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Interesting structures of self-assembled gadolinium coordination polymers with tuned stoichiometric ratios

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Hydrothermal reactions of gadolinium(III) salts with 2,6-naphthalenedisulfonate (nds) and 1,10-phenanthroline with varying mole ratios led to five different compounds, $\{\text{Gd}(\text{phen})(\text{nds})(\text{OH})\}_n$ (**1**), $\{[\text{Gd}_2(\text{phen})_4(\text{nds})_3(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Gd}(\text{phen})_2(\text{nds})_{0.5}(\text{OH})(\text{H}_2\text{O})] \cdot 0.5(\text{nds})\}_n$ (**3**), $\{[\text{Gd}_2(\text{phen})_4(\text{nds})_2(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**4**), and $\{[\text{Gd}(\text{nds})(\text{phen})(\text{H}_2\text{O})_4] \cdot 0.5(\text{nds}) \cdot (\text{phen}) \cdot 2\text{H}_2\text{O}\}_n$ (**5**). In the case of **1**, nds coordinates as $\eta^2\mu^2-\eta^2\mu^2$ bridging ligand to adjacent dimers, leading to a three-dimensional network. In **2**, nds bridges with each SO_3^- coordinated as a $\eta^3\mu^1$ -bridging group, creating a two-dimensional polymer. For **3**, 1-D infinite chains with dinuclear units connected by nds results in a 3-D framework based on hydrogen-bond interactions. 0-D **4** and 1-D **5** contain dinuclear clusters, which are further assembled into 3-D supramolecular networks via weak hydrogen bonds and aromatic packing interactions.

Keywords: Organodisulfonate complexes; Stoichiometric ratios; Gadolinium; Self-assembly

1. Introduction

Design and controlled synthesis of coordination polymers show potential applications for new functional materials in absorption [1–5], magnetism [6–9], catalysis [10–14], anion/guest exchange [15–20], optics [21–23], and single-crystal to single-crystal conversion [24] – an exciting and expanding branch in the realm of crystal engineering and supramolecular chemistry. Hydrothermal reactions have many advantages [25]. Metal-organic frameworks constructed from rigid and flexible ligands have been shown to affect structures by reaction variables, such as pressure, temperature, pH of solution, source of the metal ion, template molecule, ligand type, the metal-to-ligand ratio, *etc.* [26–30]. However, dimensionality control of the resulting complexes is still a challenge [31].

Ligands with organosulfonates are less explored, regarded as weakly coordinating [32, 33], and there are limited numbers of references on structures of metal organosulfonates. Assembling metal complexes through hydrogen bonds to create extended solids between the supramolecular chemistry of the organosulfonate group has achieved progress [34–38]. There are some examples of main group and transition metal arenesulfonates, broadly dis-

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cussed in a review [39]. However, reports on lanthanide arenedisulfonates are still limited, with a report on 2,6-naphthalenedisulfonate coordinated to lanthanide ions by directional covalent bond [40, 41]. In order to help sulfonates compete with water and coordinate to gadolinium ions, additional functional groups have been attached [42–51]. With this in mind, gadolinium disulfonate incorporating phen as auxiliaries with structures ranging from 0-D clusters, 1-D chains, 2-D layers to 3-D frameworks are particularly attractive.

We have focused our attention on reactions of different ratios of the reactants to achieve controllable assembly of such crystalline systems with desired structures and properties; appropriate choice of well-designed organic ligands as bridges or terminal groups is one of the most effective ways. The main reason we chose different ratios is that nds has variable bridging modes and terminal groups in the layer structure, and hence metal coordination might be combined. Herein, we report synthesis, crystal structure, and characterization of five naphthalenedisulfonate compounds – $\{\text{Gd}(\text{phen})(\text{nds})(\text{OH})\}_n$ (**1**), $\{[\text{Gd}_2(\text{phen})_4(\text{nds})_3(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Gd}(\text{phen})_2(\text{nds})_{0.5}(\text{OH})(\text{H}_2\text{O})] \cdot 0.5(\text{nds})\}_n$ (**3**), $\{[\text{Gd}_2(\text{phen})_4(\text{nds})_2(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**4**), and $\{[\text{Gd}(\text{nds})(\text{phen})(\text{H}_2\text{O})_4] \cdot 0.5(\text{nds}) \cdot (\text{phen}) \cdot 2\text{H}_2\text{O}\}_n$ (**5**).

2. Experimental

2.1. Materials and methods

Solvents and starting materials were purchased commercially and used without purification unless otherwise noted. The FT-IR spectra were recorded from KBr pellets (4500–400 cm^{-1}) on a Nicolet 5DX spectrometer. C, H, N elemental analyses were performed on a PerkinElmer 2400 elemental analyzer. Thermogravimetric analysis was performed on a PerkinElmer TGA7 analyzer with a heating rate of 10 $^\circ\text{C min}^{-1}$ in flowing air.

2.2. Crystal structure determination

Single crystal X-ray diffraction data collections of **1–5** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and reduction were performed using APEX II software. Multi-scan absorption corrections were applied for all the data-sets using APEX II. All five structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package [52, 53]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogens on water were located from difference Fourier maps and also refined using a riding model. The occupancy factor for O(5W) in **2** was reduced to 50% due to its very high thermal parameters. The crystallographic data and refinement parameters of **1–5** are listed in table 1 and selected bond distances and angles listed in table S1, Supplementary Material. Hydrogen-bonding data of **1–5** are listed in tables S2–S6 Supplementary material.

2.3. Synthesis of $\{\text{Gd}(\text{phen})(\text{nds})(\text{OH})\}_n$ (**1**)

A mixture of 2,6-naphthalenedisulfonate sodium salt (0.199 g, 0.6 mmol), 1,10-phenanthroline (0.120 g, 0.6 mmol), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.270 g, 0.6 mmol), and H_2O (14 mL) was

Table 1. Crystal data and structure refinement parameters of **1–5**.

