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In situ ligand synthesis and the first crystallographically characterized lanthanide 3-D pillared networks containing benzene-1,4-disulfonate as a building block †

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The reaction of $Eu(NO_3)_3\cdot6H_2O$ with 4-sulfobenzoic acid (4-H_2SB) yields an unprecedented pillar-like 3-D network, Eu_2(1,4-BDS)(4-SB)$_2\cdot3H_2O$ (1) in which benzene-1,4-disulfonate (1,4-BDS) was synthesized *in situ*; 1 displays very high thermal stability (stable up to 573 °C) and a strong red fluorescence emission in the solid-state, Gd_2(1,4-BDS)(4-SB)$_2\cdot3H_2O$ (2) was also prepared.

In situ ligand preparation not only provides a powerful synthesis method for organic ligands which are not readily accessible but also represents a potential new direction for novel inorganic–organic hybrid network construction through crystal engineering.[1] Benzene-1,4-disulfonic acid (1,4-H_2BDS) can be prepared from a variety of starting materials, such as 1-sulfonato-4-aminobenzene (diazo reaction), phenol (alkali metal salt melting process) and the sodium salt of *p*-chlorobenzenesulfonate (catalysis by $CuSO_4$).[2]

To our surprise, the reaction of 4-sulfobenzoic acid (4-H_2SB) with $Eu(NO_3)_3\cdot6H_2O$ yields an unprecedented three-dimensional pillar-like network Eu_2(1,4-BDS)(4-SB)$_2\cdot3H_2O$ (**1**) in which **1** contains the *in situ* synthesized ligand 1,4-BDS. To the best of our knowledge, **1** represents the first 3-D pillar-like metal coordination polymer containing disulfonate groups or sulfonatobenzoates as building blocks. This is despite the fact that there are many reported 3-D metal coordination networks containing di- or tri-carboxylate groups (1,4-benzenecarboxylate and 1,3,5-tribenzenecarboxylate) as building blocks[3] and 3-D clay-like organic solid-state architectures assembled from azobenzene-4,4′-disulfonate and biphenyl-4,4′-disulfonate building blocks.[4] Here we report the synthesis, solid-state structure, thermal stability and fluorescent properties of **1**. To confirm similarities in lanthanide chemistry, Gd_2(1,4-BDS)-(4-SB)$_2\cdot3H_2O$ (**2**) was also prepared.

Pale-yellow crystals of **1** were obtained by treating 4-H_2SB, H_2SO_4 and $Eu(NO_3)_3\cdot6H_2O$ under hydrothermal reaction conditions.‡ 1,4-BDS was synthesized *in situ* in this case and the Eu^{3+} catalysis effect may play an important role in its formation, similar to that found in the preparation of 1,4-H_2BDS from the sodium salt of *p*-chlorobenzenesulfonate in the presence of $CuSO_4$.[2] The presence of the sulfonate group was confirmed by two strong peaks at 1220 and 1180 cm^{-1}, respectively. Two strong peaks at 1542 and 1420 cm^{-1} suggest that both carboxylic and sulfonic acid groups in 4-H_2SB and 1,4-H_2BDS are deprotonated based on the absence of a peak at *ca.* 1700 cm^{-1}. Gd_2(1,4-BDS)(4-SB)$_2\cdot3H_2O$ (**2**) was prepared by a similar procedure to **1**.‡ The detected molecular weight peak in the mass spectrum further confirms the existence of 1,4-BDS while the solution is obtained by ligand exchange reaction with EDTA in ethanol–water.

