# Supramolecular Assembly of Double-Stranded Chains, Helical Chains and Catenane-like Layers with Flexible Ligands

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**Abstract.** Four new transition metal coordination polymers,  $[Co(bpndc)(phen)(H_2O)]_n$  (1),  $[Co_3(bpndc)_3(2,2'-bpy)_2]_n \cdot 0.5n(i-C_3H_7OH)$  (2), and  $[M(bpndc)(2,2'-bpy)_2]_n$  (M = Zn, 3; Cu, 4; H<sub>2</sub>bpndc = benzophenone -4,4'-dicarboxylic acid; phen = 1,10-phenanthroline; 2,2'-bpy = 2,2'-bipyridine) have been synthesized by the hydrothermal reactions and characterized by single crystal X-ray diffraction, elemental analysis, and IR spectrum. Because of the introduction of different terminal auxiliary ligands, bpndc ligands in complexes 1 and 2 adopt different coordination modes. In complex 1, bpndc ligands act as tridentate ligand and

bridge  $Co^{II}$  ions into 1D double-stranded chains; while complex 2 possesses 2D (4,4) grids, where bpndc ligands adopt tetradente and pentadentate modes. Two such grids interpenetrate to form a novel catenane-like layer. Complexes 3 and 4 are isostructural. Bpndc ligands adopt tetradentate mode and bridge metal ions forming 1D helical chains.

**Keywords:** Cobalt; Zinc; Copper; Benzophenone-4,4'-dicarboxylic acid; Flexible ligands; Catenane-like layers; Helical chains

## Introduction

The design and assembly of coordination polymers is still attractive, not only due to the fascinating structures, but also their potential applications in the areas of catalysis, magnetism, adsorption, and separation [1-8]. Transition metal ions, for their low coordination number and stable coordination geometry, have been extensively used to construct coordination polymers with interesting structures and desirable properties [9-15].

It is evident that ligands not only function in balancing the charge in coordination polymers, but also play an important role in deriving structural diversity. Long flexible ligands are excellent structure directing ligands because of their flexible bridging capability, and usually lead to large voids, which may further result in interpenetrated or entangled structures [16-20]. Benzophenone-4,4'-dicarboxylic acid (H<sub>2</sub>bpndc) is a typical long flexible ligand. Although there are only a few reports about its coordination chemistry [21-24], it can coordinate metal ions with tridentate, tetradentate and hexadentate modes. The typical coordination modes are summarized in Scheme 1(a-e). It's said that the introduction of auxiliary ligands will effect the construction of coordination polymers. Bridging auxiliary ligands often extend the structures, while terminal auxiliary ligands usually result in lower-dimensional structures. In

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Scheme 1 The coordination modes of bpndc ligands.

this work, we selected H<sub>2</sub>bpndc to react with Co<sup>II</sup> ions, and introduced terminal ligands 1,10-phenanthroline (phen) and 2,2'-bipyridine (2,2'-bpy) to the system, respectively. In order to determine the effect of metal ions on the construction of coordination polymers, Zn<sup>II</sup> and Cu<sup>II</sup> ions were introduced, too. Four new coordination polymers [Co(bpndc)(phen)-(H<sub>2</sub>O)]<sub>n</sub> (1), [Co<sub>3</sub>(bpndc)<sub>3</sub> (2,2'-bpy)<sub>2</sub>]<sub>n</sub>  $\cdot$  0.5n(i-C<sub>3</sub>H<sub>7</sub>OH) (2), and [M(bpndc)(2,2'-bpy)<sub>2</sub>]<sub>n</sub> (M = Zn, 3; Cu, 4) were obtained. Their synthesis and structures will be reported in this paper.

## **Experimental Section**

#### Materials and equipment

All reagents were used as received without further purification. The C, H, N microanalyses were carried out with a Vario EL elemental analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique. Thermogravi-



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metric analyses were conducted on a ZRY-2P Thermal Analyzer using a heating rate of 10 °C/min from room temperature to 900 °C.

