

Synthesis, Structure, and Fluorescence of the Novel Cadmium(II)–Trimesate Coordination Polymers with Different Coordination Architectures

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Three novel complexes, $\text{Cd}_3\text{tma}_2 \cdot 13\text{H}_2\text{O}$ (**1**), $\text{Cd}_3\text{tma}_2 \cdot \text{dabco} \cdot 2\text{H}_2\text{O}$ (**2**), and $\text{Cd}_3\text{Htma}_3 \cdot 8\text{H}_2\text{O}$ (**3**) (tma = trimesate), of cadmium(II)–trimesate coordination polymers are obtained from hydrothermal reaction. **1** ($\text{C}_{18}\text{H}_{32}\text{O}_{25}\text{Cd}_3$) crystallizes in the monoclinic $C2/c$ space group [$a = 18.985(2)$ Å, $b = 7.3872(6)$ Å, $c = 20.432(2)$ Å, $\beta = 97.1660(10)^\circ$, and $Z = 4$]. **2** ($\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_{14}\text{Cd}_3$) crystallizes in the monoclinic $P2(1)/c$ space group [$a = 10.1323(2)$ Å, $b = 19.5669(5)$ Å, $c = 13.15880(10)$ Å, $\beta = 108.9810(10)^\circ$, and $Z = 4$]. **3** ($\text{C}_{27}\text{H}_{28}\text{O}_{26}\text{Cd}_3$) belongs to the trigonal $P31c$ space group [$a = 15.7547(3)$ Å, $b = 15.7547(3)$ Å, $c = 7.93160(10)$ Å, and $Z = 2$]. The Cd(II) centers in the three complexes are bridged by tma ligands in the coordination fashion of unidentate, bridging unidentate, bidentate, chelating bis-bidentate, chelating/bridging bis-bidentate, or chelating/bridging bidentate to form the T-shaped molecular bilayer motif for **1**, chicken-wire-like motif for **2**, and honeycomb-like porous structure for **3**, respectively, in which the T-shaped molecular bilayer motif and chicken-wire-like motif are further interlinked in interdigitating or alternating fashion to construct the different coordination architectures. These three complexes exhibit strong fluorescent emission bands at 355 nm ($\lambda_{\text{ex}} = 220$ nm) for **1**, 437 nm ($\lambda_{\text{ex}} = 365$ nm) for **2**, and 353 nm ($\lambda_{\text{ex}} = 218$ nm) for **3** in the solid state at room temperature.

Introduction

Coordination polymer solids are currently of considerable interest and importance because of the scope they offer for the generation by design of new materials with a range of potentially useful properties.^{1,2} Some very interesting examples of coordination solids with cyclic structures based

on the concept of molecular squares using metal ions and bridging ligands containing N-donors such as 4,4'-bipyridine, 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl)ethane, pyrazine, and related species have been reported.^{3–6} Another approach to obtain analogic coordination polymers with

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cavity or porosity structures⁷ is the reaction of metal ions with multifunctional ligands containing O-donors such as polycarboxylates.⁸ As a building block to construct some porous or cyclic coordination polymer, trimesate (tma) ligand exhibits a variety of coordination fashions⁹ and the capability of forming coordination architectures^{1g,8a-c} of diverse sizes and shapes. Although there have been a lot of reports^{1g,8a,9,10} on the infinite 1D, 2D, and 3D coordination solids assembled by trimesate, so far their functionalities remain, with the exception of a few reports,¹¹ largely unexplored. We have been particularly concerned with the functionalities of coordination polymer solids introduced by different coordination architectures, and wish to prepare some materials with an excellent photoactivity. In this paper, we report three novel compounds of cadmium(II)–trimesate coordination polymers, displaying strong fluorescent emissions, based on different coordination architectures.

Experimental Section

General Considerations. All the syntheses were performed in poly(tetrafluoroethylene)-lined stainless steel autoclaves under autogenous pressure. Chemicals were commercially purchased and used as received. Infrared spectra were recorded on a Magna 750 spectrometer using KBr pellets, elemental analyses were carried out by the Elemental Analysis Laboratory of our Institute, fluorescent data were collected on an Edinburgh FL-FS920 TCSPC system by the Spectroscopy Laboratory of Fuzhou University, and TGA (thermal gravimetric analysis) was performed under nitrogen with a heating rate of 10 °C·min⁻¹ using a TA5200/MDSC2910 system by the Thermal Analysis Laboratory of Huaqiao University.

Cd₃tma₂·13H₂O (1). Complex **1** was synthesized hydrothermally from the static reaction of cadmium acetate dihydrate, H₃tma, Na₂tp (tp = terephthalate), and water in a molar ratio of 3:1:2:278 at 180 °C for 2 days, and then the reactant was cooled at a rate of ca. 3 °C·h⁻¹ to give a 12% yield of **1** based on Cd as primrose yellow crystals, which were collected by mechanical isolation and washed with water and absolute alcohol. Anal. Calcd (Found): C, 21.93 (21.49); O, 40.58 (40.06); H, 3.27 (3.18). IR (KBr pellet, cm⁻¹): 3400(vs, br), 2470(vw, sh), 2378(vw), 2351(vw), 2301(vw, br),

1876(w), 1618(vs), 1564(vs), 1439(vs), 1367(vs), 1205(m), 1109(s), 1059(w), 1020(vw), 1001(w), 937(m), 895(m), 833(m), 795(s), 760(vs), 733(vs), 532(s), 461(m), 424(m).

