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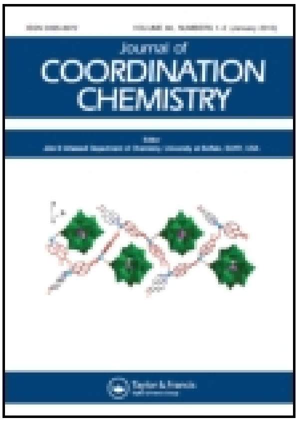

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Ligand-directed assembly of distinct 1-D Cd^{II} coordination polymers with a bent dipyridyl derivative and two isophthalates bearing different 5-substituents

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Ligand-directed assembly of distinct 1-D Cd^{II} coordination polymers with a bent dipyridyl derivative and two isophthalates bearing different 5-substituents

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Two 1-D Cd^{II} coordination polymers, $\{[Cd(4\text{-abpt})(hip)(H_2O)_2](H_2O)_{7/2}\}_n$ (**1**) and $\{[Cd(4\text{-Habpt})(sip)(H_2O)](H_2O)_2\}_n$ (**2**) (4-abpt = 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole, H_2hip = 5-hydroxyisophthalic acid, H_3sip = 5-sulfoisophthalic acid), have been hydrothermally synthesized and structurally characterized. Complex **1** has a comb-like 1-D coordination chain, while **2** presents a 1-D dual-track motif. The structural modulation of the coordination polymers can be achieved by simply changing the 5-substituent of the isophthalate from a hydroxyl group to a sulfonate group. Further, supramolecular architectures with higher dimensionality are constructed via hydrogen bonding and/or aromatic π-stacking interactions. Both complexes have been characterized by IR, microanalysis, and powder X-ray diffraction techniques. In addition, the solid fluorescence properties of both complexes have also been investigated.

Keywords: Cd^{II} Coordination complexes; Substituent effect; Hydrogen bonding; Aromatic stacking

1. Introduction

Crystalline solids of inorganic–organic hybrids have attracted widespread attention in the fields of electronics, optics, and magnetism and have the potential to provide new materials for use in areas such as separation science, catalysis, and chemical sensing [1–5]. Generally, relevant properties of the solids depend on their supramolecular network structures, which may be properly controlled by the appropriate choice of building blocks [6–8]. In other words, the selection of organic ligands plays an important role in assembling these crystalline materials. In this context, dipyridyl-type ligands, such as 4,4′-bipyridine and its derivatives, have been shown to be excellent linkers for coordination assemblies [9, 10]. In addition, carboxylate-containing organic ligands have also been used as typical building blocks in preparing coordination polymers due to their versatile coordination ability [11–13]. Dipyridyl- and carboxylate-based organic ligands are often mixed together (namely mixed-ligand systems) to assemble coordination polymers [14, 15]. Our previous work has shown that using these types of organic ligands as mixed ligands is an effective strategy to construct diverse coordination assemblies [16–18].

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In this work, a bent dipyridyl derivative 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (4-abpt) and aromatic dicarboxylic acids (H_2hip = 5-hydroxyisophthalic acid and H_3sip = 5-sulfoisophthalic acid) have been used as the mixed ligands with $Cd(OAc)_2$ to assemble coordination polymers under hydrothermal conditions. As a result, two different coordination polymers, $\{[Cd(4\text{-abpt})(hip)(H_2O)_2](H_2O)_{7/2}\}_n$ (**1**) and $\{[Cd(4\text{-Habpt})(sip)(H_2O)](H_2O)_2\}_n$ (**2**), have been obtained. Their structures can be regulated by changing the 5-substituent of the isophthalate from a hydroxyl to a sulfonate group. The complexes have been characterized by IR, microanalysis, and powder X-ray diffraction (PXRD) techniques. Moreover, the solid-state fluorescent properties of both complexes have also been explored and discussed.

2. Experimental

2.1. *Materials and methods*

With the exception of the ligand 4-abpt that was prepared according to the literature method [19], all reagents and solvents were commercially available and used as received without further purification. C, H, and N elemental analyses were carried out with a CE-440 (Leemanlabs) analyzer. FTIR spectra (KBr pellets) were obtained on an AVATAR-370 (Nicolet) spectrometer. PXRD patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 mA for a Cu-target tube ($\lambda = 1.5406$ Å). The calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software. Fluorescence spectra of the solid samples were measured on a Cary Eclipse spectrofluorimeter (Varian) at room temperature.