## Synthesis of the complexes

**[Co(bpndc)(phen)(H<sub>2</sub>O)]**<sub>n</sub> (1). A mixture of H<sub>2</sub>bpndc (0.027 g, 0.1 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.024 g, 0.1 mmol), phen·H<sub>2</sub>O (0.020 g, 0.1 mmol), triethylamine (Et<sub>3</sub>N, 0.028 ml), isopropanol (5 mL) and deionized water (5 mL) was sealed in a Teflon-lined stainless vessel (25 mL) and heated at 140 °C for 72 h under autogenous pressure. The vessel was then cooled slowly to room temperature. Dark red single crystals were obtained by filtration, washed with isopropanol, and dried in air. Yield: 0.022 g (41.9 %). Anal. Calcd for C<sub>27</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Co (%): C, 61.69; H, 3.43; N, 5.33; found (%): C, 61.54; H, 3.51; N, 5.22. IR data (KBr pellet, cm<sup>-1</sup>): 3350(m), 3071(w), 1654(m), 1600(s), 1547(m), 1519(w), 1430(w), 1386(s), 1336(m), 1304(m), 1275(s), 1127(w), 933(m), 849(m), 812(m), 735(s).

**[Co<sub>3</sub>(bpndc)<sub>3</sub>(2,2'-bpy)<sub>2</sub>]<sub>n</sub>·0.5n(i-C<sub>3</sub>H<sub>7</sub>OH) (2).** A mixture of H<sub>2</sub>bpndc (0.027 g, 0.1 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.024 g, 0.1 mmol), 2,2'-bpy (0.016 g, 0.1 mmol), NaOH aqueous solution (0.3 ml, 0.65 mol L<sup>-1</sup>), isopropanol (5 mL) and deionized water (5 mL) was sealed in a Teflon-lined stainless vessel (25 mL) and heated at 180 °C for 72 h under autogenous pressure. The vessel was then cooled slowly to room temperature. Dark red single crystals were obtained by filtration, washed with isopropanol, and dried in air. Yield: 0.017 g (38.5 %). Anal. Calcd for C<sub>66.50</sub>H<sub>44</sub>N<sub>4</sub>O<sub>15.50</sub>Co<sub>3</sub> (%): C, 60.28; H, 3.32; N, 4.23; found (%): C, 60.62; H, 3.41; N, 4.26. IR data (KBr pellet, cm<sup>-1</sup>): 3453(s), 1663(m), 1646(m), 1608(s), 1553(m), 1536(w), 1443(m), 1393(s), 1305(w), 1278(m), 934(w), 837(w), 769(m), 738(m).

 $[Zn(bpndc)(2,2'-bpy)_2]_n$  (3). The synthesis of complex 3 followed the similar procedure for complex 2 except that  $Zn(Ac)_2 \cdot 2H_2O$  was used instead of  $CoCl_2 \cdot 6H_2O$  and the temperature was 140 °C. Yield: 0.034g (69.4 %). Anal. Calcd for  $C_{25}H_{16}N_2O_5Zn$  (%): C, 61.25; H, 3.27; N, 5.72; found (%): C, 60.97; H, 3.43; N, 5.57. IR data (KBr pellet, cm<sup>-1</sup>): 3449(m), 3074(m), 1660(s), 1591(s), 1542(s), 1506(m), 1448(m), 1413(s), 1309(m), 1273(m), 1164(w), 1097(w), 1028(m), 933(m), 853(s), 759(s), 735(s).

**[Cu(bpndc)(2,2'-bpy)<sub>2</sub>]**<sub>n</sub> (4). The synthesis of complex 4 followed the similar procedure for complex 2 except using Cu(Ac)<sub>2</sub>·H<sub>2</sub>O instead of CoCl<sub>2</sub>·6H<sub>2</sub>O. Yield: 0.022 g (45.1%). Anal. Calcd for C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>Cu (%): C, 61.48; H, 3.28; N, 5.74; found (%): C, 61.04; H, 3.59; N, 5.58. IR data (KBr pellet, cm<sup>-1</sup>): 3429(m), 3067(m), 1657(s), 1593(s), 1549(s), 1499(m), 1450(m), 1384(s), 1306(m), 1274(m), 1165(w), 1129(w), 1099(w), 1034(w), 934(m), 845(s), 771(s), 737(s).