Cd₃tma₂·dabco·2H₂O (2). Similar to the preparation of **1**, the hydrothermal reaction of cadmium acetate dihydrate, H₃tma, dabco, and water in a molar ratio of 3:1:2:278 was performed at 200 °C for 4 days, and then the reactant was cooled at a rate of 3.5 °C·h⁻¹ to give a ca. 48% yield of **2** based on Cd as primrose yellow platelike crystals, which were mechanically separated from the reaction mixture of white solid and washed with water and absolute alcohol. The sample was allowed to air-dry and was stable indefinitely in air. Anal. Calcd (Found): C, 32.04 (32.18); N, 3.11 (3.02); O, 24.90(24.65); H, 2.46 (2.39). IR (KBr pellet, cm⁻¹): 3442(vs), 1622(vs), 1560(vs), 1439(vs), 1371(vs), 1245(vw, sh), 1205(w), 1184(vw), 1169(vw), 1109(m), 1053(m), 1024(w), 995(w), 935(w), 845(w), 764(s), 733(vs), 677(m), 607(m), 523(m).

Cd₃Htma₃·8H₂O (3). Similar to the synthesis of **1**, the hydrothermal reaction of cadmium acetate dihydrate, H₃tma, hexamethylenetetraamine, and water in a molar ratio of 3:1:2:278 was performed at 200 °C for 4 days, and then the reactant was cooled at a rate of 3.5 °C·h⁻¹. The resulting colorless crystals were mechanically separated from the reaction mixture of white powder and then washed with water and absolute alcohol to give a ca. 14% yield of **3** based on Cd. Anal. Calcd (Found): C, 29.33 (29.22); O, 37.62 (37.46); H, 2.55 (2.53). IR (KBr pellet, cm⁻¹): 3431(s, sh), 3215(s, br), 1650(vw), 1612(vs), 1551(vs), 1441(vs), 1371(vs), 1109(m), 931(w), 839(w), 808(w), 768(s), 735(vs), 586(vw), 523(m), 445(m).

Crystallographic Studies. Intensity data for the three complexes were collected at 293(2) K on a Siemens Smart CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97¹² and were refined by full-matrix least-squares methods using SHELXL-97.¹³ Anisotropic displacement parameters were refined for all non-hydrogen atoms. No attempt was made to locate the hydrogen atoms of water; the other hydrogen atoms were added in the riding model and not refined. Final $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, and $R_w = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ [where $P = (F_o^2 + 2F_c^2)/3$]. The structure for **1** has not gotten a satisfying reliability factor ($R = 0.0814$), probably as a result of the presence of 13 water molecules. The crystallographic data are summarized in Table 1, and the selected bond lengths and bond angles of the three complexes are listed in Tables 2 and 3, respectively.

Results and Discussion

Comments on the Synthesis and Crystal Structures. As mentioned above, tma has a great ability to construct coordination architectures with metal ions, adopting several different coordination fashions, ranging from unidentate to chelating to bridging, sometimes in more than one way in the same architecture. Chart 1 shows four coordination fashions of tma observed in this work. Although the synthetic conditions are very similar, complexes **1–3** exhibit different architectures displaying different coordination fashions.

For complex **1**, one bonding carboxylate group is unidentate and the others are chelating bis-bidentate in the coordination fashions of tma (Chart 1a). As shown in Figure

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Table 1. Crystal, Data Collection, and Structure Refinement Parameters for **1**–**3**

	1	2	3
empirical formula	C ₁₈ H ₃₂ O ₂₅ Cd ₃	C ₂₄ H ₂₂ N ₂ O ₁₄ Cd ₃	C ₂₇ H ₂₈ O ₂₆ Cd ₃
fw	985.64	899.64	1105.69
cryst syst	monoclinic	monoclinic	trigonal
space group	C2/c	P2(1)/c	P31c
<i>a</i> , Å	18.985(2)	10.1323(2)	15.7547(3)
<i>b</i> , Å	7.3872(6)	19.5669(5)	15.7547(3)
<i>c</i> , Å	20.432(2)	13.15880(10)	7.93160(10)
α (deg)	90.00	90.00	90.00
β (deg)	97.1660(10)	108.9810(10)	90.00
γ (deg)	90.00	90.00	120.00
<i>V</i> , Å ³	2843.1(4)	2466.98(8)	1704.95(5)
<i>Z</i>	4	4	2
ρ _{calcd} , g·cm ⁻³	2.303	2.422	2.154
<i>T</i> , K	293(2)	293(2)	293(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
μ, cm ⁻¹	0.2333	0.2647	0.1964
<i>R</i> ^a	0.0814	0.0397	0.0267
<i>R</i> _w ^b	0.1972	0.0978	0.0576

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$, ^b $R_w = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) for **1**^a, **2**^b and **3**^c

