

# Synthesis, Crystal Structures and Photoluminescent Properties of Three Novel Cadmium(II) Compounds Constructed from 5-Sulfoisophthalic Acid (H<sub>3</sub>SIP)

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**Keywords:** Cadmium compounds / Hydrothermal synthesis / Crystal structures / Photoluminescent properties

Hydrothermal reactions of Cd(NO<sub>3</sub>)<sub>2</sub> and NaH<sub>2</sub>SIP (5-sulfoisophthalic acid monosodium salt) at pH = 2 and 7 produce [Cd<sub>2</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(HSIP)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] (1) and [Cd<sub>5</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(SIP)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>]<sub>n</sub> (2), respectively. A similar hydrothermal reaction in the presence of dpp [1,3-bis(4-pyridyl)propane] yields {[Cd<sub>3</sub>(SIP)<sub>2</sub>(dpp)<sub>6</sub>·4(H<sub>2</sub>O)]<sub>n</sub> (3). Single-crystal X-ray diffraction reveals that compound 1 has a discrete dinuclear structure with the [Cd<sub>2</sub>(μ<sub>2</sub>-OH)<sub>2</sub>] unit. Polymer 2 features an inorganic layer, which has centrosymmetric 12- and 24-membered rings composed of chair-shaped [Cd<sub>4</sub>(μ<sub>3</sub>-OH)<sub>2</sub>] units and Cd(μ<sub>2</sub>-OH)<sub>2</sub>(CO<sub>2</sub>) units, and is interconnected by SIP into

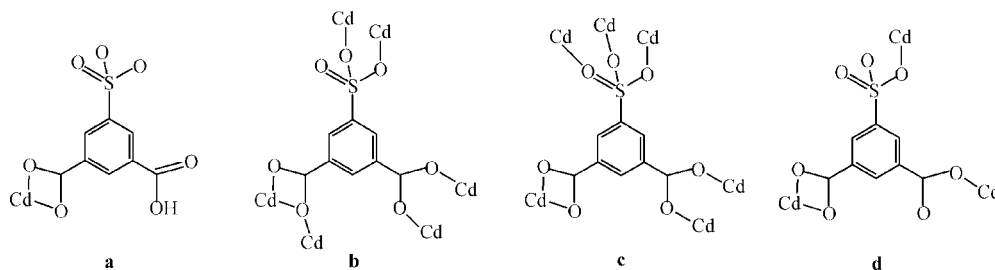
a 3D framework. Complex 3 contains a 1D ladder-like [Cd<sub>4</sub>(SIP)<sub>4</sub>]<sub>n</sub> unit with four cadmium atoms co-planar, which is interconnected by dpp into a 2D nanosized layered structure. In the solid state, compounds 1 and 3 exhibit blue-violet photoluminescence with maxima at 436 and 409 nm upon excitation at 342 and 350 nm, respectively. However, compound 2 shows photoluminescence with the maximum at 306 nm upon excitation at 270 nm.

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## Introduction

The design and construction of metal–organic frameworks (MOFs) has been one of the most active areas of materials research in recent years. The intense interest in these materials is driven by their potential applications as functional materials (catalysis, magnetism, electric conductivity and nonlinear optics) and intriguing structural diversities.<sup>[1–4]</sup> Assembly of these metal–organic coordination polymers allows for a wide choice of various parameters

including diverse electronic properties and coordination geometries of the metal ions as well as versatile functions of organic ligands.<sup>[5–7]</sup> Consequently, a wide variety of coordination architectures with interesting structures and desired properties have been prepared through judicious choice of organic ligands and metal ions.<sup>[8–11]</sup> Recently, 5-sulfoisophthalic acid (H<sub>3</sub>SIP) has been successfully used to investigate the lanthanide contraction effect<sup>[12]</sup> and the coordination polymer chemistry of a main group metal



Scheme 1. Coordination modes of 5-sulfoisophthalic acid observed in compounds 1–3.

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(Pb<sup>2+</sup>),<sup>[13]</sup> because of its multiple coordinating modes and the sensitivity of the sulfonate group to the surrounding chemical environment. In this contribution, SIP will serve as a probe to examine the coordination polymer chemistry of the late transition metal Cd<sup>2+</sup>. Three novel (SIP)Cd compounds, [Cd<sub>2</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(HSIP)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] (1), [Cd<sub>5</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(SIP)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>]<sub>n</sub> (2) and {[Cd<sub>3</sub>(SIP)<sub>2</sub>(dpp)<sub>6</sub>·4(H<sub>2</sub>O)]<sub>n</sub> (3), will be described with regard to syntheses, crystal structures, and IR spectroscopic and photolumines-

cent properties. Two unprecedented bridging coordination modes of SIP (Scheme 1, **b** and **c**) are observed in polymer **2**.

## Results and Discussion

### Preparation of the Compounds

Hydrothermal synthesis is widely employed to produce new materials with diverse structural architectures, but is still a kind of black box. This method can minimise the problems associated with ligand solubility and enhance the reactivity of reactants in favour of efficient molecular building during the crystallisation process. There are a variety of hydrothermal parameters such as reaction time, temperature, pH value, templates and molar ratio of reactants, and small changes in one or more of these parameters can have a profound influence on the final reaction outcome. Compounds **1** and **2**, with very different structures, were obtained from similar reactions but at different pH values, indicating that the hydrothermal reaction outcome of the Cd/H<sub>3</sub>SIP system is pH-dependent. We also notice that N-containing auxiliary ligands such as dpp [1,3-bis(4-pyridyl)propane] are also able to tune the framework structures. At a ratio of Cd/SIP/dpp = 3:2:6, the 2D polymer **3** is formed. Reducing the corresponding ratio to 3:2:2 results in the 1D compound  $\{[\text{Cd}(\text{SIP})(\text{dpp})(\text{H}_2\text{O})_3] \cdot 0.5\text{Cd}(\text{H}_2\text{O})_6 \cdot 5\text{H}_2\text{O}\}_n$ ,<sup>[14]</sup> indicating that the reaction products are ratio-dependent. The preparative reactions were carried out at different temperatures (140 °C, 160 °C and 180 °C) to examine the temperature dependence of their solid structures. X-ray diffraction analyses of these reaction products indicate that the same results were obtained under these reaction temperatures although the purity and yields were slightly different, indicative of the thermodynamic nature of the hydrothermal reactions.<sup>[15]</sup>

### Crystal Structure of $[\text{Cd}_2(\mu_2\text{-OH})_2(\text{HSIP})_2(\text{H}_2\text{O})_6] \text{ (1)}$

The dinuclear structure of **1** is shown in Figure 1; it has a crystallographically imposed *C*<sub>2h</sub> symmetry, which has the

