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A rare case of 2D+1D → 2D Cd(II) coordination polymer without any entanglements: Synthesis, structure and luminescent property

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The reactions of $CdCl_2{\cdot}2.5H_2O$ with mixed ligands, H_2tfbdc and hmt, under different metal-to-ligand ratios, afford two coordination polymers, namely, $[Cd(hmt)(tfbdc)(H_2O)_2]_2{\cdot}3H_2O$ (**1**) and $\{[NH_4]_2[Cd_2(H_2hmt)(tfbdc)_2Cl_4][Cd(H_2hmt)(tfbdc)Cl_2]\}{\cdot}2H_2O$ (**2**). Both the complexes have been structurally characterized by X-ray data. Complex **1** has a 2D rectangular grid built up by tfbdc^{2-} and hmt ligands, while **2** consists of distinct 1D anionic ladder $[Cd_2(H_2hmt)(tfbdc)_2Cl_4]^{2-}$ and 2D grid $[Cd(H_2hmt)(tfbdc)Cl_2]$ in a crystal. Further, in **2**, the 2D net is parallel to the 1D ladder without mutual entanglement or interdigitation. Despite the hydrogen bond interactions and the F···F interactions, only a 2D supermolecular structure is formed in **2**. Thus, compound **2** is the first case of 2D+1D→2D coordination polymer without any entanglements.

Keywords: Coordination polymers, Metal organic frameworks, Supramolecular chemistry, Luminescence, Crystal structures, 1D+2D→2D, Cadmium

The current interest in coordination polymers stems not only from their potential applications in adsorption, electrical conductivity, smart optoelectronics, magnetism, and catalysis, but also from their intriguing variety of architectures and fascinating new topologies[1-10]. Some coordination networks are particularly interesting because of the presence of two or more diverse independent motifs, such as “0D+2D”, “1D+1D”, “1D+2D”, “1D+3D”, “2D+2D”, “2D+3D”, “3D+3D”, “1D+1D+2D” and “1D+2D+2D” types[11-38]. In most of these compounds, different independent motifs are entangled with each other in different modes, for example, $\{[Cd(btre)Cl][CdCl(dca)_2]{\cdot}0.5H_2O\}_n$ (btre = 1,2-bis (1,2,4-triazol-4-yl)ethane, dca = dicyanamide)[15] exhibits a polythreading coordination array formed from a 3D microporous cation network and 1D anion ladders, while in $[Co(HL)(H_2O)_4]_n[Co_3(L)_2(H_2O)_{10}]_n{\cdot}4nH_2O$ (H_3L = 5-(4-carboxy-2-nitrophenoxy) isophthalic acid)[33], 1D chains are simultaneously threaded into one pleated 2D sheet in parallel to generate a 2D dense polythreading aggregation. Only one example of a crystal containing two independent 2D polymers without mutual interpenetration has been reported so far, in which two distinct 2D motifs are assembled in an ABCD sequence[11]. Coordination polymers involving two or more independent motifs without any entanglements are still very rare.

Using 1,4-benzenedicarboxylic acid (H_2bdc) and 1-(4-carboxybenzyl)-4,4-bipyridinium (BCbpy) ligands, Zhang *et al*[16]. have successfully synthesized a Cd(II) coordination polymer based on two independent motifs: $[Cd_2(BCbpy)_2(bdc)Cl_2][Cd(BCbpy)_2(BDC)]$ $18H_2O$ (2D+2D+1D→2D). We have been interested in the construction of novel topologies using derivatives of H_2bdc by introducing the electron-withdrawing substituent, tetrafluoroterephthalatic acid (H_2tfbdc) as a organic ligand, and we achieved a 3D pillar-layered framework with rare (3,5)-connected gra topology[39]. Besides, several Cd(II) coordination polymers based on two independent motifs, such as the previously mentioned compound $\{[Cd(btre)Cl][CdCl(dca)_2]{\cdot}0.5H_2O\}_n$[15] (1D+3D→3D), as well as $[Cd(NCS)_2(\mu\text{-}4\text{-py-pzH})]_n$[36] (4-py-pzH = 4-(4-pyridyl) pyrazole) (1D+2D→2D), $[Cd_2(bpea)(pt)(phen)_2][Cd(pt)(phen)]{\cdot}2H_2O$[38] (pt = phthalate, bpea = biphenylethene-4,4’-dicarboxylic acid, phen = 1,10-phenanthroline) (1D+2D, interdigitated), are reported.

