# Electronic Supplementary Information (ESI)

# Luminescence of Samarium(III) Bis-dithiocarbamate Frameworks: Codoped Lanthanide Emitters that Cover Visible and Near-Infrared Domains

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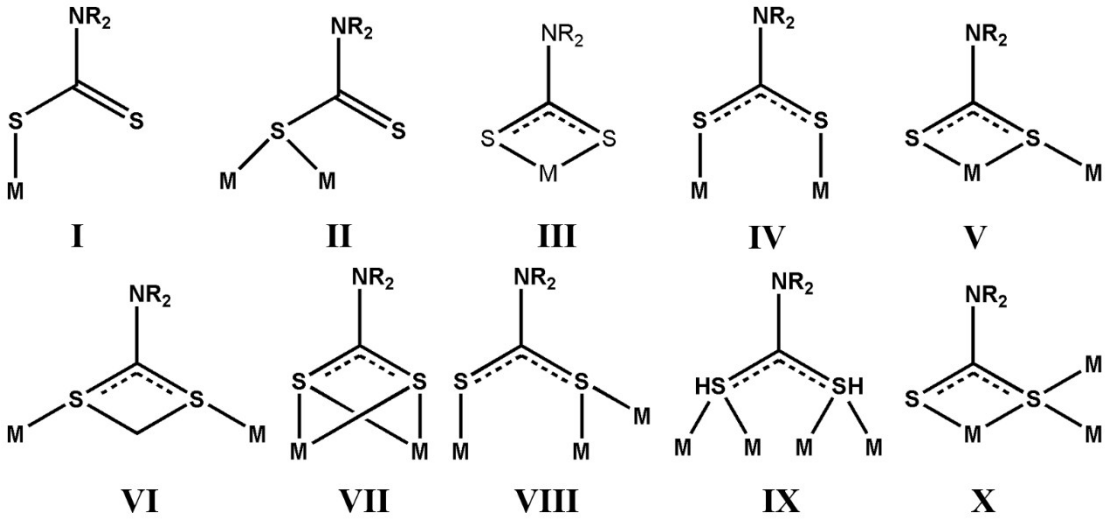
## *Contents of ESI*

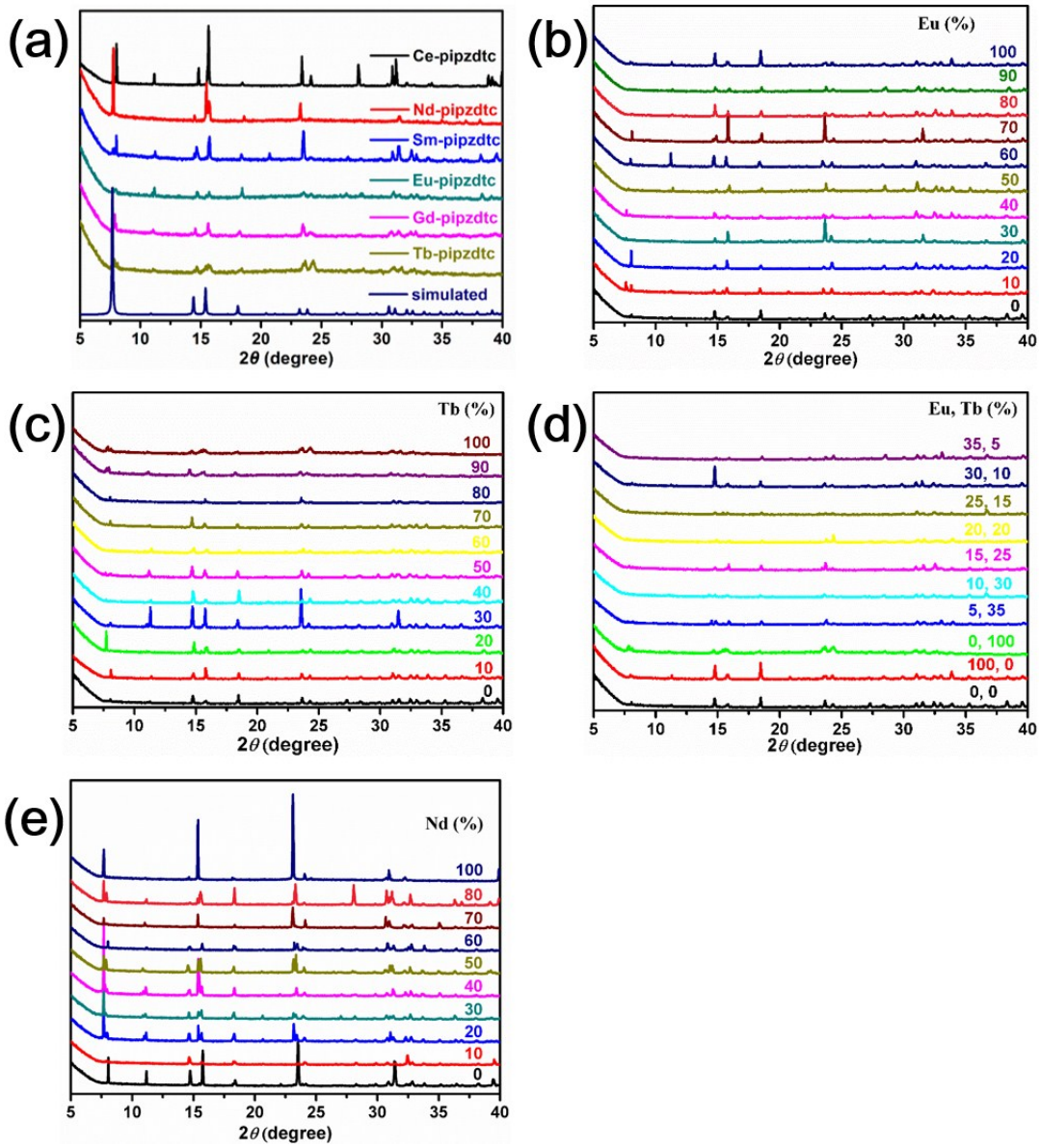



Scheme S1 Various bonding modes of Dtc$^{2-}$ based ligands.

**Table S1** Summary of crystallographic data for the **Ln-S-MOFs**.

| Complex | **Ce-S-MOF** | **Nd-S-MOF** | **Sm-S-MOF** |
|---|---|---|---|
| Formula | $C_{14.5}H_{29.5}CeN_{6.5}O_5S_8$ | $C_{14.5}H_{29.5}NdN_{6.5}O_5S_8$ | $C_{14.5}H_{29.5}SmN_{6.5}O_5S_8$ |
| Fw | 771.54 | 775.661 | 781.77 |
| space group | $P4_2/nnm$ | $P4_2/nnm$ | $P4_2/nnm$ |
| *a* (Å) | 16.4500(8) | 16.3046(9) | 16.2583(8) |
| *b* (Å) | 16.4500(8) | 16.3046(9) | 16.2583(8) |
| *c* (Å) | 6.6223(6) | 6.6306(7) | 6.6354(6) |
| *β* (deg) | 90 | 90 | 90 |
| v (Å$^3$) | 1792.0(2) | 1762.7(3) | 1754.0(2) |
| Z | 2 | 2 | 2 |
| ρcalc (Mg/m$^3$) | 1.430 | 1.461 | 1.480 |
| $\mu$ (mm$^{-1}$) | 1.767 | 1.978 | 2.181 |
| *F* (000) | 776.0 | 780.0 | 784.0 |
| *R*int | 0.0789 | 0.1648 | 0.1014 |
| $R_1$, w$R_2$ [$I > 2\sigma(I)$] | 0.0214, 0.0394 | 0.0382, 0.0750 | 0.0276, 0.0537 |
| $R_1$, w$R_2$ (all data) | 0.0352, 0.0425 | 0.0704, 0.0864 | 0.0488, 0.0601 |
| Complex | **Eu-S-MOF** | **Gd-S-MOF** | **Tb-S-MOF** |
| Formula | $C_{14.5}H_{29.5}EuN_{6.5}O_5S_8$ | $C_{14.5}H_{29.5}GdN_{6.5}O_5S_8$ | $C_{14.5}H_{29.5}TbN_{6.5}O_5S_8$ |
| Fw | 783.38 | 788.67 | 790.34 |
| space group | $P4_2/nnm$ | $P4_2/nnm$ | $P4_2/nnm$ |
| *a* (Å) | 16.1859(7) | 16.1903(12) | 16.120(3) |
| *b* (Å) | 16.1859(7) | 16.1903(12) | 16.120(3) |
| *c* (Å) | 6.6288(6) | 6.6421(11) | 6.633(2) |
| *β* (deg) | 90 | 90 | 90 |
| v (Å$^3$) | 1736.6(2) | 1741.1(4) | 1723.5(8) |
| Z | 2 | 2 | 2 |
| ρcalc (Mg/m$^3$) | 1.498 | 1.504 | 1.523 |
| $\mu$ (mm$^{-1}$) | 2.318 | 2.416 | 2.568 |
| *F* (000) | 786.0 | 788.0 | 790.0 |
| *R*int | 0.0728 | 0.0897 | 0.2027 |
| $R_1$, w$R_2$ [$I > 2\sigma(I)$] | 0.0203, 0.0404 | 0.0250, 0.0501 | 0.0458, 0.1002 |
| $R_1$, w$R_2$ (all data) | 0.0299, 0.0429 | 0.0384, 0.0539 | 0.0779, 0.1145 |

