Electronic supplementary information

Luminescence, magnetocaloric effect and single-molecule magnet behavior in lanthanide complexes based on tridentate ligand derived from 8-hydroxyquinoline

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Supplementary Experimental Section.

Synthesis of 2-(2′-benzothiazole)-8-hydroxyquinoline. This procedure is a modification of a previously published synthetic method.[1] 2-Aminothiophenol (1.86 mL, 17.33 mmol) was added to a solution of 8-hydroxyquinoline-2-carboxaldehyde (3.0 g, 17.32 mmol) in DMSO (10 mL, dried over 4 Å molecular sieves) under nitrogen. The mixture was heated and stirred at 130°C for 2 h, and then, the reaction mixture was cooled to room temperature and some of the product precipitated. The solid was filtered and washed with cold ethanol, yielding approximately 2.0 g of pure product. The filtrate was evaporated and then dissolved in ethyl acetate (100 mL). The ethyl acetate solution was washed with brine (3 times) and dried with anhydrous sodium sulfate. After filtering and evaporation, the crude product was suspended in ethanol (20 mL) and stirred for 1 h. The solid was filtered, yielding another 2.2 g of pure product. The combined product was 4.2 g (87.1%) in total. Anal. Calcd. for $C_{16}H_{10}N_2OS$ (fw = 278.33): C, 69.04; H, 3.62; N, 10.06. Found: C, 69.07; H, 3.58; N, 9.77%. ^{1}H NMR (400 MHz, d_6-DMSO, δ/ppm): 10.00 (s, 1H), 8.50 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.53-7.49 (m, 4H), 7.22 (d, J = 6.8 Hz, 1H).

Preparations of Ln(hfac)$_3$·2H$_2$O (Ln = Eu, Gd, Tb, Dy, Ho, Er, Lu).[2] To aqueous solutions of the lanthanide acetates (pH = 5 – 7), 3 equiv of hfac was added dropwise to produce a precipitate. Upon stirring at room temperature for 4 h, the precipitate was filtered, and the solid was washed with water and dried under vacuum to afford the product.

Table S1 Selected bond lengths (Å) and angles (°) for $[Eu_2(hfac)_4L_2]$ (**1**)

Eu(1)–O(1)#1	2.336(2)	Eu(1)–O(2)	2.414(2)
Eu(1)–O(5)	2.386(2)	Eu(1)–N(1)	2.492(3)
Eu(1)–O(4)	2.388(2)	Eu(1)–N(2)	2.608(3)
Eu(1)–O(3)	2.390(2)	Eu(1)–Eu(1)#1	3.8195(8)
Eu(1)–O(1)	2.396(2)		
O(1)#1–Eu(1)–O(5)	106.30(8)	O(1)–Eu(1)–N(2)	131.18(8)
O(1)#1–Eu(1)–O(4)	84.27(8)	O(2)–Eu(1)–N(2)	96.78(8)
O(5)–Eu(1)–O(4)	70.49(8)	N(1)–Eu(1)–N(2)	64.03(8)
O(1)#1–Eu(1)–O(3)	85.65(8)	O(1)#1–Eu(1)–Eu(1)#1	36.70(5)
O(5)–Eu(1)–O(3)	145.24(7)	O(5)–Eu(1)–Eu(1)#1	92.07(6)
O(4)–Eu(1)–O(3)	78.66(8)	O(4)–Eu(1)–Eu(1)#1	111.42(6)
O(1)#1–Eu(1)–O(1)	72.35(8)	O(3)–Eu(1)–Eu(1)#1	114.33(6)
O(5)–Eu(1)–O(1)	77.51(8)	O(1)–Eu(1)–Eu(1)#1	35.65(5)
O(4)–Eu(1)–O(1)	132.82(8)	O(2)–Eu(1)–Eu(1)#1	79.78(6)
O(3)–Eu(1)–O(1)	136.96(8)	N(1)–Eu(1)–Eu(1)#1	102.83(6)
O(1)#1–Eu(1)–O(2)	89.88(8)	N(2)–Eu(1)–Eu(1)#1	166.83(6)
O(5)–Eu(1)–O(2)	140.68(8)	C(16)–S(1)–C(10)	89.23(15)
O(4)–Eu(1)–O(2)	148.14(8)	C(2)–O(1)–Eu(1)#1	132.29(18)
O(3)–Eu(1)–O(2)	69.66(8)	C(2)–O(1)–Eu(1)	119.84(18)
O(1)–Eu(1)–O(2)	73.69(8)	Eu(1)#1–O(1)–Eu(1)	107.64(8)
O(1)#1–Eu(1)–N(1)	139.40(8)	C(18)–O(2)–Eu(1)	136.3(2)
O(5)–Eu(1)–N(1)	69.38(8)	C(20)–O(3)–Eu(1)	137.1(2)
O(4)–Eu(1)–N(1)	127.25(8)	C(23)–O(4)–Eu(1)	135.8(2)
O(3)–Eu(1)–N(1)	121.70(8)	C(25)–O(5)–Eu(1)	134.9(2)
O(1)–Eu(1)–N(1)	67.28(8)	C(9)–N(1)–C(1)	119.3(3)
O(2)–Eu(1)–N(1)	75.06(8)	C(9)–N(1)–Eu(1)	123.8(2)
O(1)#1–Eu(1)–N(2)	156.46(8)	C(1)–N(1)–Eu(1)	116.69(19)
O(5)–Eu(1)–N(2)	82.54(8)	C(10)–N(2)–C(11)	110.6(3)
O(4)–Eu(1)–N(2)	78.16(8)	C(10)–N(2)–Eu(1)	115.8(2)
O(3)–Eu(1)–N(2)	75.69(8)	C(11)–N(2)–Eu(1)	133.6(2)