*C*<sub>2</sub> axis passing through O7 and O7A (for symmetry code see Table 1). The two Cd<sup>II</sup> atoms are linked by two bridging water molecules to form the rhomboidal  $[\text{Cd}_2(\mu_2\text{-OH})_2]$  core with a Cd–O distance of 2.412(1) Å and O(7)–Cd(1)–O(7A) bond angle of 75.48(8)°. Each cadmium ion is bonded to two bridging water molecules, three terminal water molecules and one HSIP<sup>2–</sup> dianion through the chelating carboxylate group. The Cd–O distances range from 2.412(1) to 2.567(3) Å, which is consistent with those found in comparable structures.<sup>[16–19]</sup> The uncoordinated carboxylate group is protonated for charge balance, as suggested by the strong absorption at 1710 cm<sup>–1</sup>.<sup>[20]</sup> As shown in Figure 2a, a 3D supramolecular framework is formed through three types of hydrogen bonds between (a) coordinated water molecules and sulfonate oxygen atoms [O(7)⋯O(5B) 2.732(2) Å, O(8)⋯O(6C) 2.832(2) Å and O(9)⋯O(6D) 2.808(2) Å]; (b) coordinated water molecules and carboxylate oxygen atoms [O(9)⋯O(4B) 2.867(3) Å]; and (c) a carboxylate group and a carboxylate oxygen atom [O(3)⋯O(2E) 2.581(3) Å]. Of particular interest is the infinite tape formed by hydrogen bonds between the  $[\text{Cd}_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]$  units and the sulfonate groups along the crystallographic *b* axis (Figure 2b). The hydrogen-bonded tape features an eight-membered ring [the bridging H<sub>2</sub>O(7), O(5) and their equivalents], which is nearly perpendicular to the  $[\text{Cd}_2(\mu_2\text{-OH})_2]$  plane (95.7°). The tape is strengthened by the O(8)⋯O(6C) hydrogen bonds, as shown in Figure 2b. The 3D supramolecular structures are further stabilised by  $\pi$ – $\pi$  interactions between the parallel aromatic rings in an off-set fashion with a face-to-face distance of 3.44(2) Å and a centre-to-centre distance of 3.66(3) Å. This indicates that noncovalent interactions can play a crucial role in constructing the whole packing.

### Crystal Structure of $[\text{Cd}_5(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{SIP})_2(\text{H}_2\text{O})_5]_n \text{ (2)}$

Compound **2** contains five unique Cd<sup>II</sup> ions, four of which are six-coordinate and one [Cd(3)] five-coordinate.

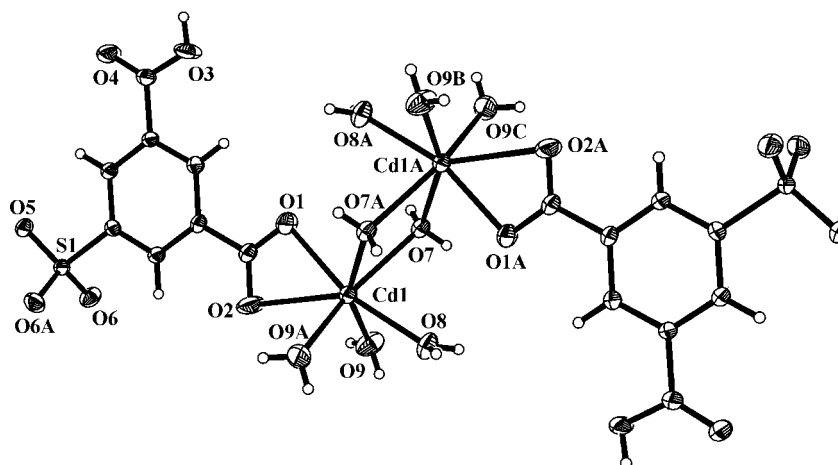


Figure 1. ORTEP drawing of **1** with 40% probability displacement ellipsoids. Hydrogen atoms are shown as small spheres of arbitrary radii.

As shown in Figure 3, Cd(1) has a distorted octahedral coordination geometry with the equatorial positions taken up by one chelating carboxylate group [O(10A) and O(11A)],

