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Novel Eclipsed 2D Cadmium(II) Coordination Polymers with Open-Channel Structure Constructed from Terephthalate and 3-(2-Pyridyl)pyrazole: Crystal Structures, Emission Properties, and Inclusion of Guest Molecules

Ru-Qiang Zou, Xian-He Bu,* and Ruo-Hua Zhang

Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

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Five new eclipsed two-dimensional (2D) coordination polymers, $\{[Cd_2(TPT)_2\mathbf{L}_2](GM^1)_{3/2}(H_2O)\}_\infty$ (**1**) (TPT = terephthalate, **L** = 3-(2-pyridyl)pyrazole, GM^1 = terephthalic acid), $\{[Cd(TPT)\mathbf{L}](GM^2)(H_2O)_2\}_\infty$ (**2**) (GM^2 = **L** = 3-(2-pyridyl)pyrazole), $\{[Cd(TPT)\mathbf{L}](GM^3)_{1/2}(H_2O)\}_\infty$ (**3**) (GM^3 = mesitylene), $\{[Cd_4(TPT)_4\mathbf{L}_4](GM^4)_{7/2}\}_\infty$ (**4**) (GM^4 = tetramethylbenzene), and $\{[Cd(TPT)\mathbf{L}](GM^5)_{1/2}\}_\infty$ (**5**) (GM^5 = naphthalene), have been synthesized and characterized by X-ray diffraction. All the five complexes take the similar eclipsed 2D open-channel framework with different guest molecules included in the cavities of their channels. TGA analysis indicates that the eclipsed open-channel frameworks are thermally stable up to 300 °C. The porous property of the 2D framework of **5** was also investigated by the XRPD technique, which indicated that the guest molecules included in the open-channel frameworks are removable and the framework is maintained after the removal of the guest molecules. Moreover, complexes **1**–**5** also display strong blue emission in the solid state.

Introduction

The design of coordination networks with porous structures or open frameworks including removable solvents or exchangeable ions that provide new sizes, shapes, and chemical environments has been of great interest in recent years, due to their potential for many applications,[1,2] for example, mimicking zeolites. In this regard, various carboxylate ligands have been used to design such moderately robust frameworks,[3−6] among which terephthalato, exhibiting a variety of bridging modes and strong tendency to form large, tightly bound metal cluster aggregates, has been used as building block to construct porous coordination frameworks.[7−11] On the other hand, so far most of the coordination polymers have been built with homoleptic ligands. There are also a few interesting examples that have been reported, including some bridging ligand combinations;[12] however, the development of systems containing both chelating and

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* Author to whom correspondence should be addressed. E-mail: buxh@nankai.edu.cn. Tel.: +86-22-23502809. Fax: +86-22-23502458.

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bridging ligands is still less explored. Considering most of the reported complexes containing the terephthalate (TPT) ligands and Cd^{II} ions are apt to form 3D networks when geometry permits and the seventh coordinated ligand is labile, which is very similar to the case of $[Cu_3(TMA)_2(H_2O)_3]_n$ (TMA = 1,3,5-benzenetricarboxylic acid) and $[Cd(py)(TPT)]_n$ (py = pyridine) in which the lability of the aqua ligands allows their replacement by other groups,[13] we attempted to use some chelating bidentate ligands, such as 3-(2-pyridyl)-pyrazole (**L**), to occupy two coordination sites of Cd^{II} to design novel 2D networks. We have successfully obtained five new eclipsed 2D coordination polymers, $\{[Cd_2(TPT)_2\mathbf{L}_2](GM^1)_{3/2}(H_2O)\}_\infty$ (**1**) (**L** = 3-(2-pyridyl)pyrazole, GM^1 = terephthalic acid), $\{[Cd(TPT)\mathbf{L}](GM^2)(H_2O)_2\}_\infty$ (**2**) (GM^2 = **L** = 3-(2-pyridyl)pyrazole), $\{[Cd(TPT)\mathbf{L}](GM^3)_{1/2}(H_2O)\}_\infty$ (**3**) (GM^3 = mesitylene), $\{[Cd_4(TPT)_4\mathbf{L}_4](GM^4)_{7/2}\}_\infty$ (**4**) (GM^4 = tetramethylbenzene), and $\{[Cd(TPT)\mathbf{L}](GM^5)_{1/2}\}_\infty$ (**5**) (GM^5 = naphthalene), with different guest molecules accommodated in their open-channel structures. Moreover, such complexes display strong blue emission in the solid state. Herein, we report the synthesis, structure, and emission properties of **1**−**5**, which represent typical controllable examples of metal coordination polymers with open-channel structures.

