Self-Assembly of 1D to 3D Cadmium Complexes: Structural Characterization and Properties

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Self-assembly reactions of 5-sulfoisophthalic monosodium salt (NaH_2sipa), $Cd(NO_3)_2 \cdot 4H_2O$ and 2,2′-bipyridine (or 4,4′-bipyridine) under hydrothermal condition give rise to four polymeric complexes, namely $\{[Cd_3(sipa)_2(2,2'\text{-bpy})_4(H_2O)_2] \cdot 6H_2O\}_n$ (**1**), $\{[Cd(sipa)(H\text{-}4,4'\text{-bpy})(H_2O)] \cdot 2H_2O\}_n$ (**2**); $\{[Cd_2(sipa)(4,4'\text{-bpy})_3(H_2O)_3] \cdot [Cd(sipa)(4,4'\text{-bpy})(H_2O)] \cdot 8H_2O\}_n$ (**3**), and $\{[Cd_3(sipa)_2(4,4'\text{-bpy})_4(H_2O)_2] \cdot 3H_2O\}_n$ (**4**), respectively. X-ray diffraction analyses reveal that complex **1** possesses a 1D rail-like chain structure, **2** is a 1D double chain, **3** has a 2D network consisting of an independent $[Cd_2(sipa)(4,4'\text{-bpy})_3(H_2O)_3]_n^{n+}$ cationic layer and a $[Cd(sipa)(4,4'\text{-bpy})(H_2O)]_n^{n-}$ anionic layer, and **4** is a novel 3D self-penetrating network constructed from two mixed bridging ligands. Thermogravimetric analyses (TGA) and fluorescent measurements of complexes **1**–**4** have also been performed.

Introduction

The rational design and synthesis of metal–organic coordination polymers with different dimensional topological structures is of great current interest because these complexes are potential candidates as new materials with uses in fluorescence, magnetism, catalysis, nonlinear optics, gas absorption, as semiconductors, and so on.[1] In recent decades, these studies have been developed rapidly and have produced delightful outcomes in which the structures or properties of a great number of reported compounds have been finely tuned by controlling the inorganic/organic component properties such as size, coordination geometries of the metal ions, flexibility, symmetry, and functionality of the organic ligands.[2] However, there are many seemingly insurmountable challenges regarding the preparation of polymeric complexes with directed dimensional networks containing inorganic or organic components exhibiting distinct physical and/or chemical properties. One of the key steps to assemble unusual architectures is to select appropriate organic ligands containing functional coordinating groups, and rigid multidentate ligands are a good choice.[3] The carboxylate groups have a strong ability to bond various metal ions and afford abundant coordination modes, thus rigid multi-carboxylate ligands have been widely used for the design and synthesis of a great variety of structures.[4] Introduction of a sulfonate group into rigid multi-carboxylate ligands may result in the formation of unexpected frameworks as the sulfonic group has a different shape and properties in terms of its coordination ability compared to the carboxylate group. Studies on the coordination chemistry of multi-carboxylate-sulfonic ligands are not very common. 5-Sulfoisophthalic acid (H_3sipa) has three distinct properties: (1) it has multiple coordination sites that may lead to high dimensional structures; (2) it possesses a symmetric geometry and rigidity that may yield novel topological structures; (3) it contains two kinds of coordinating functional groups that may form diverse supramolecular networks. However, only a few coordination polymers containing this ligand have been reported in the past few decades.[5] By employing 5-sulfoisophthalic acid as an organic ligand, we have successfully prepared two unusual planar tetracopper(II) SBUs that were further extended into an infinite metal–organic framework by the bridging carboxylates of the $sipa^{3-}$ ligand, as well as two new zeolite-like supramolecular compounds.[6] Our previous work spurred us on to systematically study metal–sipa coordination chemistry and to investigate the correlation between structures and properties. It has been well-documented that the introduction of terminal ligands into a reaction system can result in the formation of low-dimensional networks as the terminal ligands reduce the available metal binding sites and restrict the polymer's growth in this direction,[7] and that long bridging ligands can induce a single unit to grow into high dimensional frameworks.[8] Thus, the terminal ligand 2,2′-pyridine (2,2′-bpy) or the rigid bridging ligand 4,4′-bipyridine (4,4′-bpy) were introduced into a reaction system containing Cd^{II} ions and the $sipa^{3-}$ ligand with the hope of isolating polymeric complexes with different dimensional structures. Here we report the syntheses, structural

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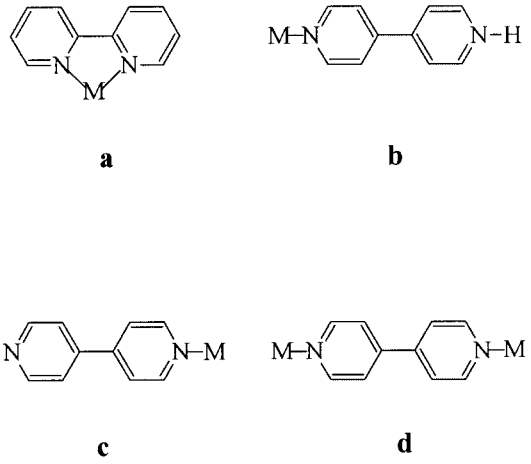
characterizations, and fluorescent properties of four novel cadmium complexes $\{[Cd_3(sipa)_2(2,2'\text{-bpy})_4(H_2O)_2]\cdot 6H_2O\}_n$ (**1**), $\{[Cd(sipa)(H\text{-}4,4'\text{-bpy})(H_2O)]\cdot 2H_2O\}_n$ (**2**), $\{[Cd_2(sipa)(4,4'\text{-bpy})_3(H_2O)_3]\cdot[Cd(sipa)(4,4'\text{-bpy})(H_2O)]\cdot 8H_2O\}_n$ (**3**), and $\{[Cd_3(sipa)_2(4,4'\text{-bpy})_4(H_2O)_2]\cdot 3H_2O\}_n$ (**4**). Complexes **1** and **2** possess one-dimensional structures, **3** contains a two-dimensional network consisting of independent cationic and anionic layers, and **4** assumes a novel self-penetrating three-dimension framework and has been briefly reported by us.[9]

Results and Discussion

Preparation of the Complexes

Coordination complexes of $sipa^{3-}$ with transition metals have been reported by our group and others recently,[5,6] but systematic studies on the coordination chemistry of $sipa^{3-}$ have been ignored. Our aim is to employ the hydrothermal method, which has been proven to be a very effective way for the synthesis of zeolite frameworks and high dimensional polymers, and to obtain novel structures by utilizing the $sipa^{3-}$ ligand's abundant coordination modes. It is well known that reaction parameters such as temperature, pH, and the ratio of reactants, as well as the addition of other ligands, can exert a profound influence on the final products under supercritical conditions. In this work, we focus on the influence of a second ligand and the molar ratio of the starting reactants. We started our work by using 2,2′-bpy as second ligand in the hydrothermal reaction of H_2sipa^-, Cd^{2+}, EtOH, and H_2O. Complex **1**, which possesses a 1D rail-like structure was prepared and no influence of the molar ratio of the reactants was observed. 2,2′-Bpy usually acts as a terminal ligand that chelates a metal ion to give low-dimensional structures, whereas 4,4′-bpy can assume different coordination modes (Scheme 1) and may generate 1D to 3D structures. Thus, 4,4′-bpy was employed instead of 2,2′-bpy with the hope of isolating different structures with varied coordination modes of 4,4′-bpy. When 4,4′-bpy replaces 2,2′-bpy in the hydrothermal reaction of H_2sipa^-, Cd^{2+}, and H_2O (H_2sipa^-/Cd^{2+}/4,4′-bpy = 1:1:1), complex **2**, with 1D double-chain, was isolated, which contains a protonated pyridine nitrogen atom with the 4,4′-bpy ligand acting as a monodentate ligand to a metal ion (Scheme 1b). When the molar ratio H_2sipa^-/Cd^{2+}/4,4′-bpy was changed to 2:3:5, the reaction yielded complex **3** with a 2D layer structure. In **3**, the 4,4′-bpy ligand displays two kinds of coordination modes: monodentate to coordinate a single metal ion and bidentate to bridge two metal ions (Scheme 1c and d). When the molar ratio H_2sipa^-/Cd^{2+}/4,4′-bpy was 4:3:4, complex **4**, which contains a 3D self-penetrating framework, was obtained, where the 4,4′-bpy acts as bidentate ligand to link two metal ions (Scheme 1, part d). Hence, by changing the molar ratio of reactants and utilizing a terminal or bridging secondary ligand, we have prepared 1D to 3D cadmium coordination complexes. In this reaction system the bpy ligands not only play the role of chelating or linking metal ions but also control the base/acid balance by protonating/deprotonating reactions between the pyridine nitrogen atoms and carboxylate groups.[5b] To confirm the purity, X-ray powder diffraction analyses (XRPD) were performed for all four complexes (see Supporting Information). These results show that the purity of the complexes is good enough to support our conclusions.



