Self-Assembly of Five Cadmium(II) Coordination Polymers from 4,4′-Diaminodiphenylmethane

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Five cadmium(II) coordination polymers formed from dadpm (dadpm = 4,4′-diaminodiphenylmethane), namely, $[Cd(dadpm)(I)_2]_n$ (**1**), $[\{Cd(dadpm)_2(Cl)\}(dca)]_n$ (**2**) [dca = dicyanamide anion, $N(CN)_2^-$], $[\{Cd(dadpm)_2(Br)\}(dca)]_n$ (**3**), $[Cd(dadpm)(SCN)_2]_n$ (**4**) and $[Cd(dadpm)(dca)_2]_n$ (**5**) have been synthesized and characterized by NMR, IR, and fluorescence spectroscopy as well as TG analysis. The ligand dadpm in **1** bridges the metal centers to form a zigzag chain where the halide anion I^- acts as a terminal ligand. Weak Cd···I interactions between adjacent chains extend the zigzag chains into a wave-like layer. Complexes **2** and **3** are isomorphous, the metal centers are bridged by dadpm to generate a double-stranded chain containing the metallacycles of $[Cd_2(dadpm)_2]$, and the halide anions (Cl^- in **2** and Br^- in **3**) link adjacent chains into 2D layer structures in a *trans* mode. Dicyanamide anions in the two complexes lie between the layers as supported anions and link the adjacent layers into 3D structures through hydrogen bonds. In complex **4**, the metal centers are bonded by the thiocyanate anions to form double-stranded chains, which are linked by dadpm in different orientations resulting in a cross-linked 3D structure. In **5**, dicyanamide anions connect the cadmium(II) centers to form a $[Cd(dca)_2]_n$ 2D layer, which contains 24-membered ring units $[Cd_4(\mu_{1,1}\text{-dca-}N,N)_4]$. The dadpm ligand links the adjacent layers into an α-Po-like 3D network structure.

Introduction

In the research of supramolecular chemistry, much interest has recently been focused on the crystal engineering of coordination frameworks because of their intriguing architectures, fascinating topologies, intertwining phenomena, and potential application in functional materials.[1] Self-assembly based on molecules has emerged as an attractive approach to the fabrication of these new materials, and considerable effort has been made towards the supramolecular networks assembled by covalent and hydrogen bonds or other molecular interactions.[2] The family of metallacyclic nanostructures assembled from transition metal junctions and bridging ligands is now a well-established group of coordination polymers,[3] and the diversity of such coordination nanostructures makes them remarkable examples in the growing library of self-assembled entities.[4] Although many topologically promising architectures have been constructed from building blocks containing nitrogen donors,[5] such as 4,4′-bipyridine,[6] pyrazine,[7] bis(4-pyridyl)ethane,[8] 1,4-bis(4-pyridyl)benzene,[9] 2,4,6-tri(pyridyl)-1,3,5-triazine[10] and 4,4′-azobis(pyridine),[11] few coordination polymers based on bifunctional neutral ligands containing aromatic NH_2 donors are documented. The involvement of oligoaniline in the assembly of supramolecular chemistry is limited because of its instability, as it is easily oxidized in an aqueous solution and/or in air. Although the aromatic diamine ligand dadpm has a poorer donor ability than the corresponding pyridyl-type ligands used before, it can still coordinate to transitional metal ions by one NH_2 group to act as a terminal ligand as in $[Cu_2(C_2H_4N_2O_2)(dadpm)_2(Br)_2]$ [$C_2H_4N_2O_2$ = bis(2-aminoethyl)oxamidato][12a] or two NH_2 groups to act as a bridging ligand as in $\{[Cu(dadpm)(C_3H_4O_4)Cl]Cl\}_2$ ($C_3H_4O_4$ = malonic acid)[12b] and $[Cu_2(dadpm)_2(PyCH_2NHCOCONHCH_2Py)]\cdot 2NO_3\cdot 6H_2O$.[12c] The ligand dadpm may be utilized as a building block for the construction of novel organic/inorganic hybrid materials. In this paper, we report on the self-assembly reactions of dadpm and cadmium(II) halides in the presence of dca^- or SCN^- ions, and the structural characterizations of five coordination polymers, $[Cd(dadpm)(I)_2]_n$ (**1**), $[\{Cd(dadpm)_2(Cl)\}(dca)]_n$ (**2**), $[\{Cd(dadpm)_2(Br)\}(dca)]_n$ (**3**), $[Cd(dadpm)(SCN)_2]_n$ (**4**) and $[Cd(dadpm)(dca)_2]_n$ (**5**).