The symmetry code: #1 -x+1/2, -y+1/2, -z

Table S2 Selected bond lengths (Å) and angles (°) for $[Gd_2(hfac)_4L_2]$ (**2**)

Gd(1)–O(1)#1	2.325(2)	Gd(1)–O(4)	2.407(2)
Gd(1)–O(2)	2.375(2)	Gd(1)–N(1)	2.481(2)
Gd(1)–O(3)	2.376(2)	Gd(1)–N(2)	2.594(3)
Gd(1)–O(5)	2.381(2)	Gd(1)–Gd(1)#1	3.8037(8)
Gd(1)–O(1)	2.386(2)		
O(1)#1–Gd(1)–O(2)	105.86(8)	O(1)–Gd(1)–N(2)	131.63(7)
O(1)#1–Gd(1)–O(3)	83.97(8)	O(4)–Gd(1)–N(2)	96.72(8)
O(2)–Gd(1)–O(3)	70.68(7)	N(1)–Gd(1)–N(2)	64.29(8)

O(1)#1–Gd(1)–O(5)	85.56(8)	O(1)#1–Gd(1)–Gd(1)#1	36.71(5)
O(2)–Gd(1)–O(5)	145.40(8)	O(2)–Gd(1)–Gd(1)#1	91.66(6)
O(3)–Gd(1)–O(5)	78.44(7)	O(3)–Gd(1)–Gd(1)#1	111.21(5)
O(1)#1–Gd(1)–O(1)	72.34(8)	O(5)–Gd(1)–Gd(1)#1	114.28(6)
O(2)–Gd(1)–O(1)	77.28(8)	O(1)–Gd(1)–Gd(1)#1	35.63(5)
O(3)–Gd(1)–O(1)	132.77(7)	O(4)–Gd(1)–Gd(1)#1	80.09(6)
O(5)–Gd(1)–O(1)	136.96(8)	N(1)–Gd(1)–Gd(1)#1	103.00(6)
O(1)#1–Gd(1)–O(4)	90.31(8)	N(2)–Gd(1)–Gd(1)#1	167.26(5)
O(2)–Gd(1)–O(4)	140.54(7)	C(10)–S(1)–C(11)	89.34(15)
O(3)–Gd(1)–O(4)	148.09(7)	C(2)–O(1)–Gd(1)#1	132.30(19)
O(5)–Gd(1)–O(4)	69.82(8)	C(2)–O(1)–Gd(1)	119.82(18)
O(1)–Gd(1)–O(4)	73.77(8)	Gd(1)#1–O(1)–Gd(1)	107.66(8)
O(1)#1–Gd(1)–N(1)	139.59(8)	C(18)–O(2)–Gd(1)	134.8(2)
O(2)–Gd(1)–N(1)	69.45(7)	C(20)–O(3)–Gd(1)	135.63(19)
O(3)–Gd(1)–N(1)	127.30(8)	C(23)–O(4)–Gd(1)	136.1(2)
O(5)–Gd(1)–N(1)	121.86(8)	C(25)–O(5)–Gd(1)	137.0(2)
O(1)–Gd(1)–N(1)	67.46(8)	C(9)–N(1)–C(1)	119.6(3)
O(4)–Gd(1)–N(1)	74.95(8)	C(9)–N(1)–Gd(1)	123.8(2)
O(1)#1–Gd(1)–N(2)	156.03(8)	C(1)–N(1)–Gd(1)	116.48(19)
O(2)–Gd(1)–N(2)	82.96(8)	C(10)–N(2)–C(16)	110.6(3)
O(3)–Gd(1)–N(2)	77.97(8)	C(10)–N(2)–Gd(1)	115.6(2)
O(5)–Gd(1)–N(2)	75.55(8)	C(16)–N(2)–Gd(1)	133.78(19)

The symmetry code: #1 -x+1/2, -y+1/2, -z

Table S3 Selected bond lengths (Å) and angles (°) for $[Tb_2(hfac)_4L_2]$ (**3**)