Scheme 1.

Description of Crystal Structures

$\{[Cd_3(sipa)_2(2,2'\text{-bpy})_4(H_2O)_2]\cdot 6H_2O\}_n$ (1)

Single crystal X-ray diffraction reveals that complex **1** possesses a one-dimensional structure constructed from Cd ions and $sipa^{3-}$ and 2,2′-bpy ligands, in which there are two types of coordination environments around the Cd ions. As shown in Figure 1, Cd1 is coordinated by two oxygen atoms from two SO_3 groups of $sipa^{3-}$ ligands and four nitrogen atoms from two 2,2′-bpy ligands. The two oxygen atoms occupy the axial positions, with an O1–Cd1–O1A bond angle of 180°, while the four nitrogen atoms are located in the equatorial plane, with the bond angles N1–Cd1–N1A and N2–Cd1–N2A being 180° and N1–Cd1–O1 and N2–Cd1–O1 being 87.6° and 89.7°, respectively, thus forming a slightly distorted octahedral geometry). The 2,2′-bpy ligand

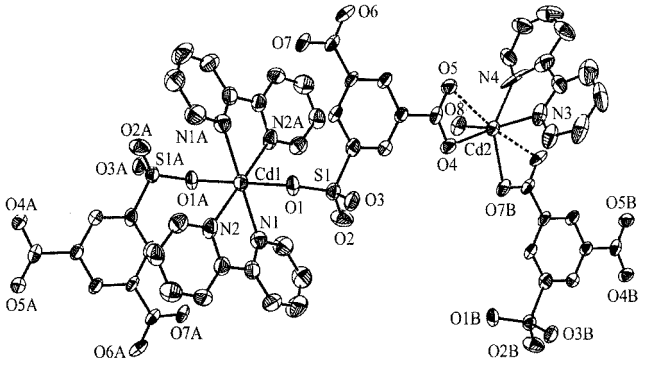


Figure 1. Ortep drawing of the coordination environments around the Cd ions in **1** with thermal ellipsoids at 30% probability. The isolated water molecules have been omitted for clarity.

binds in a chelate fashion to the metal ion and its two pyridine rings suffer from distortion, with a dihedral angle of 21°. Cd2 is in a distorted pentagonal-bipyramidal coordination environment and is coordinated by two nitrogen atoms (N3 and N4) from the bpy ligand, four oxygen atoms (O4–O7) from chelating carboxylates, and one oxygen atom (O8) (Table 1) from a water molecule, with the four carboxylate oxygen atoms and a nitrogen atom (N4) being located in the equatorial plane with Cd–O distances ranging from 2.292 to 2.616 Å and Cd2–N4 being 2.112 Å; O8 and N3 occupy the axial positions with bond lengths of 2.269 and 2.313 Å, respectively. Here, the long distances of Cd2···O6B (2.560 Å) and Cd2···O5 (2.616 Å) indicate a weak chelating interaction with the metal ions, which may be regarded as a semi-chelate coordination mode.[10] Therefore, Cd2 can also be described as having a pseudo pentagonal bipyramidal coordination geometry. The average bond lengths around Cd1 (2.317 Å) are somewhat shorter than those of Cd2 (2.354 Å), which is understandable due to the weak chelate interaction of the carboxylates in Cd2. The bond lengths S1–O1 (1.452 Å), S1–O2 (1.441 Å), and S1–O3 (1.449 Å) fall within the typical range of S–O bond lengths in a sulfonate ion (1.40–1.50 Å), and the distance C1–S1 (1.788 Å) is also as expected for a $sipa^{3-}$ ligand.[11] Due to the chelating carboxylate and the monodentate sulfonate, the $sipa^{3-}$ unit acts as three-armed connector that links a

Table 1. Selected bond lengths [Å] and angles [°] for **1**.[a]

Cd(1)–N(2)	2.284(9)	Cd(2)–O(4)	2.314(7)
Cd(1)–N(1)	2.327(10)	Cd(2)–O(6)#2	2.560(7)
Cd(1)–O(1)	2.341(7)	Cd(2)–O(5)	2.616(7)
Cd(2)–N(4)	2.112(17)	S(1)–O(2)	1.441(8)
Cd(2)–O(8)	2.269(8)	S(1)–O(3)	1.449(8)
Cd(2)–O(7)#2	2.292(8)	S(1)–O(1)	1.452(7)
Cd(2)–N(3)	2.313(10)	S(1)–C(1)	1.788(11)
N(2)–Cd(1)–N(2)#1	180.000(2)	N(3)–Cd(2)–O(4)	99.2(3)
N(2)–Cd(1)–N(1)	72.3(4)	N(4)–Cd(2)–O(6)#2	90.6(4)
N(2)#1–Cd(1)–N(1)	107.7(4)	O(8)–Cd(2)–O(6)#2	88.1(3)
N(1)#1–Cd(1)–N(1)	180.000(1)	O(7)#2–Cd(2)–O(6)#2	53.1(3)
N(2)–Cd(1)–O(1)#1	90.3(3)	N(3)–Cd(2)–O(6)#2	87.6(3)
N(1)–Cd(1)–O(1)#1	92.4(3)	O(4)–Cd(2)–O(6)#2	136.7(3)
N(2)–Cd(1)–O(1)	89.7(3)	N(4)–Cd(2)–O(5)	80.0(4)
N(1)–Cd(1)–O(1)	87.6(3)	O(8)–Cd(2)–O(5)	91.7(3)
O(1)#1–Cd(1)–O(1)	180.000(1)	O(7)#2–Cd(2)–O(5)	136.1(3)
N(4)–Cd(2)–O(8)	89.9(4)	N(3)–Cd(2)–O(5)	89.5(3)
N(4)–Cd(2)–O(7)#2	142.9(4)	O(4)–Cd(2)–O(5)	52.6(2)
O(8)–Cd(2)–O(7)#2	96.0(3)	O(6)#2–Cd(2)–O(5)	170.7(3)
N(4)–Cd(2)–N(3)	71.0(4)	O(2)–S(1)–O(3)	111.9(6)
O(8)–Cd(2)–N(3)	160.4(4)	O(2)–S(1)–O(1)	113.8(5)
O(7)#2–Cd(2)–N(3)	96.7(4)	O(3)–S(1)–O(1)	110.8(4)
N(4)–Cd(2)–O(4)	132.1(4)	O(2)–S(1)–C(1)	106.3(5)
O(8)–Cd(2)–O(4)	97.0(3)	O(3)–S(1)–C(1)	106.2(5)
O(7)#2–Cd(2)–O(4)	83.6(3)	O(1)–S(1)–C(1)	107.5(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z + 1$; #2 $x, y + 1, z$.