Complex	1	2	3	4	5
Empirical formula	C ₂₂ H ₁₅ GdN ₂ O ₇ S ₂	C ₇₈ H ₆₈ Gd ₂ N ₈ O ₂₇ S ₆	C ₃₄ H ₂₅ GdN ₄ O ₈ S ₂	C ₆₈ H ₅₄ Gd ₂ N ₈ O ₁₈ S ₄	C ₃₉ H ₃₇ GdN ₄ O ₁₅ S ₃
Formula weight	640.75	2056.32	838.97	1713.97	1055.19
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 21/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.011(2)	10.3270(12)	10.3450(7)	12.9188(9)	7.703(2)
<i>b</i> /Å	11.367(3)	10.5425(13)	12.9394(9)	14.9110(10)	13.141(4)
<i>c</i> /Å	12.148(3)	18.902(2)	13.0824(9)	17.4264(12)	20.842(6)
<i>a</i>	117.119(2)	75.5390(10)	89.7030(10)	90	106.783(3)
β /°	92.224(3)	82.8530(10)	76.6800(10)	108.6800(10)	91.475(3)
γ /°	101.687(3)	83.3280(10)	70.9530(10)	90	94.815(3)
V/Å ³	1072.2(5)	1969.5(4)	1606.11(19)	3184.0(4)	2010.0(10)
<i>Z</i>	2	1	2	2	2
<i>D</i> _c /g cm ³	1.985	1.734	1.735	1.790	1.743
μ /mm ⁻¹	3.338	1.918	2.255	2.282	1.884
GOF	1.047	1.031	1.057	1.072	1.121
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0285/0.0715	0.0280/0.0694	0.0249/0.0562	0.0219/0.0513	0.0296/0.0737
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0312/0.0730	0.0311/0.0709	0.0284/0.0576	0.0270/0.0535	0.0340/0.0756

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = \{ \sum (w(F_o^2 - F_c^2)^2) / \sum (F_o^2)^2 \}^{1/2}$$

heated to 180 °C for 72 h in a 23 ml Teflon-lined stainless-steel autoclave, then the reaction mixture was cooled to room temperature at a rate of 5 °C/h. Yellow block crystals were collected and dried in air in *ca.* 38% yield based on Gd. Anal. Calcd: C, 41.23; H, 2.36; N, 4.37%. Found: C, 41.25; H, 2.37; N, 4.38%. IR frequencies (KBr, cm⁻¹): 3605 w, 1590 w, 1519 w, 1428 w, 1237 s, 1202 m, 1159 m, 1140 m, 1089 m, 1028 s, 905 w, 850 w, 827 w, 729 w, 658 s, 620 m, 612 m, 561 w, 536 w.

2.4. Synthesis of $\{[Gd_2(phen)_4(nds)_3(H_2O)_2] \cdot 7H_2O\}_n$ (**2**)

The hydrothermal procedure for preparation of **2** was similar to that for **1** except that molar numbers of *nds* and *phen* were changed to 0.3 mmol (0.100 g) and 1.2 mmol (0.240 g), respectively. Yellow block crystals were collected in *ca.* 68% yield based on Gd. Anal. Calcd: C, 45.56; H, 3.33; N, 5.45%. Found: C, 45.60; H, 3.34; N, 5.46%. IR frequencies (KBr, cm⁻¹): 3495 m, 1626 w, 1592 w, 1522 w, 1428 m, 1255 m, 1156 s, 1088 m, 1032 s, 903 w, 843 w, 825 w, 728 m, 664 s, 625 m, 539 w.

2.5. Synthesis of $\{[Gd(phen)_2(nds)_{0.5}(OH)(H_2O)] \cdot 0.5(nds)\}_n$ (**3**)

Compound **3** was prepared by following the same procedure as for **1** except that the molar number of *phen* was changed to 0.8 mmol (0.160 g). Yellow block crystals were collected in *ca.* 43% yield based on Gd. Anal. Calcd: C, 48.68; H, 3.00; N, 6.68%. Found: C, 48.80; H, 3.00; N, 6.67%. IR frequencies (KBr, cm⁻¹): 3443 m, 1620 w, 1591 w, 1521 w, 1423 m, 1236 s, 1206 w, 1156 w, 1088 m, 1029 s, 842 w, 733 m, 655 s, 625 m, 536 w.

2.6. Synthesis of $\{[Gd_2(phen)_4(nds)_2(OH)_2(H_2O)_2] \cdot 2H_2O\}_n$ (**4**)

Compound **4** was also prepared in the same manner as for **1** except that the molar number of phen was changed to 1.2 mmol (0.240 g). Yellow block crystals were collected in *ca.* 73% yield based on Gd. Anal. Calcd: C, 47.65; H, 3.18; N, 6.54%. Found: C, 47.72; H, 3.17; N, 6.55%. IR frequencies (KBr, cm^{-1}): 3440 m, 1626 w, 1592 w, 1520 w, 1427 m, 1236 m, 1160 w, 1088 m, 1031 s, 846 w, 729 m, 663s, 622 m, 537 w.

2.7. Synthesis of $\{[Gd(nds)(phen)(H_2O)_4] \cdot 0.5(nds) \cdot (phen) \cdot 2H_2O\}_n$ (**5**)

Compound **5** was prepared in the same manner as that for **1** except that the molar numbers of nds and phen were changed to 0.9 mmol (0.300 g) and 1.2 mmol (0.240 g), respectively. Yellow block crystals were collected in *ca.* 4% yield based on Gd. Anal. Calcd: C, 44.39; H, 3.53; N, 5.31%. Found: C, 45.35; H, 3.53; N, 5.30%.