## X-ray diffraction determination

Diffraction intensities for the four complexes were collected at 293K on a Bruker SMART 1000 CCD area detector diffractometer employing graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) in  $\phi$  and  $\omega$  scan modes. Semi-empirical absorption correction was applied using the SADABS program [25]. The structures were solved by direct methods [26] and refined by full-matrix least squares method on  $|F|^2$  using SHELXS 97 and SHELXL 97 programs, respectively [26, 27]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for the four complexes are listed in Table 1, and selected bond lengths/Å and bond angles/° in Tables 2 and 3.

#### **Results and Discussion**

## Description of the structures

In complexes 1-4, bpndc ligands adopt tridentate, tetradentate, and pentadentate coordination modes, as shown in Scheme 1a, c, f and g. Complexes 3 and 4 are isostructural, so only the structures of complexes 1-3 will be described in detail.

Structural description of  $[Co(bpndc)(phen)(H_2O)]_n$  (1). The coordination environment of  $Co^{II}$  ion in complex 1 is shown in Figure 1. Each  $Co^{II}$  is six-coordinated to three oxygen atoms of three bpndc ligands, one oxygen atom of one coordinated water molecule, and two nitrogen atoms of one phen ligand. The coordination can be described as

Table 1	Crystal data	and structure	refinement	parameters	for complexes 1	l-4
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	1	2	3	4
Chemical Formula	C <sub>27</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> Co	C <sub>66.50</sub> H <sub>44</sub> N <sub>4</sub> O <sub>15.50</sub> Co <sub>3</sub>	C <sub>25</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub> Zn	C <sub>25</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub> Cu
Formula weight	525.36	1323.84	489.77	487.94
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	ΡĪ	C2/c	$P2_1/c$	P21/c
a/Å	7.736(3)	15.424(2)	12.508(2)	12.730(4)
b/Å	11.519(4)	16.664(2)	15.142(2)	14.872(5)
c/Å	13.543(5)	23.997(3)	11.464(2)	11.539(4)
α/°	83.152(7)			
β/°	83.910(7)	97.477(2)	93.421(2)	95.077(5)
γ/°	71.006(6)			
V/Å <sup>3</sup>	1130.0(8)	6115.3(1)	2167.4(5)	2175.9(1)
Z	2	4	4	4
F(000)	538	2702	1000	996
$D_c/mg m^{-3}$	1.544	1.437	1.501	1.489
$\mu$ , mm <sup>-1</sup>	0.808	0.877	1.174	1.044
T/K	293(2)	293(2)	293(2)	293(2)
θ range/°	1.52 to 26.40	1.71 to 26.36	1.63 to 26.44	2.11 to 26.42
GOF	1.084	1.056	1.069	1.029
Final R indices	$R_I = 0.0542,$	$R_I = 0.0451,$	$R_I = 0.0396,$	$R_I = 0.0400,$
[I>2σ(I)]	$wR_2 = 0.1153$	$wR_2 = 0.1411$	$wR_2 = 0.0761$	$wR_2 = 0.0835$

