

# Counterion-induced controllable assembly of 2D and 3D metal–organic frameworks: effect of coordination modes of dinuclear Cu(II) paddle-wheel motifs†

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Reactions of 4,4'-(hexa-fluoroisopropylidene)bis(benzoic acid) with Cu(II) salts controllably yielded 2D and 3D pillared-layer MOFs, respectively, with or without available unsaturated metal centers by modulating the axial coordination modes of the dinuclear Cu(II) paddlewheel SBU, which strongly depends on the counterions of Cu(II) precursors/sources. In contrast, only a 3D Co(II) counterpart can be obtained with various Co(II) salts under similar reaction conditions. The research results demonstrate that the nature of the counterions has subtle effects for different metal ions to assemble with the same ligand. The novel 1D helical chains/channels were contained in all these compounds due to the inducement of the pre-designed V-type ligand.

## Introduction

The design and synthesis of porous metal–organic frameworks (MOFs) are a focus of great interests not only because of their intriguing architectures and topologies, as well as tremendous potential applications, but also owing to the intrinsic correlation between structures and properties.<sup>1–3</sup> The geometries of the organic ligand and the metal/metal-cluster secondary building unit (SBU) are two important factors that always influence the topology of the final structure.<sup>4</sup> By pre-designing and selecting the organic ligand and SBU, it is possible to construct novel coordination networks possessing a desired topology.<sup>4</sup> As a typical paddle-wheel SBU, four acetate-anions are each coordinated as dimonodentate ligand to two M(II) ions forming the  $D_{4h}$ -symmetrical structure having the appearance of a paddle-wheel with four blades, whereas in axial positions, various ending or bridging ligands are coordinated, modulating the resultant structures ranging from 2D layer to 3D pillared-layer structure, consequently affecting particular properties. On the other hand, helical structures attract increased attention in coordination chemistry and materials chemistry owing to their importance in biological systems, asymmetric catalysis and optical devices.<sup>5–7</sup> Many chemists have dedicated to design helical coordination polymers through the self-assembly of metal ions and ligands.<sup>6–8</sup> However, the occurrence of pillared-layer complexes with helical character is especially rare. Even though the helical layer has already been reported several years ago as a new 2D structure,<sup>7</sup> whereas entangling it into interpenetrated networks or extending it into 3D open frameworks remained less explored.<sup>8</sup>

Inspired by the aforementioned considerations, our synthetic strategies are to introduce helices by selecting a flexible V-shaped ligand, 4,4'-(hexa-fluoroisopropylidene)bis(benzoic acid)

(simplified as  $H_2hfpbb$  hereafter),<sup>9</sup> as genesis and tune the structural dimensions by changeable axial coordination modes of paddlewheel SBU. In the present work, with copper(II) acetate as a precursor, we have prepared Cu( $hfpbb$ )( $H_2O$ ) (**1**), a 2D helical compound with a dicopper(II) paddlewheel cluster as the SBU, in which the two axial positions of Cu(II) paddlewheel are coordinated by ending aqua molecules. With copper(II) nitrate or chloride as sources, the coordinated aqua molecules in the dicopper SBU are replaced by the bridging  $H_2hfpbb$  ligands, a pillared-layer 3D open framework of Cu( $hfpbb$ )( $H_2hfpbb$ )<sub>0.5</sub> (**2**) was successfully obtained. In contrast, only the isostructural pillared-layer 3D open framework of Co( $hfpbb$ )( $H_2hfpbb$ )<sub>0.5</sub> (**3**) can be produced and identified when different cobalt(II) precursors were investigated. Although there are limited reports on the effects of the counterions on the assembly process of ligands with metal ions,<sup>10</sup> to the best of our knowledge, this is the first time to present the totally different effects of various counterions for the assembly of the similar transition metals ( $Cu^{2+}$  and  $Co^{2+}$ ) with the same organic ligand.

## Experimental

### Materials and general methods

All chemicals were obtained from commercial sources and used without further purification. IR spectra were recorded on an attenuated total reflectance (ATR) FT-IR spectrometer (SensIR Technologies). Elemental analyses were performed on a Perkin-Elmer 2400 Series II analyzer. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-50 thermal analyzer from room temperature to 500 °C at a ramp rate of 5 °C min<sup>-1</sup> in air. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku X-ray diffractometer at 40 kV, 40 mA for Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Solid state emission spectra were taken on a Perkin-Elmer LS50B luminescence spectrophotometer.

