Electronic Supplementary Information for Dalton Transactions


Supporting Information

For

# Synthesis, crystal structures, luminescent and magnetic properties of homodinuclear lanthanide complexes with a flexible tripodal carboxylate ligand

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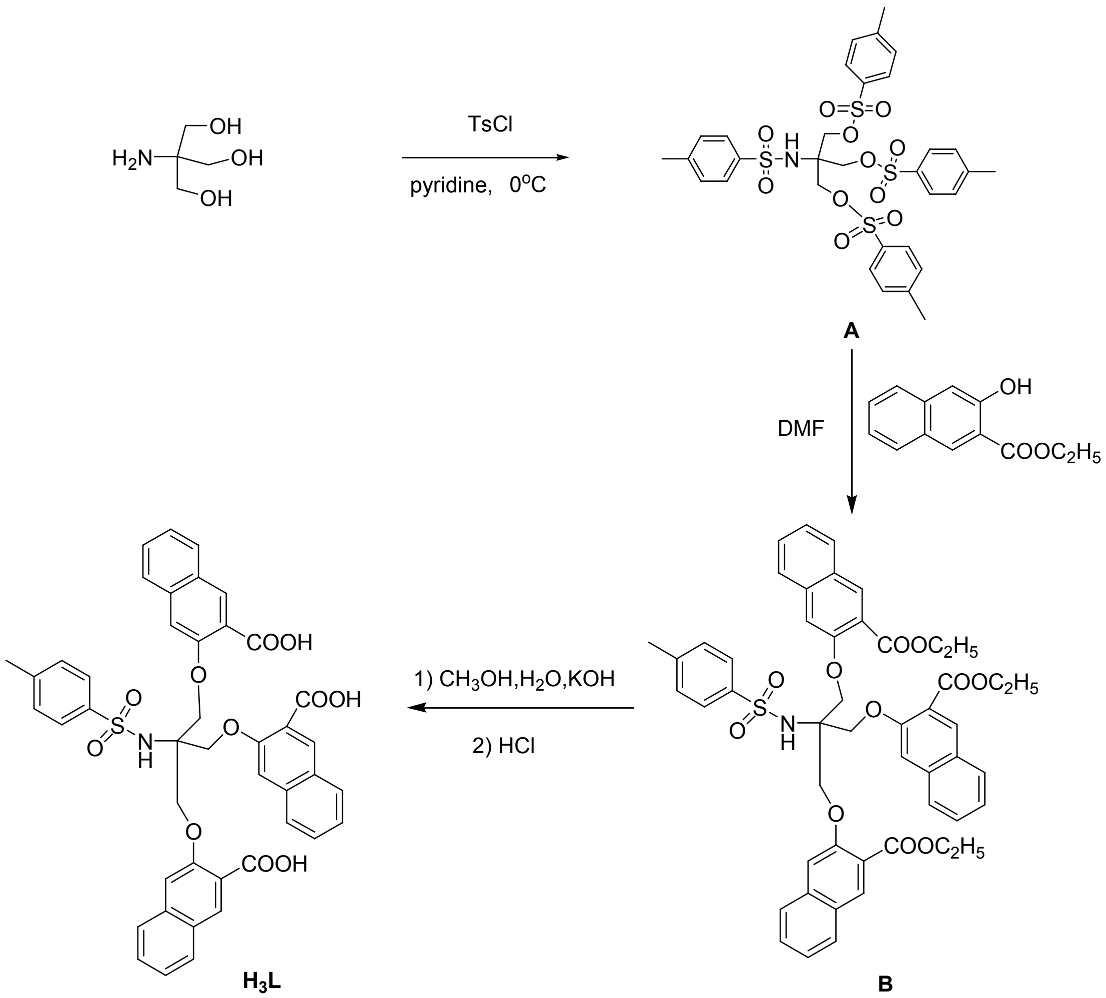



**Scheme S1** Synthetic procedure for **$H_3L$**.

**Synthesis of ligand:** The ligand (**$H_3L$**) was readily prepared according to Scheme S1. Ethyl 3-hydroxynaphthalene-2-carboxylate (2.0 g, 9.2 mmol) was added to the dry DMF solution (5 mL), $K_2CO_3$ (2.5 g, 18 mmol) was added and afterwards, the mixture was stirred and heated at 95 °C for 8 hours, then a solution of compound **A**[21] (2.1 g, 2.8 mmol) in dry DMF (25 mL) was added dropwise to the above solution over 30 min. The mixture was stirred and maintained at 85 °C for 2 days. When cooled, DMF was removed by evaporation and the crude residue was purified through silica gel chromatography (Petroleum ether / AcOEt = 6:1 to 3:1) to afford the pale yellow solid **B**. Yield, 1.0 g (40%). m. p.: 92-94 °C. Anal. Calcd (Found) for $C_{50}H_{47}NO_{11}S$