*Note.* $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$


(a)
Ce-pipzdtc
Nd-pipzdtc
Sm-pipzdtc
Eu-pipzdtc
Gd-pipzdtc
Tb-pipzdtc
simulated
2θ (degree)
(b)
Eu (%)
100
90
80
70
60
50
40
30
20
10
0
2θ (degree)
(c)
Tb (%)
100
90
80
70
60
50
40
30
20
10
0
2θ (degree)
(d)
Eu, Tb (%)
35, 5
30, 10
25, 15
20, 20
15, 25
10, 30
5, 35
0, 100
100, 0
0, 0
2θ (degree)
(e)
Nd (%)
100
80
70
60
50
40
30
20
10
0
2θ (degree)

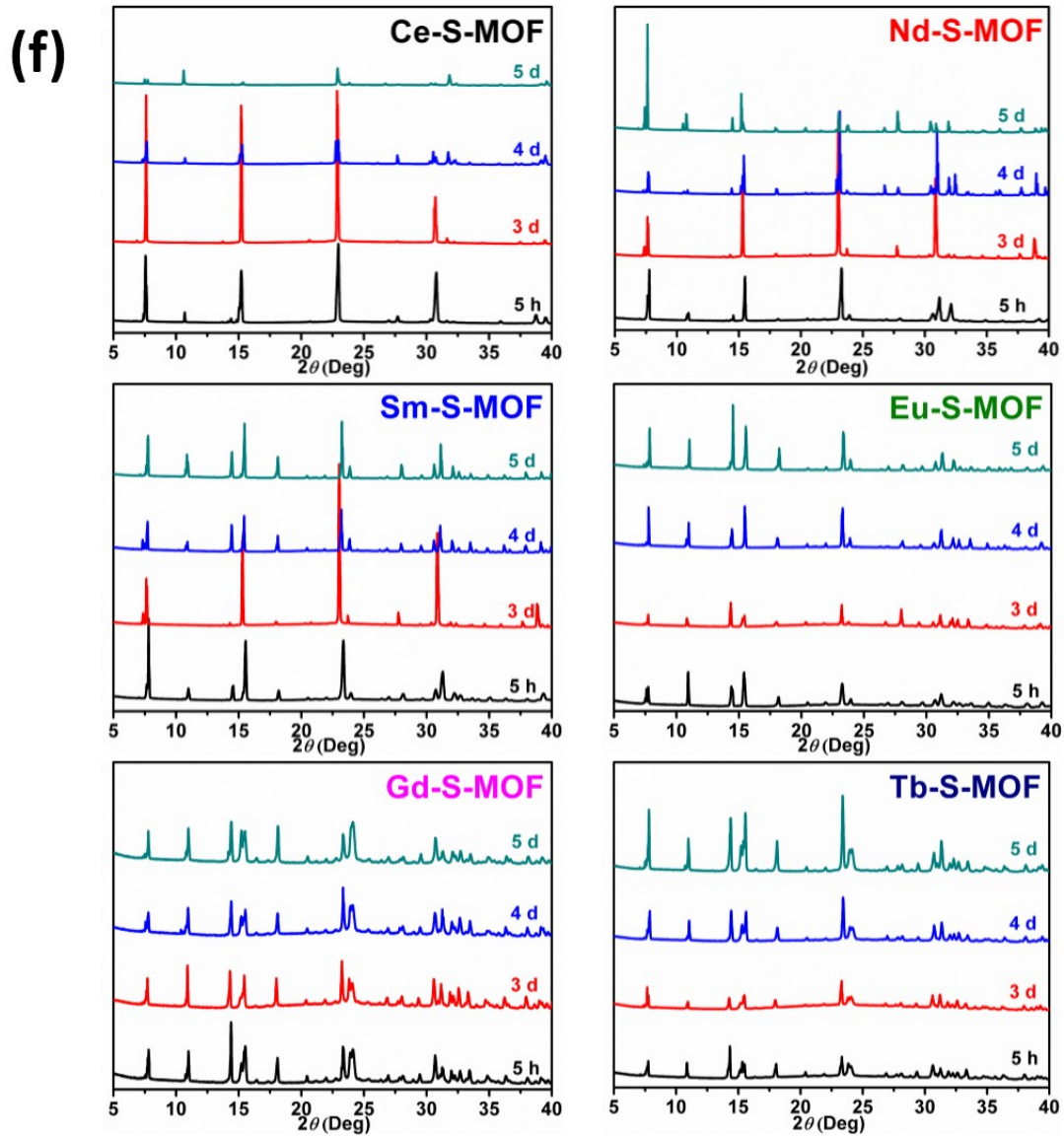



**Fig. S1** PXRD patterns for **Ln-S-MOFs** (a) and their corresponding codoped M'Ln-S-MOFs: **$Sm_{1-x}Eu_x$-S-MOFs** (b), **$Sm_{1-y}Tb_y$-S-MOFs** (c), **$Sm_{1-x-y}Eu_xTb_y$-S-MOFs** (d), and **$Sm_{1-z}Nd_z$-S-MOFs** (e), **Ln-S-MOFs** exposed to the air for different days (f).

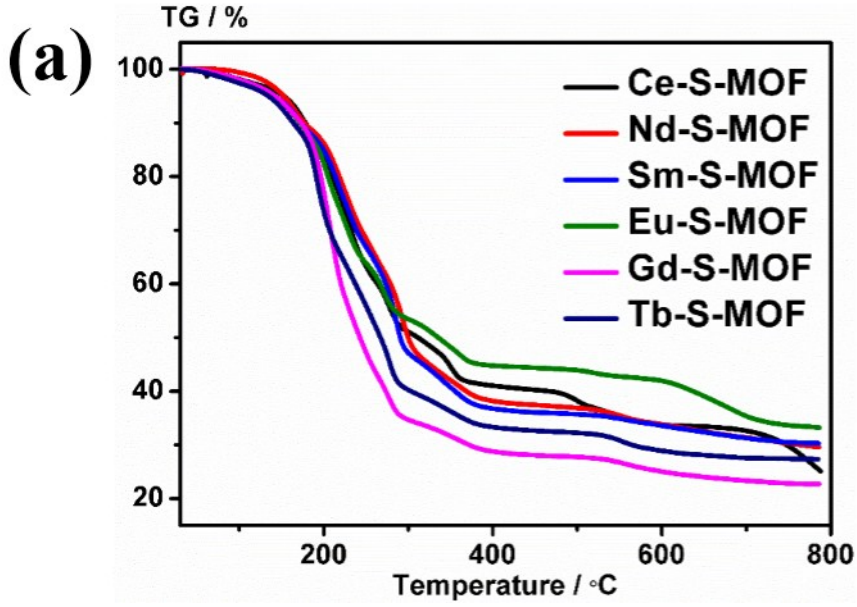
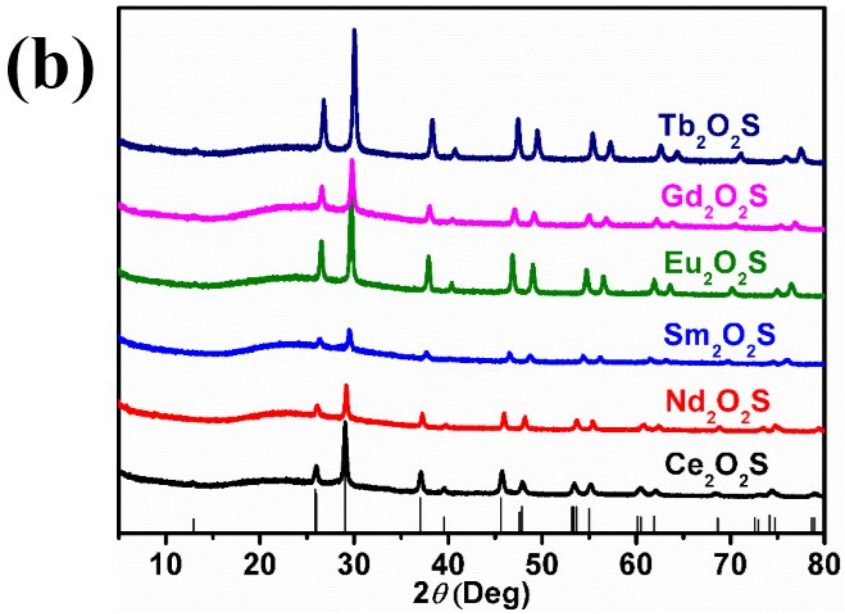