### Syntheses of compounds 1–3

As displayed in Table 1, under similar reaction conditions (160 °C and 3 d of hydrothermal treatment), compound **1** as

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**Table 1** The influences on reaction products by using the various metal precursors under similar reaction conditions.<sup>a</sup>

Run I	Cu(CH <sub>3</sub> COO) <sub>2</sub> (mmol)	0.1	0.33	0.5	0.5
	H <sub>2</sub> hfipbb (mmol)	0.3	1	1.5	1
	H <sub>2</sub> O amount (mL)	5	10	10	10
	Product	<b>1</b>	<b>1</b>	<b>1 + 2</b>	<b>1 + few 2</b>
Run II	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O (mmol)	0.1	0.1	0.15	0.5
	H <sub>2</sub> hfipbb (mmol)	0.2	0.3	0.3	1
	H <sub>2</sub> O amount (mL)	5	5	5	10
	Product	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>
Run III	CuCl <sub>2</sub> (mmol)	0.1	0.15	0.5	
	H <sub>2</sub> hfipbb (mmol)	0.2	0.3	1	
	H <sub>2</sub> O amount (mL)	5	5	10	
	Product	<b>2</b>	<b>2</b>	<b>2</b>	
Run IV	Co(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O (mmol)	0.1	0.3	0.5	0.5
	H <sub>2</sub> hfipbb (mmol)	0.3	1	1	1.5
	H <sub>2</sub> O amount (mL)	5	10	10	10
	Product	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>
Run V	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (mmol)	0.1	Run VI	CoCl <sub>2</sub> ·6H <sub>2</sub> O (mmol)	0.5
	H <sub>2</sub> hfipbb (mmol)	0.3		H <sub>2</sub> hfipbb (mmol)	1
	H <sub>2</sub> O amount (mL)	5		H <sub>2</sub> O amount (mL)	10
	Product	<b>3</b>		Product	Unknown and very low yield

<sup>a</sup> Acetone is required to remove the white solid in the products whereas plate-like colourless crystals contained in the products resulted from Co-precursors can be manually removed. The phases were identified by powder X-ray diffraction.

a pure or main (occasionally accompanying with a few concomitants of compound **2**) product was obtained although the molar ratio of Cu(OAc)<sub>2</sub>/H<sub>2</sub>hfipbb was widely changed. Compound **2** was obtained as the only product although variational metal/ligand ratios were investigated when Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O or CuCl<sub>2</sub> was used to replace Cu(OAc)<sub>2</sub>. In contrast, the only cobalt(II) analog to compound **2** was prepared and identified either cobalt(II) acetate or cobalt(II) nitrate was reacted. The typical synthesis procedures for compounds **1–3** are described as follows.

**Cu(hfipbb)(H<sub>2</sub>O) (1).** Cu(OAc)<sub>2</sub> (60.5 mg, 0.33 mmol) and H<sub>2</sub>hfipbb (392 mg, 1 mmol) in 10 mL of distilled water were sealed

in a Teflon-lined autoclave (24 mL) and heated at 160 °C for 3 d, and the as-obtained product was ultrasonic cleaned and rinsed with acetone and ethanol, giving blue crystals of **1**. Yield of **1**: 90 mg based on Cu, 58%. Elemental analysis calcd (%) of **1**: C 43.28, H 2.14; found: C 42.89, H 2.08. IR data of **1** (cm<sup>-1</sup>): 3682 b, 1964 b, 1609 s, 1559 m, 1402 vs, 1323 w, 1292 m, 1256 s, 1237 s, 1210 s, 1169 vs, 1136 s, 1021 w, 974 m, 963 m, 947 m, 928 m, 858 m, 845 m, 779 s, 748 s, 723 vs, 693 w, 556 w, 532 m, 515 vs, 494 vs, 424 m.