Table 2 Selected bond lengths/Å and angles/° for complexes 1 and 2

1 <sup>a)</sup>			
Co(1)-O(1)	2.047(3)	Co(1)-N(1)	2.145(3)
Co(1)-O(4)#1	2.101(3)	Co(1)-N(2)	2.108(3)
Co(1)-O(4)#2	2.123(3)	Co(1)-O(6)	2.081(3)
O(1)-Co(1)-O(4)#1	90.44(11)	O(4)#2-Co(1)-N(1)	168.32(11)
O(1)-Co(1)-O(4)#2	97.74(11)	O(6)-Co(1)-O(4)#1	165.34(11)
O(1)-Co(1)-O(6)	87.95(11)	O(6)-Co(1)-O(4)#2	88.52(11)
O(1)-Co(1)-N(1)	88.68(12)	O(6)-Co(1)-N(1)	101.51(12)
O(1)-Co(1)-N(2)	165.39(12)	O(6)-Co(1)-N(2)	90.22(12)
O(4)#1-Co(1)-O(4)#2	77.26(10)	N(2)-Co(1)-O(4)#2	96.70(11)
O(4)#1-Co(1)-N(1)	93.02(11)	N(2)-Co(1)-N(1)	77.48(12)
O(4)#1-Co(1)-N(2)	94.89(11)		
<b>2</b> <sup>b)</sup>			
Co(1)-O(1)	2.021(2)	Co(2)-O(2)	2.118(2)
Co(1)-O(4)#1	2.143(2)	Co(2)-O(2)#2	2.118(2)
Co(1)-O(5)#1	2.188(3)	Co(2)-O(4)#1	2.175(2)
Co(1)-O(6)	2.024(3)	Co(2)-O(4)#3	2.175(2)
Co(1)-N(1)	2.090(3)	Co(2)-O(7)	2.128(3)
Co(1)-N(2)	2.128(3)	Co(2)-O(7)#2	2.128(3)
O(1)-Co(1)-O(6)	91.42(11)	O(2)-Co(2)-O(2)#2	180.0
O(1)-Co(1)-N(1)	95.27(12)	O(2)-Co(2)-O(7)	94.12(10)
O(6)-Co(1)-N(1)	90.60(12)	O(2)#2-Co(2)-O(7)	85.88(10)
O(1)-Co(1)-N(2)	172.49(13)	O(2)-Co(2)-O(7)#2	85.88(10)
O(6)-Co(1)-N(2)	88.46(13)	O(2)#2-Co(2)-O(7)#2	94.12(10)
N(1)-Co(1)-N(2)	77.22(13)	O(7)-Co(2)-O(7)#2	180.0
O(1)-Co(1)-O(4)#1	94.84(10)	O(2)-Co(2)-O(4)#3	86.06(10)
O(6)-Co(1)-O(4)#1	101.78(10)	O(2)#2-Co(2)-O(4)#3	93.94(10)
N(1)-Co(1)-O(4)#1	163.79(11)	O(7)-Co(2)-O(4)#3	88.25(10)
N(2)-Co(1)-O(4)#1	92.53(12)	O(7)#2-Co(2)-O(4)#3	91.76(10)
O(1)-Co(1)-O(5)#1	89.80(11)	O(2)-Co(2)-O(4)#1	93.94(10)
O(6)-Co(1)-O(5)#1	162.53(11)	O(2)#2-Co(2)-O(4)#1	86.06(10)
N(1)-Co(1)-O(5)#1	106.63(11)	O(7)-Co(2)-O(4)#1	91.75(10)
N(2)-Co(1)-O(5)#1	92.57(12)	O(7)#2-Co(2)-O(4)#1	88.24(10)
O(4)#1-Co(1)-O(5)#1	60.76(10)	O(4)#3-Co(2)-O(4)#1	180.0

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2, -y+1/2, z-1/2 #2 -x+3/2, -y+1/2, -z+1 #3 -x+2, y, -z+3/2

<sup>a)</sup> Symmetry transformations used to generate equivalent atoms: #1 x,y,z+1 #2 - x, -y+1, -z;

<sup>b)</sup> Symmetry transformations used to generate equivalent atoms: #1 x-1/2, -y+1/2,z-1/2 #2 - x+3/2, -y+1/2, -z+1 #3 - x+2, y, -z+3/2.

distorted octahedral. In complex 1, bpndc ligand adopts a tridentate mode (see Scheme 1a), bridging three  $Co^{II}$  ions. Because one carboxylate oxygen atom of bpndc bridges two