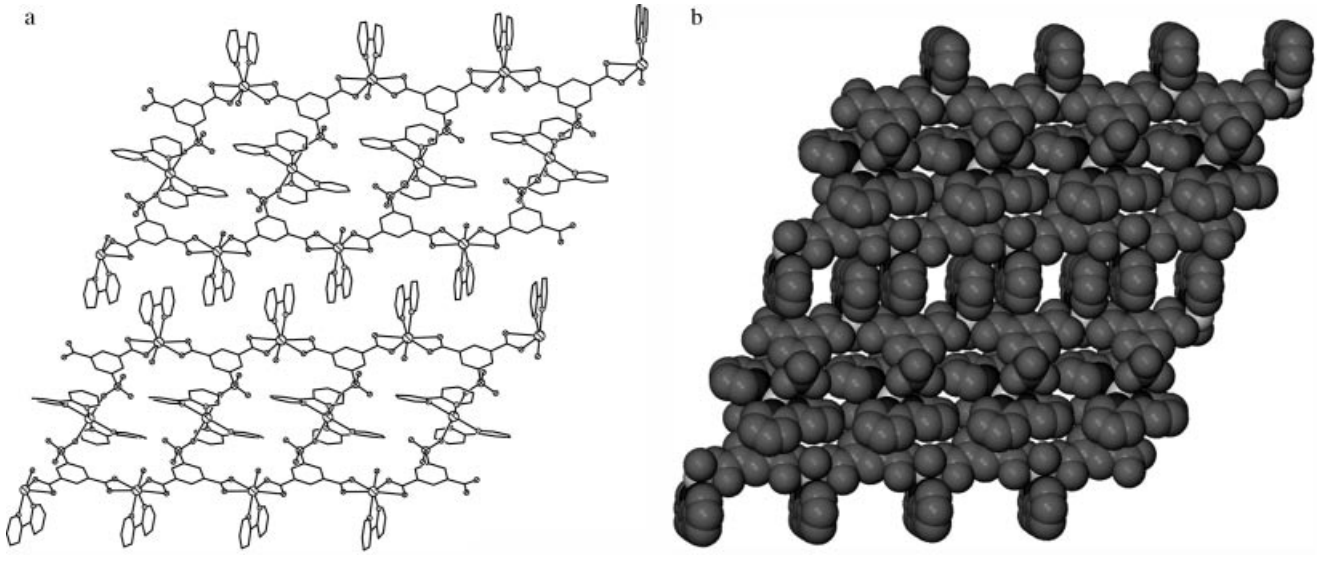


Figure 2. (a) Two-dimensional layer structure of **1**. (b) Space-filling diagram.

Cd1 and two Cd2. Two Cd1 and four Cd2 centers form a grid unit $[Cd_6(sipa)_4]$ with the shortest Cd2–Cd2A and Cd1–Cd2 distances being 10.211 Å and 9.997 Å, respectively. Such units are extended into a 1D rail-like sheet by connection with a $sipa^{3-}$ ligand, with all metal ions located in the same plane. As expected, the presence of 2,2′-bipy and the coordinated water molecules around Cd2 prevents the one-dimensional chain from being further extended into a higher-dimensional network by covalent bonding (e.g. 2D or 3D), similar to those found in other metal/carboxylate/bpy reaction systems.[12] All pyridine rings of the 2,2′-bpy linking Cd2 orientate toward the outside of the one-dimensional sheet. The nearest distance of a pyridine ring to the adjacent sheet (3.383 Å) suggests a strongly offset face-to-face π···π stacking interaction and results in a 2D network (Figure 2). Complex **1** finally forms a 3D packing structure by hydrogen bonding and off-set face-to-face π···π stacking interactions.

{[Cd(sipa)(H-4,4′-bpy)(H$_2$O)]·2H$_2$O}$_n$ (2)

Compared with that in **1**, the $sipa^{3-}$ ligand in **2** shows different coordination modes: one carboxylate group chelates a Cd ion and the other bridges two Cd ions; the sulfonate group remains uncoordinated. In complex **2**, the 4,4′-bpy ligand is protonated at one end and acts as a monodentate ligand to coordinate to the metal ion; H_2sipa^- transfers its proton to a pyridine nitrogen atom for charge balance, which may be regarded as an acid-base reaction similar to those in previous reports.[5b,13] The Cd ion in **2** adopts a distorted octahedral geometry (Figure 3) and is coordinated in the equatorial plane by one monodentate carboxylate oxygen (O3A–Cd1 = 2.278 Å), one chelating carboxylate group (O1–Cd1 = 2.261 Å; O2···Cd1 = 2.535 Å), and one pyridine nitrogen (N1–Cd1 = 2.287 Å). The axial positions are occupied by one carboxylate oxygen (O4B–Cd1 = 2.389 Å) and one coordinated water molecule (O8–Cd1 = 2.324 Å; Table 2). Each two Cd ions are bridged by two carboxylate groups to form a binuclear cluster unit with a Cd–Cd distance of 3.877 Å. Each binuclear unit is interconnected by two $sipa^{3-}$ ligands to form a one-dimensional double chain along the diagonal of the *a*- and *b*-axes (Figure 4). Although 4,4′-bpy has replaced 2,2′-bpy, one of its nitrogen atoms is protonated and the sulfonate group remains uncoordinated, which results in the one-dimensional chain structure of **2**. The 1D double chain is extended into a 2D layer by hydrogen-bonding interactions, and a three dimensional framework is finally formed by hydrogen bonding and off-set face-to-face π···π stacking interactions between the benzene rings and the pyridine rings of adjacent 2D layers, with distance of about 3.40 Å.

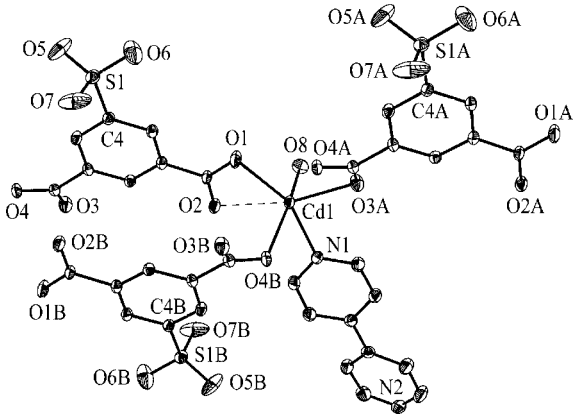


Figure 3. Ortep view of the coordination environment around the Cd ion in **2** with thermal ellipsoids at 30% probability. The isolated water molecules have been omitted for clarity.

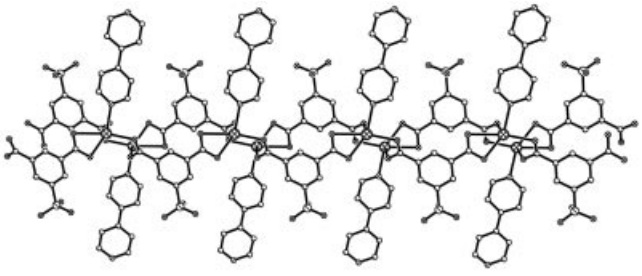


Figure 4. The 1D double-chain along the diagonal of the *a*- and *b*-axes in **2**.

Table 2. Selected bond lengths [Å] and angles [°] for **2**.[a]

Cd(1)–O(1)	2.261(4)	Cd(1)–O(2)	2.535(3)
Cd(1)–O(3)#1	2.278(4)	S(1)–O(6)	1.417(5)
Cd(1)–N(1)	2.287(4)	S(1)–O(5)	1.418(5)
Cd(1)–O(8)	2.324(4)	S(1)–O(7)	1.425(5)
Cd(1)–O(4)#2	2.389(3)	S(1)–C(4)	1.779(5)
O(1)–Cd(1)–O(3)#1	116.89(13)	O(1)–Cd(1)–O(8)	94.29(16)
O(1)–Cd(1)–N(1)	154.97(14)	O(3)#1–Cd(1)–O(8)	86.79(15)
O(3)#1–Cd(1)–N(1)	88.13(14)	N(1)–Cd(1)–O(8)	85.95(15)
O(1)–Cd(1)–O(4)#2	90.96(14)	O(4)#2–Cd(1)–O(2)	82.26(12)
O(3)#1–Cd(1)–O(4)#2	107.93(14)	O(6)–S(1)–O(5)	113.0(4)
O(8)–Cd(1)–O(4)#2	160.02(13)	O(6)–S(1)–O(7)	110.7(4)
O(1)–Cd(1)–O(2)	53.87(12)	O(5)–S(1)–O(7)	112.8(4)
O(3)#1–Cd(1)–O(2)	167.21(14)	O(6)–S(1)–C(4)	107.4(3)
N(1).–Cd(1)–O(2)	101.32(13)	O(5)–S(1)–C(4)	107.0(3)
O(8)–Cd(1)–O(2)	85.32(13)	O(7)–S(1)–C(4)	105.4(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1$, $y + 1$, z; #2 $-x$, $-y$, $-z + 1$.