**Cu(hfipbb)(H<sub>2</sub>hfipbb)<sub>0.5</sub> (2).** Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (22.5 mg, 0.1 mmol) or CuCl<sub>2</sub> (13.5 mg, 0.1 mmol) and H<sub>2</sub>hfipbb (117.7 mg, 0.3 mmol) in 5 mL of distilled water were sealed in a Teflon-lined autoclave (24 mL) and heated at 160 °C for 3 d,

**Table 2** Crystallographic parameters for compounds **1–3** from single-crystal X-ray diffraction

Complexes	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>17</sub> H <sub>10</sub> CuF <sub>6</sub> O <sub>5</sub>	C <sub>51</sub> H <sub>26</sub> Cu <sub>2</sub> F <sub>18</sub> O <sub>12</sub>	C <sub>51</sub> H <sub>26</sub> Co <sub>2</sub> F <sub>18</sub> O <sub>12</sub>
Formula weight	471.79	1299.80	1290.58
Color	Brown-blue	Sky blue	Dark purple
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2/c</i>	<i>P2/c</i>	<i>P2/c</i>
<i>a</i> /Å	12.710(3)	18.760(4)	19.030(4)
<i>b</i> /Å	6.9800(14)	7.2800(15)	7.2300(14)
<i>c</i> /Å	23.624(7)	23.402(9)	23.644(9)
$\alpha$ /°	90	90	90
$\beta$ /°	118.50(2)	123.12(2)	123.76(2)
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	1841.8(8)	2676.8(13)	2704.5(13)
<i>Z</i>	4	2	2
<i>d</i> <sub>c</sub> /g cm <sup>-3</sup>	1.701	1.613	1.585
$\mu$ /mm <sup>-1</sup>	1.271	0.917	0.735
<i>F</i> (000)	940	1296	1288
Reflections collected	15 560	23 981	35 901
Independent reflections	4093 [ <i>R</i> <sub>int</sub> = 0.1333]	6073 [ <i>R</i> <sub>int</sub> = 0.0582]	6177 [ <i>R</i> <sub>int</sub> = 0.0456]
Observed data [ <i>I</i> > 2σ( <i>I</i> )]	3000	3630	4962
Data/restraints/parameters	4093/3/276	6073/0/375	6177/0/375
GOF on <i>F</i> <sup>2</sup>	1.049	1.085	1.029
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0704, 0.1264	0.0418, 0.0862	0.0393, 0.0906
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0981, 0.1410	0.1051, 0.1219	0.0531, 0.0982

and the as-obtained product was ultrasonic cleaned and rinsed with acetone, giving blue crystals of **2**. Yield: 43 mg based on Cu, 67%. Elemental analysis calcd (%): C 47.13, H 2.02; found: C 46.83, H 1.95. IR data (cm<sup>-1</sup>): 2560 b, 2039 b, 1686 m, 1626 s, 1570 w, 1514 w, 1416 s, 1389 vs, 1333 w, 1285 m, 1252 vs, 1213 vs, 1175 vs, 1140 vs, 1022 w, 966 m, 947 m, 932 m, 845 m, 779 m, 745 m, 725 vs, 559 w, 540 m, 517 vs, 494 s.

**Co(hfipbb)(H<sub>2</sub>hfipbb)<sub>0.5</sub> (3)**. Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (29.1 mg, 0.1 mmol) or Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (24.9 mg, 0.1 mmol) and H<sub>2</sub>hfipbb (117.7 mg, 0.3 mmol) in 5 mL of distilled water were sealed in a Parr Teflon-lined autoclave (24 mL) and heated at 160 °C for 3 d, and the as-obtained product was ultrasonic cleaned and rinsed with acetone and ethanol, giving dark-purple crystals of **3**. Yield: 20 mg based on Co, 16%. Elemental analysis calcd (%): C 47.46, H 2.03; found: C 46.71, H 2.03. IR data (cm<sup>-1</sup>): 2579 b, 2159 m, 2018 m, 1655 w, 1622 m, 1561 w, 1420 m, 1387 m, 1341 m, 1314 w, 1292 w, 1250 s, 1213 vs, 1175 vs, 1138 s, 1020 w, 968 m, 945 m, 930 m, 855 m, 777 m, 747 s, 721 vs, 546 s, 511 s, 482 s.

### X-Ray crystallography

The crystal data were collected on a R-AXIS RAPID II diffractometer at room temperature with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å).<sup>11</sup> The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.<sup>12</sup> Metal atoms in all compounds were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal

parameters on *F*<sup>2</sup>. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of the water molecules were located using the difference Fourier method and refined freely. Crystallographic data and structural refinement details are summarized in Table 2. Selected bond lengths and bond angles are given in Table 3.

