Synthesis, Crystal Structures and Photoluminescent Properties of Three Novel Cadmium(II) Compounds Constructed from 5-Sulfoisophthalic Acid (H₃SIP)

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Hydrothermal reactions of $Cd(NO_3)_2$ and NaH_2SIP (5-sulfoisophthalic acid monosodium salt) at pH = 2 and 7 produce $[Cd_2(\mu_2\text{-}OH_2)_2(HSIP)_2(H_2O)_6]$ (**1**) and $[Cd_5(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(SIP)_2(H_2O)_5]_n$ (**2**), respectively. A similar hydrothermal reaction in the presence of dpp [1,3-bis(4-pyridyl)propane] yields $\{[Cd_3(SIP)_2(dpp)_6]\cdot4(H_2O)\}_n$ (**3**). Single-crystal X-ray diffraction reveals that compound **1** has a discrete dinuclear structure with the $[Cd_2(\mu_2\text{-}OH_2)_2]$ unit. Polymer **2** features an inorganic layer, which has centrosymmetric 12- and 24-membered rings composed of chair-shaped $[Cd_4(\mu_3\text{-}OH)_2]$ units and $Cd(\mu_2\text{-}OH)_2(CO_2)$ units, and is interconnected by SIP into

a 3D framework. Complex **3** contains a 1D ladder-like $[Cd_4(SIP)_4]_n$ 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.[1–4] 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.[5–7] 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.[8–11] Recently, 5-sulfoisophthalic acid (H₃SIP) has been successfully used to investigate the lanthanide contraction effect[12] and the coordination polymer chemistry of a main group metal
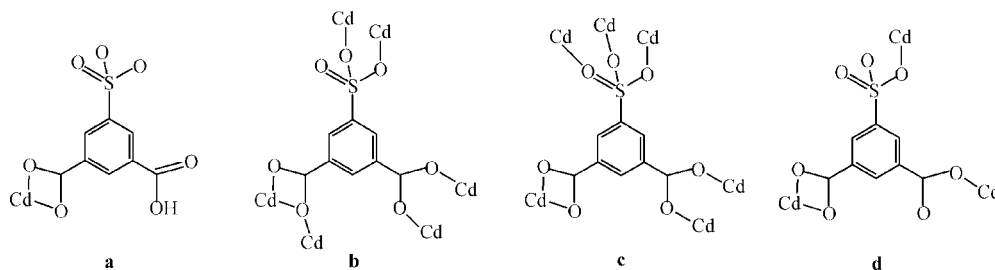
Scheme 1. Coordination modes of 5-sulfoisophthalic acid observed in compounds **1**–**3**.

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(Pb^{2+}),[13] 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^{2+}. Three novel (SIP)Cd compounds, $[Cd_2(\mu_2\text{-}OH_2)_2(HSIP)_2(H_2O)_6]$ (**1**), $[Cd_5(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(SIP)_2(H_2O)_5]_n$ (**2**) and $\{[Cd_3(SIP)_2(dpp)_6]\cdot4(H_2O)\}_n$ (**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$_3$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 {[Cd(SIP)(dpp)(H$_2$O)$_3$]·0.5Cd(H$_2$O)$_6$·5H$_2$O}$_n$,[14] 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.[15]

Crystal Structure of [Cd$_2$(μ$_2$-OH$_2$)$_2$(HSIP)$_2$(H$_2$O)$_6$] (1)

The dinuclear structure of **1** is shown in Figure 1; it has a crystallographically imposed C_{2h} symmetry, which has the

C_2 axis passing through O7 and O7A (for symmetry code see Table 1). The two Cd^{II} atoms are linked by two bridging water molecules to form the rhomboidal [Cd$_2$(μ$_2$-OH$_2$)$_2$] 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$^{2–}$ 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.[16–19] The uncoordinated carboxylate group is protonated for charge balance, as suggested by the strong absorption at 1710 cm$^{–1}$.[20] 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 [Cd$_2$(μ$_2$-OH$_2$)$_2$-(H$_2$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$_2$O(7), O(5) and their equivalents], which is nearly perpendicular to the [Cd$_2$(μ$_2$-OH$_2$)$_2$] 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 π–π 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 [Cd$_5$(μ$_2$-OH)$_2$(μ$_3$-OH)$_2$(SIP)$_2$(H$_2$O)$_5$]$_n$ (2)