{[Cd_2(sipa)(4,4′-bpy)$_3$(H_2O)$_3$]·[Cd(sipa)(4,4′-bpy)-(H_2O)]·8H_2O}$_n$ (3)

X-ray diffraction analysis shows that complex **3** has a two-dimensional structure that is different from those in a great number of 2D complexes previously reported[14] – it consists of independent cationic [Cd_2(sipa)(4,4′-bpy)$_3$-(H_2O)$_3$]$_n^{n+}$ and anionic [Cd(sipa)(4,4′-bpy)(H_2O)]$_n^{n-}$ layers. In the cationic layer, two crystallographically different coordinatio environments are observed around Cd1 and Cd2 (Figure 5). Cd1 is six-coordinate, with three carboxylate oxygen atoms and one nitrogen atom in the equatorial plane and one water molecule and one nitrogen atom occupying the axial positions to form a distorted octahedral coordination geometry. Cd2 also adopts a distorted octahedral coordination geometry and is coordinated in the equatorial plane by three nitrogen atoms from pyridine rings and one oxygen atom from a sulfonate group, with two coordinated water molecules located in the axial positions. However, Cd3 in the anionic layer has a slightly distorted pentagonal-bipyramidal coordination environment, with

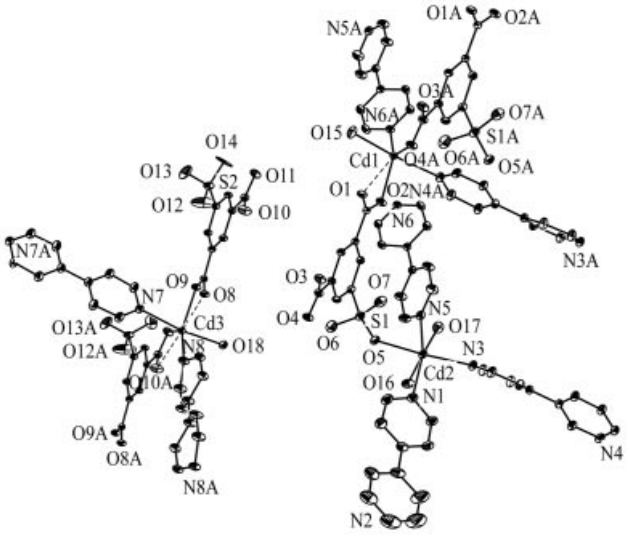


Figure 5. Ortep views of the coordination environments around the Cd ions in **3** with thermal ellipsoids at 30% probability. The isolated water molecules have been omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for **3**.[a]

Cd(1)–O(4)#1	2.296(10)	Cd(3)–O(10)#4	2.559(13)
Cd(1)–O(15)	2.298(11)	Cd(3)–O(8)	2.583(13)
Cd(1)–N(6)#2	2.314(11)	S(1)–O(6)	1.445(8)
Cd(1)–O(2)	2.345(9)	S(1)–O(7)	1.447(7)
Cd(1)–N(4)#3	2.354(12)	S(1)–O(5)	1.465(7)
Cd(1)–O(1)	2.504(12)	S(1)–C(4)	1.776(9)
Cd(2)–N(3)	2.299(11)	S(2)–O(12′)	1.409(12)
Cd(2)–O(5)	2.323(11)	S(2)–O(13)	1.411(9)
Cd(2)–N(5)	2.327(11)	S(2)–O(14)	1.415(10)
Cd(2)–O(16)	2.330(12)	S(2)–O(12)	1.422(12)
Cd(2)–O(17)	2.363(12)	S(2)–O(14′)	1.422(8)
Cd(2)–N(1)	2.368(10)	S(2)–O(13′)	1.460(9)
Cd(3)–N(8)	2.317(11)	S(2)–C(12)	1.780(9)
Cd(3)–O(18)	2.319(11)	N(8)–C(56)	1.372(11)
Cd(3)–O(11)#4	2.344(10)	N(8)–C(56′)	1.430(9)
Cd(3)–O(9)	2.356(9)	C(54)–C(55)	1.408(11)
Cd(3)–N(7)	2.368(12)	C(54)–C(55′)	1.485(11)
O(4)#1–Cd(1)–O(15)	82.1(4)	O(5)–Cd(2)–N(5)	86.8(5)
O(4)#1–Cd(1)–N(6)#2	133.6(2)	N(3)–Cd(2)–O(16)	93.9(3)
O(15)–Cd(1)–N(6)#2	89.5(5)	O(5)–Cd(2)–O(16)	96.1(3)
O(4)#1–Cd(1)–O(2)	84.0(4)	N(5)–Cd(2)–O(16)	86.6(3)
O(15)–Cd(1)–O(2)	94.2(4)	N(3)–Cd(2)–O(17)	86.3(3)
N(6)#2–Cd(1)–O(2)	142.3(2)	O(5)–Cd(2)–O(17)	83.4(3)
O(2)–Cd(1)–N(4)#3	85.3(4)	N(5)–Cd(2)–O(17)	99.0(3)
O(4)#1–Cd(1)–O(1)	136.0(3)	O(16)–Cd(2)–O(17)	174.34(11)
O(15)–Cd(1)–O(1)	90.0(3)	N(3)–Cd(2)–N(1)	94.7(5)
N(6)#2–Cd(1)–O(1)	89.1(3)	O(5)–Cd(2)–N(1)	82.8(5)
O(2)–Cd(1)–O(1)	53.4(2)	N(5)–Cd(2)–N(1)	165.44(13)
N(4)#3–Cd(1)–O(1)	98.6(3)	O(16)–Cd(2)–N(1)	84.5(3)
N(3)–Cd(2)–O(5)	169.38(12)	O(17)–Cd(2)–N(1)	89.8(3)
N(3)–Cd(2)–N(5)	97.4(5)	N(8)–Cd(3)–O(18)	92.4(5)
N(8)–Cd(3)–O(11)#4	137.9(2)	O(18)–Cd(3)–O(10)#4	92.5(3)
O(18)–Cd(3)–O(11)#4	85.4(4)	O(11)#4–Cd(3)–O(10)#4	52.7(3)
N(8)–Cd(3)–O(9)	139.4(2)	O(9)–Cd(3)–O(10)#4	135.1(2)
O(18)–Cd(3)–O(9)	85.8(4)	N(7)–Cd(3)–O(10)#4	89.7(3)
O(11)#4–Cd(3)–O(9)	82.5(4)	N(8)–Cd(3)–O(8)	87.1(2)
N(8)–Cd(3)–N(7)	100.4(5)	O(18)–Cd(3)–O(8)	92.4(3)
O(18)–Cd(3)–N(7)	167.18(10)	O(11)#4–Cd(3)–O(8)	135.0(2)
O(11)#4–Cd(3)–N(7)	85.9(4)	O(9)–Cd(3)–O(8)	52.5(2)
O(9)–Cd(3)–N(7)	83.7(4)	N(7)–Cd(3)–O(8)	87.1(3)
N(8)–Cd(3)–O(10)#4	85.5(3)	O(10)#4–Cd(3)–O(8)	171.34(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1$, y, z; #2 $-x + 2$, $-y + 1$, $-z + 1$; #3 $-x + 2$, $-y + 1$, $-z$; #4 $x - 1$, y, z.

one pyridine nitrogen and a water molecule in the axial positions and two chelating carboxylate groups and one nitrogen atom in the equatorial plane (Figure 5). The distances Cd3···O10A, Cd3···O8, and Cd1···O1 are 2.559, 2.584, and 2.504 Å, respectively, indicating a weak chelate interaction similar to that in **1**.[5,6] C55 and C56 of the 4,4′-bipyridine ring and O12, O13, and O14 of the SO_3 group of the sipa^{3-} ligand are disordered over two positions with bond length C55–C54 = 1.408 Å, C55′–C54 = 1.485 Å and C56–N8 = 1.372 Å, C56′–N8 = 1.430 Å (Table 3).