Complex 1			
Cd(1)–O(3)	2.239(10)	Cd(2)–O(10)	2.287(10)
Cd(1)–O(3b)	2.239(10)	Cd(2)–O(11)	2.287(14)
Cd(1)–O(7)	2.270(13)	Cd(2)–O(1)	2.293(12)
Cd(1)–O(7b)	2.270(13)	Cd(2)–O(12)	2.296(12)
Cd(1)–O(8)	2.276(19)	Cd(2)–O(2)	2.532(11)
Cd(2)–O(5a)	2.261(11)	Cd(2)–O(6a)	2.614(12)
Complex 2			
Cd(1)–O(13)	2.260(5)	Cd(2)–O(2)	2.330(5)
Cd(1)–O(1)	2.316(5)	Cd(2)–O(21)	2.361(5)
Cd(1)–O(15)	2.339(5)	Cd(2)–N(1)	2.441(6)
Cd(1)–O(24)	2.355(5)	Cd(3)–O(25)	2.216(6)
Cd(1)–O(22)	2.361(5)	Cd(3)–O(1)	2.220(5)
Cd(1)–O(21)	2.513(5)	Cd(3)–O(23)	2.366(6)
Cd(2)–O(11)	2.241(5)	Cd(3)–O(24c)	2.423(6)
Cd(2)–O(14)	2.299(5)	Cd(3)–O(15c)	2.465(5)
Cd(2)–O(1)	2.327(5)	Cd(3)–O(26)	2.536(6)
Complex 3			
Cd(1)–O(5)	2.210(4)	Cd(1)–O(4)	2.384(5)
Cd(1)–O(3)	2.299(5)	Cd(1)–O(3a)	2.457(5)
Cd(1)–O(1)	2.345(5)	O(3)–Cd(1d)	2.457(5)
Cd(1)–O(2)	2.356(5)		

^a Key: (a) *x* – 1/2, *y* – 1/2, *z*; (b) –*x*, *y*, –*z* + 3/2. ^b Key: (c) *x*, –*y* + 3/2, *z* – 1/2. ^c Key: (a) *y*, *x*, *z* + 1/2; (d) *y*, *x*, *z* – 1/2.

1, the fundamental building unit of the crystal structure for **1** is composed of two different Cd(II) centers (Cd1, Cd2) that are linked by tma ligands, in which the Cd1 center is five-coordinated by three aqua molecules (O7, O7b, O8) as well as two oxygen atoms (O3, O3b) belonging to two different unidentate carboxylate groups from two separated tma ligands, and the other Cd(II) center (Cd2) is seven-coordinated by three other aqua molecules (O10, O11, O12) as well as four oxygen atoms (O1 and O2, O5a and O6a) of two different chelating bis-bidentate carboxylate groups from two separated tma ligands. The remaining water molecule (O001) is in an isolated form and not linked to the building unit. In such a way, each fundamental building unit of the crystal structure is linked to the others to form a typical T-shaped molecular bilayer motif^{6a} subunit (Figure 2a,b), which is, to our knowledge, still rare so far. The adjacent

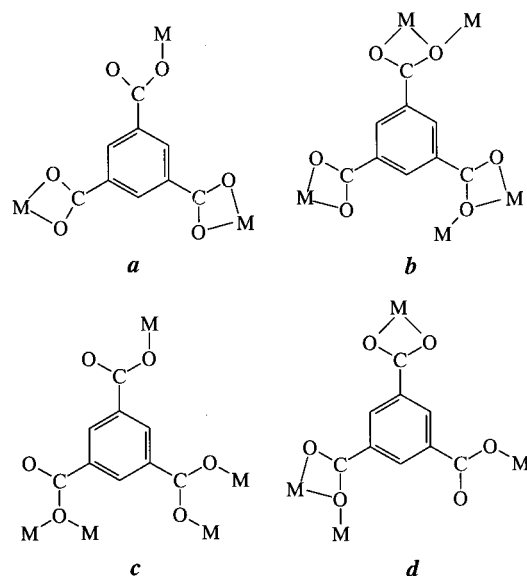
Table 3. Selected Bond Angles (deg) for **1**^a, **2**^b and **3**^c