Tb(1)–O(1)#1	2.303(2)	Tb(1)–O(2)	2.384(2)
Tb(1)–O(1)	2.370(2)	Tb(1)–N(1)	2.460(3)
Tb(1)–O(3)	2.361(2)	Tb(1)–N(2)	2.581(2)
Tb(1)–O(5)	2.354(2)	Tb(1)–Tb(1)#1	3.7709(8)
Tb(1)–O(4)	2.360(2)		
O(1)#1–Tb(1)–O(1)	72.41(8)	O(4)–Tb(1)–N(2)	77.57(8)
O(1)#1–Tb(1)–O(3)	84.89(8)	O(2)–Tb(1)–N(2)	97.05(8)
O(1)–Tb(1)–O(3)	136.65(8)	N(1)–Tb(1)–N(2)	64.60(8)
O(1)#1–Tb(1)–O(5)	106.14(8)	O(1)#1–Tb(1)–Tb(1)#1	36.80(5)
O(1)–Tb(1)–O(5)	77.32(8)	O(1)–Tb(1)–Tb(1)#1	35.61(5)
O(3)–Tb(1)–O(5)	145.60(7)	O(3)–Tb(1)–Tb(1)#1	113.74(6)
O(1)#1–Tb(1)–O(4)	83.88(8)	O(5)–Tb(1)–Tb(1)#1	91.82(6)
O(1)–Tb(1)–O(4)	132.95(8)	O(4)–Tb(1)–Tb(1)#1	111.29(6)

O(3)–Tb(1)–O(4)	78.15(8)	O(2)–Tb(1)–Tb(1)#1	79.75(6)
O(5)–Tb(1)–O(4)	71.02(8)	N(1)–Tb(1)–Tb(1)#1	103.26(6)
O(1)#1–Tb(1)–O(2)	90.21(8)	N(2)–Tb(1)–Tb(1)#1	167.84(6)
O(1)–Tb(1)–O(2)	73.34(8)	C(10)–S(1)–C(16)	89.07(15)
O(3)–Tb(1)–O(2)	70.25(8)	C(2)–O(1)–Tb(1)#1	132.23(18)
O(5)–Tb(1)–O(2)	140.08(8)	C(2)–O(1)–Tb(1)	119.97(18)
O(4)–Tb(1)–O(2)	148.24(8)	Tb(1)#1–O(1)–Tb(1)	107.59(8)
O(1)#1–Tb(1)–N(1)	139.94(8)	C(18)–O(2)–Tb(1)	136.2(2)
O(1)–Tb(1)–N(1)	67.74(8)	C(20)–O(3)–Tb(1)	136.8(2)
O(3)–Tb(1)–N(1)	122.19(8)	C(23)–O(4)–Tb(1)	135.4(2)
O(5)–Tb(1)–N(1)	69.26(8)	C(25)–O(5)–Tb(1)	134.6(2)
O(4)–Tb(1)–N(1)	127.26(8)	C(9)–N(1)–C(1)	119.3(3)
O(2)–Tb(1)–N(1)	74.85(8)	C(9)–N(1)–Tb(1)	123.8(2)
O(1)#1–Tb(1)–N(2)	155.36(8)	C(1)–N(1)–Tb(1)	116.80(19)
O(1)–Tb(1)–N(2)	132.23(8)	C(10)–N(2)–C(11)	110.4(3)
O(3)–Tb(1)–N(2)	75.59(8)	C(10)–N(2)–Tb(1)	115.64(19)
O(5)–Tb(1)–N(2)	83.11(8)	C(11)–N(2)–Tb(1)	133.9(2)

The symmetry code: #1 -x+1/2,-y+1/2,-z

Table S4 Selected bond lengths (Å) and angles (°) for $[Dy_2(hfac)_4L_2]$ (**4**)