## Results and discussion

### Structural descriptions

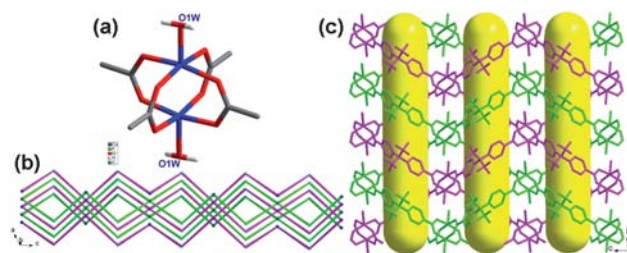
Compound **1** was prepared with copper(II) acetate as precursor under hydrothermal conditions. Single-crystal X-ray analysis showed that **1** was composed of an interpenetrated polymeric structure in the absence of any isolated solvent molecule. There is one copper(II), one hfipbb ligand, and one aqua molecule in the asymmetric unit. The basic SBU of each dicopper(II) paddle-wheel cluster is coordinated by two aqua molecules and four carboxylic oxygen atoms from four hfipbb<sup>2-</sup> anions (Fig. 1a). Such tetracarboxylate-bridged dimetallic (*e.g.*, Cu<sub>2</sub><sup>4+</sup> and Zn<sub>2</sub><sup>4+</sup>) paddlewheels have been investigated as SBUs for the construction of porous MOFs that displays gas storage and separation properties.<sup>13</sup> In the dicopper(II) structure, the bond distances between Cu and carboxylic oxygen atoms are in the range of 1.952(3)–1.973(3) Å, whereas Cu–O<sub>1w</sub> distance of 2.146(3) Å is slightly longer. The intradimer Cu–Cu separation is 2.6056(9) Å, all of which are comparative to those in reported ones.<sup>13</sup> The H<sub>2</sub>hfipbb ligand in bent conformation gives a dihedral angle of 71.14° between two benzene rings and bridges four Cu(II), where each oxygen is in a monodentate fashion. Notably, each dinuclear Cu(II) paddle-wheel cluster connects with the other four neighbouring ones by the bent hfipbb ligands, leading to an undulating (4, 4) net with a rhombic window (Fig. 1b). The distances between adjacent centers of dinuclear copper subunits of the net are 13.720(3) × 13.720(3) Å<sup>2</sup>. As shown in Fig. 1, the left- and right-hand helical chains appear alternatively by sharing the paddle-wheel clusters in covalent skeleton of this 2D sheet. Such two identical helical layers are interpenetrated to present parallel 2D to 2D layers. Upon 2-fold parallel interpenetration, the 1D double helical channels in skeleton are formed (Fig. 1).

With copper(II) acetate replaced by copper(II) nitrate or chlorate under the similar reaction conditions, unexpectedly, ending-coordinated aqua molecules in Cu<sub>2</sub><sup>4+</sup> SBUs in **1** were substituted by H<sub>2</sub>hfipbb ligands, and the parallel interpenetrating helical double layers of **1** were successfully extended into a 3D

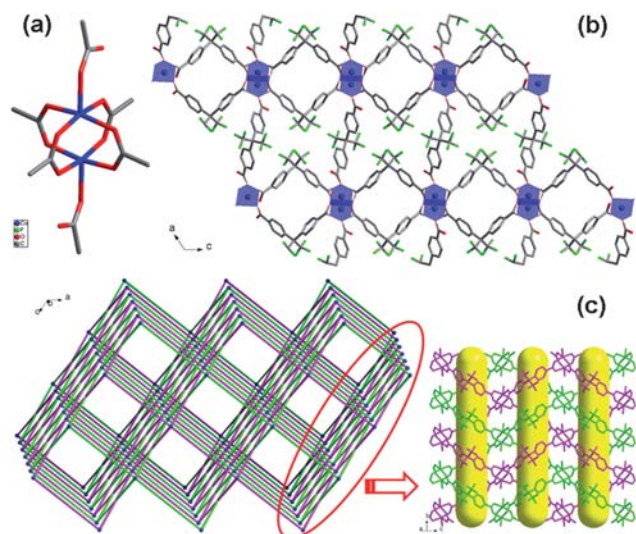
**Table 3** Selected bond lengths (Å) and bond angles (°) for compounds **1–3**<sup>a,b</sup>