Compound **2** contains five unique Cd^{II} ions, four of which are six-coordinate and one [Cd(3)] five-coordinate.
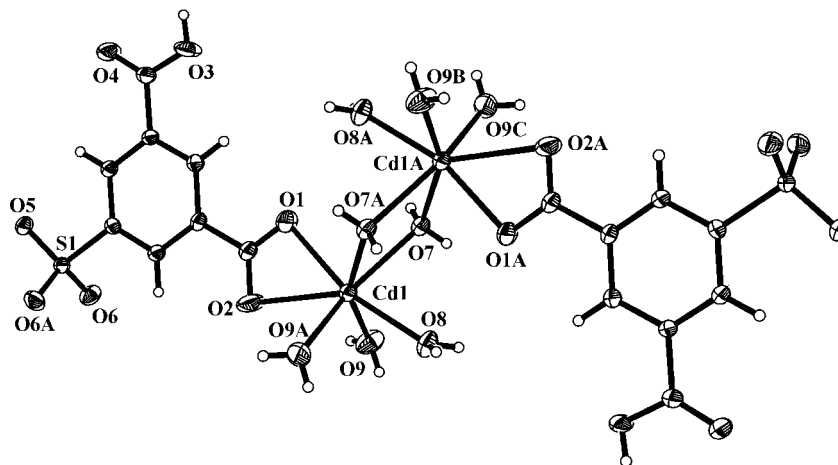

Figure 1. ORTEP drawing of **1** with 40% probability displacement ellipsoids. Hydrogen atoms are shown as small spheres of arbitrary radii.

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**.[a]

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(9)
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 μ₃-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 [CdO₆] octahedron. Cd(5) has a similar coordination environment to that of Cd(1). Cd(2) also has a distorted [CdO₆] octahedral coordination geometry in which a pair of symmetrically related μ₃-hydroxy oxygen atoms [O(16) and O(16C)], a μ₂-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 μ₂-hydroxy oxygen atom [O(20)] occupies the apical position. The Cd(3) atom is coordinated by one μ₂-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 μ₂-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 μ₂-η²:η¹ 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,
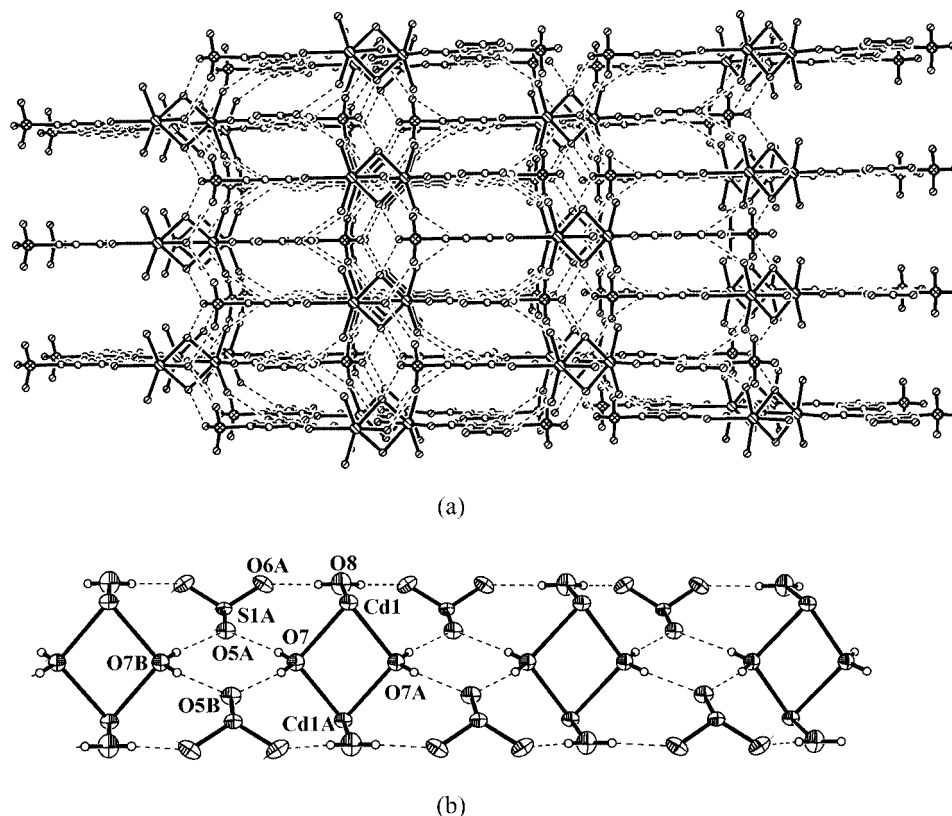
(a)