To continue our previous efforts in constructing novel architectures[39-46], we have reacted H_2tfbdc with $CdCl_2 \cdot 2.5H_2O$ and hexamethylenetetramine (hmt) in different metal-to-ligand ratios, and isolated two coordination polymers $[Cd(hmt)(tfbdc)(H_2O)_2]_2 \cdot 3H_2O$ (**1**) and $\{[NH_4]_2[Cd_2(H_2hmt)(tfbdc)_2Cl_4][Cd(H_2hmt)(tfbdc)Cl_2]\} \cdot 2H_2O$ (**2**). **1** forms a 2D rectangular grid, whereas **2** exhibits a 1D+2D→2D layer structure, formed from the parallel packing of a 2D grid and 1D anionic ladder without any mutual entanglements.

Materials and Methods

All reagents and solvents for synthesis and analysis were commercially available and used as received. Infrared spectra were recorded on a Nicolet ESP 460 FT-IR spectrometer on KBr pellets in the range of 4000–400 cm^{-1}. X-ray single crystal diffraction data were collected on a Bruker Smart Apex CCD diffractometer. Carbon, hydrogen, and nitrogen analyses were performed on a PE-2400II (Perkin-Elmer) analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on an X-ray diffractometer (D/max 2500 PC, Rigaku) with Cu-Kα radiation (1.5406 Å). The luminescent spectra were recorded at room temperature on a Sahimadzu RF-5301PC fluorescence spectrofluorometer.

Preparation of $[Cd(hmt)(tfbdc)(H_2O)_2]_2 \cdot 3H_2O$ (1)

$CdCl_2 \cdot 2.5H_2O$ (0.1142 g, 0.50 mmol) was added to the solution of H_2tfbdc (0.1191 g, 0.50 mmol) in 5 mL H_2O. Then, a solution of hmt (0.0700 g, 0.50 mmol) in 5 mL H_2O was added to the mixture. The resulting colorless aqueous was kept at room temperature for 5 days, to yield colorless block crystals of **1** (0.174 g, 63%). Anal.(%): Found: C 30.70, H 3.89, N 10.26; Calcd. for $C_{28}H_{38}Cd_2F_8N_8O_{15}$: C 30.48, H 3.47, N 10.15. IR (KBr, cm^{-1}): 3438(s), 2964(m), 2370(w), 1633(vs), 1466(vs), 1374(vs), 1258(m), 1236(s), 1062(m), 1018(s), 997(s), 982(s), 929(w), 830(w), 801(m), 739(s), 701(m), 677(m), 625(m), 513(m), 482(m).

Preparation of $\{[NH_4]_2[Cd_2(H_2hmt)(tfbdc)_2Cl_4][Cd(H_2hmt)(tfbdc)Cl_2]\} \cdot 2H_2O$ (2)

To a solution of H_2tfbdc (0.1191 g, 0.5 mmol) and $CdCl_2 \cdot 2.5H_2O$ (0.1142 g, 0.5 mmol) in 5 mL water, was added a solution of hmt (0.3505 g, 2.5 mmol) in water (5 mL). The mixture was stirred at room temperature for 30 min. Slow evaporation of the solvents from the resulting solution produced colorless prismatic crystals of **2**, which were collected by filtration, washed thoroughly with Et_2O and dried in air (yield 0.153 g, 57% based on Cd). Anal.(%) Found: C 27.21, H 2.14, N 8.92; Calcd. for $C_{36}H_{40}Cd_3Cl_6F_{12}N_{10}O_{14}$: C 26.78, H 2.50, N 8.67. IR (KBr, cm^{-1}): 3456(s), 2356(w), 2149(w), 1637(s), 1467(s), 1371(s), 1236(s), 1057(m), 1018(s), 998(s), 979(s), 927(m), 831(m), 822(w), 801(m), 779(w), 741(s), 701(s), 693(s), 677(w), 665(w), 620(w), 514(m), 482(m).

X-ray crystallography

Crystal structures were solved by direct methods and *SHELXTL*[47] was used for structure solution and least-squares refinement with anisotropic displacement parameters for all non-hydrogen atoms. The solvent water molecule O(7) in **1** was fixed with constrained parameters and refined with an occupancy factor of 0.5. In **2**, one of the two solvent ater molecules was disordered over three sites with an occupancy ratio of 0.40/0.30/0.30 for O(2W)/O(3W)/(O4W). H atoms attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times *U*eq of the parent atoms. All other hydrogen atoms bonded to O or N atoms were located from difference maps and refined with isotropic thermal parameters 1.5 times that of their carrier atoms. The crystallographic data for **1** and **2** are listed in Table 1.

