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Solvothermal Syntheses, Crystal Structures and Luminescence Properties of Three New Lanthanide Sulfate Fluorides

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Thermal analysis

Thermal analysis shows that the total weight loss of compound **1** in the range of 50-1100°C is 75.03%, which is in good agreement with the calculated value (73.39%). As shown in Fig. S1, the weight loss of 34.02 % in the range of 50-400°C corresponds to the loss of the organic amine and HF (the calculated value is 33.11 %). The weight loss of 41.01 % in the range of 500-1100°C can be attributed to the loss of SO_3 (the calculated value is 42.70 %). The final product is Sm_2O_3.

Thermal analysis shows that the total weight loss of compound **2** in the range of 50-1100°C is 34.02 %, which is in agreement with the calculated value (36.90 %). As shown in Fig. S2, the weight loss of 9.40 % in the range of 190-780 °C corresponds to the removal of coordination water and HF (the calculated value is 9.50 %). The weight loss of 24.62 % in the range of 781-1100°C can be attributed to the loss of SO_3 (the calculated value is 27.40 %). As shown in Fig. S3, the TG curve of **3** is very similar with 2 due to the same topological structure.

IR spectra

The IR spectrum of **1** exhibits characteristic bands of the organic amine. The typical sharp peaks for diethylenetriamine are in the region 1460-1590 cm^{-1}, and

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characteristic bands due to the SO_4^{2-} are in the 1065 and 608 cm^{-1} regions. The bands at 3180 cm^{-1} are due to N-H bonding vibrations. Absorption at 415 cm^{-1} can be attributed to Sm-O vibration.

The IR spectra of **2** and **3** show that the band at 3380 cm^{-1} is due to the presence of water. The characteristic bands due to the SO_4^{2-} are in the 1079 and 610 cm^{-1} regions. The bands at 3149 cm^{-1} are due to O-H bonding vibrations. Absorption at 420 cm^{-1} can be attributed to Ln-O vibration.

Table S1 Hydrogen bonds for **1**/ Å and °.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1 - H1C ··· O (19a)	0.8894	2.1311	2.948(8)	152.45
N1 - H1C ··· O(21a)	0.8894	2.3881	3.104(8)	137.73
N1 - H1D ··· O12	0.8894	2.1963	2.777(8)	122.51
N1 - H1D ··· O(2a)	0.8894	2.5892	3.215(8)	128.06
N1 - H1D ··· O(24a)	0.8894	2.4505	3.038(8)	123.96
N1 - H1E ··· O(16a)	0.8902	2.1832	2.957(8)	145.03
N2 - H2C ··· O2	0.9006	2.3725	3.024(8)	129.23
N2 - H2C ··· O12	0.9006	2.4117	3.035(9)	126.50
N2 - H2C ··· O(24a)	0.9006	2.3927	3.008(8)	125.66
N2 - H2D ··· O11	0.9000	2.1273	2.963(8)	154.00
N2 - H2D ··· O28	0.9000	2.3257	3.076(9)	140.75
N3 - H3C ··· O18	0.8897	2.0500	2.837(7)	146.89
N3 - H3D ··· O2	0.8901	2.0821	2.927(9)	158.12
N3 - H3D ··· O(24a)	0.8901	2.5891	2.885(8)	100.36
N3 - H3E ··· O(22b)	0.8895	2.3361	3.099(8)	143.78
N3 - H3E ··· O(23b)	0.8895	2.3179	2.929(8)	125.83
N3 - H3E ··· O(24a)	0.8895	2.4672	2.885(8)	109.24
N4 - H4C ··· O(10a)	0.8910	2.0447	2.918(8)	166.15
N4 - H4D ··· O(1c)	0.8899	2.5832	2.885(8)	100.75

N4 - H4D ··· O(14b)	0.8899	2.3619	2.946(11)	123.30
N4 - H4E ··· O(1c)	0.8901	2.3846	2.885(8)	115.74
N4 - H4E ··· O(26a)	0.8901	2.5458	3.044(10)	116.07
N5 - H5C ··· O16	0.8998	1.9820	2.835(8)	157.55
N5 - H5D ··· O3	0.8999	2.4406	2.995(9)	120.11
N5 - H5D ··· O(9b)	0.8999	2.0601	2.912(9)	157.42
N6 - H6C ··· O(22d)	0.8894	1.9907	2.844(8)	160.33
N6 - H6D ··· O(21e)	0.8903	2.2409	3.115(9)	166.99
N6 - H6E ··· O(25e)	0.8906	1.9395	2.760(8)	152.52
N7 - H7C ··· O1	0.8896	1.9589	2.730(9)	144.10
N7 - H7C ··· O4	0.8896	2.4884	3.291(8)	150.34
N7 - H7D ··· O(25f)	0.8904	2.0220	2.806(8)	146.20
N7 - H7E ··· O26	0.8898	2.1042	2.748(8)	128.56
N8 - H8C ··· O(4g)	0.8896	2.5008	3.209(8)	136.96
N8 - H8C ··· O(15g)	0.8896	1.9105	2.714(9)	149.40
N8 - H8D ··· O(6g)	0.8900	2.4328	3.010(8)	122.83
N8 - H8D ··· O(7g)	0.8900	1.9711	2.772(9)	148.95
N8 - H8E ··· O13	0.8888	1.9588	2.784(8)	153.78
N9 - H9C ··· O(28h)	0.8989	2.1691	2.995(10)	152.49
N9 - H9D ··· O(7g)	0.9001	1.9946	2.832(8)	154.24