Table 1. Selected bond lengths [Å] and bond angles [°] of **1–3**.<sup>[a]</sup>

Compound 1			
Cd(1)–O(1)	2.265(2)	Cd(1)–O(2)	2.567(3)
Cd(1)–O(7)	2.4121(13)	Cd(1)–O(8)	2.284(2)
Cd(1)–O(9)	2.2683(18)		
O(1)–Cd(1)–O(2)	52.45(8)	O(1)–Cd(1)–O(7)	83.93(5)
O(1)–Cd(1)–O(8)	163.71(9)	O(1)–Cd(1)–O(9)	107.82(6)
O(7)–Cd(1)–O(7A)	75.48(8)	O(9)–Cd(1)–O(7)	85.73(7)
O(9)–Cd(1)–O(8)	81.13(6)	O(7)–Cd(1)–O(8)	83.21(5)
O(9)–Cd(1)–O(2)	78.00(6)	O(2)–Cd(1)–O(8)	143.84(8)
O(7)–Cd(1)–O(2)	123.84(4)	O(9)–Cd(1)–O(9A)	108.51(11)
Cd(1)–O(7)–Cd(1A)	104.52(8)		
Compound 2			
Cd(1)–O(1)	2.258(3)	Cd(1)–O(15)	2.327(3)
Cd(1)–O(16)	2.198(2)	Cd(1)–O(10A)	2.405(3)
Cd(1)–O(11A)	2.317(3)	Cd(1)–O(5B)	2.445(2)
Cd(2)–O(2)	2.315(3)	Cd(2)–O(16)	2.276(2)
Cd(2)–O(16C)	2.260(2)	Cd(2)–O(17)	2.398(4)
Cd(2)–O(18)	2.200(3)	Cd(2)–O(6B)	2.412(2)
Cd(3)–O(3)	2.260(2)	Cd(3)–O(12)	2.432(2)
Cd(3)–O(18)	2.201(3)	Cd(3)–O(19)	2.287(3)
Cd(3)–O(20)	2.182(3)	Cd(4)–O(13)	2.416(2)
Cd(4)–O(20)	2.237(2)	Cd(4)–O(21)	2.276(3)
Cd(4)–O(22)	2.286(2)	Cd(4)–O(9E)	2.345(2)
Cd(4)–O(22D)	2.235(2)	Cd(5)–O(14)	2.517(2)
Cd(5)–O(22)	2.193(2)	Cd(5)–O(23)	2.279(3)
Cd(5)–O(8E)	2.270(2)	Cd(5)–O(3F)	2.507(2)
Cd(5)–O(4F)	2.309(3)		
O(1)–Cd(1)–O(16)	118.75(9)	O(1)–Cd(1)–O(11A)	82.70(9)
O(10A)–Cd(1)–O(11A)	54.97(9)	O(16)–Cd(1)–O(10A)	101.87(9)
O(15)–Cd(1)–O(16)	97.29(10)	O(15)–Cd(1)–O(1)	99.84(12)
O(15)–Cd(1)–O(10A)	85.45(13)	O(15)–Cd(1)–O(11A)	93.96(11)
O(5B)–Cd(1)–O(1)	90.71(9)	O(5B)–Cd(1)–O(16)	79.69(8)
O(5B)–Cd(1)–O(10A)	84.97(11)	O(5B)–Cd(1)–O(11A)	84.72(10)
O(16C)–Cd(2)–O(16)	81.20(8)	O(6B)–Cd(2)–O(16)	174.23(9)
O(18)–Cd(2)–O(6B)	90.15(11)	O(16C)–Cd(2)–O(18)	93.27(11)
O(2)–Cd(2)–O(16)	78.61(9)	O(2)–Cd(2)–O(16C)	92.43(9)
O(2)–Cd(2)–O(18)	108.43(11)	O(2)–Cd(2)–O(6B)	82.08(9)
O(17)–Cd(2)–O(16)	90.06(15)	O(17)–Cd(2)–O(16C)	100.81(16)
O(17)–Cd(2)–O(18)	84.41(15)	O(17)–Cd(2)–O(6B)	84.14(15)
O(3)–Cd(3)–O(12)	103.64(8)	O(3)–Cd(3)–O(18)	129.41(11)
O(12)–Cd(3)–O(18)	121.49(11)	O(19)–Cd(3)–O(3)	78.58(9)
O(19)–Cd(3)–O(12)	73.32(9)	O(19)–Cd(3)–O(18)	92.68(11)
O(20)–Cd(2)–O(3)	92.98(9)	O(20)–Cd(3)–O(12)	98.00(9)
O(20)–Cd(3)–O(18)	101.49(11)	O(13)–Cd(4)–O(21)	82.07(10)
O(13)–Cd(4)–O(22)	100.35(8)	O(22D)–Cd(4)–O(21)	92.43(9)
O(22D)–Cd(4)–O(22)	83.20(8)	O(22)–Cd(4)–O(20)	100.88(9)
O(13)–Cd(4)–O(20)	82.62(9)	O(22D)–Cd(4)–O(20)	110.23(9)
O(21)–Cd(4)–O(20)	88.06(10)	O(22)–Cd(4)–O(9E)	79.23(8)
O(13)–Cd(4)–O(9E)	77.61(9)	O(22D)–Cd(4)–O(9E)	89.83(9)
O(21)–Cd(4)–O(9E)	92.88(10)	O(3F)–Cd(5)–O(4F)	54.08(8)
O(4B)–Cd(5)–O(8E)	83.71(9)	O(3F)–Cd(5)–O(22)	97.64(8)
O(8E)–Cd(5)–O(22)	120.34(9)	O(14)–Cd(5)–O(3F)	79.74(8)
O(14)–Cd(5)–O(4F)	85.51(9)	O(14)–Cd(5)–O(22)	78.12(8)
O(14)–Cd(5)–O(8E)	87.58(9)	O(23)–Cd(5)–O(3F)	94.46(11)
O(23)–Cd(5)–O(4F)	97.71(11)	O(23)–Cd(5)–O(22)	94.77(10)
O(23)–Cd(5)–O(8E)	102.12(11)	Cd(1)–O(16)–Cd(2)	105.56(9)
Cd(1)–O(16)–Cd(2C)	124.45(11)	Cd(2)–O(16)–Cd(2C)	98.80(8)
Cd(2)–O(18)–Cd(3)	142.54(16)	Cd(3)–O(20)–Cd(4)	111.16(11)
Cd(4)–O(22)–Cd(5)	105.06(9)	Cd(4)–O(22)–Cd(4D)	96.80(8)
Cd(5)–O(22)–Cd(4D)	121.22(10)	Cd(3)–O(3)–Cd(5F)	121.56(10)

Table 1. (continued).

Compound 3			
Cd(1)–O(5)	2.317(2)	Cd(1)–N(1)	2.372(3)
Cd(1)–N(3)	2.338(3)	Cd(2)–O(1)	2.302(2)
Cd(2)–O(3B)	2.539(2)	Cd(2)–O(4B)	2.346(2)
Cd(2)–N(5)	2.300(3)	Cd(2)–N(4C)	2.351(3)
Cd(2)–N(6D)	2.356(3)		
N(1)–Cd(1)–N(3)	82.75(10)	N(1)–Cd(1)–N(3A)	97.25(10)
N(1)–Cd(1)–O(5)	90.22(9)	N(3)–Cd(1)–O(5)	95.57(9)
N(1A)–Cd(1)–O(5)	89.78(9)	N(3A)–Cd(1)–O(5)	84.43(9)
O(1)–Cd(2)–N(5)	129.70(9)	O(1)–Cd(2)–O(4B)	84.90(8)
O(3B)–Cd(2)–O(4B)	53.47(7)	N(5)–Cd(2)–O(3B)	91.42(8)
N(6D)–Cd(2)–O(1)	86.42(10)	N(6D)–Cd(2)–O(3B)	83.31(9)
N(6D)–Cd(2)–O(4B)	83.89(9)	N(6D)–Cd(1)–N(5)	91.61(10)
N(4C)–Cd(2)–O(1)	84.90(8)	N(4C)–Cd(2)–O(3B)	85.97(9)
N(4C)–Cd(2)–O(4B)	84.37(9)	N(4C)–Cd(1)–N(5)	95.33(10)
N(4C)–Cd(2)–O(6D)	167.37(10)		

[a] Symmetry transformation for equivalent atoms: Compound **1**: A:  $-x, -y + 1, -z + 2$ ; Compound **2**: A:  $x + 1, y, z - 1$ ; B:  $-x, -y + 2, -z + 1$ ; C:  $-x - 1, -y + 3, -z + 1$ ; D:  $-x, -y + 2, -z + 2$ ; E:  $-x - 1, -y + 3, -z + 2$ ; F:  $-x - 1, -y + 2, -z + 2$ ; Compound **3**: A:  $-x - 1, -y + 1, -z + 1$ ; B:  $x - 1, y, z$ ; C:  $-x - 1, -y, -z + 1$ ; D:  $x, y + 1, z$ .