<b>1</b>			
Cu(1)–O(3)#1	1.952(3)	Cu(1)–O(4)#2	1.964(3)
Cu(1)–O(1)	1.965(3)	Cu(1)–O(2)#3	1.973(3)
Cu(1)–O(1W)	2.146(3)	Cu(1)–Cu(1)#3	2.6056(9)
O(3)#1–Cu(1)–O(4)#2	169.10(11)	O(3)#1–Cu(1)–O(1)	91.20(13)
O(4)#2–Cu(1)–O(1)	89.50(13)	O(3)#1–Cu(1)–O(2)#3	89.41(13)
O(4)#2–Cu(1)–O(2)#3	87.84(14)	O(1)–Cu(1)–O(2)#3	168.89(11)
O(3)#1–Cu(1)–O(1W)	96.98(11)	O(4)#2–Cu(1)–O(1W)	93.60(11)
O(1)–Cu(1)–O(1W)	100.15(11)	O(2)#3–Cu(1)–O(1W)	90.78(11)
<b>2</b>			
Cu(1)–O(3)#1	1.938(3)	Cu(1)–O(4)#2	1.940(3)
Cu(1)–O(2)#3	1.949(2)	Cu(1)–O(1)	2.004(2)
Cu(1)–O(5)	2.212(3)	Cu(1)–Cu(1)#3	2.6473(10)
O(3)#1–Cu(1)–O(4)#2	168.05(12)	O(3)#1–Cu(1)–O(2)#3	91.26(11)
O(4)#2–Cu(1)–O(2)#3	89.03(11)	O(3)#1–Cu(1)–O(1)	88.76(11)
O(4)#2–Cu(1)–O(1)	88.48(11)	O(2)#3–Cu(1)–O(1)	167.96(11)
O(3)#1–Cu(1)–O(5)	99.32(11)	O(4)#2–Cu(1)–O(5)	92.35(11)
O(2)#3–Cu(1)–O(5)	100.95(10)	O(1)–Cu(1)–O(5)	90.92(10)
<b>3</b>			
Co(1)–O(3)#1	1.9752(17)	Co(1)–O(4)#2	1.9913(16)
Co(1)–O(2)#3	2.0044(15)	Co(1)–O(5)	2.0488(15)
Co(1)–O(1)	2.1809(15)	Co(1)–Co(1)#3	2.9150(7)
O(3)#1–Co(1)–O(4)#2	159.45(8)	O(3)#1–Co(1)–O(2)#3	94.12(8)
O(4)#2–Co(1)–O(2)#3	90.61(8)	O(3)#1–Co(1)–O(5)	103.19(7)
O(4)#2–Co(1)–O(5)	94.42(7)	O(2)#3–Co(1)–O(5)	107.32(7)
O(3)#1–Co(1)–O(1)	85.53(7)	O(4)#2–Co(1)–O(1)	83.67(7)
O(2)#3–Co(1)–O(1)	161.34(7)	O(5)–Co(1)–O(1)	90.86(6)

<sup>a</sup> Symmetry codes for **1**: #1 *x*, *−y* − 1, *z* + 1/2; #2 *−x* + 1, *y* + 1, *−z* − 1/2; #3 *−x* + 1, *−y*, *−z*. <sup>b</sup> Symmetry codes for **2** and **3**: #1 *−x* − 1, *y* − 1, *−z* − 3/2; #2 *x*, *−y*, *z* + 1/2; #3 *−x* − 1, *−y* − 1, *−z* − 1.

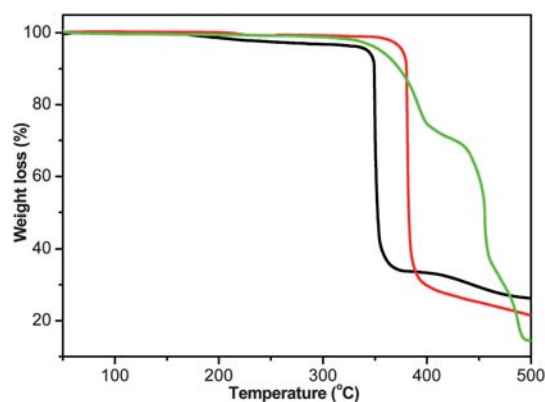


**Fig. 1** (a) A Cu<sub>2</sub> paddle-wheel SBU in **1**. (b) Schematic representation of 1D double helical channels in 2D layers of **1**. (c) View of 2-fold parallel interpenetration of **1** with double-stranded helical structures.