**Fig. S2 a)** TGA of **Ln-S-MOFs** (Ln = $Ce^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$ and $Tb^{3+}$).

Complexes in this work were heated under air in the temperature range of 30-800 ºC at a heating rate of 10 ºC $min^{-1}$ (Fig. S2a). The 66.77-77.27% weight loss of **Ln-S-MOFs** from 30 ºC to 800 ºC corresponds to the loss of guest molecules and organic ligands.




**The powder diffraction patterns of the annealed sample.**

**Fig. S2 b**) Powder X-ray diffraction shows that Ln-S-MOFs were converted into $Ln_2O_2S$ after calcination in air at 800 ºC.

**Table S2** SHAPE analysis of eight-coordinate geometry in compound **Sm-S-MOF**.

| OP ($D_{8h}$) | HPY ($C_{7v}$) | HBPY ($D_{6h}$) | CU ($O_h$) | SAPR ($D_{4d}$) | **TDD ($D_{2d}$)** | JGBF ($D_{2d}$) | JETBPY ($D_{3h}$) | JBTP ($C_{2v}$) | BTPR ($C_{2v}$) | JSD ($D_{2d}$) | TT ($T_d$) | ETBP Y ($D_{3h}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 34.778 | 21.920 | 16.005 | 9.338 | 3.246 | **1.316** | 14.211 | 29.021 | 3.708 | 3.110 | 4.059 | 9.588 | 22.789 |

Abbreviations: OP – Octagon, HPY – Heptagonal pyramid, HBPY – Hexagonal bipyramid, CU – Cube, SAPR – Square antiprism, TDD – Triangular dodecahedron, JGBF – Johnson – Gyrobifastigium (J26), JETBPY – Johnson Elongated triangular bipyramid (J14), JBTP – Johnson Biaugmented trigonal prism (J50), BTPR – Biaugmented trigonal prism, JSD – Snub disphenoid (J84), TT – Triakis tetrahedron, ETBPY – Elongated trigonal pyramid

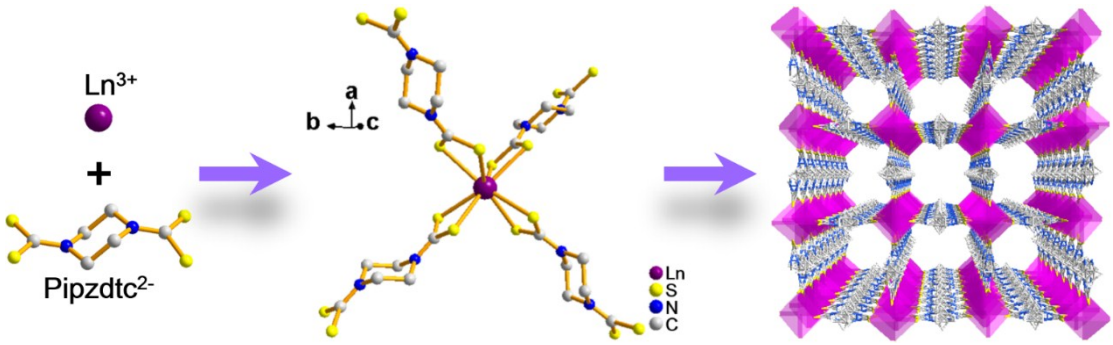



**Fig. S3** Crystal structure of **Ln-S-MOFs** (Ln = $Ce^{3+}$, $Nd^{3+}$, $Eu^{3+}$, $Gd^{3+}$ and $Tb^{3+}$).

**Table S3** Selected bond distances (Å) and angles (°) for **Ce-S-MOF**.

| | | | | | |
|---|---|---|---|---|---|
| Ce(1)-S(1)#1 | 2.9120(16) | Ce(1)-S(1)#5 | 2.9120(16) | Ce(1)-S(2)#3 | 2.9662(9) |
| Ce(1)-S(1)#2 | 2.9120(16) | Ce(1)-S(1)#6 | 2.9120(16) | Ce(1)-S(2)#7 | 2.9662(9) |
| Ce(1)-S(1)#3 | 2.9120(16) | Ce(1)-S(1)#7 | 2.9120(16) | Ce(1)-S(2)#5 | 2.9662(9) |
| Ce(1)-S(1)#4 | 2.9120(16) | Ce(1)-S(1) | 2.9121(16) | Ce(1)-S(2) | 2.9662(9) |
| S(1)#1-Ce(1)-S(1)#2 | 153.38(4) | S(1)#2-Ce(1)-S(1) | 152.40(18) | S(2)#3-Ce(1)-S(2)#7 | 122.34(2) |
| S(1)#1-Ce(1)-S(1)#3 | 152.40(18) | S(1)#3-Ce(1)-S(1) | 153.38(4) | S(1)#1-Ce(1)-S(2)#5 | 82.8(2) |
| S(1)#2-Ce(1)-S(1)#3 | 7.2(7) | S(1)#4-Ce(1)-S(1) | 100.0(7) | S(1)#2-Ce(1)-S(2)#5 | 77.8(2) |
| S(1)#1-Ce(1)-S(1)#4 | 93.039(10) | S(1)#5-Ce(1)-S(1) | 93.039(10) | S(1)#3-Ce(1)-S(2)#5 | 82.8(2) |
| S(1)#2-Ce(1)-S(1)#4 | 93.039(10) | S(1)#6-Ce(1)-S(1) | 86.1(7) | S(1)#4-Ce(1)-S(2)#5 | 146.16(4) |
| S(1)#3-Ce(1)-S(1)#4 | 86.1(7) | S(1)#7-Ce(1)-S(1) | 93.039(10) | S(1)#5-Ce(1)-S(2)#5 | 60.41(3) |
| S(1)#1-Ce(1)-S(1)#5 | 100.0(7) | S(1)#1-Ce(1)-S(2)#3 | 146.16(4) | S(1)#6-Ce(1)-S(2)#5 | 60.41(3) |
| S(1)#2-Ce(1)-S(1)#5 | 86.1(7) | S(1)#2-Ce(1)-S(2)#3 | 60.41(3) | S(1)#7-Ce(1)-S(2)#5 | 146.16(4) |
| S(1)#3-Ce(1)-S(1)#5 | 93.039(10) | S(1)#3-Ce(1)-S(2)#3 | 60.41(3) | S(1)-Ce(1)-S(2)#5 | 77.8(2) |
| S(1)#4-Ce(1)-S(1)#5 | 152.40(18) | S(1)#4-Ce(1)-S(2)#3 | 77.8(2) | S(2)#3-Ce(1)-S(2)#5 | 122.344(19) |
| S(1)#1-Ce(1)-S(1)#6 | 93.039(10) | S(1)#5-Ce(1)-S(2)#3 | 77.8(2) | S(2)#7-Ce(1)-S(2)#5 | 85.99(3) |
| S(1)#2-Ce(1)-S(1)#6 | 93.039(10) | S(1)#6-Ce(1)-S(2)#3 | 82.8(2) | S(1)#1-Ce(1)-S(2) | 60.41(3) |
| S(1)#3-Ce(1)-S(1)#6 | 100.0(7) | S(1)#7-Ce(1)-S(2)#3 | 82.8(2) | S(1)#2-Ce(1)-S(2) | 146.16(4) |
| S(1)#4-Ce(1)-S(1)#6 | 153.38(4) | S(1)-Ce(1)-S(2)#3 | 146.16(4) | S(1)#3-Ce(1)-S(2) | 146.16(4) |
| S(1)#5-Ce(1)-S(1)#6 | 7.2(7) | S(1)#1-Ce(1)-S(2)#7 | 77.8(2) | S(1)#4-Ce(1)-S(2) | 82.8(2) |
| S(1)#1-Ce(1)-S(1)#7 | 86.1(7) | S(1)#2-Ce(1)-S(2)#7 | 82.8(2) | S(1)#5-Ce(1)-S(2) | 82.8(2) |
| S(1)#2-Ce(1)-S(1)#7 | 100.0(7) | S(1)#3-Ce(1)-S(2)#7 | 77.8(2) | S(1)#6-Ce(1)-S(2) | 77.8(2) |
| S(1)#3-Ce(1)-S(1)#7 | 93.039(10) | S(1)#4-Ce(1)-S(2)#7 | 60.41(3) | S(1)#7-Ce(1)-S(2) | 77.8(2) |
| S(1)#4-Ce(1)-S(1)#7 | 7.2(7) | S(1)#5-Ce(1)-S(2)#7 | 146.16(4) | S(1)-Ce(1)-S(2) | 60.41(3) |
| S(1)#5-Ce(1)-S(1)#7 | 153.38(4) | S(1)#6-Ce(1)-S(2)#7 | 146.16(4) | S(2)#3-Ce(1)-S(2) | 85.98(3) |
| S(1)#6-Ce(1)-S(1)#7 | 152.40(18) | S(1)#7-Ce(1)-S(2)#7 | 60.41(3) | S(2)#7-Ce(1)-S(2) | 122.345(19) |
| S(1)#1-Ce(1)-S(1) | 7.2(7) | S(1)-Ce(1)-S(2)#7 | 82.8(2) | S(2)#5-Ce(1)-S(2) | 122.345(19) |