Results and Discussion

Complex 1 was obtained as colorless crystals by the reaction of $CdCl_2 \cdot 2.5H_2O$, H_2tfbdc and hmt in a molar ratio of 1:1:1. Keeping other reaction conditions unchanged, and only metal-to-ligand ratio changed to 1:1:5, 2 was obtained. In this system, we found that the metal-to-ligand ratio had a dramatic influence over the direct synthetic products. On altering the ratios of hmt-to-metal from 1:1 to 5:1, NH_4^+cations were formed from the decomposition of hmt and H_2O in acidic solution and some hmt ligands were protonated for charge balance at the same time[48], which affects the coordination environment of the metal, as well as the dimensionality of the coordination polymer. In the IR spectra of **1** and **2**, the strong and broad absorption bands around 3200–3600 cm^{-1} region are assigned as characteristic peaks of OH vibration, indicating the presence of water molecules (Supplementary Data, Fig. S1). The absorption peak between 1690 cm^{-1} and 1730 cm^{-1} was not observed, showing all carboxylic groups are deprotonated in **1** and **2**. The peaks at 1633 and 1466 cm^{-1} (**1**), 1637 and 1467 cm^{-1} (**2**) are the asymmetric stretching vibration $\nu_{as}(COO^-)$ and the symmetric stretching vibration ν_s (COO^-) of $tfbdc^{2-}$,

Table 1—Crystal data and structure refinement for **1** and **2**

	1	**2**
Emp. formula	$C_{28}H_{38}Cd_2F_8N_8O_{15}$	$C_{36}H_{40}Cd_3Cl_6F_{12}N_{10}O_{14}$
Formula mass	1103.46	1614.68
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.4353(12)	11.728(2)
b (Å)	10.5002(17)	13.126(18)
c (Å)	13.135(2)	19.630(2)
α (°)	86.875(3)	98.198(2)
β (°)	81.479(3)	93.278(3)
γ (°)	79.819(2)	92.635(2)
V (Å^3)	997.8(3)	2981.7(8)
Z	1	2
D_{calc} (g cm^{-3})	1.836	1.798
F(000)	550	1584
μ [Mo K, cm^{-1}]	11.79	14.30
Total no. of reflns	5240	23297
No. of unique reflns	3360 (R_{int} = 0.0141)	11569 (R_{int} = 0.0202)
No. of obs reflns	2994 (I>2.00σ(I))	6093 (I>2.00σ(I))
No. of variables	283	751
$R_1{}^a$	0.0303	0.0522
$wR_2{}^b$	0.0975	0.1144
GOF^c	1.076	1.005
Residual peaks (e Å^{-3})	0.759 and –0.397	0.585 and –0.857

[a] $R = ||F_o|-|F_c|/|F_o|$. [b] $wR = \{w(F_o{}^2-F_c{}^2)^2/w(F_o{}^2)^2\}^{1/2}$. [c] $\mathrm{GOF} = \{w((F_o{}^2-F_c{}^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

respectively. The elemental analyses were consistent with their chemical formulae. The structures of **1** and **2** were identified by X-ray diffraction.

Crystal structure of 1

The X-ray structural analysis of **1** reveals that a 2D coordination polymer of rectangular grid is built up by tfbdc^{2-} and hmt ligands lying in the crystallographic *bc* plane (Fig. 1). The asymmetric unit of **1** contains two halves of Cd(II) ion, a hmt ligand, a tfbdc^{2-} ligand, two coordination water molecules and one and a half lattice water molecules. In the (4,4) net, since Cd(1) (Fig. 2) and Cd(2) (Supplementary Data, Fig. S2) are in a similar coordination environment, only the coordination geometry of Cd(1) is discussed in detail. Cd(1) is attached to two hmt ligands, two tfbdc^{2-} anions, and two coordinated water molecules in a distorted octahedral environment. The two N atoms (N(3) and N(3A), Cd–N = 2.453(3) Å) (Table 2) from two hmt

