligand, led to the demonstration of the significant role that the dicarboxylate connectors had in their

preparation and structure. Compound **1** exhibits a (6,3) topological metal network, whereas **2** is a 3-connected (8<sup>2</sup>10) metal net. Dpap exhibits similar coordination modes in **1** and **2**. The presence of mal acid was essential to construct hetero-chiral helical chains and semi-rigid V-shaped sdba was also significant to build crossing bilayers because without it, the cornu(V-shape) was not formed. Compound **3** was obtained by different metal salts introduced to **2**, which was not tampered with metal effect. A comparison of polymers **2** and **4**, with the same dicarboxylate connectors, showed that changes in flexibility, and length of organic ligands have a significant influence on the overall structure.

# 3.2. Fluorescence properties

Compounds constructed from d<sup>10</sup> metal centers and conjugated organic links are promising candidates for hybrid photoactive materials with potential applications such as light-emitting diodes [31]. The solid-state emission spectra of dpap, **1** and **2**, have been investigated at room temperature, as depicted in Fig. 7. The peak of 466 nm ( $\lambda_{ex}$  = 390 nm) for compound **1** may be assigned to the intraligand fluorescent emission [32] of dpap (442 nm,  $\lambda_{ex}$  = 390 nm). Complex **2** exhibits a broad emission band with the maximal emission at 455 nm ( $\lambda_{ex}$  = 390 nm), which is redshifted compared with free dpap and sdba (329 nm) [18b]. According to the Ref. [18b], the emission of **2** may be attributed to the ligand-to-metal charge transfer. The different emission bands of **1**, **2** may be due to the significant difference of their topological structure because the fluorescence behavior is closely associated with the metal ions and the ligands coordinated around them [33].

#### 3.3. TGA analyses

Thermogravimetric analyses (TGA) of complexes **1–4** were performed on single crystal samples. Complex **1** exhibits high thermal stability, as there is no weight loss below 352 °C (Fig. S6). The TGA indicates that**2** lost 5.2% of total weight in the 80–110 °C temperature range, corresponding to the loss of two H<sub>2</sub>O molecules per formula unit (expected 5.0%). When the temperature is above 285 °C, the product begins to decompose and oxidize, all assigned to the decomposition of organic ligands (Fig. S7). The TGA of **3** are similar to that of **2. Compound 3** experienced 4.3% weight loss in the 85– 118 °C temperature range for H<sub>2</sub>O molecules per formula unit (expected 4.1%). The decomposition of the organic ligands occurs at 275.8 °C (Fig. S8). While, TGA display that the weight of **4** remains almost unchanged from 40 to 190 °C. In the temperature range of



Fig. 3. ORTEP drawing of Cd center of 2 at the 30% probability level (hydrogen atoms and water molecules are omitted for clarity).



**Fig. 4.** (a) Two-dimensional bilayer (A and B) structure of **2** with dpap ligands link two layers; (b) dpap are omitted for clarity. The purple and blue color show the A and B layers, respectively (for clarity, only two chains are represented by color codes in (a)).

190–240 °C, the complex undergoes large weight loss of 56.5%, which belongs to sdba and coordinated H<sub>2</sub>O molecules losing together (calculated: 59.7%) (Fig. S9). Then, the bpp begin to decompose and oxidize above 290 °C.

# 3.4. Conclusion

Two polymers of Cd(II),  $[Cd(dpap)(mal)]_n$  (1) and  $\{[Cd(dpap)(sdba)] \cdot 2H_2O\}_n$  (2) exhibit novel framework due to different dicarboxylate anions. Same direction and relative short distance of dicarboxylate species in **1** help to generate Cd-carboxylate

helical chains, which are alternately arranged to form a 2D (6,3) framework. While the semi-rigid V-shaped and relatively long ligand sdba results in two different layers (A and B) of **2**. The regular crossing bilayers are parallel and stacked without interpenetrating with ( $8^210$ ) topology. Compound **3** was obtained by different metal salts introduced to **2**, which was not tampered with metal effect. The formation of the 1-D chains of {[Co(bpp)(H<sub>2</sub>O)<sub>4</sub>] · sdba}<sub>n</sub> (**4**) herein obviously resulted from the flexible nature of bpp as well as metal effect. It is noteworthy that a variety of framework structures can be achieved on the basis of the choice of the different nature of ligand and dicarboxylate groups as building blocks.



**Fig. 5.** The butterfly network of **2** along *a* axis.



**Fig. 6.** (a) ORTEP drawing of **4** showing Co(II) octahedra (30% ellipsoids) and free sdba dianions. Hydrogen atoms are omitted for clarity; (b) a left-handed 2<sub>1</sub> helix of complex **4** along the crystallographic *a* axis, emphasizing the left-handed (red) helix chain; (c) 2D hydrogen-bonding sheet in *bc* plane.



Fig. 7. Solid-state fluorescence emissions recorded at room temperature for dpap (red), 1 (black) and 2 (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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#### **Appendix A. Supplementary material**

CCDC 655401, 655402, 655403 and 655404 contain the supplementary crystallographic data for 1, 2, 3 and 4. 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.2008.05.001.

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