Symmetry transformations used to generate equivalent atoms: *#1, y+1/2,x-1/2,z; #2, -y+1,-x+1,z; #3, -x+3/2,-y+1/2,z; #4, -x+3/2,y,-z+1/2; #5, y+1/2,-x+1,-z+1/2; #6, x,-y+1/2,-z+1/2; #7, -y+1,x-1/2,-z+1/2; #8, -x+1,-y,-z+1*.

**Table S4** Selected bond distances (Å) and angles (°) for **Sm-S-MOF**.

| | | | | | |
|---|---|---|---|---|---|
| Sm(1)-S(1) | 2.844(2) | Sm(1)-S(1)#4 | 2.844(2) | Sm(1)-S(2)#3 | 2.9005(13) |
| Sm(1)-S(1)#1 | 2.844(2) | Sm(1)-S(1)#5 | 2.844(2) | Sm(1)-S(2)#7 | 2.9005(13) |
| Sm(1)-S(1)#2 | 2.844(2) | Sm(1)-S(1)#6 | 2.844(2) | Sm(1)-S(2)#4 | 2.9005(13) |
| Sm(1)-S(1)#3 | 2.844(2) | Sm(1)-S(1)#7 | 2.844(2) | Sm(1)-S(2) | 2.9005(13) |
| S(1)-Sm(1)-S(1)#1 | 8.2(6) | S(1)#1-Sm(1)-S(1)#7 | 85.3(6) | S(2)#3-Sm(1)-S(2)#7 | 123.40(3) |
| S(1)-Sm(1)-S(1)#2 | 151.50(19) | S(1)#2-Sm(1)-S(1)#7 | 101.2(6) | S(1)-Sm(1)-S(2)#4 | 77.1(2) |
| S(1)#1-Sm(1)-S(1)#2 | 152.74(7) | S(1)#3-Sm(1)-S(1)#7 | 93.183(15) | S(1)#1-Sm(1)-S(2)#4 | 82.7(2) |
| S(1)-Sm(1)-S(1)#3 | 152.74(7) | S(1)#4-Sm(1)-S(1)#7 | 152.74(7) | S(1)#2-Sm(1)-S(2)#4 | 77.1(2) |
| S(1)#1-Sm(1)-S(1)#3 | 151.50(19) | S(1)#5-Sm(1)-S(1)#7 | 151.50(19) | S(1)#3-Sm(1)-S(2)#4 | 82.7(2) |
| S(1)#2-Sm(1)-S(1)#3 | 8.2(6) | S(1)#6-Sm(1)-S(1)#7 | 8.2(6) | S(1)#4-Sm(1)-S(2)#4 | 61.64(4) |
| S(1)-Sm(1)-S(1)#4 | 93.183(15) | S(1)-Sm(1)-S(2)#3 | 145.56(5) | S(1)#5-Sm(1)-S(2)#4 | 61.64(4) |
| S(1)#1-Sm(1)-S(1)#4 | 101.2(6) | S(1)#1-Sm(1)-S(2)#3 | 145.56(5) | S(1)#6-Sm(1)-S(2)#4 | 145.56(5) |
| S(1)#2-Sm(1)-S(1)#4 | 85.3(6) | S(1)#2-Sm(1)-S(2)#3 | 61.64(4) | S(1)#7-Sm(1)-S(2)#4 | 145.56(5) |
| S(1)#3-Sm(1)-S(1)#4 | 93.183(15) | S(1)#3-Sm(1)-S(2)#3 | 61.64(4) | S(2)#3-Sm(1)-S(2)#4 | 123.40(3) |
| S(1)-Sm(1)-S(1)#5 | 85.3(6) | S(1)#4-Sm(1)-S(2)#3 | 77.1(2) | S(2)#7-Sm(1)-S(2)#4 | 84.21(5) |
| S(1)#1-Sm(1)-S(1)#5 | 93.183(15) | S(1)#5-Sm(1)-S(2)#3 | 82.7(2) | S(1)-Sm(1)-S(2) | 61.64(4) |
| S(1)#2-Sm(1)-S(1)#5 | 93.183(15) | S(1)#6-Sm(1)-S(2)#3 | 77.1(2) | S(1)#1-Sm(1)-S(2) | 61.64(4) |
| S(1)#3-Sm(1)-S(1)#5 | 101.2(6) | S(1)#7-Sm(1)-S(2)#3 | 82.7(2) | S(1)#2-Sm(1)-S(2) | 145.56(5) |
| S(1)#4-Sm(1)-S(1)#5 | 8.2(6) | S(1)-Sm(1)-S(2)#7 | 82.7(2) | S(1)#3-Sm(1)-S(2) | 145.56(5) |
| S(1)-Sm(1)-S(1)#6 | 101.2(6) | S(1)#1-Sm(1)-S(2)#7 | 77.1(2) | S(1)#4-Sm(1)-S(2) | 82.7(2) |
| S(1)#1-Sm(1)-S(1)#6 | 93.183(15) | S(1)#2-Sm(1)-S(2)#7 | 82.7(2) | S(1)#5-Sm(1)-S(2) | 77.1(2) |
| S(1)#2-Sm(1)-S(1)#6 | 93.183(15) | S(1)#3-Sm(1)-S(2)#7 | 77.1(2) | S(1)#6-Sm(1)-S(2) | 82.7(2) |
| S(1)#3-Sm(1)-S(1)#6 | 85.3(6) | S(1)#4-Sm(1)-S(2)#7 | 145.56(5) | S(1)#7-Sm(1)-S(2) | 77.1(2) |
| S(1)#4-Sm(1)-S(1)#6 | 151.50(19) | S(1)#5-Sm(1)-S(2)#7 | 145.56(5) | S(2)#3-Sm(1)-S(2) | 84.21(5) |
| S(1)#5-Sm(1)-S(1)#6 | 152.74(7) | S(1)#6-Sm(1)-S(2)#7 | 61.64(4) | S(2)#7-Sm(1)-S(2) | 123.40(3) |
| S(1)-Sm(1)-S(1)#7 | 93.183(15) | S(1)#7-Sm(1)-S(2)#7 | 61.64(4) | S(2)#4-Sm(1)-S(2) | 123.40(3) |

Symmetry transformations used to generate equivalent atoms: *#1, y+1/2,x-1/2,z; #2, -y+1,-x+1,z; #3, -x+3/2,-y+1/2,z; #4, y+1/2,-x+1,-z+1/2; #5, x,-y+1/2,-z+1/2; #6, -x+3/2,y,-z+1/2; #7, -y+1,x-1/2,-z+1/2; #8, -x+1,-y,-z+1*.

