

Novel Supramolecular Frameworks Self-Assembled from One-Dimensional Polymeric Coordination Chains

Xin Shi,^[a] Guangshan Zhu,^{*[a]} Qianrong Fang,^[a] Gang Wu,^[a] Ge Tian,^[a] Renwei Wang,^[a] Daliang Zhang,^[a] Ming Xue,^[a] and Shilun Qiu^{*[a]}

Keywords: Supramolecular chemistry / Coordination modes / Fluorescence / Polymers

The novel supramolecular frameworks $[\text{Cd}(\text{BDC})(\text{phen})\cdot(\text{H}_2\text{O})]_n$ (**2**) and $[\text{Cd}_2(\text{HBTC})_2(\text{phen})_2]_{2n}\cdot n\text{Cd}(\text{HBTC})(\text{phen})_2$ (**3**) have been synthesized by reaction of the metal source $\text{Cd}(\text{phen})_2(\text{NO}_3)_2$ (**1**) with benzene-1,4-dicarboxylic acid (H_2BDC) and benzene-1,3,5-tricarboxylic acid (H_3BTC), respectively in a mixed solution of DMF/ $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$. The three-dimensional supramolecular structure of **2** is constructed through hydrogen-bond and aromatic π - π interactions between adjacent metal-organic polymeric coordination chains. Conversely, interestingly, the supramolecular

architecture **3** is formed by extending 1-D metal-organic polymeric coordination chains into a 3-D framework by hydrogen-bond interactions between polymeric coordination chains and metal-organic coordination complexes instead of by interchain hydrogen-bond interactions. Additionally, these three compounds exhibit strong fluorescence at room temperature in the solid state.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Metal-organic coordination frameworks with various intriguing topologies have been extensively studied for their versatile chemical and physical properties and potential applications in functional materials.^[1–8] With the development of supramolecular chemistry, self-assembly based on molecules has become an effective approach to construct functional coordination frameworks. Hydrogen bonds provide an ideal synthetic example for the rational design of an organic crystalline framework.^[9] Recently, attempts have been made to combine metal–ligand coordination and hydrogen bond interactions to self-assemble multidimensional metal-organic supramolecular frameworks.^[10–12] Some 3-D supramolecular frameworks have been self-assembled from one-dimensional polymeric coordination chains, which are generated by transition metal ions and multidentate units, through hydrogen bonding and π - π interactions.^[11,12]

Metal-organic coordination compounds as reactants provide not only transition metal ions but also segmental organic ligands in synthesis systems. Hence novel topologies and, particularly, chemical and physical properties may be obtained if metal-organic coordination compounds are used as the metal source to prepare supramolecular frameworks; however, we could not find any reported examples.

We report here the two novel fluorescent supramolecular frameworks $[\text{Cd}(\text{BDC})(\text{phen})(\text{H}_2\text{O})]_n$ (**2**) and $[\text{Cd}_2$

$(\text{HBTC})_2(\text{phen})_2]_{2n}\cdot n\text{Cd}(\text{HBTC})(\text{phen})_2$ (**3**), which are self-assembled from metal-organic coordination compound $\text{Cd}(\text{phen})_2(\text{NO}_3)_2$ (**1**) with benzene-1,4-dicarboxylic acid (H_2BDC) and benzene-1,3,5-tricarboxylic acid (H_3BTC), respectively.

Results and Discussion

Description of Crystal Structure

$\text{Cd}(\text{phen})_2(\text{NO}_3)_2$ (**1**)

In the asymmetric unit of coordination compound **1** (Figure 1) the seven-coordinate cadmium center is chelated by four nitrogen atoms (N1, N2; N3, N4) of two chelating

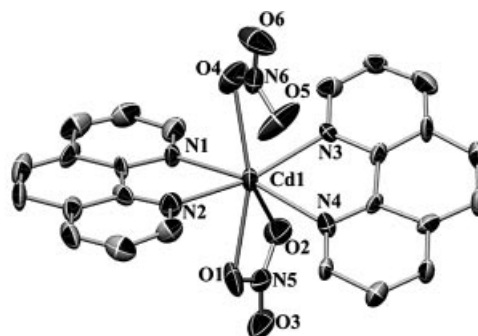


Figure 1. Asymmetry unit of **1**; thermal ellipsoids are drawn at the 50% probability level; all hydrogen atoms are omitted for clarity

^[a] Key Laboratory of Inorganic Synthesis & Preparative Chemistry Jilin University, Changchun 130023, P. R. China
Fax: (internat.) + 86-431-5671974
E-mail: sqiu@mail.jlu.edu.cn

phen ligands and three oxygen atoms (O1, O2; O4) of two NO_3^- anions in different ways.

$[\text{Cd}(\text{BDC})(\text{phen})(\text{H}_2\text{O})]_n$ (**2**)

A single-crystal X-ray analysis revealed that **2** is self-assembled from 1-D zig-zag polymeric coordination chains. In the asymmetric unit of **2**, there are one Cd atom, one BDC ligand, one phen ligand and one coordinated H_2O molecule. [Figure 2 (a)] The cadmium atom is seven-coordinate through coordination to five oxygen atoms (O1, O2; O3, O4; O5) of two chelating carboxylate groups of two BDC ligands, one water molecule and two nitrogen atoms (N1, N2) of one chelating phen ligand. The bond lengths of Cd1–O2 and Cd1–O3 are 2.567 and 2.401 Å, which are longer than those in other cadmium carboxylate coordination polymers.^[13a] The distortion of the Cd–O bond may be due to the severe steric hindrance caused by the bulky phen group.