Results and Discussion

Syntheses

During the preparation of the dadpm/Cd complexes, direct treatment of dadpm with various cadmium halides

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failed to produce a complex, which may be ascribed to the poor coordination ability of dadpm. As the dicyanamide anion has various coordination modes,[13] and thus can provide a suitable "building block" for assembling novel inorganic/organic hybrid materials, we want to introduce this anion ligand into the Cd halide/dadpm reaction mixture as a co-ligand in order to prepare some novel dadpm−Cd complexes. Mixing of $CdX_2 \cdot nH_2O$ ($X = I$, $n = 0$; $X = Br$, $n = 4$; $X = Cl$, $n = 2.5$) with 4,4′-diaminodiphenylmethane and sodium dicyanamide in a 1:2:1 ratio in hot aqueous solution resulted in the crystalline complexes **1**, **2** and **3** with 1D to 2D structures. As in our recent report on Cd coordination frameworks,[15] the larger radius of I^- results in the cadmium atom adopting a tetracoordinated geometry upon coordination, while with the halide ions Cl^- and Br^-, the cadmium ion adopts a six-coordinate geometry. The dca^- anion is not incorporated into complex **1**, but acts as a supported anion in both **2** and **3**. The effect of the dca^- anion in the formation of **1** is still unclear. While we changed the reaction sequence, namely, first mixing the Cd salt with the dadpm ligand, then adding the dicyanamide anion to the reaction mixture, complex **5** with an α-P_o-like 3D net structure was obtained, which is completely different from those of **1**, **2** and **3**. Using another anion ligand with a different size and shape, the SCN^- anion, complex **4** with a cross-linked 3D structure was obtained.

Description of the Structures

The X-ray analysis revealed that the cadmium atoms in complex **1** are bridged by a dadpm ligand with the occurrence of an 1D coordination polymeric chain along the *a* axis. An ORTEP view of the chain with atom labeling is shown in Figure 1 (a). Each cadmium atom is tetracoordinated by two nitrogen atoms of two dadpm ligands and two I^- anions with square-planar coordination geometry. The Cd−N(dadpm) bond length is 2.32(2) Å, and the Cd−I distance 2.794(3) Å. The Cd···Cd separation is 13.131 Å through the bridging dadpm ligand. The inter-chains are tightly packed (Cd···Cd = 4.520 Å) by the weak interaction between the Cd^{II} center and the I^- anion belonging to neighbor chains [Cd(E)−I = 3.587 Å, symmetry code: (E) *x*, *y*, 1 + *z*], forming a quasi-2D wave-like sheet as shown in Figure 1 (b). In the sheet structure, there are a four-membered ring and a 28-membered ring, the former contains two cadmium(II) ions and two I^- anions, and the latter two cadmium(II) ions, two I^- anions and two dadpm ligands.

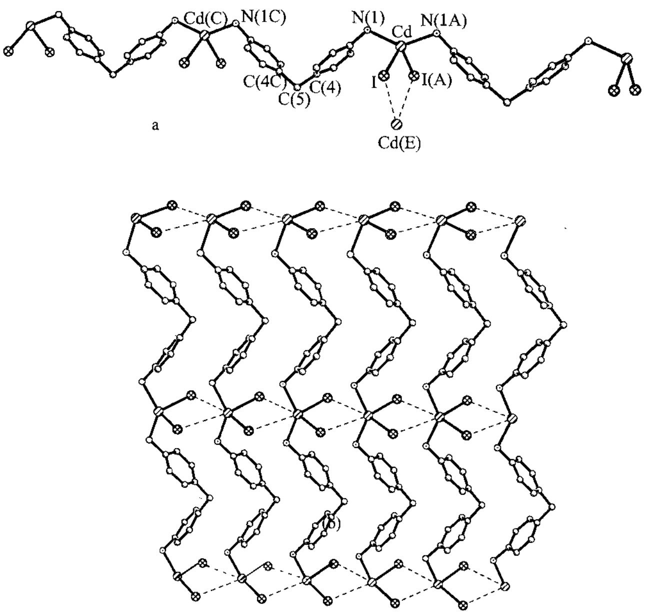

Figure 1. (a) ORTEP drawing of the zigzag chain in **1** with atom numbering scheme, showing the cadmium coordination environment; (b) quasi-two dimensional sheet of **1** formed through weak Cd···I interactions