(b)

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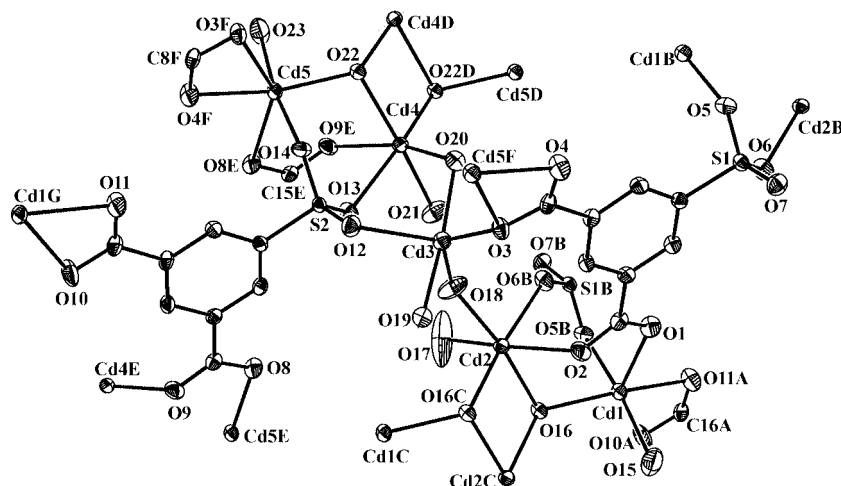

Figure 3. ORTEP drawing of **2** with 40% probability displacement ellipsoids.

neither type of coordination mode of the SIP ligands is observed in the reported SIP complexes.

The 3D framework structure shown in Figure 4a is constructed by inorganic oxide layers pillared by the SIP ligands, reminiscent of reported metal biphosphonate compounds.[21,22] The inorganic oxide layer contains two types of chair-like [Cd$_4$(μ$_3$-OH)$_2$] cluster units formed by Cd(1)/Cd(2) and Cd(4)/Cd(5), respectively, and features two types of centrosymmetric rings: 12-membered (A) and 24-membered (B). As shown in Figure 4b, each μ$_3$-hydroxy group