2.2. *Preparation of the complexes*

2.2.1. Synthesis of $\{[Cd(4\text{-abpt})(hip)(H_2O)_2](H_2O)_{7/2}\}_n$ (1). A mixture of 4-abpt (24.0 mg, 0.1 mmol), H_2hip (18.2 mg, 0.1 mmol), and $Cd(OAc)_2 \cdot 2H_2O$ (26.6 mg, 0.1 mmol) in water (10 mL) was sealed in a Teflon-lined stainless steel vessel (20 mL), which was heated to 140 °C for 24 h and then gradually cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block-shaped single crystals of **1** (15.6 mg, 25% yield) were obtained. Anal. Calcd for $C_{20}H_{25}CdN_6O_{10.5}$ (**1**): C, 38.14; H, 4.00; N, 13.34%. Found: C, 38.21; H, 4.06; N, 13.29%. IR (cm^{-1}): 3434 b, 1614 s, 1568 vs, 1391 w, 1370 w, 1306 w, 1284 w, 1221 m, 980 w, 826 m, 787 vs, 723s, 696 w, 607 w, 510 w.

2.2.2. Synthesis of $\{[Cd(4\text{-Habpt})(sip)(H_2O)](H_2O)_2\}_n$ (2). The same synthetic method as that for **1** was used except that H_2hip was replaced by H_3sip (24.6 mg, 0.1 mmol), affording colorless block-shaped single crystals (21.4 mg, 33% yield) of **2**. Anal. calcd for $C_{20}H_{20}CdN_6O_{10}S$ (**2**): C, 37.02; H, 3.11; N, 12.95%. Found: C, 37.18; H, 3.09; N, 12.89%. IR (cm^{-1}): 3438 b, 1640 w, 1608 s, 1551 vs, 1435 s, 1369 vs, 1190 vs, 1104 m, 1040 vs, 830 m, 736 s, 690 s, 621 s, 508 m.

2.3. *X-ray crystallography*

X-ray single-crystal diffraction data for **1** and **2** were collected on a Bruker Apex II CCD diffractometer at $T = 296$ K with Mo Kα radiation ($\lambda = 0.71073$ Å). There was no

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evidence of crystal decay during data collection. Semiempirical absorption corrections were applied (SADABS) and the program SAINT was used for integration of the diffraction profiles [20]. Both structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [21, 22]. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms on F^2. Generally, C-bound hydrogen atoms were placed geometrically and refined as riding atoms, whereas O- and N-bound hydrogen atoms were first determined in difference Fourier maps and then fixed in the calculated positions. Notably, the lattice water molecule of O10 in **1** is disordered over three sites, with the site occupancy factors of 0.50/0.25/0.25. In addition, the lattice water molecule of O12 in **1** was assigned to 1/2 occupancy to obtain the appropriate thermal parameters. Thus, the affiliated H atoms for both water molecules O10 and O12 were not determined. Further crystallographic details are summarized in table 1 and selected bond lengths and angles are shown in table 2.

3. Results and discussion

3.1. *Description of crystal structure of 1*

Single-crystal X-ray diffraction analysis indicated that **1** has a comb-like 1-D coordination chain. The asymmetric unit of **1** consists of one Cd^{II} ion, one hip^{2-} anion, one 4-abpt ligand, two coordinated water molecules, and three and a half lattice water molecules. As shown in figure 1(a), the Cd^{II} center has a distorted pentagonal bipyramidal geometry, defined by four carboxylate O donors from two hip^{2-} ligands (Cd1–O: 2.278(3)–2.633(2) Å) and one N donor from 4-abpt (Cd1–N1: 2.308(3) Å) in the equatorial plane and two

Table 1. Crystallographic and data refinement parameters for **1** and **2**.

	1	**2**
Chemical formula	$C_{20}H_{25}CdN_6O_{10.5}$	$C_{20}H_{20}CdN_6O_{10}S$
Formula mass	629.86	648.88
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/n$
a/Å	8.130(2)	13.331(1)
b/Å	10.239(2)	9.9441(7)
c/Å	15.439(4)	19.374(2)
α/°	85.849(3)	90.00
β/°	84.128(4)	109.609(2)
γ/°	83.612(4)	90.00
Unit cell volume/Å^3	1268.0(5)	2419.4(3)
No. of formula units per unit cell, Z	2	4
No. of reflections measured	6425	12,134
No. of independent reflections	4396	4262
R_{int}	0.0144	0.0612
Final R_1 values ($I > 2\sigma(I)$)	0.0324	0.0365
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0870	0.0629
Final R_1 values (all data)	0.0367	0.0810
Final $wR(F^2)$ values (all data)	0.0898	0.0755
Goodness of fit on F^2	1.072	0.977