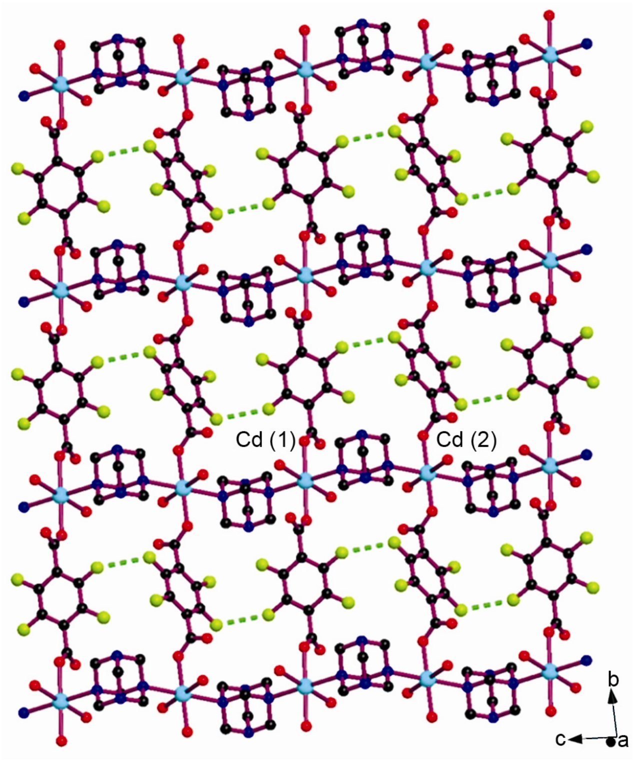

Fig. 1—2D grid structure of complex **1** along the *a*-axis. The F···F interactions are shown in bright green dashed line. All solvent water molecules and hydrogen atoms are omitted for clarity.

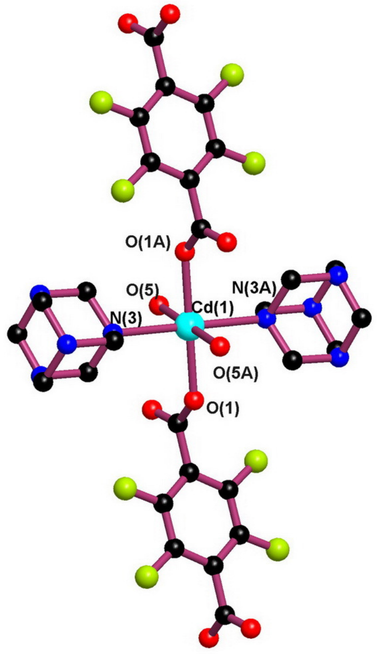

Fig. 2—The coordination environment of Cd(1) in **1**. All hydrogen atoms are omitted for clarity. [Symmetry code: A: –*x*, –*y*+2, –*z*+2.].

Table 2—Selected bond lengths (Å) for **1**

Cd(1)–O(1)	2.247(3)	Cd(1)–O(5)	2.321(3)
Cd(1)–N(3)	2.453(3)	Cd(2)–O(3)	2.252(3)
Cd(2)–O(6)	2.307(2)	Cd(2)–N(2)	2.456(3)

and two O atoms (O(5) and O(5A), Cd(1)–O(5) = 2.321(3) Å) from two aqua molecules in the equatorial positions, and the axial sites which are occupied by two O atoms (O(1) and O(1A), Cd–O = 2.247(3) Å) from two $tfbdc^{2-}$, are ligated in 4+2 coordination with the CdN_2O_4 chromophore. Each hmt molecule acts as an N,N'-bis(monodentate) ligand, bridging the Cd(II) ions in the $[0\ 0\ \bar{1}]$ direction, whereas each carboxylate group of each $tfbdc^{2-}$ anion adopts the monodentate coordination mode, making the $tfbdc^{2-}$ ligand bridge the Cd^{2+}ions in the $[1\ \bar{1}\ 0\ ]$ direction. In the resulting 2D grid, the Cd(II)···Cd(II) separation along Cd(II)···hmt···Cd(II) and Cd(II)···$tfbdc^{2-}$···Cd(II) is 6.57 Å and 11.74 Å, respectively. Moreover, the F···F contact (F(1)···F(3) = 2.875(4) Å) of all $tfbdc^{2-}$ is found in the 2D layer (Fig. 1). The contact is close to the sum of the van der Waals radii (2.94 Å)[49,50] and is rather weak, therefore the F···F interaction does not contribute significantly to the crystal packing.