Experimental Section

Materials and General Methods. All the solvents and reagents for synthesis, including terephthalic acid, were commercially available and used as received. 3-(2-Pyridyl)pyrazole (**L**) was synthesized by the literature method.[14] FT-IR spectra (KBr pellets) were taken on a 170SX (Nicolet) spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was carried out on a Dupont thermal analyzer from room temperature to 600 °C under nitrogen atmosphere. X-ray powder diffraction (XRPD) studies were recorded on a Rigaku RU200 diffractometer at 60 kV and 300 mA for Cu Kα radiation ($\lambda = 1.5406$ Å). Emission spectra were taken on a Stetlofluorometer FL111AI spectrometer.

Synthesis of $\{[Cd_2(TPT)_2L_2](GM^1)_{3/2}(H_2O)\}_\infty$ (1) (TPT = Terephthalate, L = 3-(2-Pyridyl)pyrazole, GM^1 = Terephthalic Acid). Complex **1** was obtained by the reaction of $Cd(NO_3)_2{\cdot}6H_2O$, terephthalic acid, 3-(2-pyridyl)pyrazole (L), and NaOH in the molar ratio of 1:2:1:4 mixed with 12 mL of water under hydrothermal conditions at 120 °C for 2 days. The colorless crystals were washed by water and acetone and dried in air. Yield: ~50%. Anal. Calcd for $C_{44}H_{33}Cd_2N_6O_{15}$: C, 47.59; H, 2.99; N, 7.57. Found: C, 47.91; H, 3.13; N, 7.84. IR (KBr, cm^{-1}): 3335 m, 3161 w, 2666 m, 1648 vs, 1607 m, 1463 s, 1291 s, 1023 m, 1003 m, 743 s, 696 w. TGA data (peak positions): 163, 329, 401, and 459 °C.

$\{[Cd(TPT)L](GM^2)(H_2O)_2\}_\infty$ (2) (GM^2 = L = 3-(2-Pyridyl)-pyrazole). The colorless crystals of complex **2** were obtained by the reaction of $Cd(NO_3)_2{\cdot}6H_2O$, terephthalic acid, 3-(2-pyridyl)-pyrazole (**L**), and NaOH in the molar ratio of 1:1:2:4 using a procedure similar to that of **1**. Yield: ~55%. Anal. Calcd for $C_{24}H_{22}CdN_6O_6$: C, 47.81; H, 3.68; N, 13.94. Found: C, 47.46; H, 3.53; N, 13.67. IR (KBr, cm^{-1}): 3412 m, 3104 m, 3064 m, 2964 m, 2823 m, 1972 w, 1682 vs, 1574 s, 1287 s, 1113 m, 1019 m, 781 s, 560 w. TGA data (peak positions): 172, 380, 415, and 462 °C.

$\{[Cd(TPT)L](GM^3)_{1/2}(H_2O)\}_\infty$ (3) (GM^3 = Mesitylene), $\{[Cd_4(TPT)_4L_4](GM^4)_{7/2}\}_\infty$ (4) (GM^4 = Tetramethylbenzene), and $\{[Cd(TPT)L](GM^5)_{1/2}\}_\infty$ (5) (GM^5 = Naphthalene). These three complexes were synthesized by the reactions of $Cd(NO_3)_2{\cdot}6H_2O$, terephthalic acid, 3-(2-pyridyl)pyrazole, NaOH, and corresponding guest molecules in the molar ratio of 1:1:1:2:4 using a synthetic method similar to that of **1** and **2**.