Dy(1)–O(1)#1	2.296(2)	Dy(1)–O(2)	2.370(3)
Dy(1)–O(5)	2.340(2)	Dy(1)–N(1)	2.450(3)
Dy(1)–O(4)	2.351(2)	Dy(1)–N(2)	2.572(3)
Dy(1)–O(3)	2.354(3)	Dy(1)–Dy(1)#1	3.7657(8)
Dy(1)–O(1)	2.365(2)		
O(1)#1–Dy(1)–O(5)	105.25(9)	O(1)–Dy(1)–N(2)	132.72(9)
O(1)#1–Dy(1)–O(4)	83.53(9)	O(2)–Dy(1)–N(2)	96.72(9)
O(5)–Dy(1)–O(4)	71.27(9)	N(1)–Dy(1)–N(2)	64.85(10)
O(1)#1–Dy(1)–O(3)	85.03(9)	O(1)#1–Dy(1)–Dy(1)#1	36.72(6)
O(5)–Dy(1)–O(3)	145.88(9)	O(5)–Dy(1)–Dy(1)#1	91.04(7)
O(4)–Dy(1)–O(3)	77.90(9)	O(4)–Dy(1)–Dy(1)#1	111.00(7)
O(1)#1–Dy(1)–O(1)	72.20(9)	O(3)–Dy(1)–Dy(1)#1	113.82(7)
O(5)–Dy(1)–O(1)	76.93(9)	O(1)–Dy(1)–Dy(1)#1	35.48(6)
O(4)–Dy(1)–O(1)	132.85(9)	O(2)–Dy(1)–Dy(1)#1	80.35(7)
O(3)–Dy(1)–O(1)	136.65(8)	N(1)–Dy(1)–Dy(1)#1	103.40(7)
O(1)#1–Dy(1)–O(2)	91.00(9)	N(2)–Dy(1)–Dy(1)#1	168.20(6)
O(5)–Dy(1)–O(2)	139.82(9)	C(10)–S(1)–C(16)	89.22(18)
O(4)–Dy(1)–O(2)	148.24(9)	C(2)–O(1)–Dy(1)#1	132.4(2)

O(3)–Dy(1)–O(2)	70.46(9)	C(2)–O(1)–Dy(1)	119.6(2)
O(1)–Dy(1)–O(2)	73.51(9)	Dy(1)#1–O(1)–Dy(1)	107.80(9)
O(1)#1–Dy(1)–N(1)	140.01(9)	C(18)–O(2)–Dy(1)	136.1(2)
O(5)–Dy(1)–N(1)	69.57(9)	C(20)–O(3)–Dy(1)	136.7(3)
O(4)–Dy(1)–N(1)	127.44(9)	C(23)–O(4)–Dy(1)	135.3(2)
O(3)–Dy(1)–N(1)	122.26(10)	C(25)–O(5)–Dy(1)	134.7(2)
O(1)–Dy(1)–N(1)	67.99(9)	C(9)–N(1)–C(1)	119.5(3)
O(2)–Dy(1)–N(1)	74.42(9)	C(9)–N(1)–Dy(1)	123.6(2)
O(1)#1–Dy(1)–N(2)	155.08(9)	C(1)–N(1)–Dy(1)	116.7(2)
O(5)–Dy(1)–N(2)	83.83(9)	C(10)–N(2)–C(11)	110.6(3)
O(4)–Dy(1)–N(2)	77.45(9)	C(10)–N(2)–Dy(1)	115.7(2)
O(3)–Dy(1)–N(2)	75.42(9)	C(11)–N(2)–Dy(1)	133.7(2)

The symmetry code: #1 -x+1/2,-y+1/2,-z

Table S5 Selected bond lengths (Å) and angles (°) for $[Ho_2(hfac)_4L_2]$ (**5**)

Ho(1)–O(1)#1	2.288(2)	Ho(1)–O(2)	2.365(2)
Ho(1)–O(5)	2.338(2)	Ho(1)–N(1)	2.442(3)
Ho(1)–O(3)	2.343(2)	Ho(1)–N(2)	2.562(3)
Ho(1)–O(4)	2.343(2)	Ho(1)–Ho(1)#1	3.7549(8)
Ho(1)–O(1)	2.354(2)		
O(1)#1–Ho(1)–O(5)	105.41(8)	O(1)–Ho(1)–N(2)	133.32(8)
O(1)#1–Ho(1)–O(3)	84.88(8)	O(2)–Ho(1)–N(2)	96.88(8)
O(5)–Ho(1)–O(3)	145.83(8)	N(1)–Ho(1)–N(2)	65.06(9)
O(1)#1–Ho(1)–O(4)	83.44(8)	O(1)#1-Ho(1)-Ho(1)#1	36.61(5)
O(5)–Ho(1)–O(4)	71.46(8)	O(5)–Ho(1)–Ho(1)#1	91.15(7)
O(3)–Ho(1)–O(4)	77.67(8)	O(3)–Ho(1)–Ho(1)#1	113.67(6)
O(1)#1–Ho(1)–O(1)	72.03(8)	O(4)–Ho(1)–Ho(1)#1	110.83(6)
O(5)–Ho(1)–O(1)	76.93(8)	O(1)–Ho(1)–Ho(1)#1	35.42(5)
O(3)–Ho(1)–O(1)	136.66(8)	O(2)–Ho(1)–Ho(1)#1	80.36(6)
O(4)–Ho(1)–O(1)	132.72(8)	N(1)–Ho(1)–Ho(1)#1	103.72(7)
O(1)#1–Ho(1)–O(2)	91.08(8)	N(2)–Ho(1)–Ho(1)#1	168.73(6)
O(5)–Ho(1)–O(2)	139.46(8)	C(10)–S(1)–C(16)	89.34(16)
O(3)–Ho(1)–O(2)	70.84(8)	C(2)–O(1)–Ho(1)#1	132.3(2)
O(4)–Ho(1)–O(2)	148.40(8)	C(2)–O(1)–Ho(1)	119.56(19)
O(1)–Ho(1)–O(2)	73.41(8)	Ho(1)#1–O(1)–Ho(1)	107.97(8)
O(1)#1–Ho(1)–N(1)	140.23(8)	C(18)–O(2)–Ho(1)	136.0(2)
O(5)–Ho(1)–N(1)	69.25(8)	C(20)–O(3)–Ho(1)	136.4(2)
O(3)–Ho(1)–N(1)	122.46(9)	C(23)–O(4)–Ho(1)	135.3(2)