3. Results and discussion

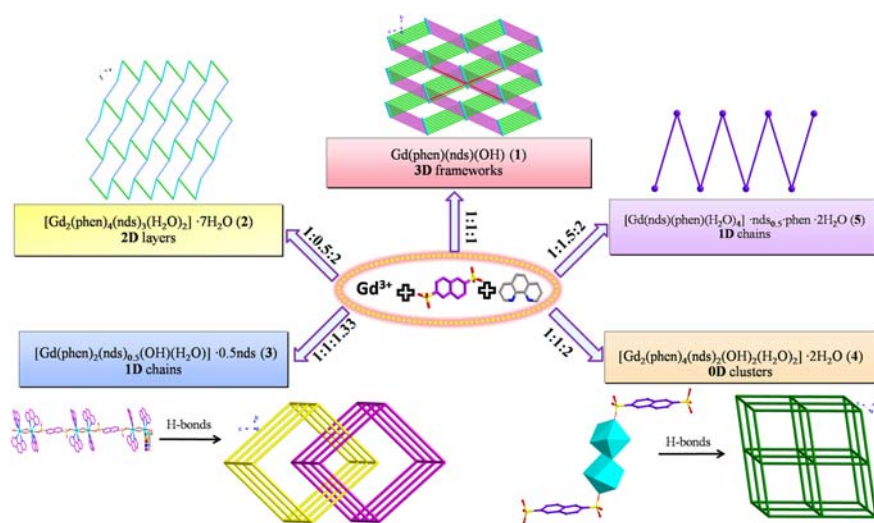
3.1. Overview

Product composition depends on critical factors such as stoichiometry between metal salts and ligands, pH, temperature, reaction time, and counterions. By exploiting hydrothermal reactions, **1–4** were obtained in good yields by using the same procedure with changing stoichiometric ratio of the reactants. In our experiments, the only difference in synthesis of **1–5** was Gd/nds/phen ratios (scheme 1).

The nds has three kinds of coordination modes: (i) Each nds is bonded to only two lanthanide atoms, leaving four free oxygens (scheme 2(a)). (ii) The nds–sulfonate linker adopts $\eta^2\mu^2-\eta^2\mu^2$ coordination, leaving two uncoordinated oxygens (scheme 2(b)). (iii) Each nds is terminal with SO_3^- being monodentate, leaving five free oxygens (scheme 2(c)). All coordination modes are crucial in constructing these complexes; nds is a good choice for understanding the role of intermolecular interactions because of the existence of extensive hydrogen bonds and $\pi \cdot \pi$ interactions within the solid structures.

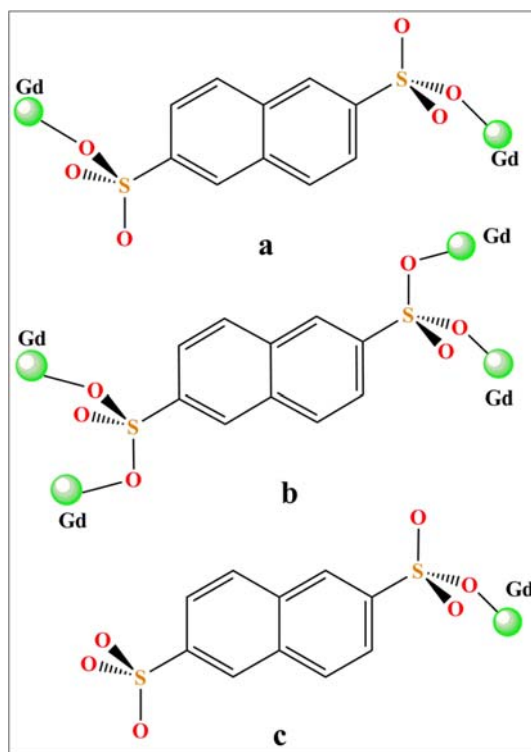
3.2. Structural descriptions

3.2.1. Structure of $\{Gd(phen)(nds)(OH)\}_n$ (1**).** Compound **1** crystallizes in the triclinic system with space group $P\bar{1}$. An ORTEP view of **1** is shown in figure 1(a). Gd(III) is eight-coordinate by two μ_2 -OH groups, four oxygens from nds, and one bidentate chelating phen. The Gd–O and Gd–N bond lengths are within normal ranges (table S1); bond lengths formed by hydroxide and Gd(III) ions [Gd(1)–O(2) = 2.264(3) Å, Gd(1)–O(2A) = 2.271(3) Å] are much shorter than other Gd–O bond distances 2.383(3)–2.502(3) Å. It is not appropriate to use the terms *syn* and *anti* to describe coordination of metal arenedisulfonate; instead, torsion angles of C–S–O–Eu are used [54–61]. The torsion angles of C(18)–S(2)–O(1)–Gd(1), C(18)–S(2)–O(3)–Gd(1), C(13)–S(1)–O(4)–Gd(1), and C(13)–S(1)–O(6)–Gd(1) are $-144.852(235)^\circ$, $-132.354(307)^\circ$, $-118.728(556)^\circ$, and $-144.072(252)^\circ$, respectively. Two Gd(III) centers are linked through a pair of hydroxides,



Scheme 1. Assembly of compounds tuned by stoichiometric ratio of the reactants.

phen and nds, resulting in a $[\text{Gd}_2(\text{OH})_2(\text{nds})_2(\text{phen})_2]$ dinuclear unit with a $\text{Gd} \cdots \text{Gd}$ distance of 3.6563(7) Å. The connection of adjacent dinuclear units through nds (color in red)



Scheme 2. Coordination modes of nds.