(O16) as a metal linker bridges the neighbouring three Cd atoms to generate a chair-shaped tetranuclear [Cd$_4$(μ$_3$-OH)$_2$] cluster with Cd(2), O(16) and their equivalents related by an inversion centre defining a plane and with the two Cd(1) atoms above and below the [Cd$_2$(μ$_3$-OH)$_2$] plane. The Cd(1)–O(16), Cd(2)–O(16) and Cd(2C)–O(16) distances are 2.198(2), 2.276(2) and 2.260(2) Å, respectively, with surrounding angles of 105.56(9)°, 124.45(11)° and 98.80(8)° for Cd(1)–O(16)–Cd(2), Cd(1)–O(16)–Cd(2C) and Cd(2)–O(16)–Cd(2C), respectively. The chair-shaped
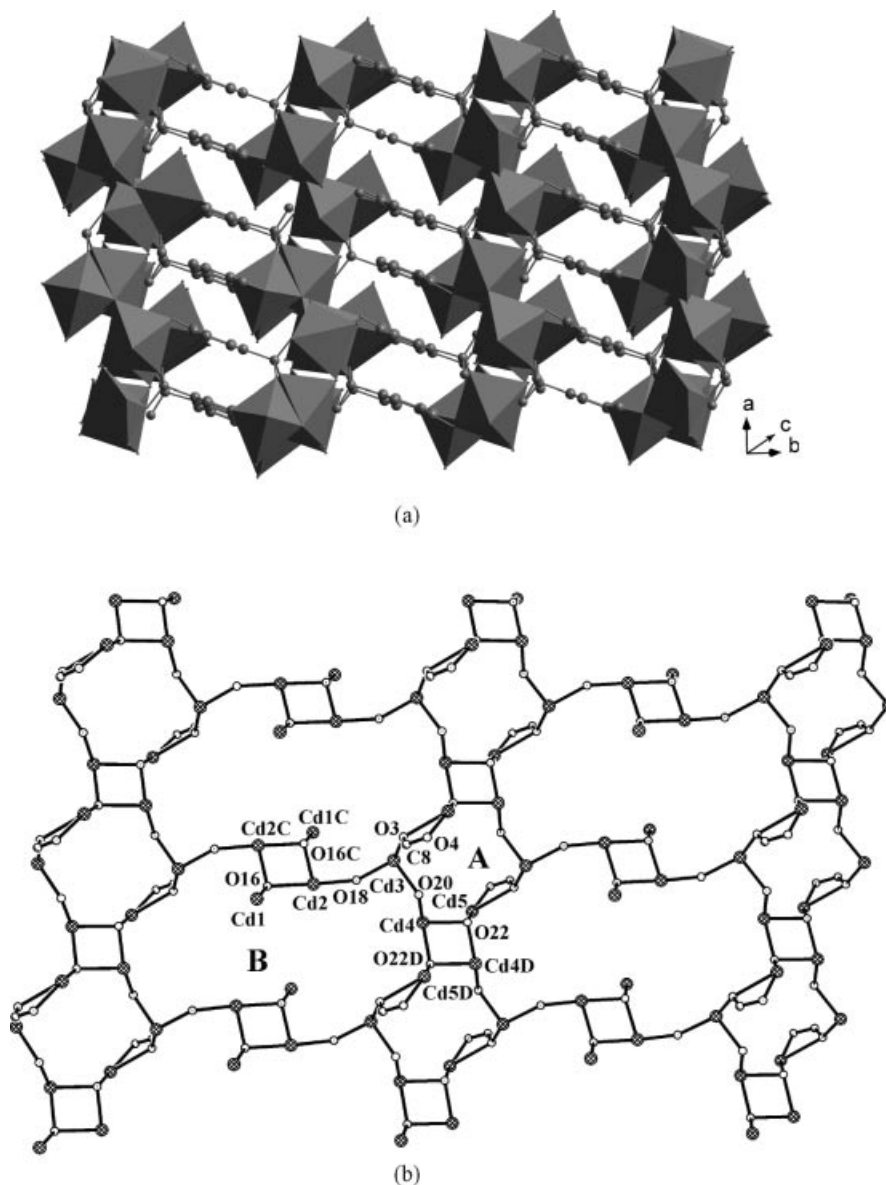
Figure 4. (a) 3D structure of **2** (the polyhedral presentation indicates the coordination environments for the Cd centre). (b) Perspective view of the 2D metal–oxide inorganic layer featuring the chair-shaped $[Cd_4(\mu_3\text{-OH})_2]$ clusters and two types of large rings.