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Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cd1–O4A	2.278(3)	Cd1–O2	2.284(2)
Cd1–N1	2.308(3)	Cd1–O6	2.323(3)
Cd1–O7	2.340(3)	Cd1–O5A	2.566(2)
Cd1–O1	2.633(2)		
O4A–Cd1–O2	86.5(1)	O4A–Cd1–N1	138.2(1)
O2–Cd1–N1	135.1(1)	O4A–Cd1–O6	87.4(1)
O2–Cd1–O6	94.8(1)	N1–Cd1–O6	91.4(1)
O4A–Cd1–O7	99.4(1)	O2–Cd1–O7	79.4(1)
N1–Cd1–O7	87.7(1)	O6–Cd1–O7	170.7(1)
O4A–Cd1–O5A	53.2(1)	O2–Cd1–O5A	135.8(1)
N1–Cd1–O5A	86.1(1)	O6–Cd1–O5A	100.1(1)
O7–Cd1–O5A	89.1(1)	O4A–Cd1–O1	137.1(1)
O2–Cd1–O1	52.6(1)	N1–Cd1–O1	84.1(1)
O6–Cd1–O1	84.3(1)	O7–Cd1–O1	86.4(1)
O5A–Cd1–O1	169.3(1)		
2			
Cd1–N1	2.268(4)	Cd1–O6A	2.289(3)
Cd1–O8	2.311(3)	Cd1–O2	2.357(3)
Cd1–O1	2.379(3)	Cd1–O6B	2.477(3)
Cd1–O7A	2.587(3)		
N1–Cd1–O6A	121.4(1)	N1–Cd1–O8	92.3(1)
O6A–Cd1–O8	113.9(1)	N1–Cd1–O2	152.6(1)
O6A–Cd1–O2	80.4(1)	O8–Cd1–O2	93.1(1)
N1–Cd1–O1	98.5(1)	O6A–Cd1–O1	133.1(1)
O8–Cd1–O1	85.5(1)	O2–Cd1–O1	55.3(1)
N1–Cd1–O6B	80.5(1)	O6A–Cd1–O6B	75.9(1)
O8–Cd1–O6B	170.0(1)	O2–Cd1–O6B	90.4(1)
O1–Cd1–O6B	88.8(1)	N1–Cd1–O7A	84.9(1)
O6A–Cd1–O7A	53.3(1)	O8–Cd1–O7A	79.5(1)
O2–Cd1–O7A	122.5(1)	O1–Cd1–O7A	164.7(1)
O6B–Cd1–O7A	106.5(1)		

Symmetry codes for **1**: A = *x*, *y*–1, *z*; for **2**: A = *x*, *y*–1, *z*; B = 1–*x*, 1–*y*, –*z*.

water O atoms (Cd–O6: 2.323(3) Å; Cd–O7: 2.340(3) Å) at the axial sites. The Cd1–O1 (2.633(2) Å) and Cd1–O5A (2.566(2) Å) bond lengths of the carboxylate groups are significantly longer than those of other Cd-O bond distances (Cd–$O_{carboxylate}$, 2.278(3)–2.323(3) Å and Cd–O_{water}, 2.340(3) Å), indicating an asymmetric coordination mode for the carboxylate groups. Both carboxylate groups of the hip^{2-} ligand adopt a chelating coordination mode and the adjacent Cd^{II} ions are interconnected by the hip^{2-} ligands to afford a 1-D coordination motif with a Cd···Cd distance of 10.239(2) Å. 4-Abpt adopts a monodentate bonding mode to decorate the 1-D chain, resulting in the final comb-like array (see figure 1(b)). The adjacent 1-D arrays are connected via O3–H3···N6 and O7–H7A···O5 hydrogen bonds, between the hydroxyl group of a hip^{2-} ligand and pyridyl group of 4-abpt and between coordinated water molecules and the carboxylate group of the hip^{2-} ligand, respectively, to generate a 2-D double-layer framework (see figure 1(c)). The 2-D double-layers are further extended to afford a 3-D supramolecular architecture (see figure 1(d)) via N5–H5A···O1 and O6–H6A···N2 interactions involving the amino and carboxylate groups, coordinated water molecules, and the triazole rings. In addition, this structure is further stabilized by multiple hydrogen bonding interactions between the lattice water guest molecules and the host structure (see table 3).