**Table S5** Selected bond distances (Å) and angles (°) for **Nd-S-MOF**.

| | | | | | |
|---|---|---|---|---|---|
| Nd(1)-S(1) | 2.865(4) | Nd(1)-S(1)#4 | 2.865(4) | Nd(1)-S(2)#3 | 2.9265(18) |
| Nd(1)-S(1)#1 | 2.865(4) | Nd(1)-S(1)#5 | 2.865(4) | Nd(1)-S(2)#7 | 2.9265(18) |
| Nd(1)-S(1)#2 | 2.865(4) | Nd(1)-S(1)#6 | 2.865(4) | Nd(1)-S(2)#6 | 2.9265(18) |
| Nd(1)-S(1)#3 | 2.865(4) | Nd(1)-S(1)#7 | 2.865(4) | Nd(1)-S(2) | 2.9265(18) |
| S(1)-Nd(1)-S(1)#1 | 6(2) | S(1)#1-Nd(1)-S(1)#7 | 99(2) | S(2)#3-Nd(1)-S(2)#7 | 122.99(4) |
| S(1)-Nd(1)-S(1)#2 | 152.2(5) | S(1)#2-Nd(1)-S(1)#7 | 88(2) | S(1)-Nd(1)-S(2)#6 | 81.9(8) |
| S(1)#1-Nd(1)-S(1)#2 | 152.75(9) | S(1)#3-Nd(1)-S(1)#7 | 93.18(2) | S(1)#1-Nd(1)-S(2)#6 | 78.1(8) |
| S(1)-Nd(1)-S(1)#3 | 152.75(9) | S(1)#4-Nd(1)-S(1)#7 | 6(2) | S(1)#2-Nd(1)-S(2)#6 | 81.9(8) |
| S(1)#1-Nd(1)-S(1)#3 | 152.2(5) | S(1)#5-Nd(1)-S(1)#7 | 152.2(5) | S(1)#3-Nd(1)-S(2)#6 | 78.1(8) |
| S(1)#2-Nd(1)-S(1)#3 | 6(2) | S(1)#6-Nd(1)-S(1)#7 | 152.75(9) | S(1)#4-Nd(1)-S(2)#6 | 145.99(10) |
| S(1)-Nd(1)-S(1)#4 | 88(2) | S(1)-Nd(1)-S(2)#3 | 145.99(10) | S(1)#5-Nd(1)-S(2)#6 | 61.23(6) |
| S(1)#1-Nd(1)-S(1)#4 | 93.18(2) | S(1)#1-Nd(1)-S(2)#3 | 145.99(10) | S(1)#6-Nd(1)-S(2)#6 | 61.23(6) |
| S(1)#2-Nd(1)-S(1)#4 | 93.18(2) | S(1)#2-Nd(1)-S(2)#3 | 61.23(6) | S(1)#7-Nd(1)-S(2)#6 | 145.99(10) |
| S(1)#3-Nd(1)-S(1)#4 | 99(2) | S(1)#3-Nd(1)-S(2)#3 | 61.23(6) | S(2)#3-Nd(1)-S(2)#6 | 122.99(4) |
| S(1)-Nd(1)-S(1)#5 | 99(2) | S(1)#4-Nd(1)-S(2)#3 | 81.9(8) | S(2)#7-Nd(1)-S(2)#6 | 84.90(7) |
| S(1)#1-Nd(1)-S(1)#5 | 93.18(2) | S(1)#5-Nd(1)-S(2)#3 | 78.1(8) | S(1)-Nd(1)-S(2) | 61.23(6) |
| S(1)#2-Nd(1)-S(1)#5 | 93.18(2) | S(1)#6-Nd(1)-S(2)#3 | 81.9(8) | S(1)#1-Nd(1)-S(2) | 61.23(6) |
| S(1)#3-Nd(1)-S(1)#5 | 88(2) | S(1)#7-Nd(1)-S(2)#3 | 78.1(8) | S(1)#2-Nd(1)-S(2) | 145.99(10) |
| S(1)#4-Nd(1)-S(1)#5 | 152.75(9) | S(1)-Nd(1)-S(2)#7 | 78.1(8) | S(1)#3-Nd(1)-S(2) | 145.99(10) |
| S(1)-Nd(1)-S(1)#6 | 93.18(2) | S(1)#1-Nd(1)-S(2)#7 | 81.9(8) | S(1)#4-Nd(1)-S(2) | 78.1(8) |
| S(1)#1-Nd(1)-S(1)#6 | 88(2) | S(1)#2-Nd(1)-S(2)#7 | 78.1(8) | S(1)#5-Nd(1)-S(2) | 81.9(8) |
| S(1)#2-Nd(1)-S(1)#6 | 99(2) | S(1)#3-Nd(1)-S(2)#7 | 81.9(8) | S(1)#6-Nd(1)-S(2) | 78.1(8) |
| S(1)#3-Nd(1)-S(1)#6 | 93.18(2) | S(1)#4-Nd(1)-S(2)#7 | 61.23(6) | S(1)#7-Nd(1)-S(2) | 81.9(8) |
| S(1)#4-Nd(1)-S(1)#6 | 152.2(5) | S(1)#5-Nd(1)-S(2)#7 | 145.99(10) | S(2)#3-Nd(1)-S(2) | 84.90(7) |
| S(1)#5-Nd(1)-S(1)#6 | 6(2) | S(1)#6-Nd(1)-S(2)#7 | 145.99(10) | S(2)#7-Nd(1)-S(2) | 122.99(4) |
| S(1)-Nd(1)-S(1)#7 | 93.18(2) | S(1)#7-Nd(1)-S(2)#7 | 61.23(6) | S(2)#6-Nd(1)-S(2) | 122.99(4) |

Symmetry transformations used to generate equivalent atoms: *#1, y+1/2,x-1/2,z; #2, -y+1,-x+1,z; #3, -x+3/2,-y+1/2,z; #4, x,-y+1/2,-z+1/2; #5, -x+3/2,y,-z+1/2; #6, -y+1,x-1/2,-z+1/2; #7, y+1/2,-x+1,-z+1/2; #8, -x+1,-y,-z+1*.