Complex 3. Yield: ~50%. Anal. Calcd for $C_{20.25}H_{18.25}CdN_3O_5$: C, 49.03; H, 3.71; N, 8.47. Found: C, C, 39.41; H, 3.56; N, 8.69. IR (KBr, cm^{-1}): 3401 m, 3121 m, 2832 m, 2543 m, 1681 vs, 1543 s, 1385 s, 1133 m, 1108 w, 813 s, 685 m. TGA data (peak positions): 173, 282, 339, 398, and 435 °C.

Complex 4. Yield: ~40%. Anal. Calcd for $C_{99}H_{93}Cd_4N_{12}O_{16}$: C, 55.14; H, 4.35; N, 7.79. Found: C, 54.79; H, 4.47; N, 7.98. IR (KBr, cm^{-1}): 3105 m, 3061 m, 2832 m, 1972 w, 1688 vs, 1423 vs, 1285 s, 1133 m, 1008 m, 791 s, 525 m. TGA data (peak positions): 187, 305, 340, and 422 °C.

Complex 5. Yield: ~40%. Anal. Calcd for $C_{21}H_{15}CdN_3O_4$: C, 51.92; H, 3.11; N, 8.65. Found: C, 51.56; H, 3.01; N, 9.01. IR (KBr, cm^{-1}): 3423 w, 3117 w, 3045 w, 2914 w, 1712 w, 1605 m, 1563 vs, 1505 s, 1432 s, 1386 vs, 1290 m, 1094 w, 840 m, 746 s, 520 m. TGA data (peak positions): 201, 317, 337, and 439 °C.

X-ray Data Collection and Structure Determinations. X-ray single-crystal diffraction data for complexes **1**−**5** were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo Kα radiation ($\lambda = 0.710\ 73$ Å) by the ω scan mode. The program SAINT[15] was used for integration of the diffraction profiles. All 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 (semiempirical absorption corrections were applied using the SADABS program).[16] Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen atoms of ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors (the hydrogen atoms of water molecules were located using the difference Fourier method). Further details for structural analysis are summarized in Table 1.

Results and Discussion

Description of Structures. Complex 1. The structure of **1** consists of a 2D neutral coordination network $\{[Cd_2(TPT)_2\mathbf{L}_2](GM^1)_{3/2}(H_2O)\}_\infty$ with terephthalic acid and lattice water molecules included in the open-channel framework (Figure 1). The local coordination environment around Cd^{II} ion in **1** is the chelating **L** and chelating/bridging carboxylates (Figure 1a). The *b* axial direction of **1** is occupied by the chelating bidentate **L** ligands, and each terephthalato (TPT)

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Table 1. Crystallographic Data and Structural Refinement Summary for Complexes **1**−**5**

	1	**2**	**3**	**4**	**5**
chem formula	$C_{44}H_{33}Cd_2N_6O_{15}$	$C_{24}H_{22}CdN_6O_6$	$C_{20.25}H_{18.25}CdN_3O_5$	$C_{99}H_{93}Cd_4N_{12}O_{16}$	$C_{21}H_{15}CdN_3O_4$
fw	1110.56	602.88	482.52	2156.45	485.76
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.347(4)	10.329(4)	10.325(3)	10.347(5)	10.352(3)
b/Å	10.390(4)	10.354(4)	10.372(3)	20.500(9)	10.373(4)
c/Å	21.833(8)	12.222(5)	12.344(3)	23.426(10)	12.158(4)
α/deg	77.937(5)	113.765(6)	67.148(4)	102.858(7)	94.659(5)
β/deg	88.261(5)	92.672(7)	72.038(4)	95.683(7)	114.699(5)
γ/deg	72.257(5)	108.919(6)	74.932(5)	103.896(7)	105.995(5)
V/Å^3	2184.8(13)	1107.7(8)	1143.9(5)	4641(4)	1111.0(7)
T /K	293(2)	293(2)	293(2)	293(2)	293(2)
D_c/g cm^{-3}	1.695	1.808	1.401	1.543	1.452
Z	2	2	2	2	2
μ(Mo Kα)/mm^{-1}	1.053	1.044	0.983	0.977	1.012
R^a/wR^b	0.0278/0.0612	0.0712/0.1949	0.0520/0.1038	0.0460/0.0736	0.0428/0.1055