In the anionic layer each 4,4′-bpy ligand bridges two cadmium ions to yield a zigzag chain along the *c* axis. This chain forms a two dimensional step-like network by the linkage of the sipa^{3-} ligand through its two chelating carboxylate groups in the *ac* plane; the sulfonate groups do not engage in coordination and stand at the zygomorphic sides of the layer (Figure 6, part a). The layer contains two kinds of grids with different dimensions: side lengths 10.237 × 11.813 Å and diagonal distances 15.342 × 15.916 Å based on the metal–metal interval for **A**, and side 10.237 × 11.731 Å and diagonal 15.286 × 15.865 Å for **B**. The dihedral angle between **A** and **B** is 105.50°. On the other hand, the parallelogram 34-membered $Cd_4(sipa)_2(4,4'\text{-bpy})_2$ macro grid can be regarded as a basic building block for the whole 2D step-like structure. Each two $Cd_4(sipa)_2(4,4'\text{-bpy})_2$ units are linked together to form a ladder-like chain by sharing a Cd-bpy-Cd side, and the adjacent ladders are connected by 4,4′-bpy ligands to generate the final 2D step-like layer (Figure 6, part b).

In the cationic layer the sipa^{3-} acting as a three-armed ligand utilizes its monodentate and chelating carboxylate groups to link Cd1 to produce a one-dimensional cationic chain. Each two such chains are connected together by bridges formed by monodentate sulfonate, 4,4′-bpy, and Cd2 to yield a double chain along the *a* axis (Figure 7, part a). In fact, the double chain is an infinite brick-like sheet with a width of about 17.204 Å and height of about 3.710 Å from the closest pyridine ring center to the benzene ring center (the height is almost equal to the sum of the S–O and O–Cd distances). The uncoordinated end of 4,4′-bpy points outside of the brick-like sheet. On the other hand, the cadmium ions and the 4,4′-bpy ligands propagate into a zigzag chain along the *c* axis, and two such chains are fastened together by a sipa^{3-} ligand through its chelating carboxylates and monodentate sulfonate groups to yield a double zigzag cationic chain (Figure 7, part b). The infinite brick-like sheets (Figure 7, part a) and the double zigzag chains (Figure 7, part b) are connected by the sipa^{3-} ligands as linkers and the cadmium ions as nodes to form a two-dimensional cationic step-like network; the uncoordinated pyridine ends of 4,4′-bpy ligands fall on different sides of the step-like plane (Figure 7, part c).

The step-like cationic layer and the step-like anionic layer have an alternate arrangement, where the uncoordinated end of 4,4′-pyridine from the cationic layer penetrates into the cavities of the anionic layer to form a tightly stacked neutral structure through electrostatic forces as well as hydrogen-bonding interactions between carboxylate oxygen atoms, pyridine nitrogen atoms, and free water molecules that are present between the cationic and anionic layers (Figure 8).

It's interesting that the 4,4′-bpy ligands in **3** play different roles in the cationic layer: one acts as a bridging ligand results in the formation of the two dimensional structure,

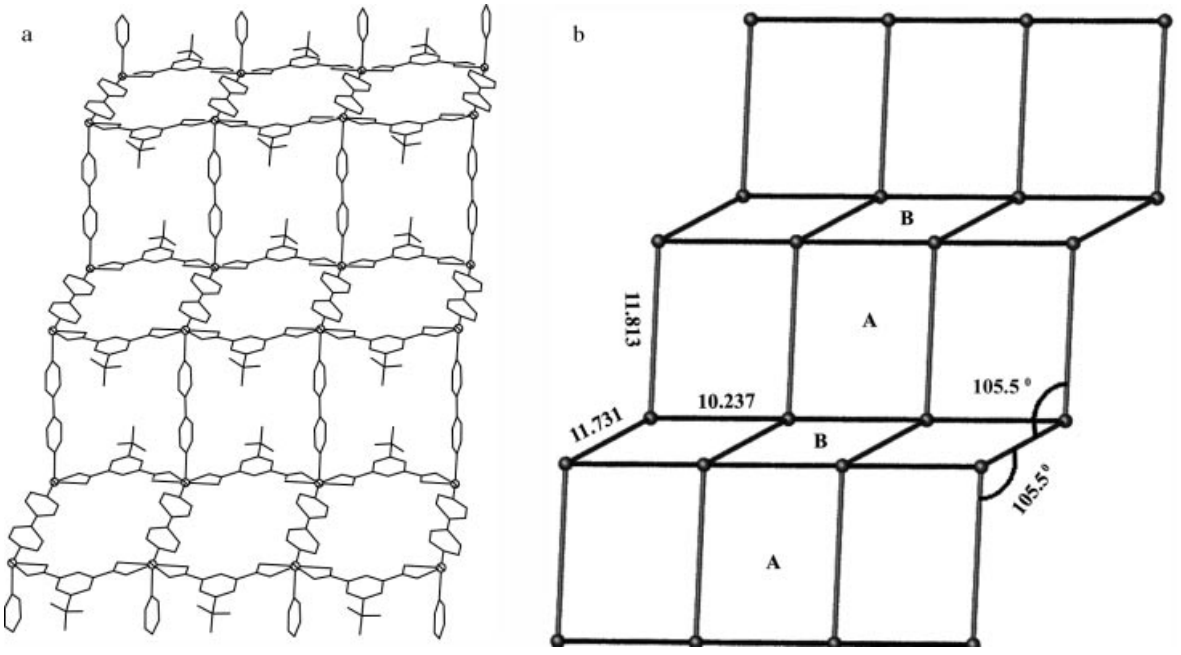


Figure 6. (a) The 2D step-like structure along the *a* axis of **3**. (b) Schematic plot of the 2D step-like structure.