one monodentate carboxylate oxygen atom [O(1)] and one  $\mu_3$ -hydroxy oxygen atom [O(16)]. The axial positions are occupied by one water molecule [O(15)] and one sulfonate oxygen atom [O(5B)] from the third SIP ligand. The angles formed by the equatorial atoms range from 54.97(9)° [O(10A)–Cd(1)–O(11A)] to 118.75(9)° [O(1)–Cd(1)–O(16)], indicative of a serious distortion of the [CdO<sub>6</sub>] octahedron. Cd(5) has a similar coordination environment to that of Cd(1). Cd(2) also has a distorted [CdO<sub>6</sub>] octahedral coordination geometry in which a pair of symmetrically related  $\mu_3$ -hydroxy oxygen atoms [O(16) and O(16C)], a  $\mu_2$ -hydroxy oxygen atom [O(18)] and a sulfonate oxygen atom [O(6B)] form the equatorial plane. The water molecule [O(17)] and the carboxylate oxygen atom [O(2)] occupy the apical positions. The coordination environment of Cd(4) is similar to that of Cd(2) but the terminal water molecule [O(21)] is located at the equatorial plane and the  $\mu_2$ -hydroxy oxygen atom [O(20)] occupies the apical position. The Cd(3) atom is coordinated by one  $\mu_2$ -hydroxy oxygen atom [O(18)], a sulfonate oxygen atom [O(12)] and one carboxylate oxygen atom [O(3)] in an equatorial plane, and the other  $\mu_2$ -hydroxy oxygen atom [O(20)] and the water molecule [O(19)] in the apical positions to complete its trigonal-bipyramidal coordination environment. The Cd–O distances range from 2.182(3) to 2.517(2) Å, as listed in Table 1. Two crystallographically unique SIP ligands exhibit two different coordination modes (Scheme 1, **b** and **c**). One SIP (**b**) acts as a hexadentate ligand with the bidentate sulfonate and carboxylate groups, and one  $\mu_2$ - $\eta^2$ : $\eta^1$  carboxylate group (one oxygen atom bridges two metal atoms, the other connects one metal atom and the carboxylate group coordinates to two metal atoms). The other SIP ligand also adopts a hexadentate bridging coordination mode through its one bidentate carboxylate group, one chelate carboxylate group and the tridentate sulfonate group. To the best of our knowledge,

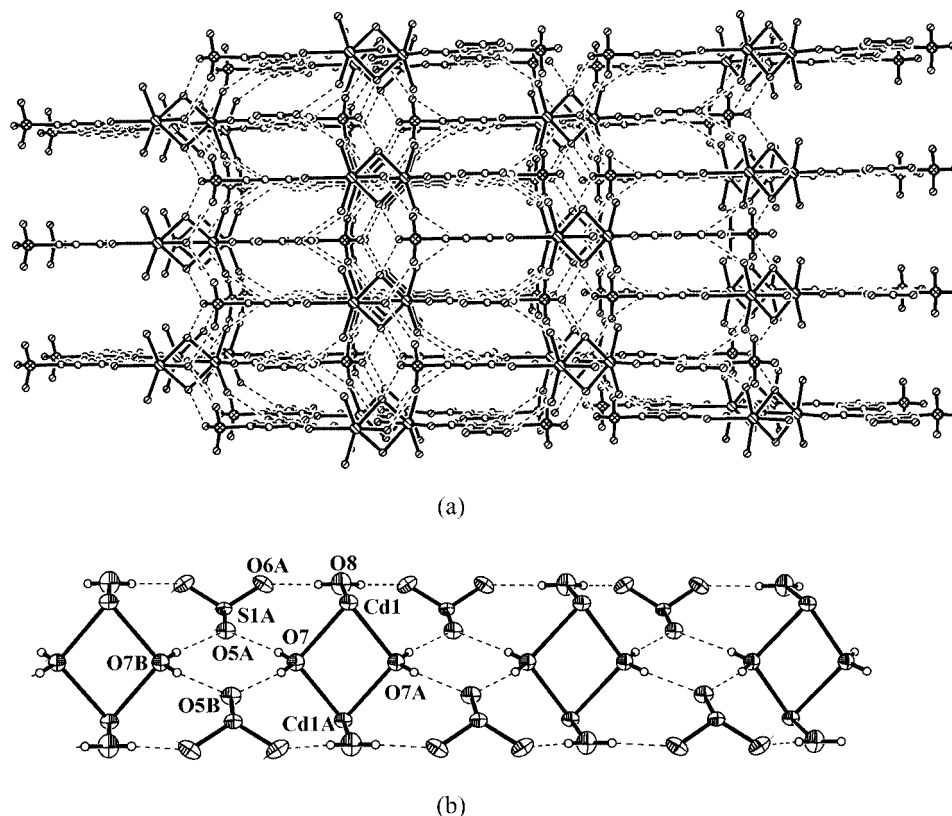
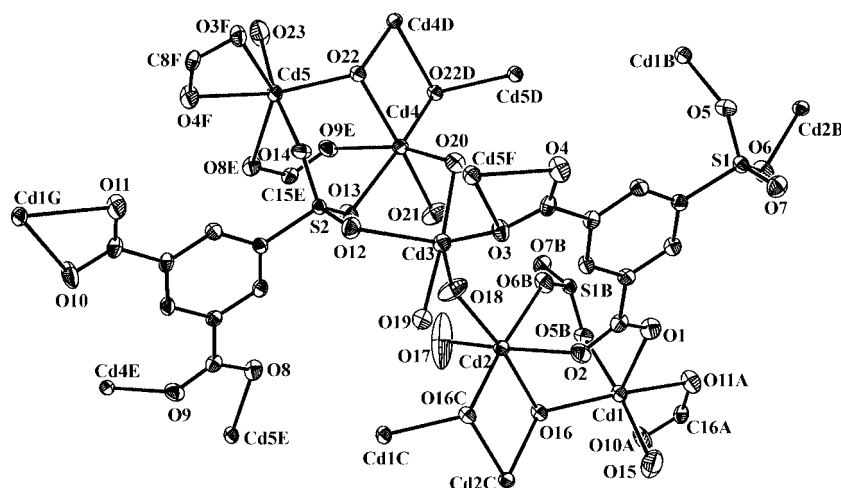


Figure 2. (a) 3D porous supramolecular open framework of **1** viewed along the *c* axis. (b)  $[\text{Cd}_2(\mu_2\text{-OH}_2)_2]$  cores bridged by sulfonate groups through hydrogen bonds to form a 1D tape.