$[Cd_4(\mu_3\text{-OH})_2]$ cluster formed by Cd(4)/Cd(5) has a similar geometry to that of the $[Cd_4(\mu_3\text{-OH})_2]$ 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,[23–25] but those with two capping μ_3-OH groups are rare. It is even more interesting that the $[Cd_4(\mu_3\text{-OH})_2]$ cluster units are interconnected by the $Cd(3)(\mu_2\text{-OH})_2(CO_2)$ unit into an unusual inorganic oxide layer. Although cadmium cluster units have been known to be present in coordination polymers,[6,26–28] 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 3.8×4.9 Å^2, which is composed of Cd(3), Cd(4) and Cd(5) atoms and their equivalents linked by two μ_3-OH, two μ_2-OH and two carboxylate groups. It also contains a large 24-membered ring (B) with approximate dimensions of 4.7×14.3 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 $\{[Cd_3(SIP)_2(dpp)_6]\cdot 4(H_2O)\}_n$ (3)

As shown in Figure 5, **3** contains two crystallographically independent cadmium ions; Cd(1) lies on the crystallographic inversion centre. Both 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^{2+} ions in coordination mode **d** (Scheme 1) into an infinite ladder structure along the *a* axis, which features the cyclic [Cd$_4$(SIP)$_4$] unit with dimensions of 7.5 × 12.8 Å^2. 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)]$_n$ 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$_2$ groups, such as *TT*, *TG*, *GG* and *GG′* (*T* = *trans*; *G* =*gauche*), with quite different N···N separations (6.7–10.1 Å).[29,30] 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.
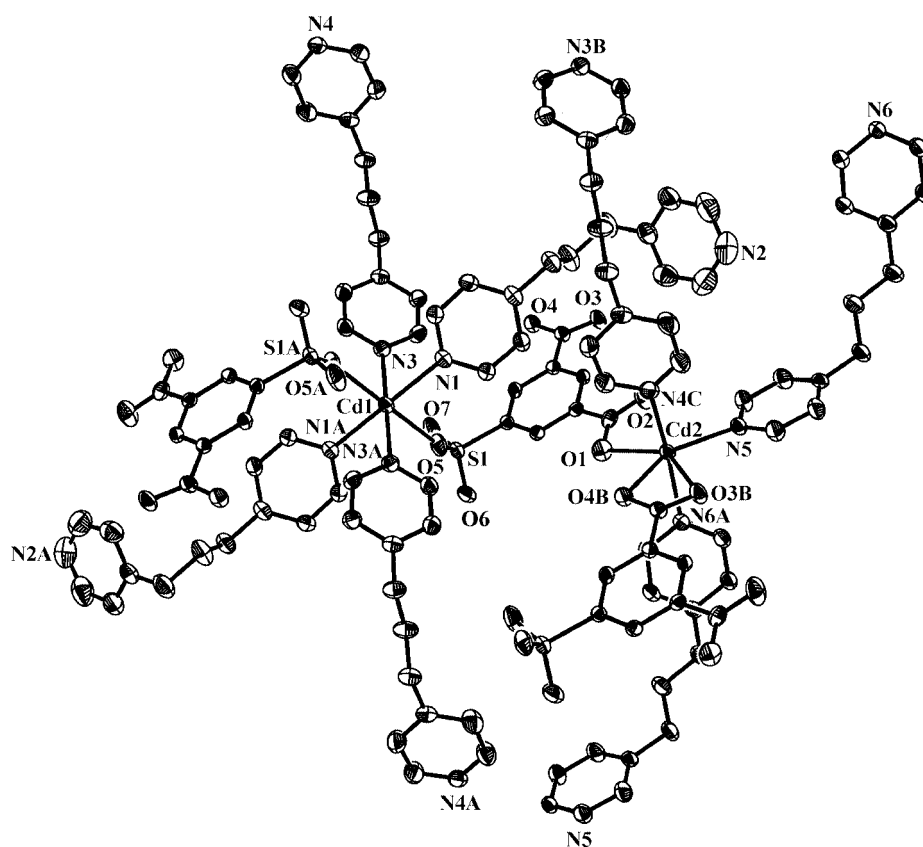