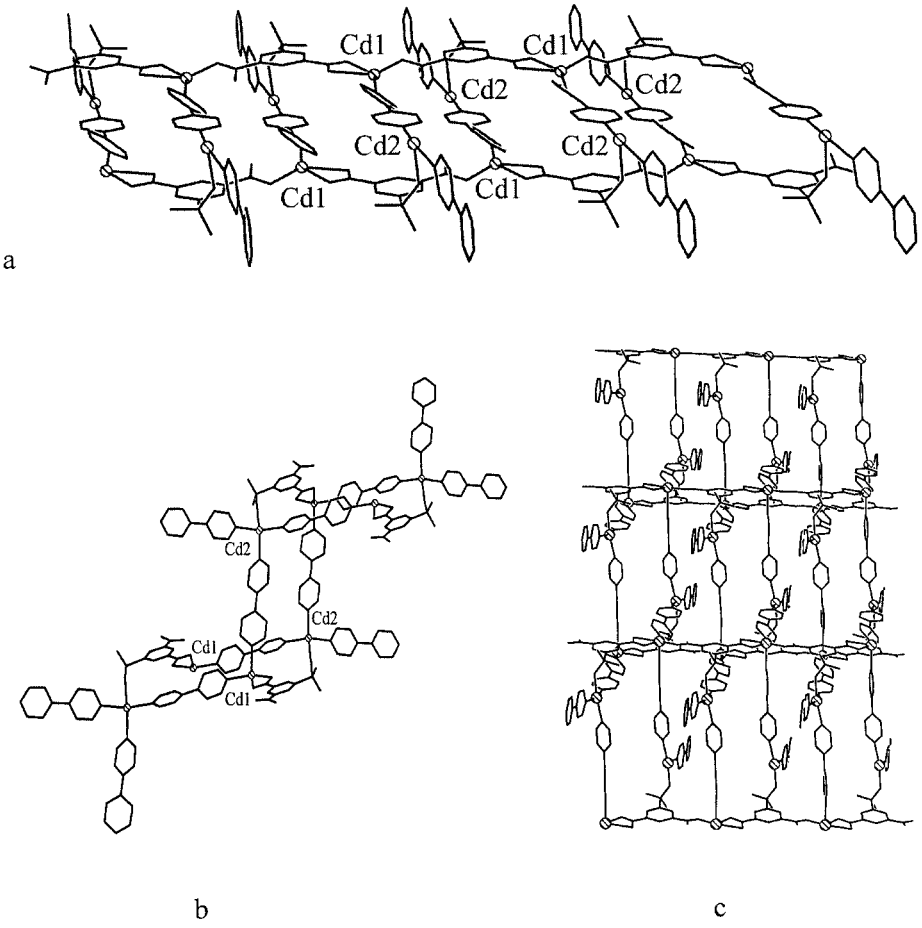


Figure 7. (a) The infinite brick-like sheet along the *c* axis of **3**. (b) The double zigzag chain along the *a* axis. (c) The step-like network.

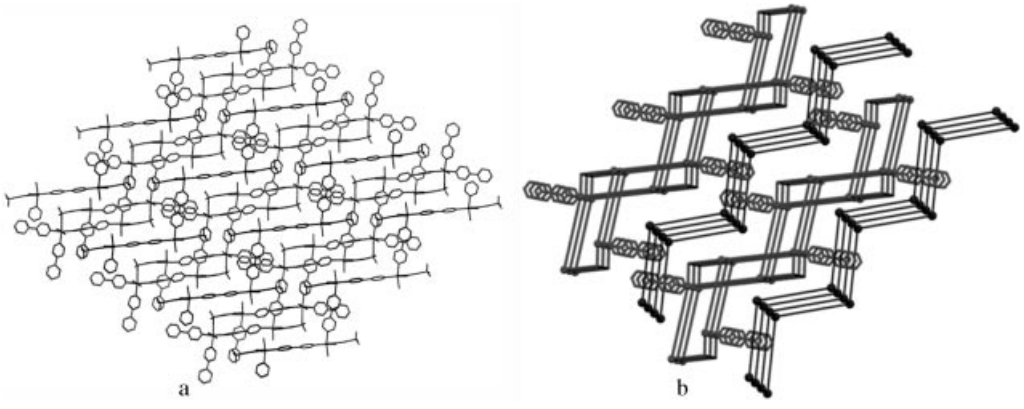


Figure 8. (a) Profile of the stacking structure along the *a* axis of **3**. (b) The stacking structure of **3**, with red representing the step-like cationic layer and blue representing the step-like anionic layer.

whereas the other, in which one nitrogen remains free and does not engage in coordination to the metal ion, acts as a terminal ligand that prevents the formation of three dimensional networks, although the $sipa^{3-}$ ligands employ all their coordination functional groups. In the anionic layer, one 4,4′-bpy bridges two metal ions and two carboxylate groups of $sipa^{3-}$ chelate one metal ion, leading to the formation of a two-dimensional structure; the sulfonate group remains uncoordinated to prevent the formation of three-dimensional frameworks. To the best of our knowledge, **3** is the first example of independent cationic and anionic layers in the structural framework of cadmium sulfonate-carboxylate complexes, which have only rarely been reported in other metal–organic compounds.[15]

{[Cd_3(sipa)$_2$(4,4′-bpy)$_4$(H_2O)$_2$]·3H_2O}$_n$ (4)

The structure of **4** has already been described in our previous report[9] and a detailed discussion will not be made here. In **4**, four $sipa^{3-}$ ligands and four cadmium ions form a 32-membered-ring $Cd_4(sipa)_4$ unit, which then propagates into a one-dimensional ladder-like double chain by sharing the $sipa^{3-}$ ligands as sides. Four cadmium ions and four bpy ligands encircle a $Cd_4(bpy)_4$ unit[16,17] and the $Cd_4(bpy)_4$ units are further extended into a one-dimensional twisted 8-like chain by sharing vertex cadmium ions. The two types of one-dimensional chains are interlocked and interwoven into a two-dimensional framework by sharing cadmium ions in the *ab* plane (Figure 9 and Table 4). The most intriguing feature is that the two kinds of $Cd_4(sipa)_4$ and $Cd_4(bpy)_4$ units interlock and interconnect each other to produce a pseudocatenate structure. Each $Cd_4(bpy)_4$ unit interlocks two $Cd_4(sipa)_4$ units and each $Cd_4(sipa)_4$ interlocks two $Cd_4(bpy)_4$ through cadmium ion nodes to yield an interwoven structure that is further magnified in different directions into a new three-dimensional, self-penetrating topological network (Figure 10).[18]

Both $sipa^{3-}$ and 4,4′-bpy ligands in **4** take full advantage of their coordination functional groups to link metal ions and generate a new self-penetrating three-dimensional framework, whereas in **1** the presence of the 2,2′-bipy ligand prevents the one-dimensional chain from being further extended into a 2D or 3D network even though the $sipa^{3-}$ ligands employ all their functional groups in coordination. In **2** and **3**, although 4,4′-bpy replaces 2,2′-bpy, one nitrogen atom of the pyridine ligand does not engage in coordination or the sulfonate group remains uncoordinated, which results in preventing the formation of a 3D structure. Thus, the design and syntheses of coordination complexes with different dimensional structures may be carried out by the control or modification of the properties of e coordinating functional groups and/or introduction of a second organic ligand.

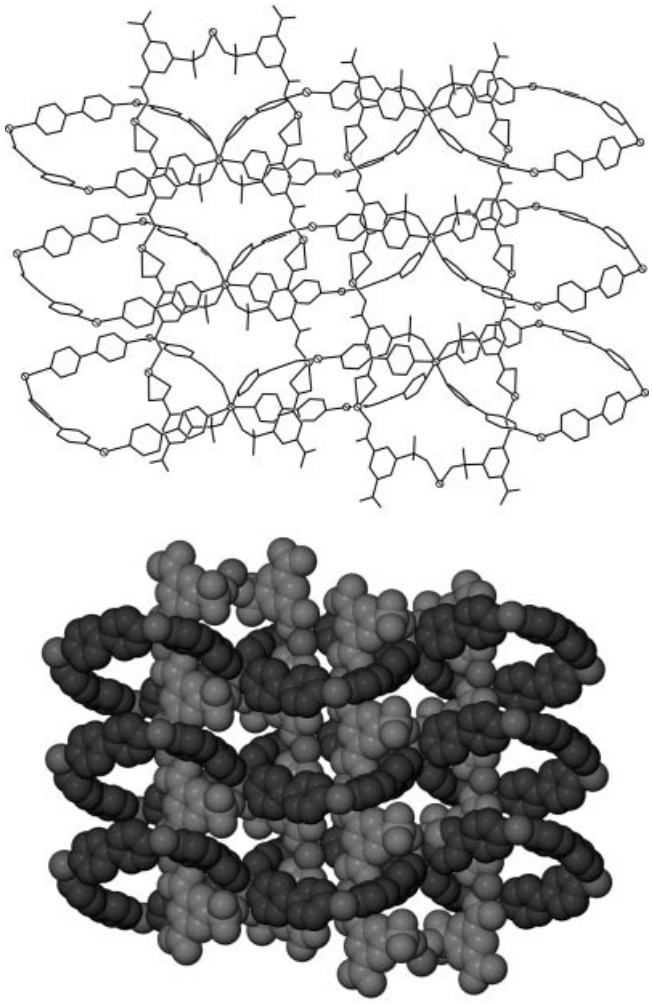


Figure 9. (a) 2D view showing the interlocking and interweaving of two kinds of units [$Cd_4(sipa)_4$ and $Cd_4(bpy)_4$] in the *ab* plane of **4**. (b) Space-filling diagram.