(%): C, 69.03 (69.21); H, 5.45 (5.50); N, 1.61 (1.56). $^1$H NMR ($CDCl_3$, 400 MHz, ppm): $\delta$ 8.33 (s, 3H, Ar–H), 7.81 (d, *J* = 8.0 Hz, 3H, Ar–H), 7.70 (d, *J* = 8.4 Hz, 3H, Ar–H), 7.64 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.53-7.49 (m, 3H, Ar–H), 7.40-7.36 (m, 3H, Ar–H), 7.21 (s, 3H, Ar–H), 6.99 (s, 1H, –NH–), 6.65(d, *J* = 8.0 Hz, 2H, Ar–H), 4.78(s, 6H, $–CH_2O–$), 4.34 (q, *J* = 7.2 Hz, 6H, $–CH_2–$), 1.88 (s, 3H, $–CH_3$), 1.32(t, *J* = 7.2Hz, 9H, $–CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz, ppm): $\delta$ 166.0 (3C), 154.4 (3C), 142.8, 139.2, 136.2 (3C), 133.5 (3C), 129.0 (2C), 128.9 (3C), 128.7 (3C), 127.9 (3C), 126.8 (3C), 126.6 (2C), 124.8 (3C), 121.5 (3C), 108.6 (3C), 67.6 (3C), 61.9, 61.3 (3C), 21.2, 14.6 (3C). ESI–MS: *m*/*z* 870.8 ($[M + H]^+$). To a solution of KOH (3.1 g, 22 mmol) in methanol (75 mL) and water (25 mL), **B** (2.2 g, 2.5 mmol) was added and refluxed for 12 h. After cooled to room temperature, concentrated HCl (12 mL) was added to the mixture to yield pale yellow solid that was filtered, washed with water 5 × 50 mL) and dried to obtain the pale yellow pure product **$H_3L$**. Yield, 2.0 g (89%). m. p.: 164-167 $^o$C. Anal. Calcd (Found) for $C_{44}H_{35}NO_{11}S$ (%): C, 67.25 (67.41); H, 4.49 (4.36); N, 1.78 (1.85). $^1$H NMR (DMSO, 400 MHz, ppm): $\delta$ 12.92 (s, 3H, –COOH), 8.28 (s, 3H, Ar–H), 7.94 (d, *J* = 8.0 Hz, 3H, Ar–H), 7.83 (d, *J* = 8.0Hz, 3H, Ar–H), 7.62 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.57-7.53 (m, 3H, Ar–H), 7.42-7.37 (m, 3H, Ar–H), 7.28(s, 1H, –NH–), 6.69 (d, *J* = 8.4 Hz, 2H, Ar–H), 4.64(s, 6H, $–CH_2O–$), 1.65(s, 3H, $–CH_3$). $^{13}$C NMR (DMSO, 100 MHz, ppm): $\delta$ 167.3 (3C), 153.9 (3C), 141.8, 139.9, 135.6 (3C), 132.1 (3C), 128.9 (2C), 128.7 (3C), 128.4 (3C), 127.4 (3C), 126.7 (3C), 126.0 (2C), 124.6 (3C), 122.8 (3C), 107.8 (3C), 67.4 (3C), 61.3, 20.5. HRMS (ESI) *m/z* obsd 786.2004 ([M + H]$^+$), calcd 785.1913 for $C_{32}H_{29}NO_{11}S$.

**Table S1** Representative bond lengths (Å) and angles (˚) for [$La_2$ $L_2(DMF)_4$]·4DMF

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| La(1)-O(1) | 2.505(5) | La(1)-O(2) | 2.543(4) | La(1)-O(3) | 2.562(4) | La(1)-O(4) | 2.531(4) |
| La(1)-O(5) | 2.485(4) | La(1)-O(5)#1 | 2.723(4) | La(1)-O(6)#1 | 2.612(4) | La(1)-O(7) | 2.521(4) |
| La(1)-O(8)#1 | 2.513(4) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O(5)-La(1)-O(1) | 150.13(14) | O(5)-La(1)-O(8)#1 | 71.22(13) | O(1)-La(1)-O(8)#1 | 138.35(14) |
| O(5)-La(1)-O(7) | 77.65(13) | O(1)-La(1)-O(7) | 76.37(15) | O(8)#1-La(1)-O(7) | 132.01(13) |
| O(5)-La(1)-O(4) | 78.94(13) | O(1)-La(1)-O(4) | 78.40(15) | O(8)#1-La(1)-O(4) | 134.90(14) |
| O(5)-La(1)-O(2) | 136.13(15) | O(1)-La(1)-O(2) | 71.04(16) | O(8)#1-La(1)-O(2) | 72.84(14) |
| O(7)-La(1)-O(2) | 146.22(15) | O(4)-La(1)-O(2) | 111.18(15) | O(5)-La(1)-O(3) | 81.66(13) |
| O(1)-La(1)-O(3) | 98.81(15) | O(8)#1-La(1)-O(3) | 90.88(14) | O(7)-La(1)-O(3) | 119.92(13) |
| O(4)-La(1)-O(3) | 51.16(13) | O(2)-La(1)-O(3) | 74.56(14) | O(5)-La(1)-O(6)#1 | 120.40(12) |
| O(1)-La(1)-O(6)#1 | 72.11(14) | O(8)#1-La(1)-O(6)#1 | 79.63(14) | O(7)-La(1)-O(6)#1 | 85.98(13) |
| O(4)-La(1)-O(6)#1 | 145.45(14) | O(2)-La(1)-O(6)#1 | 75.92(14) | O(3)-La(1)-O(6)#1 | 150.46(13) |
| O(1)-La(1)-O(5)#1 | 109.36(14) | O(8)#1-La(1)-O(5)#1 | 70.53(13) | O(7)-La(1)-O(5)#1 | 65.62(12) |
| O(4)-La(1)-O(5)#1 | 130.64(12) | O(2)-La(1)-O(5)#1 | 117.46(13) | O(3)-La(1)-O(5)#1 | 151.16(13) |
| O(6)#-La(1)-O(5)#1 | 49.06(12) | O(5)-La(1)-O(5)#1 | 72.24(14) | O(7)-La(1)-O(4) | 69.66(14) |