Complex 1			
O(3)–Cd(1)–O(3b)	171.0(7)	O(5a)–Cd(2)–O(12)	96.5(5)
O(3)–Cd(1)–O(7)	80.5(5)	O(10)–Cd(2)–O(12)	82.8(5)
O(3b)–Cd(1)–O(7)	105.9(4)	O(11)–Cd(2)–O(12)	173.1(5)
O(3)–Cd(1)–O(7b)	105.9(4)	O(1)–Cd(2)–O(12)	86.7(5)
O(3b)–Cd(1)–O(7b)	80.5(4)	O(5a)–Cd(2)–O(2)	136.5(4)
O(7)–Cd(1)–O(7b)	93.3(8)	O(10)–Cd(2)–O(2)	86.5(4)
O(3)–Cd(1)–O(8)	85.5(3)	O(11)–Cd(2)–O(2)	82.9(4)
O(3b)–Cd(1)–O(8)	85.5(3)	O(1)–Cd(2)–O(2)	52.7(4)
O(7)–Cd(1)–O(8)	133.4(4)	O(12)–Cd(2)–O(2)	90.2(4)
O(7b)–Cd(1)–O(8)	133.4(4)	O(5a)–Cd(2)–O(6a)	52.5(4)
O(5a)–Cd(2)–O(10)	136.9(5)	O(11)–Cd(2)–O(6a)	84.7(4)
O(5a)–Cd(2)–O(11)	89.2(5)	O(11)–Cd(2)–O(6a)	89.6(4)
O(10)–Cd(2)–O(11)	95.7(6)	O(1)–Cd(2)–O(6a)	137.3(4)
O(5a)–Cd(2)–O(1)	84.8(4)	O(12)–Cd(2)–O(6a)	97.0(4)
O(10)–Cd(2)–O(1)	137.8(4)	O(2)–Cd(2)–O(6a)	167.8(4)
O(11)–Cd(2)–O(1)	90.0(6)		
Complex 2			
O(13)–Cd(1)–O(1)	97.00(19)	O(2)–Cd(2)–O(21)	165.58(19)
O(13)–Cd(1)–O(15)	127.49(19)	O(11)–Cd(2)–N(1)	89.4(2)
O(1)–Cd(1)–O(15)	107.03(19)	O(14)–Cd(2)–N(1)	77.5(2)
O(13)–Cd(1)–O(24)	83.3(2)	O(1)–Cd(2)–N(1)	165.59(19)
O(1)–Cd(1)–O(24)	175.54(18)	O(2)–Cd(2)–N(1)	84.7(2)
O(15)–Cd(1)–O(24)	76.08(19)	O(21)–Cd(2)–N(1)	95.9(2)
O(13)–Cd(1)–O(22)	146.2(2)	O(25)–Cd(3)–O(1)	145.01(19)
O(1)–Cd(1)–O(22)	90.82(19)	O(25)–Cd(3)–O(23)	91.0(2)
O(15)–Cd(1)–O(22)	80.4(2)	O(1)–Cd(3)–O(23)	108.5(2)
O(24)–Cd(1)–O(22)	86.5(2)	O(25)–Cd(3)–O(24c)	127.67(19)
O(13)–Cd(1)–O(21)	95.21(18)	O(1)–Cd(3)–O(24c)	86.93(18)
O(1)–Cd(1)–O(21)	78.59(17)	O(23)–Cd(3)–O(24c)	55.06(18)
O(15)–Cd(1)–O(21)	134.51(18)	O(25)–Cd(3)–O(15c)	90.4(2)
O(24)–Cd(1)–O(21)	96.95(17)	O(1)–Cd(3)–O(15c)	107.33(18)
O(22)–Cd(1)–O(21)	54.15(19)	O(23)–Cd(3)–O(15c)	112.80(18)
O(13)–Cd(1)–Cd(2)	81.00(13)	O(24c)–Cd(3)–O(15c)	72.56(18)
O(11)–Cd(2)–O(14)	163.6(2)	O(25)–Cd(3)–O(26)	55.16(19)
O(11)–Cd(2)–O(1)	104.63(19)	O(1)–Cd(3)–O(26)	92.65(18)
O(14)–Cd(2)–O(1)	88.15(19)	O(23)–Cd(3)–O(26)	137.07(18)
O(11)–Cd(2)–O(2)	77.8(2)	O(24c)–Cd(3)–O(26)	166.49(19)
O(14)–Cd(2)–O(2)	110.1(2)	O(15c)–Cd(3)–O(26)	94.75(19)
O(1)–Cd(2)–O(2)	101.37(19)	Cd(3)–O(1)–Cd(1)	109.5(2)
O(11)–Cd(2)–O(21)	87.74(19)	Cd(3)–O(1)–Cd(2)	127.1(2)
O(14)–Cd(2)–O(21)	84.04(19)	Cd(1)–O(1)–Cd(2)	96.90(19)
O(1)–Cd(2)–O(21)	81.55(18)	Cd(2)–O(21)–Cd(1)	90.90(17)
Complex 3			
O(5)–Cd(1)–O(3)	85.26(17)	O(1)–Cd(1)–O(4)	79.56(18)
O(5)–Cd(1)–O(1)	178.91(18)	O(2)–Cd(1)–O(4)	131.95(17)
O(3)–Cd(1)–O(1)	94.21(19)	O(5)–Cd(1)–O(3a)	90.45(16)
O(5)–Cd(1)–O(2)	123.53(17)	O(3)–Cd(1)–O(3a)	135.95(12)
O(3)–Cd(1)–O(2)	113.36(17)	O(1)–Cd(1)–O(3a)	90.58(18)
O(1)–Cd(1)–O(2)	55.83(18)	O(2)–Cd(1)–O(3a)	105.42(17)
O(5)–Cd(1)–O(4)	101.32(18)	O(4)–Cd(1)–O(3a)	53.73(16)
O(3)–Cd(1)–O(4)	84.19(17)		

^a Key: (a) *x* – 1/2, *y* – 1/2, *z*; (b) –*x*, *y*, –*z* + 3/2. ^b Key: (c) *x*, –*y* + 3/2, *z* – 1/2. ^c Key: (a) *y*, *x*, *z* + 1/2.

bilayer subunits are further interdigitated with each other to generate a 2D coordination architecture (Figure 2c).