Table 4. Selected bond lengths [Å] and angles [°] for **4**.[a]

Cd(1)–O(5)	2.300(5)	Cd(2)–N(4)#3	2.335(5)
Cd(1)–O(5)#1	2.300(5)	Cd(2)–O(2)	2.355(4)
Cd(1)–N(1)#1	2.358(5)	Cd(2)–N(2)#4	2.375(5)
Cd(1)–N(1)	2.358(5)	Cd(2)–O(1)	2.464(4)
Cd(1)–N(3)	2.397(5)	S(1)–O(7)	1.437(5)
Cd(1)–N(3)#1	2.397(5)	S(1)–O(6)	1.438(5)
Cd(2)–O(4)#2	2.250(4)	S(1)–O(5)	1.466(5)
Cd(2)–O(8)	2.327(4)	S(1)–C(1)	1.775(6)
O(5)–Cd(1)–O(5)#1	86.0(2)	O(8)–Cd(2)–N(4)#3	91.93(17)
O(5)–Cd(1)–N(1)#1	174.27(16)	O(4)#2–Cd(2)–O(2)	136.18(16)
O(5)–Cd(1)–N(1)	93.39(17)	O(8)–Cd(2)–O(2)	87.98(16)
O(5)#1–Cd(1)–N(1)	174.27(16)	N(4)#3–Cd(2)–O(2)	93.03(17)
N(1)#1–Cd(1)–N(1)	87.8(3)	O(8)–Cd(2)–N(2)#4	164.27(17)
O(5)–Cd(1)–N(3)	84.51(16)	O(2)–Cd(2)–N(2)#4	104.00(17)
O(5)#1–Cd(1)–N(3)	81.92(16)	O(4)#2–Cd(2)–O(1)	84.08(16)
N(1)#1–Cd(1)–N(3)	89.75(17)	O(8)–Cd(2)–O(1)	91.98(16)
N(1)–Cd(1)–N(3)	103.70(17)	N(4)#3–Cd(2)–O(1)	146.66(17)
N(3)–Cd(1)–N(3)#1	161.4(2)	O(2)–Cd(2)–O(1)	54.05(14)
O(4)#2–Cd(2)–O(8)	80.44(16)	N(2)#4–Cd(2)–O(1)	87.07(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z + 1/2$; #2 x, $y - 1$, z; #3 $-x + 1/2$, $y - 1/2$, $-z + 1/2$; #4 x, $-y$, $z - 1/2$.

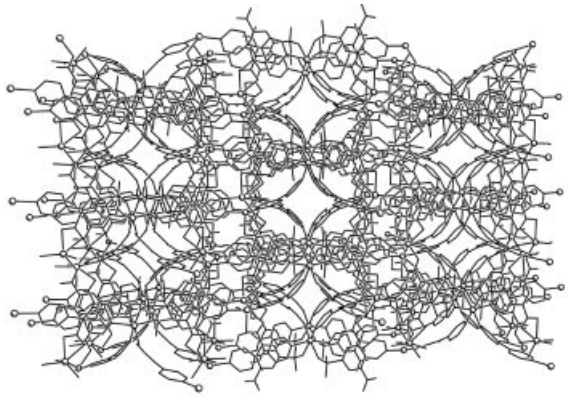


Figure 10. The three-dimensional self-penetrating structure along the *c* axis of **4**. Isolated water molecules are located in the channels.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses for complexes **1**–**4** were performed under a flow of nitrogen gas from room temperature to 1000 °C at a heating rate of 15 °C min^{-1}. Complex **1** begins to lose free water molecules at 184 °C and then loses further weight with increasing temperature. Differential thermal analysis (DTA) studies show two strongly endothermic reactions at 395 and 440 °C, respectively, which indicates that the framework collapses at 395 °C. For **2**, the first weight loss of 6.87% (calcd.: 6.36%) from 111 to 154 °C corresponds to the loss of two guest water molecules per formula unit ($2H_2O$/[Cd(sipa)(Hbpy)(H_2O)]·$2H_2O$ along with a strong absorption heat reaction; the coordination water molecules are slowly lost over the range 154–375 °C. DTA shows that one strong heat-absorption reaction takes place at 417 °C because of the collapse of the framework of **2**. Complex **3** starts losing weight at 50 °C and loses further weight with increasing temperature. DTA shows that a strongly endothermic reaction occurs at 436 °C, which indicates that the framework of **3** collapses. For **4**, the first weight loss of 5.75% (calcd. 5.86%) from 63 to 144 °C, which is accompanied by heat absorption, corresponds to the loss of three free waters and coordination water molecules per formula unit ($5H_2O$/{[Cd_3(sipa)$_2$-(bpy)$_4$(H_2O)$_2$]·$3H_2O$}). Strong heat absorption takes place in the range 340–420 °C, indicating the collapse of the structural framework at 340 °C.

Fluorescence Measurements

Previous studies have shown that polymeric compounds containing cadmium exhibit photoluminescent properties.[18] Hence, we also investigated the photoluminescent properties of complexes **1**–**4** (Figure 11). In the solid state, complex **1** displays two intense broadband fluorescent emissions at 335 and 351 nm, respectively, upon photoexcitation at 310 nm. Since NaH_2sipa exhibits photoluminescence emission at 355 nm, and free 2,2′-bipyridine exhibits emission at 362 nm, the emission bands at 351 and 335 nm of **1** can be attributed to the ligand donation. Strong photoluminescence emission bands at 510, 458, and 455 nm are observed for complexes **2**, **3**, and **4**, respectively, while free 4,4′-pyridine ligand presents weak photoluminescence emission at 486 nm. The photoluminescent emission of **2**–**4** may therefore be assigned to the nonradiative decay of the intraligand (π–π*) excited state and/or to ligand-to-metal charge transition, similar to previous reports.[5,19,20]

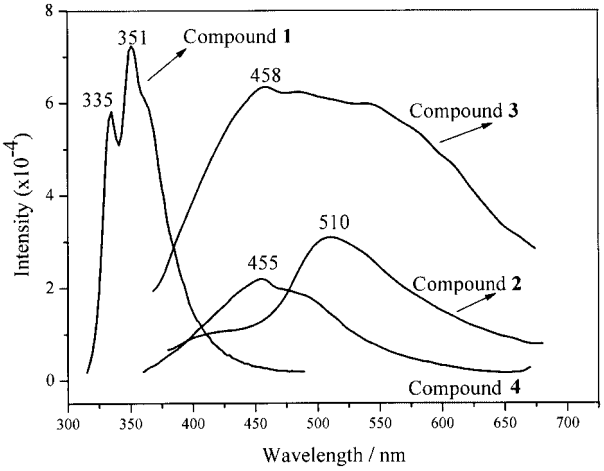


Figure 11. The photoluminescent spectra of **1**–**4** in the solid state at room temperature.

Conclusions

In conclusion, by selecting H_2sipa$^-$, 2,2′-bpy, and 4,4′-bpy as organic ligands, and the cadmium ion as knots, four polymeric complexes have been successfully isolated under hydrothermal conditions. Complex **1** possesses a 1D rail-like chain structure, **2** is a 1D double chain, **3** has a 2D network consisting of independent cationic [Cd_2(sipa)(4,4′-bpy)$_3$(H_2O)$_3$]$_n^{n+}$ and anionic [Cd(sipa)(4,4′-bpy) (H_2O)]$_n^{n-}$ layers, and **4** is a novel 3D self-penetrating network constructed from two mixed bridging ligands. The present work shows that a novel structure can be designed and assembled by combining the topology of organic ligands and the coordination geometry of metal ions.

Experimental Section

General: All chemicals were used as purchased without purification. The IR spectra were recorded as KBr pellets in the 4000–400 cm^{-1} region on a Magna 750 FT-IR spectrophotometer. The C, H, and N microanalyses were carried out with a Perkin–Elmer 240-element analyzer at this institute. Thermogravimetric analyses (TGA) were carried out on a Netzsch STA449C instrument. Fluorescent properties of **1**–**4** were measured on an Edinburgh Instruments analyzer model FL920.