There are abundant hydrogen bonds between coordinated water molecules, solvent water molecules as well as uncoordinated carboxylate O atom of $tfbdc^{2-}$ and the uncoordinated nitrogen atom of hmt in **1** (Table 3). Thus, the adjacent sheets are held together to afford a 3D supramolecular network, with the lattice water molecules located between two layers. (Supplementary Data, Fig. S3).

Crystal structure of 2

The structural determination of a single crystal of **2** shows that as compared to **1**, complex **2** had a more complex and interesting structure, consisting of two independent polymers; a 2D grid $[Cd(H_2hmt)(tfbdc)Cl_2]$ (A) and a 1D anionic ladder $[Cd_2(H_2hmt)(tfbdc)_2Cl_4]^{2-}$ (B). In total, complex **2** can be formulated as $[(NH_4)_2(A)(B)]\cdot 2H_2O$. The polymer (A) comprises a simple 2D (4,4) grid, consisting of two independent Cd(II) ions. The asymmetric unit of **2** contain two halves of Cd(II) ions, two Cd(II) ions, two hmt ligands, three $tfbdc^{2-}$ ligands, six Cl^- ions, two NH_4^+ cations and two lattice water molecules. Both Cd(1) and Cd(2) atoms have an octahedral geometry, coordinated by two O atoms from different $tfbdc^{2-}$ ligands (Cd(1)–O = 2.277(4) Å, Cd(2)–O = 2.228(3) Å), and two terminal Cl atoms (Cd(1)–Cl = 2.2925(13) Å, Cd(2)–Cl = 2.3180(13) Å) and two nitrogen atoms from H_2hmt^{2+}ligands (Cd(1)–N = 2.488(4) Å, Cd(2)–N = 2.424(4) Å) (Table 4), which are protonated for charge balance (Fig. 3). Similar to that in **1**, each $tfbdc^{2-}$ anion adopts bis-monodentate coordination mode bridging the Cd(II) ions in the [1 0 0] direction. The bis-monodentate H_2hmt^{2+}ligands bridges these Cd(II) ions in the [0 1 0] direction, and forms a 2D grid (Fig. 4a). The polymer (B) consists of infinite anionic ladders which are packed between the 2D layers of polymer (A). As shown in Fig. 4b, the 1D anionic ladder features $tfbdc^{2-}$ ligands as the supports and H_2hmt^{2+}ligands as the rungs. Two adjacent linear $[Cd(\mu\text{-}tfbdc)]_\infty$ chains are interlinked by bis-monodentate H_2hmt^{2+}ligands to form the ladder. The coordination mode of the $tfbdc^{2-}$ anion is very similar to that found in **1**. The 1D anionic ladder consists of two independent Cd atoms, Cd(3) and Cd(4) are in square pyramidal geometry coordinated by two O atoms from different $tfbdc^{2-}$ ligands (average Cd(3)–O = 2.256(4) Å, average Cd(4)–O = 2.279(4) Å), and two terminal Cl atoms (average Cd(3)–Cl = 2.320(1) Å, average Cd(4)–Cl = 2.286(1) Å) while an N atom from H_2hmt^{2+}ligand (Cd(3)–N = 2.391(4) Å, Cd(4)–N = 2.446(4) Å) occupies the remaining apical site (Fig. 3). Unlike Cd(II) ions which are six-coordinated in **1** or in the polymer (A)

Table 3—Hydrogen bond distances (Å) for the complex **1**

D–H···A	D–H	H···A	D···A
O(6)–H(6Y)···N(1D)	0.82	2.06	2.853(4)
O(5)–H(5X)···O(2F)	0.82	2.47	2.908(5)
O(5)–H(5Y)···O(8E)	0.82	1.98	2.768(6)
O(8)–H(8Y)···O(8C)	0.85	2.38	3.065(7)
C(4)–H(4a)···O(2F)	0.97	2.41	3.338(7)
C(3)–H(3a)···O(3B)	0.97	2.57	3.388(5)
C(2)–H(2a)···O(1A)	0.97	2.57	3.149(5)
C(1)–H(1a)···F(3)	0.97	2.51	3.371(4)

Symmetry code: A: $-x$, $-y+2$, $-z+2$; B: $-x$, $-y+2$, $-z+1$; C: $-x$, $-y+1$, $-z$; D: $-x+1$, $-y+2$, $-z+1$; E: x, $y+1$, $z+1$; F: $-x+1$, $-y+2$, $-z+2$