O(4)–Ho(1)–N(1)	127.29(8)	C(25)–O(5)–Ho(1)	134.7(2)
O(1)–Ho(1)–N(1)	68.37(8)	C(9)–N(1)–C(1)	119.7(3)
O(2)–Ho(1)–N(1)	74.44(8)	C(9)–N(1)–Ho(1)	123.8(2)
O(1)#1–Ho(1)–N(2)	154.65(8)	C(1)–N(1)–Ho(1)	116.4(2)
O(5)–Ho(1)–N(2)	83.86(9)	C(10)–N(2)–C(11)	110.1(3)
O(3)–Ho(1)–N(2)	75.21(8)	C(10)–N(2)–Ho(1)	115.8(2)
O(4)–Ho(1)–N(2)	77.19(8)	C(11)–N(2)–Ho(1)	134.0(2)

The symmetry code: #1 -x+1/2,-y+1/2,-z

Table S6 Selected bond lengths (Å) and angles (°) for $[Er_2(hfac)_4L_2]$ (**6**)

Er(1)–O(1)#1	2.273(2)	Er(1)–O(2)	2.354(2)
Er(1)–O(5)	2.327(2)	Er(1)–N(1)	2.429(2)
Er(1)–O(3)	2.331(2)	Er(1)–N(2)	2.552(3)
Er(1)–O(4)	2.333(2)	Er(1)–Er(1)#1	3.7369(8)
Er(1)–O(1)	2.343(2)		
O(1)#1–Er(1)–O(5)	105.04(7)	O(1)–Er(1)–N(2)	133.87(7)
O(1)#1–Er(1)–O(3)	84.83(7)	O(2)–Er(1)–N(2)	96.95(8)
O(5)–Er(1)–O(3)	146.04(7)	N(1)–Er(1)–N(2)	65.32(8)
O(1)#1–Er(1)–O(4)	83.27(8)	O(1)#1–Er(1)–Er(1)#1	36.59(5)
O(5)–Er(1)–O(4)	71.66(7)	O(5)–Er(1)–Er(1)#1	90.79(6)
O(3)–Er(1)–O(4)	77.55(7)	O(3)–Er(1)–Er(1)#1	113.62(6)
O(1)#1–Er(1)–O(1)	71.91(8)	O(4)–Er(1)–Er(1)#1	110.71(5)
O(5)–Er(1)–O(1)	76.72(8)	O(1)–Er(1)–Er(1)#1	35.31(5)
O(3)–Er(1)–O(1)	136.57(7)	O(2)–Er(1)–Er(1)#1	80.44(6)
O(4)–Er(1)–O(1)	132.66(7)	N(1)–Er(1)–Er(1)#1	103.92(6)
O(1)#1–Er(1)–O(2)	91.34(7)	N(2)–Er(1)–Er(1)#1	169.17(5)
O(5)–Er(1)–O(2)	139.15(7)	C(10)–S(1)–C(16)	89.27(15)
O(3)–Er(1)–O(2)	71.11(7)	C(2)–O(1)–Er(1)#1	132.49(19)
O(4)–Er(1)–O(2)	148.55(7)	C(2)–O(1)–Er(1)	119.23(18)
O(1)–Er(1)–O(2)	73.28(7)	Er(1)#1–O(1)–Er(1)	108.10(8)
O(1)#1–Er(1)–N(1)	140.40(8)	C(18)–O(2)–Er(1)	136.0(2)
O(5)–Er(1)–N(1)	69.48(7)	C(20)–O(3)–Er(1)	136.2(2)
O(3)–Er(1)–N(1)	122.37(8)	C(23)–O(4)–Er(1)	135.28(19)
O(4)–Er(1)–N(1)	127.39(8)	C(25)–O(5)–Er(1)	134.1(2)
O(1)–Er(1)–N(1)	68.67(8)	C(9)–N(1)–C(1)	119.9(3)
O(2)–Er(1)–N(1)	74.10(8)	C(9)–N(1)–Er(1)	123.6(2)
O(1)#1–Er(1)–N(2)	154.22(8)	C(1)–N(1)–Er(1)	116.39(19)
O(5)–Er(1)–N(2)	84.34(8)	C(10)–N(2)–C(11)	110.2(3)