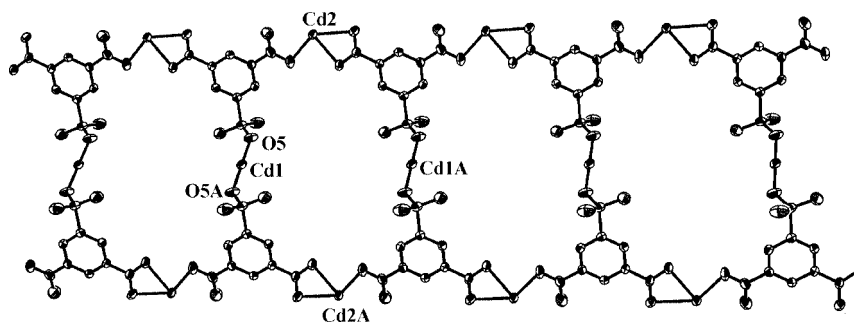Figure 5. ORTEP drawing of **3** with 35% probability displacement ellipsoids.

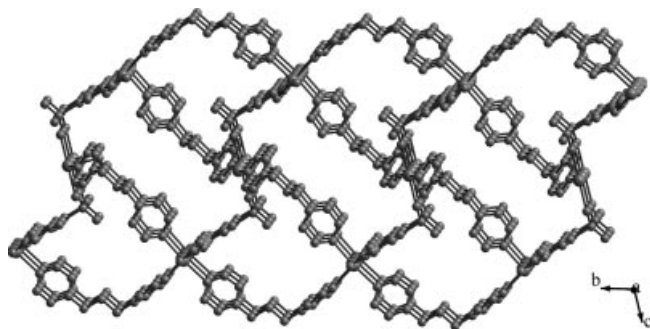Figure 6. 1D ladder structure in compound **3** featuring the cyclic [Cd$_4$(SIP)$_4$] unit.

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 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 cm^{-1}. The IR spectra of **1**–**3** display the typical stretching bands of carboxylate groups between 1400 and 1622 cm^{-1}. The characteristic band at 1710 cm^{-1} in **1** is attributable to the protonated carboxylate group of H$_3$SIP ligand. The absorptions in the region 1000–1230 cm^{-1} in **1**–**3** are typical for the sulfonate groups. The strong absorptions at about 620 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.[31–33] In the present work, we have examined the photoluminescent properties of **1**–**3** and the free H$_3$SIP ligand in the solid state at room temperature. Free NaH$_2$SIP displays a photoluminescent emission at 320 nm upon excitation at 286 nm.[17] 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 π-stacking interactions, as described above. In other words, the π-electrons of the aromatic rings are delocalised over the 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 [Cd$_2$(μ_2-OH)$_2$] cluster, which compares to our recently reported (SIP)lead compound.[13] The emission peak of **3** at 409 nm,

which is similar to that of the analogue {[Cd(SIP)(H$_2$O)$_3$]·0.5(H$_2$en)(H$_2$O)}$_n$[17] (412 nm), can be assigned to ligand-to-metal charge transfer (LMCT). This is consistent with the fact that the Cd^{II} or Zn^{II} coordination complexes with aromatic carboxylate ligands may possess an LMCT photoluminescent property.[34–36] In the case of **2**, the emission at 306 nm upon excitation at 270 nm is similar to that of the free H$_3$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[35] because the μ_2/μ_3-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.
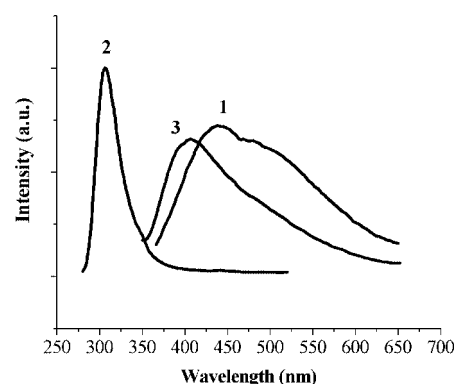

Figure 8. Solid-state emission photoluminescent spectra of **1**–**3** at room temperature.