For complex **2**, the tma ligand has two coordination fashions. In one fashion the ligand contains a chelating bidentate carboxylate group and two chelating/bridging bis-bidentate carboxylate groups (Chart 1b). In the other the ligand has three different carboxylate groups which are unidentate, bridging unidentate, and bidentate (Chart 1c). The local coordination environment around the Cd(II) centers (Cd1, Cd2, Cd3) is depicted in Figure 3. Each Cd(II) atom is in a distorted octahedral coordination geometry, and three Cd centers are bridged by a capped μ₃-O atom (O1) [Cd1–O1 = 2.316(5) Å, Cd2–O1 = 2.327(5) Å, and Cd3–O1

Chart 1. Coordination Fashions of tma^{3-} 

^a Key: (a) chelating bis-bidentate and unidentate; (b) chelating/bridging bis-bidentate and chelating bidentate; (c) unidentate, bridging unidentate, and bidentate; (d) chelating bidentate, chelating/bridging bidentate, and unidentate.

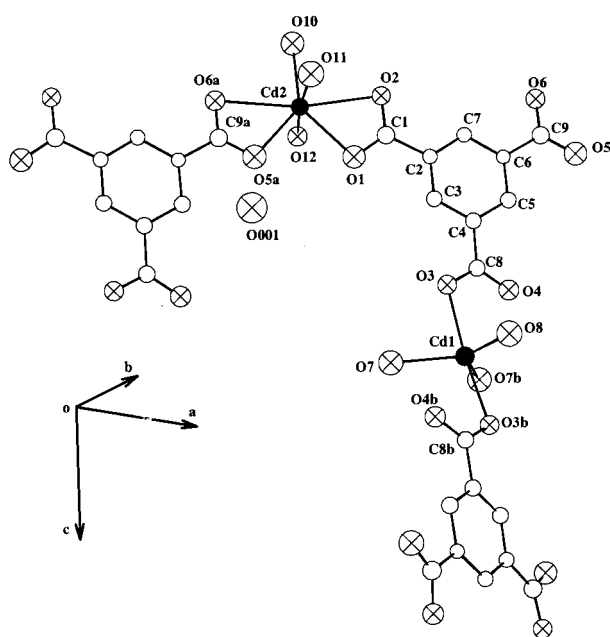


Figure 1. ORTEP drawing (at 50% probability) of the coordination environment of Cd1 and Cd2 in **1**: (a) $x - 1/2, y - 1/2, z$; (b) $-x, y, -z + 3/2$.

$=2.220(5) \text{ \AA}$] to construct a trinuclear Cd_3O core with a distorted triangular prism, in which the distances of $\text{Cd}\cdots\text{Cd}$ separation are 3.475 \AA ($\text{Cd1}\cdots\text{Cd2}$), 3.704 \AA ($\text{Cd1}\cdots\text{Cd3}$), and 4.072 \AA ($\text{Cd2}\cdots\text{Cd3}$). The Cd1 atom is coordinated by six oxygen atoms, three [(O21, O22) and (O24)] of which come from two different chelating/bridging bidentate carboxylate groups (Chart 1b) of two separated tma ligands. The others come from a bridging unidentate (O15) and a bidentate (O13) carboxylate group (Chart 1c) of two different tma ligands with the exception of a unitary $\mu_3\text{-O}$ atom (O1). Different from Cd1, besides coordination with five oxygen atoms, a $\mu_3\text{-O}$ atom (O1), an O atom from the terminal aqua

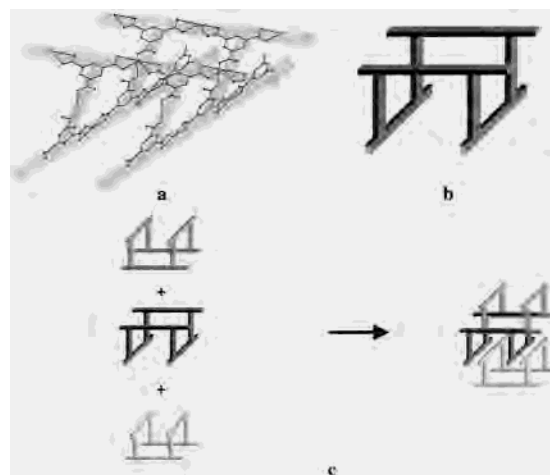


Figure 2. (a) A view of the T-shaped molecular bilayer in **1**. Hydrogen atoms, guests, and coordination water molecules are omitted for clarity. (b) Schematic diagram showing a pillared bilayer motif based upon **1**. (c) The 3-fold interdigitation model for **1**.