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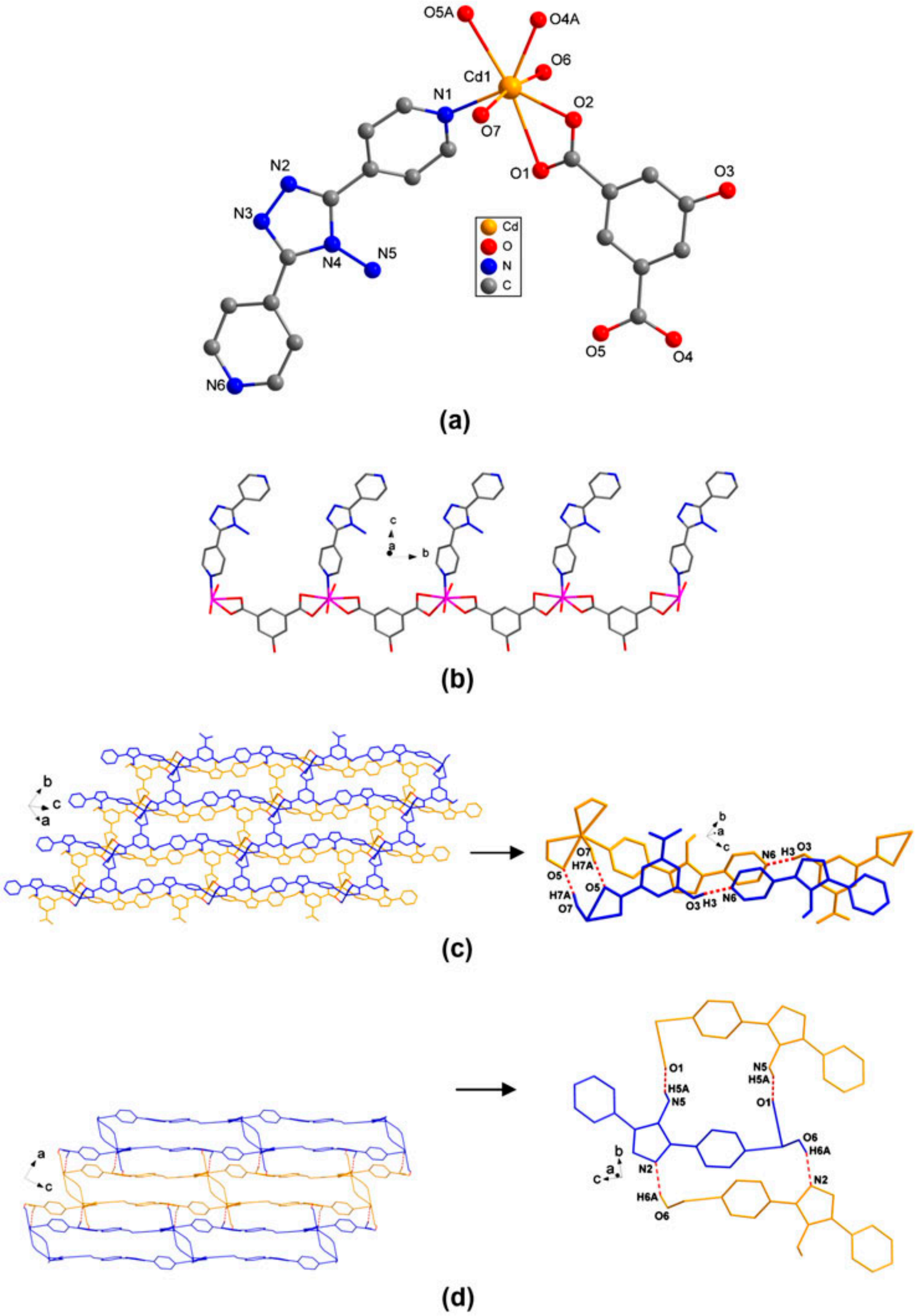

Figure 1. Crystal structure of **1**. (a) View of the asymmetric coordination unit and the coordination sphere of Cd(II). Hydrogens are removed for clarity. (b) 1-D comb-like coordination chain. (c) 2-D double-layer network constructed via O3–H3…N6 and O7–H7A…O5 hydrogen bonding interactions. (The adjacent chains are represented in different colors and hydrogen bonds are shown as red dashed lines.) (d) 3-D hydrogen-bonded network connected via N5–H5A…O1 and O6–H6A…N2 interactions. (The adjacent layers are represented in different colors and hydrogen bonds are shown as red dashed lines (see http://dx.doi.org/10.1080/00206814.2013.797078 for color version).)