Conclusions

In conclusion, hydrothermal reactions of the Cd/H$_3$SIP system are pH-dependent. Incomplete deprotonation of the H$_3$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 [Cd$_4$(μ_3-OH)$_2$] cluster units are interconnected by the [Cd(μ_2-OH)$_2$(CO$_2$)] unit into an unprecedented inorganic oxide layer, which is pillared by the 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 [Cd$_4$(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 Cd/SIP coordination polymers and thus potential application in LED technology.

Experimental Section

General Remarks: All chemicals were purchased commercially and used without further purication, 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 [Cd$_2$(μ-OH$_2$)$_2$(HSIP)$_2$(H$_2$O)$_6$] (1): A mixture of Cd^{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). C$_{16}$H$_{24}$Cd$_2$O$_{22}$S$_2$ (857.27): calcd. C 22.33, H 2.81; found C 22.31, H 2.76. IR (KBr pellet): ṽ = 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 w cm^{-1}.

Synthesis of [Cd$_5$(μ$_2$-OH)$_2$(μ$_3$-OH)$_2$(SIP)$_2$(H$_2$O)$_5$]$_n$ (2): A mixture of Cd^{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). C$_{16}$H$_{20}$Cd$_5$O$_{23}$S$_2$ (1206.44): calcd. C 15.82, H 1.66; found C 15.76, H 1.63. IR (KBr pellet): ṽ = 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 w cm^{-1}.

Synthesis of {[Cd$_3$(SIP)$_2$(dpp)$_6$]·4(H$_2$O)}$_n$ (3): A mixture of Cd^{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). C$_{94}$H$_{98}$Cd$_3$N$_{12}$O$_{18}$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): ṽ = 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 w 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 Mo-K_a radiation (λ = 0.71073 Å). CrystalClear software was used for data reduction and empirical absorption correction.[37] 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[38]). The H atoms bonded to C atoms and N atoms were assigned to calculated positions and refined using a riding model [C–H = 0.93 Å, U_{iso}(H) = 1.2U_{iso}(C); N–H = 0.89 Å, U_{iso}(H) = 1.2U_{iso}(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**.

	1	2	3
Empirical formula	C$_{16}$H$_{24}$Cd$_2$O$_{22}$S$_2$	C$_{16}$H$_{20}$Cd$_5$O$_{23}$S$_2$	C$_{94}$H$_{98}$Cd$_3$N$_{12}$O$_{18}$S$_2$
Formula mass	857.27	1206.44	2085.16
Temperature [K]	293(2)	293(2)	293(2)
Crystal size [mm]	0.40 × 0.28 × 0.05	0.38 × 0.30 × 0.20	0.45 × 0.25 × 0.10
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/m	P1̄	P1̄
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)
α [°]	90	78.749(5)	101.562(4)
β [°]	107.007(14)	85.824(6)	99.637(5)
γ [°]	90	72.229(5)	104.124(6)
V [Å^3]	1326.4(5)	1399.56(4)	2316.5(6)
$D_{calcd.}$ [g/cm^3]	2.146	2.863	1.495
μ [mm^{-1}]	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
2θ range [°]	3.10–27.49	3.19–27.48	3.06–27.48
h/k/l ranges	–29/29	–10/10	–13/12
	–8/8	–9/15	–13/16
	–6/11	–18/19	–24/24
R_{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/Å^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.

Acknowledgments

[1] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658.

[2] O. R. Evans, R. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem.* **1999**, *111*, 557–559; *Angew. Chem. Int. Ed.* **1999**, *38*, 536–538.

[3] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330.

[4] C. D. Wu, W. B. Lin, *Angew. Chem. Int. Ed.* **2005**, *44*, 1958–1961.

[5] S. Kitagawa, R. Kitaura, S. I. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375.

[6] O. R. Evans, W. B. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522.

[7] C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem. Int. Ed.* **2004**, *43*, 1466–1496.

[8] J. P. Zhang, Y. Y. Lin, X. C. Huang, X. M. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 5495.

[9] G. H. Li, Z. Shi, X. M. Liu, Z. M. Dai, S. H. Feng, *Inorg. Chem.* **2004**, *43*, 6884–6886.