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $wR = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

adopts a μ_6-bridging mode to connect four Cd^{II} ions to extend along the *ac* directions to form an eclipsed 2D network structure (Figure 1b). The seven-coordinated geometry of Cd^{II} is as follows: Two oxygen atoms of the two distinct TPT carboxylate anions coordinate to Cd^{II} almost equally in a bidentate chelating mode. The Cd−O distances (2.364−2.518 Å) are quite similar to normal Cd−OCO distances (2.251−2.879 Å).[17] Second, the bridging Cd−O distances (2.359(2) Å) are shorter than the chelating ones. Third, the Cd−N distances (2.311(2) and 2.377(2) Å, respectively) are also falling into the normal range (2.32−2.39 Å).[18] The TPT anion acts as bis-tridentate ligand to bridge the two coplanar Cd^{II} ions and other two Cd^{II} ions in the same layer, resulting in the formation of a 2D network with channel dimensions of 10.43 × 10.43 Å^2 passing the eclipsed 2D layers. It can be seen from a perspective view of **1** down the *b* axis that the green layer (see Figure 1b) is completely covered by the red one, indicating that the adjacent 2D layers are eclipsed each other. When viewed from the *c* axis (Figure 1c), the separation between the adjacent **L** ligands located in the adjacent 2D layers is about 3.638 Å, indicating the existence of weak $\pi-\pi$ stacking interactions.[19] Water molecules and terephthalic acid molecules were included in the channel (Figure 1d).

Application of a continuous solvent-area model to calculate the channels containing diffuse electron density led to the same result,[21] suggesting a contribution of ca. 279 electrons/unit cell from the channel region. This is consistent with ca. three molecules, including terephthalic acid and two water molecules per unit cell, which is also consistent with the result of elemental analysis.

Complex 2. Similar to complex **1**, the structure of **2** consists of a 2D neutral coordination network with lattice water molecules and guest (3-(2-pyridyl)pyrazole) (**L**) included in the channel (Figure 2a). The 2D eclipsed framework and the local coordination environment around Cd^{II} in **2** are similar to that of **1**, but different guest molecules are included in their framework channels. The channels contain diffuse electron density, which is difficult to model as discrete atoms. Application of a continuous solvent-area model led to satisfactory refinement, suggesting a contribution of ca. 193 electrons/unit cell from the channel region. This is consistent with ca. two included **L** and four lattice water molecules per unit cell, which is consistent with the result of elemental analysis.

Complexes 3−5. The frameworks of **3**−**5** are similar to that of **1** and **2**, but different guest molecules are included in their open-channel frameworks (see Figure 2b−d). The diffuse electron density included in the open-channel frameworks has been calculated to lead to satisfactory results (Table 2), which are also consistent with the result of elemental analysis.

Exclusion of Guest Molecules of 5: TGA and XRPD Studies. As described above, all five complexes have the 2D eclipsed frameworks exhibiting open channels filled with guest molecules. To verify whether the framework will be maintained after the removal of the guest molecules, which is important for new microporous materials, TGA and XRPD techniques have been used to investigate the framework stability and the removal of the guest molecules of **5** according to the sublimation properties of naphthalene. The TGA result reveals that **5** is stable up to 180 °C where decomposition starts, and there is a weight loss of 8.8% (calcd: 8.0%) from ca. 180 to 210 °C, being consistent with the removal of the included naphthalene rings, which is also confirmed by elemental analyses (Figure 4). As shown in Figure 4, the eclipsed open-channel frameworks are thermally stable up to almost 300 °C, which is well confirmed by the TGA results of complexes **1**−**4**. The similarity between the XRPD pattern recorded at this point and that of the original starting sample suggests the dried solid $\{[Cd(TPT)\mathbf{L}]\}_\infty$ retains the initial framework of **5**. The slight shift and splitting of some peaks may be attributed to the removal of naphthalene rings and the subtle change of the relative positions of some atoms in the crystal lattice (Figure 3).[20]