**Table S6** Selected bond distances (Å) and angles (°) for **Eu-S-MOF**.

| | | | | | |
|---|---|---|---|---|---|
| Eu(1)-S(1)#1 | 2.8293(12) | Eu(1)-S(1)#5 | 2.8293(12) | Eu(1)-S(2) | 2.8944(9) |
| Eu(1)-S(1)#2 | 2.8293(12) | Eu(1)-S(1)#6 | 2.8293(12) | Eu(1)-S(2)#3 | 2.8944(9) |
| Eu(1)-S(1)#3 | 2.8293(12) | Eu(1)-S(1)#7 | 2.8293(12) | Eu(1)-S(2)#7 | 2.8944(9) |
| Eu(1)-S(1)#4 | 2.8293(12) | Eu(1)-S(1) | 2.8293(12) | Eu(1)-S(2)#4 | 2.8944(9) |
| S(1)#1-Eu(1)-S(1)#2 | 152.50(5) | S(1)#2-Eu(1)-S(1) | 150.95(7) | S(2)-Eu(1)-S(2)#3 | 83.39(3) |
| S(1)#1-Eu(1)-S(1)#3 | 150.95(7) | S(1)#3-Eu(1)-S(1) | 152.50(5) | S(1)#1-Eu(1)-S(2)#7 | 76.66(7) |
| S(1)#2-Eu(1)-S(1)#3 | 9.2(2) | S(1)#4-Eu(1)-S(1) | 93.237(11) | S(1)#2-Eu(1)-S(2)#7 | 82.87(7) |
| S(1)#1-Eu(1)-S(1)#4 | 102.21(19) | S(1)#5-Eu(1)-S(1) | 84.34(19) | S(1)#3-Eu(1)-S(2)#7 | 76.66(7) |
| S(1)#2-Eu(1)-S(1)#4 | 84.34(19) | S(1)#6-Eu(1)-S(1) | 102.21(19) | S(1)#4-Eu(1)-S(2)#7 | 145.22(3) |
| S(1)#3-Eu(1)-S(1)#4 | 93.238(11) | S(1)#7-Eu(1)-S(1) | 93.238(11) | S(1)#5-Eu(1)-S(2)#7 | 145.22(3) |
| S(1)#1-Eu(1)-S(1)#5 | 93.238(11) | S(1)#1-Eu(1)-S(2) | 62.20(3) | S(1)#6-Eu(1)-S(2)#7 | 62.20(3) |
| S(1)#2-Eu(1)-S(1)#5 | 93.238(11) | S(1)#2-Eu(1)-S(2) | 145.22(3) | S(1)#7-Eu(1)-S(2)#7 | 62.20(3) |
| S(1)#3-Eu(1)-S(1)#5 | 102.21(19) | S(1)#3-Eu(1)-S(2) | 145.22(3) | S(1)-Eu(1)-S(2)#7 | 82.87(7) |
| S(1)#4-Eu(1)-S(1)#5 | 9.2(2) | S(1)#4-Eu(1)-S(2) | 82.87(7) | S(2)-Eu(1)-S(2)#7 | 123.89(2) |
| S(1)#1-Eu(1)-S(1)#6 | 93.238(11) | S(1)#5-Eu(1)-S(2) | 76.66(7) | S(2)#3-Eu(1)-S(2)#7 | 123.89(2) |
| S(1)#2-Eu(1)-S(1)#6 | 93.238(11) | S(1)#6-Eu(1)-S(2) | 82.87(7) | S(1)#1-Eu(1)-S(2)#4 | 82.87(7) |
| S(1)#3-Eu(1)-S(1)#6 | 84.34(19) | S(1)#7-Eu(1)-S(2) | 76.66(7) | S(1)#2-Eu(1)-S(2)#4 | 76.66(7) |
| S(1)#4-Eu(1)-S(1)#6 | 150.95(7) | S(1)-Eu(1)-S(2) | 62.20(3) | S(1)#3-Eu(1)-S(2)#4 | 82.87(7) |
| S(1)#5-Eu(1)-S(1)#6 | 152.50(5) | S(1)#1-Eu(1)-S(2)#3 | 145.22(3) | S(1)#4-Eu(1)-S(2)#4 | 62.20(3) |
| S(1)#1-Eu(1)-S(1)#7 | 84.34(19) | S(1)#2-Eu(1)-S(2)#3 | 62.20(3) | S(1)#5-Eu(1)-S(2)#4 | 62.20(3) |
| S(1)#2-Eu(1)-S(1)#7 | 102.21(19) | S(1)#3-Eu(1)-S(2)#3 | 62.20(3) | S(1)#6-Eu(1)-S(2)#4 | 145.22(3) |
| S(1)#3-Eu(1)-S(1)#7 | 93.238(11) | S(1)#4-Eu(1)-S(2)#3 | 76.66(7) | S(1)#7-Eu(1)-S(2)#4 | 145.22(3) |
| S(1)#4-Eu(1)-S(1)#7 | 152.50(5) | S(1)#5-Eu(1)-S(2)#3 | 82.87(7) | S(1)-Eu(1)-S(2)#4 | 76.66(7) |
| S(1)#5-Eu(1)-S(1)#7 | 150.95(7) | S(1)#6-Eu(1)-S(2)#3 | 76.66(7) | S(2)-Eu(1)-S(2)#4 | 123.89(2) |
| S(1)#6-Eu(1)-S(1)#7 | 9.2(2) | S(1)#7-Eu(1)-S(2)#3 | 82.87(7) | S(2)#3-Eu(1)-S(2)#4 | 123.89(2) |
| S(1)#1-Eu(1)-S(1) | 9.2(2) | S(1)-Eu(1)-S(2)#3 | 145.22(3) | S(2)#7-Eu(1)-S(2)#4 | 83.39(3) |

Symmetry transformations used to generate equivalent atoms: *#1, y+1/2,x-1/2,z; #2, -y+1,-x+1,z; #3, -x+3/2,-y+1/2,z; #4, y+1/2,-x+1,-z+1/2; #5, x,-y+1/2,-z+1/2; #6, -x+3/2,y,-z+1/2; #7, -y+1,x-1/2,-z+1/2; #8, -x+1,-y,-z+1.*

**Table S7** Selected bond distances (Å) and angles (°) for **Gd-S-MOF**.

| | | | | | |
|---|---|---|---|---|---|
| Gd(1)-S(1) | 2.817(2) | Gd(1)-S(1)#4 | 2.817(2) | Gd(1)-S(2)#2 | 2.8826(13) |
| Gd(1)-S(1)#1 | 2.817(2) | Gd(1)-S(1)#5 | 2.817(2) | Gd(1)-S(2)#5 | 2.8826(13) |
| Gd(1)-S(1)#2 | 2.817(2) | Gd(1)-S(1)#6 | 2.817(2) | Gd(1)-S(2)#7 | 2.8826(13) |
| Gd(1)-S(1)#3 | 2.817(2) | Gd(1)-S(1)#7 | 2.817(2) | Gd(1)-S(2) | 2.8826(13) |
| S(1)-Gd(1)-S(1)#1 | 7.0(12) | S(1)#1-Gd(1)-S(1)#7 | 86.5(11) | S(2)#2-Gd(1)-S(2)#5 | 123.77(3) |
| S(1)-Gd(1)-S(1)#2 | 152.41(7) | S(1)#2-Gd(1)-S(1)#7 | 93.260(16) | S(1)-Gd(1)-S(2)#7 | 82.1(4) |
| S(1)#1-Gd(1)-S(1)#2 | 151.5(3) | S(1)#3-Gd(1)-S(1)#7 | 100.1(11) | S(1)#1-Gd(1)-S(2)#7 | 77.4(4) |
| S(1)-Gd(1)-S(1)#3 | 151.5(3) | S(1)#4-Gd(1)-S(1)#7 | 7.0(12) | S(1)#2-Gd(1)-S(2)#7 | 77.4(4) |
| S(1)#1-Gd(1)-S(1)#3 | 152.41(7) | S(1)#5-Gd(1)-S(1)#7 | 152.41(7) | S(1)#3-Gd(1)-S(2)#7 | 82.1(4) |
| S(1)#2-Gd(1)-S(1)#3 | 7.0(12) | S(1)#6-Gd(1)-S(1)#7 | 151.5(3) | S(1)#4-Gd(1)-S(2)#7 | 62.08(5) |
| S(1)-Gd(1)-S(1)#4 | 100.1(11) | S(1)-Gd(1)-S(2)#2 | 145.46(7) | S(1)#5-Gd(1)-S(2)#7 | 145.46(7) |
| S(1)#1-Gd(1)-S(1)#4 | 93.260(16) | S(1)#1-Gd(1)-S(2)#2 | 145.46(7) | S(1)#6-Gd(1)-S(2)#7 | 145.46(7) |
| S(1)#2-Gd(1)-S(1)#4 | 86.5(11) | S(1)#2-Gd(1)-S(2)#2 | 62.08(5) | S(1)#7-Gd(1)-S(2)#7 | 62.08(5) |
| S(1)#3-Gd(1)-S(1)#4 | 93.260(17) | S(1)#3-Gd(1)-S(2)#2 | 62.08(5) | S(2)#2-Gd(1)-S(2)#7 | 123.77(3) |
| S(1)-Gd(1)-S(1)#5 | 93.261(16) | S(1)#4-Gd(1)-S(2)#2 | 77.4(4) | S(2)#5-Gd(1)-S(2)#7 | 83.59(5) |
| S(1)#1-Gd(1)-S(1)#5 | 100.1(11) | S(1)#5-Gd(1)-S(2)#2 | 77.4(4) | S(1)-Gd(1)-S(2) | 62.08(5) |
| S(1)#2-Gd(1)-S(1)#5 | 93.260(16) | S(1)#6-Gd(1)-S(2)#2 | 82.1(4) | S(1)#1-Gd(1)-S(2) | 62.08(5) |
| S(1)#3-Gd(1)-S(1)#5 | 86.5(11) | S(1)#7-Gd(1)-S(2)#2 | 82.1(4) | S(1)#2-Gd(1)-S(2) | 145.46(7) |
| S(1)#4-Gd(1)-S(1)#5 | 151.5(3) | S(1)-Gd(1)-S(2)#5 | 77.4(4) | S(1)#3-Gd(1)-S(2) | 145.46(7) |
| S(1)-Gd(1)-S(1)#6 | 86.5(11) | S(1)#1-Gd(1)-S(2)#5 | 82.1(4) | S(1)#4-Gd(1)-S(2) | 82.1(4) |
| S(1)#1-Gd(1)-S(1)#6 | 93.260(17) | S(1)#2-Gd(1)-S(2)#5 | 82.1(4) | S(1)#5-Gd(1)-S(2) | 82.1(4) |
| S(1)#2-Gd(1)-S(1)#6 | 100.1(11) | S(1)#3-Gd(1)-S(2)#5 | 77.4(4) | S(1)#6-Gd(1)-S(2) | 77.4(4) |
| S(1)#3-Gd(1)-S(1)#6 | 93.260(17) | S(1)#4-Gd(1)-S(2)#5 | 145.46(7) | S(1)#7-Gd(1)-S(2) | 77.4(4) |
| S(1)#4-Gd(1)-S(1)#6 | 152.41(7) | S(1)#5-Gd(1)-S(2)#5 | 62.08(5) | S(2)#2-Gd(1)-S(2) | 83.59(5) |
| S(1)#5-Gd(1)-S(1)#6 | 7.0(12) | S(1)#6-Gd(1)-S(2)#5 | 62.08(5) | S(2)#5-Gd(1)-S(2) | 123.77(3) |
| S(1)-Gd(1)-S(1)#7 | 93.258(16) | S(1)#7-Gd(1)-S(2)#5 | 145.46(7) | S(2)#7-Gd(1)-S(2) | 123.77(3) |