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3.2. *Description of crystal structure of 2*

If the 5-substituent group of the isophthalate is changed from a hydroxyl to a sulfonate group, a distinct 1-D dual-track motif is formed for **2**. As shown in figure 2(a), each Cd^{II} ion is surrounded by six oxygens from three different sip^{3-} ligands and one water molecule, and one nitrogen atom from a protonated 4-abpt (4-Habpt) ligand, which generate a distorted pentagonal bipyramidal geometry. The Cd–O bond distances fall in a range from 2.289(3) to 2.587(3) Å and the Cd–N bond distance is 2.268(4) Å. Compound **2** is a formal zwitterion, as the angular ligand H_3sip is fully deprotonated (sip^{3-}) and the non-coordinating pyridyl N atom of 4-abpt is protonated (4-Habpt), balancing the charge of the overall complex. Notably, for sip^{3-}, the two carboxylate groups take chelating and μ-O,O-η-O,O′ coordination modes [17, 23]. The chelating carboxylate group is symmetrically bound (Cd1–O1, 2.379(3) Å; Cd1-O2, 2.357(3) Å), while the chelate-bridging carboxylate is asymmetrically coordinated. In the latter, the bridging Cd1–O6A and Cd1–O6B distances are 2.289(3) Å and 2.477(3) Å, respectively, but the second chelating O atom has an even longer bond distance (Cd1–O7A, 2.587(3) Å). As a result of the two carboxylate coordination modes for sip^{3-}, the adjacent Cd^{II} ions are interlinked to construct a 1-D dual-track motif (see figure 2(b)) with dimeric Cd_2O_2 units. The Cd···Cd separation (3.7601(5) Å) is longer than the 3.683(1) Å distance found in a similar structure formed with 2,5-bis(3-pyridyl)-1,3,4-oxadiazole instead of 4-abpt [17]. A shorter Cd-Cd distance (3.4064(5) Å) within the Cd_2O_2 core was observed when pyridine-2,6-dicarboxylic acid was used instead of H_3sip [24]. The protonated 4-abpt (4-Habpt) adopts the common monodentate coordination mode, serving as the side arms of this 1-D motif. Notably, there are intrachain N5–H5A···O5 bonds between the amino group of 4-abpt and the sulfonate groups of sip^{3-}, interchain N5–H5B···O7 bonds between the amino group of 4-abpt and a carboxylate group of sip^{3-}, as well as interchain O8–H8A···O4, O8–H8B···N2, and

Table 3. Hydrogen-bonding parameters (Å, °) for **1** and **2**.

D–H…A	*d*(D–H)	*d*(H…A)	*d*(D…A)	D–H…A
1				
O3–H3…N6[a]	0.82	1.90	2.687(4)	160
N5–H5A…O1[b]	0.89	2.17	3.025(4)	162
N5–H5B…O8[b]	0.89	2.29	3.045(5)	143
O6–H6A…N2[c]	0.86	1.99	2.810(4)	158
O6–H6B…O8	0.85	2.07	2.917(5)	171
O7–H7A…O5[d]	0.84	1.86	2.700(4)	175
O7–H7B…O9[e]	0.84	2.00	2.806(4)	161
O8–H8A…O2[f]	0.84	2.47	2.852(4)	109
O8–H8B…O10	0.84	1.86	2.645(1)	155
O9–H9B…O1[b]	0.84	2.08	2.897(4)	165
2				
N5–H5A…O5[a]	0.89	2.25	3.131(5)	173
N5–H5B…O7[b]	0.89	2.05	2.938(6)	175
N6–H6…O9	0.86	1.81	2.634(5)	161
O8–H8A…O4[c]	0.85	1.86	2.705(5)	177
O8–H8B…N2[d]	0.85	1.96	2.811(5)	176
O9–H9A…O2[e]	0.85	1.93	2.742(5)	159
O9–H9B…O10	0.85	2.04	2.784(7)	146

Symmetry codes for **1**: a = *x*–1, *y*, *z*–1; b = –*x* + 1, –*y* + 2, –*z* + 1; c = –*x* + 1, –*y* + 1, –*z* + 1; d = –*x*, –*y* + 2, –*z* + 1; e = *x*–1, *y*, *z*; f = *x* + 1, *y*, *z*; for **2**: a = –*x* + 1, –*y* + 1, –*z*; b = –*x* + 3/2, *y*–1/2, –*z* + 1/2; c = *x* + 1/2, –*y* + 1/2, *z* + 1/2; d = –*x* + 3/2, *y* + 1/2, –*z* + 1/2; e = *x*, *y*, *z* + 1.