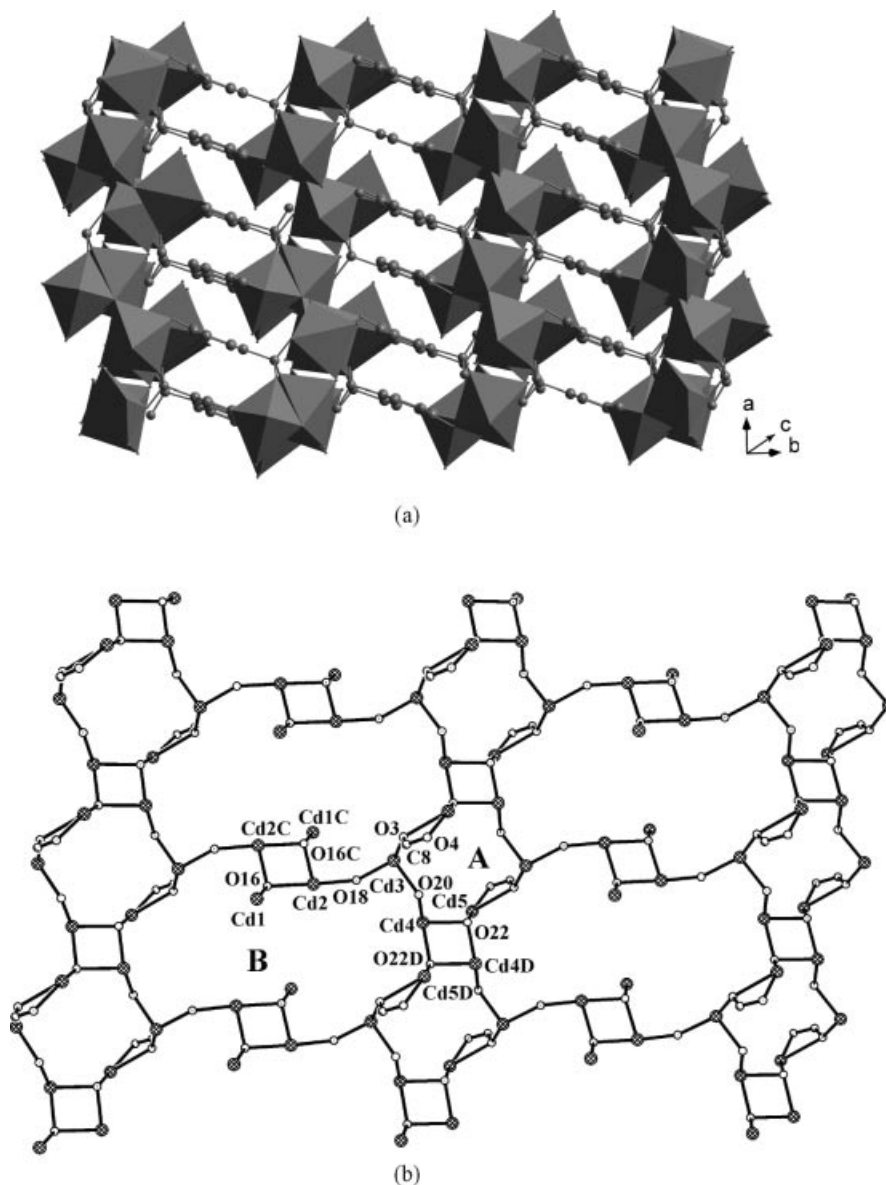


Figure 4. (a) 3D structure of **2** (the polyhedral presentation indicates the coordination environments for the Cd centre). (b) Perspective view of the 2D metal-oxide inorganic layer featuring the chair-shaped  $[\text{Cd}_4(\mu_3\text{-OH})_2]$  clusters and two types of large rings.

$[\text{Cd}_4(\mu_3\text{-OH})_2]$  cluster formed by Cd(4)/Cd(5) has a similar geometry to that of the  $[\text{Cd}_4(\mu_3\text{-OH})_2]$  cluster formed by Cd(1)/Cd(2), with Cd(5)–O(22), Cd(4)–O(20) and Cd(4)–O(22) bond lengths of 2.193(2), 2.286(2) and 2.237(2) Å, respectively, and surrounding angles of 105.06(9)°, 121.22(10)° and 96.80(8)° for Cd(4)–O(22)–Cd(5), Cd(5)–O(22)–Cd(4D) and Cd(4)–O(22)–Cd(4D), respectively. There are several compounds containing a chair-shaped tetranuclear cadmium cluster,<sup>[23–25]</sup> but those with two capping  $\mu_3\text{-OH}$  groups are rare. It is even more interesting that the  $[\text{Cd}_4(\mu_3\text{-OH})_2]$  cluster units are interconnected by the Cd(3)( $\mu_2\text{-OH})_2(\text{CO}_2)$  unit into an unusual inorganic oxide layer. Although cadmium cluster units have been known to be present in coordination polymers,<sup>[6,26–28]</sup> such cluster-based inorganic layers as subunits of a coordination polymer are still scarce. The layer has a 12-membered ring (A)

with approximate dimensions of  $3.8 \times 4.9 \text{ Å}^2$ , which is composed of Cd(3), Cd(4) and Cd(5) atoms and their equivalents linked by two  $\mu_3\text{-OH}$ , two  $\mu_2\text{-OH}$  and two carboxylate groups. It also contains a large 24-membered ring (B) with approximate dimensions of  $4.7 \times 14.3 \text{ Å}^2$ . The inorganic oxide layer is linked by the carboxylate and sulfonate groups of the SIP ligands to form a 3D pillared framework.

### Crystal Structure of $\{[\text{Cd}_3(\text{SIP})_2(\text{dpp})_6] \cdot 4(\text{H}_2\text{O})\}_n$ (**3**)

As shown in Figure 5, **3** contains two crystallographically independent cadmium ions; Cd(1) lies on the crystallographic inversion centre. Both  $\text{Cd}^{2+}$  ions are octahedrally coordinated but their coordination environments are different. Cd(1) is coordinated to four equatorial pyridine ni-

trogen atoms [Cd–N = 2.372(3) and 2.338(3) Å] in a square-planar arrangement and two apical sulfonate oxygen atoms from two *trans*-SIP ligands [Cd–O = 2.317(2) Å]. Cd(2) is coordinated by one chelating and one monodentate carboxylate group from two different SIP ligands, and one pyridine nitrogen atom in equatorial positions with Cd–O distances of 2.346(2), 2.539(2) and 2.302(2) Å, respectively, and a Cd–N distance of 2.300(3) Å. The axial positions are taken up by two other pyridine nitrogen atoms, with Cd–N distances of 2.351(3) and 2.356(3) Å. As illustrated in Figure 6, the SIP ligands interconnect the Cd<sup>2+</sup> ions in coordination mode **d** (Scheme 1) into an infinite ladder structure along the *a* axis, which features the cyclic [Cd<sub>4</sub>(SIP)<sub>4</sub>] unit with dimensions of 7.5 × 12.8 Å<sup>2</sup>. It is interesting that the four Cd ions [Cd(1), Cd(2), Cd(1A) and Cd(2A)] are

co-planar. The 1D ladder can also conveniently be regarded as resulting from two antiparallel [Cd(SIP)]<sub>n</sub> single chains bridged by Cd(1) (Figure 6).