In the crystal structure of **2**, each cadmium(II) center is bridged by four dadpm ligands to give rise to a double stranded chain as shown in Figure 2 (a). The dadpm adopts a *trans*-gauche conformation and two dadpm ligands bridge two cadmium(II) ions to form a distorted square metallacyclic ring with a Cd−Cd distance of 12.401 Å. In the square ring, each of the two opposite phenyl rings of the two dadpm ligands are parallel and the two adjacent phenyl rings are almost perpendicular with a torsion angle of 89.7°. The dimensions of the ring are approximately 7.15 × 4.15 $Å^2$ based on the distance of the two opposite phenyl rings, which is slightly shorter than those of the $[Cu_2(dadpm)_2]$ macrocycle (8.36 × 4.15 $Å^2$) in $[Cu(dadpm)\{CH_2(COOH)_2Cl\}Cl]_2$.[12b] The cadmium atom is six-coordinate in an elongated octahedral environment. The equatorial plane is defined by four N atoms from four dadpm ligands with two short Cd−N bonds [Cd−N(4A), 2.357(5) Å] and two long Cd−N bonds [Cd−N(5), 2.3852(4) Å]. The four equatorial donor atoms and the central cadmium(II) atom are almost coplanar with a mean deviation of 0.012 Å and N−Cd−N bond angles of 86.1(2) and 93.9(2)°. Two chloride anions are at the axial positions and link the adjacent double-stranded chains into an unprecedented 2D layer with a Cd−Cl bond length of 2.752(6) Å, as shown in Figure 2 (b). The channels are viewed through the metallacycles packing along the *b* axis. The Cl−Cd−N bond angles vary from 80.0(1) to 100.0(1)° and the Cd−Cd separation of adjacent chains is 5.505 Å with a Cd−Cl−Cd bond angle of 180°.

The dicyanamide anion is disordered in the structure. It does not engage in coordination and acts as a supported anion between the 2D layers through the hydrogen bond interactions between the N atoms (N1 and N3) of the dicyanamide anion and the N atoms (N4) of dadpm as in Figure 2 (c) [N3···N4B, 2.821 Å; N1···N4 H, 2.832 Å, symmetry code: (H) −*x*, *y*, −1 + *z*]. Through these hydrogen bonds, a 32-membered ring constructed by two dadpm ligands, four Cd^{II} centers and two N−C≡N groups of two dca^- anions is formed and the other C≡N groups of the dca^- anions protrude into the cavity of the ring.

An X-ray crystal analysis revealed that complex **3** exhibits a similar structure to that of complex **2** except that **2** has a Br^- bridge instead of a Cl^- bridge. An ORTEP drawing of the molecular structure of **3** with atom labeling is shown in Figure 3 (a). The Cd−N bond lengths [Cd−N(4) 2.38(1)

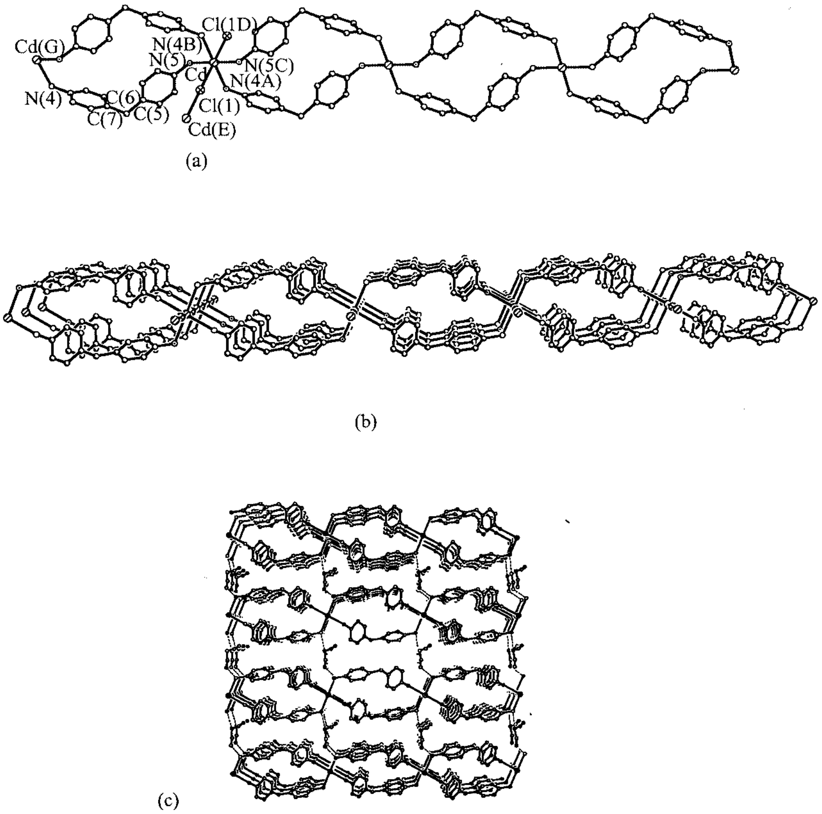

Figure 2. (a) ORTEP drawing of the double-stranded chain in **2** with atom numbering; (b) ORTEP drawing of the layer structure of **2** to view the channels in the *b* axis direction; (c) perspective view of the dicyanamide anion's supported 3D structure of **2**

Å and Cd−N(5A) 2.38(1) Å] in the equatorial plane are slightly longer than those in **2**, and the N−Cd−N bond angles are 85.7(4) and 94.3(4)°. The separation between the two Cd^{II} atoms in the$[Cd_2(dadpm)_2]$ macrocycle is 12.452 Å, similar to that in **2**, and the dimensions of the macrocycle are about 7.25 × 4.06 Å. The Br^- anions coordinate axially with the cadmium centers in a *trans* geometry to link the adjacent chains into a 2D layer with Cd−Br−Cd bond angles of 180°. The Cd−Cd separation of adjacent chains is 5.505 Å, which is larger than the corresponding value in **2** through the Cl^- bridge because of the larger radius of the Br^- ion. Similar to **2** the dicyanamide anions in **3** lie between two adjacent layers acting as supporting anions.