Table 3 Selected bond lengths/Å and angles/° for complexes 3 and 4

3 <sup>c)</sup>			
Zn(1)-O(1)	2.085(2)	Zn(1)-O(5)#1	2.224(2)
Zn(1)-O(2)	2.239(2)	Zn(1)-N(1)	2.092(2)
Zn(1)-O(4)#1	2.127(2)	Zn(1)-N(2)	2.075(2)
O(1)-Zn(1)-O(2)	60.68(8)	O(2)-Zn(1)-N(2)	94.50(9)
O(1)-Zn(1)-O(4)#1	101.45(8)	O(5)#1-Zn(1)-O(4)#1	60.46(8)
O(1)-Zn(1)-O(5)#1	152.48(9)	O(5)#1-Zn(1)-N(1)	93.42(8)
O(1)-Zn(1)-N(1)	108.93(9)	O(5)#1-Zn(1)-N(2)	92.44(9)
O(1)-Zn(1)-N(2)	107.21(9)	N(1)-Zn(1)-O(4)#1	92.81(9)
O(2)-Zn(1)-O(4)#1	98.89(8)	N(2)-Zn(1)-O(4)#1	151.33(8)
O(2)-Zn(1)-O(5)#1	99.56(8)	N(2)-Zn(1)-N(1)	78.74(9)
O(2)-Zn(1)-N(1)	165.65(8)		
4 <sup>c)</sup>			
Cu(1)-O(1)	2.464(2)	Cu(1)-O(5)#1	1.988(2)
Cu(1)-O(2)	1.976(2)	Cu(1)-N(1)	1.991(2)
Cu(1)-O(4)#1	2.409(2)	Cu(1)-N(2)	1.991(2)
O(1)-Cu(1)-O(2)	58.51(8)	O(5)#1-Cu(1)-O(4)#1	58.75(8)
O(1)-Cu(1)-O(4)#1	157.50(8)	O(5)#1-Cu(1)-N(1)	96.35(9)
O(1)-Cu(1)-O(5)#1	105.36(9)	O(5)#1-Cu(1)-N(2)	162.89(9)
O(1)-Cu(1)-N(1)	108.93(9)	N(1)-Cu(1)-O(4)#1	99.91(9)
O(2)-Cu(1)-O(5)#1	96.54(9)	N(1)-Cu(1)-N(2)	81.39(9)
O(2)-Cu(1)-N(1)	154.95(9)	N(2)-Cu(1)-O(1)	91.75(9)
A (A) A (4) A (4)	02 10(0)	$N(2) C_{2}(1) O(4) \# 1$	104 75(9)
O(2)-Cu(1)-N(2)	92.19(9)	IN(2)-Cu(1)-O(4)#1	104.75(7)

<sup>c)</sup> Symmetry transformations used to generate equivalent atoms: #1 x-1,-y+1/2,z-1/2

 $Co^{II}$  ions, a rhombic  $Co_2O_2$  core is formed, in which the Co<sup>...</sup>Co distance is 3.300 Å. These  $Co_2O_2$  cores are linked by bpndc ligands to form 1D double-stranded chains, as shown in Figure 2a. There are hydrogen bonds between the coordinated water molecules and uncoordinated carboxylate oxygen atoms (the O<sup>...</sup>O distance is 2.742 Å), which results in the formation of 2D layers (see Figure 2b).

Structural description of  $[Co_3(bpndc)_3(2,2'-bpy)_2]_n$ . 0.5n(i-C<sub>3</sub>H<sub>7</sub>OH) (2). There are two kinds of crystallographically independent Co<sup>II</sup> ions in complex 2, as shown in Figure 3. Although both Co(1) and Co(2) are six-coordinated and their coordination can be described as distorted octahedral, their coordination environments are different. Co(1) is surrounded by four oxygen atoms of three bpndc ligands



Figure 1 The coordination environment of Co<sup>II</sup> ion in complex 1 with 30 % thermal ellipsoids, all hydrogen atoms are omitted for clarity.