Compound **3** contains one monodentate [N(1)⋯N(2)] and two bridging dpp ligands [N(3)⋯N(4) and N(5)⋯N(6)]. The flexible dpp ligand can adopt several conformations based on the orientations of the CH<sub>2</sub> groups, such as *TT*, *TG*, *GG* and *GG'* (*T* = *trans*; *G* = *gauche*), with quite different N⋯N separations (6.7–10.1 Å).<sup>[29,30]</sup> In the present case, the monodentate dpp has a conformation of *TG* with an N⋯N distance of 8.9 Å and the bridging ones adopt *TT* conformation with an N⋯N separation of 9.5 Å. The 1D ladders are connected by the bridging dpp ligands to form a 2D nanolayer with a thickness of about 1.5 nm, as shown in Figure 7; the cavity is filled in by the monodentate dpp.

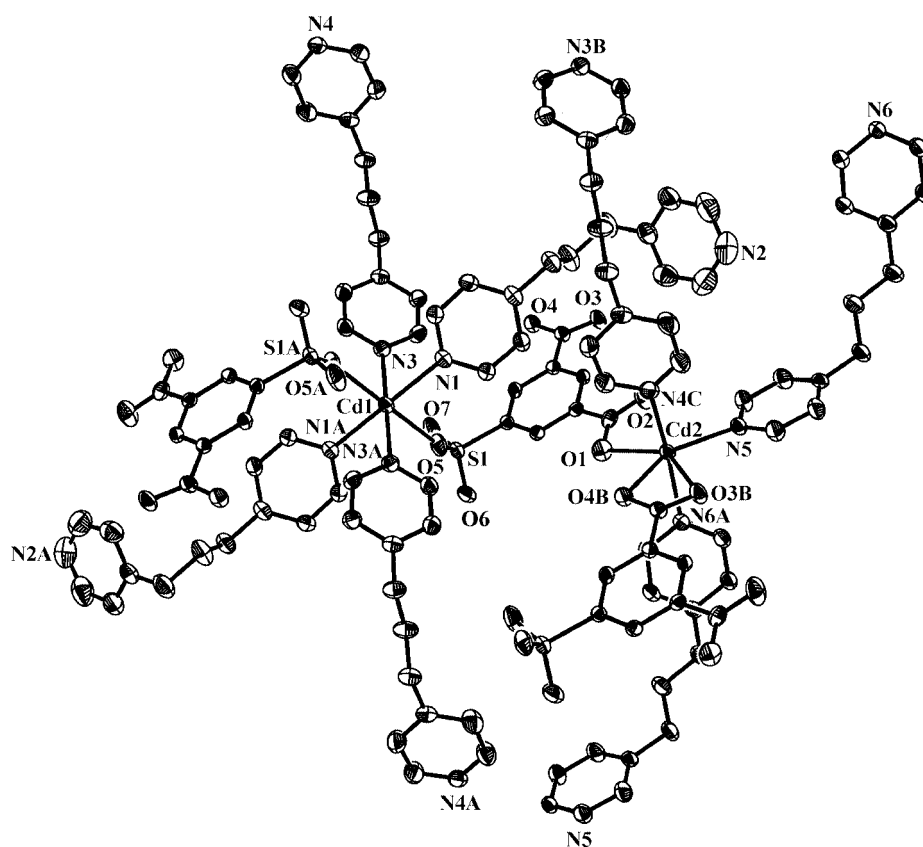


Figure 5. ORTEP drawing of **3** with 35% probability displacement ellipsoids.

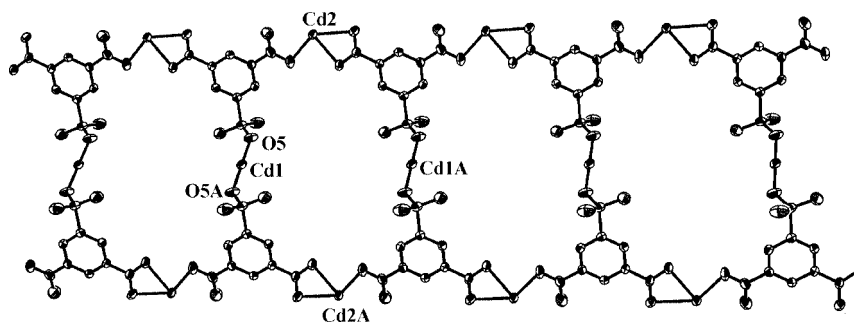


Figure 6. 1D ladder structure in compound **3** featuring the cyclic [Cd<sub>4</sub>(SIP)<sub>4</sub>] unit.

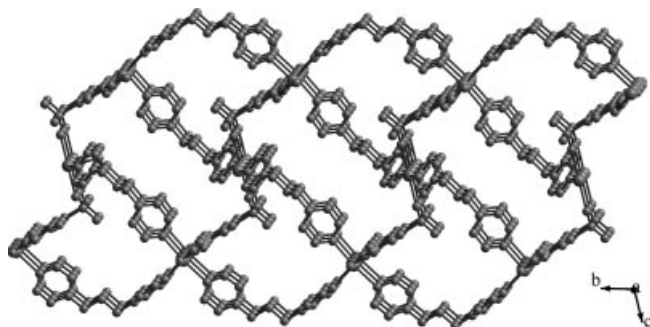


Figure 7. Perspective view of the 2D structure of **3**. Lattice water molecules and monodentate dpp molecules omitted for clarity.

### FTIR Spectra

The FTIR spectra of **1** and **3** exhibit broad absorptions centred at 3498 and 3399  $\text{cm}^{-1}$  for **1** and **3**, respectively, because of the existence of water molecules in the structures. The O–H stretching vibrations of the water molecules and hydroxy group in **2** appear at 3435 and 3159  $\text{cm}^{-1}$ . The IR spectra of **1–3** display the typical stretching bands of carboxylate groups between 1400 and 1622  $\text{cm}^{-1}$ . The characteristic band at 1710  $\text{cm}^{-1}$  in **1** is attributable to the protonated carboxylate group of  $\text{H}_3\text{SIP}$  ligand. The absorptions in the region 1000–1230  $\text{cm}^{-1}$  in **1–3** are typical for the sulfonate groups. The strong absorptions at about 620  $\text{cm}^{-1}$  in **1–3** can be assigned to the S–O stretching vibrations.