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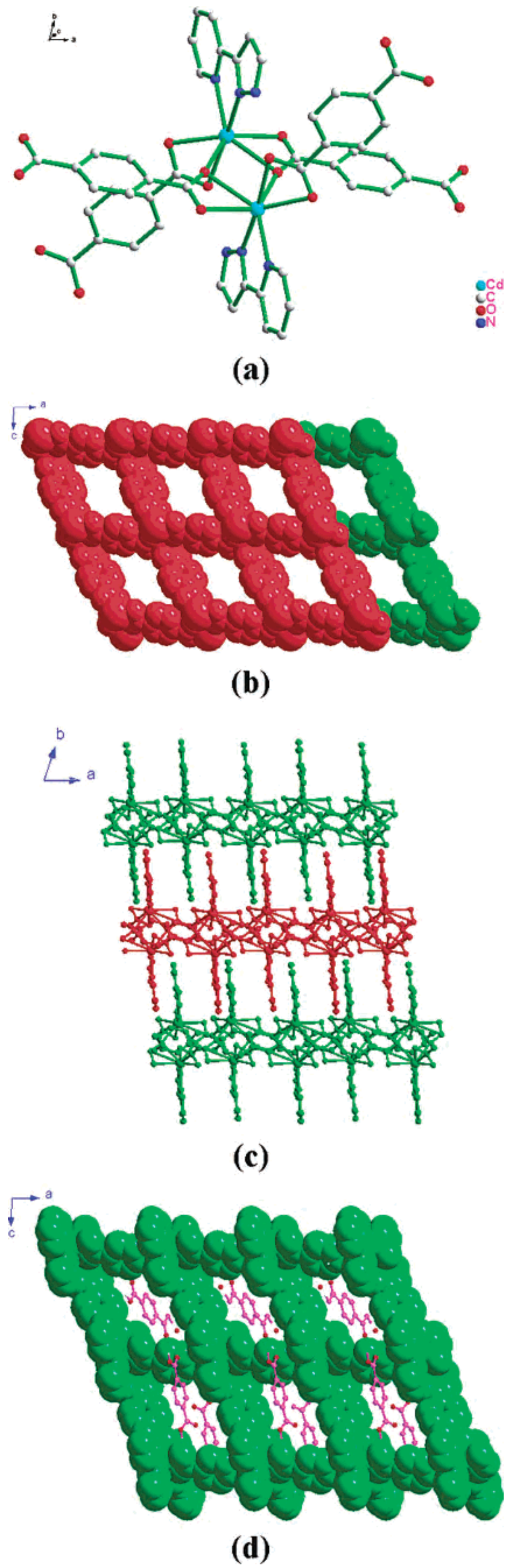

Figure 1. (a) View of the Cd^{II} coordination environment. (b) Eclipsed 2D coordination networks (different color used to show the adjacent 2D layers). (c) Stacking diagram along the *c* axis (H atoms and guest molecules omitted for clarity). (d) 2D eclipsed network with TPT and water molecules included in the open channels of complex **1**.