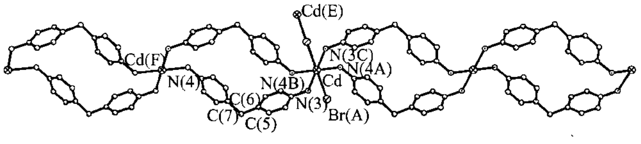

Figure 3. ORTEP drawing of **3** with atom labeling, showing the cadmium coordination environment

An ORTEP view of a Cd center of **4** is shown in Figure 4 (a). Each cadmium(II) atom is located on an inversion center, and coordinated by two thiocyanate nitrogen atoms [Cd−N(SCN), 2.335(7) Å] and two thiocyanate sulfur atoms [Cd−S, 2.746(2) Å] in a *trans* geometry in the equatorial plane, resulting in a chain structure containing eight-membered $[Cd_2(SCN)_2]$ rings as in Figure 4 (a), which have been well documented in Cd^{II}/L/SCN systems.[17] Two nitrogen atoms of two dadpm groups complete the remaining two axial positions around the six-coordinate Cd^{II} center and the distance of Cd−N(dadpm) is slightly longer than Cd−N(SCN) with a bond length of 2.354(6) Å. The cadmium thiocyanate chains are cross-linked by the dadpm with different orientations into a 3D polymer as in Figure 4 (c). The Cd···Cd separation is 13.518 Å through the dadpm ligand. In the 3D structure, four SCN^- ions and four dadpm ligands link eight cadmium ions into a 64-membered ring with dimensions of 30.57 × 6.2 Å, as shown in Figure 4 (b).

Each cadmium(II) center in **5** is in a distorted octahedral environment, being coordinated by four nitrogen atoms of four dca^- ligands in the equatorial plane and two nitrogen atoms of two *trans*-related dadpm ligands at the axial positions as shown in Figure 5 (a). The Cd−N(dadpm) bond length is 2.39(1) Å, and Cd−N(dca) bond lengths are 2.31(1) and 2.33(1) Å. The dca^- ligands and Cd centers are interlinked into a 2D layer, resulting in an hourglass-shaped, 24-membered $[Cd_4(\mu_{1,1}\text{-dca-}N,N)_4]$ metallacycle, as shown in Figure 5 (b), different from other reported Cd−dca coordination polymers in which the Cd centers and dca^- ligands are interconnected into $[Cd(dca)_2]_n$ chains.[18] The Cd···Cd separation through the dca^- ligand in **5** is 7.597 Å. For comparison, $Zn[N(CN)_2]$ features a 2D

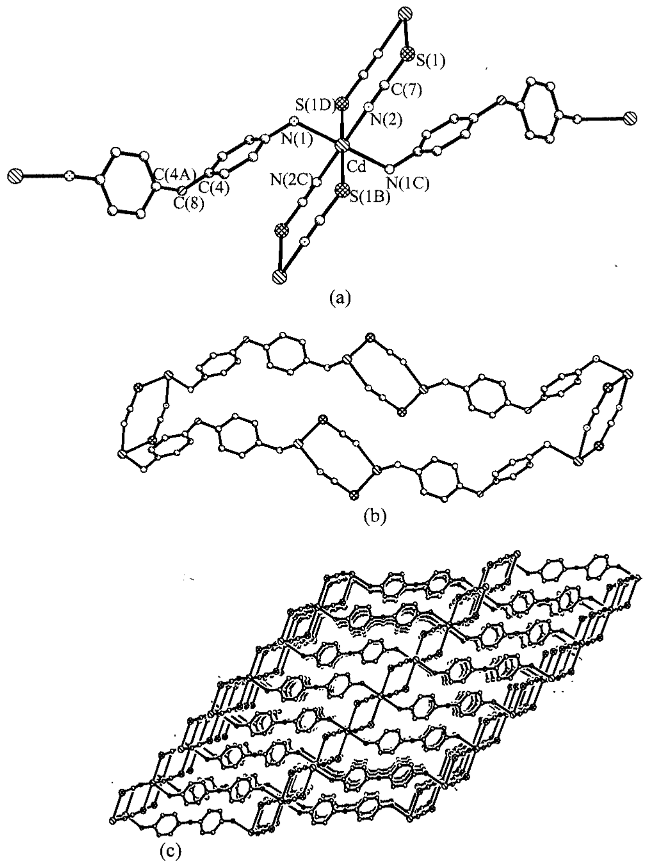

Figure 4. (a) ORTEP drawing of **4** with atom numbering, showing the cadmium coordination environment; (b) perspective of the metallacycle in **4**; (c) view of the 3D structure of **4**