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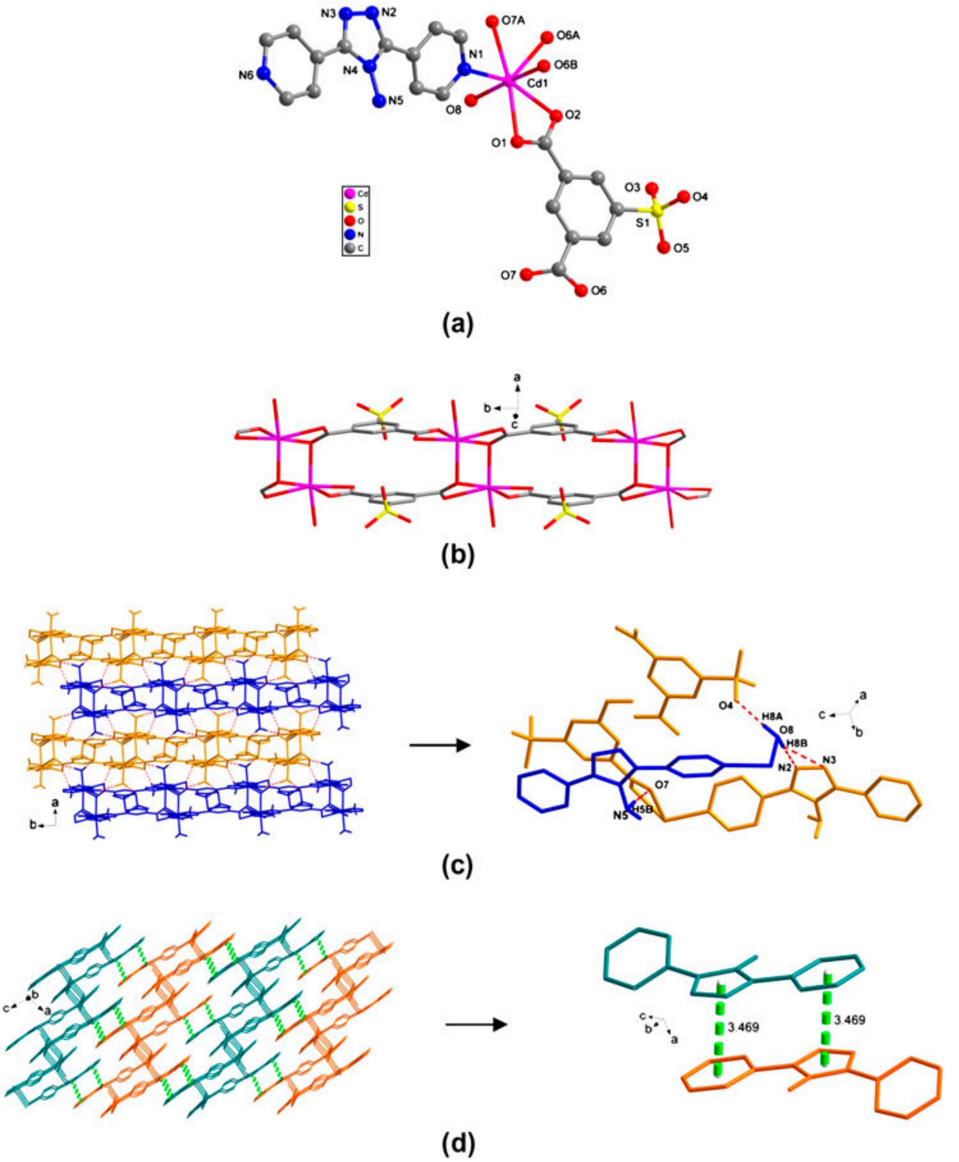