Symmetry transformations used to generate equivalent atoms: a: -x,2-y,1-z; b: 1-x,1-y,1-z; c: x,y,1+z; d: 1-x,-y,1-z; e: -x,1-y,1-z; f: -x,2-y,-z; g: 1-x,1-y,-z; h: 1-x,2-y,-z; i: x,1+y,z; j: 1+x,y,z

Table S2 Hydrogen bonds for **2**/ Å and °.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O1W - H1WB ··· O(2a)	0.85(5)	2.00(5)	2.831(5)	167(5)
O1W - H1WA ··· O(2b)	0.85(2)	2.49(4)	3.256(5)	150(5)
O1W - H1WA ··· O(3b)	0.85(2)	2.19(4)	2.901(5)	141(5)

Symmetry transformations used to generate equivalent atoms: a: -1/2+x, 3/2-y,-1/2+z; b:

-1/2-x,-1/2+y, 1/2-z; c: -x, 1-y,-z.

Table S3 Hydrogen bonds for **3** / Å and °.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O1W - H1WB ··· O(2a)	0.85(6)	2.06(6)	2.833(7)	151(5)
O1W - H1WA ··· O(2b)	0.85(4)	2.46(5)	3.257(7)	156(7)
O1W - H1WA ··· O(3b)	0.85(4)	2.20(6)	2.897(7)	138(7)

Symmetry transformations used to generate equivalent atoms: a: -1/2+x, 3/2-y,-1/2+z; b:

-1/2-x,-1/2+y, 1/2-z.

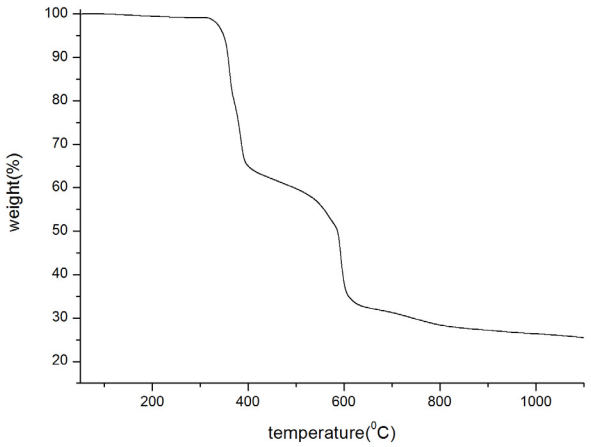

Fig. S1 TGA curve of compound **1** (Temperature vary from 50 to 1100°C at a heating rate of 10°C/min in N_2 atmosphere)

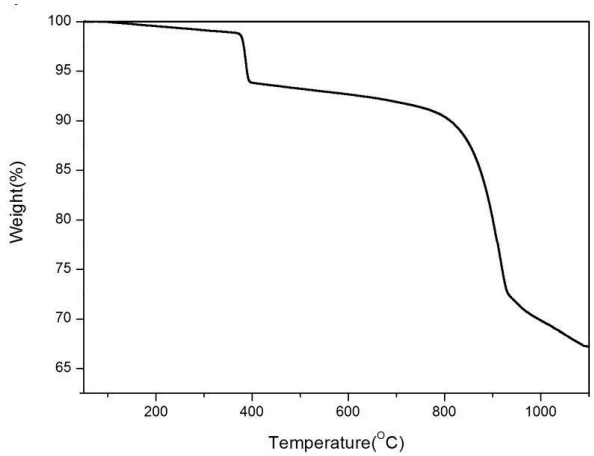

Fig. S2 TGA curve of compound **2** (Temperature vary from 50 to 1100°C at a heating rate of

10°C/min in N_2 atmosphere)

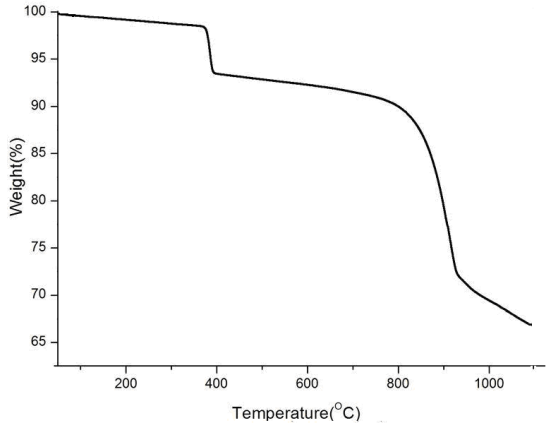

Fig. S3 TG curve of compound **3** (Temperature vary from 50 to 1100°C at a heating rate of 10°C/min in N_2 atmosphere)

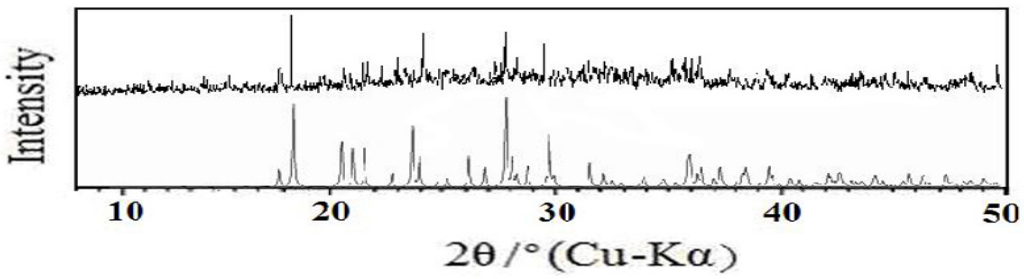

Fig. S4 The experimental (a) and simulated (b) XRD patterns of $Nd(SO_4)F(H_2O)$ **3**