Symmetry transformations used to generate equivalent atoms: *#1, y+1/2,x-1/2,z; #2, -x+3/2,-y+1/2,z; #3 -y+1,-x+1,z; #4, -x+3/2,y,-z+1/2; #5, y+1/2,-x+1,-z+1/2; #6, x,-y+1/2,-z+1/2; #7, -y+1,x-1/2,-z+1/2; #8, -x+1,-y,-z+1*.

**Table S8** Selected bond distances (Å) and angles (°) for **Tb-S-MOF**.

| | | | | | |
|---|---|---|---|---|---|
| Tb(1)-S(1)#1 | 2.802(4) | Tb(1)-S(1)#5 | 2.802(4) | Tb(1)-S(2) | 2.865(2) |
| Tb(1)-S(1)#2 | 2.802(4) | Tb(1)-S(1)#6 | 2.802(4) | Tb(1)-S(2)#2 | 2.865(2) |
| Tb(1)-S(1)#3 | 2.802(4) | Tb(1)-S(1)#7 | 2.802(4) | Tb(1)-S(2)#5 | 2.865(2) |
| Tb(1)-S(1)#4 | 2.802(4) | Tb(1)-S(1) | 2.802(4) | Tb(1)-S(2)#4 | 2.865(2) |
| S(1)#1-Tb(1)-S(1)#2 | 150.8(3) | S(1)#2-Tb(1)-S(1) | 152.04(13) | S(2)-Tb(1)-S(2)#2 | 83.30(9) |
| S(1)#1-Tb(1)-S(1)#3 | 152.04(13) | S(1)#3-Tb(1)-S(1) | 150.8(3) | S(1)#1-Tb(1)-S(2)#5 | 76.8(3) |
| S(1)#2-Tb(1)-S(1)#3 | 8.4(9) | S(1)#4-Tb(1)-S(1) | 93.35(3) | S(1)#2-Tb(1)-S(2)#5 | 76.8(3) |
| S(1)#1-Tb(1)-S(1)#4 | 101.5(9) | S(1)#5-Tb(1)-S(1) | 93.35(3) | S(1)#3-Tb(1)-S(2)#5 | 82.4(3) |
| S(1)#2-Tb(1)-S(1)#4 | 93.35(3) | S(1)#6-Tb(1)-S(1) | 101.5(9) | S(1)#4-Tb(1)-S(2)#5 | 145.45(9) |
| S(1)#3-Tb(1)-S(1)#4 | 85.2(9) | S(1)#7-Tb(1)-S(1) | 85.2(9) | S(1)#5-Tb(1)-S(2)#5 | 62.45(8) |
| S(1)#1-Tb(1)-S(1)#5 | 85.2(9) | S(1)#1-Tb(1)-S(2) | 62.45(8) | S(1)#6-Tb(1)-S(2)#5 | 62.45(8) |
| S(1)#2-Tb(1)-S(1)#5 | 93.35(3) | S(1)#2-Tb(1)-S(2) | 145.45(9) | S(1)#7-Tb(1)-S(2)#5 | 145.45(9) |
| S(1)#3-Tb(1)-S(1)#5 | 101.5(9) | S(1)#3-Tb(1)-S(2) | 145.45(9) | S(1)-Tb(1)-S(2)#5 | 82.4(3) |
| S(1)#4-Tb(1)-S(1)#5 | 152.04(13) | S(1)#4-Tb(1)-S(2) | 82.4(3) | S(2)-Tb(1)-S(2)#5 | 123.94(6) |
| S(1)#1-Tb(1)-S(1)#6 | 93.35(3) | S(1)#5-Tb(1)-S(2) | 76.8(3) | S(2)#2-Tb(1)-S(2)#5 | 123.94(6) |
| S(1)#2-Tb(1)-S(1)#6 | 85.2(9) | S(1)#6-Tb(1)-S(2) | 82.4(3) | S(1)#1-Tb(1)-S(2)#4 | 82.4(3) |
| S(1)#3-Tb(1)-S(1)#6 | 93.35(3) | S(1)#7-Tb(1)-S(2) | 76.8(3) | S(1)#2-Tb(1)-S(2)#4 | 82.4(3) |
| S(1)#4-Tb(1)-S(1)#6 | 150.8(3) | S(1)-Tb(1)-S(2) | 62.45(8) | S(1)#3-Tb(1)-S(2)#4 | 76.8(3) |
| S(1)#5-Tb(1)-S(1)#6 | 8.4(9) | S(1)#1-Tb(1)-S(2)#2 | 145.45(9) | S(1)#4-Tb(1)-S(2)#4 | 62.45(8) |
| S(1)#1-Tb(1)-S(1)#7 | 93.35(3) | S(1)#2-Tb(1)-S(2)#2 | 62.45(8) | S(1)#5-Tb(1)-S(2)#4 | 145.45(9) |
| S(1)#2-Tb(1)-S(1)#7 | 101.5(9) | S(1)#3-Tb(1)-S(2)#2 | 62.45(8) | S(1)#6-Tb(1)-S(2)#4 | 145.45(9) |
| S(1)#3-Tb(1)-S(1)#7 | 93.35(3) | S(1)#4-Tb(1)-S(2)#2 | 76.8(3) | S(1)#7-Tb(1)-S(2)#4 | 62.45(8) |
| S(1)#4-Tb(1)-S(1)#7 | 8.4(9) | S(1)#5-Tb(1)-S(2)#2 | 82.4(3) | S(1)-Tb(1)-S(2)#4 | 76.8(3) |
| S(1)#5-Tb(1)-S(1)#7 | 150.8(3) | S(1)#6-Tb(1)-S(2)#2 | 76.8(3) | S(2)-Tb(1)-S(2)#4 | 123.94(6) |
| S(1)#6-Tb(1)-S(1)#7 | 152.04(13) | S(1)#7-Tb(1)-S(2)#2 | 82.4(3) | S(2)#2-Tb(1)-S(2)#4 | 123.94(6) |
| S(1)#1-Tb(1)-S(1) | 8.4(9) | S(1)-Tb(1)-S(2)#2 | 145.45(9) | S(2)#5-Tb(1)-S(2)#4 | 83.30(9) |

Symmetry transformations used to generate equivalent atoms: *#1, y+1/2,x-1/2,z; #2, -x+3/2,-y+1/2,z; #3, -y+1,-x+1,z; #4, y+1/2,-x+1,-z+1/2; #5, -y+1,x-1/2,-z+1/2; #6, -x+3/2,y,-z+1/2; #7, x,-y+1/2,-z+1/2; #8, -x+1,-y,-z+1*.

**DFT Calculations**

The geometrical configuration optimization and frequency calculations of the sulphur-donor ligand ($Na_2$(pipzdtc)) and Oxygen-donor ligand (piperazinium carboxamide trihydrate: $PZH^+CO^{2-}\cdot 3H_2O$[1]) were conducted by density functional methods using B3LYP[2]/6-31G** basis set. HOMO, HOMO-1, LUMO, LUMO+1 orbitals were calculated to obtain the gap energy of the ligands. These DFT calculations were carried out with the Gaussian 09[3] program package.