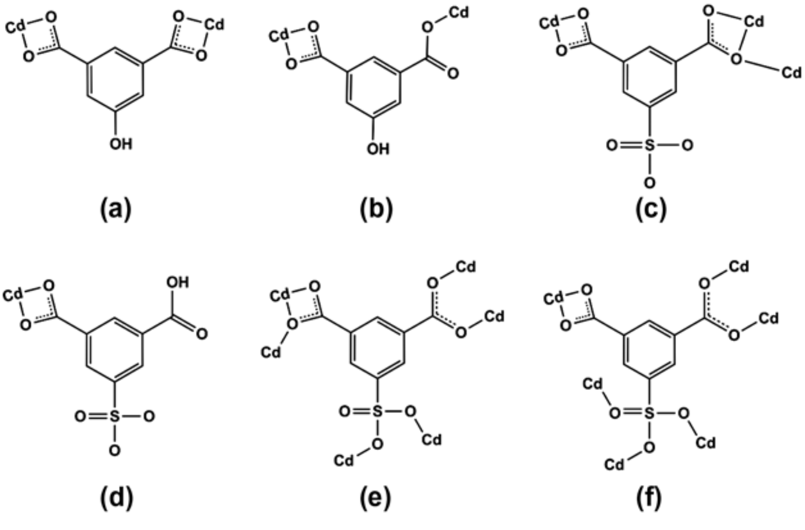
Figure 2. Crystal structure of **2**. (a) View of the asymmetric unit and the coordination environment of Cd(II). Hydrogens are removed for clarity. (b) 1-D dual-track motif linked by sip^{3-} omitting the coordinated 4-Habpt ligand. (c) 2-D H-bonding network constructed via N–H…O, O–H…O, and O–H…N hydrogen bonding interactions. (The adjacent chains are represented in different colors and hydrogen bonds are shown as red dashed lines.) (d) 3-D supramolecular network showing interlayer aromatic staking interactions. (The adjacent layers are represented in different colors and aromatic staking interactions are shown as green dashed lines. (see http://dx.doi.org/10.1080/00206814.2013.797078 for color version).)

O8–H8B···N3 H-bonds between the coordinated water molecule and the sulfonate/triazole/triazole groups, respectively, which extend the adjacent 1-D motifs into a 2-D layered network (see figure 2(c)). The lattice water guest molecules (O9 and O10) are involved in host–guest (N6–H6···O9 and O9–H9A···O2) and guest–guest (O9–H9B···O10) H-bonding interactions. Additionally, interlayer aromatic π-stacking interactions are observed between triazole and pyridyl rings to link the 2-D layers into a 3-D supramolecular network (see figure 2(d)).

3.3. *Comparison of the structure features for 1 and 2*

Assembling the bent dipyridyl derivative 4-abpt and $Cd(OAc)_2$ with the distinct aromatic dicarboxylic acids 5-hydroxyisophthalic acid and 5-sulfoisophthalic acid resulted in formation of different structures. Notably, 4-abpt (4-Habpt) serves as a monodentate ligand at each metal center. However, subtle differences in the binding modes of carboxylate groups can be observed, namely the chelating mode (scheme 1(a)) in **1** and chelating and μ-O,O-η-O,O′ modes (scheme 1(c)) in **2** [17, 23]. Additionally, for both **1** and **2**, the Cd^{II} ion has similar pentagonal bipyramidal geometries. All the Cd–O (2.278(3)-2.633(2) Å) and Cd–N (2.268(4) and 2.308(3) Å) bond lengths (see table 2) in both species are within the normal range found for similar complexes in the literature [25–27]. The mean deviation from planarity of the planes containing the five equatorial donor atoms and the metal ion is small, 0.0331 Å in **1** and 0.1154 Å in **2**. Angles involving the adjacent donor atoms of the equatorial plane and the Cd^{II} center in **1** and **2** are not very close to the ideal value of 72°, as can be seen in table 2, due to the constrained O–Cd–O angles of the chelating carboxylate groups. Finally, the axial oxygen atoms are somewhat distorted from linearity with angles of O6–Cd1–O7 of 170.7(1)° for **1** and O6B–Cd1–O8 of 170.0(1)° for **2**.

As previously reported [28–30], 5-hydroxyisophthalic acid and 5-sulfoisophthalic acid have been investigated in the assembly of coordination polymers with Cd^{II} salts. Consequently, various coordination motifs have been found because of the multiple coordination modes for H_2hip and H_3sip, and especially the sensitivity towards bonding of the sulfonate group for H_3sip. Compared to previously reported complexes, the introduction of the 4-abpt linker into the assembled system affords somewhat different structures, especially



Scheme 1. The coordination modes of the hip^{2-} and sip^{3-} ligands.