Table 4—Selected bond lengths (Å) for **2**

Cd(1)–O(1)	2.277(4)	Cd(1)–Cl(1)	2.2925(13)
Cd(1)–N(1)	2.488(4)	Cd(2)–O(3)	2.228(3)
Cd(2)–Cl(2)	2.3180(13)	Cd(2)–N(2)	2.424(4)
Cd(3)–O(5)	2.225(4)	Cd(3)–O(7B)	2.286(4)
Cd(3)–Cl(3)	2.3207(15)	Cd(3)–Cl(4)	2.3295(14)
Cd(3)–N(5)	2.391(4)	Cd(4)–O(9)	2.278(4)
Cd(4)–O(11D)	2.280(4)	Cd(4)–Cl(6)	2.2805(14)
Cd(4)–Cl(5)	2.2919(14)	Cd(4)–N(8)	2.446(4)

Symmetry code: A: $-x+1$, $-y+1$, $-z+1$; B: $x-1$, y, z; C: $-x+1$, $-y$, $-z+1$; D: $x+1$, y, z.

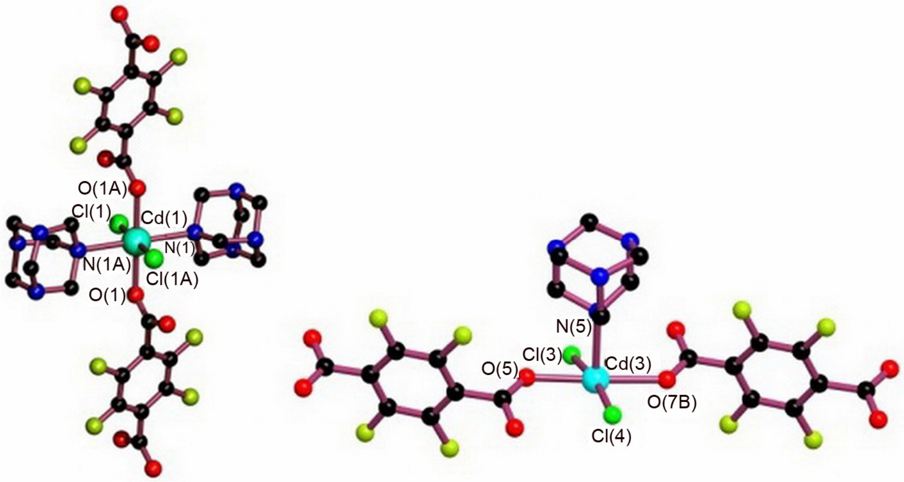

Fig. 3—The coordination environment of Cd(1) and Cd(3) atoms in **2**. All hydrogen atoms are omitted for clarity. [Symmetry code: A: –*x*+1, –*y*+1, –*z*+1; B: *x* – 1, *y*, *z*.].

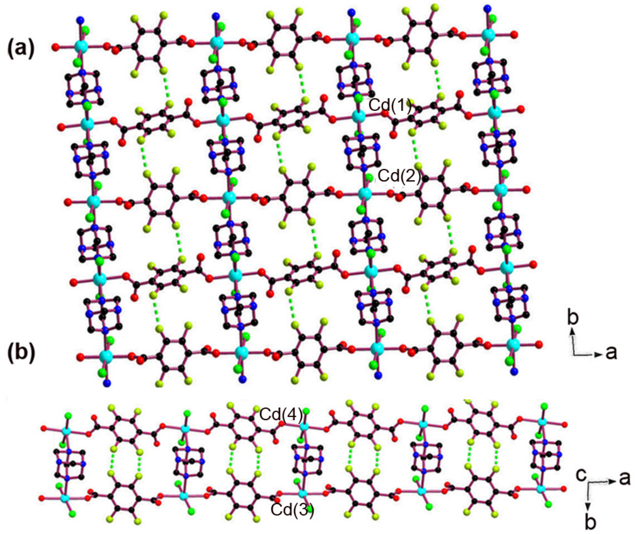

Fig. 4— (a) 2D Grid structure of polymer (A) viewed along the *c*-axis and (b) the 1D anionic ladder structure of polymer (B) viewed along the *c*-axis. The F···F interactions are shown in bright green dashed line. All solvent water molecules and hydrogen atoms are omitted for clarity.