**Fig. 2** (a) A  $\text{Co}_2$  paddle-wheel SBU in **3**. (b) View of the 3D pillared-layer structure of **3** along the  $b$ -axis. (c) Topological view of the 3D 2-fold interpenetrated network of **3** (left) and schematic representation of the included helical layer (right).

pillared-layer framework of **2**. In contrast, either cobalt(II) acetate or cobalt(II) nitrate reacting with  $\text{H}_2\text{hfipbb}$  can only afford **3** with a 3D pillared-layer framework. It should be noted here that although synthesis, gas adsorption and separation properties of **2** have been reported by Li *et al.*,<sup>13a</sup> we prepared **2** under different conditions. Considering the system of our study, it is also listed and its characterizations were performed. Single-crystal X-ray analyses reveal that **2** and **3** are isostructural, therefore, the structure of **3** is discussed here as a representative. Compared to **1**, the aqua molecule in **1** is replaced by half a  $\text{H}_2\text{hfipbb}$  in the asymmetric unit. As a result, the dicobalt(II) paddle-wheel SBU in **3** is coordinated by six carboxylic oxygen atoms from planar four  $\text{hfipbb}^{2-}$  anions and axial two  $\text{H}_2\text{hfipbb}$  ligands (Fig. 2a). In  $\text{Co}_2$  SBU, the bond distances between Co and carboxylic oxygen atoms range from 1.975(2) to 2.181(2) Å and the intradimer Co–Co separation is 2.915(1) Å. The dihedral angle of  $68.57^\circ$  between the two benzene rings in  $\text{H}_2\text{hfipbb}$  is smaller than that of  $73.53^\circ$  in  $\text{hfipbb}^{2-}$  anion. The ligands display various coordinated modes, where  $\text{hfipbb}^{2-}$  binds four Co(II), the same as that in **1**, whereas  $\text{H}_2\text{hfipbb}$  bridges two Co(II) by two oxygen atoms, the other two oxygen atoms are assigned to hydroxyl groups for requirements of charge balance.<sup>14</sup> As expected, identical to that of **1**, the  $\text{hfipbb}^{2-}$  anions connect with Co(II) into a planar helical layer with 1D double helical channels. While with the additional coordinated  $\text{H}_2\text{hfipbb}$  ligands as pillars, the interpenetrating helical layer was extended into a 3D pillared-layer network (Fig. 2b). Interestingly, if we take the dicobalt(II) paddle wheel cluster as a single node, each such cluster is linked by six ligands, whereas each ligand only bridges two clusters simplified to be a line. Therefore, the whole network can be extended to a 3D six-connected net with the Schläfli symbol of  $(4^{12}\cdot 6^3)$ .<sup>15</sup> Because of the presence of the interpenetrated helical layers in **3**, the overall structure gives a six-connected 2-fold interpenetrated network (Fig. 2c). PLATON calculation gives effective free volume in **3** of 12.1% (total



**Fig. 3** TG curves for compounds **1** (black), **2** (red) and **3** (green).

potential solvent volume of  $327.0 \text{ \AA}^3$  out of each unit cell volume of  $2704.5 \text{ \AA}^3$ , slightly lower than that of **1** (14.4%), probably due to free interlayer space occupied by additional  $\text{H}_2\text{hfipbb}$  ligands.

### Thermogravimetric analyses

Thermogravimetric (TG) analyses indicated the robust frameworks of compounds **1–3** (Fig. 3). The first step of weight loss (3.70%) of **1** observed in the range of 100–330 °C corresponds to evacuation of coordinated water molecules (3.82%). Beyond that, the residue host framework starts to decompose and does not end until 500 °C. It is evidenced that the unsaturated metal centers can be available upon removal of coordinated  $\text{H}_2\text{O}$  molecules by simple heating. While no obvious weight loss happens to **2** and **3** before the decomposed temperatures of their host frameworks of 350 °C and 300 °C, respectively, owing to absences of isolated and coordinated solvent molecules.