Symmetry transformations used to generate equivalent atoms: #1 1–x, -y, 2-z

**Table S2** Representative bond lengths (Å) and angles (˚) for [$Nd_2$ $L_2(DMF)_4$]·4DMF

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Nd(1)-O(1) | 2.451(5) | Nd (1)-O(2) | 2.487(5) | Nd(1)-O(3)#1 | 2.468(4) | Nd(1)-O(4)#1 | 2.510(4) |
| Nd(1)-O(5) | 2.683(4) | Nd(1)-O(5)#1 | 2.428(4) | Nd(1)-O(6) | 2.545(4) | Nd(1)-O(7)#1 | 2.466(4) |
| Nd(1)-O(8) | 2.460(4) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O(5)#1-Nd(1)-O(1) | 149.70(15) | O(5)#1-Nd(1)-O(8) | 71.49(14) | O(1)-Nd(1)-O(8) | 138.67(15) |
| O(5)#1-Nd(1)-O(7)#1 | 78.46(14) | O(1)-Nd(1)-O(7)#1 | 75.85(15) | O(8)-Nd(1)-O(7)#1 | 132.70(14) |
| O(5)#1-Nd(1)-O(3)#1 | 78.10(14) | O(1)-Nd(1)-O(3)#1 | 78.10(15) | O(8)-Nd(1)-O(3)#1 | 134.53(15) |
| O(7)#1-Nd(1)-O(3)#1 | 69.62(14) | O(5)#1-Nd(1)-O(2) | 136.45(15) | O(8)-Nd(1)-O(2) | 73.05(15) |
| O(7)#1-Nd(1)-O(2) | 145.09(15) | O(3)#1-Nd(1)-O(2) | 111.45(15) | O(5)#1-Nd(1)-O(4)#1 | 81.74(14) |
| O(5)#1-Nd(1)-O(4)#1 | 81.74(14) | O(1)-Nd(1)-O(4)#1 | 98.09(16) | O(8)-Nd(1)-O(4)#1 | 89.90(15) |
| O(7)#1-Nd(1)-O(4)#1 | 121.23(14) | O(3)#1-Nd(1)-O(4)#1 | 52.27(14) | O(2)-Nd(1)-O(4)#1 | 73.71(15) |
| O(5)#1-Nd(1)-O(6) | 121.25(13) | O(1)-Nd(1)-O(6) | 72.30(15) | O(8)-Nd(1)-O(6) | 80.43(14) |
| O(7)#1-Nd(1)-O(6) | 85.19(14) | O(3)#1-Nd(1)-O(6) | 145.02(15) | O(2)-Nd(1)-O(6) | 75.86(14) |
| O(4)#1-Nd(1)-O(6) | 149.56(14) | O(5)#1-Nd(1)-O(5) | 72.07(15) | O(1)-Nd(1)-O(5) | 110.76(15) |
| O(8)-Nd(1)-O(5) | 70.43(13) | O(7)#1-Nd(1)-O(5) | 65.94(13) | O(3)#1-Nd(1)-O(5) | 130.15(13) |
| O(2)-Nd(1)-O(5) | 117.79(14) | O(4)#1-Nd(1)-O(5) | 151.02(14) | O(6)-Nd(1)-O(5) | 49.91(13) |

Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, -z

**Table S3** Representative bond lengths (Å) and angles (˚) for [$Eu_2$ $L_2(DMF)_4$]·4DMF

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Eu(1)-O(1) | 2.409(3) | Eu(1)-O(2) | 2.464(3) | Eu(1)-O(3) | 2.462(3) | Eu(1)-O(4) | 2.444(3) |
| Eu(1)-O(5) | 2.384(3) | Eu(1)-O(5)#1 | 2.653(3) | Eu(1)-O(6)#1 | 2.507(3) | Eu(1)-O(7) | 2.435(3) |
| Eu(1)-O(8)#1 | 2.415(3) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O(5)-Eu(1)-O(1) | 148.83(10) | O(5)-Eu(1)-O(8)#1 | 72.09(9) | O(1)-Eu(1)-O(8)#1 | 139.00(10) |
| O(5)-Eu(1)-O(7) | 78.09(9) | O(1)-Eu(1)-O(7) | 75.76(11) | O(8)#1-Eu(1)-O(7) | 132.88(9) |
| O(5)-Eu(1)-O(4) | 77.86(10) | O(1)-Eu(1)-O(4) | 77.56(11) | O(8)#1-Eu(1)-O(4) | 134.16(10) |
| O(7)-Eu(1)-O(4) | 70.21(10) | O(5)-Eu(1)-O(3) | 82.09(10) | O(1)-Eu(1)-O(3) | 97.93(11) |
| O(8)#1-Eu(1)-O(3) | 88.77(11) | O(7)-Eu(1)-O(3) | 122.47(10) | O(4)-Eu(1)-O(3) | 52.92(10) |
| O(5)-Eu(1)-O(2) | 137.39(10) | O(4)-Eu(1)-O(6) | 144.69(10) | O(1)-Eu(1)-O(2) | 70.47(11) |
| O(8)#1-Eu(1)-O(2) | 72.88(10) | O(7)-Eu(1)-O(2) | 144.52(11) | O(4)-Eu(1)-O(2) | 111.63(11) |
| O(3)-Eu(1)-O(2) | 73.66(10) | O(5)-Eu(1)-O(6)#1 | 121.03(9) | O(1)-Eu(1)-O(6)#1 | 72.75(10) |
| O(8)#1-Eu(1)-O(6)#1 | 81.13(10) | O(7)-Eu(1)-O(6)#1 | 84.14(10) | O(3)-Eu(1)-O(6)#1 | 149.52(10) |
| O(2)-Eu(1)-O(6)#1 | 75.89(10) | O(5)-Eu(1)-O(5)#1 | 71.38(9) | O(1)-Eu(1)-O(5)#1 | 111.94(10) |
| O(8)#1-Eu(1)-O(5)#1 | 70.31(9) | O(7)-Eu(1)-O(5)#1 | 65.96(9) | O(4)-Eu(1)-O(5)#1 | 130.31(9) |
| O(3)-Eu(1)-O(5)#1 | 150.05(9) | O(2)-Eu(1)-O(5)#1 | 117.52(9) | O(6)#1-Eu(1)-O(5)#1 | 50.13(8) |

Symmetry transformations used to generate equivalent atoms: #1 -x, 1-y, 1-z

**Table S4** Representative bond lengths (Å) and angles (˚) for [$Gd_2$ $L_2(DMF)_4$]·4DMF

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Gd(1)-O(1) | 2.3977(15) | Gd(1)-O(2) | 2.4402(16) | Gd(1)-O(3) | 2.4456(14) | Gd(1)-O(4) | 2.4341(15) |
| Gd(1)-O(5)#1 | 2.6506(13) | Gd(1)-O(5) | 2.3670(14) | Gd(1)-O(6)#1 | 2.4907(14) | Gd(1)-O(7) | 2.4197(13) |
| Gd(1)-O(8)#1 | 2.4052(13) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O(5)-Gd(1)-O(1) | 148.63(5) | O(5)-Gd(1)-O(8)#1 | 72.28(5) | O(1)-Gd(1)-O(8)#1 | 139.03(5) |
| O(5)-Gd(1)-O(7) | 78.40(5) | O(1)-Gd(1)-O(7) | 75.48(5) | O(8)#1-Gd(1)-O(7) | 133.12(5) |
| O(5)-Gd(1)-O(4) | 77.90(5) | O(1)-Gd(1)-O(4) | 77.23(5) | O(8)#1-Gd(1)-O(4) | 134.20(5) |
| O(7)-Gd(1)-O(4) | 70.48(5) | O(5)-Gd(1)-O(2) | 137.47(5) | O(1)-Gd(1)-O(2) | 70.47(5) |
| O(8)#1-Gd(1)-O(2) | 72.75(5) | O(7)-Gd(1)-O(2) | 144.11(5) | O(4)-Gd(1)-O(2) | 111.56(5) |
| O(5)-Gd(1)-O(3) | 82.11(5) | O(1)-Gd(1)-O(3) | 97.87(5) | O(8)#1-Gd(1)-O(3) | 88.34(5) |
| O(7)-Gd(1)-O(3) | 123.12(5) | O(4)-Gd(1)-O(3) | 53.28(5) | O(2)-Gd(1)-O(3) | 73.45(5) |
| O(5)-Gd(1)-O(6)#1 | 121.42(5) | O(1)-Gd(1)-O(6)#1 | 72.62(5) | O(8)#1-Gd(1)-O(6)#1 | 81.46(5) |
| O(7)-Gd(1)-O(6)#1 | 83.72(5) | O(4)-Gd(1)-O(6)#1 | 144.33(5) | O(2)-Gd(1)-O(6)#1 | 75.72(5) |
| O(3)-Gd(1)-O(6)#1 | 149.15(5) | O(5)-Gd(1)-O(5)#1 | 71.29(5) | O(1)-Gd(1)-O(5)#1 | 112.23(4) |
| O(8)#1-Gd(1)-O(5)#1 | 70.47(4) | O(7)-Gd(1)-O(5)#1 | 65.82(4) | O(4)-Gd(1)-O(5)#1 | 130.28(5) |
| O(1)-Gd(1)-O(5)#1 | 117.62(5) | O(3)-Gd(1)-O(5)#1 | 149.83(5) | O(6)#1-Gd(1)-O(5)#1 | 50.57(5) |