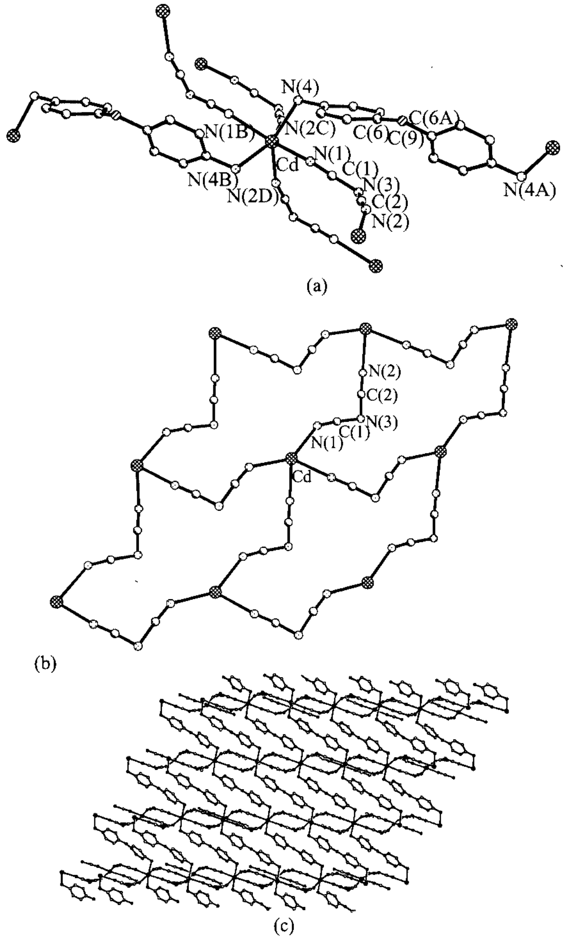

Figure 5. (a) ORTEP drawing of the cadmium(II) coordination in **5** with atom numbering; (b) perspective of the 2D sheet in **5**; (c) view of the α-P$_o$-like 3D structure of **5**

layer structure with linkages similar to the [Cd(dca)$_2$] layer in **5**, but the layers are markedly buckled and packed in a staggered fashion due to the tetrahedral configuration of Zn^{II}.[19] To the best of our knowledge, such a [Cd$_4$(μ$_{1,1}$-dca-*N,N*)$_4$] arrangement of the metallacycle is unprecedented, and only a few similar structures have been reported, such as [Mn$_4$(SCN)$_4$] in [Mn(EtOH)$_2$(NCS)$_2$],[20a] [Mn$_4$(N$_3$)$_4$] in [Mn(4-acpy)$_2$(N$_3$)$_2$] (4-acpy = 4-acetylpyridine),[20b] and [Cd$_4$(NCS)$_4$] in [Cd(SCN)$_2$(3-PyCONH$_2$)$_2$] (3-PyCONH$_2$ = nicotinamide).[20c]

As shown in Figure 5 (c), the [Cd(μ$_{1,1}$-dca-*N,N*)$_2$]$_n$ layers are further linked by the dadpm ligands into an α-P$_o$-like 3D net as in [Mn(dca)$_2$(pz)].[21] A 36-membered ring is formed through four cadmium ions linked by two single μ$_{1,1}$-dca-*N,N* bridges and two dadpm ligands. The Cd···Cd distance is 12.328 Å through the bridging dadpm ligand.

The C(Ph)−C−C(Ph) bond angles, the dihedral angles between the two phenyl rings of dadpm and the M···M distances through the dadpm ligand in the five complexes are listed in Table 3. The C(Ph)−C−C(Ph) bond angles show slight differences, which range from 102.0(1)° in **5** to 115.9(1)° in **3**. But the dihedral angles between the two phenyl rings in the dadpm ligand show large differences in the five complexes, ranging from 55.3(2)° in **5**, 57.2(3)° in **4** to 81.6(4)°in **1**, 87.7(6)° in **3** and 89.7(5)° in **2**, which may be ascribed to the different coordination schemes of dadpm. In **1**, **4** and **5** the dadpm ligand links the metal atoms into a zigzag chain, but in **2** and **3**, the dadpm ligand connects the metal atoms into a double-stranded chain. The Cd···Cd distances through the dadpm ligand range from 12.328 Å in **5** to 13.131 Å in **1**. The structural data show the flexibility of the dadpm ligand in the five coordination polymers. The flexibility of dadpm induces a small effective cavity volume of the channels in the five dadpm−Cd complexes and no guest molecules are accommodated in the channels.