(a)



Figure 2 (a) The simple representation of 1D double-stranded chain constructed by bpndc ligands linking  $Co_2O_2$  cores in complex 1; (b) The 2D layers formed by 1D chains via hydrogen bonds viewed along the *b* axis (the dotted lines represent hydrogen bonds).

and two nitrogen atoms of one 2,2'-bpy ligand, while Co(2) is coordinated to six oxygen atoms of six bpndc ligands. Co(1) and Co(2) are bridged by three carboxylate groups with the distance of 3.466 Å. Co(2) is in a symmetrical center. So the trinuclear Co(1)Co(2)Co(1B) shown in Figure 3 can be regarded as the second building block. In complex **2**, bpndc ligands adopt two kinds of coordination modes, tetradentate and pentadentate (see Scheme 1c and f). The later has not been reported before. The trinuclear



Figure 4 The representation of 2D catenane-like layer in complex 2 (The ball represents the trinuclear building block, and the line represents bpndc ligand).

building blocks are linked by bpndc ligands to form a 2D (4, 4) grid. It's interesting that in this grid one side is connected by tetradentate bpndc ligand, and the other is double-connected by two pentadentate bpndc ligands.

Noticeably, two such (4,4) grids interpenetrate each other to generate a novel 2D catenane-like layer, as shown in Figure 4. The layers are stacked parallel resulting in the formation of a 3D supramolecular network. There are cavities between the layers, at which free isopropanol molecules are located.

Structural description of  $[Zn(bpndc)(2,2'-bpy)_{2]_n}$  (3). The coordination environment of Zn<sup>II</sup> ion in complex 3 is shown in Figure 5. Each Zn<sup>II</sup> ion is six-coordinated, in which four oxygen atoms come from two bpndc ligands, and two nitrogen atoms come from one 2,2'-bpy ligand. In complex 3, bpndc ligand adopts a new tetradentate mode (see Scheme 1g), and Zn<sup>II</sup> ions are bridged by bpndc ligands forming a 1D infinite helical chain, as shown in Figure 6a. There are  $\pi$ - $\pi$  stacking interactions between the helical chains (the 2,2'-bpy ligands are parallel and the face-to-face distance is 3.51 Å), resulting in the formation of a 3D supramolecular network (see Figure 6b).

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Figure 3 The coordination environment of Co<sup>II</sup> ions in complex 2 with 30 % thermal ellipsoids, all hydrogen atoms are omitted for clarity.



Figure 5 The coordination environment of  $Zn^{II}$  ion in complex 3 with 30 % thermal ellipsoids, all hydrogen atoms are omitted for clarity.



Figure 6 (a) The 1D helical chain in complex 3; (b) The 3D supramolecular structure of complex 3 viewed along the a axis (Every helical chain is represented by one colour).

#### Thermogravimetric analyses

Complexes 1-4 are very stable in air at ambient temperature and almost insoluble in common solvents such as water. alcohol, and acetone. In order to examine their thermal stability, we carried out thermal gravimetric analyses (TGA) of complexes 1 and 2. The result shows that complex 1 is stable up to 208 °C. A weight loss of 3.5 % occurred in the temperature of 208-265 °C corresponds to the loss of the one coordinated water molecule in complex 1 (calc. 3.4 %). While for complex 2, the first weight loss of 2.0 % from 46 to 60 °C corresponds to the loss of free isopropanol molecule (calc. 2.3 %). The low decomposition temperature of complex 2 is consistent with the structure since there are no hydrogen bonds between the free isopropanol molecule and the framework. The further decomposition took place at 340 °C and 320 °C for complexes 1 and 2, respectively, giving the powder of CoO.

# Conclusions

In this work, we report the syntheses and structures of four new coordination polymers,  $[Co(bpndc)(phen)(H_2O)]_n$ 

(1),  $[Co_3(bpndc)_3(2,2'-bpy)_2]_n \cdot 0.5n(i-C_3H_7OH)$  (2), and  $[M(bpndc)(2,2'-bpy)_2]_n$  (M = Zn, 3; Cu, 4). Complex 1 is of 1D double-stranded chains, while complex 2 possesses 2D catenane-like layers, which is contributed to the introduction of different auxiliary terminal ligands phen and 2,2'-bpy. Complexes 3 and 4 are isostructural. Bpndc ligands bridge metal ions forming 1D helical chains. The  $\pi$ - $\pi$  stacking interactions result in the construction of 3D supramolecular networks.