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for H_3sip. For example, synthesis of $[Cd_2(\mu_2\text{-}OH_2)_2(Hsip)_2(H_2O)_6]$ at pH 2 formed a discrete dinuclear structure, while synthesis of $[Cd_5(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(sip)_2(H_2O)_5]_n$ at pH 7 produced a complex with an inorganic layer, interconnected by sip^{3-} into a 3D framework [28]. Three bridging coordination modes of sip^{3-} were observed in these polymers (scheme 1(d)–(f)). As described above, the combination of 4-abpt and H_3sip with Cd^{II} resulted in a 1-D dual-track coordination motif linked by sip^{3-} ligand and a new type of coordination mode for sip^{3-} (scheme 1(c)). Regarding the hip^{2-} linker, $[Cd(hip)(H_2O)_3]_n$ formed a 1-D coordination chain [29]. The carboxylate groups of hip^{2-} in this complex adopted monodentate and bidentate chelating coordination modes (scheme 1(b)). When 4-abpt is introduced into the assembly, one coordinated water was formally replaced by 4-abpt, affording a 1-D comb-like chain. Both carboxylate groups of hip^{2-} adopt bidentate chelating modes (scheme 1(a)). In **1** and **2**, the 4-abpt ligand is monodentate and just plays the role of decorating the polymer chain.

3.4. *IR, PXRD, and fluorescence*

In the IR spectra of **1** and **2** (figure S1), the absence of a characteristic absorption band between 1650 and 1700 cm^{-1} indicated complete deprotonation of the carboxylic acid groups. The phase purities of the complexes were also confirmed by PXRD patterns (figure S2). The solid-state photoluminescent spectra for 4-abpt, **1**, and **2** were measured at room temperature (see figure 3). Upon excitation at 320 nm, comparable maximum emissions appeared at 360 nm for **1** and 361 nm for **2**. A similar fluorescent behavior was also observed for 4-abpt, which displayed emission at 366 nm upon excitation at 270 nm. No obvious fluorescent emissions for H_2hip and H_3sip were found under similar conditions. Thus, the photoluminescent mechanism of **1** and **2** can be ascribed to the ligand-based emissions and the blue-shift compared to that of 4-abpt should be attributed to the incorporation of metal-ligand (4-abpt) interactions. Notably, the maximum fluorescence emission

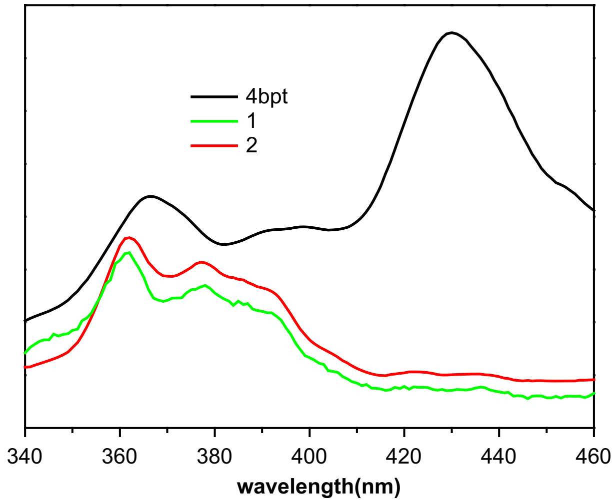

Figure 3. Solid-state fluorescent emission spectra of 4-abpt, **1**, and **2**.

at 430 nm of 4-abpt was quenched in **1** and **2**, which may be caused by the heavy-atom effect of Cd^{II} ions and/or the effect of incorporating isophthalates [31, 32].

4. Conclusion

Two different Cd^{II} coordination polymers based on 4-abpt and 5-hydroxyisophthalic acid or 5-sulfoisophthalic acid were synthesized under hydrothermal conditions. Interestingly, distinct coordination modes of the aromatic dicarboxylates can be observed by altering the non-coordinating 5-substituent of the isophthalate, which resulted in the different coordination arrays and extended lattice structures of both complexes. These results will prompt us to further explore the substituent effect on directing the coordination supramolecular assemblies.

Supplementary material

Figures of IR spectra and experimental and simulated PXRD patterns for **1** and **2**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, 909658 and 909659 for **1** and **2,** respectively. Copies of this information may be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: C44 1223 336 066; E-mail: deposit@ccdc.cam.ac.uk].

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