IR, ^{1}H NMR and Fluorescent Spectra

All of the five complexes show strong C≡N stretching vibrations of the dca$^-$ or SCN$^-$ ions in the region 2000−2300 cm^{-1}, except complex **1**. The strong C≡N stretching vibration of thiocyanate in **4** at 2116 cm^{-1} suggests a bridging mode.[22] The C≡N stretching vibrations of [N(CN)$_2$]$^-$ are at 2260, 2210, 2148 cm^{-1} in **2**, and 2258, 2213, 2149 cm$^-$ in **3**, but shifted to 2301, 2248, 2176 cm^{-1} in **5**, which are assigned to ν$_{sym}$ + ν$_{asym}$ (C≡N), ν$_{asym}$ (C≡N) and ν$_{sym}$ (C≡N), respectively. Compared with the corresponding spectroscopic data of free [N(CN)$_2$]$^-$,[23] the

$[N(CN)_2]^-$ ligand acts as a supported anion in **2** and **3**, but a $\mu_{1,1}$-end-to-end bridge in **5** and **6**, which is consistent with the results of X-ray analyses. The aromatic C−H stretching vibrations are in the region 2800−3000 cm^{-1}. The strong bands in 3100−3350 cm^{-1} are ascribed to ν_{N-H} stretching vibrations in the five complexes.

The ^1H NMR spectra of **1**, **2**, **3**, and **5** show resonance signals at $\delta = 6.80$ and 6.45 [m, 8 H, 2 (C_6H_4)], 4.837 [s, 4 H, 2 (NH_2)] and 3.547 (s, 2 H, CH_2) ppm for the dadpm ligand. The ^1H NMR signals for the NH_2 group protons of all five complexes are slightly shifted downfield relative to the free ligand, while the signals of other protons remain essentially unchanged in the five complexes.

The fluorescent characterization shows that each complex has a strong or medium yellow fluorescent emission[24] [585 (m) in **1**, 590 (s) in **2**, 593 (s) in **3**, 567 (m) in **4**, and 570 nm (m) in **5** and the wavelength at which the complex is excited is 310 nm], which may be ascribed to ligand-to-metal charge transfer (LMCT) bands.

Thermogravimetric Analysis

Thermogravimetric analyses show that all five of the complexes are stable. Complex **1** remains stable up to 190 °C, and then it slowly decomposes with the loss of the ligand dadpm. Complex **2** and **3** are stable up to 153 and 168 °C . The TGA trace displays a gradual weight loss of 11.5% (calculated 10.81%) from 153 to 209 °C for complex **2** and 10.08% (calculated 10.5%) from 168 to 235 °C for complex **3**, which corresponds to the weight loss of one dca^- supported anion. When the temperature exceeds about 250 °C, both of them begin to decompose. Complex **4** decomposes from 220 °C with a weight loss of 49.5% (calculated 44.71%) corresponding to the decomposition of the dadpm ligand. Subsequent weight loss from 350 °C may correspond to the decomposition of the thiocyanate groups. The TG curve of **5** shows that the complex is stable below 238 °C, and that from this temperature the compound decomposes and loses the dadpm and dca ligands almost simultaneously.

Conclusion

In spite of the similarity of the building blocks used, the products display quite different structures. The isolated five coordination compounds include one- or three-dimensional polymeric structures sustained only by coordinative bonds (**1**, **4** and **5**), and three-dimensional arrays connected both by coordinative and hydrogen bonds (**2** and **3**). The variety of the observed structural motifs confirms that rationalization of the resulting topologies is still difficult. Many factors play a role in the formation of the final product: (i) the anions effects (I^-, Cl^- and Br^- in **1**, **2** and **3**, and also dca and SCN^- anions in **4** and **5**); (ii) the conformational flexibility of the dadpm ligand; (iii) the versatility of the metal coordination sphere (the cadmium coordination geometry is tetrahedral in **1**, but octahedral in **2**, **3**, **4** and **5**); and (iv) the reaction sequence (in **2** and **5**). This work demonstrates the feasibility of achieving various polymeric frameworks by self-assembly of the flexible aromatic diamine ligand and metal salts and may provide useful information for crystal engineering.