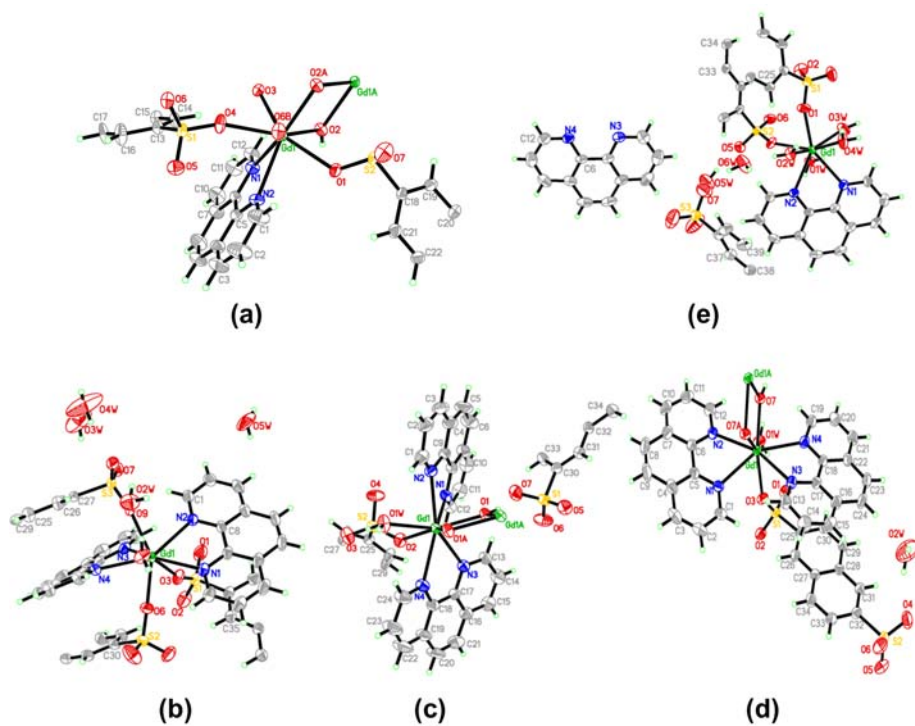


Figure 1. ORTEP drawings for 1–5 (50% thermal ellipsoids). Symmetry code: (a) $-x, 1-y, 1-z$; (b) $1-x, 1-y, 1-z$. (c) $-x, 1-y, 1-z$. (d) $1-x, -y, -z$.

adopting a symmetric $\eta^2\mu^2-\eta^2\mu^2$ mode generate an infinite 1-D zigzag string as shown in figure 2(a). These nds (color in green) ligands also bridge two Gd from each one of the dimers into a 2-D structure of $[\text{Gd}_2(\text{OH})_2(\text{nds})]^{2+}$ layer (figure 2(b)). The geometry imposed by position of the sulfonate in the nds connector is the first example of 2-D $[\text{Gd}_2(\text{OH})_2(\text{nds})]^{2+}$ sheets by a directional covalent bond. Dinuclear Gd centers can be seen as six-connected nodes (figure 3(a)), the nds as the ditopic linker, and the whole framework can be rationalized as 6-connected topology with Schläfli symbol of $(4^{12}.6^3)$ (figure 3(b)).

3.2.2. Structure of $\{[\text{Gd}_2(\text{phen})_4(\text{nds})_3(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}\}_n$ (2). Complex 2 crystallizes in the triclinic system, space group $P\bar{1}$. An ORTEP view of 2 is shown in figure 1(b). Gd(III) is eight-coordinate by three oxygens from nds, four nitrogens from two bidentate chelating phen, and one oxygen from a coordinated water. The Gd–O bond distances ranging from 2.309(2) to 2.354(2) Å and the Gd–N bond lengths ranging from 2.562(3) to 2.588(3) Å are comparable to those reported in other lanthanum(III) sulfonates [62–66]. The torsion angles of C(36)–S(1)–O(3)–Gd(1), C(30)–S(2)–O(6)–Gd(1), and C(27)–S(3)–O(9)–Gd(1) are $108.749(543)^\circ$, $-35.369(921)^\circ$, and $52.113(494)^\circ$, respectively. Nds bridges with each SO_3^- coordinated as a $\eta^3\mu^1$ -bridging group. Three Gd(III) ions construct a $[\text{Gd}_3]$ unit and Gd1···Gd1A and Gd1···Gd1B distances are 12.0854 and 12.6886 Å, respectively. Adjacent $[\text{Gd}_3]$ units are further connected into a 2-D Gd(III)-layer in the ac plane by nds

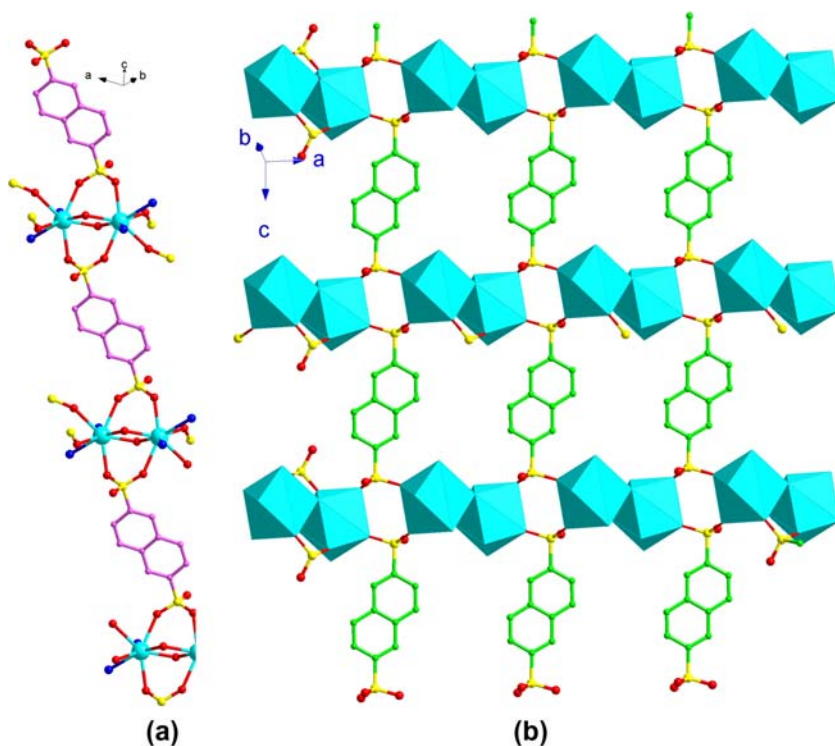


Figure 2. (a) Infinite 1-D chain; each nds adopts a $\eta^2\mu^2-\eta^2\mu^2$ mode between dinuclear units. (b) $[\text{Gd}_2(\text{OH})_2(\text{nds})]^{2+}$ layers formed in **1**.

bridges. Considering $[\text{Gd}_3]$ as a node, the 2-D sheet can be viewed as linkages of the SBUs; $[\text{Gd}_6(\text{nds})_6]^{6+}$ (figure 4(a)), can also be interpreted as a 6^3 -net, as shown in figure 4(b). A 3-D supramolecular network is generated by 2-D layers through the O–H \cdots O and C–H \cdots O hydrogen bonds (figure 4(c)).