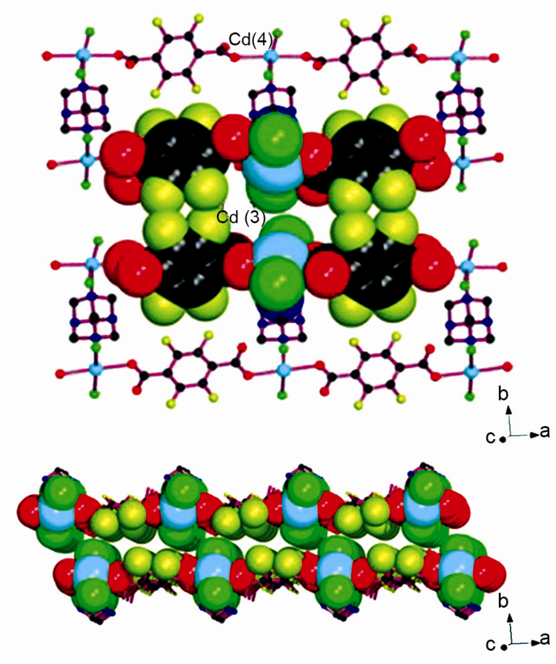

Fig. 5—The hydrophobic environment of Cd(3) and Cd(4) atoms in **2**.

of **2**, atoms Cd(3) and Cd(4) in polymer (B) are in five-coordinated square pyramidal geometry. We tentatively ascribe this difference to the fact that the hydrophobic environment (Fig. 5) created by the F and Cl atoms may hamper the water molecules or other ligands to further coordinate to the Cd atoms, leading to the formation of the novel mixed 1D+2D structure in **2**.

The F···F contacts, (F(1)···F(3C)/F(3)···F(1C) = 2.866(4) Å), of tfbdc^{2-} are also found in the polymer (A) (Fig. 4A), which are similar to those in the 2D layer of **1**. Besides, there are two much shorter F···F contacts in polymer (B), i. e., F(7)···F(9C)/F(9)···F(7B) (2.384(4) Å) and F(8)···F(10C)/F(10)···F(8B) (2.509(4) Å) of the tfbdc^{2-} anions from the adjacent linear [Cd(μ-tfbdc)]$_{\infty}$chains (Fig. 4B). Two other F···F contacts (F(5)···F(11C)/F(11)···F(5B) = 2.329(4) Å and F(6)···F(12C)/F(12)···F(6B) = 2.534(4) Å) linked the adjacent 1D ladders to form a 2D layer parallel to the crystallographic *ab* plane (Fig. 4A), which is also parallel to the 2D grid of polymer (A) without any entanglements. Additionally, the intramolecular hydrogen bonds between the

Table 5—Hydrogen bond distances (Å) for 2

D–H···A	D–H	H···A	D···A
N(3)–H(3)···Cl(6)	0.91	1.93	2.817(5)
N(6)–H(6)···Cl(1)	0.91	2.02	2.880(5)
N(10)–H(10Y)···Cl(5)	0.90	2.44	2.955(5)
O(1W)–H(1X)···N(9A)	0.90	2.38	2.882(6)
O(1W)–H(1Y)···O(7B)	0.90	2.47	2.984(5)
N(9)–H(9Y)···O(10A)	0.90	2.52	3.045(6)
N(9)–H(9V)···F(9A)	0.90	2.34	2.901(5)
C(1)–H(1b)···F(1)	0.97	2.53	3.211(5)
C(3)–H(3a)···O(3)	0.97	2.51	3.066(7)
C(6)–H(6a)···O(9)	0.97	2.48	3.293(7)
C(15)–H(15b)···O(5)	0.97	2.48	3.045(7)
C(5)–H(5b)···Cl(2C)	0.97	2.38	2.872(6)
C(19)–H(19a)···F(10D)	0.97	2.48	3.322(5)
C(20)–H(20a)···O(4A)	0.97	2.40	3.341(7)
C(2)–H(2b)···O(8E)	0.97	2.36	3.305(7)

Symmetry code: A: – x+1, –y+1, –z+1; B: x –1, y, z; C: –x+1 , –y, –z+1; D: x+1, y, z; E: x – 1, y – 1, z

protonated tertiary amino functions $\equiv N^+$–H and two terminal Cl$^-$ anions, N(6)–H(6)···Cl(1) (2.817(5) Å) and N(3)–H(3)···Cl(6) (2.880(5) Å) (Fig. 6, Table 5) in compound **2** extend the structure into 2D tri-layer supramolecular architecture, as it infinite sandwiches are put together in an orderly manner. As shown in Fig. S4 (Supplementary Data), the free solvent water molecules and NH_4^+cations are linked to the polymer (B) by five other kinds of strong hydrogen bonds, between the solvent water molecules and the uncoordinated O atoms of the tfbdc^{2-} anions or NH_4^+cations, between the NH_4^+cations and F atoms of the tfbdc^{2-} anions or Cl$^-$ anion from polymer (B) to form a 2D layer supramolecular architecture, like some huge sandwiches embellished with sesame.