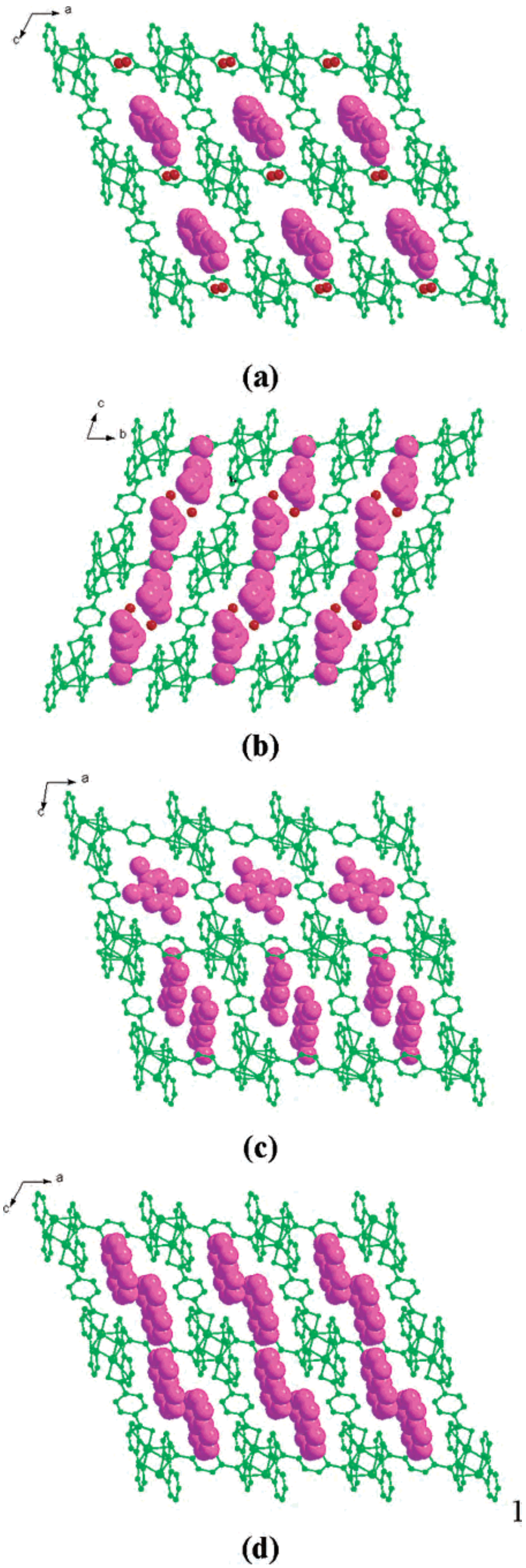

Figure 2. Eclipsed 2D networks of (a) **2** with the **L** and water molecules, (b) **3** with mesitylene molecules and water molecules, (c) **4** with tetramethylbenzene molecules, and (d) **5** with naphthalene molecules included in their open channels.

Table 2. Structural Parameters

	before *SQUEEZE* procedure			resid electrons/ unit cell	no. of included molecules	after *SQUEEZE* procedure		
	R1	wR2	$\Delta\rho$(max, min)			R1	wR2	$\Delta\rho$(max, min)
1	0.0278	0.0612	1.016, −0.436	279	1.5 GM^1, H_2O	0.0265	0.0587	0.534, −0.389
2	0.0712	0.1949	1.669, −1.884	193	GM^2, 0.2 H_2O	0.0437	0.0862	0.436, −0.994
3	0.0520	0.1038	0.664, −0.530	88	0.5 GM^3, H_2O	0.0383	0.0574	0.457, −0.497
4	0.0460	0.0736	0.591, −0.729	550	3.5GM^4	0.0362	0.0584	0.606, −0.667
5	0.0428	0.1055	0.843, −0.361	58	0.5 GM^5	0.0319	0.0660	0.596, −0.314

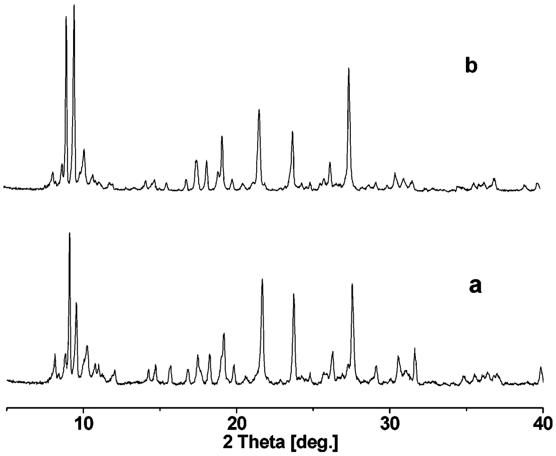

Figure 3. XRPD patterns for **5**: (a) before removal of the guest naphthalene molecules; (b) after removal of the guest naphthalene molecules.