3.2.3. Structure of $\{[\text{Gd}(\text{phen})_2(\text{nds})_{0.5}(\text{OH})(\text{H}_2\text{O})] \cdot 0.5(\text{nds})\}_n$ (3**).** The X-ray structural analysis reveals that **3** is triclinic, space group $P\bar{1}$. An ORTEP view of **3** is shown in figure 1(c). It is a μ_2 -OH bridged dinuclear compound in which an inversion center locates between Gd(III) ions. The two Gd(III) ions and hydroxides are strictly coplanar. Each Gd(III) is eight-coordinate, anti-prismatic geometry, formed by two chelating phen, two hydroxides, one water, and one nds. Gd–O bond distances range from 2.2514(18) to 2.493(2) Å and Gd–N bond lengths range from 2.557(2) to 2.617(2) Å. The C(25)–S(2)–O(2)–Gd(1) torsion angle is 160.5(2)°. The connection of adjacent dinuclear units through nds adopting symmetric $\eta^1\mu^1-\eta^1\mu^1$ mode generate infinite 1-D strings as shown in figure 5(a). These 1-D chains are connected by H-bonds from coordinated water to free sulfonate and from hydroxide to sulfonate [O(1W)–H \cdots O(5), O(1)–H \cdots O(7): 1.90 Å, 2.732(3) Å, 164.3°; 1.90 Å, 2.817(3) Å, 167.5°], giving rise to a 2-D layer (figure 5(b)). These 2-D layers are packed into a 3-D supramolecular network via H-bonds from phen to sulfonates and hydroxide [C(21)–H \cdots O(3), C(15)–H \cdots O(4), C(3)–H \cdots O(5): 2.56 Å, 3.473(4) Å,

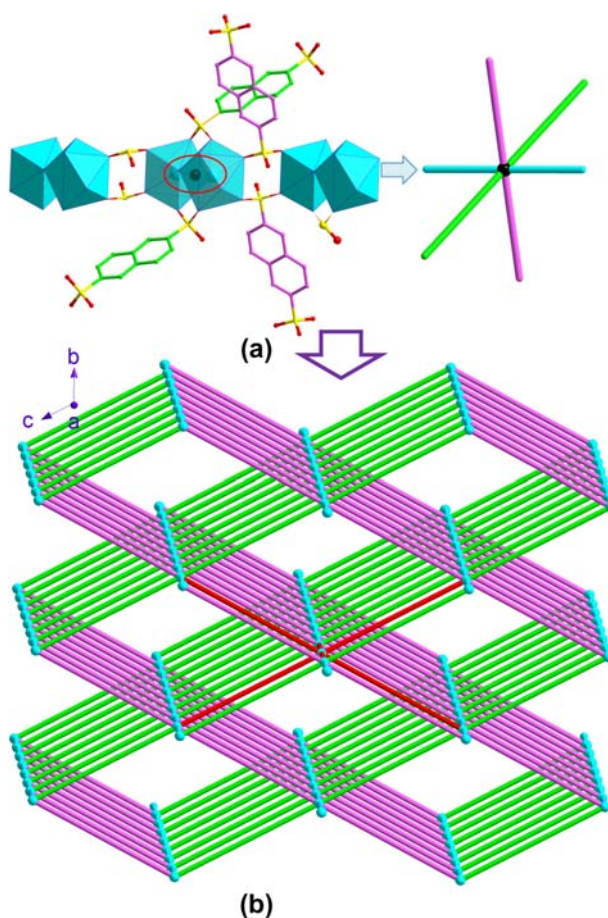


Figure 3. (a) Dinuclear Gd centers as six-connected nodes. (b) Diagram for the (2,6)-connected net of **1**.

166.5°; 2.37 Å, 3.303(4) Å, 178.5°; 2.58 Å, 3.378(4) Å, 144.1°] (figure 5(c)). Therefore, the dinuclear Gd centers can be seen as the six-connected node and nds as the connected bridge; the whole network is a doubly interpenetrated six-connected 2-fold pcu network (figure 6). Frameworks with pcu topology have been demonstrated to show remarkable physical properties, such as porous hydrogen storage and magnetic properties of the Prussian blue family [67–70].

3.2.4. Structure of $\{[\text{Gd}_2(\text{phen})_4(\text{nds})_2(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (4**).** Compound **4** crystallizes in the monoclinic system, space group $P2_1/c$; an ORTEP of **4** is shown in figure 1 (d). Gd(III) is eight-coordinate to two μ_2 -OH, two chelating phen, one water and one terminal nds. Every two of these polyhedra share an OH–OH edge in a dimer. The Gd–O and Gd–N bond distances are within normal ranges and the C(25)–S(1)–O(3)–Gd(1) torsion angle is 99.685(213)°. Intermolecular H-bonds from terminal water to sulfonate and from hydroxide to sulfonate link dinuclear units [O(1W)–H···O(5), O(7)–H···O(6): 1.93 Å, 2.787(3) Å, 173.8°; 1.92 Å, 2.843(3) Å, 174.2°], forming 1-D chains (figure 7(a)).