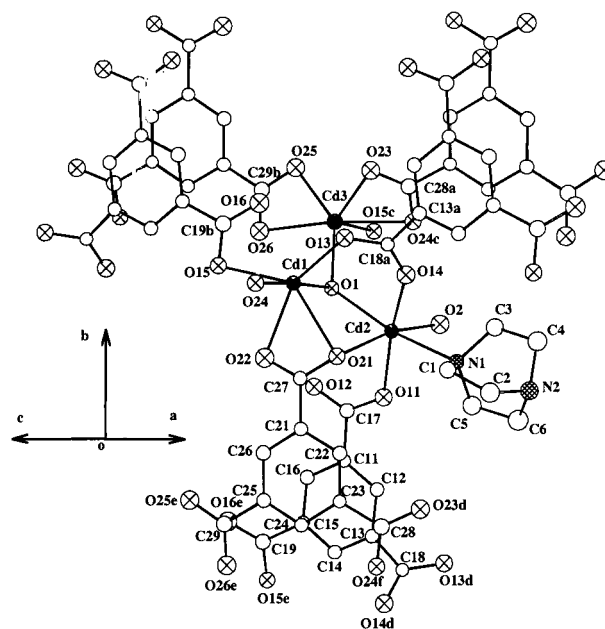


Figure 3. ORTEP drawing (at 50% probability) of **2** around the Cd centers: (a) $-x + 1, y + 1/2, -z + 1/2$; (b) $-x, y + 1/2, -z + 1/2$; (c) $x, -y + 3/2, z - 1/2$; (d) $-x + 1, y - 1/2, -z + 1/2$; (e) $-x, y - 1/2, -z + 1/2$; (f) $-x + 1, -y + 1, -z + 1$.

molecule (O2), and unidentate (O11), chelating/bridging bidentate (O21), and bidentate (O14) oxygens of three different carboxylate groups of three separated tma ligands, the six-coordinated Cd2 atom is bound by a nitrogen (N1) atom from a dabco molecule. The Cd3 atom is also six-coordinated by six oxygen atoms from chelating bidentate (O25, O26), chelating/bridging bidentate (O23, O24c), and bridging unidentate (O15c) carboxylate groups of three separated tma ligands as well as a $\mu_3\text{-O}$ atom (O1). In this way, the fundamental building units, which are constructed by two tma ligands with two coordination fashions (Chart 1b,c) and three Cd(II) centers (Cd1, Cd2, and Cd3), of the crystal structure for **2** are interconnected along the ab plane to yield an interesting “chicken-wire-like” motif subunit with a cavity dimension of ca. $8 \times 8 \text{ \AA}$ (Figure 4a,b). These

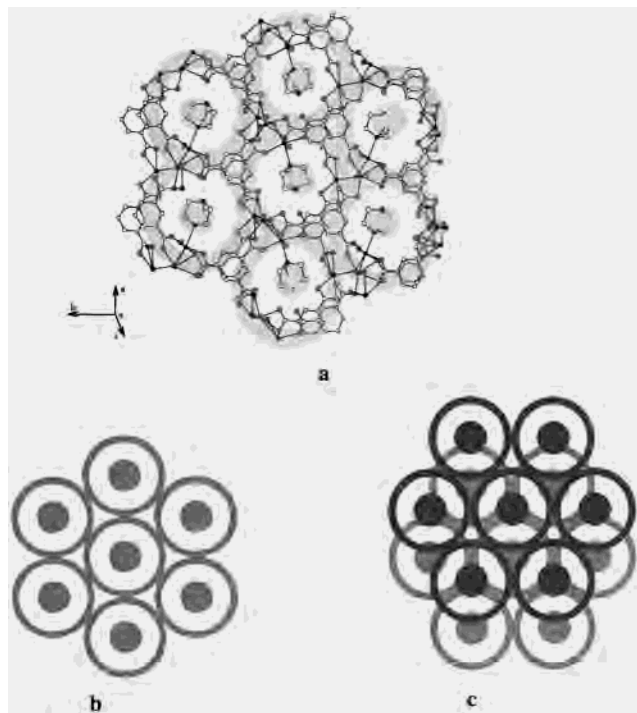


Figure 4. (a) A side view of a single network sheet subunit of **2**. Hydrogen atoms and coordination water molecules are omitted for clarity. (b) Schematic diagram showing a chicken-wire-like motif based upon **2**. (c) The 2-fold alternate sheets model for **2**.

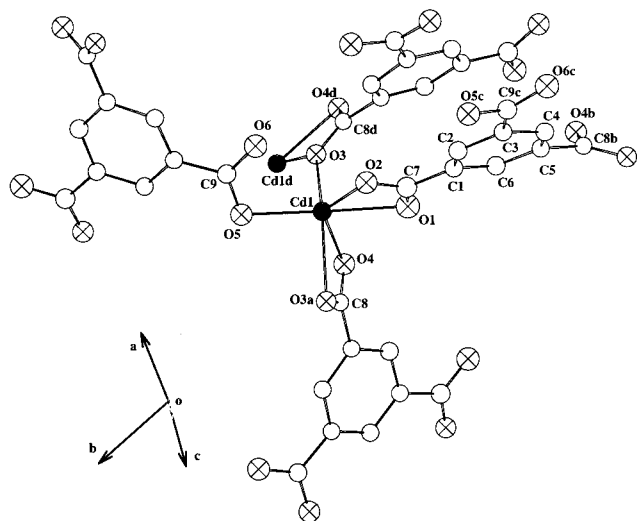


Figure 5. Local coordination of Cd1 in **3** (at 50% probability): (a) $y, x, z + 1/2$; (b) $-x + y, -x, z$; (c) $-x + 1, -x + y, z + 1/2$; (d) $y, x, z - 1/2$.

adjacent chicken-wire-like sheet subunits are further linked alternately to stack in a 3D coordination framework (Figure 4c).