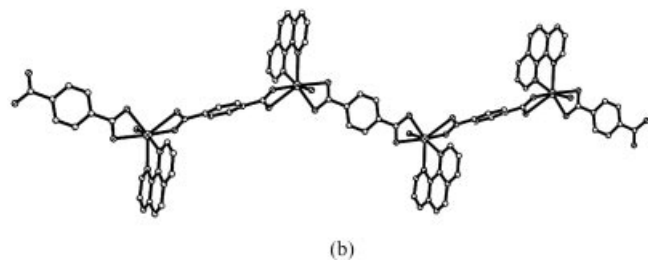
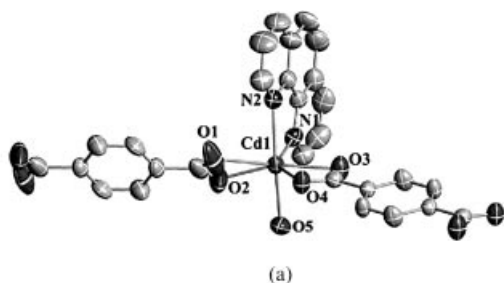


Figure 2. (a) Perspective view of the coordination environment of the cadmium atom in **2**; thermal ellipsoids are drawn at the 50% probability level; all hydrogen atoms are omitted for clarity; (b) 1-D zig-zag polymeric chain

Each BDC ligand bridges two cadmium atoms in bis(bidentate) fashion to form a 1-D infinite zig-zag chain [Figure 2(b)]. The coordinated H_2O molecules of the polymeric chains are well positioned to form interchain hydrogen bonds with the carboxylate oxygen atoms. The oxygen atoms of coordinated H_2O molecules and carboxylate oxygen atoms of BDC ligands from adjacent chains form strong hydrogen bonds ($\text{O2}\cdots\text{O5}$ 2.704 Å), which combine the 1-D zig-zag chains into 2-D undulating layers. Between neighboring 2-D undulating layers, C atoms with hydrogen atoms of phen ligands and carboxylate oxygen atoms of BDC ligands from neighboring layers form interlayer $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds ($\text{C9}-\text{H9}\cdots\text{O4}$). The $\text{C9}\cdots\text{O4}$ in

$\text{C9}-\text{H9}\cdots\text{O4}$ hydrogen bond is 3.219 Å long and the $\text{C9}-\text{H9}\cdots\text{O4}$ angle is 147.20° , which are acceptable according to recent studies.^[12b,14] There are also aromatic $\pi-\pi$ stacking interactions between neighboring undulating layers. The plane–plane distance between adjacent two phen ligands of two neighboring layers is 3.517 Å, which is reasonable.^[12b,15] All lateral phen ligands from neighboring undulating layers are intercalated in a zipper-like manner, which is similar to some previous examples.^[12b,12c] Thus, the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds along with aromatic $\pi-\pi$ interactions further extend the 2-D undulating layers into a 3-D supramolecular framework (Figure 3).

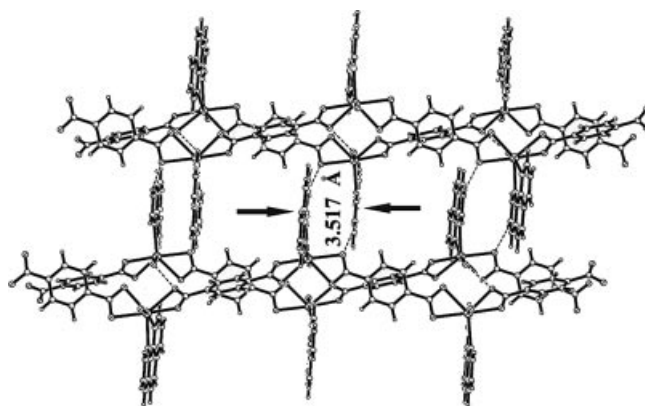


Figure 3. 3-D supramolecular framework along the [010] direction; neighboring undulating 2-D layers are intercalated in a zipper-like manner through $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ interactions

$[\text{Cd}_2(\text{HBTC})_2(\text{phen})_2]_{2n} \cdot n\text{Cd}(\text{HBTC})(\text{phen})_2$ (**3**)

X-ray crystallography reveals that **3** consists of 1-D polymeric coordination chains $[\text{Cd}_2(\text{HBTC})_2(\text{phen})_2]_n$ and metal-organic coordination complexes $n\text{Cd}(\text{HBTC})(\text{phen})_2$. There are three six-coordinate cadmium centers in each asymmetric unit of **3**. Cd1 adopts a distorted octahedral geometry by coordinating to four nitrogen atoms (N1, N2; N3, N4) of two chelating phen ligands and two oxygen atoms (O14; O17) of two monodentate carboxylate groups from two H_3BTC ligands.

Two carboxylate groups from each of two crystallographically equivalent H_3BTC ligands bridge two cadmium atoms (Cd1 and Cd1A) to form a metal-organic coordination complex but the third carboxy group is uncoordinated. From the difference in bond lengths between $\text{C57}-\text{O15}$ [1.209(9) Å] and $\text{C57}-\text{O16}$ [1.326(9) Å] in the uncoordinated carboxy group, $\text{C57}-\text{O15}$ can be assigned to a double bond and $\text{C57}-\text{O16}$ to a single bond, and the hydrogen atom H16 should be linked to O16 [Figure 4 (a)].