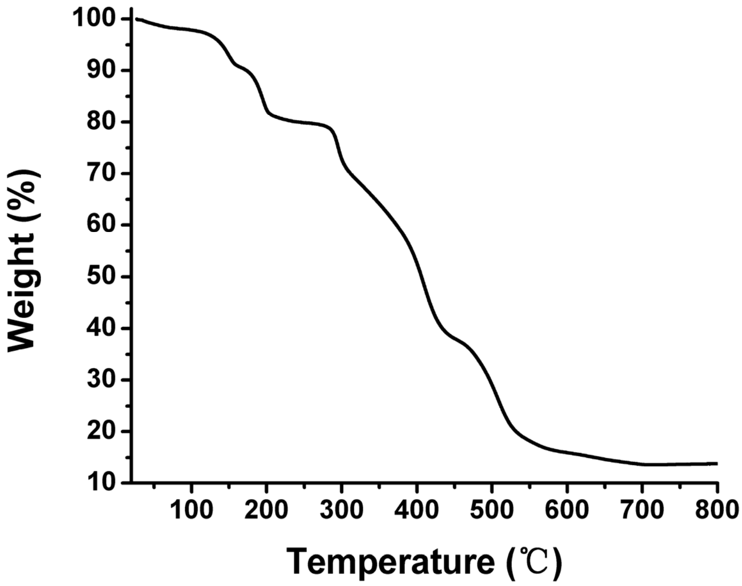
Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, 2-z.

**Table S5** Representative bond lengths (Å) and angles (˚) for[ $Dy_2L_2(DMF)_4$]·4DMF

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Dy(1)-O(1) | 2.374(4) | Dy(1)-O(2) | 2.434(4) | Dy(1)-O(3)#1 | 2.418(4) | Dy(1)-O(4)#1 | 2.419(4) |
| Dy(1)-O(5) | 2.651(4) | Dy(1)-O(5)#1 | 2.332(4) | Dy(1)-O(6) | 2.458(4) | Dy(1)-O(7)#1 | 2.391(4) |
| Dy(1)-O(8) | 2.378(4) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O(5)#1-Dy(1)-O(1) | 148.29(14) | O(5)#1-Dy(1)-O(8) | 72.52(13) | O(1)-Dy(1)-O(8) | 139.14(14) |
| O(5)#1-Dy(1)-O(7)#1 | 78.58(13) | O(1)-Dy(1)-O(7)#1 | 75.35(14) | O(8)-Dy(1)-O(7)#1 | 132.88(13) |
| O(5)#1-Dy(1)-O(3)#1 | 82.04(13) | O(1)-Dy(1)-O(3)#1 | 97.71(15) | O(8)-Dy(1)-O(3)#1 | 88.34(15) |
| O(7)#1-Dy(1)-O(3)#1 | 123.75(14) | O(5)#1-Dy(1)-O(4)#1 | 77.33(14) | O(1)-Dy(1)-O(4)#1 | 77.25(15) |
| O(8)-Dy(1)-O(4)#1 | 134.28(14) | O(7)#1-Dy(1)-O(4)#1 | 70.67(14) | O(3)#1-Dy(1)-O(4)#1 | 53.65(14) |
| O(5)#1-Dy(1)-O(2) | 137.58(14) | O(1)-Dy(1)-O(2) | 70.46(15) | O(8)-Dy(1)-O(2) | 72.87(14) |
| O(7)#1-Dy(1)-O(2) | 143.84(15) | O(3)#1-Dy(1)-O(2) | 73.19(14) | O(4)#1-Dy(1)-O(2) | 111.78(15) |
| O(5)#1-Dy(1)-O(6) | 121.49(13) | O(1)-Dy(1)-O(6) | 72.91(15) | O(8)-Dy(1)-O(6) | 81.36(14) |
| O(7)#1-Dy(1)-O(6) | 83.11(13) | O(3)#1-Dy(1)-O(6) | 149.16(14) | O(4)#1-Dy(1)-O(6) | 144.33.(14) |
| O(2)-Dy(1)-O(6) | 76.01(14) | O(5)#1-Dy(1)-O(5) | 71.08(14) | O(1)-Dy(1)-O(5) | 113.00(14) |
| O(8)-Dy(1)-O(5) | 69.82(13) | O(7)#1-Dy(1)-O(5) | 65.93(12) | O(3)#1-Dy(1)-O(5) | 149.25(13) |
| O(4)#1-Dy(1)-O(5) | 130.06(13) | O(2)-Dy(1)-O(5) | 117.72(13) | O(6)-Dy(1)-O(5) | 50.76(12) |

Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, -z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Weight (%)
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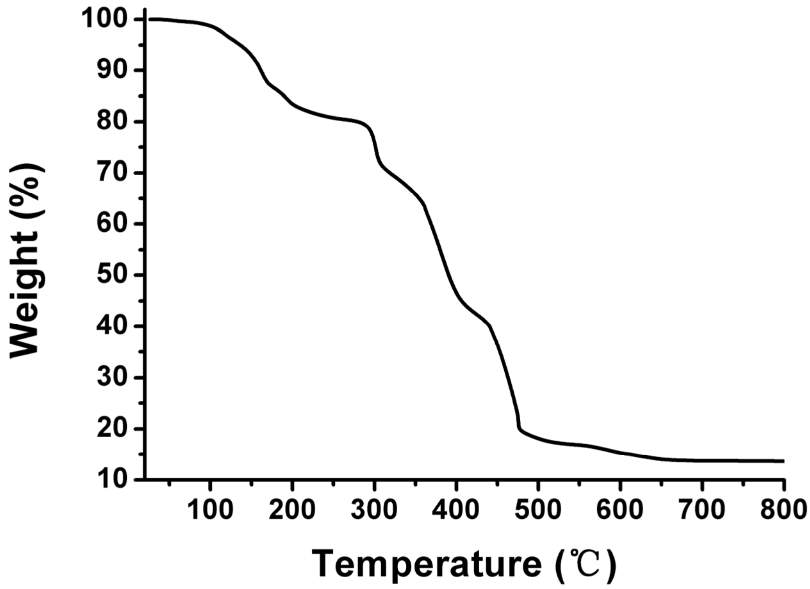
Temperature (℃)