[10] Y. M. Song, T. Zhou, X. S. Wang, X. N. Li, R. G. Xiong, *Cryst. Growth Des.* **2006**, *6*, 14–17.

[11] X. H. Bu, M. L. Tong, H. Chang, S. Kitagawa, S. R. Batten, *Angew. Chem. Int. Ed.* **2004**, *43*, 192–195.

[12] Q. Y. Liu, L. Xu, *Eur. J. Inorg. Chem.* **2005**, 3458–3466.

[13] Q. Y. Liu, L. Xu, *Eur. J. Inorg. Chem.* **2006**, 1620–1628.

[14] Q. Y. Liu, L. Xu, *CrystEngComm* **2005**, *7*, 87–89.

[15] R. M. Barrer, *Hydrothermal Chemistry of Zeolite*, Academic Press, London, **1982**.

[16] Z. M. Sun, J. G. Mao, Y. Q. Sun, H. Y. Zeng, A. Clearfield, *Inorg. Chem.* **2004**, *43*, 336–341.

[17] Q. Y. Liu, L. Xu, *Inorg. Chem. Commun.* **2005**, *8*, 401–405.

[18] J. Tao, X. Yin, Z. B. Wei, R. B. Huang, L. S. Zheng, *Eur. J. Inorg. Chem.* **2004**, 125–133.

[19] X. Li, R. Cao, W. H. Bi, D. Q. Yuan, D. F. Sun, *Eur. J. Inorg. Chem.* **2005**, 3156–3166.

[20] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, **1958**.

[21] E. V. Bakhmutova, X. Ouyang, D. G. Medvedev, A. Clearfield, *Inorg. Chem.* **2003**, *42*, 7046–7051.

[22] Z. M. Sun, J. G. Mao, Y. Q. Sun, H. Y. Zeng, A. Clearfield, *New J. Chem.* **2003**, *27*, 1326–1330.

[23] M. Weidenbruch, M. Herrndorf, A. Schäfer, S. Pohl, W. Saak, *J. Organomet. Chem.* **1989**, *361*, 139–145.

[24] S. Boulmaaz, R. Papiernik, L. G. H. Vaissermann, J. C. Daran, *Polyhedron* **1992**, *11*, 1331–1336.

[25] D. C. Liles, M. McPartlin, P. A. Tasker, H. C. Lip, L. F. Lindoy, *J. Chem. Soc., Chem. Commun.* **1976**, 549–551.

[26] W. B. Lin, Z. Y. Wang, L. Ma, *J. Am. Chem. Soc.* **1999**, *121*, 11249–11250.

[27] X. Xue, X. S. Wang, L. Z. Wang, R. G. Xiong, B. F. Abrahams, X. Z. You, Z. L. Xue, C. M. Che, *Inorg. Chem.* **2002**, *41*, 6544–6546.

[28] S. Lulin'ski, I. Madura, J. Serwatowski, J. Zachara, *Inorg. Chem.* **1999**, *38*, 4937–4941.

[29] L. Carlucci, G. Ciani, D. W. v. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812–3813.

[30] M. F. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2001**, *123*, 11982–11990.

[31] P. C. Ford, A. Vogler, *Acc. Chem. Res.* **1993**, *26*, 220–226.

[32] C. M. Che, S. W. Lai, *Coord. Chem. Rev.* **2005**, *249*, 1296–1309.

[33] R. Bertoncello, M. Bettinelli, M. Casarin, A. Gulino, E. Tondello, A. Vittadini, *Inorg. Chem.* **1992**, *31*, 1558–1565.

[34] G. A. Crosby, R. G. Highland, K. A. Truesdell, *Coord. Chem. Rev.* **1985**, *64*, 41–52.

[35] S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen, W. T. Wong, *Inorg. Chem.* **2004**, *43*, 830–838.

[36] B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2002**.

[37] *CrystalClear*, version 1.3, Rigaku Corp., **2000**.

[38] G. M. Sheldrick, *SHELXS 97*, *Program for Crystal Structure Solution*, University of Göttingen, **1997**.