### Fluorescence properties

All three compounds display considerable solid-state fluorescent emissions at room temperature. The emission maximum of **1** is at 618 nm under  $\lambda_{\text{ex}} = 446 \text{ nm}$ , whereas the weaker emissions of **2** and **3** similarly located around 593 nm under the same conditions. To further understand the nature of the emission bands, the photoluminescence properties of free  $\text{H}_2\text{hfipbb}$  ligand were also studied and results showed that the weak emission at 595 nm could be observed under  $\lambda_{\text{ex}} = 435 \text{ nm}$ . Thus, we assume that these emissions originate from the intraligand transitions.

### Conclusions

In conclusion, we have presented three MOFs with helical channels by using a pre-designed V-shaped ligand. For Cu compounds, the coordinated modes of dinuclear Cu(II) paddle-wheel SBUs changed by simply changing the metal precursors, leading to variational dimensions and structures of resultant compounds. The available unsaturated metal centers in the 2D Cu-MOF could be used as Lewis acid sites for potential catalysis applications.<sup>16</sup> While the only 3D cobalt(II) counterpart was obtained by applying different Co(II) salts as reactants. The results reveal that counterions with various sizes and nucleophilic features have subtle effects on supramolecular architectures



constructed by different metal ions. Furthermore, the successful preparation of these MOFs induced by various counterions provides a valuable approach for the construction of novel MOFs with different structures and functional properties.