Cd2 also adopts a distorted octahedral geometry by coordinating to four oxygen atoms (O1, O2; O5, O8) of one chelating carboxylate group of one H_3BTC ligand, two bis(monodentate) carboxylate groups of two different H_3BTC ligands and two nitrogen atoms (N5, N6) of one chelating phen ligand. The coordination environment of Cd3 is same

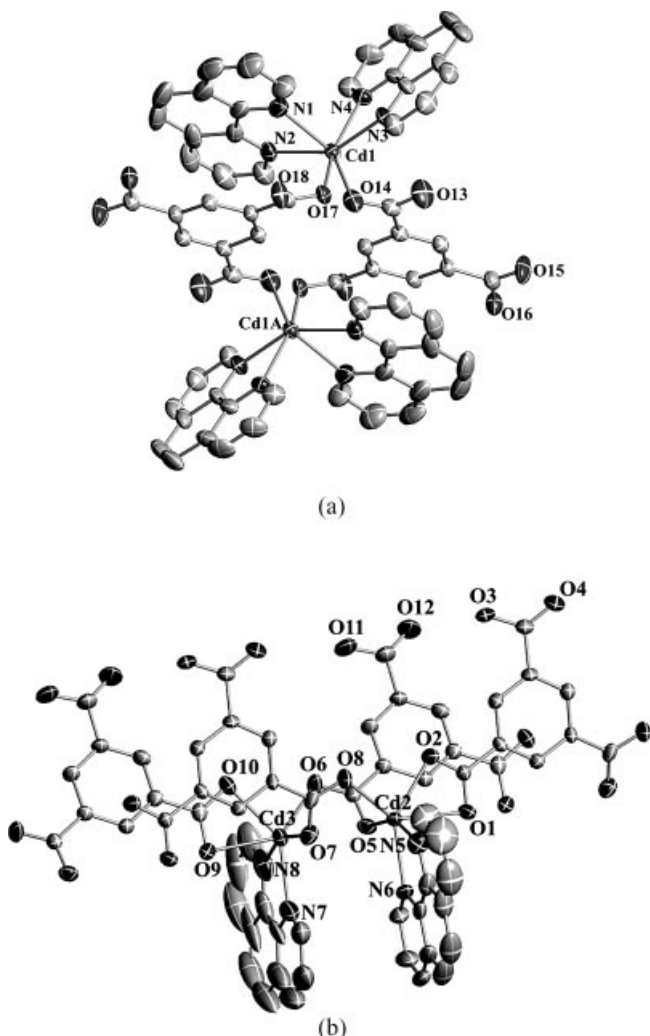


Figure 4. Perspective view of (a) the coordination environment of Cd1 in **3** and (b) the coordination environment of Cd2 and Cd3 in **3**; thermal ellipsoids are drawn at the 50% probability level; all hydrogen atoms are omitted for clarity

as that of Cd2 [Figure 4 (b)]. The bond lengths and angles of Cd–O are similar to those of cadmium trimesate polymers.^[13b]

The coordinated H₃BTC ligands have two unchelated carboxy groups. The C–O bonds [C5–O3 1.298(9) Å, C40–O11 1.303(10) Å] are much longer than C=O [C5–O4 1.203(9) Å, C40–O12 1.195(10) Å] in the carboxy groups, so C5–O4 and C40–O12 can be assigned as double bonds and C5–O3 and C40–O11 as single bonds, with H3 and H11 linked to O3 and O11. The IR spectrum of **3** exhibits a broad band at ca. 3200 cm^{−1}, which is typical of the O–H vibration of a carboxy group. This shows that deprotonation of the H₃BTC ligands is incomplete, which is in good agreement with the uncoordinated carboxy groups in the structure of **3**.

Incompletely deprotonated H₃BTC ligands using the carboxylate functionality link Cd2 and Cd3 to form 1-D infinite polymeric chains [Cd₂(HBTC)₂(phen)₂]_n. Two adjacent 1-D chains are intercalated in a zipper-like manner^[12b,12c] to form a double polymeric chain [Cd₂(HBTC)₂(phen)₂]_{2n}

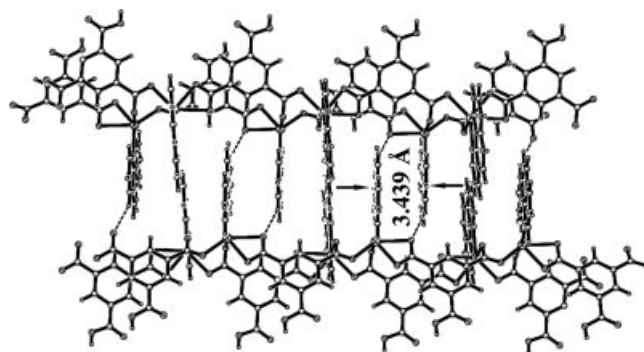


Figure 5. Double chain formed by intercalating two adjacent 1-D chains in a zipper-like manner through hydrogen bonds and π – π interactions

through C–H $\cdots$ O hydrogen bonds (C17 $\cdots$ O1 2.217 Å, C17–H17 $\cdots$ O1 154.77°)^[14] and aromatic π – π stacking interactions (plane–plane distance 3.439 Å)^[15] (Figure 5).