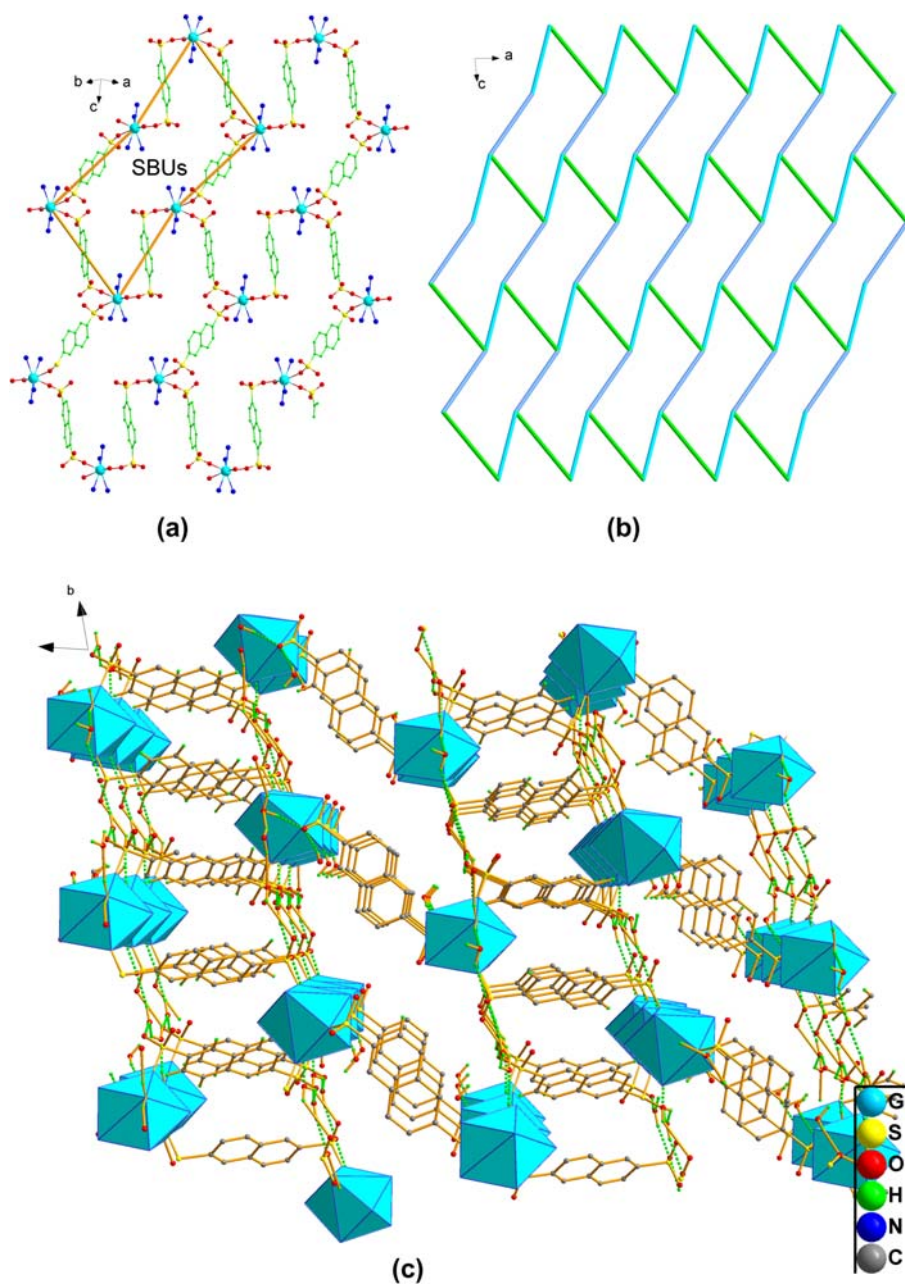


Figure 4. (a) The 2-D sheet constructed by $\eta^3\mu^1$ -bridging nds, linking $[Gd_6(nds)_6]^{6+}$ SBUs. (b) Schematic illustration of the 2-D 6^3 layer. (c) Stacking of the 3-D framework from the *a* direction.

Both the aromatic plane of naphthalene containing C25–C28 and the plane containing C4–C7 are nearly parallel to the phen plane containing N(3)/N(4) (dihedral angles $3.7418(16)^\circ$ and $3.7477(17)^\circ$, respectively) and the inter-planar distances are 3.5363(11) and 3.6294(11) Å, separately, which show intramolecular $\pi \cdots \pi$ interactions (figure 7(b)). The nds

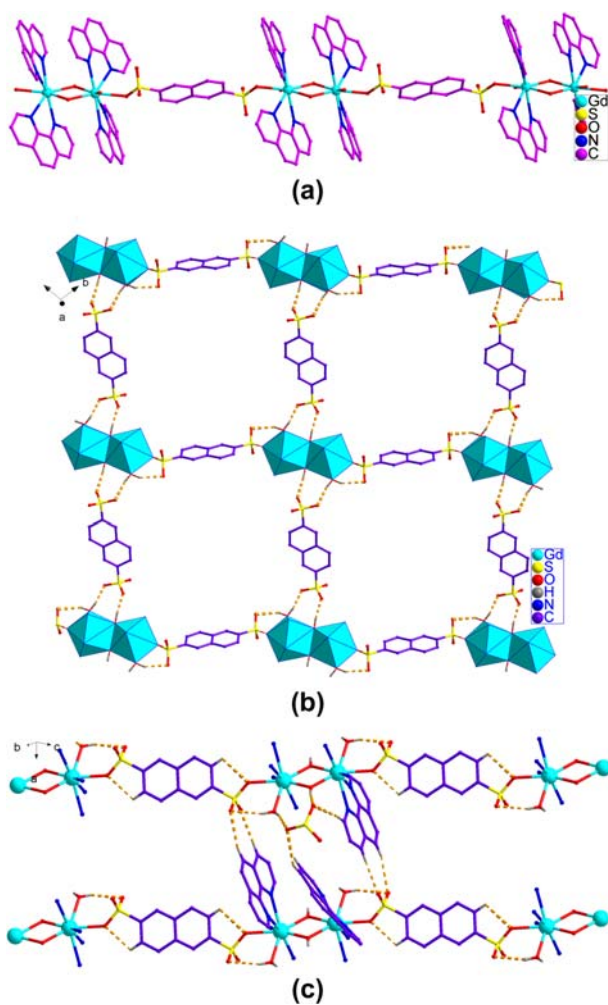


Figure 5. (a) View of the 1-D infinite chain linked by nds of **3**. (b) The 2-D layer formed by O–H···O bonds. (c) View of 2-D sheet formed by C–H···O bonding.

interacting with water and phen link to sulfonates through hydrogen bonding. The layers are linked by interlamellar hydrogen bonds to form a 3-D supramolecular network. Dinuclear Gd centers also can be seen as six-connected nodes with a Schläfli symbol of $(4^{12}.6^3)$ (figure 7(c)).