In principle, for crystal packing between 1D chains and 2D nets, the nets can be either parallel or inclined[31-38]. The parallel packing of covalent 1D+2D→2D is reported only in $[Hg_2(\mu\text{-bpdh})(\mu\text{-SCN})_4]_n[Hg_2(\mu\text{-bpdh})(\mu\text{-SCN})_4]_{2n}$ (bpdh = 2,5-bis (3-pyridyl)-3,4-diaza-2,4-hexadiene)[31], but herein the 2D net is polycatenated by the 1D double chain. However, in **2**, the 2D net (part A) is parallel to the 1D ladder (part B) without mutual entanglement or interdigitation. Eventhough the hydrogen bond interactions and the F···F interactions are present, only a 2D supermolecular structure is formed in **2**. Hence, compound **2** is the first case of 2D+1D→2D coordination polymer without any entanglements.

PXRD and luminescent properties

For **1** and **2**, the X-ray powder diffraction Patterns showed good correlation between the experimental patterns and the simulated ones (Supplementary Data, Fig. S5), indicating reasonably good phase purity of these compounds.

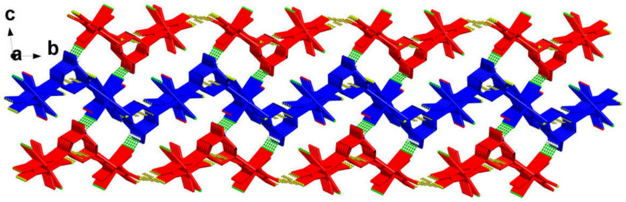

Fig. 6—2D Tri-layer supramolecular architecture via F···F (dark yellow dashed line) and N–H···Cl (bright green dashed line) interactions in **2**. Side view of polymer (A) and polymer (B) are shown in blue and red, respectively.

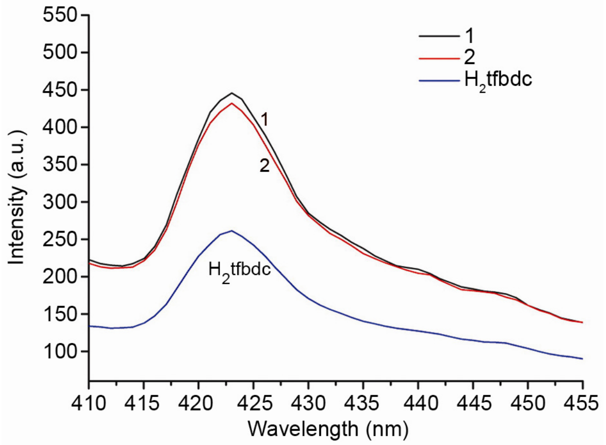

Fig. 7—Solid-state emission spectra for free ligand H_2tfbdc and complexes **1** and **2** (λ_{ex} = 370 nm) at room temperature.

The solid-state luminescent properties of organic ligands H_2tfbdc and complexes **1** and **2** were investigated at room temperature, and are depicted in Fig. 7. H_2tfbdc and both the complexes exhibit purple fluorescence with emission maximal at 423 nm upon excitation at 370 nm. The emissions of the two complexes can be rationally assigned to π*–π transition of tfbdc^{2-} ligand, due to their similarity in emissions[39-46]. Moreover, the emission intensity of two complexes is remarkably stronger than that of the free ligand, which may be assigned to the increased rigidity of the ligand when it is bound to a metal center, which effectively reduces the loss of energy[51, 52].

Conclusions

In conclusion, two distinct Cd(II) coordination polymers, including a 2D rectangular grid (**1**), and a new type of 1D+2D→2D layer structure (**2**), have been successfully assembled. **2** is the first case of 2D coordination polymer consisting of 1D ladders and 2D layers in one crystal without any entanglements. Clearly, the different organization of such two 2D layers is controlled only by the metal-to-ligand ratios.

Supplementary Data

CCDC 1059251 and 1059252 for **1** and **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223–336033, or deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article, i.e. Figs S1–S5 are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(02) 203-210_SupplData.pdf.

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