Experimental Section

General: All chemicals were of an analytical grade and used without further purification. Elemental analyses of C, H N and S were performed with an Elementar Vario ELIII elemental analyzer. IR spectra were recorded as KBr pellets with a Nicolet Magna 750 FT-IR spectrometer in the range of 200−4000 cm^{-1}. Thermogravimetric analyses (TGA) were performed with a NETSCHZ STA-449C thermoanalyzer under N_2 (26−1000 °C range) at a heating

Table 1. Crystallographic data for complexes **1−5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{13}H_{14}CdI_2N_2$	$C_{28}H_{28}CdClN_7$	$C_{28}H_{28}BrCdN_7$	$C_{15}H_{14}CdS_2N_4$	$C_{17}H_{14}CdN_8$
Formula mass	564.48	610.42	654.88	428.8	444.74
Crystal system	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
Space group	*Imm*2	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a [Å]	12.828(4)	5.5052(5)	5.7166(8)	9.411(2)	13.337(2)
b [Å]	13.131(4)	9.9187(9)	9.702(2)	8.059(2)	7.277(1)
c [Å]	4.520(1)	12.166(1)	11.965(2)	20.589(4)	10.214(2)
α [°]	90	88.449(2)	87.302(2)	90	90
β [°]	90	79.453(2)	80.340(2)	93.495(0)	118.557(3)
γ [°]	90	83.843(2)	84.058(2)	90	90
V [$Å^3$]	761.5(4)	649.3(1)	650.4(2)	1558.5(5)	870.7(3)
Z	4	2	2	8	4
μ [mm^{-1}]	2.737	0.976	2.407	1.669	1.273
No. of reflections:					
total	975	3396	2145	2316	929
unique	508	2270	1222	1375	634
$R[I > 2\sigma(I)]$					
*R*1	0.0546	0.0550	0.0630	0.0603	0.0630
*wR*2	0.1251	0.1538	0.1480	0.1286	0.1788

rate of 10°/min. NMR spectra were carried out with a Varian 500 spectrometer. Fluorescent spectra were measured with an Edinburgh F900 analytical instrument at Fuzhou University.

Syntheses

[Cd(dadpm)(I)$_2$]$_n$ (1): Ligand dadpm (0.10 g, 0.5 mmol) was added to an aqueous solution (30 mL) of CdI_2 (0.09 g, 0.25 mmol). After stirring the mixture for about 30 min, a DMF (5 mL) solution of sodium dicyanamide (0.03 g, 0.25 mmol) was added. The above mixture was stirred and heated for 1 h and then filtered while still hot. The filtrate was allowed to stand at room temperature. On concentration for about one week, colorless block crystals of **1** were obtained. Yield: 0.10 g (72%). $C_{13}H_{14}CdI_2N_2$ (564.48): calcd. C 27.64, H 2.48, N 4.96; found C 28.45, H 2.57, N 5.06.

[{Cd(dadpm)$_2$(Cl)}(dca)]$_n$ (2): This compound was prepared as light-yellow block crystals in a similar manner to that of **1** except $CdCl_2{\cdot}2.5H_2O$ was used instead of CdI_2 Yield 0.12 g (78%). $C_{28}H_{28}CdClN_7$ (610.42): calcd. C 55.04, H 4.59, N 16.05; found C 55.14, H 4.66, N 16.14.

[{Cd(dadpm)$_2$(Br)}(dca)]$_n$ (3): This compound was prepared as light-yellow block crystals in a similar manner to that of **1** except $CdBr_2{\cdot}4H_2O$ was used instead of CdI_2. Yield 0.13 g (82%). $C_{28}H_{28}CdBrN_7$ (654.88): calcd. C 51.31, H 4.28, N 14.96; found C 51.42, H 4.26, N 15.04.

[Cd(dadpm)(SCN)$_2$]$_n$ (4): Sodium thiocyanate (0.05 g, 0.5 mmol) was added to an aqueous (30 mL) solution of $CdCl_2{\cdot}2.5H_2O$ (0.057 g, 0.25 mmol). After stirring of the mixture for about 30 min, a DMF (5 mL) solution of the ligand dadpm (0.05 g, 0.25 mmol) was added. The above mixture was stirred and heated for 1 h and then filtered while still hot. Well-shaped light-yellow crystals of **4** were obtained from the filtrate by slow concentration at room temperature for several days. Yield 0.078 g (73%). $C_{15}H_{14}CdN_4S_2$ (428.8): calcd. C 41.98, H 3.26, N 13.06; found C 42.07, H 3.35, N 13.16.

[Cd(dadpm)(dca)$_2$]$_n$ (5): This compound was prepared as pale yellow prismatic crystals in a similar manner to that of **4** except that sodium dicyanamide was used instead of sodium thiocyanate. Yield 0.074 g (67%). $C_{17}H_{14}CdN_8$ (444.74): calcd. C 45.87, H 3.15, N 25.18; found C 45.92, H 3.22, N 25.28.