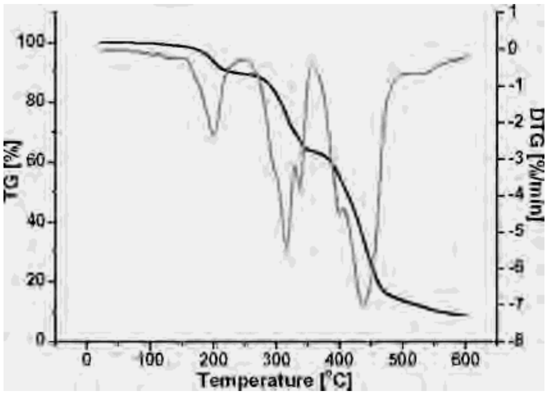

Figure 4. TG-DTG patterns for **5**: black line for TG (%); gray line for DTG (% min).

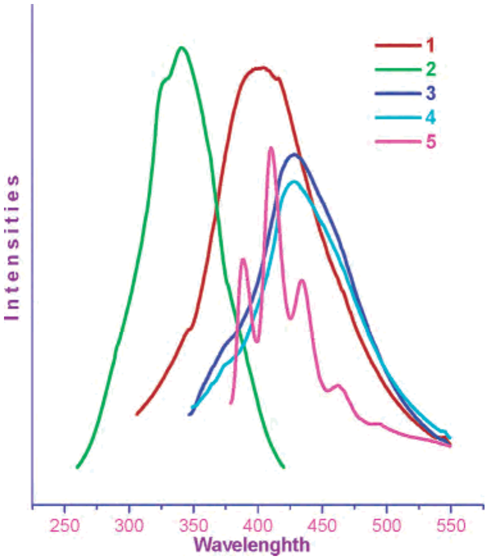

Figure 5. Emission spectra of **1**−**5** in the solid state at room temperature (λ_{ex} = 332 nm).

During this exclusion, a subtle color change occurs, from faint yellow to colorless. The XRPD pattern for the desolvated **5** has been indexed, and the cell parameters (a = 10.3343(0.020918) Å, b = 10.39048(0.017942) Å, c = 12.12345(0.021629) Å, α = 95.0398(0.19738)°, β = 114.4947(0.18284)°, γ = 106.1486(0.12519)°)) compare well with those of compound **5,** further indicating that the framework is maintained after the removal of the guest molecules.

Emission Properties. Complexes **1**−**5** exhibit significant blue fluorescent emission. As shown in Figure 5, the emission spectra of complexes **1**−**5** consist of similar broad emission bands in the UV−vis region that extend beyond 550 nm. The emission maxima (λ_{max}) are 398 (**1**), 428 (**3**), and 428 nm (**4**) (λ_{ex} = 332 nm), respectively. The emission bands of **1**, **3**, and **4** reveal hypsochromic absorption and significant enhancement of fluorescent intensities comparing with those of free TPT and **L**, because of the symmetry decrease of TPT in the two-dimensionally condensed polymeric structure. Unlike **1**, **3**, and **4**, the maxima emission band of **2** at 340 nm may be caused by the cooperated emission of TPT and the included **L**. The emission spectrum of **5** is much more complicated: four emission bands (λ_{max}, 389, 410, 434, 485 nm; λ_{ex}, 332 nm) were found, which may arise from the emissions of TPT ligand and the included naphthalene.

Owing to the blue emission of **1**−**5**, they may be potential materials for blue-light-emitting diode devices. These condensed polymeric materials may be good candidates for thermally stable and solvent-resistant blue fluorescent material because **1**−**5** are insoluble in the common solvents such as ethanol, chloroform, acetone, acetonitrile, benzene, and water.

In conclusion, five new 2D Cd^{II} coordination polymers with the mixed ligands terephthalic acid and 3-(2-pyridyl)-pyrazole have been prepared and structurally characterized. Their 2D eclipsed open-channel frameworks can accommodate suitable guest molecules, and the structures of these inclusion complexes display similar behaviors. The open-channel frameworks are retained after the removal of the guest molecules. They also exhibit strong blue emissions and may be potentially applicable as materials for blue-light-emitting diode devices.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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