3.2.5. Structure of $\{[\text{Gd}(\text{nds})(\text{phen})(\text{H}_2\text{O})_4] \cdot 0.5(\text{nds}) \cdot (\text{phen}) \cdot 2\text{H}_2\text{O}\}_n$ (5**).** X-ray analysis reveals that **5** crystallizes in the $P\bar{1}$ space group; an ORTEP of **5** is shown in figure 1 (e). The asymmetric unit contains one Gd(III), four terminal waters, one phen, two half-contained nds anions, two free waters, one free phen, and one half-contained nds anion. The unique Gd(III) is eight-coordinate by two nds groups, four waters, and one chelating phen. Gd–O bond lengths vary from 2.351(3) to 2.408(4) Å and Gd–N bond lengths range from 2.555(4) to 2.573(4) Å. The torsion angles of C(31)–S(2)–O(4)–Gd(1) and C(26)–S

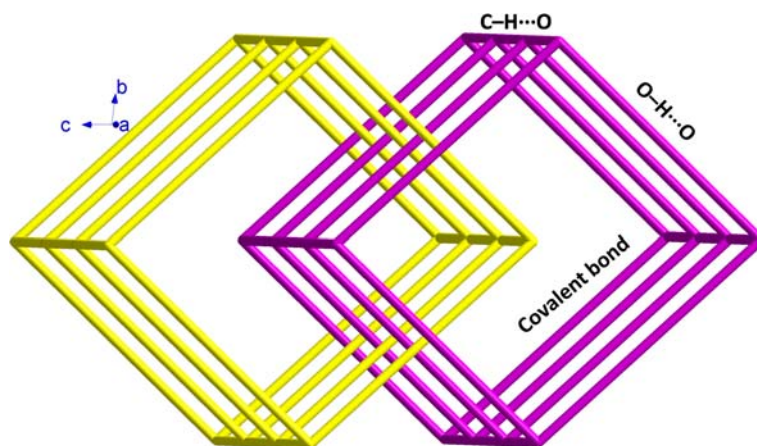


Figure 6. Six-connected 2-fold interpenetrated **pcu** net topology of **3** (dinuclear Gd as the six-connected node, nds as the connected bridge).

(1)–O(1)–Gd(1) are $115.245(409)^\circ$ and $162.053(781)^\circ$, respectively. Adjacent Gd(III) ions are bridged by nds adopting a symmetric $\eta^2\mu^1-\eta^2\mu^1$ mode to form 1-D $[\text{Gd}(\text{nds})(\text{phen})(\text{H}_2\text{O})_4]^+$ chains with Gd–nds–Gd connectivity (figure 8(a)). These 1D chains are connected by H-bonds from free water to sulfonates $[\text{O}(5\text{W})-\text{H}\cdots\text{O}(8)$, $\text{O}(5\text{W})-\text{H}\cdots\text{O}(5)$: 2.48 Å, 3.150(9) Å, 134.8° ; 2.04 Å, 2.848(7) Å, 155.5°], giving a 2-D layer (figure 8(b)). These 2-D subunits are further extended to a 3-D organic–inorganic hybrid supramolecular network via $\text{O}_{\text{water}}-\text{H}\cdots\text{O}_{\text{nds}}$ hydrogen bonds (figure 8(c)).

3.3. Thermogravimetric analysis

TGA of **1–4** were performed under air from 50 to 750 °C with a heating rate of 10 °C/min, as shown in Supplementary Material. For **1**, there is no weight loss between 50 and 425 °C; consecutive weight loss from 425 to 675 °C is probably caused by decomposition of nds and phen, resulting in collapse of framework. The TGA curve of **2** shows release of seven crystalline waters from 74–135 °C (found 6.2%, calcd 6.1%). The next two overlapping steps from 135–165 °C show that two coordinated waters are released (found 7.7%, calcd 7.9%). The TGA curve of **3** also shows two overlapping steps, the first between 220–250 °C corresponds to release of one coordinated water with weight loss of 2.17% very close to the calculated value of 2.15%. The second step (250–350 °C) corresponds to combustion of free nds (found 17.9%, calcd 17.4%). The TGA curve of **4** shows a total weight loss of 4.1% from 120 to 250 °C (calcd 4.2%), which corresponds to loss of all non-coordinated and coordinated waters.

4. Conclusions

Reactions of gadolinium(III) arenedisulfonates with tuned stoichiometric ratios gave five new complexes which are different from other metal naphthylidicarbonylates/naphthylidicarbonylates [71, 72]. Crystal engineering principles provide a facile approach to controlled assembly of 0-D to 3-D extended networks due to nds as connectors or terminal groups.