X-ray Crystallography: Colorless crystals of **1** and light-yellow crystals of **2**, **3**, **4** and **5** were selected for diffraction analyses. The data collections were performed with a Siemens Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K. All the structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELX-97 program.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically. The crystallographic data for compounds **1−5** are listed in Table 1, and selected bond lengths and angles in Table 2. Additional crystallographic details and complete listings of the five complexes have been deposited with the Cambridge Crystallographic Data Centre. CCDC-177678 (**1**), -175521 (**2**), -177947 (**3**), -177679 (**4**) and

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1−5**; symmetry codes: **1** (A) $-x, -y, z$; (B) $-x, y, z$; (C) $-x, -y - 1, z$; **2** (A) $-x, -y, -z + 1$; (B) $x + 1, y, z - 1$; (C) $- x + 1, -y, -z$; (D) $x + 1, y, z$; (E) $x - 1, y, z$; (F) $-x, -y + 1, -z$; (G) $x - 1, y, z + 1$; **3** (A) $x + 1, y, z - 1$; (B) $-x, -y, -z + 1$; (C) $- x + 1, -y, -z$; (D) $x + 1, y, z$; (E) $x - 1, y, z$; (F) $-x, -y + 1, -z$; (G) $x - 1, y, z + 1$; **4** (A) $- x - 1, y, -z + 1/2$; (B) $x - 1/2, y - 1/2, z$; (C) $-x, -y, -z + 1$; (D) $-x + 1/2, -y + 1/2, -z + 1$; (E) $x + 1/2, y + 1/2, z$; **5** (A) $- x + 1, y, -z + 1$; (B) $-x, y, -z$; (C) $x - 1/2, y + 1/2, z$; (D) $-x + 1/2, y + 1/2, -z$; (E) $x + 1/2, y - 1/2, z$)

Complex **1**:			
Cd−N(1)	2.32(2)	Cd−I	2.794(3)
N(1)−Cd−N(1A)	137.0(1)	N(1)−Cd−I(A)	102.8(3)
N(1)−Cd−I	102.8(3)	I−Cd−I(A)	104.9(1)
C(4)−C(5)−C(4C)	109(3)		
Complex **2**:			
Cd−N(4A)	2.357(5)	Cd−N(5)	2.385(4)
Cd−Cl(1)	2.7526(3)		
N(4A)−Cd−N(5)	93.9(2)	N(5)−Cd−Cl(1)	100.0(1)
N(4A)−Cd−Cl(1)	99.4(1)	N(4A)−Cd−N(5C)	86.1(2)
N(4B)−Cd−Cl(1)	80.6(1)	N(5)−Cd−Cl(1D)	80.0(1)
Cl(1D)−Cd−Cl(1)	180.0	Cd(E)−Cl(1)−Cd	180.0
C(5)−C(6)−C(7)	115.8(4)		
Complex **3**:			
Cd−N(3)	2.38(1)	Cd−N(4A)	2.38(1)
Cd-Br	2.8583(4)		
N(3)−Cd−N(4A)	85.7(4)	N(3)−Cd−Br	98.1(3)
N(3)−Cd−N(4B)	94.3(4)	N(3C)−Cd−Br	81.9(3)
N(4B)−Cd−Br	99.0(3)	N(4A)−Cd−Br	81.0(3)
Br−Cd−Br(D)	180.0	Cd(E)−Br−Cd	180.0
C(5)−C(6)−C(7)	116.0(1)		
Complex **4**:			
Cd−N(2)	2.336(7)	Cd−N(1)	2.353(6)
Cd−S(1B)	2.746(2)		
N(1)−Cd−S(1D)	84.0(2)	N(1)−Cd−S(1B)	96.0(2)
N(2)−Cd−N(1C)	91.6(3)	N(2)−Cd−S(1B)	92.4(2)
N(2)−Cd−N(1)	88.4(3)	N(2)−Cd−S(1D)	87.6(2)
N(2)−C(7)−S(1)	177.8(8)	C4−C(8)−C(4A)	114.9(9)
Complex **5**:			
Cd−N(1)	2.32(2)	Cd−N(2C)	2.34(3)
Cd−N(4)	2.38(2)		
N(1B)−Cd−N(1)	144.0(1)	N(2D)−Cd−N(4)	145.8(7)
N(1)−Cd−N(2C)	120.9(7)	N(1)−Cd−N(4B)	89.5(6)
N(1)−Cd−N(2D)	88.0(8)	N(1)−Cd−N(4)	72.1(7)
N(2C)−Cd−N(4)	87.4(8)	N(2D)−Cd−N(2C)	79.4(1)
N(4B)−Cd−N(4)	119.0(1)	C(6)−C(9)−C(6A)	99.3(5)

Table 3. C(Ph)−C−C(Ph) bond angles [°] and the dihedral angles of the two phenyl rings [°], M···M separations through dadpm [Å] for the five complexes

Complex	C(Ph)−C−C(Ph) bond angles	Dihedral angles of the two phenyl rings	M···M separations through dadpm
1	109.5(3)	81.6(4)	13.131
2	115.8(4)	87.7(6)	12.401
3	115.9(1)	89.7(5)	12.452
4	105.5(4)	57.2(3)	12.33
5	102.0(1)	55.3(2)	12.328

-177680 (**5**), 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.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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