Each double polymeric chain is surrounded by metal-organic coordination complexes (Figure 6). Uncoordinated

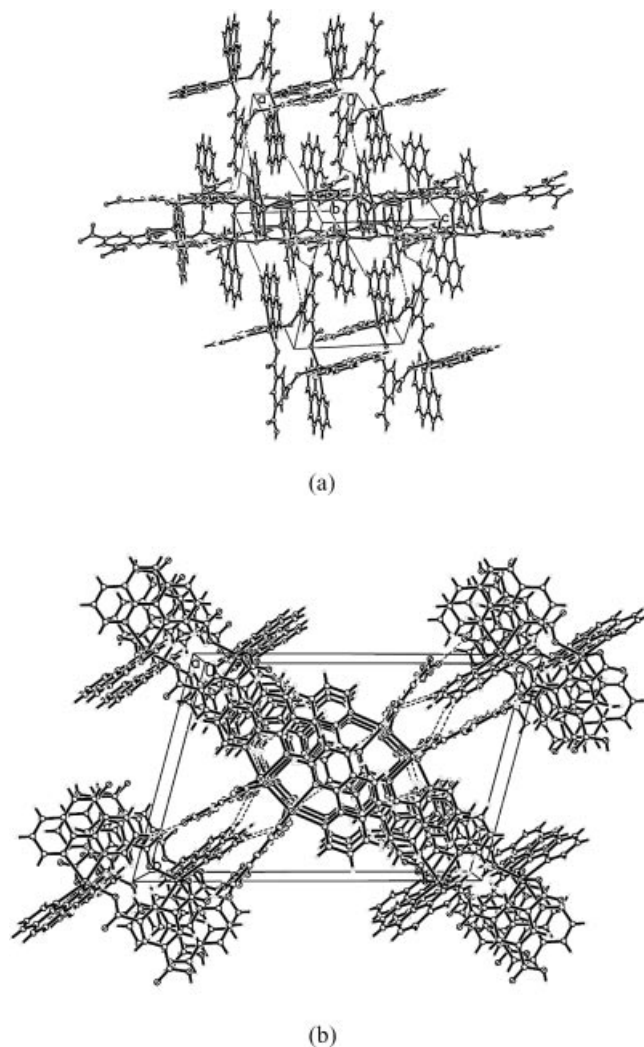


Figure 6. Perspective view of hydrogen bonds between 1-D double polymeric chains and metal-organic coordination complexes from different directions

carboxy oxygen atoms (O3–H3 and O11–H11) of H₃BTC ligands from the double polymeric chains point outward to form hydrogen bonds (O3–H3...O18, O11–H11...O13) with the carboxylate oxygen atoms (O18 and O13) from surrounding metal-organic coordination complexes. At the same time, uncoordinated carboxy oxygen atoms (O16–H16) from the metal-organic coordination complexes are well positioned to form hydrogen bonds (O16–H16...O9) with carboxylate oxygen atoms (O9) from the double polymeric chains. The O...O distances and O–H...O angles are listed in Table 1.

Table 1. O–O distances [Å] and O–H...O angles [°] of O...O hydrogen bonds in **3** (symmetry transformations used to generate equivalent atoms: #1: $x - 1, y, z$; #2: $-x + 1, -y + 1, -z$)

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
O(3)–H(3)...O(18)	0.82	1.73	2.532(7)	166.6
O(11)–H(11)...O(13)#1	0.82	1.77	2.551(8)	158.9
O(16)–H(16)...O(9)#2	0.82	1.82	2.617(7)	163.4

In addition to O...O hydrogen bonds, C–H...O hydrogen bonds exist between double polymeric chains and metal-organic coordination complexes. Double polymeric chains and their surrounding metal-organic coordination complexes intercalate so as to form hydrogen bonds between them. C atoms with hydrogen atoms (C10–H10 and C16–H16a) of a phen ligand from double polymeric chains form C–H...O hydrogen bonds (C10–H10...O18 and C16–H16a...O16) with carboxylate oxygen atoms (O18 and O16) from coordination complexes. Simultaneously, C atoms with hydrogen atoms (C42–H42, C49–H49 and C72–H72) of a phen ligands from coordination complexes also form C–H...O hydrogen bonds (C42–H42...O2, C49–H49...O10 and C72–H72...O12) with carboxylate oxygen atoms (O2, O10 and O12) from double polymeric chains. The C...O distances (2.438–2.546 Å) of C–H...O hydrogen bonds (C10–H10...O18, C16–H16a...O16, C42–H42...O2, C49–H49...O10, C72–H72...O12) and the C–H...O angles (148.22–159.34°) are both within acceptable ranges.^[14] Thus, two kinds of complementary hydrogen bonds form multi-linked hydrogen-bond interactions between double polymeric chains and metal-organic coordination complexes, which ultimately extend one-dimensional double polymeric chains into a three-dimensional supramolecular framework along [011] and [0–11] (Figure 7).

Fluorescent Properties

Solid-state **1**, **2** and **3** exhibit strong fluorescence at room temperature. The free phen·H₂O also fluoresces in the solid state. The emission bands for free phen·H₂O are at 365 and 388 nm ($\lambda_{\text{exc.}} = 310$ nm), which may be attributed to the $\pi^* \rightarrow \pi$ transition [Figure 8 (a)]. Of the emission bands for **1** at 366, 389 and 410 nm ($\lambda_{\text{exc.}} = 384$ nm) [Figure 8 (b)] the first two are obviously due to intraligand charge transfer of coordinated phen ligands, similarly to the emission of free phen·H₂O. The band at 410 nm for **1** is neither LMCT (ligand-to-metal charge transfer) nor MLCT (metal-to-ligand