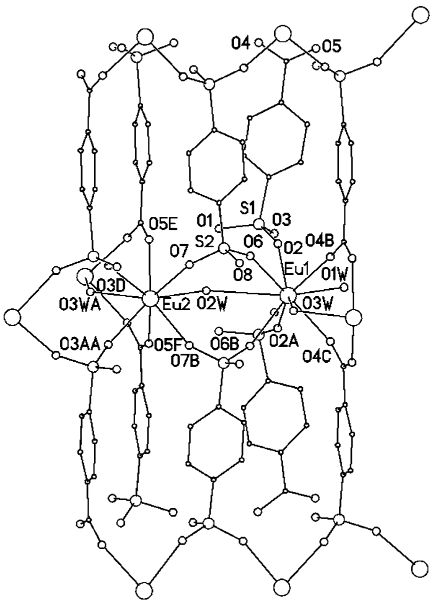

Fig. 1 A local perspective view of Eu_2(1,4-BDS)(4-SB)$_2\cdot3H_2O$ (**1**). Selected bond lengths (Å) and angles (°): Eu(1)–O(4B) 2.296(7), Eu(1)–O(6) 2.385(7), Eu(1)–O(2) 2.392(6), Eu(1)–O(1W) 2.561(13), Eu(1)–O(2W) 2.815(10), Eu(1)–O(3W) 3.106(12), Eu(2)–O(5E) 2.352(6), Eu(2)–O(7) 2.360(7), Eu(2)–O(3D) 2.432(6), Eu(2)–O(2W) 2.530(11), Eu(2)–O(3WA) 2.531(9); O(4C)–Eu(1)–O(6) 138.5(3), O(2)–Eu(1)–O(6) 75.8(3), O(4B)–Eu(1)–O(1W) 68.7(3), O(6)–Eu(1)–O(1W) 135.52(19), O(2)–Eu(1)–O(1W) 71.5(3), O(4B)–Eu(1)–O(2W) 70.8(2), O(4B)–Eu(1)–O(3W) 136.31(19), O(1W)–Eu(1)–O(2W) 123.3(4), O(1W)–Eu(1)–O(3W) 126.6(3), O(2W)–Eu(1)–O(3W) 110.1(3), O(5E)–Eu(2)–O(7) 144.4(3), O(5E)–Eu(2)–O(3D) 139.5(3), O(7)–Eu(2)–O(3D) 75.9(2), O(5E)–Eu(2)–O(3WA) 71.3(2), O(7)–Eu(2)–O(3WA) 78.9(2), O(3D)–Eu(2)–O(3WA) 142.95(15), O(5E)–Eu(2)–O(2W) 72.5(2), O(7)–Eu(2)–O(2W) 139.60(19), O(3D)–Eu(2)–O(2W) 72.2(3), O(2W)–Eu(2)–O(3WA) 113.8(4).

The single-crystal X-ray analysis of complex **1** revealed that there are two crystallographically independent Eu atom centers in the structure, each having a different coordination environment (Fig. 1).§ One Eu center (Eu1) binds to nine oxygen donor atoms, four of which belong to sulfonate groups from two 1,4-BDS and 4-SB ligands, two to carboxylate groups from two 4-SB ligands and the remaining three to three water molecules. Thus, the coordination geometry around the Eu(1) atom is a distorted tricapped trigonal prism in which O(2), O(6) and O(4B) form the top plane of the trigonal prism and the bottom plane is completed by O(2A), O(6B) and O(4C), while O(1W),

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† Electronic supplementary information (ESI) available: a view of **1** showing the unique molecular ‘floor’. See http://www.rsc.org/suppdata/dt/b0/b009542g/

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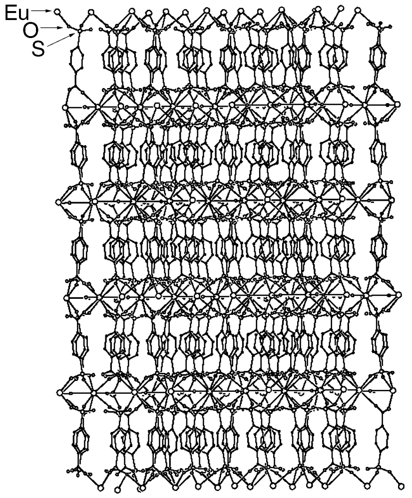

Fig. 2 A pillar-like representation of $Eu_2(1,4\text{-}BDS)(4\text{-}SB)_2\cdot 3H_2O$ (**1**). The increasing size of the open circles represent the C, O, S and Eu atoms, respectively.

O(2W) and O(3W) cap each quadrilateral face of the trigonal prism. The other Eu2 coordinates to four oxygen atoms of sulfonate groups from two 1,4-BDS and 4-SB ligands, to two oxygen atoms of carboxylate groups from two 4-SB ligands and to two water molecules. The coordination geometry around the Eu2 center can be best described as a distorted square antiprism. Both 1,4-BDS and 4-SB ligands in **1** act as a tetradentate bridging spacer to link four different Eu atoms, resulting in the formation of a 3-D pillar-like coordination polymer (Fig. 2). In addition, both the sulfonate and carboxylate group in 1,4-BDS and 4-SB ligands adopt a bidentate bridging mode rather than a chelating mode due to the steric demand on the metal center.

If the pillars (benzene rings) are omitted for clarity (see ESI),† the remaining layer can be regarded as a unique molecular 'floor'. Thus, pillars can directly link the floor to give rise to a 3-D pillar-like network. The distance between two adjacent floors is about 6.023–6.055 Å. The formation of **1** may be due to the high coordination number of rare earth elements allowing them to adopt a 'pseudo-double layer' coordination mode (see ESI).† Furthermore, the space below or above the layer around the Eu atom center can be linked by pillars, leading to the formation of a 3-D pillared network. Thus, **1**, as we are aware, represents the first example of pillar-like coordination polymer containing disulfonate or sulfobenzoate groups as building blocks not only in transition or main group metal but also in lanthanide chemistry. Similarly, **2** is isostructural to **1**.§

The most important feature of **1** is that the dehydrated framework $[Eu_2(1,4\text{-}BDS)(4\text{-}SB)_2]$ displays the highest thermal stability (stable up to 573 °C) of all the known coordination polymers,[3,5] demonstrated by a thermogravimetric analysis (TGA) study which showed an onset of weight loss at *ca.* 210 °C that terminated at *ca.* 364 °C. A 5.20% total weight loss was observed during the TGA study, equivalent to the removal of three water molecules per formula unit (calculated loss is 5.43%), with no further weight loss being detected from *ca.* 364 to 573 °C. More interestingly, the dehydrated framework can regenerate **1** after absorbtion of water (identical X-ray powder diffraction patterns were obtained for samples of **1** before and after the removal of water molecules). This makes **1** an excellent candidate for microporous lanthanide–organic frameworks which find widespread applications in catalysis, adsorption and host–guest chemistry.[3] As expected, **1** displays strong red fluorescent emission in the solid state, and these emissions at different wavelengths are all characteristic of the Eu^{3+} ion, as shown in Fig. 3.