(a)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40
30
20
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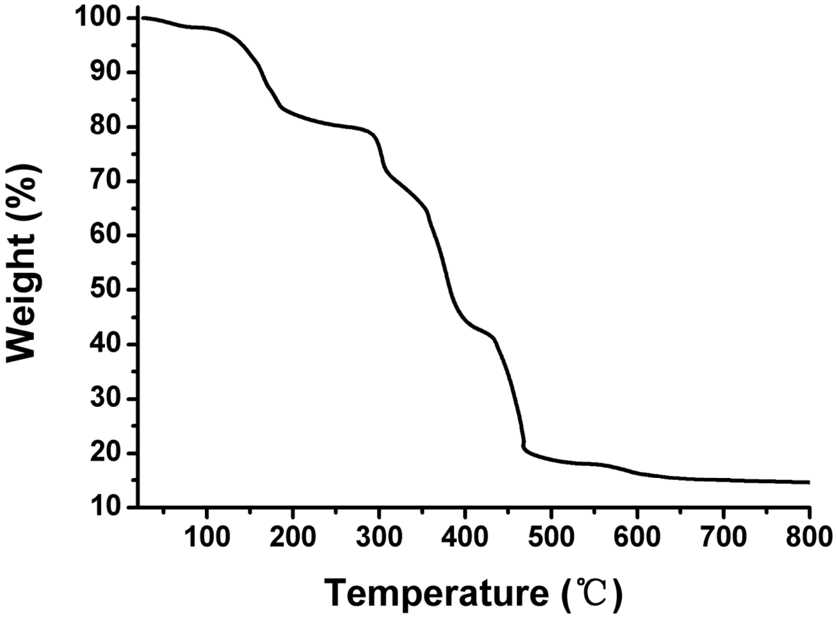
Weight (%)
100 200 300 400 500 600 700 800
Temperature (℃)

(b)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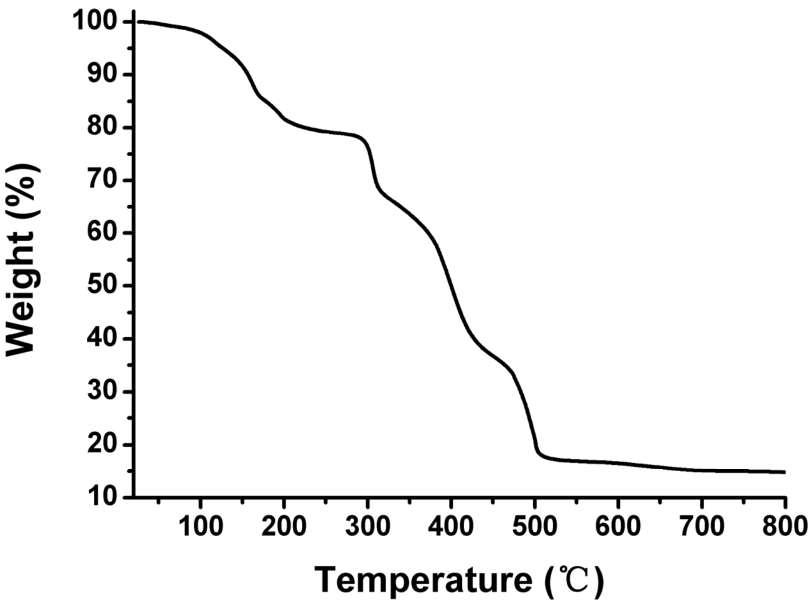
Temperature (℃)