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## References

- (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040; (c) R. Kitaura, K. Seki, G. Akiyama and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2003, **42**, 428; (d) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (e) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, *Adv. Mater.*, 2007, **19**, 1693; (f) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (g) P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 16842; (h) H.-L. Jiang, Y. Tatsu, Z.-H. Lu and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5586.
- (a) L. Pan, B. Parker, X. Y. Huang, D. H. Olson, J. Y. Lee and J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4180; (b) D. Zacher, O. Shekhah, C. Wöll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418; (c) J. R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (d) M. Du, X. J. Jiang and X. J. Zhao, *Chem. Commun.*, 2005, 5521; (e) Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315; (f) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; (g) H. L. Jiang, B. Liu, T. Akita, M. Haruta, H. Sakurai and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 11302.
- (a) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (b) C. Y. Su, A. M. Goforth, M. D. Smith, P. J. Pellechia and H. C. zur Loye, *J. Am. Chem. Soc.*, 2004, **126**, 3576; (c) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (d) X. Lin, J. Jia, P. Hubberstey, M. Schröder and N. R. Champness, *CrystEngComm*, 2007, **9**, 438; (e) J. Zhang, Z.-J. Li, Y. Kang, J.-K. Cheng and Y.-G. Yao, *Inorg. Chem.*, 2004, **43**, 8085; (f) M. R. Kishan, J. Tian, P. K. Thallapally, C. A. Fernandez, S. J. Dalgarno, J. E. Warren, B. P. McGrail and J. L. Atwood, *Chem. Commun.*, 2010, **46**, 538; (g) P. K. Thallapally, C. A. Fernandez, R. K. Motkuri, S. K. Nune, J. Liu and C. H. F. Peden, *Dalton Trans.*, 2010, **39**, 1692.
- (a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (b) H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem.-Eur. J.*, 2005, **11**, 3521; (c) Q.-R. Fang, G.-S. Zhu, M. Xue, Q.-L. Zhang, J.-Y. Sun, X.-D. Guo, S.-L. Qiu, S.-T. Xu, P. Wang, D.-J. Wang and Y. Wei, *Chem.-Eur. J.*, 2006, **12**, 3754.
- (a) V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, **259**, 1596; (b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (c) T. E. Gier, X. Bu, P. Feng and G. D. Stucky, *Nature*, 1998, **395**, 154; (d) S. Neeraj, S. Natarajan and C. N. R. Rao, *Chem. Commun.*, 1999, 165; (e) Z. Shi, S. H. Feng, S. Gao, L. Zhang, G. Yang and J. Hua, *Angew. Chem., Int. Ed.*, 2000, **39**, 2325; (f) D. Kumaran, S. Eswaramoorthy, F. W. Studier and S. Swaminathan, *Protein Sci.*, 2005, **14**, 719; (g) Y.-P. Cai, X.-X. Zhou, Z.-Y. Zhou, S.-Z. Zhu, P. K. Thallapally and J. Liu, *Inorg. Chem.*, 2009, **48**, 6341.
- (a) P. Braunstein, B. Oswald, A. Tiripicchio and M. T. Camellini, *Angew. Chem., Int. Ed.*, 1990, **29**, 1140; (b) Y. Cui, S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 6014; (c) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *Chem. Commun.*, 2005, 1258; (d) X. L. Wang, C. Qin, E. B. Wang, L. Xu, Z. M. Su and C. W. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036; (e) D. F. Sun, R. Cao, Y. Q. Sun, W. H. Bi, X. Li, M. C. Hong and Y. J. Zhao, *Eur. J. Inorg. Chem.*, 2003, 38.
- (a) L. Han, M. C. Hong, R. H. Wang, J. H. Luo, Z. Z. Lin and D. Q. Yuan, *Chem. Commun.*, 2003, 2580; (b) J. Liang, Y. Wang, J. H. Yu, Y. Li and R. R. Xu, *Chem. Commun.*, 2003, 882.
- (a) D.-R. Xiao, E.-B. Wang, H.-Y. An, Y.-G. Li, Z.-M. Su and C.-Y. Sun, *Chem.-Eur. J.*, 2006, **12**, 6528; (b) L. Han, Y. Zhou, W. N. Zhao, X. Li and Y. X. Liang, *Cryst. Growth Des.*, 2009, **9**, 660.
- (a) P. Pachfule, C. Dey, T. Panda, K. Vanka and R. Banerjee, *Cryst. Growth Des.*, 2010, **10**, 1351; (b) C. A. Fernandez, P. K. Thallapally, R. K. Motkuri, S. K. Nune, J. C. Sumrak, J. Tian and J. Liu, *Cryst. Growth Des.*, 2010, **10**, 1037; (c) H.-L. Jiang, B. Liu and Q. Xu, *Cryst. Growth Des.*, 2010, **10**, 806; (d) D.-S. Li, Y.-P. Wu, P. Zhang, M. Du, J. Zhao, C.-P. Li and Y.-Y. Wang, *Cryst. Growth Des.*, 2010, **10**, 2037.
- (a) X.-D. Chen, J.-H. Guo, M. Du and T. C. W. Mak, *Inorg. Chem. Commun.*, 2005, **8**, 766; (b) D.-L. Long, R. J. Hill, A. J. Blake, N. R. Champness, P. Hubberstey, C. Wilson and M. Schröder, *Chem.-Eur. J.*, 2005, **11**, 1384; (c) Y.-N. Chi, K.-L. Huang, F.-Y. Cui, Y.-Q. Xu and C.-W. Hu, *Inorg. Chem.*, 2006, **45**, 10605; (d) R. Wang, D. Yuan, F. Jiang, L. Han, Y. Gong and M. Hong, *Cryst. Growth Des.*, 2006, **6**, 1351.
- T. Higashi, *Program for Absorption Correction*; Rigaku Corporation: Tokyo, Japan, 1995.
- G. M. Sheldrick, *SHELXTL NT, Program for Solution and Refinement of Crystal Structures*, version 5.1; University of Göttingen: Göttingen, Germany, 1997.
- (a) L. Pan, M. B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath and J. K. Johnson, *J. Am. Chem. Soc.*, 2004, **126**, 1308; (b) H. J. Park and M. P. Suh, *Chem.-Eur. J.*, 2008, **14**, 8812; (c) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charamant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (d) B. Moulton, H. Abourahma, M. W. Bradner, J. J. Lu, G. J. McManus and M. J. Zaworotko, *Chem. Commun.*, 2003, 1342.
- (a) X. Duan, J. Lin, Y. Li, C. Zhu and Q. Meng, *CrystEngComm*, 2008, **10**, 207; (b) K. S. Gavrilenko, S. V. Punin, O. Cadour, S. Golhen, L. Ouahab and V. V. Pavlishchuk, *J. Am. Chem. Soc.*, 2005, **127**, 12246; (c) T. Fiedler, M. Hilder, P. C. Junk, U. H. Kynast, M. M. Lezhnina and M. Warzala, *Eur. J. Inorg. Chem.*, 2007, 291.
- (a) A. F. Wells, *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977; (b) R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735.
- R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 8402–8403.