O(3)–Er(1)–N(2)	74.97(8)	C(10)–N(2)–Er(1)	115.5(2)
O(4)–Er(1)–N(2)	76.94(8)	C(11)–N(2)–Er(1)	134.32(19)

The symmetry code: #1 -x+1/2,-y+1/2,-z

Table S7 Selected bond lengths (Å) and angles (°) for $[Lu_2(hfac)_4L_2]$ (**7**)

Lu(1)–O(1)#1	2.243(2)	Lu(1)–O(2)	2.322(2)
Lu(1)–O(5)	2.293(2)	Lu(1)–N(1)	2.399(3)
Lu(1)–O(3)	2.305(2)	Lu(1)–N(2)	2.529(3)
Lu(1)–O(4)	2.306(2)	Lu(1)–Lu(1)#1	3.7004(8)
Lu(1)–O(1)	2.321(2)		
O(1)#1–Lu(1)–O(5)	104.41(8)	O(1)–Lu(1)–N(2)	135.11(8)
O(1)#1–Lu(1)–O(3)	84.43(8)	O(2)–Lu(1)–N(2)	96.91(9)
O(5)–Lu(1)–O(3)	146.34(9)	N(1)–Lu(1)–N(2)	65.97(9)
O(1)#1–Lu(1)–O(4)	82.90(9)	O(1)#1–Lu(1)–Lu(1)#1	36.53(6)
O(5)–Lu(1)–O(4)	72.11(8)	O(5)–Lu(1)–Lu(1)#1	90.20(7)
O(3)–Lu(1)–O(4)	77.01(8)	O(3)–Lu(1)–Lu(1)#1	113.25(6)
O(1)#1–Lu(1)–O(1)	71.65(9)	O(4)–Lu(1)–Lu(1)#1	110.48(6)
O(5)–Lu(1)–O(1)	76.42(9)	O(1)–Lu(1)–Lu(1)#1	35.12(5)
O(3)–Lu(1)–O(1)	136.33(8)	O(2)–Lu(1)–Lu(1)#1	80.77(6)
O(4)–Lu(1)–O(1)	132.63(8)	N(1)–Lu(1)–Lu(1)#1	104.32(7)
O(1)#1–Lu(1)–O(2)	91.98(8)	N(2)–Lu(1)–Lu(1)#1	170.21(6)
O(5)–Lu(1)–O(2)	138.64(8)	C(10)–S(1)–C(16)	89.17(17)
O(3)–Lu(1)–O(2)	71.68(8)	C(2)–O(1)–Lu(1)#1	132.5(2)
O(4)–Lu(1)–O(2)	148.63(8)	C(2)–O(1)–Lu(1)	119.0(2)
O(1)–Lu(1)–O(2)	73.20(8)	Lu(1)#1–O(1)–Lu(1)	108.35(9)
O(1)#1–Lu(1)–N(1)	140.75(9)	C(18)–O(2)–Lu(1)	135.4(2)
O(5)–Lu(1)–N(1)	69.63(9)	C(20)–O(3)–Lu(1)	136.1(2)
O(3)–Lu(1)–N(1)	122.75(9)	C(23)–O(4)–Lu(1)	135.3(2)
O(4)–Lu(1)–N(1)	127.46(9)	C(25)–O(5)–Lu(1)	134.3(2)
O(1)–Lu(1)–N(1)	69.26(9)	C(9)–N(1)–C(1)	119.5(3)
O(2)–Lu(1)–N(1)	73.71(9)	C(9)–N(1)–Lu(1)	123.7(2)
O(1)#1–Lu(1)–N(2)	153.24(9)	C(1)–N(1)–Lu(1)	116.6(2)
O(5)–Lu(1)–N(2)	85.29(9)	C(10)–N(2)–C(11)	110.4(3)
O(3)–Lu(1)–N(2)	74.62(9)	C(10)–N(2)–Lu(1)	115.0(2)
O(4)–Lu(1)–N(2)	76.39(9)	C(11)–N(2)–Lu(1)	134.5(2)

The symmetry code: #1 -x+1/2, -y+1/2, -z

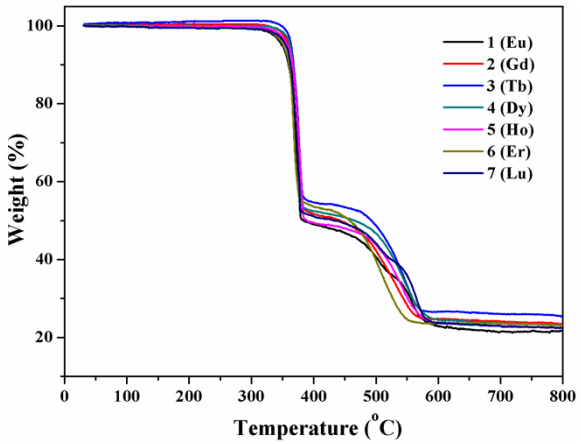

Fig. S1 TGA curves for complexes **1–7**.