### Photoluminescent Properties

Metal–organic frameworks (MOFs) are promising photoluminescent materials because of their high thermal stability, and structure- and metal-dependent emission. The combination of organic linkers and metal centres in coordination polymers provides an efficient route to a new type of photoluminescent materials with potential applications as light-emitting diodes (LEDs). The  $d^{10}$  metal compounds have been shown to exhibit interesting photoluminescent properties.<sup>[31–33]</sup> In the present work, we have examined the photoluminescent properties of **1–3** and the free  $\text{H}_3\text{SIP}$  ligand in the solid state at room temperature. Free  $\text{NaH}_2\text{SIP}$  displays a photoluminescent emission at 320 nm upon excitation at 286 nm.<sup>[17]</sup> Compound **1** exhibits a broad photoluminescent emission centred at 436 nm upon excitation at 342 nm and **3** displays an emission at 409 nm upon excitation at 350 nm (Figure 8). The emissions of **1** (436 nm) and **3** (409 nm) occur at much longer wavelengths than that of the free ligand (320 nm). Such a large bathochromic shift indicates that the aromatic rings of the ligand effectively interact with the metal ion and/or with each other through  $\pi$ -stacking interactions, as described above. In other words, the  $\pi$ -electrons of the aromatic rings are delocalised over the  $\text{Cd}^{2+}$  ion and/or the neighbouring ligand. With the above concerns in mind, the fluorescence emission of **1** may tentatively be assigned to the formation of the  $[\text{Cd}_2(\mu_2\text{-OH})_2]$  cluster, which compares to our recently reported (SIP)lead compound.<sup>[13]</sup> The emission peak of **3** at 409 nm,

which is similar to that of the analogue  $\{[\text{Cd}(\text{SIP})(\text{H}_2\text{O})_3] \cdot 0.5(\text{H}_2\text{en})(\text{H}_2\text{O})\}_n$ <sup>[17]</sup> (412 nm), can be assigned to ligand-to-metal charge transfer (LMCT). This is consistent with the fact that the  $\text{Cd}^{\text{II}}$  or  $\text{Zn}^{\text{II}}$  coordination complexes with aromatic carboxylate ligands may possess an LMCT photoluminescent property.<sup>[34–36]</sup> In the case of **2**, the emission at 306 nm upon excitation at 270 nm is similar to that of the free  $\text{H}_3\text{SIP}$  ligand. This indicates that the emission band of **2** is an intraligand transition. The further lifetime measurements at room temperature of each emission maximum give results of 0.61, 18 and 0.56 ns for compounds **1**, **2** and **3**, respectively. The lifetime of **2** is significantly longer than those of **1** and **3**. This is consistent with the fact that metal hydroxide (or oxide) clusters usually have longer emission lifetimes<sup>[35]</sup> because the  $\mu_2/\mu_3\text{-OH}$  ligands can tighten the whole framework and thus result in weaker vibrations. These observations clearly reveal the structure-dependent photoluminescent properties of coordination polymers.

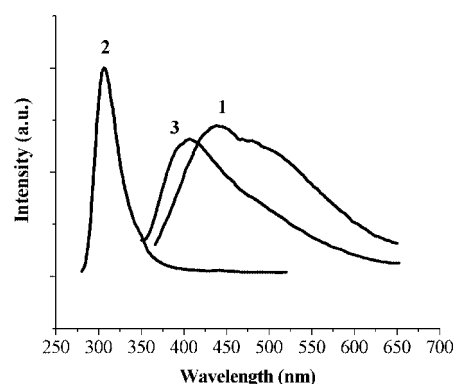


Figure 8. Solid-state emission photoluminescent spectra of **1–3** at room temperature.

### Conclusions

In conclusion, hydrothermal reactions of the  $\text{Cd}/\text{H}_3\text{SIP}$  system are pH-dependent. Incomplete deprotonation of the  $\text{H}_3\text{SIP}$  ligand occurs under acidic conditions, leading to lowered connectivity of the SIP ligand and the formation of the discrete dinuclear compound **1**. The ligand is fully deprotonated under neutral or basic conditions, accompanied by the formation of the hydroxy-bridged cadmium clusters **2**. In **2**, the chair-like  $[\text{Cd}_4(\mu_3\text{-OH})_2]$  cluster units are interconnected by the  $[\text{Cd}(\mu_2\text{-OH})_2(\text{CO}_2)]$  unit into an unprecedented inorganic oxide layer, which is pilared by the  $\text{SIP}^{3-}$  ligand into a 3D framework structure. Two unprecedented coordination modes are observed in compound **2**. The addition of the auxiliary ligand dpp leads to the 2D structure of **3** containing a cyclic  $[\text{Cd}_4(\text{SIP})_4]$  unit with the Cd atoms co-planar. Compounds **1–3** display different photoluminescent emissions at room temperature, indicating structure-dependent photoluminescent properties of the  $\text{Cd}/\text{SIP}$  coordination polymers and thus potential application in LED technology.

## Experimental Section

**General Remarks:** All chemicals were purchased commercially and used without further purification, including 5-sulfoisophthalic acid monosodium salt (Alfa) and 1,3-bis(4-pyridyl)propane (Acros). Elemental analyses were carried out with an Elementar Vario EL III analyser and IR spectra (KBr pellets) were recorded with a Perkin–Elmer Spectrum One. Fluorescent spectra were measured at room temperature with an Edinburgh FL-FS90 TCSPC system. All complexes were synthesised by a hydrothermal method under autogenous pressure.