**Supplementary Data.** Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 661654-661657 for **1–4** respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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#### References

- O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* 2003, 423, 705–714.
- [2] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* 2005, 309, 2040–2042.
- [3] M. B. Zhang, J. Zhang, S. T. Zheng, G. Y. Yang, Angew. Chem. 2005, 117, 1409–1412; Angew. Chem. Int. Ed. 2005, 44, 1385–1388.
- [4] S. Hu, J. C. Chen, M. L. Tong, B. Wang, Y. X. Yan, S. R. Batten, Angew. Chem. 2005, 117, 5607–5611; Angew. Chem. Int. Ed. 2005, 44, 5471–5475.
- [5] H. B. Cui, Z. M. Wang, K. Takahashi, Y. Okano, H. Kobayashi, A. Kobayashi, J. Am. Chem. Soc. 2006, 128, 15074–15075.
- [6] X. S. Wang, S. Ma, D. Sun, S. Parkin, H. C. Zhou, J. Am. Chem. Soc. 2006, 128, 16474–16475.
- [7] Z. M. Wang, B. Zhang, K. Inoue, H. Fujiwara, T. Otsuka, H. Kobayashi, M. Kurmoo, *Inorg. Chem.* 2007, 46, 437–445.
- [8] S. M. Humphrey, J. S. Chang, S. H. Jhung, J. W. Yoon, P. T. Wood, Angew. Chem. 2007, 119, 276–279; Angew. Chem. Int. Ed. 2007, 46, 272–275.

- [9] C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. 2004, 116, 1490–1521; Angew. Chem. Int. Ed. 2004, 43, 1466–1496.
- [10] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. 2004, 116, 2388–2430; Angew. Chem. Int. Ed. 2004, 43, 2334–2375.
- [11] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, J. Am. Chem. Soc. 2005, 127, 1504–1518.
- [12] J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, *Inorg. Chem.* 2007, 46, 2988–2997.
- [13] D. R. Xiao, Y. G. Li, E. B. Wang, L. L. Fan, H. Y. An, Z. M. Su, L. Xu, *Inorg. Chem.* 2007, 46, 4158–4166.
- [14] H. Q. Tan, Y. G. Li, Z. M. Zhang, C. Qin, X. L. Wang, E. B. Wang, Z. M. Su, J. Am. Chem. Soc. 2007, 129, 10066-10067.
- [15] J. J. Perry IV, V. C. Kravtsov, G. J. McManus, M. J. Zaworotko, J. Am. Chem. Soc. 2007, 129, 10076-10077.
- [16] S. R. Batten, A. R. Harris, P. Jensen, K. S. Murray, A. Ziebell, *J. Chem. Soc., Dalton Trans.* 2000, 3829–3836.
- [17] F. A. A. Paz, Y. Z. Khimyak, A. D. Bond, J. Rocha, J. Klinowski, Eur. J. Inorg. Chem. 2002, 2823–2828.

- [18] J. F. Ma, J. Yang, G. L. Zheng, L. Li, J. F. Liu, *Inorg. Chem.* 2003, 42, 7531-7534.
- [19] X. J. Cao, R. Li, D. F. Sun, W. H. Bi, Y. Q. Wang, X. Li, M. C. Hong, *Cryst. Growth Des.* **2004**, *4*, 775–780.
- [20] Y. Y. Liu, J. F. Ma, J. Tang, Z. M. Su, Inorg. Chem. 2007, 46, 3027–3037.
- [21] Y. B. Wang, Z. M. Wang, C. H. Yan, L. P. Jin, J. Mol. Struct. 2004, 692, 177–186.
- [22] Y. B. Wang, L. P. Jin, Chin. J. Chem. 2004, 22, 1272-1278.
- [23] C. Y. Sun, L. P. Jin, J. Mol. Struct. 2005, 733, 63-68.
- [24] C. Y. Sun, L. P. Jin, J. Mol. Struct. 2006, 782, 171-176.
- [25] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area detector Data, University of Göttingen, Germany, 1997.
- [26] G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [27] G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.