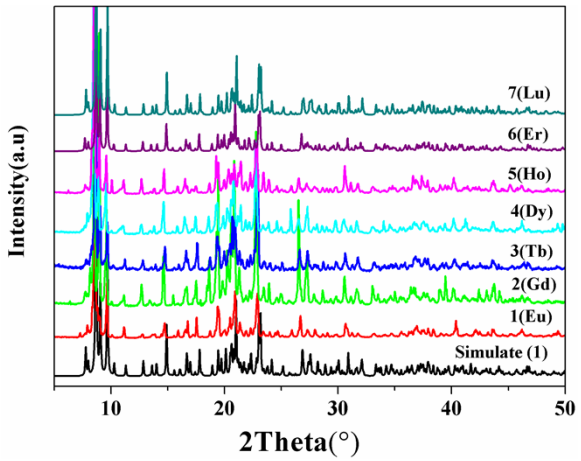

Fig. S2 PXRD patterns of complexes **1–7**.

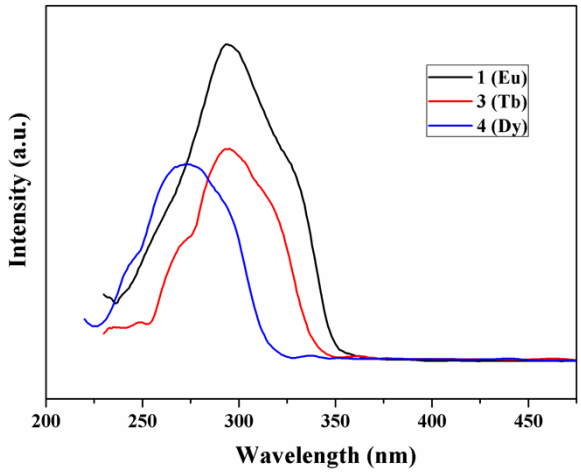

Fig. S3 Excitation spectra of complex **1** (λ_{em} = 617 nm), complex **3** (λ_{em} = 545 nm) and complex **4** (λ_{em} = 575 nm).

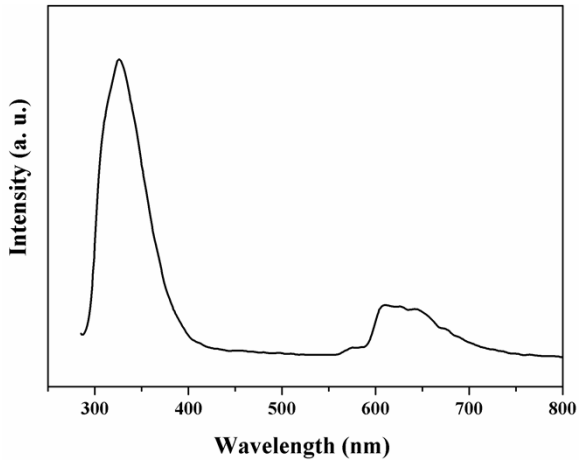

Fig. S4 Room-temperature luminescence spectra of **4** (λ_{ex} = 275 nm) in methanol.

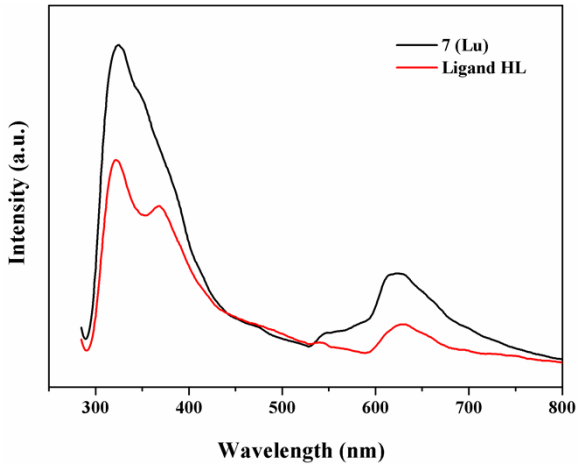

Fig. S5 Room-temperature luminescence spectra of **7** (λ_{ex} = 275 nm) in methanol.