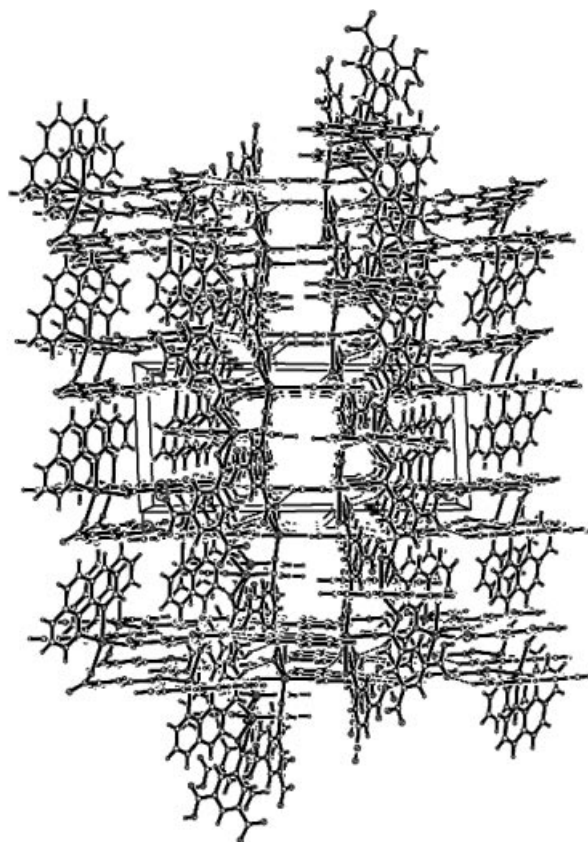


Figure 7. 3-D supramolecular architecture of **3** along [010] direction

charge transfer) in nature, and tentatively can be assigned to the intraligand fluorescent emission of coordinated phen ligands due to the planar configuration of excimeric phen molecules maintained by the cadmium ion.^[16] The emission bands for **2**, at 367, 385 and 404 nm ($\lambda_{\text{exc.}} = 332$ nm), can be assigned like those of **1** [Figure 8 (c)].^[16] It is reported that free H₂BDC and free H₃BTC show fluorescence emission in the solid state. Their emission bands are mainly located at about 390 nm, with a shoulder at 370 nm for free H₃BTC (H₂BDC: $\lambda_{\text{exc.}} = 350$ nm; H₃BTC: $\lambda_{\text{exc.}} = 334$ nm) and are attributed to a $\pi^* \rightarrow n$ transition.^[17] For **2**, the H₂BDC ligands show almost no contribution to the fluorescent emission, due to very weak fluorescent emission, resulting from a $\pi^* \rightarrow n$ transition of H₂BDC, compared with the $\pi^* \rightarrow \pi$ transition of phen and/or fluorescence quenching of carboxy groups of H₂BDC (which are strong electron-withdrawing groups). Interestingly, **3** has a single broad emission band at 380 nm ($\lambda_{\text{exc.}} = 330$ nm), which is obviously different from the multi-bands of **2**, and may tentatively be assigned to intraligand charge transfer of coordinated phen ligands [Figure 8 (d)]. Here H₃BTC ligands also show almost no contribution to the fluorescent emission of **3**, as with **2**. The large difference between the emission bands of **2** and **3**, although they are both mixed-ligand systems, may be due to the uniquely complicated structure of **3**, with attachment of the dicadmium complex to the 1-D polymeric chain through hydrogen bonds. This complicated structure

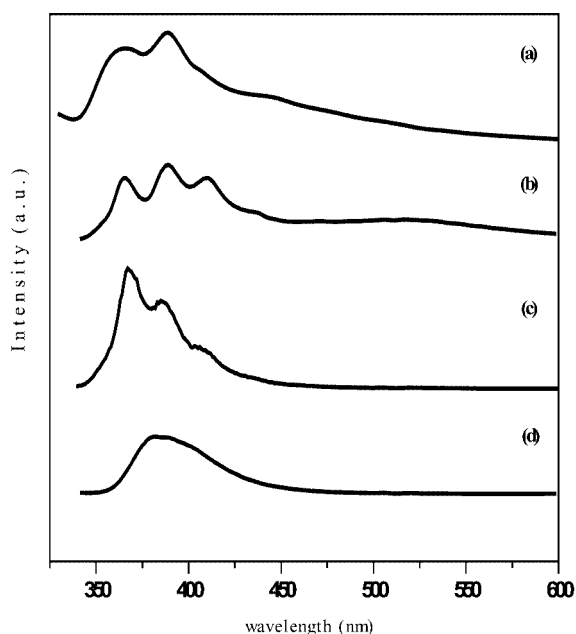


Figure 8. Solid-state fluorescent emission spectra of (a) free phen·H₂O, (b) Cd(phen)₂(NO₃)₂, (c) [Cd(BDC)(phen)(H₂O)]_n and (d) [Cd₂(HBTC)₂(phen)₂]_{2n}·nCd(HBTC)(phen)₂ at room temperature

causes multiple charge-transfer with close transition energies, which might ultimately result in a single broad emission band.

Conclusions

Two 3-D supramolecular frameworks have been synthesized by using a metal-organic coordination compound as the metal source under mild conditions. Notably for **3**, it is the hydrogen-bonding interactions between polymeric coordination chains and coordination complexes that extend the

1-D double chains into a 3-D supramolecular framework – in contrast to previously reported supramolecular structures constructed through interchain hydrogen bonds. Moreover, these compounds exhibit strong fluorescence at room temperature in the solid state.