In conclusion, this one-pot *in situ* ligand synthesis reaction in a supramolecular chemistry system provides a robust strategy for the construction of coordination polymers with promising physical properties.

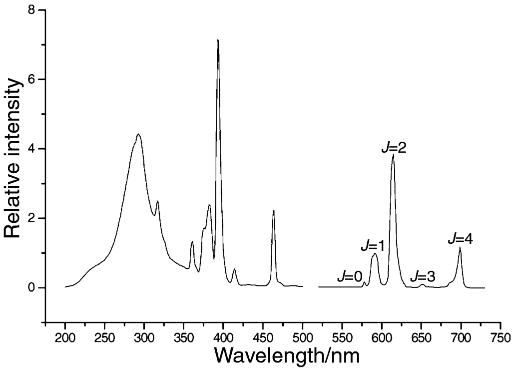

Fig. 3 Fluorescence spectrum of $Eu_2(1,4\text{-}BDS)(4\text{-}SB)_2\cdot 3H_2O$ (**1**) in the solid-state.

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Notes and references

‡ Compound **1**: Samples of $Eu(NO_3)_3\cdot 6H_2O$ (1 mmol) and 4-H_2SB (3 mmol) were thoroughly mixed using a pestle and mortar, and placed in a thick-walled Pyrex tube (*ca.* 20 cm long). After addition of 0.5 ml of EtOH and 2 ml of H_2SO_4 (5 N), the tube was frozen with liquid N_2, evacuated under vacuum and sealed with a torch. The tube was heated at 130 °C for two days to give pale-yellow block crystals (only one phase) in 75% yield based on 4-H_2SB. (Found: C, 24.24; H, 1.92. Calc.: C, 24.15; H, 1.82%). Solid reflectance UV-vis: 290.6 and 226.6 nm. IR (KBr, cm^{-1}): 3400(m), 1590(m), 1542(s), 1420(s), 1220(vs), 1180(vs), 1120(m), 1040(m), 1014(m), 865(w), 790(w), 740(m), 708(m), 640(m) 570(w) and 480(m).

Compound **2**: The procedures used were identical to those for **1** but using $Gd(NO_3)_3\cdot 6H_2O$ as starting material. The pale-yellow block crystals (one phase) were harvested with a yield of 85% based on 4-H_2SB. (Found: C, 23.84; H, 1.87. Calc.: C, 23.90; H, 1.81%). IR (KBr, cm^{-1}): 3400(m), 1590(m), 1542(s), 1420(s), 1220(vs), 1180(vs), 1120(m), 1040(m), 1014(m), 865(w), 790(w), 740(m), 708(m), 640(m), 570(w) and 480(m).

§ Crystal data for **1**: $C_{20}H_{18}Eu_2O_{19}S_4$, $M_r = 994.50$, orthorhombic, space group *Pnma*, $a = 15.90190(19)$, $b = 20.5627(3)$, $c = 8.14890(10)$ Å, $V = 2664.58(5)$ Å^3, $Z = 4$, $\rho_{calc} = 2.479$ g cm^{-3}. Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 293(2)$ K, $\mu = 5.072$ mm^{-1}, $R1 = 0.0620$, $wR2 = 0.1580$ for 3482 observed reflections from 3576 independent reflections, GOF = 1.232.

Crystal data for **2**: $C_{20}H_{18}Gd_2O_{19}S_4$, $M_r = 1005.11$, orthorhombic, space group *Pnma*, $a = 15.855(2)$, $b = 20.492(3)$, $c = 8.1388(11)$ Å, $V = 2644.3(6)$ Å^3, $Z = 4$, $\rho_{calc} = 2.525$ g cm^{-3}. Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 293(2)$ K, $\mu = 5.383$ mm^{-1}, $R1 = 0.0838$, $wR2 = 0.2570$ for 2101 observed reflections from 2383 independent reflections, GOF = 2.090 [The relatively high R value is probably due to disorder of ghost peaks Q1 (5.04 e Å^{-3}) close to S1 and O5 (1.240 and 1.382 Å), Q2 (3.38 e Å^{-3}) is very close to O2 (0.687 Å). In addition, the single crystal quality of **2** is inferior to that of **1**]. CCDC reference numbers 153699 and 153700. See http://www.rsc.org/suppdata/dt/b0/b009542g/ for crystallographic data in CIF or other electronic format.

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