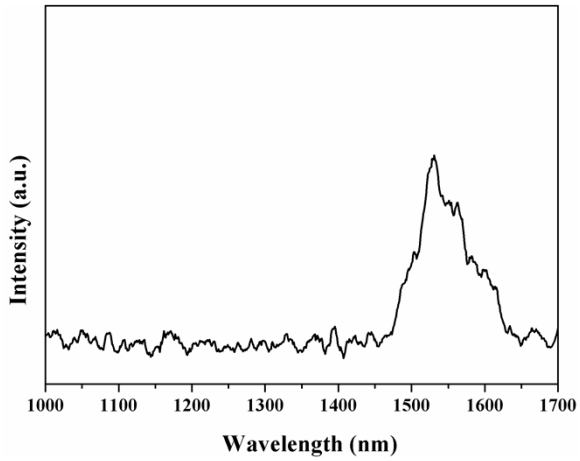

Fig. S6 The room-temperature NIR emission spectrum of complex **6** in the solid-state under 310 nm excitation.

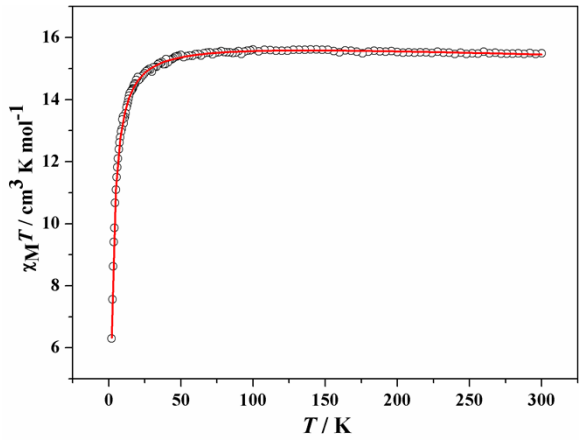

Fig. S7 Temperature dependence of the $\chi_M T$ product for complex **2**; The red line is the best fits to the experimental data.

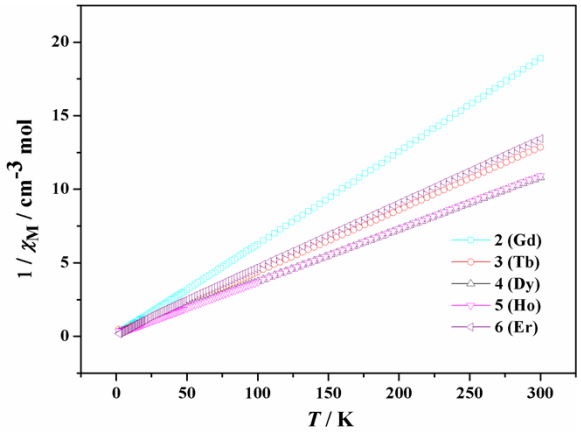

Fig. S8 χ_M^{-1} *vs T* for complexes **2**–**6**.

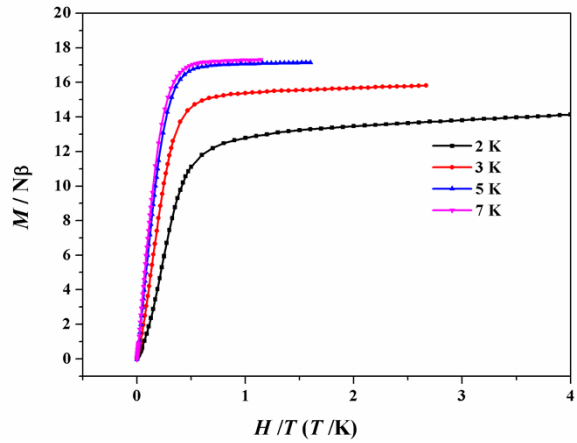

Fig. S9 *M* vs *H*/*T* plots of **4** measured at 2, 3, 5 and 7 K.

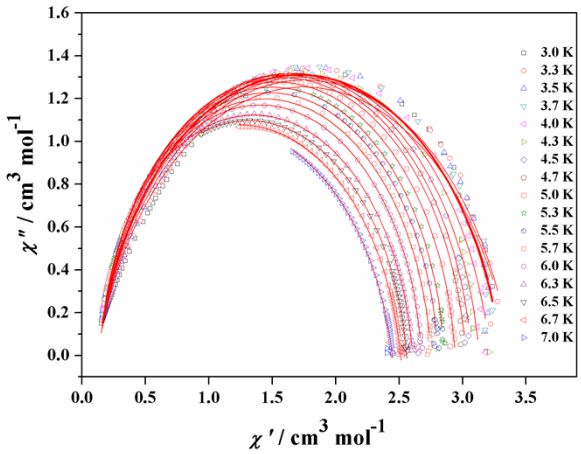

Fig. S10 Cole-Cole plots for **4**. The solid lines are the best fits to the experimental data obtained using the generalized Debye model.

References

1. N. M. Shavaleev, R. Scopelliti, F. Gumy and J.-C. G. Bünzli, *Inorg. Chem.*, 2009, **48**, 2908.

2. H.-B. Xu, J. Li, L.-Y. Zhang, X. Huang, B. Li and Z.-N. Chen, *Cryst. Growth Des.*, 2010, **10**, 4101.