Figure 5 reveals the local coordination of the Cd(II) center (Cd1) in complex **3**. Each tma ligand in **3** has three carboxylate groups with different coordination fashions—chelating/bridging bidentate, chelating bidentate, and unidentate (Chart 1d). Each tma ligand coordinates to four Cd1 centers through the three different coordination fashions mentioned above. Each six-coordinated Cd1 atom connects to six oxygen atoms belonging to four different carboxylate groups of four separated tma ligands, where three oxygen

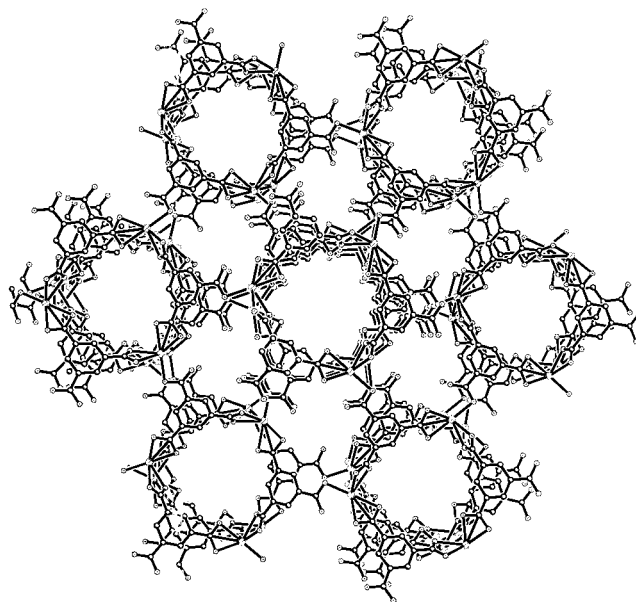


Figure 6. Honeycomb-like channels in **3** viewed along the c axis.

atoms (O3a, O4, and O3) come from two different chelating/bridging bidentate carboxylate groups, two oxygen atoms (O1, O2) come from a chelating bidentate carboxylate group, and one oxygen atom (O5) belongs to a unidentate carboxylate group (Figure 5). Extension of the coordination geometry around each Cd1 center and each tma ligand will therefore give a 3D “honeycomb-like” porous coordination polymer with channel dimensions of ca. $8 \times 8 \text{ \AA}$ (Figure 6).

The elemental analysis data for the three complexes are consistent with the formulas of $\text{Cd}_3\text{tma}_2 \cdot 13\text{H}_2\text{O}$ (**1**), $\text{Cd}_3\text{tma}_2 \cdot \text{dabco} \cdot 2\text{H}_2\text{O}$ (**2**), and $\text{Cd}_3\text{Htma}_3 \cdot 8\text{H}_2\text{O}$ (**3**). The IR spectra of these complexes show the characteristic bands of the tma ligand at $1622\text{--}1551 \text{ cm}^{-1}$ for the asymmetric vibration and at $1441\text{--}1367 \text{ cm}^{-1}$ for the symmetric vibration, and the broad bands of water at $3215\text{--}3442 \text{ cm}^{-1}$. The absence of the expected characteristic bands at $1730\text{--}1690 \text{ cm}^{-1}$ attributed to the protonated carboxylate groups indicates the complete deprotonation of H_3tma on the reactions with Cd ions.¹⁴ For **2**, the absorption vibrations for the dabco ligand appeared at $1245\text{--}1024 \text{ cm}^{-1}$. The TGA of **1** shows an obvious weight loss starting at $246 \text{ }^\circ\text{C}$. Water removal continues up to $419 \text{ }^\circ\text{C}$ to give a total approximately 23.7% weight loss, corresponding to loss of 13 H_2O molecules per formula unit. The complete decomposition of **1** is finished at ca. $530 \text{ }^\circ\text{C}$. This suggests that the aqua ligands are strongly coordinated, which is consistent with the structure of **1** (also see Figure 1), and accounts for complex **1** being rather stable. Similarly, complex **2** shows an obvious weight loss starting at ca. $81 \text{ }^\circ\text{C}$ of the TGA trace with a large decline stage up to ca. $427 \text{ }^\circ\text{C}$ to give a total weight loss of ca. 16.0%, corresponding to loss of 2 H_2O molecules and a dabco molecule per formula unit. Finally, complex **2** decomposes completely at about $561 \text{ }^\circ\text{C}$. This indicates the coordination bonds of the aqua ligands in **2** are not as strong as those in

(14) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958.

1. The TGA of **3** shows two obvious weight losses. The first weight loss in **3** starts at ca. 83 °C up to 110 °C to give a total weight loss of ca. 13.1%, corresponding to loss of 8 H₂O molecules per formula unit. This is consistent with the structure of **3** in which the aqua molecules are just guests. Another weight loss starts at ca. 425 °C up to 532 °C, which accounts for the framework of **3** being rather stable.