(c)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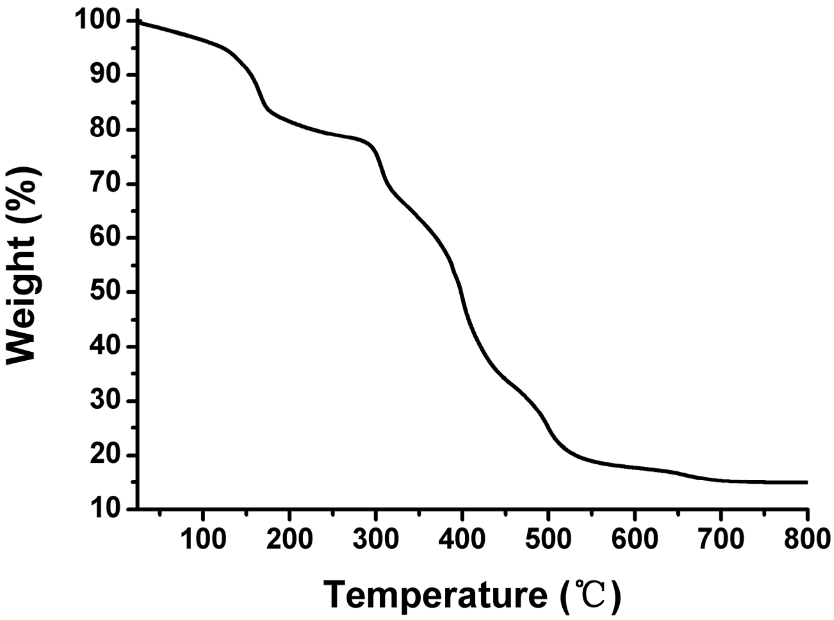
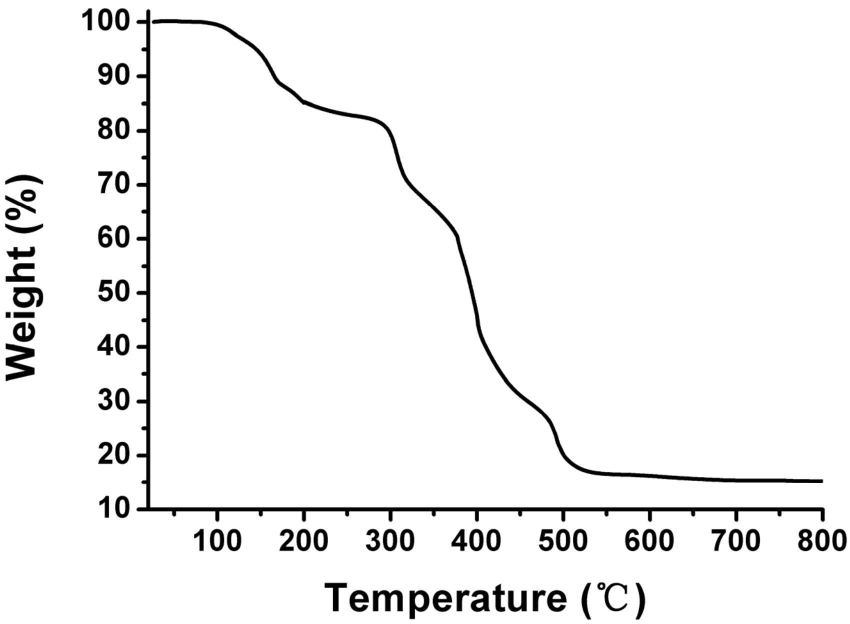
Temperature (℃)

(d)




(e)




(f)