Experimental Section

General Remarks: Elemental analyses were performed with a Perkin–Elmer 2400 element analyzer, and inductively couple plasma (ICP) analysis with a Perkin–Elmer Optima 3300DV ICP spectrometer. IR spectra were obtained with a Nicolet Impact 410 FTIR spectrometer. Fluorescence spectra were obtained with a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

Preparation

Metal Source Cd(phen)₂(NO₃)₂ (1**):** Synthesis under hydrothermal conditions. The reaction of Cd(NO₃)₂·6H₂O (0.308 g, 1.0 mmol) with 1,10-phenanthroline monohydrate (0.257 g, 1.3 mmol) in a solution of NaOH (10^{−3} mol/L, 10 mL) at 160 °C for 6 d produced large yellow block crystals in 86% yield (0.513 g). C₂₄H₁₆CdN₆O₆ (596.83): calcd. C 48.30, H 2.680, Cd 18.83, N 14.08; found C 48.36, H 2.675, Cd 18.73, N 14.12. IR (KBr): $\tilde{\nu}$ = 3066, 1600, 1588, 1495, 980, 880 cm^{−1}.

Compound 2: Preparation under mild conditions by allowing Cd(phen)₂(NO₃)₂ (0.158 g, 0.25 mmol) and H₂BDC (0.041 g, 0.25 mmol) to react in a solution of *N,N'*-dimethylformamide (DMF) (10.0 mL), absolute ethanol (2.0 mL), and distilled water (3.0 mL) at 55 °C for 4 d to produce large yellow block crystals in 59% yield (0.070 g). C₂₀H₁₄CdN₂O₅ (474.73): calcd. C 50.60, H 2.949, Cd 23.67, N 5.900; found C 50.52, H 2.941, Cd 23.72, N 5.884. IR (KBr): $\tilde{\nu}$ = 3325, 3079, 1625, 1606, 1541, 1418, 1012, 780 cm^{−1}.

Compound 3: Synthesis by allowing Cd(phen)₂(NO₃)₂ (0.158 g, 0.25 mmol) and H₃BTC (0.053 g, 0.25 mmol) to react in a solution of *N,N'*-dimethylformamide (DMF) (10.0 mL), absolute ethanol (2.0 mL), and distilled water (3.0 mL) at 55 °C for 6 d. The result-

Table 2. Crystal data and structure refinement for complexes **1–3**

	1	2	3
Empirical formula	C ₂₄ H ₁₆ CdN ₆ O ₆	C ₂₀ H ₁₄ CdN ₂ O ₅	C ₇₅ H ₄₄ Cd ₃ N ₈ O ₁₈
Formula mass	596.83	474.73	1682.38
Temperature [K]	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	Cc	C2/c	P $\bar{1}$
<i>a</i> [Å]	11.532(2)	25.502(9)	10.192(2)
<i>b</i> [Å]	15.326(3)	9.866(2)	16.074(3)
<i>c</i> [Å]	13.330(3)	21.239(5)	23.747(5)
α [°]	90	90	104.84(3)
β [°]	104.36(3)	125.75(2)	92.26(3)
γ [°]	90	90	90.80(3)
<i>V</i> [Å ³]	2282.4(8)	4337(2)	3756.6(13)
<i>Z</i>	2	4	2
$\rho_{\text{calcd.}}$ [gcm ^{−3}]	0.8680.7271.487		
μ [mm ^{−1}]	0.506	0.518	0.914
Reflections collected	2617	3034	15085
Independent reflections (<i>R</i> _{int})	2482 (0.019)	2698 (0.041)	11446 (0.050)
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0196, 0.0524	0.0617, 0.1862	0.0607, 0.2104

ant colorless block crystals were filtered off, washed with absolute ethanol and dried at room temperature. The yield was about 46% (0.064 g). $C_{75}H_{44}Cd_3N_8O_{18}$ (1682.38): calcd. C 53.54, H 2.615, Cd 20.04, N 6.660; found C 53.58, H 2.620, Cd 20.07, N 6.652. IR (KBr): $\tilde{\nu}$ = 3200, 3058, 1598, 1568, 1409, 998, 860, 676 cm^{-1} .

Single-Crystal Structure Determination: Crystallographic data for **1** and **3** were collected at 293(2) K with a Rigaku R-Axis RAPID IP diffractometer with Mo- K_{α} (λ = 0.71073 Å). Crystallographic data for **2** were collected at 293(2) K with a Bruker-AXS Smart CCD diffractometer with Mo- K_{α} radiation (λ = 0.71073 Å). The

structures were solved by direct methods^[18] and refined by full-matrix least-squares method against F^2 (SHELXL-97).^[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were located geometrically. The crystallographic data for **1–3** are listed in Table 2, and selected bond lengths and angles for **2** and **3** are presented in Tables 3 and 4, respectively. CCDC-216289 for [Cd(phen)₂(NO₃)₂], -216290 for [Cd(BDC)(phen)(H₂O)] and -216291 for [Cd₂(HBTC)₂(phen)₂·Cd(HBTC)(phen)₂] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-0333; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Selected bond lengths [Å] and angles [°] for [Cd(BDC)(phen)(H₂O)]_n