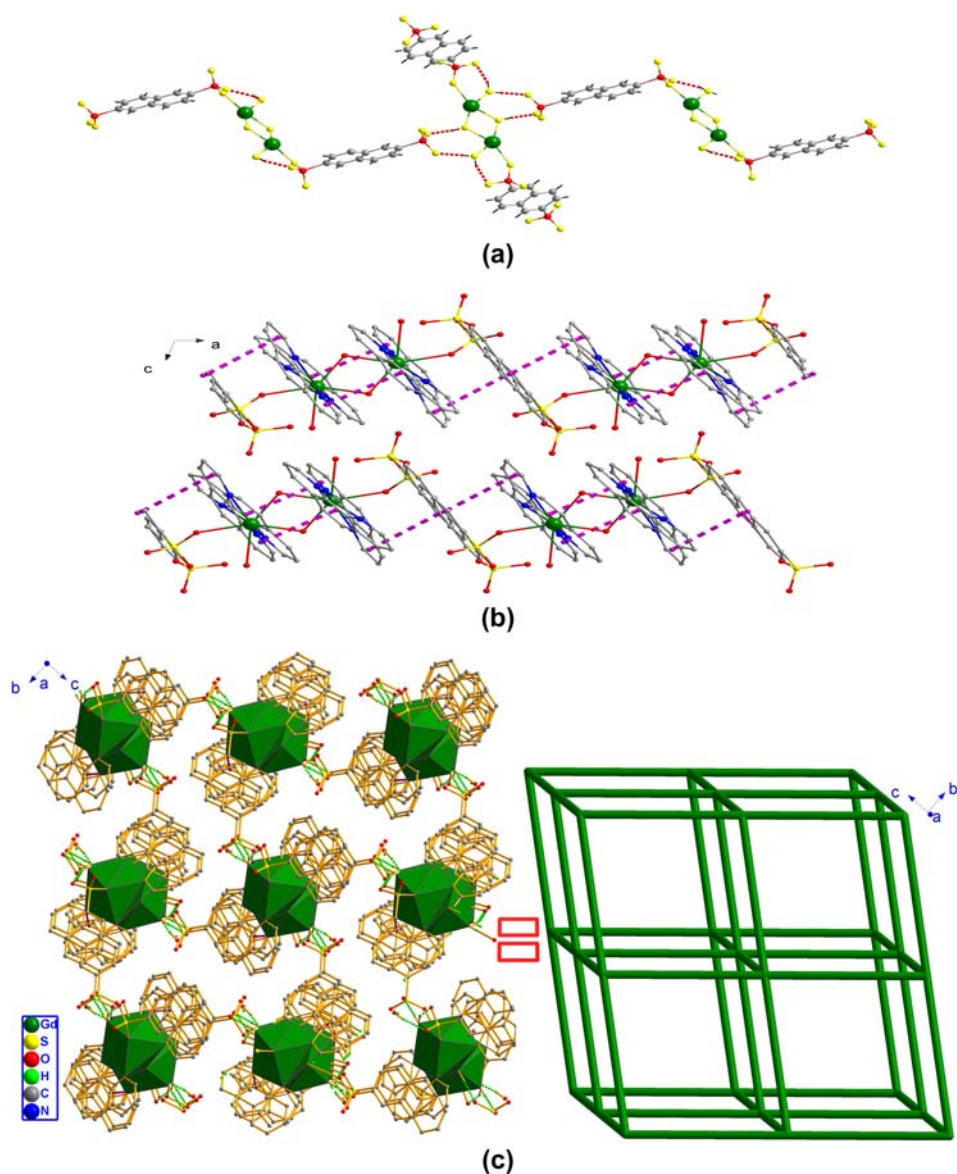


Figure 7. (a) View of the 1-D chain formed by coordinated water and nds. (b) The intramolecular $\pi\pi$ stacking interactions in **4**. (c) 3-D well-packed structure of **4** along the [100] direction.

Hydrogen bonding as well as aromatic packing interactions in these gadolinium(III) complexes further stabilize these supermolecular assemblies. Further research is in progress.

Supplementary data

CCDC-791935 (for **1**), -791937 (for **2**), -791936 (for **3**), -791938 (for **4**), and -791939 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.

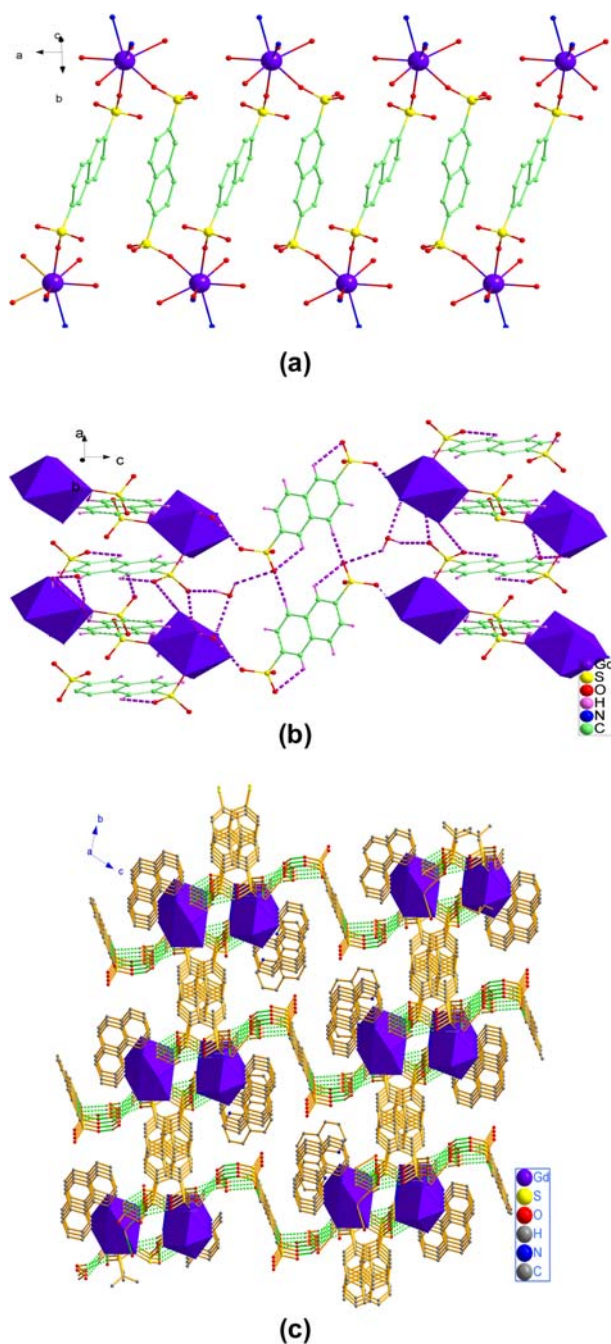


Figure 8. (a) Infinite 1-D zig-zag chain connected by nds with $\eta^2\mu^1-\eta^2\mu^1$ mode. (b) View of the 2-D layer structure by hydrogen bonds. (c) 3-D extended network of 5.

cam.ac.uk/data_request/cif; Supporting Information: TG curves and FT-IR spectra for 1–4, selected bonds distances and angles, hydrogen bonds and X-ray data files in CIF format for 1–5.

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