**Fig. S1** TGA curves of complexes **1-6**.

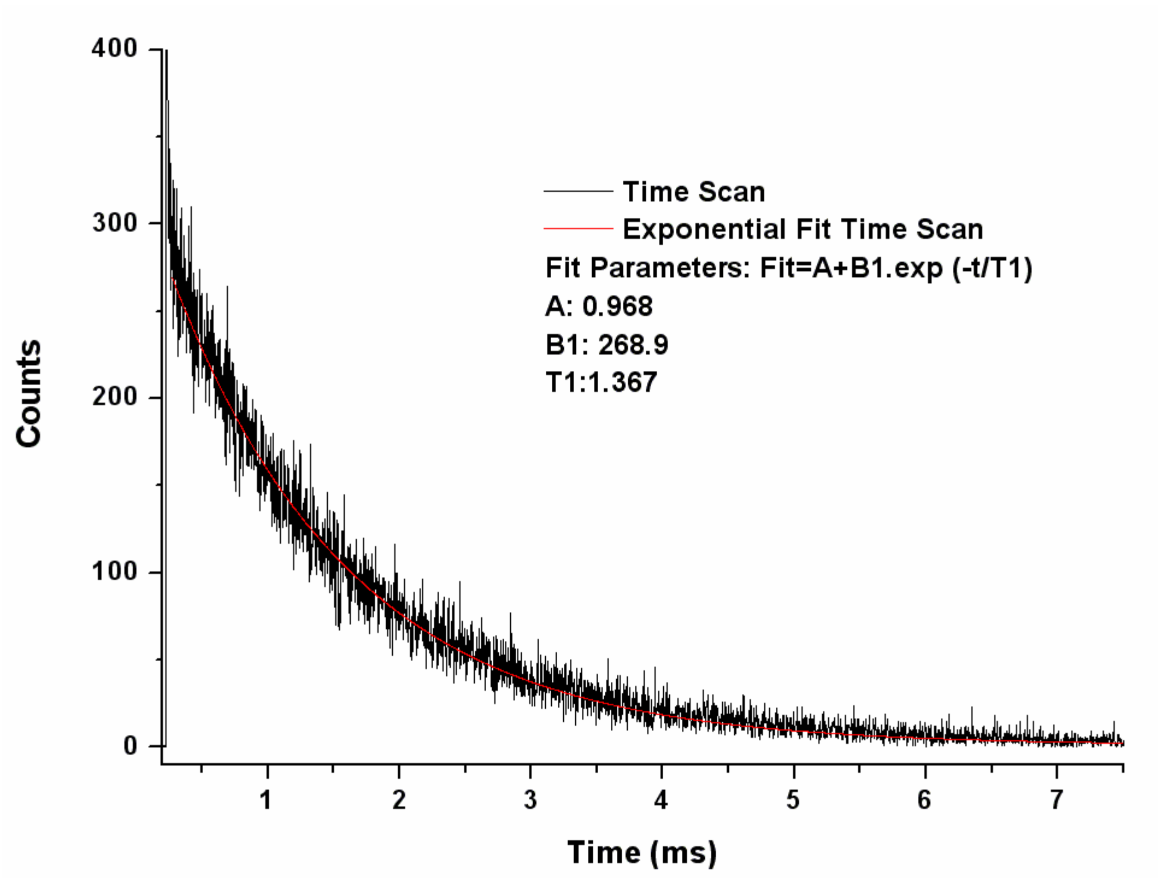



**Fig. S2** The room-temperature solid-state phosphorescence lifetime of Eu (III) complex of ligand $\mathbf{H_3L}$.

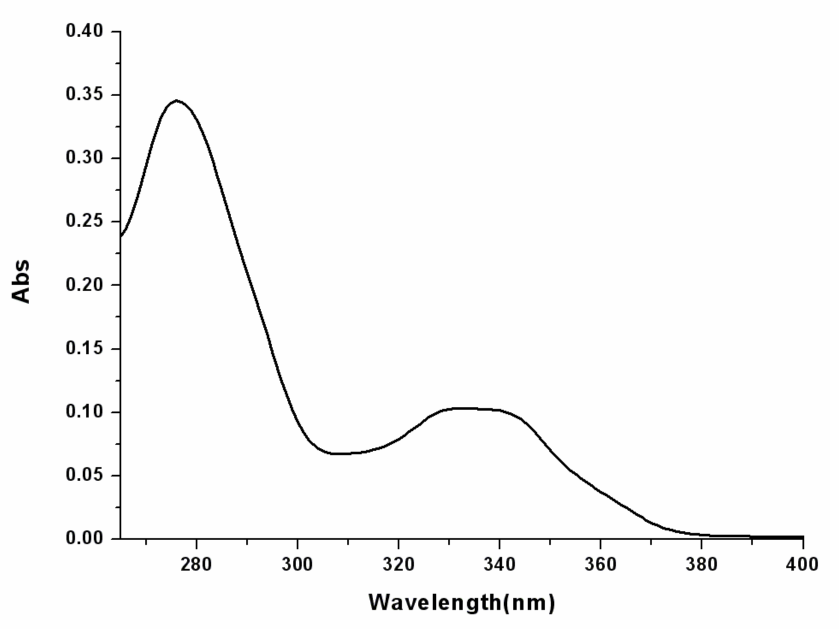



**Fig. S3** Absorption spectra of **$H_3L$** in DMF solution ($2.5 \times 10^{-5}$ M).

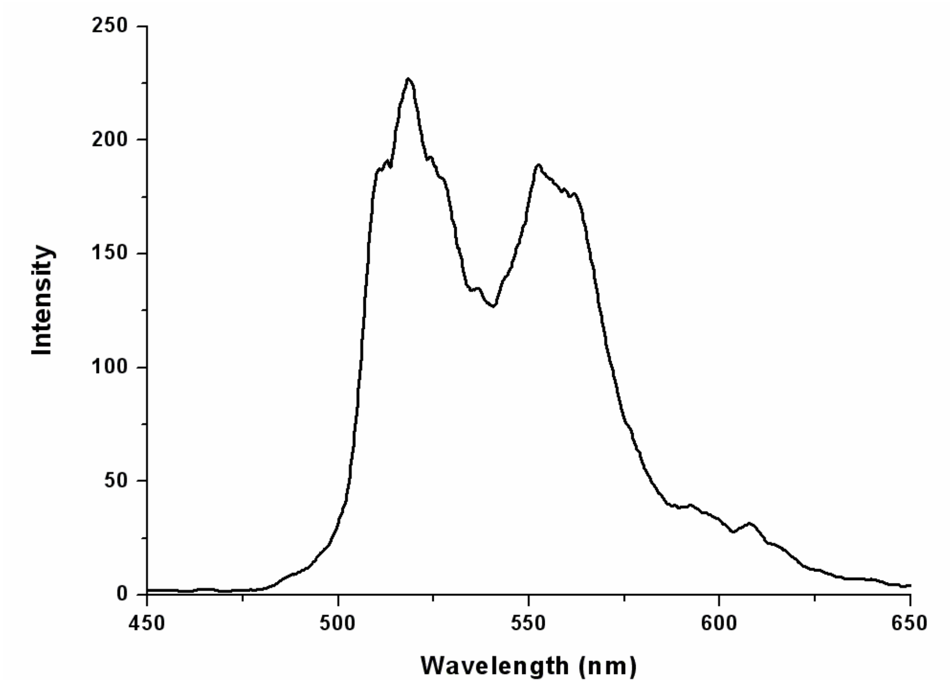



**Fig. S4** Phosphorescence spectrum of Gd(III) complex of ligand $\mathbf{H_3L}$ excited at 358 nm at 77K.