{[Cd_3(sipa)$_2$(2,2′-bpy)$_4$(H_2O)$_2$]·$6H_2O$}$_n$ (1): A mixture of NaH_2sipa (0.053 g, 0.2 mmol), $Cd(NO_3)_2$·$4H_2O$ (0.092 g, 0.3 mmol), 2,2′-bipyridine (0.047 g, 0.3 mmol), EtOH (1.0 mL), and water (15 mL) was placed in a 25-mL Teflon-lined stainless autoclave and heated under autogenous pressure at 160 °C for 3 d. It was then cooled

Table 5. Summary of crystal data for **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{56}H_{54}Cd_3N_8O_{22}S_2$	$C_{18}H_{18}CdN_2O_{10}S$	$C_{56}H_{62}Cd_3N_8O_{26}S_2$	$C_{56}H_{48}Cd_3N_8O_{19}S_2$
Formula mass	1592.39	566.80	1664.46	1538.34
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	8.0333(3)	8.8014(6)	10.24(5)	35.578(4)
b [Å]	10.2111(2)	9.2140(7)	17.97(10)	10.2327(10)
c [Å]	20.2010(7)	13.9886(10)	18.74(12)	16.2118(17)
α [°]	95.68	97.4200(10)	77.71(13)	90
β [°]	94.43	94.5960(10)	87.3(2)	108.913(2)
γ [°]	109.62	113.97	77.4(2)	90
V [Å^3]	1542.38(8)	1016.81	3287(33)	5583.5(10)
Z	1	2	2	4
D_c [g cm^{-3}]	1.714	1.851	1.682	1.830
μ [mm^{-1}]	1.177	1.238	1.113	1.293
λ (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
F(000)	798	568	1676	3072
θ range [°]	2.71–25.09	1.48–25.09	3.02–25.03	1.21–25.04
R_1 [$I > 2\sigma(I)$]	0.0769	0.0387	0.0357	0.0469
R_1 (all data)	0.1407	0.0461	0.0407	0.0850
S (F^2)	1.022	1.228	1.032	1.077

to room temperature over 24 h. The resulting colorless block-like crystals of **1** were separated from the reaction mixture in about 47% yield (0.15 g) based on NaH_2sipa. $C_{56}H_{54}Cd_3N_8O_{22}S_2$ (1592.4): calcd. C 42.24, H 3.42, N 7.04; found C 42.16, H 3.27, N 7.19. IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} m, 3088 w, 1668 vs, 1593 m, 1489 w, 1473 m, 1443 s, 1387 m, 1315 m, 1269 s, 1161 vs, 1101 m, 1049 s, 1018 m, 906 w, 864 w, 760 s, 735 m, 708 w, 634 s, 577 w, 411 w.

{[Cd(sipa)(H-4,4′-bpy)(H_2O)]·2H_2O}$_n$ (2): A mixture of NaH_2sipa (0.133 g, 0.5 mmol), $Cd(NO_3)_2$·4H_2O (0.154 g, 0.5 mmol), 4,4′-bipyridine dihydrate (0.096 g, 0.5 mmol), and water (15 mL) was placed in a 25-mL Teflon-lined stainless autoclave and heated under autogenous pressure at 160 °C for 3 d. It was then cooled to room temperature over 24 h. Colorless sheet-like crystals of **2** were separated from the reaction mixture in about 35% yield (0.10 g) based on NaH_2sipa. $C_{18}H_{18}CdN_2O_{10}S$ (566.80): calcd. C 38.14, H 3.20, N 4.94; found C 38.26, H 3.11, N 4.90. IR (KBr): $\tilde{\nu}$ = 3419 cm^{-1} m, 3089 m, 3055 m, 2567 w, 2156 w, 1603 s, 1552 s, 1495 m, 1437 m, 1373 s, 1308 w, 1221 s, 1103 m, 1036 s, 933 w, 877 w, 820 m, 769 w, 731 m, 675 w, 631 s, 580 w, 523 w, 447 w.

{[Cd_2(sipa)(4,4′-bpy)$_3$(H_2O)$_3$]·[Cd(sipa)(4,4′-bpy)(H_2O)]·8H_2O}n (3): A mixture of NaH_2sipa (0.053 g, 0.2 mmol), $Cd(NO_3)_2$·4H_2O (0.092 g, 0.3 mmol), 4,4′-bipyridine dihydrate (0.096 g, 0.5 mmol), EtOH (1.0 mL), and water (15 mL) was placed in a 25-mL Teflon-lined stainless autoclave and heated under autogenous pressure at 160 °C for 5 d. It was then slowly cooled to room temperature over 24 h. Colorless sheet-like crystals of **3** were separated from the reaction mixture in about 54% yield (0.18 g). $C_{56}H_{62}Cd_3N_8O_{26}S_2$ (1664.5): calcd. C 40.41, H 3.75, N 6.73; found C 40.29, H 3.64, N 6.61. IR (KBr): $\tilde{\nu}$ = 3417 cm^{-1} m, 3088 m, 3051 m, 2565 w, 2141 w, 1942 w, 1603 vs, 1556 s, 1491 w, 1414 m, 1363 s, 1308 w, 1221 s, 1198 s, 1147 m, 1103 m, 1043 s, 874 w, 825 m, 806 s, 769 m, 731 m, 631 s, 580 w, 492 w, 447 w.

{[Cd_3(sipa)$_2$(4,4′-bpy)$_4$(H_2O)$_2$]·3H_2O}$_n$ (4): A mixture of NaH_2sipa (0.266 g, 1.0 mmol), $Cd(NO_3)_2$·4H_2O (0.231 g, 0.75 mmol), 4,4′-bipyridine dihydrate (0.192 g, 1.0 mmol), and water (10 mL) was placed in a 25-mL Teflon-lined stainless autoclave and heated under autogenous pressure at 160 °C for 3 d. It was then slowly cooled to room temperature over 24 h. The light-yellow block-like crystals of **4** were separated from the reaction mixture in about 23% yield (0.35 g). $C_{56}H_{48}Cd_3N_8O_{19}S_2$ (1538.3): calcd. C 43.72, H 3.14, N 7.28; found C 43.60, H 2.94, N 7.31. IR (KBr): $\tilde{\nu}$ = 3377 cm^{-1} w, 3211 w, 3055 w, 1942 w, 1605 vs, 1556 s, 1491 w, 1416 m, 1363 s, 1230 s, 1198 s, 1105 w, 1043 m, 1007 w, 922 w, 806 m, 783 w, 719 w, 629 m, 582 m, 492 w, 432 w.

X-ray Crystallography: Single crystals of complexes **1**–**4** with dimensions 0.24 × 0.18 × 0.12 (**1**), 0.36 × 0.24 × 0.10 (**2**), 0.24 × 0.18 × 0.06 (**3**), and 0.28 × 0.22 × 0.18 mm (**4**) were mounted on glass fibers for crystal structure analyses. For **1**, **2**, and **4** the data collections were performed on a Siemens Smart CCD diffractometer and for **3** on a Rigaku CCD diffractometer with graphite-monochromated Mo-K_a radiation (λ = 0.71073 Å) at 293 K. Empirical absorption corrections were applied using the SADABS program for **1**, **2**, and **4** and the CrystalClear program for **3**. All structures were solved by direct methods and the heavy atoms were located from the E-maps. Other non-hydrogen atoms were derived from the successive difference Fourier syntheses. The structures were refined by full-matrix, least-squares minimizations of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed with the SHELXTL-97 program package.[21] The positions of hydrogen atoms were generated geometrically and treated isotropically. In complex **3**, C55 and C56 of the 4,4′-bipyridine ring and O12, O13, and O14 of the SO_3^- group from $sipa^{3-}$ ligand were disordered over two sets of positions and were refined with restraints. Table 5 summarizes the important crystal data for **1**–**4**.

CCDC-246223 (for **1**), -246224 (for **2**), -246225 (for **3**), and -221212 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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