**Synthesis of  $[\text{Cd}_2(\mu\text{-OH})_2(\text{HSIP})_2(\text{H}_2\text{O})_6]$  (1):** A mixture of  $\text{Cd}^{\text{II}}$  nitrate tetrahydrate (0.0616 g, 0.2 mmol), 5-sulfoisophthalic acid monosodium salt (0.0536 g, 0.2 mmol), triethylamine (0.01 mL) and water (15 mL) (pH = 2) was heated at 160 °C for 4 d. Colourless plate-like crystals of **1** were obtained when cooling to room temperature at 5 °C/h. The crystals were recovered by filtration, washed with distilled water and dried in air (yield: 0.05 g, 63% based on Cd).  $\text{C}_{16}\text{H}_{24}\text{Cd}_2\text{O}_{22}\text{S}_2$  (857.27): calcd. C 22.33, H 2.81; found C 22.31, H 2.76. IR (KBr pellet):  $\tilde{\nu}$  = 3498 s, 1710 s, 1622 s, 1580 w, 1552 s, 1436 w, 1371 s, 1231 s, 1187 s, 1118 s, 1047 s, 999 w, 857 w, 768 m, 731 w, 673 m, 624 m, 580  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{Cd}_5(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{SIP})_2(\text{H}_2\text{O})_5]_n$  (2):** A mixture of  $\text{Cd}^{\text{II}}$  nitrate tetrahydrate (0.0616 g, 0.2 mmol), 5-sulfoisophthalic acid monosodium salt (0.0536 g, 0.2 mmol), triethylamine (0.05 mL) and water (15 mL) (pH = 7) was heated at 160 °C for 4 d. Colourless prism-like crystals of **2** were obtained when cooling to room temperature at 5 °C/h. The crystals were recovered by filtration, washed with distilled water and dried in air (yield: 0.013 g, 11% based on Cd).  $\text{C}_{16}\text{H}_{20}\text{Cd}_5\text{O}_{23}\text{S}_2$  (1206.44): calcd. C 15.82, H 1.66; found C 15.76, H 1.63. IR (KBr pellet):  $\tilde{\nu}$  = 3435 s, 3159 s,

1615 s, 1569 w, 1553 m, 1400 s, 1216 w, 1182 s, 1106 m, 1044 s, 858 w, 833 w, 707 w, 673 m, 620 m, 447  $\text{cm}^{-1}$ .

**Synthesis of  $\{[\text{Cd}_3(\text{SIP})_2(\text{dpp})_6]\cdot 4(\text{H}_2\text{O})\}_n$  (3):** A mixture of  $\text{Cd}^{\text{II}}$  nitrate tetrahydrate (0.0231 g, 0.075 mmol), 5-sulfoisophthalic acid monosodium salt (0.0134 g, 0.05 mmol), 1,3-bis(4-pyridyl)propane (0.0297 g, 0.15 mmol), triethylamine (0.01 mL) and water (15 mL) was heated at 160 °C for 4 d. Colourless rod-like crystals of **3** were obtained when cooling to room temperature at 5 °C/h. The crystals were recovered by filtration, washed with distilled water and dried in air (yield: 0.023 g, 46% based on Cd).  $\text{C}_{94}\text{H}_{98}\text{Cd}_3\text{N}_{12}\text{O}_{18}\text{S}_2$  (2085.16): calcd. C 54.02, H 4.73, N 8.05; found C 54.03, H 4.71, N 8.02. IR (KBr pellet):  $\tilde{\nu}$  = 3399 s, 2943 s, 1612 s, 1560 w, 1502 w, 1428 s, 1364 s, 1224 m, 1199 m, 1103 m, 1068 w, 1042 m, 1015 m, 925 w, 846 w, 811 m, 781 w, 728 m, 624 m, 576 w, 515 w, 448  $\text{cm}^{-1}$ .

**X-ray Crystallographic Study:** X-ray diffraction data of compounds **1–3** were collected with a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated  $\text{Mo-K}_\alpha$  radiation ( $\lambda$  = 0.71073 Å). CrystalClear software was used for data reduction and empirical absorption correction.<sup>[37]</sup> The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on  $F^2$  (SHELXTL Version 5.1<sup>[38]</sup>). The H atoms bonded to C atoms and N atoms were assigned to calculated positions and refined using a riding model [ $\text{C-H}$  = 0.93 Å,  $U_{\text{iso}}(\text{H})$  = 1.2 $U_{\text{iso}}(\text{C})$ ;  $\text{N-H}$  = 0.89 Å,  $U_{\text{iso}}(\text{H})$  = 1.2 $U_{\text{iso}}(\text{N})$ ]; H atoms bonded to O atoms were located from difference maps except for one lattice water oxygen atom of compound **3**, which could not be located. The  $R_1$  values are defined as  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$  and  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ . Details of the crystal parameters, data collection and refinement are summarised in Table 2, and selected bond lengths and bond

Table 2. Crystallographic data for compounds **1–3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{16}\text{H}_{24}\text{Cd}_2\text{O}_{22}\text{S}_2$	$\text{C}_{16}\text{H}_{20}\text{Cd}_5\text{O}_{23}\text{S}_2$	$\text{C}_{94}\text{H}_{98}\text{Cd}_3\text{N}_{12}\text{O}_{18}\text{S}_2$
Formula mass	857.27	1206.44	2085.16
Temperature [K]	293(2)	293(2)	293(2)
Crystal size [mm]	$0.40 \times 0.28 \times 0.05$	$0.38 \times 0.30 \times 0.20$	$0.45 \times 0.25 \times 0.10$
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/m$	$P\bar{1}$	$P\bar{1}$
Z	2	2	1
$a$ [Å]	23.104(6)	8.16570(10)	10.2233(15)
$b$ [Å]	6.8756(11)	12.0452(2)	12.842(2)
$c$ [Å]	8.7315(18)	15.2366(3)	19.073(3)
$\alpha$ [°]	90	78.749(5)	101.562(4)
$\beta$ [°]	107.007(14)	85.824(6)	99.637(5)
$\gamma$ [°]	90	72.229(5)	104.124(6)
$V$ [Å <sup>3</sup> ]	1326.4(5)	1399.56(4)	2316.5(6)
$D_{\text{calcd.}}$ [g/cm <sup>3</sup> ]	2.146	2.863	1.495
$\mu$ [mm <sup>-1</sup> ]	1.860	3.988	0.801
Measured reflections	5133	10722	18047
Independent reflections	1645	6286	10479
Observed reflections [ $I > 2\sigma(I)$ ]	1581	5828	9017
Parameters	136	464	584
$F(000)$	848	1144	1066
Completeness [%]	99.7	97.8	98.5
$2\theta$ range [°]	3.10–27.49	3.19–27.48	3.06–27.48
$h/k/l$ ranges	–29/29 –8/8 –6/11	–10/10 –9/15 –18/19	–13/12 –13/16 –24/24
$R_{\text{int}}$	0.0258	0.0164	0.0225
$R_1$ (obsd. refl.)	0.0208	0.0267	0.0439
$wR_2$ (all refl.)	0.0550	0.0705	0.0980
Largest diff. peak/hole [ $e/\text{\AA}^3$ ]	0.390/–0.728	1.798/–1.372	1.246/–0.598



angles are listed in Table 1. CCDC-609221 to -609223 (for 1–3) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

## Acknowledgments

We gratefully acknowledge the financial support of the “One Hundred Talents Program” of the Chinese Academy of Sciences and the National Science Foundation of China (Grant No. 20473092).

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Received: June 8, 2006

Published Online: October 19, 2006