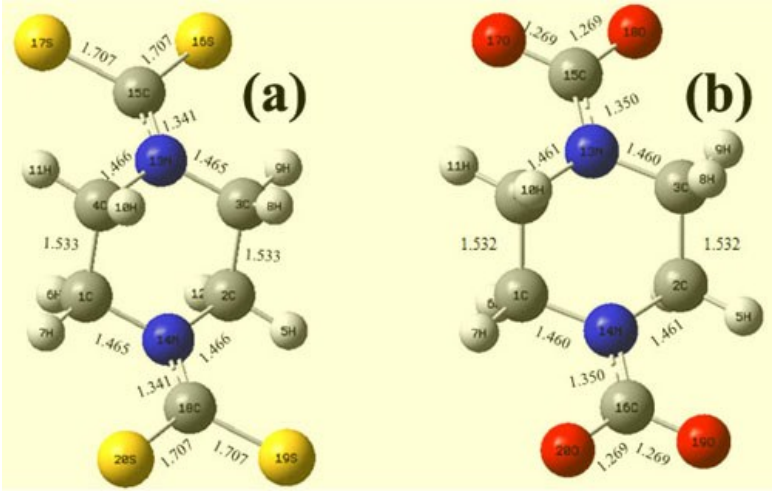



**Fig. S4** Optimized geometries of the free pipzdtc$^{2-}$ (a) and PZCO$^{2-}$ (b) ligands denoting some bond lengths (Å) around the piperazine ring.

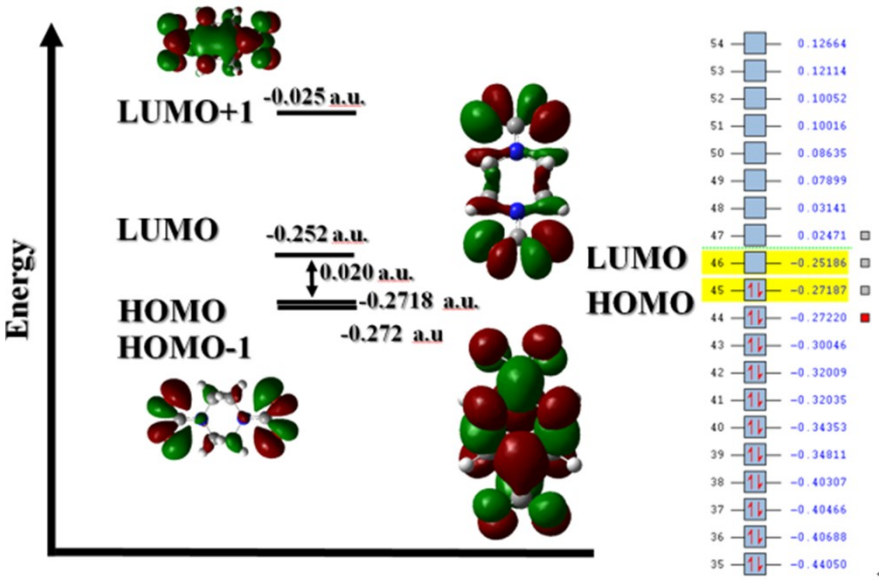



**Fig. S5** Calculated frontier orbitals of the free piperazinium carboxamide trihydrate: PZCO[2] ligand.

**Table S9** CIE coordinates of **$Sm_{1-x}Eu_x$-S-MOFs.**

| Eu% | CIE x | CIE y |
|---|---|---|
| 10 | 0.377 | 0.329 |
| 20 | 0.337 | 0.32 |
| 30 | 0.3236 | 0.3135 |
| 40 | 0.3167 | 0.3162 |
| 50 | 0.31 | 0.3143 |
| 60 | 0.3071 | 0.3164 |
| 70 | 0.3114 | 0.3199 |
| 80 | 0.3029 | 0.3125 |
| 90 | 0.2979 | 0.3009 |

**Table S10** CIE coordinates of **$Sm_{1-y}Tb_y$-S-MOFs.**

| Tb% | CIE x | CIE y |
|---|---|---|
| 10 | 0.3386 | 0.2813 |
| 20 | 0.3639 | 0.2954 |
| 30 | 0.3583 | 0.2933 |
| 40 | 0.3292 | 0.2728 |
| 50 | 0.3276 | 0.2788 |
| 60 | 0.3414 | 0.2836 |
| 70 | 0.2817 | 0.2492 |
| 80 | 0.2946 | 0.2675 |
| 90 | 0.2297 | 0.2634 |

**Table S11** CIE coordinates of **$Sm_{1-x-y}Eu_xTb_y$-S-MOFs.**

| Eu% | Tb% | CIE x | CIE y |
|---|---|---|---|
| 5 | 35 | 0.3755 | 0.3241 |
| 10 | 30 | 0.3484 | 0.3087 |
| 15 | 25 | 0.3301 | 0.3034 |
| 20 | 20 | 0.3316 | 0.3041 |
| 25 | 15 | 0.3224 | 0.3062 |
| 30 | 10 | 0.3204 | 0.3088 |
| 35 | 5 | 0.3077 | 0.2985 |

**Table S12** Partial crystal data for **$Sm_{1-z}Nd_z$-S-MOFs.**

| Nd(%) | a | b | c | α | β | γ | V |
|---|---|---|---|---|---|---|---|
| 0 | 16.37 | 16.37 | 6.72 | 90.00 | 90.00 | 90.00 | 1800 |
| 20 | 16.38 | 16.38 | 6.71 | 90.00 | 90.00 | 90.00 | 1798 |
| 30 | 16.37 | 16.37 | 6.70 | 90.00 | 90.00 | 90.00 | 1796 |
| 40 | 16.39 | 16.39 | 6.70 | 90.00 | 90.00 | 90.00 | 1798 |
| 50 | 16.38 | 16.38 | 6.70 | 90.00 | 90.00 | 90.00 | 1799 |
| 60 | 16.35 | 16.35 | 6.68 | 90.00 | 90.00 | 90.00 | 1786 |
| 70 | 16.40 | 16.40 | 6.69 | 90.00 | 90.00 | 90.00 | 1800 |
| 80 | 16.37 | 16.37 | 6.68 | 90.00 | 90.00 | 90.00 | 1790 |
| 90 | 16.41 | 16.41 | 6.68 | 90.00 | 90.00 | 90.00 | 1799 |
| 100 | 16.37 | 16.37 | 6.69 | 90.00 | 90.00 | 90.00 | 1794 |

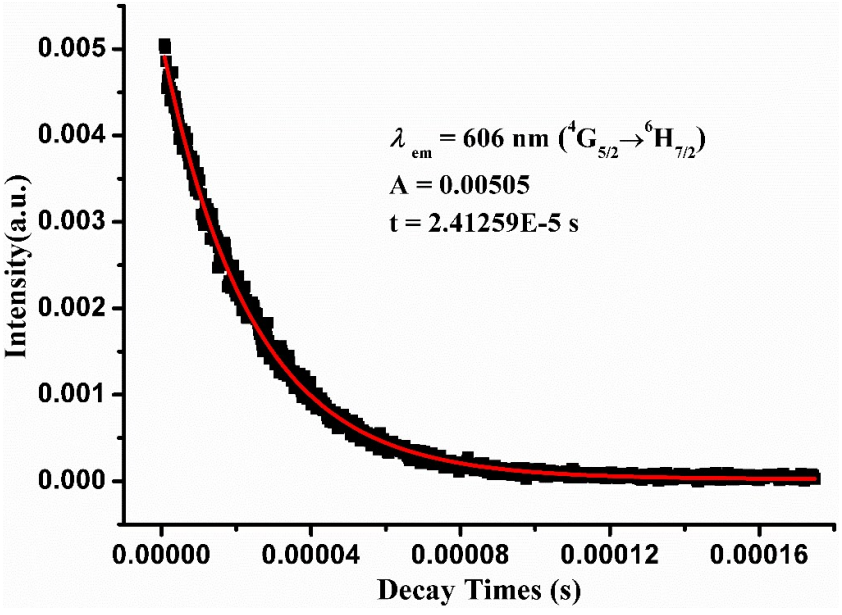



**Fig. S6** Room temperature emission decay curve of **Sm-S-MOF**.