What is the reason these different coordination architectures can be generated in similar synthesis conditions? Yaghi et al.^{9a} suggest that the dimensionality of the resulting coordination framework topology constructed by metal ions and tma is extremely dependent on the deprotonation level of H₃tma. An important characteristic of these reactions is that the basicities of the reactants have a little disparity, in which the pH value order for reactants in water is dabco (obsd, 11.0) > hexamethylenetetraamine (obsd, 9.1) > Na₂-tp (obsd, 6.1). Although the real mechanisms in these reactions are not clear yet, a reasonable assumption is therefore suggested that the strength of the base of the reactants influences the deprotonation of H₃tma and the coordination sphere of Cd atoms, resulting in the different coordination architectures assembled. Besides basicity, the steric geometry of the reactants may be another important factor for fabrication of the resulting coordination architectures. Unlike the dabco molecules for complex **2**, terephthalate for complex **1** and hexamethylenetetraamine for complex **3** are not coordinated to Cd atoms or stay as guests in the resulting coordination solids. Similarly to dabco molecules, however, their presence as reactants probably played a template or structure-directing role on the constructing coordination frameworks. In addition, an adequate reaction temperature and time were also very important for preparing these three compounds. Complex **1** cannot be obtained under the hydrothermal condition at 200 °C as complexes **2** and **3** can. Probably the conditions of temperature, time, and cooling rate not only were related to the reaction process but also influenced the necessary crystallization on the resulting coordination solids.

Fluorescent Properties. The emission spectra of complexes **1–3** in the solid state at room temperature are shown in Figure 7. It can be observed that the intense emissions occurring at 355 nm (Figure 7a, $\lambda_{\text{ex}} = 220$ nm) for **1**, 437 nm (Figure 7b, $\lambda_{\text{ex}} = 365$ nm) for **2**, and 353 nm (Figure 7c, $\lambda_{\text{ex}} = 218$ nm) for **3** are assigned to the ligand-to-metal charge-transfer (LMCT) band. Interestingly, a clearly bathochromic shift of emission occurs in **2**, compared with **1** and **3**, which is probably due to σ -donations from the cooperation of dabco and tma ligands to the Cd₃O core. It is noticeable that complex **2** exhibits a quenching of the fluorescence with $\tau = 3.35$ ns. These observations suggest that complex **2** will be an excellent candidate for potential photoactive material.

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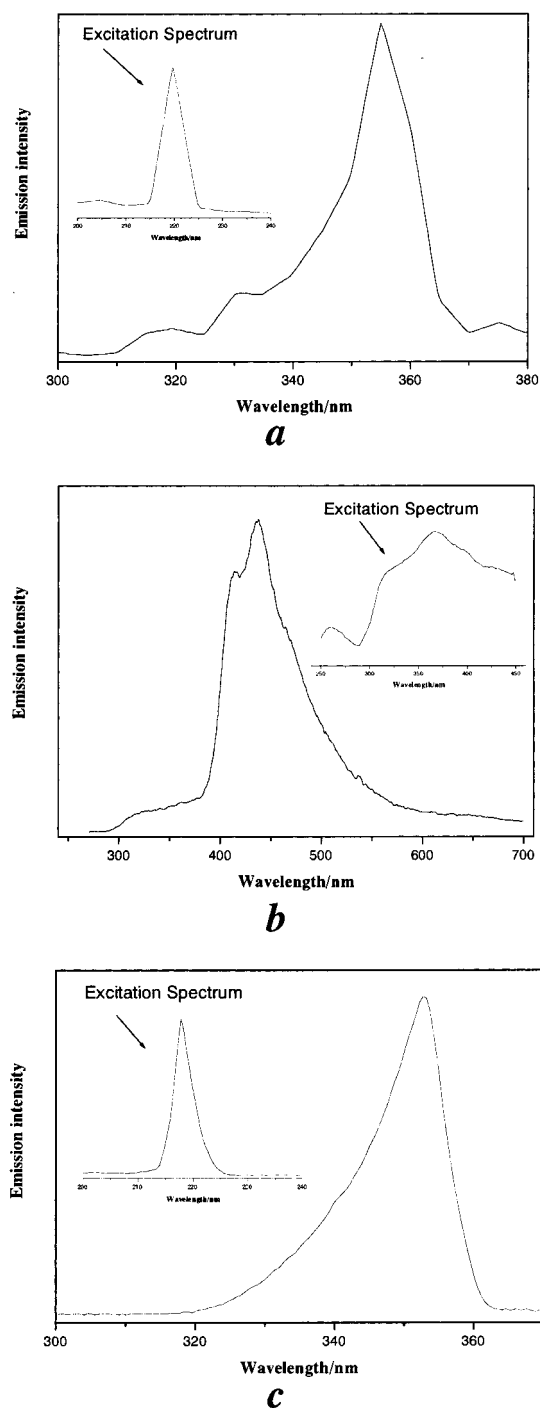


Figure 7. Solid-state emission spectra of cadmium(II)-trimesate complexes at room temperature: (a) **1**; (b) **2**; (c) **3**.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of complexes **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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