Cd(1)–O(1)	2.242(7)	Cd(1)–O(3)	2.401(5)
Cd(1)–N(2)	2.342(5)	Cd(1)–O(5)	2.408(5)
Cd(1)–O(4)	2.348(5)	Cd(1)–O(2)	2.567(8)
Cd(1)–N(1)	2.363(5)		
O(1)–Cd(1)–N(2)	93.6(3)	N(2)–Cd(1)–O(5)	91.02(19)
O(1)–Cd(1)–O(4)	161.3(2)	O(4)–Cd(1)–O(5)	87.53(17)
N(2)–Cd(1)–O(4)	86.26(18)	N(1)–Cd(1)–O(5)	161.41(17)
O(1)–Cd(1)–N(1)	103.3(2)	O(3)–Cd(1)–O(5)	95.38(18)
N(2)–Cd(1)–N(1)	70.68(18)	O(1)–Cd(1)–O(2)	52.5(3)
O(4)–Cd(1)–N(1)	94.32(18)	N(2)–Cd(1)–O(2)	128.8(2)
O(1)–Cd(1)–O(3)	126.1(3)	O(4)–Cd(1)–O(2)	138.6(2)
N(2)–Cd(1)–O(3)	140.09(17)	N(1)–Cd(1)–O(2)	80.8(2)
O(4)–Cd(1)–O(3)	54.86(17)	O(3)–Cd(1)–O(2)	85.54(19)
N(1)–Cd(1)–O(3)	100.81(18)	O(5)–Cd(1)–O(2)	109.8(2)
O(1)–Cd(1)–O(5)	73.8(2)		

Table 4. Selected bond lengths [Å] and angles [°] for [Cd₂(HBTC)₂(phen)₂]_{2n}·nCd(HBTC)(phen)₂

Cd(1)–O(14)	2.227(5)	Cd(2)–O(5)	2.328(5)
Cd(1)–O(17)	2.288(5)	Cd(2)–N(5)	2.347(7)
Cd(1)–N(3)	2.343(5)	Cd(2)–O(1)	2.459(5)
Cd(1)–N(4)	2.359(6)	Cd(3)–O(6)	2.264(5)
Cd(1)–N(1)	2.424(6)	Cd(3)–O(7)	2.318(5)
Cd(1)–N(2)	2.407(6)	Cd(3)–N(8)	2.337(8)
Cd(2)–O(2)	2.299(5)	Cd(3)–N(7)	2.346(8)
Cd(2)–O(8)	2.294(5)	Cd(3)–O(10)	2.356(6)
Cd(2)–N(6)	2.329(5)	Cd(3)–O(9)	2.433(5)
O(14)–Cd(1)–O(17)	99.1(2)	N(6)–Cd(2)–N(5)	71.2(2)
O(14)–Cd(1)–N(3)	119.1(2)	O(5)–Cd(2)–N(5)	155.6(2)
O(17)–Cd(1)–N(3)	86.04(19)	O(2)–Cd(2)–O(1)	54.24(17)
O(14)–Cd(1)–N(4)	92.0(2)	O(8)–Cd(2)–O(1)	138.50(18)
O(17)–Cd(1)–N(4)	157.12(19)	N(6)–Cd(2)–O(1)	86.67(19)
N(3)–Cd(1)–N(4)	71.1(2)	O(5)–Cd(2)–O(1)	92.3(2)
O(14)–Cd(1)–N(1)	151.4(2)	N(5)–Cd(2)–O(1)	91.6(2)
O(17)–Cd(1)–N(1)	85.0(2)	O(6)–Cd(3)–O(7)	102.9(2)
N(3)–Cd(1)–N(1)	89.3(2)	O(6)–Cd(3)–N(8)	87.3(3)
N(4)–Cd(1)–N(1)	94.8(2)	O(7)–Cd(3)–N(8)	157.9(3)
O(14)–Cd(1)–N(2)	83.2(2)	O(6)–Cd(3)–N(7)	132.7(2)
O(17)–Cd(1)–N(2)	109.30(18)	O(7)–Cd(3)–N(7)	87.9(3)
N(3)–Cd(1)–N(2)	151.3(2)	N(8)–Cd(3)–N(7)	71.1(3)
N(4)–Cd(1)–N(2)	91.8(2)	O(6)–Cd(3)–O(10)	84.57(19)
N(1)–Cd(1)–N(2)	68.9(2)	O(7)–Cd(3)–O(10)	96.28(19)
O(2)–Cd(2)–O(8)	85.31(18)	N(8)–Cd(3)–O(10)	104.3(3)
O(2)–Cd(2)–N(6)	140.71(19)	N(7)–Cd(3)–O(10)	140.6(2)
O(8)–Cd(2)–N(6)	131.9(2)	O(6)–Cd(3)–O(9)	136.61(18)
O(2)–Cd(2)–O(5)	98.95(19)	O(7)–Cd(3)–O(9)	96.73(18)
O(8)–Cd(2)–O(5)	104.1(2)	N(8)–Cd(3)–O(9)	88.7(2)
N(6)–Cd(2)–O(5)	85.0(2)	N(7)–Cd(3)–O(9)	85.8(2)
O(2)–Cd(2)–N(5)	102.8(2)	O(10)–Cd(3)–O(9)	54.81(16)
O(8)–Cd(2)–N(5)	88.5(2)		

Acknowledgments

We are grateful for the financial support of both the State Basic Research Project (G2000077507) and the National Nature Science Foundation of China (Grant no. 29873017 and 20101004).

- [1] [1a] O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484. [1b] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. Reineke, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330.
- [2] [2a] R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, *Science* **2002**, *298*, 2358–2361. [2b] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986.
- [3] [3a] H. L. Li, A. Laine, M. O’Keeffe, O. M. Yaghi, *Science* **1999**, *283*, 1145–1147. [3b] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150. [3c] O. R. Evans, R. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem. Int. Ed.* **1999**, *38*, 536–538. [3d] M. Eddaoudi, J. Kim, M. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472.
- [4] [4a] D. T. Vodak, M. E. Braun, J. Kim, M. Eddaoudi, O. M. Yaghi, *Chem. Commun.* **2001**, 2534–2535. [4b] M. Eddaoudi, J. Kim, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376–377. [4c] C. Z.-J. Lin, S. S.-Y. Chui, S. M.-F. Lo, F. I.-Y. Shek, M. Wu, K. Suwinska, J. Lipkowski, I. D. Williams, *Chem. Commun.* **2002**, 1642–1643. [4d] C. Livage, N. Guillo, J. Marrot, G. Ferey, *Chem. Mater.* **2001**, *13*, 4387–4392. [4e] C. Serre, G. Ferey, *J. Mater. Chem.* **2002**, *12*, 3053–3057.
- [5] [5a] D. P. Cheng, M. A. Khan, R. P. Houser, *Inorg. Chem.* **2001**, *40*, 6858–6859. [5b] X. M. Zhang, M. L. Tong, X. M. Chen, *Angew. Chem. Int. Ed.* **2002**, *41*, 1029–1031. [5c] G. F. Liu, B. H. Ye, Y. H. Ling, X. M. Chen, *Chem. Commun.* **2002**, 1442–1443.
- [6] [6a] S. O. H. Gutschke, D. J. Price, A. K. Powell, P. T. Wood, *Angew. Chem. Int. Ed.* **2001**, *40*, 1920–1923. [6b] S. A. Bourne, J. J. Lu, A. Mondal, B. Moulton, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2001**, *40*, 2111–2113.
- [7] [7a] P. M. Forster, A. K. Cheetham, *Angew. Chem. Int. Ed.* **2002**, *41*, 457–459. [7b] B. Moulton, J. J. Lu, R. Hajndl, S. Hariharan, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2002**, *41*, 2821–2824.
- [8] [8a] S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972. [8b] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.
- [9] [9a] K. T. Holman, A. M. Pivovar, M. D. Ward, *Science* **2001**, *294*, 1907–1911. [9b] O. Félix, M. W. Hosseini, A. De Cian, J. Fischer, *Chem. Commun.* **2000**, 281–282. [9c] R. Custelcean, M. D. Ward, *Angew. Chem. Int. Ed.* **2002**, *41*, 1724–1728.
- [10] [10a] J. C. MacDonald, P. C. Dorrestein, M. M. Pilley, M. M. Foote, J. L. Lundburg, R. W. Henning, A. J. Shultz, J. L. Manson, *J. Am. Chem. Soc.* **2000**, *122*, 11692–11702. [10b] J. C. Nov-

- eron, M. S. Lah, R. E. Del Sesto, A. M. Miller, J. S. Miller, P. J. Stang, *J. Am. Chem. Soc.* **2002**, *124*, 6613–6625.
- [11] [11a] Yong Cui, Helen L. Ngo, Peter S. White, Wenbin Lin, *Inorg. Chem.* **2003**, *42*, 652–654. [11b] Jun-Hua Luo, Mao-Chun Hong, Rui-Hu Wang, Rong Cao, Qian Shi, Jia-Bao Weng, *Eur. J. Inorg. Chem.* **2003**, 1778–1784.
- [12] [12a] Yong Cui, Helen L. Ngo, Peter S. White, Wen-bin Lin, *Chem. Commun.* **2003**, 994–995. [12b] Xiao-Ming Zhang, Ming-Liang Tong, Meng-Linan Gong, Xiao-Ming Chen, *Eur. J. Inorg. Chem.* **2003**, 138–142. [12c] S.-L. Zheng, M.-L. Tong, R.-W. Fu, X.-M. Chen, S. W. Ng, *Inorg. Chem.* **2001**, *40*, 3562–3569.
- [13] [13a] Z.-F. Chen, P. Zhang, R.-G. Xiong, D.-J. Liu, X.-Z. You, *Inorg. Chem. Commun.* **2002**, 35–37. [13b] J.-C. Dai, X.-T. Wu, Z.-Y. Fu, C.-P. Cui, S.-M. Hu, W.-X. Du, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, *Inorg. Chem.* **2002**, *41*, 1391–1396.
- [14] C. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441–449.
- [15] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.
- [16] [16a] J. Zhang, Y.-R. Xie, Q. Ye, R.-G. Xiong, Z.-L. Xue, X.-Z. You, *Eur. J. Inorg. Chem.* **2003**, 2572–2577. [16b] X.-M. Ouyang, D.-J. Liu, T. Okamura, H.-W. Bu, W.-Y. Sun, W.-X. Tang, N. Ueyama, *Dalton Trans.* **2003**, 1836–1845. [16c] Y.-P. Tian, X.-J. Zhang, J.-Y. Wu, H.-K. Fun, M.-H. Jiang, Z.-Q. Xu, A. Usman, S. Chantrapromma, L. K. Thompson, *New. J. Chem.* **2002**, *26*, 1468–1473.
- [17] [17a] W. Chen, J.-Y. Wang, C. Chen, Q. Yue, H. -M. Yuan, J.-S. Chen, S.-N. Wang, *Inorg. Chem.* **2002**, *42*, 944–946.
- [18] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, Göttingen University, Germany, **1997**.
- [19] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen University, Germany, **1997**.

Received June 23, 2003

Early View Article

Published Online October 31, 2003